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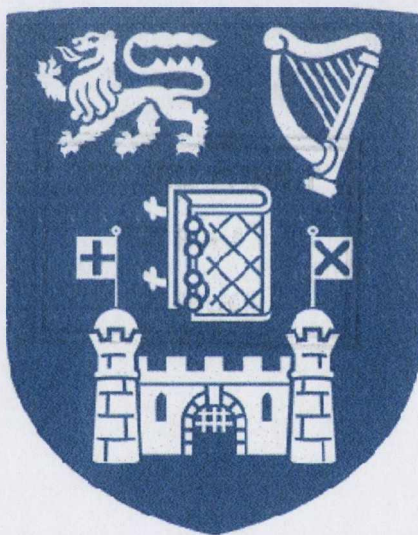
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# Novel Hetero-Fluoranthenes Towards Nitroaromatic Sensing

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A thesis submitted to the University of Dublin for the degree of  
Doctor of Philosophy

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Trinity College Dublin

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PhD  
CHEMISTRY





Thesis 11165

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## Summary

**Chapter 1:** This chapter gives a broad literature review to explosives and nitroaromatic sensing of polycyclic aromatic hydrocarbons (PAHs) particularly fluoranthenes which are discussed in subsequent chapters. The concept of fluorescence quenching is discussed, taking examples from a broad range of published work which is an important preface to the results in the following chapters.

**Chapter 2:** This chapter details the synthesis and characterisation of a novel family of nitrogen substituted *tert*-butyl fluoranthenes *via* the [2+4] Diels-Alder route and their application in nitroaromatic sensing. Static fluorescence quenching mechanism was observed between these *tert*-butyl fluoranthenes and the explosive picric acid which was supported by DFT studies. It was observed that incorporation of nitrogen atoms into the fluoranthene core increases the sensitivity towards explosives particularly picric acid, demonstrated by the increased quenching ability recorded experimentally.

**Chapter 3:** This chapter outlines the synthesis and characterisation of a novel family of 2N fluoranthenes, which vary in their peripheral functionalisation. The main body of the chapter discusses their synthesis and characterisation *via* the [2+4] Diels-Alder route and studies the photophysical properties towards nitroaromatic sensing particularly picric acid. The synthesis of a library of these compounds allowed for analysis of the best sensor and subsequent evaluation of potentialities in nitroaromatic sensing. By varying the substituents on the fluoranthene core while keeping the nitrogen loading constant, it was observed that fluoranthenes with electron donating groups show maximum amount of sensitivity.

**Chapter 4:** This chapter focuses on the design of a series of methoxy-functionalised nitrogen-substituted fluoranthenes, by systematically increasing the methoxy groups with increased synthetic control. It discusses the synthetic challenges and characterisation by 2D NMR and single crystal X-ray analysis. The photophysical and nitroaromatic studies supported by DFT are presented in the latter part of the chapter.

**Chapter 5:** This chapter introduces azafluoranthenes and outlines the synthesis and characterisation of a novel family of azafluoranthenes which vary in their peripheral functionalisation. The azafluoranthenes were synthesised *via* the [2+4] Diels-Alder route towards nitroaromatic sensing, selective to picric acid. The photophysical properties and the anomalies in nitroaromatic sensing are discussed here.

**Chapter 6:** This chapter focusses on the initial attempts to expand the family of functionalised fluoranthenes particularly bromo substituted compounds and possible synthetic routes for the design of novel complex fluoranthene systems for various applications. The second part discusses the practical use of hand-held explosive sensing devices and further possibilities.

**Chapter 7:** This chapter provides a full account of the experimental work carried out within this research.

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## Abbreviations

|                      |                                                     |
|----------------------|-----------------------------------------------------|
| <b>1D</b>            | one-dimensional                                     |
| <b>2D</b>            | two-dimensional                                     |
| <b>Å</b>             | angstrom                                            |
| <b>Ar</b>            | aryl                                                |
| <b>a.u.</b>          | arbitrary units                                     |
| <b>BODIPY</b>        | boron dipyrromethene                                |
| <b>Bu</b>            | butyl                                               |
| <b>BQ</b>            | benzoquinone                                        |
| <b>°C</b>            | degrees Celsius                                     |
| <b>cm</b>            | centimetre                                          |
| <b>COSY</b>          | correlation spectroscopy                            |
| <b>d</b>             | doublet                                             |
| <b>dd</b>            | doublet of doublets                                 |
| <b>DEPT</b>          | distortionless enhancement by polarisation transfer |
| <b>DNP</b>           | dinitro phenol                                      |
| <b>DFT</b>           | density functional theory                           |
| <b>DNT</b>           | dinitro toluene                                     |
| <b>DNB</b>           | dinitro benzene                                     |
| <b>DIPA</b>          | diisopropylamine                                    |
| <b>DMF</b>           | dimethylformamide                                   |
| <b>DMPD</b>          | 1,4-dimethylpiperazine-2,3-dione                    |
| <b>DMSO</b>          | dimethylsulfoxide                                   |
| <b>Dppz</b>          | dipyrido[3,2-a:2'-3'-c]phenazine                    |
| <b>DSC</b>           | differential scanning calorimetry                   |
| <b>e<sup>-</sup></b> | electron                                            |
| <b>E</b>             | ethanol                                             |
| <b>EDG</b>           | electron donating group                             |
| <b>EI-MS</b>         | electron impact mass spectrometry                   |
| <b>em</b>            | emission                                            |
| <b>ESI-MS</b>        | electrospray mass spectrometry                      |
| <b>EWG</b>           | electron withdrawing group                          |
| <b>Exc</b>           | excitation                                          |
| <b>F</b>             | Fluorophore                                         |

|                     |                                                                                |
|---------------------|--------------------------------------------------------------------------------|
| <b>FTIR</b>         | Fourier transform infrared spectroscopy                                        |
| <b>g</b>            | gram                                                                           |
| <b>HMBC</b>         | heteronuclear multiple-bond correlation                                        |
| <b>HMQC</b>         | heteronuclear multiple-quantum correlation                                     |
| <b>HOMO</b>         | highest occupied molecular orbital                                             |
| <b>HPLC</b>         | high-performance liquid chromatography                                         |
| <b>HRMS</b>         | high-resolution mass spectrometry                                              |
| <b>H</b>            | hour                                                                           |
| <b>Hz</b>           | Hertz                                                                          |
| <b>IR</b>           | Infrared                                                                       |
| <b><i>J</i></b>     | coupling constant                                                              |
| <b>K</b>            | Kelvin                                                                         |
| <b>kJ</b>           | kilojoule                                                                      |
| <b>L</b>            | ligand                                                                         |
| <b>LD-TOF</b>       | laser desorption –time-of-flight mass spectrometry                             |
| <b>LMCT</b>         | ligand-to-metal-charge transfer                                                |
| <b>LUMO</b>         | lowest unoccupied molecular orbital                                            |
| <b>m</b>            | multiplet                                                                      |
| <b>M</b>            | molarity                                                                       |
| <b>Min</b>          | minute                                                                         |
| <b>m.p.</b>         | melting point                                                                  |
| <b>m.u.</b>         | mass units                                                                     |
| <b><i>m/z</i></b>   | mass to charge ratio                                                           |
| <b>MALDI-TOF MS</b> | matrix-assisted laser desorption/ionisation – time of flight mass spectrometry |
| <b>Max</b>          | maximum                                                                        |
| <b>Me</b>           | methyl                                                                         |
| <b>Mg</b>           | milligram                                                                      |
| <b>MHz</b>          | megahertz                                                                      |
| <b>mL</b>           | millilitre                                                                     |
| <b>MLCT</b>         | metal to ligand charge transfer                                                |
| <b>Mmol</b>         | millimole                                                                      |
| <b>Mol</b>          | mole                                                                           |
| <b>MS</b>           | mass spectrometry                                                              |
| <b>mV</b>           | millivolt                                                                      |



|                                |                                          |
|--------------------------------|------------------------------------------|
| <b>N-HSB</b>                   | nitrogen-heterosuperbenzene              |
| <b>NAC</b>                     | nitroaromatic compounds                  |
| <b>NBA</b>                     | nitro benzaldehyde                       |
| <b>Nm</b>                      | nanometre                                |
| <b>nOe</b>                     | nuclear Overhauser effect                |
| <b>NP</b>                      | nitrophenol                              |
| <b>ns</b>                      | nanoseconds                              |
| <b>NT</b>                      | nitrotoluene                             |
| <b>OFET</b>                    | organic field effect transistor          |
| <b>OLED</b>                    | organic light emitting diode             |
| <b>OPV</b>                     | organic photovoltaics                    |
| <b>ox.</b>                     | oxidation                                |
| <b>P</b>                       | phenol                                   |
| <b>PA</b>                      | picric acid                              |
| <b>PAH</b>                     | polycyclic aromatic hydrocarbon          |
| <b>Ph</b>                      | phenyl                                   |
| <b>PIFA</b>                    | (bis(trifluoroacetoxy)iodo)benzene       |
| <b>Ppm</b>                     | parts per million                        |
| <b>Ppy</b>                     | 2-phenylpyridine                         |
| <b>QCM</b>                     | quartz crystal microbalance              |
| <b>RT</b>                      | room temperature                         |
| <b>S</b>                       | singlet                                  |
| <b>SCE</b>                     | standard calomel electrode               |
| <b>Sec</b>                     | second                                   |
| <b>Sh</b>                      | shoulder                                 |
| <b>solv.</b>                   | solvent                                  |
| <b>T</b>                       | toluene                                  |
| <b><i>t</i> or <i>tert</i></b> | tertiary                                 |
| <b>TAC</b>                     | time to amplitude converter              |
| <b>TASB</b>                    | tetraazasuperbenzene                     |
| <b>TCSPC</b>                   | time-correlated single photon counting   |
| <b>TD DFT</b>                  | time dependent density functional theory |
| <b>TFA</b>                     | trifluoroacetic acid                     |
| <b>THF</b>                     | tetrahydrofuran                          |
| <b>TLC</b>                     | thin layer chromatography                |

|               |                                |
|---------------|--------------------------------|
| <b>TMS</b>    | tetramethylsilane              |
| <b>TNT</b>    | trinitrotoluene                |
| <b>TOCSY</b>  | total correlation spectroscopy |
| <b>TPA</b>    | two-photon absorption dyes     |
| <b>Tpy</b>    | Terpyridine                    |
| <b>UV/Vis</b> | ultraviolet-visible            |
| <b>vs.</b>    | versus                         |
| <b>WAXS</b>   | wide-angle x-ray spectroscopy  |
| <b>°</b>      | degrees                        |
| <b>δ</b>      | chemical shift                 |
| <b>Δ</b>      | heat                           |
| <b>ε</b>      | molar absorption coefficient   |
| <b>λ</b>      | wavelength                     |
| <b>τ</b>      | half life                      |
| <b>μs</b>     | microsecond                    |
| <b>%</b>      | percentage                     |

**1. Introduction**





## **1.1 Introduction**

Over the previous two centuries, human activities including rapid industrialisation, and the advent of large scale chemical based manufacturing has had a huge impact on the environment. More recently, over the last few decades, the detection of explosive chemicals and their derivatives has been an active area of research due to the rise in global terrorism and environmental pollution.<sup>1</sup> The devising of advanced methods through molecular chemosensors for the detection of these chemical explosives is critical for national and international security, environmental decontamination, military operations, and for humanitarian efforts.<sup>2</sup>

The facile access to large-scale ordnance has resulted in a dramatic rise in incidents of terrorist activity. These involve the clandestine placement of explosives in a wide range of commercial and public locations including, but not limited to, shopping centres, railway stations and airports.<sup>3</sup> This evolving issue has given rise to the demand for quicker, increasingly accurate and ubiquitous explosive detection. With the ever-increasing amount of global air travel, and with millions of items of luggage scanned annually in every major and regional airport, there has been an obvious proportional rise in demand for effective, reliable and rapid methods for screening. This alone has now become an important bottleneck for powerful counter-terrorism activities.<sup>4</sup>

Novel molecular chemosensors that can rapidly detect explosives also have important potential applications in global de-mining projects, the remediation of explosives manufacturing sites, forensic and criminal investigations like post-blast residue determinations, and other military applications.<sup>5</sup> Concurrent to this, there is also a growing concern regarding the health risks associated with the passive release of explosive residues into the environment from military sites and former ammunition plants.<sup>6</sup>

Therefore, it is clear that these combined security and environmental concerns have prompted the development of new and innovative molecular chemosensors for explosive compounds.<sup>7</sup> To assist in the addressing of these global concerns, in this work, we have synthesised a set of novel fluoranthene derivatives, and have explored their physical application towards the development of quick, low-cost, and accurate devices for the detection of explosives.

## **1.2 Explosives**

Explosives may be defined as compounds that can be initiated to undergo rapid and self-propagating decomposition, resulting in the formation of more stable materials with the

sudden release of heat and pressure.<sup>8</sup> These substances contain a large amount of chemical energy that can be released by destabilising their equilibrium condition upon addition of external agents like pressure and temperature. The generated by-products are often energetically stable gases; including carbon monoxide, carbon dioxide, and molecular nitrogen, all of which possess the property of containing strong double or triple bonds having high bond strengths of approximately  $1 \text{ MJmol}^{-1}$ . Consequently, most commercial explosives are organic compounds containing  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NHNO}_2$  groups. The sensitivity of explosives is often measured by the ease with which an explosive can be ignited or detonated, *i.e.* the amount and intensity of shock, friction, or heat that is required.<sup>9</sup>

Taking into consideration their chemical structure and performance, explosives have also been routinely classified based on their burn rates, with low and high explosives being the two predominant classes as shown in Figure 1.1.<sup>10</sup>

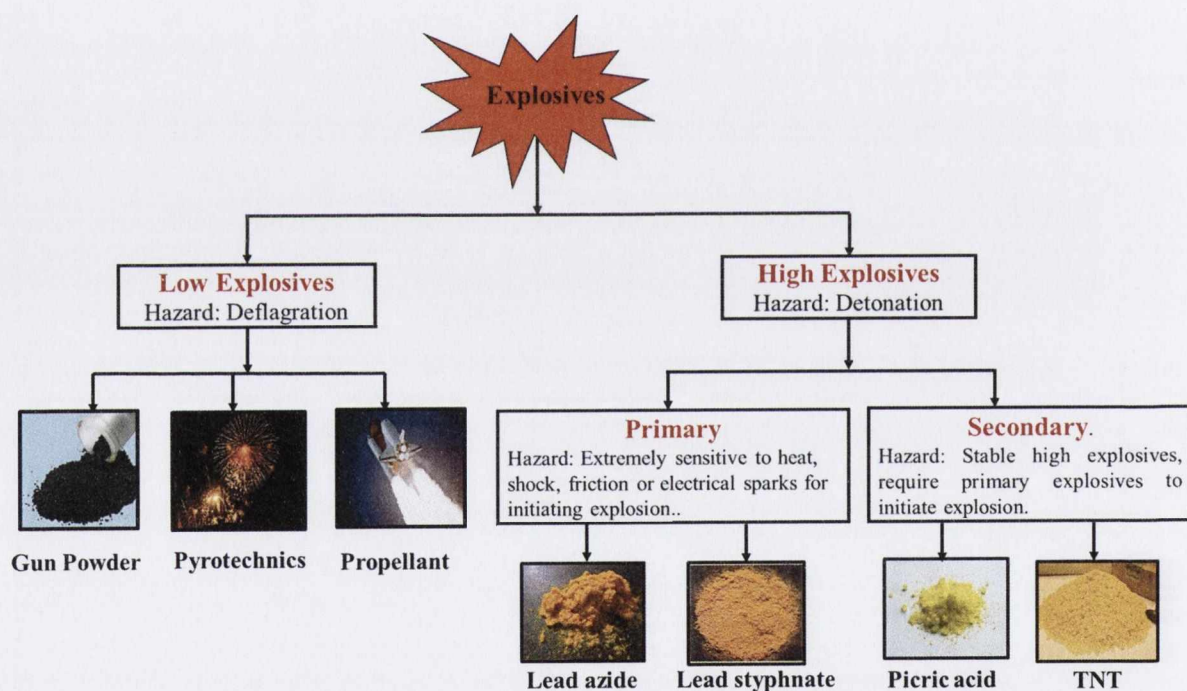


Figure 1.1: The classification and sub-classification of explosives based on their structure and performance.

Low explosives burn at relatively low velocities measured in the  $\text{cm s}^{-1}$  range, whereas high explosives detonate at dramatic velocities measurable in  $\text{km s}^{-1}$ . In these high burn rate explosives, the chemical reaction propagates with such rapidity that the rate of reaction in the material often exceeds the speed of sound.<sup>11</sup> Low burn rate explosives include propellants, smokeless powder, black powder, and common pyrotechnics. Due to the increased danger



associated with high burn rate explosives, these are further sub-divided into primary and secondary explosive classes allocated on the basis of their stability and method of detonation. Primary explosives, which include lead azide and lead styphnate, are highly susceptible to initiation and thus are often referred as ‘initiating explosives’. These explosives are commonly used therefore to ignite secondary explosives. These secondary explosives, which include nitroaromatics and nitramines, are much more prevalent at military sites. Secondary explosives are regularly used as the main charge or bolstering explosives because they are specifically formulated to detonate only under certain circumstances or conditions.<sup>10</sup>

Secondary explosives are again further categorized into two classes, melt-pour explosives or plastic bonded explosives. Melt-pour explosives include those based on the nitroaromatics group, such as trinitrotoluene (TNT) and dinitrotoluene (DNT), whilst plastic bonded explosives which are based on a binder and crystalline explosive model, include explosives such as hexahydro-1,3,5 trinitroazine (RDX).

### 1.3 Explosive materials

The purposely energetic materials used by international militaries, such as propellants and explosives, are mostly established on organic compounds containing nitro (NO<sub>2</sub>) groups. The three major classes of these energetic materials are nitroaromatics (*e.g.* TNT), nitramines (*e.g.* RDX) and nitrate esters (*e.g.* nitrocellulose and nitroglycerine). Due to the diversity of chemistry used in the manufacture of secondary explosives, the mere use of the melt-pour and plastic bonded classes generates an unsatisfactory oversimplification.<sup>9</sup> Therefore, secondary explosives can be assigned to six principle chemically derived categories (shown with examples below);

1. *Aliphatic Nitro Compounds*: Nitromethane and hydrazine nitrate.
2. *Nitroaromatic Compounds*: TNT, dinitrobenzene (DNB), hexanitrostilbene, and picric acid. This category contains the primary military-used explosives, and also the principal components of the unexploded landmines found in war zones worldwide.
3. *Nitramines or Nitrosamines*: Octogen (HMX) or RDX.
4. *Nitrate Esters*: Pentrite (PETN), ethylene glycol dinitrate (EDGN), nitroglycerine, and nitroguanidine (NQ). Nitroglycerine and NQ are the main components of highly energetic plastic explosives, such as C-4 (91% RDX) and Semtex (40–76% PETN).

5. *Acid Salts*: Ammonium nitrate. Ammonium nitrate is commonly used for industrial applications, typically in solid rocket propellants.
6. *Organic Peroxides*: Triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD). This category has grown rapidly *via* homemade explosives as they can be easily synthesized from inexpensive and readily accessible materials.

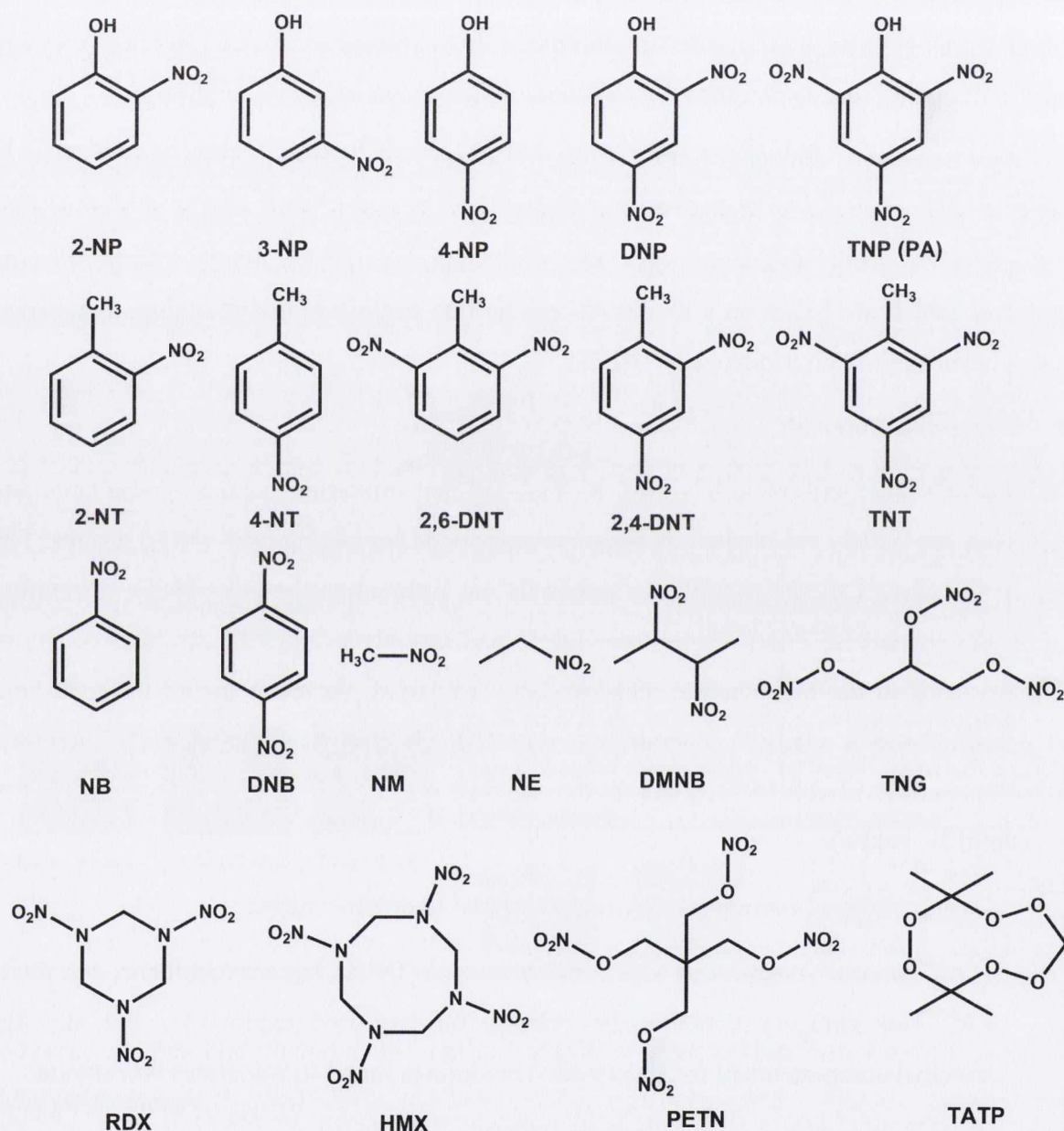


Figure 1.2: Chemical structures of selected explosives<sup>12</sup>

As these nitrated compounds are sensitive to shock, friction and impact, detection methods that permit contact-free analysis are necessary. Moreover, the need to detect hidden explosives in transportation hubs, and buried explosives in warzones, has led to further interest in the ultrasensitive detection of nitrated explosives in the vapour phase.<sup>13</sup> Explosive



vapours are notoriously difficult to detect. Firstly, most secondary explosives are found to have low volatility at ambient temperature. This is increasingly frustrating as those with the highest priority to be detected (e.g., TNT, PA) have especially low volatility. In addition, explosives are often concealed or deliberately hermetically sealed to avoid detection. This results in the vapour concentration of these explosives being potentially reduced by a factor of nearly 1000 by the simple wrapping of the material in a plastic package. Secondly, the physical properties of each class of nitrated explosive can differ significantly, making the detection of broad-class explosives a challenge.<sup>9</sup> One example is the increasing demand for the direct detection of RDX and PETN, both of which lack nitroaromatic rings. This, coupled with their low vapour pressures, and prohibitively high lowest unoccupied molecular orbital (LUMO) energies, renders them very difficult to be detected by common optically-based approaches used for NACs. Finally, as many daily used chemicals contain similar functional groups, these are likely to cause interferences and thereby lead to false alarms. In a practical field test, false positive alarms often come from environmental contaminants, and false negative alarms are directly linked to the lack of molecular selectivity. For instance, bleach is a strong oxidant and is likely to generate a false positive alarm in TATP or HMTD sensing. All of these issues combined make it extremely difficult to achieve selective detection and sensitivity of a broad range of explosives by a single molecular chemosensor.<sup>12, 13</sup>

While the optimal detection of explosives is required to be contact-free, through the vapour phase, sensing applications are also often required to be performed *via* an aqueous matrix. The sensing of explosives as an aqueous solution is increasingly found to be of a beneficial nature due to the location of underwater mines, the extension of terrorist activities from land to marine environments, and the characterization of soil and groundwater contaminations. One benefit of the aqueous requirement is that solubility in aqueous solutions is increased *versus* that of gaseous environments.<sup>14</sup> Despite this advantage, saturated concentrations are hardly ever achieved as water movement will cause various degrees of dilution, and thus ppb (or lower) levels are required as suitable detection levels for real-world application. This makes the detection of nitrated explosives in aqueous samples extremely challenging.<sup>15</sup>

### 1.3.1 Nitroaromatic Compounds

Nitroaromatic compounds (NACs) are an important class of highly energetic explosives. They also find considerable use as industrial chemicals in reagents, solvents, dyes, foams, insecticides, and herbicides. Research suggests that NACs are found as the main components of unexploded landmines.<sup>16</sup> A strong argument can be made that these landmines should have



the highest detection priority, and therefore this has guided the focus of this current research. Nitroaromatic compounds can be divided into two major compound groupings; phenolic and tolyl. The most widely studied member of the tolyl group is TNT, while a phenolic nitrocompound example is TNP, colloquially known as picric acid.<sup>17</sup>

#### 1.3.1.1 TNT

2,4,6 Trinitrotoluene (TNT) has earned the distinction of being the most commonly utilised high explosives in the last century. Other commonly used names for TNT are Tritolol, Trilite, Tolite, Trinol, and Trotyl. TNT is not only a security threat, but is also of great environmental concern as it causes soil and water contamination. The origin of its use as a large scale explosive can be traced back to World War I. Its primary use is as a booster (bursting charge) for high explosive bombs.<sup>18</sup> TNT in the solid state is a crystalline material with good thermal and chemical stability, safe to handle, has a high compatibility with other explosives, is of moderate toxicity and enjoys a low cost. The wide use of TNT as a military explosive is compounded due to the safety of its manufacture, and loading, transportation, and storage. Directly contradicting these advantages is the ability for TNT to rapidly penetrate the skin, and readily enter groundwater supplies. These sobering disadvantages have resulted in TNT being classified as toxic, with harmful effects being presented to almost all life forms. In human and mammalian life it may result in liver damage, aplastic anaemia and toxic hepatitis that can lead to death.<sup>19, 20</sup>

#### 1.3.1.2 Picric acid

A close relative to TNT is 2,4,6-trinitrophenol (TNP), more commonly known as picric acid (PA). PA's explosive nature is equivalent to 105% of TNT.<sup>21, 22</sup> PA is found as an odourless, bright yellow and crystalline material in the solid state. Despite its odourless nature, the vapours of PA are considered extremely hazardous, and cause headache, general weakness and fatigue, anemia and liver injury. When inhaled at high concentrations, the vapors may damage the entire respiratory system. More commonly, small amounts of exposure can result in skin allergies and damage to the structures of the eye. Furthermore, as PA often cannot be degraded by the body, accumulation may result in many chronic diseases such as sycosis and cancer.<sup>23</sup> Despite this, PA is widely used in dye manufacturing, pharmaceuticals, as a staining agent and as a reagent in chemical synthesis. This is of concern as due its high solubility in water, it can easily contaminate soil and groundwater when adequate care is not taken. A crucial difference to TNT is the ability of PA to react with other materials and self-assemble

explosive compounds. If PA comes in contact with certain amines, bases, forms of concrete, or particular metals, PA can generate shock sensitive unstable picrate salts. These unstable salts are often far more explosive in nature than pure PA.

This concerning property of PA as compared to TNT suggests an even greater need for a selective molecular chemosensor for PA than that for TNT. As a result, in this current volume of research we have focussed our efforts towards the development of a cost-efficient, selective,<sup>24</sup> rapid and portable detection method for PA in aqueous media.<sup>25</sup>

#### 1.4 Detection Methods

Molecular-based detection for the presence of a target or a target-related material is an important technique to determine or indicate harmful materials present in a chemical sample.<sup>3, 12</sup> The detection of explosives is often a challenging task from a chemist's perspective. Most explosives have a low vapour pressure, and the problem is complicated by the frequent introduction of novel explosive compounds, and the sealing of explosive material in novel casing materials. The trace detection of explosives typically involves collecting vapour or particulate samples, with further analysis with a sensitive sensor system. Current available methods for the detection of explosives are broadly classified into three types, (i) non-optical, (ii) instrumental and (iii) optical.

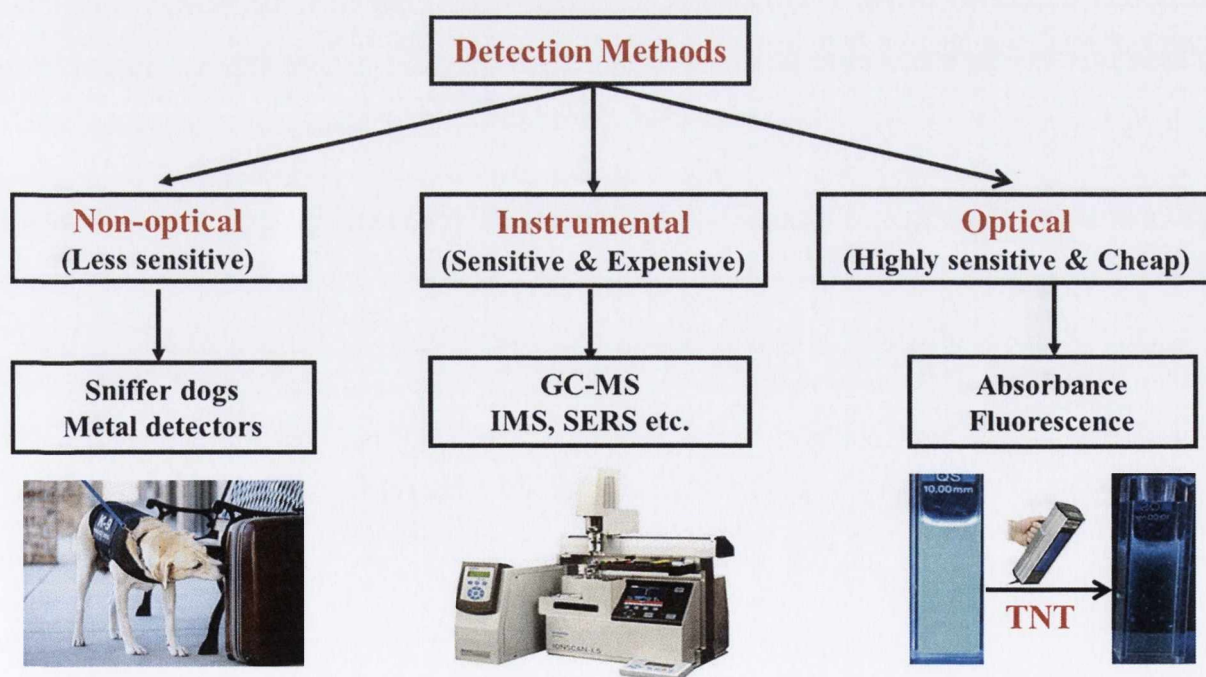


Figure 1.3: Three broad categories of detection methods.



### 1.4.1 Non-optical methods

In this class of detection, specially trained canines are often the most reliable. The canine olfactory system is found to be over four times more sensitive than that of a human, and responsive to trace vapour.<sup>26</sup> These highly-trained canines (sniffer dogs) are widely used in relevant detection test sites like airports to identify, and more importantly, discriminate between different explosive compounds.

Despite this “best in class” type of detection, canine training has a very high initial start-up cost, and the dogs require constant care and thus suffer from high maintenance costs. The dogs can also easily tire, with their use being therefore limited to short periods of the day. For these reasons, their use is completely unsuitable for continuous and large-scale sensing in areas such as transportation site screening. Other non-optical methods include the use of metal detectors to detect landmines. However, these are entirely useless if the casing material of the explosive is plastic in nature.<sup>27</sup>

### 1.4.2 Instrumental methods

Instrumental methods, often referred to as mass sensors include gas chromatography coupled with mass spectrometry (GC-MS), ion-mobility spectrometry (IMS), surface-enhanced Raman spectroscopy (SERS), quartz crystal microbalance (QCM), surface plasmon resonance (SPR), and X-ray dispersion. While these techniques enjoy considerable sensitivity and selectivity, currently available instrumental techniques are prohibitively expensive, and are often unsuitable for large-scale use.<sup>28</sup>

In one example, IMS, a “one swipe” action, is often all that is required to sufficiently detect and identify a large number of explosives. This swipe action allows the device to pick up airborne or surface bound particulates containing explosive residue which is then analysed *via* its molecular mass. Positive identification involves a comparative analysis with a library of standards. This technique has device guaranteed sensitivity of nanogram or picogram concentrations for common explosives. However, it suffers some serious limitations on a large scale. First, this technique lacks suitable sensitivity for a broad range of explosives, such as PETN and RDX, which greatly limits its overall utility.<sup>29</sup> Moreover, such instruments require sophisticated protocols for their use and suffer from time-consuming calibration. Coupled with these device limitations, the issue of poor portability and high cost prevents it being a truly feasible option for real-time field detection.<sup>30</sup> Similar limitations also apply to other laboratory explosive detection systems, such as electrochemical methods<sup>31, 32</sup> and



biosensor techniques.<sup>20, 33</sup> Therefore, it is obviously apparent that there exists an urgent need for innovative detection strategies that are not only low-cost and user-friendly, but also highly sensitive and selective.

### 1.4.3 Optical methods

Unlike the other common detection techniques, optical methods present an attractive and promising approach to explosive sensing, offering many benefits such as low-cost set up and use, good portability, and high sensitivity and selectivity. Of the many optical sensing methods, which include fibre optic sensors,<sup>28</sup> absorbance sensing, photoluminescence detection, and Laser Induced Breakdown Spectroscopy (LIBS), absorbance (colorimetric) and fluorescence sensing offer the most potential as disruptive technologies as cheap and highly selective optical sensors for explosive detection.<sup>34</sup>

In most typical set ups, fluorescence-based detection is one to three orders of magnitude more sensitive, and has wider linear ranges compared to absorbance-based methods. Moreover, the source and detector of fluorescence-based methods can be easily incorporated into a cheap handheld device for the field detection of explosives.<sup>35</sup> Thus, this fluorescence-based method has the most promise to be applied in the rapid, sensitive and selective detection of explosives, and has thus become the focus of discussion in this thesis.

Current major research focusses on the use of the fluorescence quenching technique, in which the fluorescence signal of a chromophore is diminished in the presence of the explosive molecule. A reverse method, “turn-on fluorescence” is much less common but may find use in the future for novel detection strategies.<sup>36</sup> In this method, a non-fluorescent precursor is converted to a fluorescent indicator only in the presence of explosives compounds. The challenge is therefore to identify novel synthetic methods by which explosives can selectively react with the appropriate precursors. This alternative method of fluorescence detection is highly attractive in sensory devices as sensitivity is significantly greater by the appearance of a light signal on a dark background.<sup>37</sup>

Some limitations do exist with fluorescence-based detection methods which include photodegradation and photobleaching of the fluorescent materials. Slow response times due to analyte transport, as well as a potential for non-specific responses can also cause issue. Nevertheless, fluorescence detection is intrinsically cost-effective and portable, requiring little more than the equivalent of a digital camera and a backlight.<sup>38</sup>

## 1.5 Fluorescence Quenching Detection

A physical process which results in a decrease of the fluorescence intensity of any given compound/substance/sample/chemical is called fluorescence quenching. Fluorescence quenching-based detection of nitroaromatics has become a powerful tool to detect trace amounts of explosives due to the fact that it is a reliable technique, shows high sensitivity, has easy visualization, and a very quick response time. It is an indirect method, where it utilizes the non-fluorescent properties of nitroaromatics to attenuate the fluorescence intensity of the fluorophore upon interactions with NACs.<sup>39-42</sup> In theory, any process that causes a change of fluorescence intensity (quenching or enhancement), emission wavelength, anisotropy, or excited state lifetime has the potential to be used to detect explosives.

### 1.5.1 Fluorescence Quenching Detection

Of the different fluorescence-based detection methods, fluorescence quenching has dominated the field of explosive detection to date.<sup>43</sup> There are a number of possible interactions or processes that can occur which result in fluorescence quenching. Some of these main processes are discussed below.

#### 1.5.1.1 Photo-Induced Electron Transfer (PET)

PET is one of the most widely studied processes for fluorescence quenching, and plays an important informative role in the development of fluorescence sensors for explosive detection. Following a photo-induced electron transition, the generated excited-state of the electron rich fluorophores (D) donates the electron to the ground state of an electron deficient nitrated organic compound (A) through a classical donor-acceptor (D-A) interaction. Subsequent to this, generally a charge transfer complex is formed between the electron donor and the electron acceptor before a back-transfer of the electron occurs, allowing the donor molecule to return to the ground state without radiative emission.<sup>37</sup> This process demonstrates the ability of the electron acceptor to quench the fluorescence of the donor molecule.<sup>43</sup>



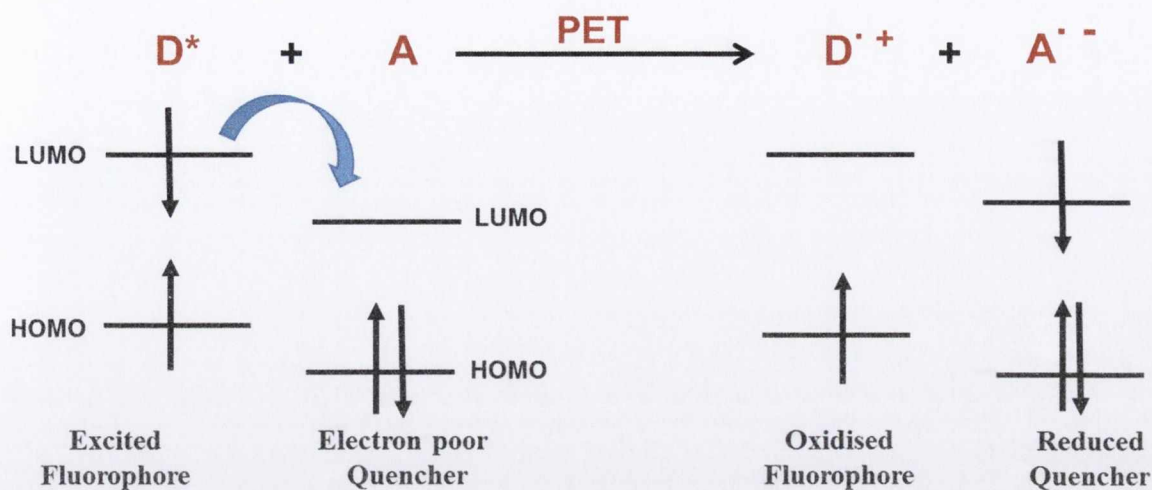


Figure 1.4: Molecular orbital schematic of photo-induced electron transfer.

The fluorescence quenching efficiency of a given sensor is determined *via* the electron transfer between the LUMO of the donor sensor to that of the accepter LUMO and is proportional to the energy gap between these energy levels.

According to Marcus theory, developed to analyse the PET process, this energy gap is the thermodynamic driving force for the oxidative electron transfer process, and the electron transfer rate ( $K_{et}$ ) is expressed as;<sup>18, 44</sup>

$$K_{et} = A \exp\left(-\frac{\Delta G^*}{kT}\right) = \frac{2\pi^{3/2}}{h\sqrt{\lambda kT}} V^2 \exp\left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda kT}\right]$$

Here,  $h$  is Planck's constant,

$k$  is the Boltzmann constant,

and,  $T$  is temperature in Kelvin.

$\Delta G^\circ$  is the standard Gibbs free energy difference of the electron transfer reaction,

$V$  is the electron coupling between the initial state ( $D^*A$ ) and the final state ( $D^+A^-$ ),

$\lambda$  is the reorganization energy of adjusting the molecular structure for producing a new stabilized state. It includes two contributions: (i) the internal part  $\lambda_e$  related to the geometry changes of  $D$  and  $A$ , and (ii) the external part  $\lambda_c$  related to changes in the surroundings.

Under the one-electron approximation,  $\Delta G^\circ$  can be obtained by the energy gap between the LUMO of  $A$  and of  $D$ . It can be readily calculated by using a quantum chemical calculation method. Electron coupling ( $V$ ) can be considered as direct LUMO coupling between  $D$  and



A, which is strongly dependent upon the distance between them and also on their relative orientation. Simply,  $\Delta G^\circ$  is considered as the thermodynamic driving force for the PET process.<sup>43</sup>

Photo-induced electron transfer contributes to the fluorescence quenching by nitro-aromatic explosives, which accounts for most of the fluorescence-based explosive detection.

### 1.5.1.2 Resonance Energy Transfer (RET)

In Förster Resonance Energy Transfer (FRET), energy transfer occurs between an excited donor fluorophore ( $D^*$ ) and acceptor quencher (A) *via* a non-radiative dipole-dipole coupling interaction. The excited fluorophore simultaneously returns to the ground state as depicted in Figure 1.5.

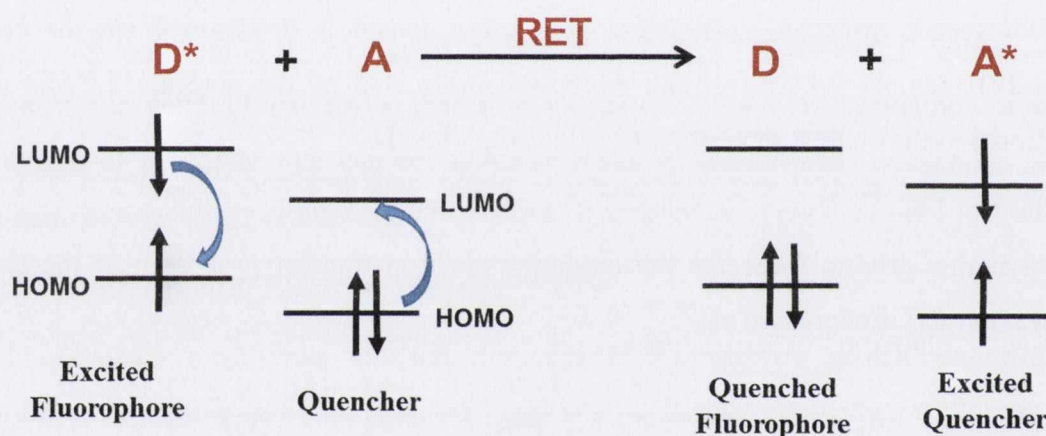


Figure 1.5: Molecular orbital schematic of Resonance Energy Transfer

According to the FRET theory, the rate of energy transfer depends on (1) the relative orientation of the donor and acceptor dipoles, (2) the extent of overlap of the fluorescence emission spectrum of the donor (the fluorophore) and the absorption spectrum of the acceptor (the analyte), and (3) the distance between the donor and the acceptor.

The efficiency (E) of energy transfer is inversely proportional to the distance between the donor and the acceptor to the power of six as shown in the following equation;

$$E = 1 - \frac{I}{I_0} = \frac{R_0^6}{R_0^6 + r_0^6}$$

where  $I$  and  $I_0$  are the relative fluorescence intensities of the donor in the presence and the absence of an acceptor, respectively;  $r_0$  represents the distance between the donor and the acceptor, and  $R_0$  is the critical distance at which energy transfer efficiency equals to 50%.

Over the last decade, the FRET process has been widely used for the detection of nitroaromatic compounds, particularly to improve the sensitivity and selectivity of the fluorophores. The mechanisms to detect trace NACs falls into two categories. The first method utilises the unique range of explosives and rationally designed fluorophore materials. Here, the emission spectrum of the fluorophore efficiently overlaps with the absorption of explosives. For example, picric acid has a different absorption spectrum from most other nitroaromatic explosives. By implementing this difference, highly sensitive and selective fluorescence sensors to detect picric acid have been developed.<sup>45, 46</sup> The second method utilises the electron-deficient properties of nitroaromatic explosives, and the subsequent formation of a Meisenheimer complex.<sup>19</sup> For example, electron-rich primary amines have been exploited as promising binding sites for TNT through a donor–acceptor interaction Meisenheimer complex.<sup>47</sup>

### 1.5.1.3 Electron Exchange (EE)

Electron exchange (Dexter interaction) is a short-range phenomenon that occurs between a donor and an acceptor. An electron in the LUMO of the donor is transferred to the LUMO of the acceptor, while the acceptor then transfers an electron back to the HOMO of the donor. This second electron comes from the HOMO of the acceptor, leaving the acceptor in an excited state. The schematic representation is shown in Figure 1.6.<sup>43</sup>

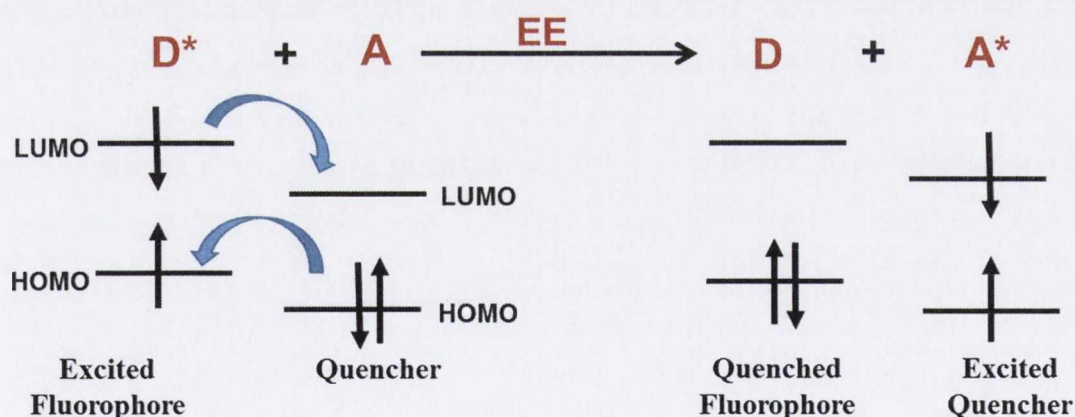


Figure 1.6: Molecular orbital schematic of Electron Exchange.

These short-range interactions fall off exponentially with distance and depend on the spatial overlap of the donor and quencher molecular orbitals, and are generally observed when the spectral overlap is small. Typically, high concentrations are necessary for significant electron exchange processes. The shapes of the absorption and fluorescence spectra of the fluorophores remain unchanged during the process. This exchange process is a quantum



mechanical effect with no analogy in classical electrodynamics.<sup>48</sup> Swager *et al.* reported on the selective detection of cyclic ketones via energy transfer, which was dominated by an electron exchange mechanism to the upper excited state of the fluorophore followed by relaxation and emission to account for the efficient energy transfer in the absence of appreciable spectral overlap.<sup>48</sup>

### 1.5.2 Fluorescence Quenching Detection

The fluorescence-quenching-based detection of explosives follows two processes; electron transfer and energy transfer where deactivation of the excited state energy of the fluorophore is observed in the presence of the quencher molecules. The quenching process occurs in two different mechanistic pathways; static quenching and dynamic quenching. Both static and dynamic quenching are simple photo-induced electron-transfer processes that occur between a fluorophore molecule and a NAC (analyte) molecule shown in Figure 1.7.

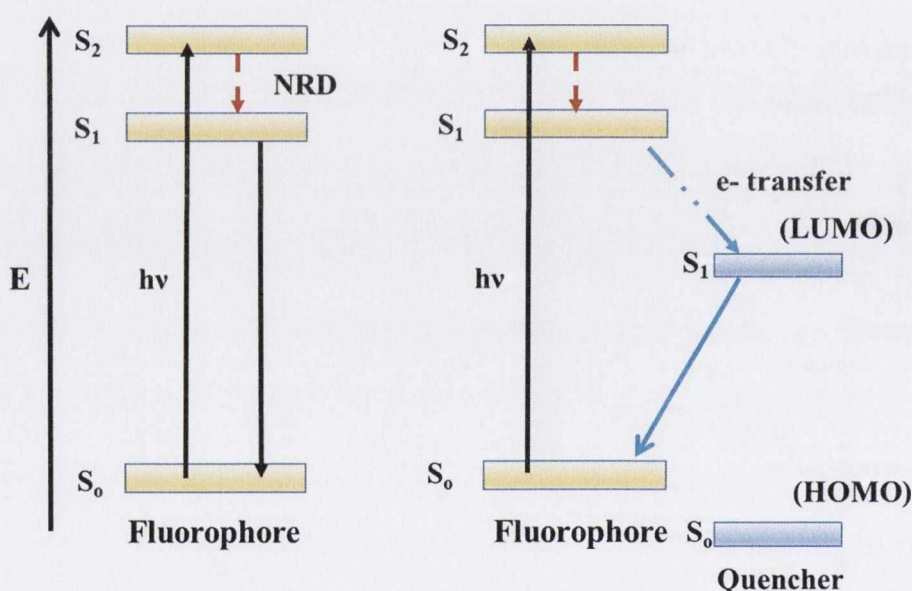


Figure 1.7: Mechanism of fluorescence quenching process. (NRD is Non radiative decay)

In general, fluorescence quenching requires molecular contact between the fluorophore and the NAC (quencher). If this contact results in complex formation, then the process is considered static quenching, whereas if contact results *via* diffusive encounter, then it is considered dynamic quenching.

Simply, if the fluorophore binds with the analyte (quencher) in the ground-state *via* the creation of a non-fluorescent electron-transfer complex formation, it results in static quenching. For dynamic quenching, an excited state electron-transfer process occurs in which



the fluorophore interacts with the analyte in the electronically excited state. These two processes can be easily distinguished by time-resolved measurements of the fluorescence decays of the fluorophores.<sup>49</sup>

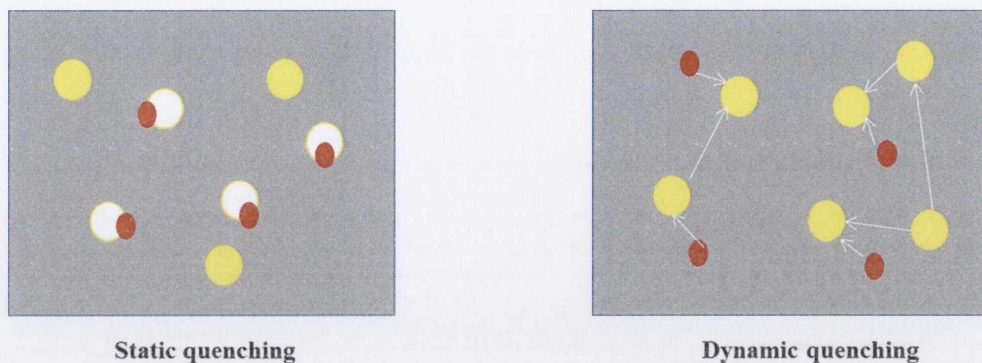


Figure 1.8: Figure depicting static and dynamic quenching processes. Yellow: fluorescent fluorophores; Red: quencher molecules; White: quenched fluorophores. With an increase in quencher concentration, the probability of associative processes and the probability of collision-based processes increase respectively.

The change in the fluorescence excited-state lifetime of the fluorophore in the absence and presence of explosive quenchers represents the simplest way to examine whether the quenching is *via* a static or dynamic process. Other prominent methods include examination of the absorption spectra of the sensing material (fluorophore). The spectrum is distorted in a static quenching process, while it remains unchanged with a dynamic quenching process. Additionally, temperature also has a direct impact on the balance of these processes. Higher temperatures lead to the dissociation of weakly bound complexes, resulting in lower amounts of fluorophore–quencher complexes *via* static quenching, whereas in dynamic quenching, the high thermal energy promotes faster diffusion leading to larger amounts of collisional dynamic quenching.

#### 1.5.2.1 Static Quenching

For static quenching, the fluorescence decay lifetime of a material will remain unchanged as the concentration of the quencher is increased. The formation of a non-fluorescent fluorophore–quencher complex is the origin of this quenching, with any molecules not bound to an analyte decaying with their intrinsic lifetime. In this process, though the steady state emission intensity of the fluorophore solution decreases, the lifetime of unbound fluorophores is not affected. The ratios of lifetime, expressed as  $\tau_0/\tau = 1$  when plotted *versus* the quencher

concentration. Here,  $\tau_0$  and  $\tau$  are the lifetimes of the fluorophore in the absence and presence of a quencher, respectively.

### 1.5.2.2 Dynamic Quenching

For dynamic quenching (collisional quenching), the collision of quencher molecules against the excited fluorophores is a necessary requirement, and therefore dynamic quenching is a diffusion controlled process. The fluorophore and the quencher are unbound, with quenching occurring when a photo-excited fluorophore interacts briefly with a colliding analyte molecule. This collision results in a direct decrease in the average fluorescence lifetime. For dynamic quenching, fluorescence intensity, expressed as  $I_0/I = \tau_0/\tau$  where  $I_0$  is the emission intensity in the absence of quencher and  $I$  is in the presence of incremental amounts of quencher ( $I$ ).

The kinetics of the above two intermolecular deactivation processes can be represented by a simple relationship *via* the Stern-Volmer equation.

### 1.5.2.3 Stern-Volmer Equation

The Stern-Volmer equation is a straight line equation, where the quenching rate constant,  $K_Q$  can be easily determined. If the two fluorescence intensities,  $I_0$  and  $I$  are measured, and the resulting ratio of emission intensities ( $I_0/I$ ) are plotted as a function of quencher concentration  $[Q]$ , the resulting graph (called a Stern-Volmer plot) will have an intercept of 1, and a slope called the Stern-Volmer constant,  $K_{SV}$ .  $K_{SV}$  is the product of the natural radiative lifetime, incorporating both  $\tau_0$  and the bimolecular quenching rate constant ( $k_q$ ). Knowing the value of the slope, and the natural radiative lifetime allows for the simplistic calculation of the quenching rate constant.

In a static quenching process, the dependence of the fluorescence intensity upon  $[Q]$  is derived by considering the association constant for complex formation, and the equation is shown;

$$\frac{I_0}{I} = 1 + K_S[Q]$$

where,  $K_s$  is the Stern–Volmer constant for the static quenching process.

Whereas in dynamic quenching, the dependence of the fluorescence intensity upon  $[Q]$  and lifetime,  $\tau_0$ , is derived by considering the extent of collision and the equation is shown;



$$\frac{I_0}{I} = 1 + K_q \tau_0 [Q] = 1 + K_D [Q]$$

where,  $K_D$  is the Stern-Volmer constant for the collision quenching process.

For systems where both dynamic and static quenching processes occur concurrently, the Stern-Volmer equation is given by,

$$\frac{I_0}{I} = (1 + K_D [Q])(1 + K_S [Q]) = 1 + (K_D + K_S)[Q] + K_D K_S [Q]^2$$

At lower quencher concentrations  $[Q]$ , the contribution of  $[Q]^2$  is less prominent resulting in linear plot, while at higher concentrations, the plot deviates from linearity and bends upwards.

It was observed experimentally that in general, static quenching occurs more commonly than dynamic processes in explosive detection. This is due to the larger  $K_{SV}$  for explosive molecules binding to many polymeric sensors. In spite of an apparent potential to lead to faster and more reversible detection, dynamic quenching processes possess much smaller  $K_{SV}$  values and suffer from a lower sensitivity.<sup>50</sup>

## 1.6 Fluorescent Compounds for Explosive Detection

A wide variety of  $\pi$ -electron-rich sensors including small-molecule fluorophores, conjugated organic/inorganic polymers, metal-organic frameworks (MOFs) and dendrimers have been specially developed for NAC detection.<sup>51-61</sup> Among all of these, conjugated polymers are considered to be the most promising materials due to their high sensitivity.<sup>62-64</sup> Despite this, the applications of conjugated polymeric sensors are limited due to their unfavourable multi-step synthesis, and poor molecular organization. In comparison, small molecule-based fluorescent sensors offer facile and straightforward synthesis, easy purification, satisfactory reproducibility, and high quantum yields.<sup>65</sup> One attractive advantage is the ability to achieve facile chemical modification by introducing specially chosen functional groups to increase the sensing selectivity and sensitivity. Moreover, unlike MOFs (metal organic frameworks) and many polymers, small molecule-based sensors are typically soluble in common organic solvents, allowing for easy fabrication towards practical application and use. In general, turn-on fluorescent sensors for explosive detection are appealing because analyte binding leads to a significant enhancement of emission intensity, and thus sensing may be easily visualized by the naked eye.<sup>66</sup> However, the design of turn-on fluorescent sensors has proven to be massively complicated, and appear limited for real-time use due to their very small Stokes



shift and lack of reversibility. Therefore, in recent years research interest has concentrated on the design of turn-off fluorescent sensors.<sup>67, 68</sup>

### 1.6.1 Chemical Sensors: Polymers

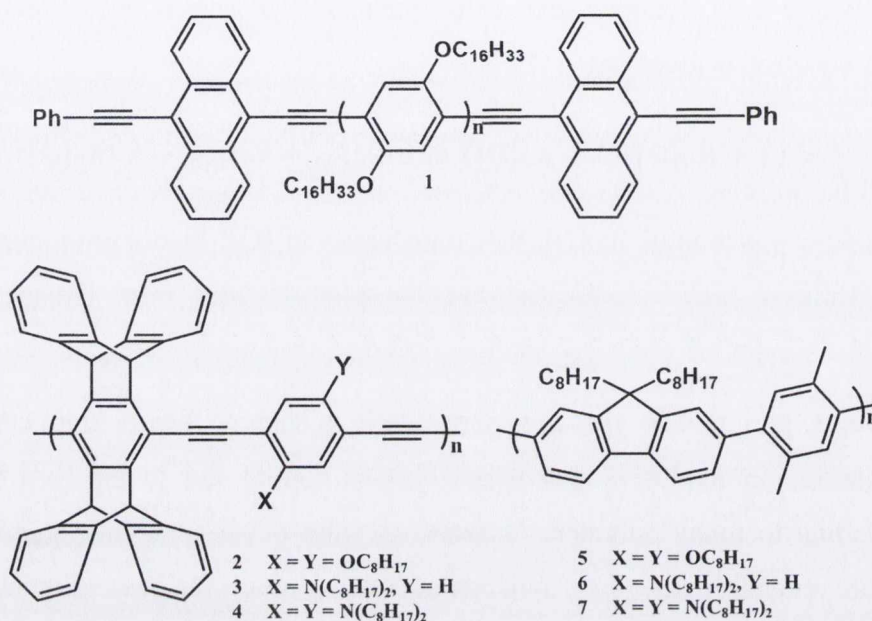


Figure 1.9: Amplifying conjugated polymers for nitroaromatic sensing.<sup>62</sup>

Several  $\pi$ -electron rich conjugated covalent polymers have been reported as promising candidates for explosive sensing, with particular sensitivity towards TNT detection. Some of these are shown in Figure 1.9. The high sensitivity of these conjugated polymers often comes from the so-called “signal amplification effect”, where the polymer backbone acts as a molecular wire to enable the rapid long range exciton migration.<sup>69</sup>

However, the real-time utilization of these polymeric materials is limited for several reasons. Firstly, the traditional covalent synthesis of organic polymers involves several multi-step syntheses. These syntheses are time consuming, and usually result in low yields of the target compounds. Secondly, there is poor synthetic control of the molecular organization or structure determination. This is compounded by issues of poor solubility.<sup>70</sup>

### 1.6.2 Chemical Sensors: Small Molecule Based Sensors

In very recent years, a plethora of small molecule-based fluorescent chemosensors have been designed, synthesized and employed successfully for NAC detection, both in solution and in the vapor phase. Although several articles highlighting the nitroaromatic sensing ability of various materials have been reported recently, this thesis is dedicated to the sensing of NACs by  $\pi$ -electron-rich small molecule based fluorescent sensors incorporating a fluoranthene

moiety. In the next chapters, this thesis aims to provide an overview of fluorescent turn-off chemosensors with particular emphasis given to poly-(hetero)cyclic aromatic hydrocarbons for nitroaromatic explosive detection.<sup>71</sup>

### 1.6.2.1 Pyrene Based Sensors

Pyrene and its derivatives have drawn substantial attention recently as fluorescent tags and probes in various applications. This is due to their interesting photo-physical properties, high stability and planar aromatic surface which tend to form strong charge transfer complexes with electron-deficient analytes (Figure 1.10). In 2001, Goodpaster *et al.* and McGuffin *et al.* demonstrated the phenomenon of selective fluorescence quenching of free pyrene **8** as an indirect detection method in combination with mass-spectrometry/gas chromatography for TNT and its derivatives.<sup>72</sup> The free pyrene **8** showed selective fluorescence quenching for NACs with Stern–Volmer quenching constants of  $K_{SV} = 307\text{--}394\text{ M}^{-1}$ . Following this, a series of pyrene based sensors were reported for NAC sensing studies by Chen *et al.* (**9**),<sup>73</sup> Mukherjee *et al.* (**10–12**),<sup>74</sup> Venkatramaiah *et al.* (**13 & 14**)<sup>75</sup> and Fang *et al.* (**17**).<sup>76</sup> Quenching constants have since increased to values of  $K_{SV} = 4.0 \times 10^6\text{ M}^{-1}$  for the thione containing pyrene **16**.<sup>77</sup>

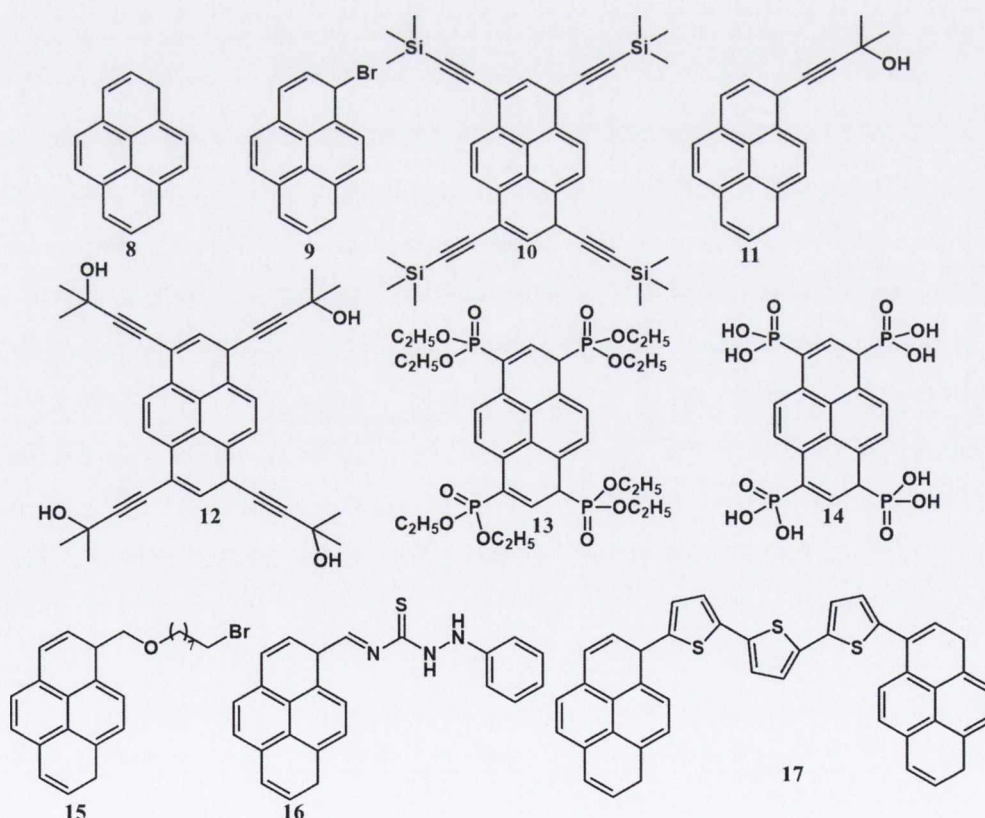


Figure 1.10: Pyrene derivatives utilised towards nitroaromatic sensing.



### 1.6.2.2 Triphenylamine Based Sensors

The freely rotatable C–N single bonds and non-planar nature of triphenylamine (TPA) helps derivatives form unique supramolecular organic electronic materials. In particular, the aggregation-induced emission provides large internal voids for the excitons to migrate within these systems<sup>78</sup>.

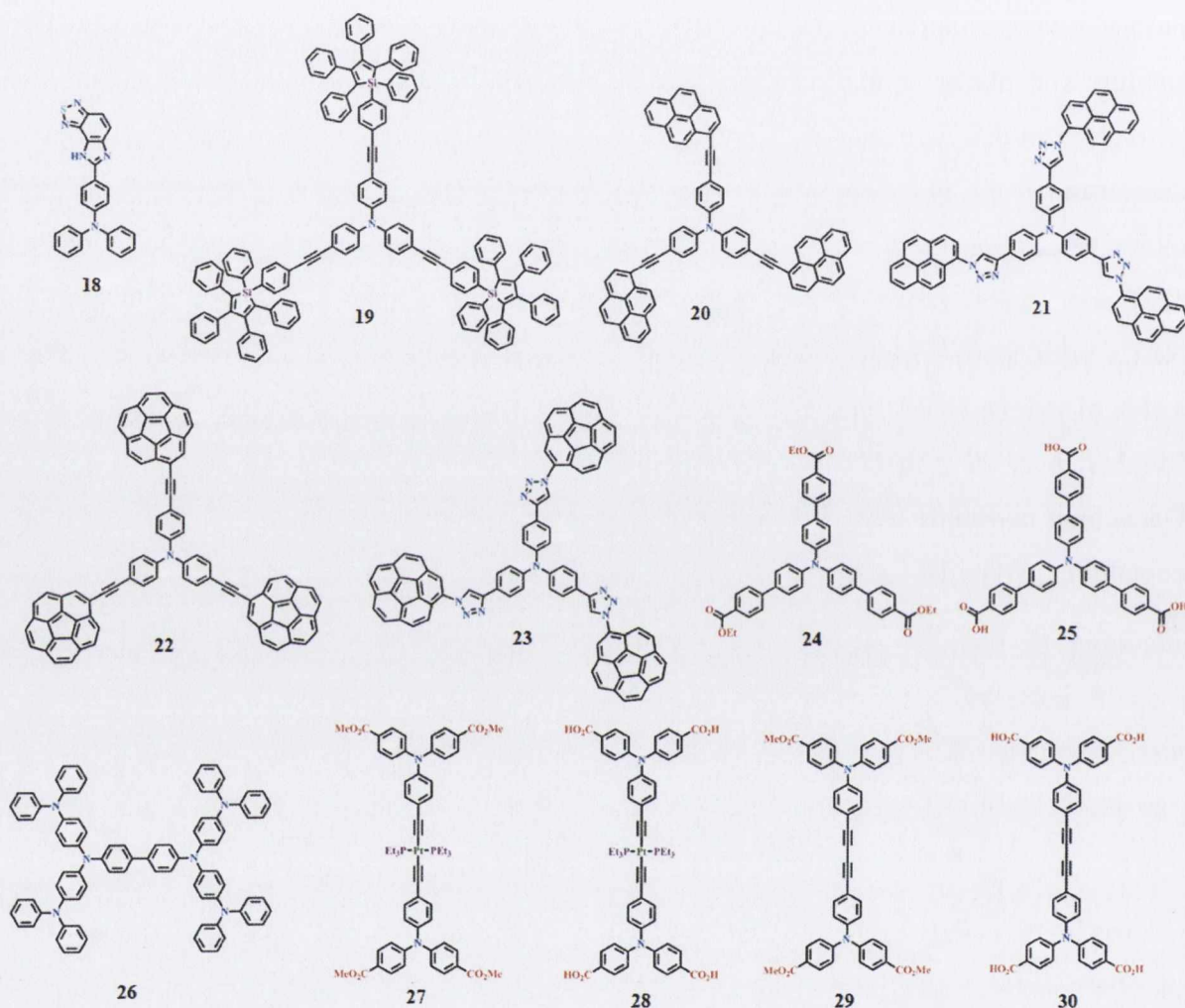


Figure 1.11: Triphenylamine derivatives utilised towards nitroaromatic sensing.

Molina *et al.* synthesized a novel TPA-based sensor, **18**, substituted with an imidazobenzothiadiazole moiety and used it to selectively detect NACs, with a discriminating ability between phenolic and non-phenolic NACs (Figure 1.11). The emission titration showed that **18** formed a 1:1 complex with picric acid (PA) and the calculated binding constant was  $K_a = 4.49 \times 10^3 \text{ M}^{-1}$ . According to a  $^1\text{H}$  NMR titration study, it was concluded that the presence of the –OH group in phenolic-NACs became involved in hydrogen-bonding interactions with



**18.** This, coupled with a strong  $\pi$ - $\pi$  stacking interaction with the TPA fluorophore, resulted in discriminating sensing behavior between phenolic and non-phenolic NACs<sup>79</sup>.

Similar tests were carried out with other TPA-derived sensors. In Figure 1.11, **19** showed a “propeller-like” shape due to the peripheral siloles, and its fluorescence was quenched upon the addition of PA even at the trace value of 1 ppm. In 2012, Sukwattanasinitt *et al.* designed a series of triskelion-shaped TPA based sensors **20-21** with pyrene, and corannulene **22-23** fluorophores.<sup>58</sup> These were found to be selective to TNT. Sensors **24** and **25** showed strong blue emission in a THF solution at 455 and 450 nm, and their quenching efficiencies wrt PA were found to be 82 % and 95 % respectively, with detection limits of 40 ppb for **24** and 5 ppb for **25**.<sup>80</sup> Zade *et al.* reported an extended  $\pi$ -conjugated TPA-based dumbbell shaped sensor **26** which showed a superior efficiency of 98% in the presence of 30 equivalents of PA and the detection limit was found to be 433 ppb.<sup>81</sup> Recently, Mukherjee *et al.* synthesized fluorophores **27-30** towards various NAC detection, both in solution as well as in the vapour phase.<sup>82</sup> Interestingly, **29** and **30** which contain carboxylic groups showed a better quenching response upon exposure to the nitrobenzene vapors over **27** and **28**. This was ascribed to the long-exciton migration through intermolecular interaction along the molecular backbone.

### 1.6.3 Polyaromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are one of the most widely studied classes of compounds in organic and material chemistry.<sup>83</sup> They are considered as two-dimensional graphitic segments composed of  $sp^2$ -hybridised carbons. They are widely found in the pollutant residues of domestic and natural combustion of coal, wood, and other organic materials,<sup>84</sup> and have even been found in interstellar space. Extended  $\pi$ -conjugation enables extensive delocalisation throughout the graphite-like discs. This, coupled with their high thermal and chemical stability, makes these highly conjugated systems excellent materials for use in optoelectronic devices,<sup>85-87</sup> and explosive sensing.<sup>18</sup> Anthracene, phenanthrene and acenaphthene (Figure 1.12) are the smallest PAH-based systems and have been extensively investigated towards their application in photochemistry, particularly in the field of molecular sensing.

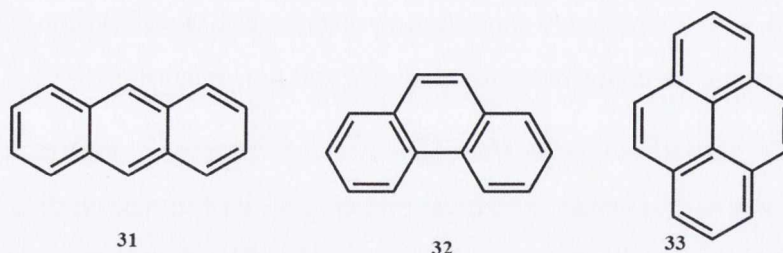


Figure 1.12: Simple PAH systems- anthracene **31**, phenanthrene **32**, pyrene **33**.

The pioneering contributions to the development of all carbon aromatic frameworks, based upon a central benzene ring around which other phenyl groups could be extended, was initially investigated by R. Scholl and E. Clar.<sup>19</sup> In their works, a correlation between the size and topology of the large aromatic systems and their electronic properties was observed. Difficulties in obtaining synthetic control over the structures of the PAHs, along with the harsh conditions required for their synthesis meant that systematic studies of larger PAH based systems were difficult. Despite their complexity, many have been fully characterized thanks to advances made in analytical techniques over recent years. More recently, many selective synthetic routes to PAHs using mild reaction conditions have emerged.<sup>88</sup>

These PAHs can be subdivided into two classes; alternant and non-alternant PAHs. Alternant PAHs comprise only six-membered rings like hexabenzocoronenes whereas non-alternant PAHs contain aromatic rings of varying size like fluoranthenes.

#### 1.6.3.1 Alternate PAH: Hexabenzocoronenes

Possibly the best known example of an alternant PAH is hexa-*peri*-hexabenzocoronene (HBC), an aromatic molecule consisting of 13 fused six-membered rings. HBC is highly symmetric and stable. The extensive electron delocalisation over its large  $\pi$ -conjugated network is analogous to the delocalisation of electrons within a benzene ring. It was this similarity to benzene that prompted researchers to call HBC “superbenzene”. Due to their planar, highly rigid and discotic core unit, they have been attracted tremendous interest in the area of materials and supramolecular chemistry.<sup>89</sup>

Unfortunately, their potential as fluorescence sensors for the trace detection of analytes is limited due to their aggregation in solution which causes fluorescence quenching through facile  $\pi$ - $\pi$  stacking interactions. One way to overcome the problem is to introduce sterically demanding functional groups which in turn, decreases the effective  $\pi$ - $\pi$  stacking between adjacent HBC moieties. Following this approach, Bhalla *et al.* synthesized HBC based fluorophores **34** and **35** with bulky *tert*-butyl groups to prevent self-quenching in solution<sup>90</sup>.



These compounds showed aggregation-induced fluorescence enhancements in THF on the addition of 40% H<sub>2</sub>O. This was attributed to the locking of phenyl group free-rotations in the mixed aqueous media. Later, the enhanced emissions of both **34** and **35** were quenched drastically in the presence of PA in THF–H<sub>2</sub>O medium resulting in quenching efficiencies of nearly 67% for **34** and 96% for **35**. A static quenching mechanism was observed in **34** *via* hydrogen bonding interactions between –OH of PA and –NH<sub>2</sub> in **34**, while a charge-transfer quenching mechanism was observed in **35** due to the lack of hydrogen-bonding interactions. Also, a triptycene-based 3D nanographene **36** bearing three HBCs was shown in Figure 1.13 which is used as a selective fluorescent sensor for PA.<sup>17</sup>

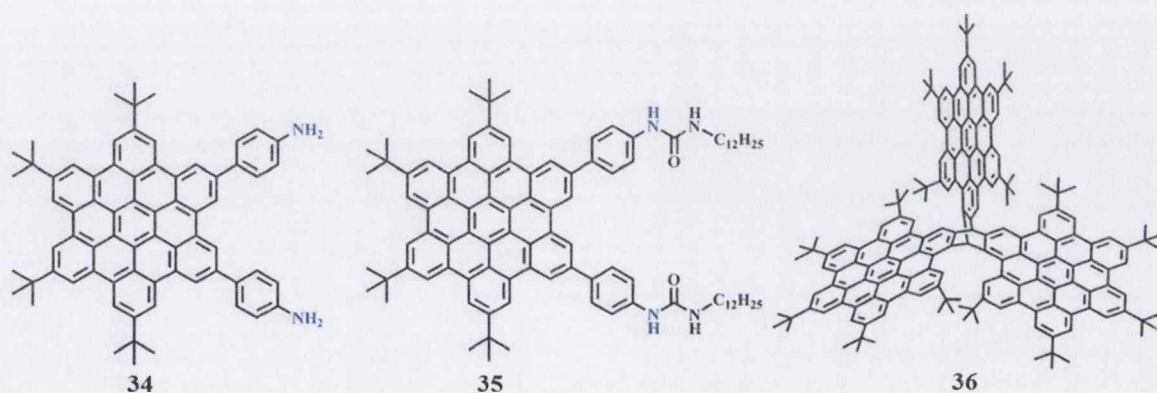


Figure 1.13: HBC systems used for nitroaromatic sensing.

#### 1.6.3.2 Non-Alternate PAH: Fluoranthenes

Fluoranthenes are non-alternant PAHs first discovered by Dumas and Laurent in 1835, and are widely found in emissions from burning of fossil fuels such as coal. It is for this reason that fluoranthenes were initially extracted from coal tar by distillation. The basic fluoranthene structure contains a benzene ring fused to a naphthalene moiety, by a five membered ring. The compound now known as fluoranthene was fully isolated as part of concurrent work undertaken by Goldschmiedt, Fittig and Gebhard.<sup>91, 92</sup>



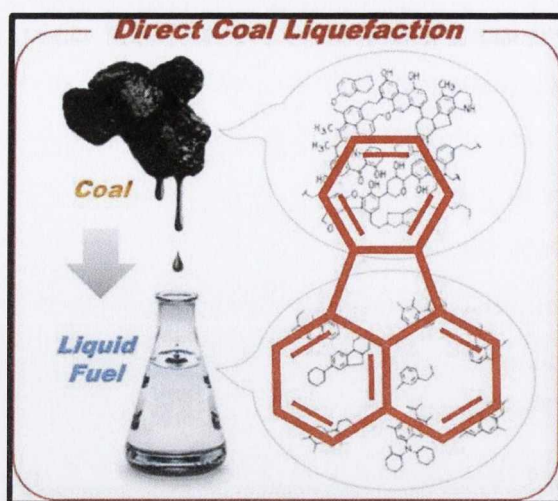


Figure 1.14: Fluoranthene structure and extraction summary<sup>93</sup>

## 1.7 Applications of Fluoranthenes

Fluoranthene segments are highly fluorescent in nature and this property can be further enhanced using polyphenylene-derived fluoranthenes which are promising scaffolds for the development of effective materials for light emitting devices, dye-sensitized solar cells (DSSCs), field effect transistors, and fluorescent sensors.

### 1.7.1 Fluoranthene for Organic electronics application

Fluorescent materials for organic light-emitting diodes (OLEDs)<sup>94,95</sup> and DSSC applications need to exhibit high solid-state luminescence and charge carrier-mobility, good thermal and oxidative stability, excellent film formation, morphology and colour purity. OLEDs can exhibit broad emission spectra that completely cover the visible region (wavelengths between 400 to 700 nm)<sup>96</sup> and many fluorescent materials emitting between 500 to 700 nm (green and red regions) have been used in this application.<sup>97, 98</sup> A variety of deep blue emitters, which typically have a simple core structure, such as anthracene,<sup>99</sup> fluorene,<sup>100</sup> pyrene,<sup>101</sup> triphenylenes,<sup>102</sup> and fluoranthene,<sup>103</sup> have been developed. As potential OLED candidates,<sup>104, 105</sup> fluoranthenes often exhibit extensive  $\pi$ -electron delocalisation, as exemplified by HBC, formed by oxidative cyclodehydrogenation of polyphenylene precursors.<sup>106</sup> Depending on the functionalisation of the fluoranthene core, the luminescence of the compounds can be finely tuned to cover a wide range of wavelengths. Fluoranthene-based asymmetric organic cyanine (**40**) has been developed as the absorbing layer in a DSSC exhibiting a solar energy to electricity conversion efficiency of 9.3%. As examples of specific application, Fluoranthene derivatives of benzo[k]fluoranthene-based linear acenes (**37-39**)

have been employed in electroluminescent device fabrication, as the emissive layer, to give the efficient deep blue fluorescent OLEDs shown in Figure 1.15.<sup>107</sup>

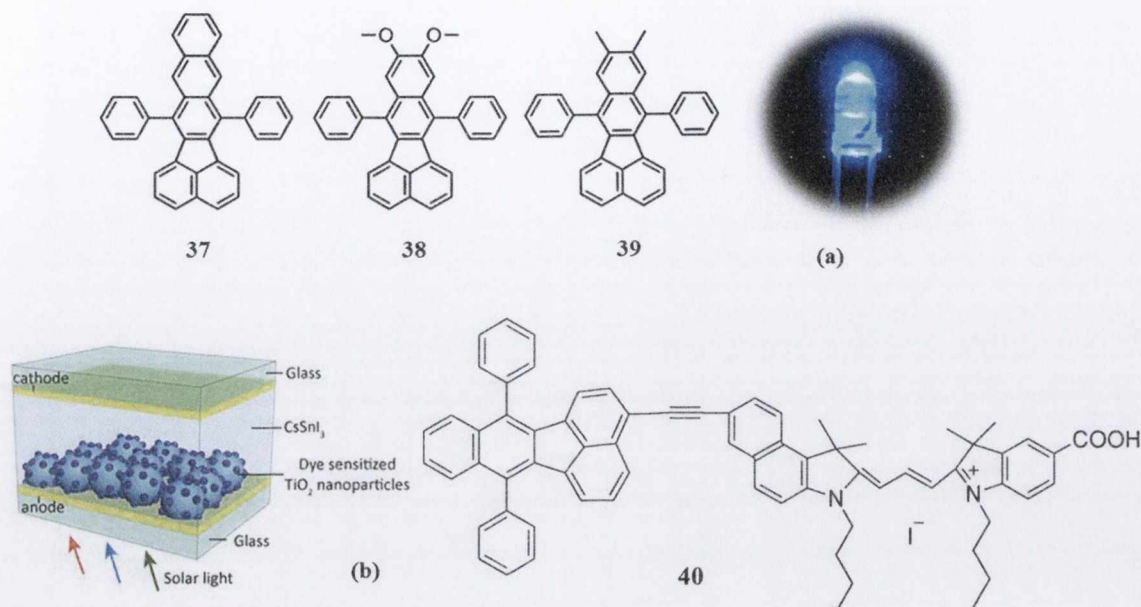


Figure 1.15: (a) Fluoranthene based derivatives **37**, **38** and **39** for OLED application and (b) Carboxylic functionalized fluoranthene **40** for DSSC application.<sup>107</sup> Inserts show bright blue fluoranthene LED and blue fluoranthene dyes in a typical solar cell set-up.

### 1.7.2 Fluoranthene Sensors for Nitroaromatic Detection

Similar to pyrene, fluoranthene and its derivatives have attracted considerable attention in recent years owing to their strong fluorescence, with small Stokes shifts and their potential applications in organic light emitting materials. Harnessing these qualities has allowed fluoranthene-based materials to be employed as sensors in the detection of explosive debris (Figure 1.16).



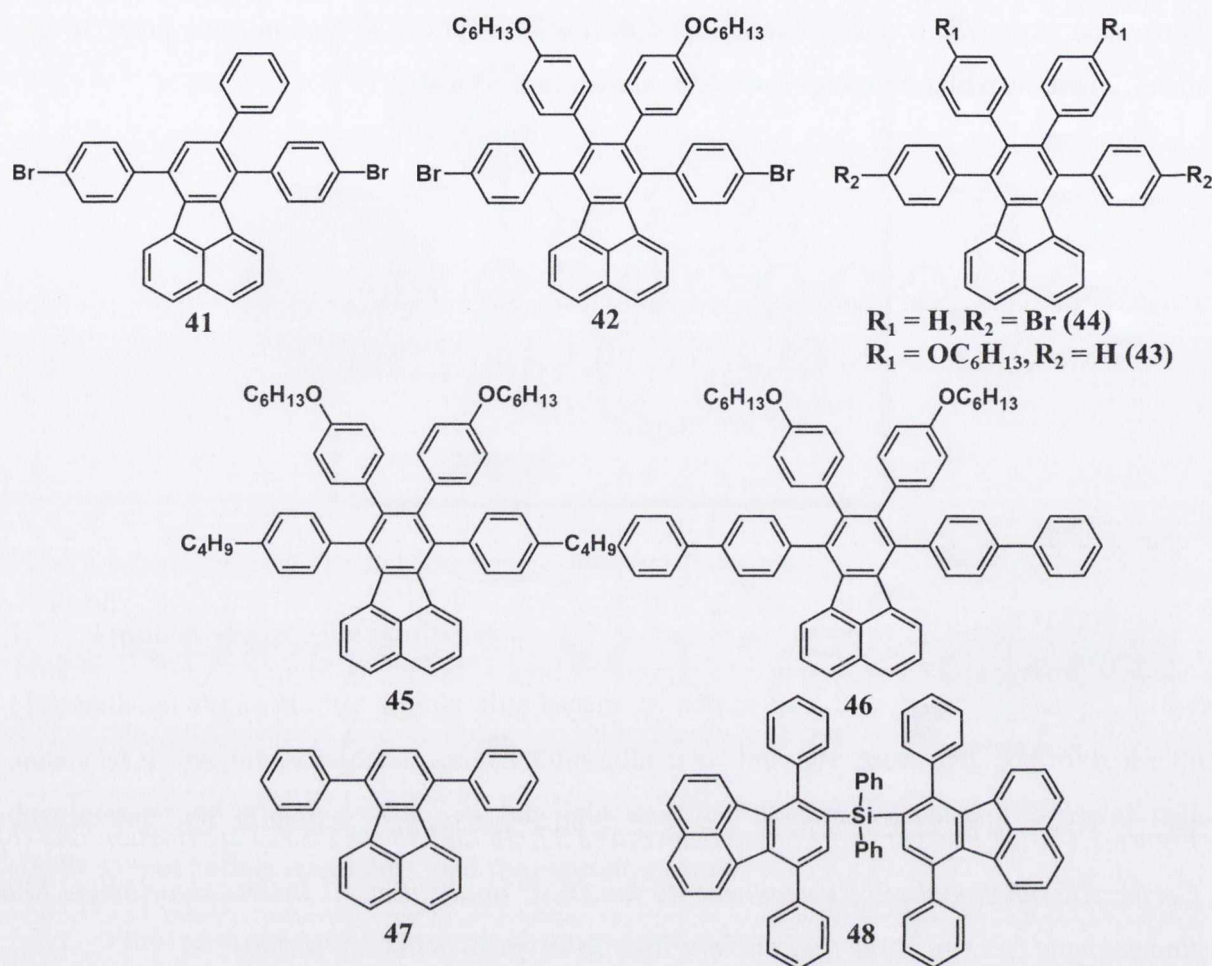


Figure 1.16: The structures of Fluoranthene derivatives that have been used as NAC sensors.

In 2012, Patil *et al.* used a  $\pi$ -electron-rich asymmetric fluoranthene **41** and a symmetric fluoranthene **42** for the selective detection of NACs. The unsymmetrical phenyl moiety in **41** aided the self-association of the fluoranthene-analyte *via*  $\pi$ - $\pi$  interactions to form a 1D-supramolecular arrangement in the solid-state, through a layer-by-layer self-assembly. In contrast the solid-state packing of **42** revealed a Z-shaped supramolecular arrangement stabilized by strong C-H $\cdots\pi$  interactions. The two sensors showed a 76% and an 80% quenching efficiency in the presence of 10  $\mu$ M and 0.1 mM concentration of PA respectively.

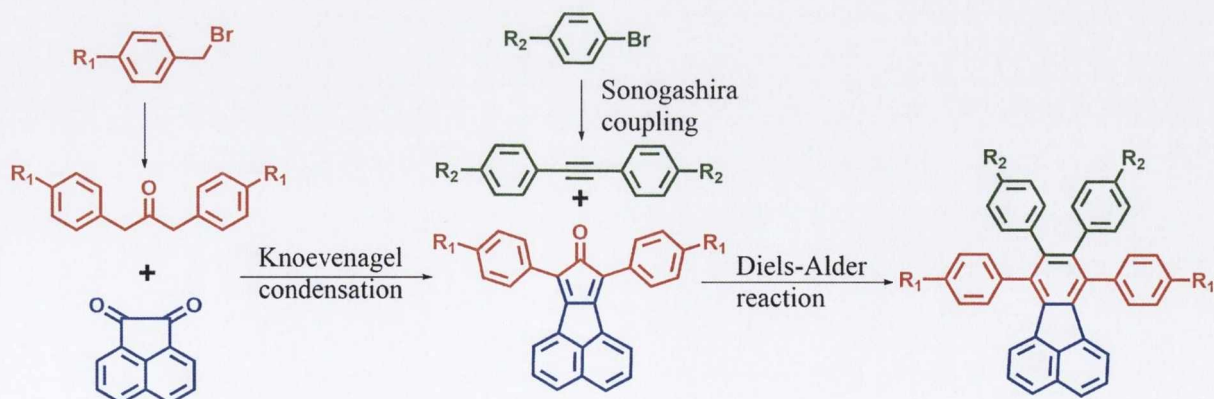
In 2013, the same group demonstrated the sensing ability of a series of fluoranthene derivatives (**44–46**).<sup>108</sup> The presence of alkoxy ( $-OC_6H_{13}$ ) chains on phenyl rings in **44–46** enhanced the solubility of these materials in common solvents and induced enough flexibility to give them unique supramolecular arrangements in the solid-state. Attachment of bulky phenyl moieties on the surface of the fluoranthene core prevents the self-aggregations *via*  $\pi$ - $\pi$  interactions in solution and maintains their photo-stability. All of the fluoranthene derivatives in Figure 1.16 showed a strong blue-emission at  $\lambda = 475$  nm, with a fluorescence lifetime in



the range 8.23 –11.87 ns. The calculated quenching constants of the sensors with PA follow the order **46** > **45** > **44** > **43**. Notably, no pronounced quenching was observed upon the addition of other electron deficient non-nitroaromatics, implying the high selectivity of these sensors for NACs. Furthermore, the initial emission intensity of the generated thin films gradually decreased as a function of the exposure time to saturated vapors of NACs. Xie *et al.* have synthesized two other fluoranthene-based sensors; non-silicon containing 7,10-diphenyl-fluoranthene (**47**) and silicon containing bis(7,10-diphenyl-fluoranthene)diphenylsilane (**48**). These sensors indicated the presence of nitrobenzene *via* fluorescence quenching at trace amounts as low as 100 ppm, and 50 ppm respectively. The quenching efficiency of **48** was found to be higher than **47** and this is directly attributable to its structure. The presence of “V” shaped non-coplanar tetrahedral structure restricts its aggregation and enhances the  $\pi$ - $\pi$  interactions between **48** and NACs.

### 1.7.3 General Synthesis of Fluoranthene based molecules

Fluoranthene-derived polyphenylenes are synthesized by a four step reaction. The single [2+4] Diels-Alder cycloaddition of generated diarylcyclopentadienones (diene) with an arylacetylene (dienophile) is a well-established method for the controlled synthesis of poly-aryl fluoranthenes (Scheme 1.1).<sup>109</sup> By altering the phenyl groups in the alkyne precursor, the size and dimensions of the poly-substituted product can be altered. The cyclopentadienone derivatives are prepared *via* a double-Knoevenagel condensation<sup>110</sup> from acenaphthenequinone and the requisite ketone under basic conditions in MeOH/EtOH, and the desired phenyl-containing mono-ketones are either purchased, or prepared by Fe(CO)<sub>5</sub>-mediated couplings of the corresponding benzyl bromides.<sup>111</sup>



Scheme 1.1: General synthetic route to fluoranthenes.

Draper *et al.* have successfully incorporated nitrogen atoms into the periphery of graphitic molecules such as HBC, leading to the formation of a family of compounds known as the nitrogen heterosuperbenzenes (N-HSBs).<sup>112</sup>

The incorporation of electroactive imines on the periphery of the carbon framework changes the electronic properties, and enhances the  $\pi$ -electron mobility within the molecules. It has been shown that the inclusion of nitrogen atoms reduces the band gap and therefore the need for extensive aromatic platforms, and simultaneously induces ligand-functionality in the formation of metal-based fluorescent materials. The presence of peripheral nitrogen atoms can cause synthetic difficulties which can be overcome by using a family of nitrogen-containing ligands based on the smaller pre-fused PAH-like fluoranthene. These novel N-fluoranthenes are prepared with the desired nitrogen atoms incorporated into the diarylacetylene. The reduction in size of these molecules improves their solubility, making characterization easier, and the incorporation of a pre-fused moiety potentially renders cyclodehydrogenation unnecessary.<sup>113</sup>

In this work the synthesis of a novel range of hetero-substituted fluoranthenes, comprising four fused rings alongside planar substituents is presented. The effects of substitution on their photophysical characteristics are explored. The large  $\pi$ -electron delocalisation character, and optical properties of these hetero-fluoranthenes, meant they could be studied for use and application in NAC sensing.<sup>108, 114</sup>

## 1.8 Aims

Draper *et al.* pioneered the development of nitrogen containing hexa-superbenzenes (N-HSBs). They were able in early work to show how this unique class of compounds exhibits interesting optical and electronic properties with potential applications in field-effect transistors, as light emitting layers in organic light emitting diodes (OLEDs) or photovoltaic devices. The research described in this thesis aimed to synthesise a library of novel N-containing fluoranthene compounds suitable as novel chemosensors for selective PA-based explosive sensing studies.

It details the generation of the first nitrogen substituted fluoranthenes and provides initial structure-property relationships in the application of these molecules towards nitroaromatic sensing.

This volume of work aims to prepare four series of nitrogen-containing fluoranthene polyphenylenes as potential chemosensors and to study the effect of varying degree of

nitrogen loading and peripheral substitution. It builds on the earlier synthetic work of Dr. Sarath Perara and Dr. Pablo Fernandez within the Draper group.<sup>115, 116</sup>

This work provides the novel fluoranthenes which were fully characterised using a range of NMR techniques, high resolution mass spectrometry, single crystal X-ray diffraction studies and elemental analysis and gives preliminary data which it is hoped can feed back into synthetic methodologies to tailor future optimised materials with the ultimate goal of enabling a real-world working device.





**2. Nitrogen Substituted *Tert*-Butyl Fluoranthenes**





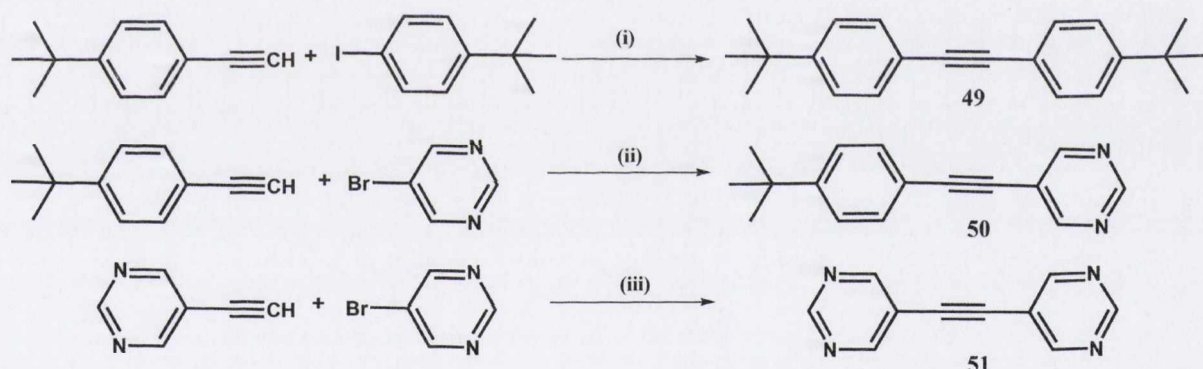
## 2.1 Introduction

In this chapter, two novel hetero-substituted fluoranthenes are presented and their all-carbon control compound. These systems comprise of four fused rings alongside planar substituents. Detailed studies into the effects of nitrogen-substitution on their photophysical characteristics, and their use as explosive chemosensors with particular emphasis on picric acid are also carried out.

## 2.2 Synthesis of N-Substituted *Tert*-Butyl Fluoranthenes

### 2.2.1 Preparation of Synthetic Precursors

The preparation of the nitrogen-substituted *tert*-butyl fluoranthene derivatives **55-57**, requires the initial assembly of the key synthetic dienone precursor, 7,9-bis(4-*tert*-butyl)phenyl)-8H-cyclopenta[*a*]acenaphthylene-8-one **54**. The appropriate acetylene precursors **49-51** shown in Scheme 2.1 for the Diels Alder [2+4] cycloaddition were synthesised previously in the Draper group through the conventional palladium-catalysed Sonogashira cross coupling procedure.<sup>116</sup>

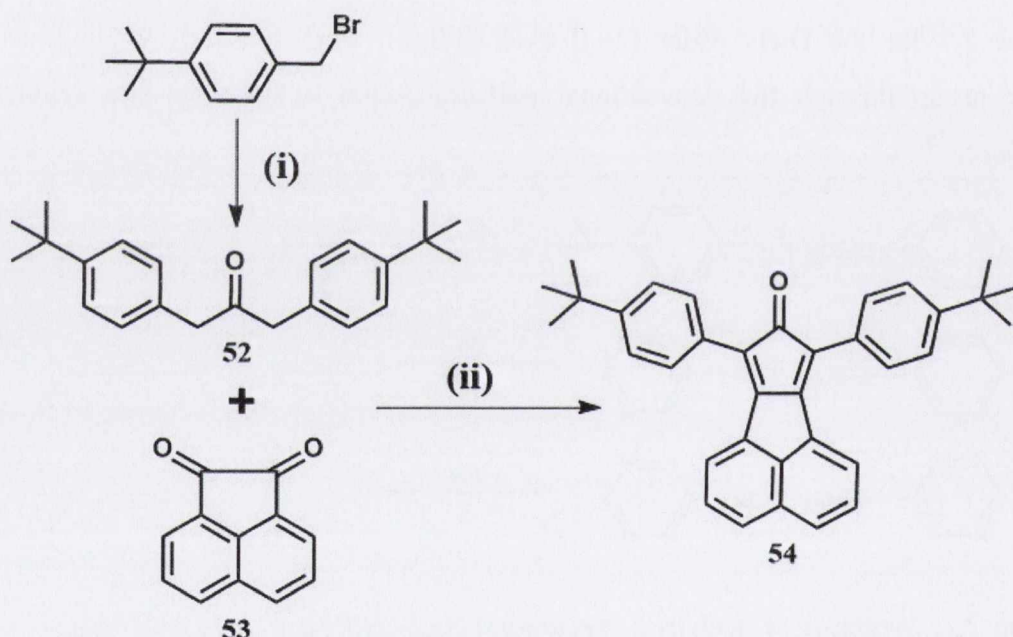


Scheme 2.1: Synthesis of acetylene precursors. (i)  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (10 mol%),  $\text{CuI}$  (5 mol%),  $\text{DMF:DIPA}$  (1:3), 65 °C, 5 h, 85% (ii)  $\text{Pd}(\text{PPh}_3)_4$  (2 mol%),  $\text{CuI}$  (2 mol%),  $\text{DMF:DIPA}$  (1:3),  $\mu\text{w}$  150 W, 115 °C, 25 min, 88% (iii)  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (2 mol%),  $\text{CuI}$  (2 mol%),  $\text{PPh}_3$ ,  $\text{DMF:DIPA}$  (1:3), 6 h, 71%.

Palladium-catalysed Sonogashira coupling reactions between the 4-*tert*-butylphenyl acetylene and 4-*tert*-butyl iodoacetylene generates **49**, whereas reaction with 5-bromopyrimidine gives **50**. The microwave mediated reaction involved, the addition of  $\text{PPh}_3$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$  (2 mol%) and  $\text{CuI}$  (2 mol%) to the starting materials followed by irradiation at 150 W at 120 °C for 25 min.<sup>117</sup> After cooling, the brown suspension was extracted with  $\text{Et}_2\text{O}$ , followed by the washing of the organic layer with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , and a final wash with water. The organic layer was dried over  $\text{MgSO}_4$  and concentrated *in vacuo* to obtain **49**

as off-white crystals. Compound **50** was prepared in a similar manner. Gourdon *et al.* reported this convenient method to synthesise pyrimidyl based aryl-acetylenes.<sup>117</sup> Purification of the two acetylene ligands was achieved by column chromatography on silica using hexane:dichloromethane (2:1 v/v) as the eluent. The product **49** was obtained as an off-white solid in 85% yield, whereas **50** was obtained in an 88% yield. The acetylene **51** was synthesised using a two-step literature procedure with 71% yield.<sup>118</sup>

The generated diene precursor, an aryl-substituted cyclopentadienone, 7,9-bis(4-(*tert*-butyl)phenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one **54**, was obtained *via* a Knoevenagel condensation reaction<sup>119</sup> between *tert*-butyl monoketone **52**<sup>111</sup> and the commercially available acenaphthenequinone **53** in EtOH with a catalytic amount of KOH (Scheme 2.2). The deliberate incorporation of tertiary butyl groups was to improve solubility.



Scheme 2.2: Synthetic route to the cyclopentadienone, **54**; (i)  $\text{Ca}(\text{OH})_2$ ,  ${}^t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$  (1:1 v/v), RT, 6 h, 74% (ii) KOH,  $\text{C}_2\text{H}_5\text{OH}$ , 80 °C, 45 min, 86%.

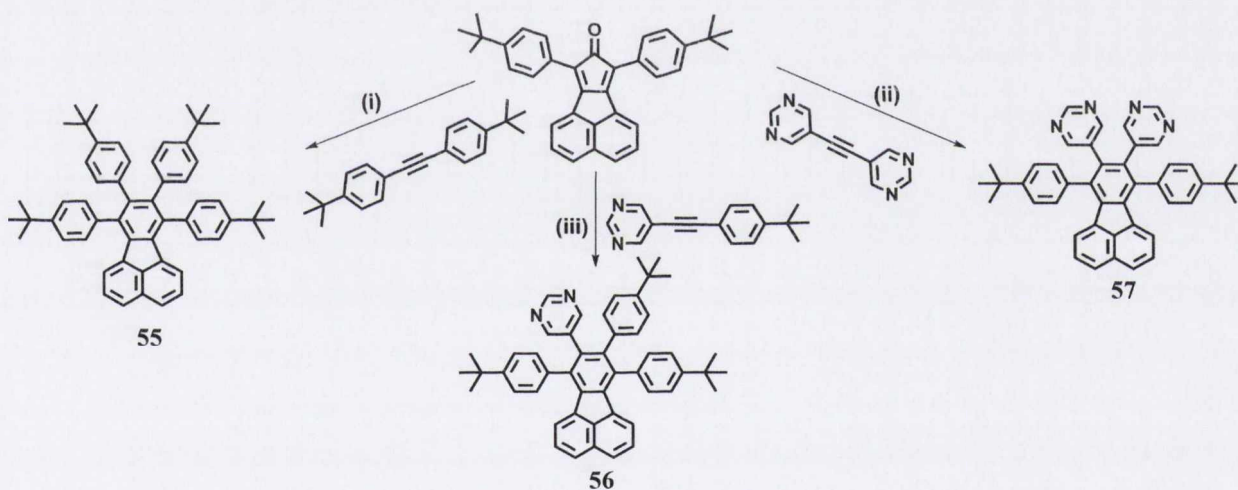
The *tert*-butylphenyl substituted monoketone **52** and the tetraarylcyclopentadienone **54** have been synthesised previously in the Draper group.<sup>112</sup> The monoketone, 1,3-bis(4-*tert*-butylphenyl)propan-2-one **52** was prepared *via* a liquid-liquid phase-transfer carbonylation reaction, with  $\text{Fe}(\text{CO})_5$  as a source of CO, with  ${}^t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$  as phase transfer catalyst. The Knoevenagel condensation successfully yielded the cyclopentadienone **54** as a dark purple crystalline solid (86%).



### 2.2.2 Synthesis of Fluoranthenes

The target *tert*-butyl fluoranthene derivatives **55-57** were synthesised in very high yields (80-90%) by the Diels Alder [2+4] cycloaddition of the appropriate acetylenes and cyclopentadienone in benzophenone melts under an argon atmosphere (Scheme 2.3).<sup>120</sup>

The Diels–Alder reaction is a reliable method that is commonly used in synthetic organic chemistry for the generation of peripheral or heteroatom-substituted six-membered ring systems with high control over regio- and stereo-chemical properties.<sup>121</sup> In a typical [2+4] cycloaddition reaction, a dienophile containing  $2\pi$  electrons regioselectively adds to a conjugated 1,4-diene containing  $4\pi$  electrons towards the generation of a new six membered ring. This occurs *via* the formation of two new C-C  $\sigma$ -bonds, with the evolution of carbon monoxide. These Diels-Alder reactions are generally carried out at high temperatures and in non-polar solvents and the ease with which these reactions occur is often found to be highly influenced by the substituents.



Scheme 2.3: Synthesis of Fluoranthene polyphenylenes by the [2+4] Diels-Alder reaction in benzophenone melts. (i) 280 °C, 8 h, 76%, (ii) 280 °C, 6 h, 74%, (iii) 300 °C, 3 h, 71%

### 2.3 Structural Characterisation of 55-57

The fluoranthene derivatives **55-57** were fully characterised by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and TOCSY, HSQC, HMBC), MALDI high resolution mass spectrometry, elemental analysis and infrared spectroscopy. The obtained NMR data of the known reactants, acetylenes **48-51**, cyclopentadienone **54** and the generated monoketone, were all in good agreement with the literature. Compound **57** was further characterised by single crystal x-ray diffraction. The photophysical investigation of these compounds will be discussed in the later sections.



2.3.1 NMR Studies of **55-57**

Due to a  $C_2$ -plane of symmetry, the  $^1\text{H}$ -NMR spectra of **55** and **57** was relatively simple. The  $^1\text{H}$  NMR spectra of **55-57** shows a doublet-pseudotriplet-doublet system characteristic of the naphthyl moiety. Free rotation of the aryl rings at positions 7, 8, 9 and 10 of the fluoranthenes is observed in all three systems. The pyrimidyl peak for compounds **56** and **57** show a singlet at  $\delta = 8.70$  and  $\delta = 8.81$  ppm respectively. The protons at positions **1** and **2** of the 5-pyrimidyl substituents in **56** and **57** are magnetically equivalent.

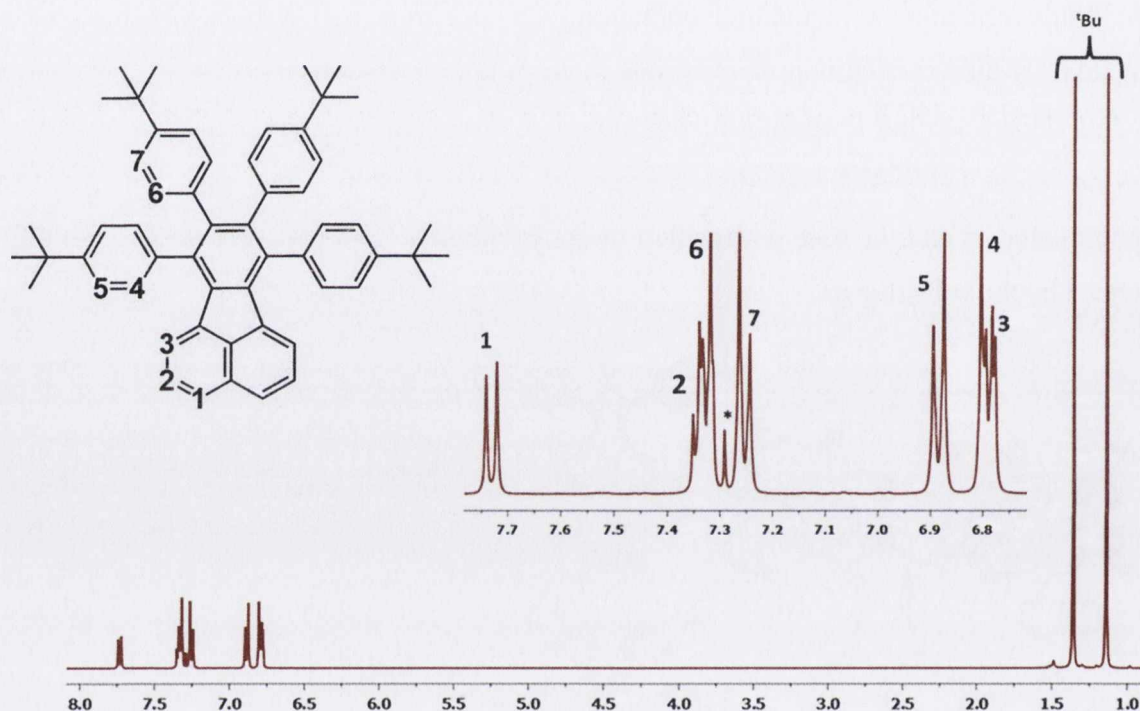


Figure 2.1: Full assignment for  $^1\text{H}$  NMR spectrum of **55**. Asterisk denotes solvent peak ( $\text{CDCl}_3$ , RT, and 400 MHz). Inset shows expansion of the aromatic region and structure of **55**.

The full proton spectrum of **55** is shown in Figure 2.1. The aromatic signals appear as a series of well-resolved singlets and doublets. From the spectrum, it is evident that the aromatic signals are considerably downfield, in the region  $\delta = 6.8 - 7.8$  ppm. The signals of *tert*-butyl protons appear as two singlet signals at  $\delta = 1.36$  and  $1.14$  ppm, integrating for a total of 18 protons each. All three spectra were assigned using various 2D NMR techniques and a similar strategy was employed in the assignment of the signals. As the same techniques were used for all three fluoranthene containing polyphenylenes, only the assignment of **56** will be discussed in detail.

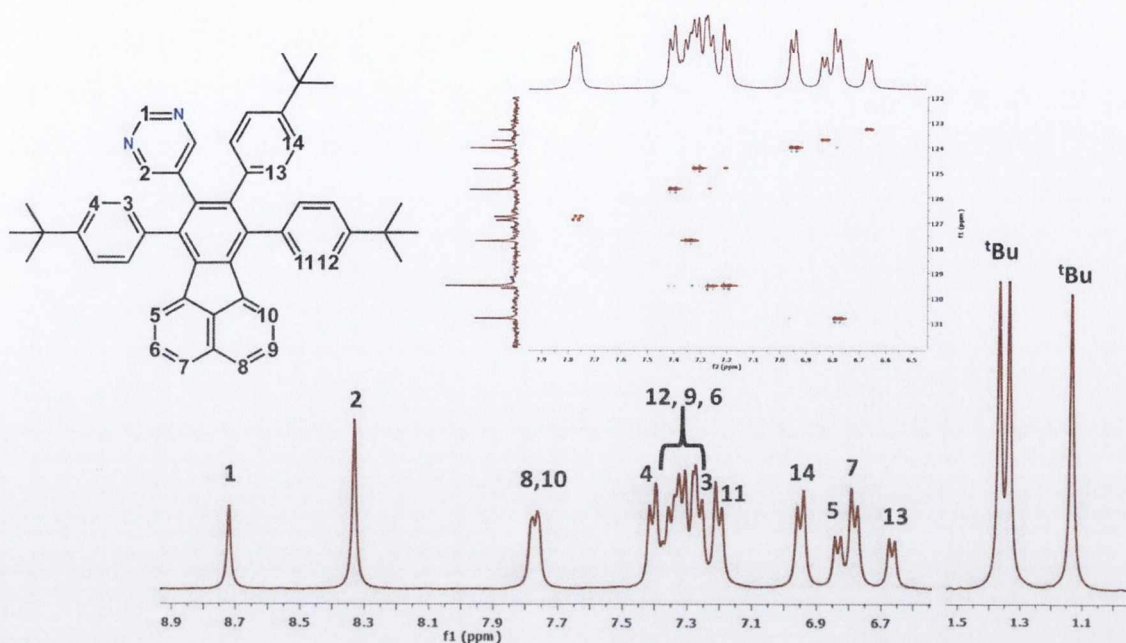


Figure 2.2: Full assignment for  $^1\text{H}$  NMR spectrum of **56**. (Solvent:  $\text{CDCl}_3$ , RT and 600 MHz). Inset shows HSQC spectrum.

The immediate difference between **55** and **56** was apparent in the  $^1\text{H}$  NMR spectra from signals of the pyrimidyl in **56**. Figure 2.2 shows the  $^1\text{H}$  NMR spectra assignment of **56**. Characterisation of the asymmetric fluoranthene **56** proved more complex, owing to the more convoluted nature of its signals. Using selective TOCSY experiments allowed for the full assignment of the proton signals, and when the spectrum was coupled with the HSQC spectrum, inset in Figure 2.2, it allowed for the assignment of all of the carbon signals.

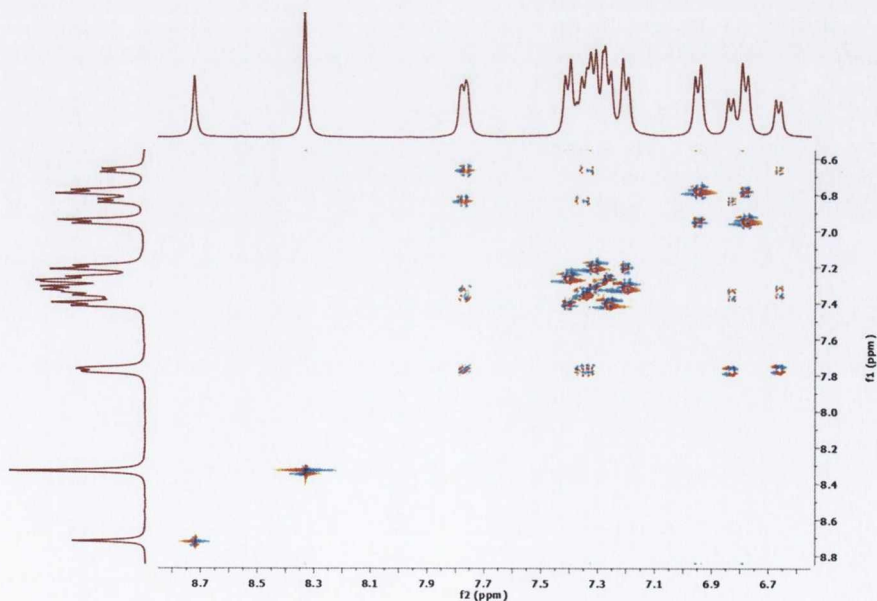


Figure 2.3:  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **56** in  $\text{CDCl}_3$ , 600 MHz, RT.



In the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **56**, the most downfield signals at  $\delta = 8.70$  ppm and  $\delta = 8.31$  ppm do not show any correlation with other aromatic signals, confirming their assignment as pyrimidyl protons. This assignment was further supported by the HSQC spectrum, with the correlated carbon signals appearing in at 155.96 and 155.30 ppm respectively (Figure 2.2). Apart from the pyrimidyl signals, compound **56** consists of 3 two spin systems *i.e.* for each *tert*-butyl substituted aromatic ring which appear as a series of doublets in the region  $\delta \sim 7.4 - 6.6$  ppm, with  $^3J$  splitting of  $\sim 8.0$  Hz. and 2 three spin systems from fluoranthene moiety.

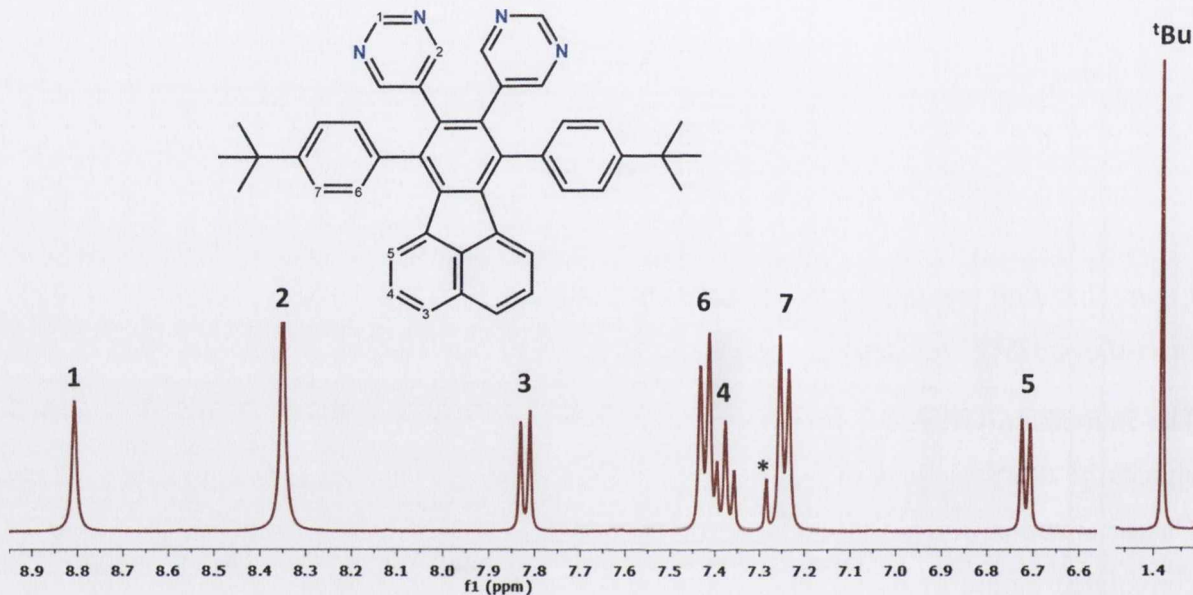


Figure 2.4: Full assignment for  $^1\text{H}$  NMR of **57**. Asterisk denotes solvent peak ( $\text{CDCl}_3$ , RT, 400 MHz).

In comparison with **56**, characterisation of the **57** was much simpler owing to its symmetric nature. The most downfield singlet at  $\delta = 8.81$  ppm (integrating to two protons) is attributed to  $\text{H}_1$ , with the second most downfield signal  $\delta = 8.35$  ppm (integrating to four protons) being attributed to  $\text{H}_2$ . These signals are directly adjacent to the pyrimidyl rings in the fluoranthene compound. The pyrimidyl protons are found as expected as the most deshielded signals due to the electron withdrawing ability of the nitrogen atoms. The resonances of the *tert*-butyl functionalised aromatic ring protons appear as two doublet signals at  $\delta = 7.41$  ( $\text{H}_6$ ) and 7.26 ( $\text{H}_7$ ) ppm, integrating for four protons each. The doublet-pseudotriplet-doublet signals characteristic of the naphthyl moiety are seen at  $\delta = 7.83$  ( $\text{H}_3$ ), 7.38 ( $\text{H}_4$ ) and 6.73 ( $\text{H}_5$ ) ppm, with each signal integrating for two protons each. Finally, the *tert*-butyl signals appear in aliphatic region as a singlet peak at  $\delta = 1.37$  ppm, integrating to 18 protons in total.



### 2.3.2 Spectroscopic studies of 55-57

The electrospray mass spectra of **55** recorded in acetonitrile, and the other two derivatives, **56** and **57** recorded in dichloromethane, reveal the major peak in each spectrum corresponding to the  $[M+H]^+$  molecular ion. Here, the compound has become positively charged by the inclusion of a proton upon ionisation in the mass spectrometer. These values are in excellent agreement with the calculated values for the molecular ion, and agree with isotopic modelling. The mass spectral data is summarised in Table 2.1.

Table 2.1: Electrospray mass spectral data for novel fluoranthene derivatives (**55** recorded in acetonitrile, **56**, **57** in  $CH_2Cl_2$ ,  $m/z$  in *m.u.*)

| Compound  | Molecular Ion | Formula           | Calculated $m/z$ | Found $m/z$ (%) |
|-----------|---------------|-------------------|------------------|-----------------|
| <b>55</b> | $[M+H]^+$     | $C_{56}H_{58}$    | 730.4539         | 730.4531        |
| <b>56</b> | $[M+H]^+$     | $C_{50}H_{49}N_2$ | 677.3896         | 677.3876        |
| <b>57</b> | $[M+H]^+$     | $C_{44}H_{38}N_4$ | 623.3175         | 623.3164        |

### 2.3.3 Crystallographic study of 57

Colourless needle-shaped crystals of **57**, suitable for single crystal X-ray diffraction studies, were grown *via* the slow evaporation of a  $CH_2Cl_2$  solution of **57** from MeOH. **57** crystallises in the triclinic space group  $P\bar{1}$ . The asymmetric unit is shown in Figure 2.5. As expected, the fluoranthene moiety is very slightly curved (C5 to C22, mean deviation from planarity = 0.113 Å). The pyrimidyl substituents lie almost perpendicular to the fluoranthene plane (80.6° and 75.4° for the C1-N3 and C23-C26 rings respectively). The phenyl ring twists are less pronounced (66.2, 68.0° for rings C27-C32, C37-C42 respectively). In comparison to similar literature structures, ring twists in **57** are more pronounced than in 7, 10-diphenylfluoranthene (58.2 and 50.2°) and less pronounced than in dimethyl 7,10-diphenylfluoranthene-8,9-dicarboxylate (69.9, 86.6°).<sup>122</sup>

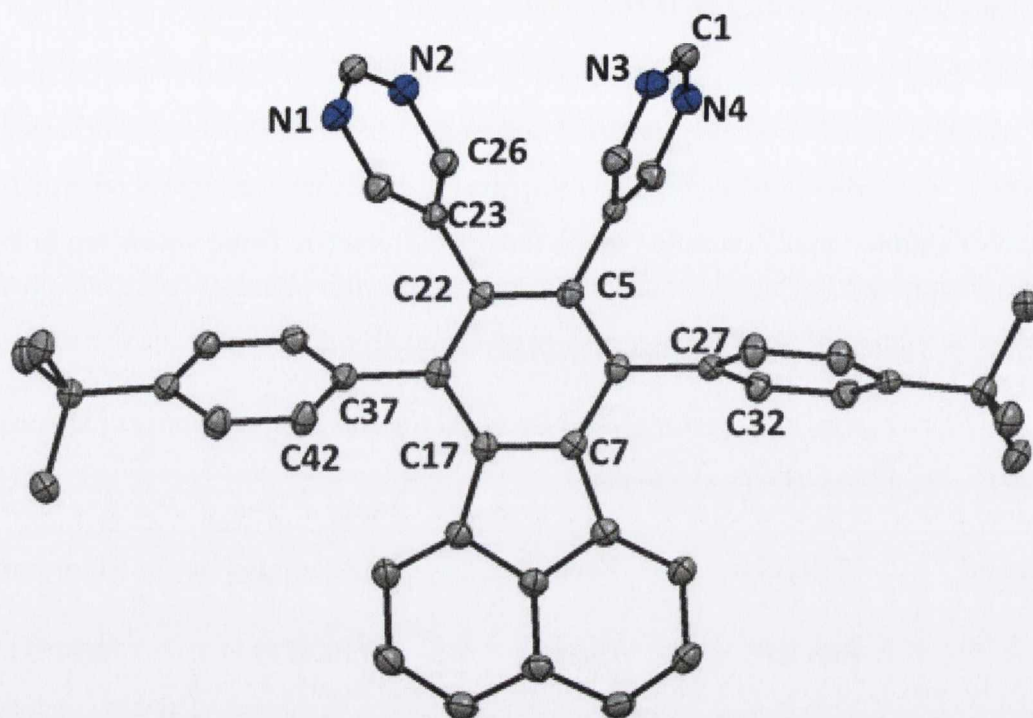


Figure 2.5: Molecular structure of **57** (ellipsoids shown at 50%).

The packing arrangement of **57** shows little significant strong interactions unlike 7,10-bis(4-bromophenyl)-8-phenylfluoranthene where weak  $\pi$ - $\pi$  interactions were reported.<sup>75</sup> In **57**, weak C-H $\cdots$  $\pi$  and C-H $\cdots$ N are found as the supramolecular influences. The molecules are packed in slipped stacks with alternating pyrimidine-pyrimidine fluoranthene-fluoranthene arrangements as shown in Figure 2.6. The interplanar distance between the adjacent fluoranthene moieties is 3.68 Å.

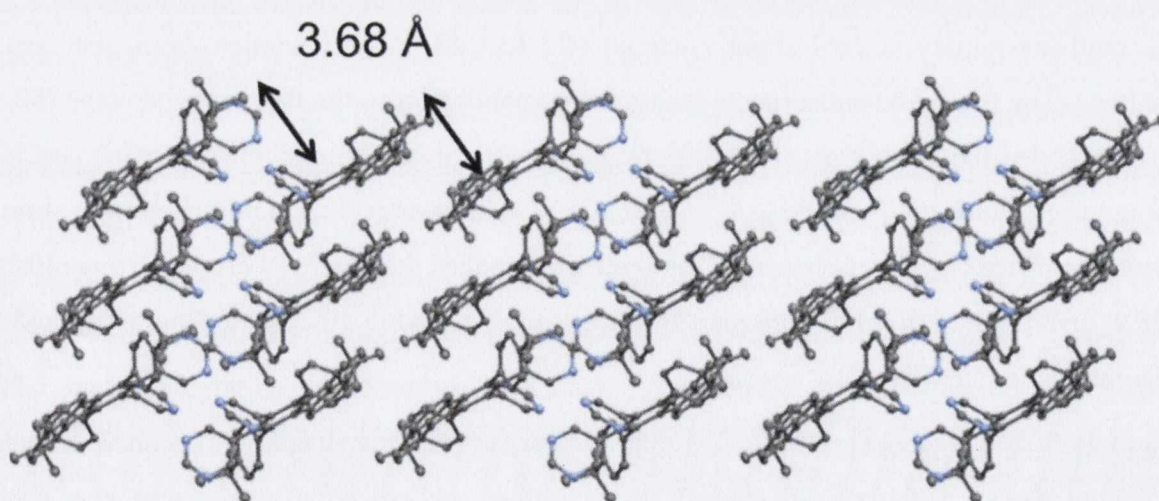


Figure 2.6: Packing arrangement of **57** along *b*-axis showing the intermolecular distance. Hydrogen atoms are omitted for clarity.



## 2.4 Photophysical Studies of 55-57

The absorption and emission spectra of **55-57** were measured in EtOH ( $1 \times 10^{-5}$  M). The absorption spectra predominantly exhibits two absorption bands at  $\lambda_{\max} = 295, 376$  nm for **55**;  $\lambda_{\max} = 294, 373$  nm for **56**;  $\lambda_{\max} = 286, 374$  nm for **57** (Figure 2.7) originating from  $\pi$ - $\pi^*$  intramolecular transitions. The high molar extinction coefficients of these bands further suggest the  $\pi$ - $\pi^*$  nature of the absorption bands, which typically display  $\epsilon$  values of  $10^3 - 10^5$   $\text{M}^{-1}\text{cm}^{-1}$ . The absorption spectra of the three ligands **55-57** feature strong bands in the near UV-region of the spectrum. In general, the absorptions are quite broad, which is indicative of free rotation of the attached phenyl rings along the molecular axis, and of rotation about the fluoranthene moiety. This data is similar to that observed for the fluoranthene unit alone ( $\lambda_{\max} = 289$  and  $360$  nm).<sup>123</sup>

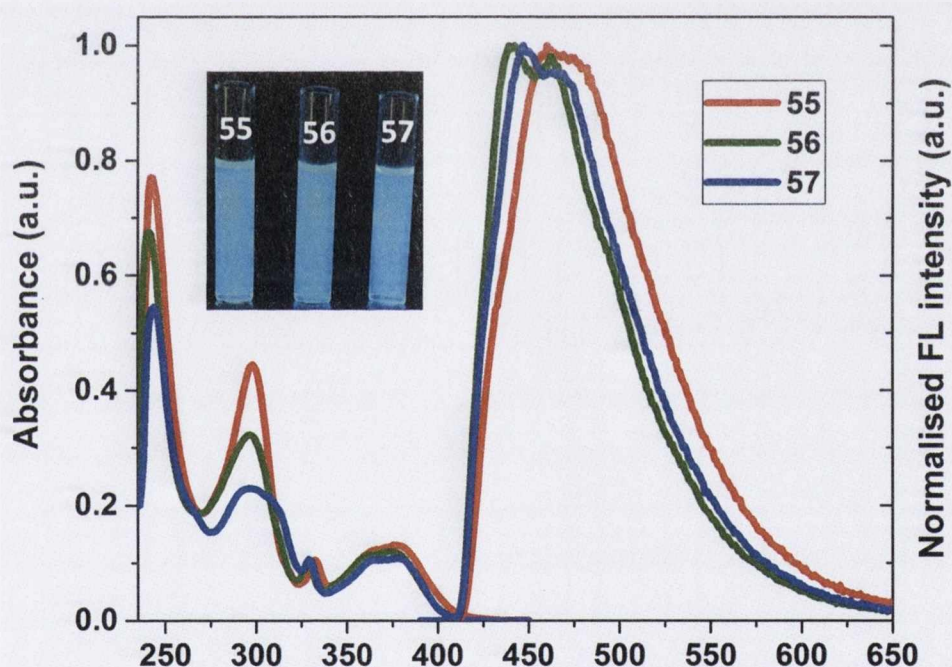


Figure 2.7: The optical absorption and fluorescence spectra of fluoranthene derivatives **55-57** in EtOH ( $\sim 10^{-5}$  M).

The  $\pi$ -conjugated nature of these fluoranthenes gives rise to a strong blue fluorescence emission in ethanol at  $\lambda_{\max} = 464$  nm for **55**,  $\lambda_{\max} = 452$  nm for **56** and  $\lambda_{\max} = 445$  nm for **57**, with a Stokes shifts of  $5044.02$   $\text{cm}^{-1}$ ,  $4685.76$   $\text{cm}^{-1}$  and  $4266.06$   $\text{cm}^{-1}$  respectively. The anomalous fluorescence characteristics such as Stokes shifts have received attention in blue-light-emitting organic light-emitting diodes (OLEDs) as discussed in Chapter 1. The quantum yields obtained in ethanol were measured by using an integration sphere and demonstrate that



the fluorescence process in each compound is quite efficient. The fluorescence lifetime measurements were carried out using 372nm NanoLED and are presented in Table 2.2 along with the photophysical data. The quantum yield and emission lifetime measurements demonstrate that the radiative process in each case is reasonably efficient, with  $k_F$  values between  $1.5 \times 10^7 \text{ s}^{-1}$  and  $1.84 \times 10^7 \text{ s}^{-1}$ .

Table 2.2: Summary of Photophysical data of **55-57** ( $\sim 10^{-5} \text{ M}$ ) in EtOH at RT.

| Compound  | $\lambda_{\text{max}}$ [nm]<br>( $\epsilon \times 10^4/\text{M}^{-1} \text{ cm}^{-1}$ ) | $\lambda_{\text{em}}$ [nm]<br>( $\lambda_{\text{ex}}$ [nm]) | $\Phi_f$ | $\tau$ /ns |
|-----------|-----------------------------------------------------------------------------------------|-------------------------------------------------------------|----------|------------|
| <b>55</b> | 243(7.70), 295(4.44),<br>329(1.05), 376(1.31)                                           | 464 (376)                                                   | 42 %     | 23         |
| <b>56</b> | 242(6.83), 294(3.27),<br>328 (1.02), 373(1.22)                                          | 452 (373)                                                   | 45 %     | 25         |
| <b>57</b> | 244(5.45), 286(2.29),<br>327(1.06), 374(1.08)                                           | 445 (374)                                                   | 41 %     | 28         |

## 2.5 Electrochemistry of **55-57**

The cyclic voltammograms recorded for the **55-57** with the internal standard, ferrocene, are shown in Figure 2.8. Cyclic voltammetric (CV) studies were carried out on 1mM solutions of the ligands in  $\text{CH}_2\text{Cl}_2$  (0.1 M nBu<sub>4</sub>NPF<sub>6</sub>). The results are summarised in Table 2.3. CVs were carried out using a Ag/AgCl electrode as reference electrode, a Pt wire counter electrode and a glassy carbon working electrode. Potentials are quoted versus the Fc/Fc<sup>+</sup> couple (0.0V) and referenced to internal ferrocene added at the end of each experiment (potentials were converted to Fc/Fc<sup>+</sup> scale by subtraction of 0.4V).

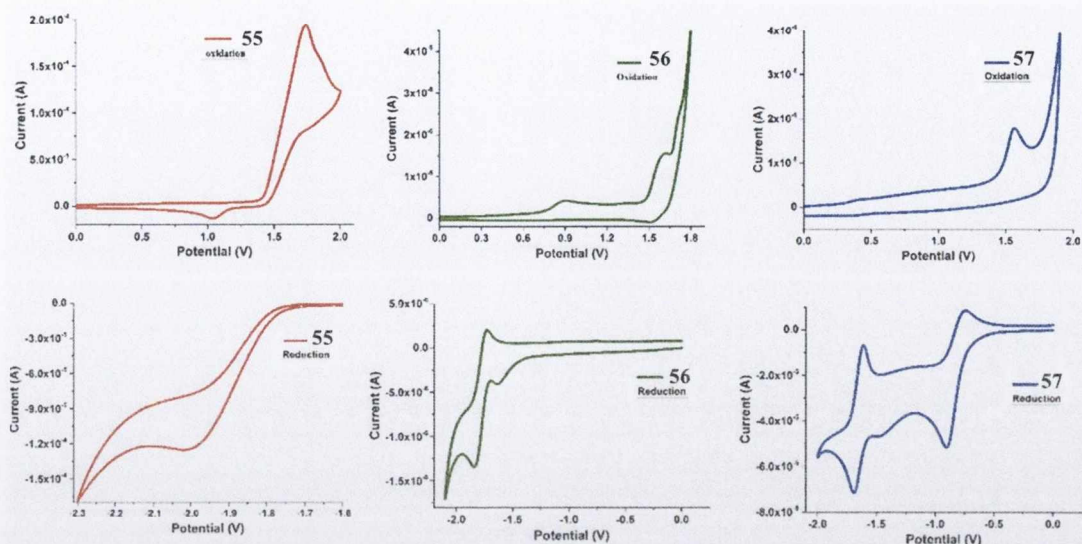


Figure 2.8: Electrochemistry plots of **55-57** compounds plotted against Ag/AgCl. Ferrocene was found to be 0.38V.

Table 2.3: Electrochemical properties of **55-57** (1mM) were recorded at room temperature, using glassy carbon working electrode, a Pt wire counter electrode with a scan rate of 100 mVs<sup>-1</sup>; Supporting electrolyte is 0.1 M TBAPF<sub>6</sub>. Potentials are quoted vs. Fc/Fc<sup>+</sup>, which was used as an internal standard. Positive oxidation sweeps resulted in periflanthene formation (*vide infra*) – onset potentials quoted.

| Compound  | Oxidation onset<br>E <sub>onset</sub> /V | Reduction potential<br>E <sub>1/2</sub> /V (ΔE/mV) | Band gap, eV | HOMO-LUMO gap, eV |
|-----------|------------------------------------------|----------------------------------------------------|--------------|-------------------|
| <b>55</b> | 1.06                                     | -2.36 <sup>a</sup>                                 | 730.454      | 730.453           |
| <b>56</b> | 1.30                                     | -1.23, <sup>a</sup> -2.21 (140)                    | 677.389      | 677.387           |
| <b>57</b> | 1.40                                     | -1.24 (160), -2.04 (74)                            | 623.317      | 623.316           |

<sup>a</sup>: irreversible reduction process, peak potentials (E<sub>p</sub>) quoted.

CV studies did not reveal any large variations in their oxidation and reduction potentials, signifying that the central fluoranthene moiety accounts for the majority of the observed redox behaviour. All of the compounds displayed irreversible oxidations, arising from the formation of a film caused by the fusion of oxidised fluoranthene molecules at the glassy-carbon working electrode surface, giving rise to periflanthene-type molecules.<sup>124</sup> The onset



potentials for this process are quoted in Table 2.3. Reduction occurs more readily with the addition of electron withdrawing pyrimidyl units. Compound **57** exhibits two clear reversible reduction waves (Figure. 2.8), whereas **55** and **56** display more sluggish kinetics.

Due to periflanthene formation, it is not very easy to predict HOMO levels from CV. The electron donating pyrimidyl groups decrease the HOMO and increase the LUMO energy levels giving a reduction in the band gap, consistent with the findings of the photophysical studies.

## 2.6 Theoretical Studies of **55-57**

In order to understand the absorption characteristics of the fluoranthenes, theoretical calculations were performed for the molecules **55**, **56** and **57** using density functional theory. Use of the B3LYP functional and the 6-31g\* basis set in both gas phase, and in ethanol, using a polarisable continuum solvent model (PCM) are displayed in Figure 2.9a and 2.9b respectively. The phenyl groups are significantly twisted from the fluoranthene core and are less involved in  $\pi$ -interactions. The higher wavelength absorption peaks observed for these compounds in ethanol agree well with the theoretically forecast values except for a minor red shift which is most probably an artefact of the solvent model used. The intense band in **55-57** around 370 nm is thought to arise from the HOMO to LUMO electronic transition. The wave functions of the frontier molecular orbitals *i.e.* the HOMO and LUMO orbitals of **55-57** are  $\pi$ -type and mainly localised on the fluoranthene core. This leads to the conclusion that the low energy transition observed for the compounds originate from a fluoranthene based  $\pi$ - $\pi^*$  transition. Also, to identify the orbital association with the electronic transitions, time-dependent DFT was performed for all the optimised structures and the prominent higher wavelength vertical transitions predicted by the theory are collected in Table 2.4, with the corresponding computed absorption spectrum in Figure 2.10.



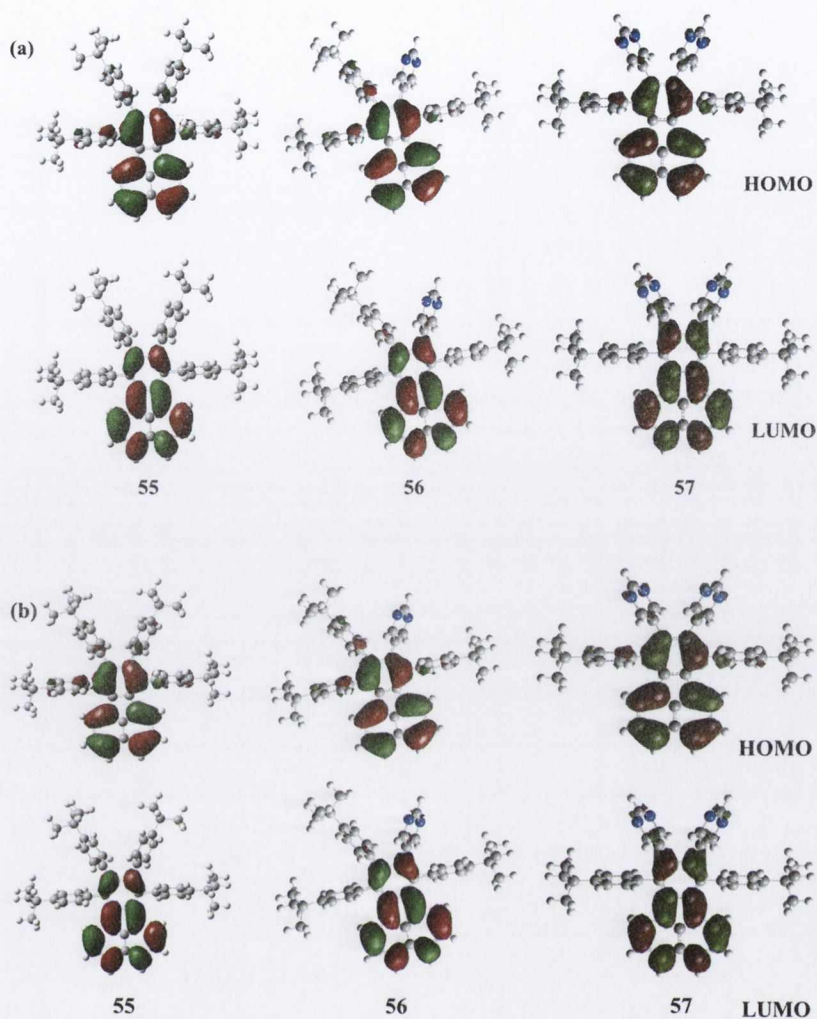


Figure 2.9: Electron density superimposed on the optimised geometry in (a) gas phase and (b) Ethanol (PCM), with B3LYP/6-31g\* basis set. (55-57)

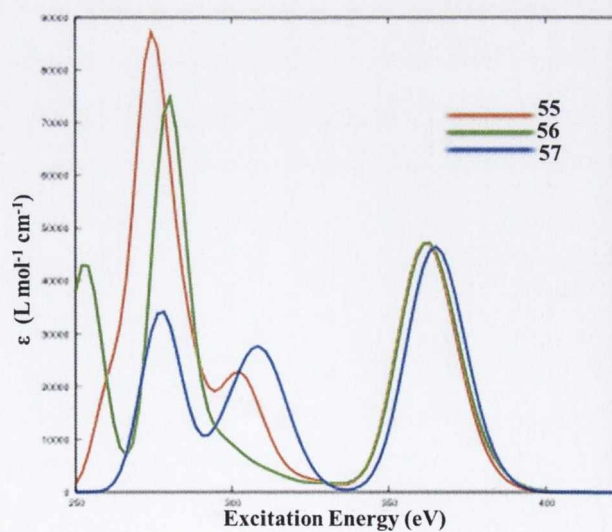


Figure 2.10: Computed absorption spectrum of 55-57

Table 2.4: Predicted (TDDFT B3LYP/6-31g\*) vertical transitions and their assignments of **55-57**. (Summary of excited state electronic transitions of the three lowest energy transitions obtained from TD-DFT Calculations in Ethanol (PCM), on the optimised geometry).

| Compound  | Wavelength,<br>$\lambda_{\text{calc}}$ (nm) | Energy, eV | Oscillator Strength, f | Assignment<br>(Dominant contribution) |
|-----------|---------------------------------------------|------------|------------------------|---------------------------------------|
| <b>55</b> | 369.71                                      | 3.3535     | 0.0355                 | HOMO-1 $\rightarrow$ LUMO             |
|           | 361.42                                      | 3.4305     | 0.3343                 | HOMO $\rightarrow$ LUMO               |
|           | 326.12                                      | 3.8018     | 0.0139                 | HOMO-2 $\rightarrow$ LUMO             |
| <b>56</b> | 374.83                                      | 3.3078     | 0.0311                 | HOMO-1 $\rightarrow$ LUMO             |
|           | 361.90                                      | 3.4259     | 0.3464                 | HOMO $\rightarrow$ LUMO               |
|           | 330.78                                      | 3.7482     | 0.0114                 | HOMO-2 $\rightarrow$ LUMO             |
| <b>57</b> | 367.02                                      | 3.3781     | 0.0251                 | HOMO-1 $\rightarrow$ LUMO             |
|           | 364.82                                      | 3.3985     | 0.3281                 | HOMO $\rightarrow$ LUMO               |
|           | 319.01                                      | 3.8866     | 0.0236                 | HOMO-2 $\rightarrow$ LUMO             |

## 2.7 Nitroaromatic Sensing Application of Fluoranthenes of **55-57**

### 2.7.1 Detection of Nitroaromatic by Fluorescence Quenching

The potential application of **55-57** as sensors for the detection of nitroaromatic compounds (NACs) based on fluorescence quenching were studied. The general mechanism of fluorescence quenching-based detection usually involves the formation of a donor-acceptor charge-transfer (CT) complex between the  $\pi$ -electron rich donor (fluoranthene) and electron deficient acceptor (nitroaromatic) *via*  $\pi$ - $\pi$  interactions.<sup>16, 125-128</sup> In this current work, we have employed three fluoranthene-based sensors **55-57** to detect NAC as per the proposed quenching mechanism.

#### Selectivity

To demonstrate the potential of these fluoranthenes in the sensing of nitroaromatics, preliminary fluorescence quenching titration experiments were carried out in EtOH with



picric acid (PA), dinitrophenol (DNP), nitrophenol (NP), dinitrotoluene (DNT), nitrotoluene (NT), dinitrobenzene (DNB), and nitrobenzaldehyde(NBA). Other common interfering electron deficient analytes such as Benzoquinone (BQ), Iodophenol (IP), Phenol (P), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), toluene (T), ethanol (E) and trifluoroacetic acid (TFA) were also used. As expected, the initial emission intensity of fluoranthenes depleted upon the gradual addition of an EtOH solution of each NAC.

The selectivity of fluoranthenes **55-57** for the detection of certain NACs was studied. Figure 2.11 shows the resulting histograms of the corresponding quenching efficiencies. Interestingly, the fluoranthenes **55-57** showed differential fluorescence quenching responses among the tested analytes. No significant decrease in the fluorescence intensity was seen with other electron deficient compounds like BQ, DDQ, IP, P and T, indicating that all three fluoranthenes show strong quenching responses for NACs, and not with other types of aromatic compounds. The reduction potential of non-nitroaromatic quenchers are similar to nitroaromatic quenchers.<sup>23</sup> Therefore, the observed higher fluorescence quenching responses of the electron-deficient nitroaromatics is due to the strong dipolar or electrostatic interaction with  $\pi$ -electron rich aromatic fluoranthenes. This observation is fully consistent with the proposed quenching mechanism in which the electron-deficient nitroaromatics act as a fluorescence quencher to electron-rich fluorophores as a result of the formation of a charge-transfer (CT) complex.

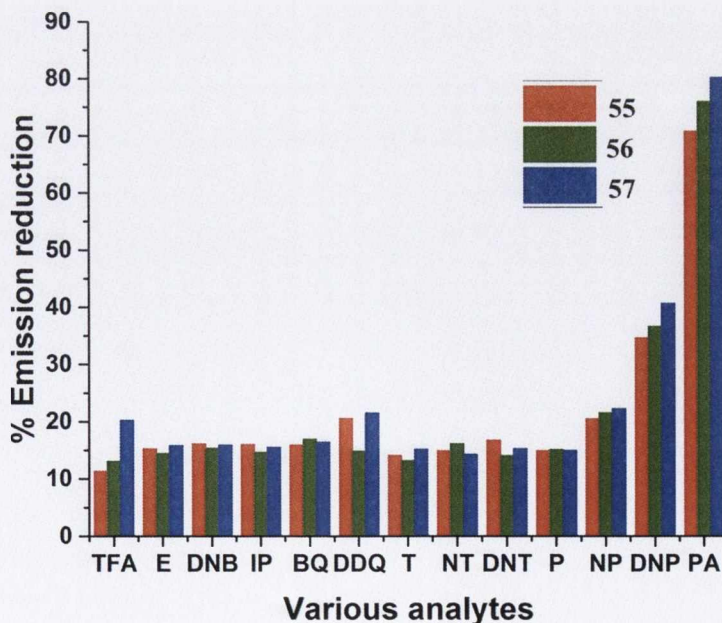


Figure 2.11: The fluorescence quenching efficiency of fluoranthene derivatives **55-57** ( $\sim 10^{-6}$  M) upon addition of different analyte solutions ( $\sim 10^{-4}$  M).



The fluorescence intensity of EtOH solutions of fluoranthenes **55-57** was found to decrease significantly upon the gradual addition of nitroaromatics, in particular with PA. Addition of a 25  $\mu$ M concentration solution of PA to **55** showed a 70% fluorescence quenching upon excitation at  $\lambda_{\text{ex}} = 373\text{nm}$ , while **56** showed a 75.5% quenching ( $\lambda_{\text{ex}} = 372\text{ nm}$ ) and **57** showed an 80% quenching ( $\lambda_{\text{ex}} = 370\text{nm}$ ). With increasing numbers of pyrimidyl rings, the fluorescence quenching efficiency is increased, indicating enhanced formation of the  $\pi$ -donor-acceptor complexes.<sup>71</sup>

### 2.7.2 Detection of Picric acid by Fluorescence Quenching

Although a few metal organic frameworks<sup>129</sup> and conjugated polymers<sup>1</sup> have been reported to show sensing of nitroaromatics, the development of efficient sensors for the selective sensing of picric acid with a very low detection limit is still a challenging task. The presence of three strong electron withdrawing  $-\text{NO}_2$  groups in the phenyl ring of picric acid makes it a very strong electron deficient analyte. This fact can be exploited however to lead to the formation of a non-fluorescent charge-transfer complex between this explosive, and the electron rich fluoranthenes **55-57** with the subsequent quenching of their fluorescence.

The pre-requisite for fluorescence quenching is molecular contact between the fluorophore and the quencher. This contact can result either from a diffusive encounter (dynamic quenching) or from complex formation (static quenching). The fluorescence decay lifetime of the fluorophores remain unchanged as the concentration of the quencher is increased. As discussed in Chapter 1, this is consistent with the formation of a static non-fluorescent fluorophore-quencher complex.<sup>128</sup>

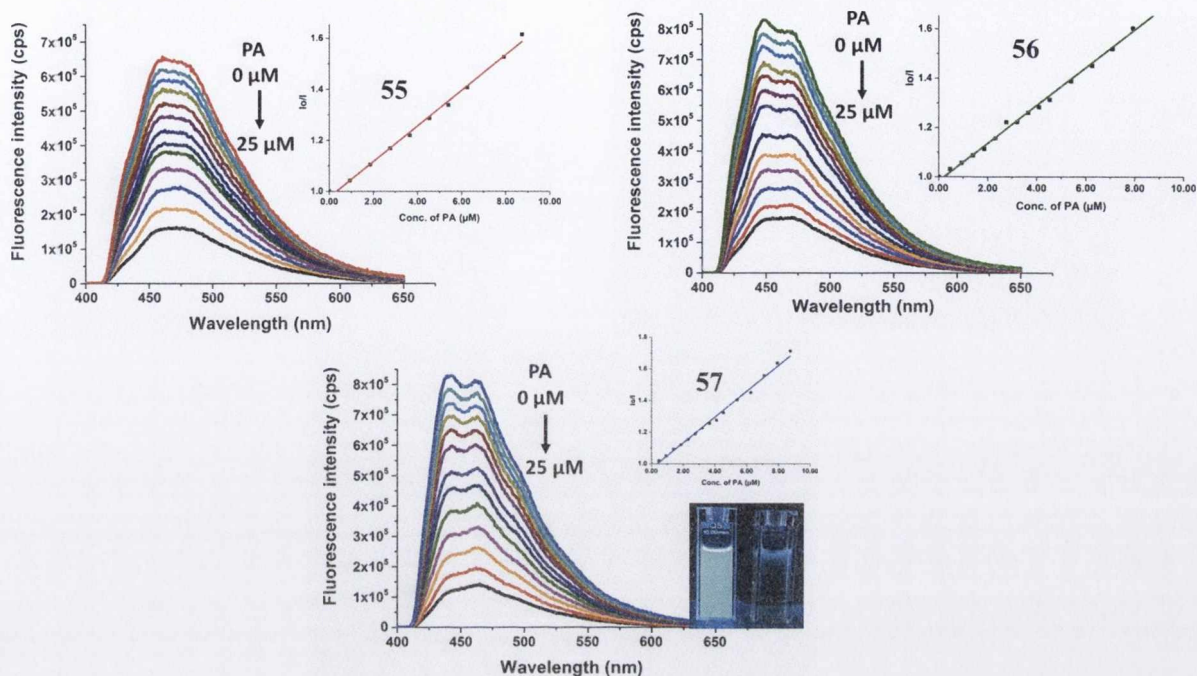


Figure 2.12: Fluorescence quenching of **55**, **56** and **57** ( $10^{-6} M$ ) upon addition of PA ( $10^{-4} M$ ) in EtOH ( $\lambda_{ex}=370$  nm). The inset shows corresponding Stern-Volmer plots for these compounds. The inset photograph shows the visual colour change observed upon the mixing of a  $\sim 10^{-5} M$  solution of fluoranthene **57** with a  $\sim 10^{-4} M$  solution of PA in EtOH under UV light.

The sensitivity of the fluoranthenes towards PA was determined via fluorescence quenching titration at parts per billion (ppb) concentrations (Figure 2.13). The detection limit was found to be as low as 2-5 ppb, in the order **57** > **56** > **55** obtained from the quantitative analysis of fluorescence titration profiles of **55-57**.

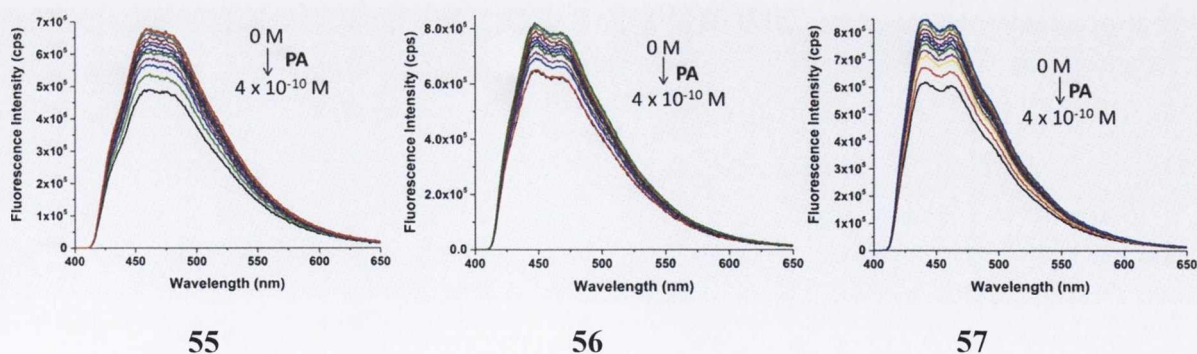


Figure 2.13: Changes in initial fluorescence intensity of **55-57** upon gradual addition of PA ( $0-4 \times 10^{-10} M$ ) in ethanol.



The fluorescence quenching was analysed by the Stern-Volmer (SV) equation given by  $I_0/I = \tau_0/\tau = 1 + K_{sv}[Q]$  (where  $I_0$ ,  $I$  are the fluorescence intensities, and  $\tau_0$ ,  $\tau$  are the fluorescence lifetimes of **55-57** in the absence and presence of PA, respectively,  $K_{sv}$  is the Stern-Volmer constant, and  $Q$  is the quencher concentration). A linear SV plot was obtained with a rate constant of  $K_{sv} = 6.9 \times 10^4 \text{ M}^{-1}$  for **55**;  $K_{sv} = 7.7 \times 10^4 \text{ M}^{-1}$  for **56**;  $K_{sv} = 8.3 \times 10^4 \text{ M}^{-1}$  for **57**. The rate constant is therefore increasing with the increasing number of pyrimidyl substituents. Due to the dilution effect of adding analyte solution, fluorophore concentration was not constant affecting the emission intensity at higher additions of analyte.

The linear SV plots at low concentrations of PA and the unaltered fluorescence life times determined by time correlated single photon counting (TCSPC) further support a static quenching mechanism (Table 2.5).

Table 2.5: Excited state lifetime measurements of **55-57** ( $\sim 10^{-6} \text{ M}$ ) with various concentrations of PA ( $\sim 10^{-4} \text{ M}$ ).

| Compound                | Life time ( $\tau$ ) (ns) |           |           |
|-------------------------|---------------------------|-----------|-----------|
| Fluoranthene (F)        | <b>55</b>                 | <b>56</b> | <b>57</b> |
| <b>F</b>                | 23                        | 25        | 28        |
| <b>F + 0.5 eq of PA</b> | 23                        | 25        | 28        |
| <b>F + 1 eq of PA</b>   | 23                        | 25        | 28        |
| <b>F + 2 eq of PA</b>   | 23                        | 25        | 28        |

The spectrophotometric titration of **57** ( $10^{-6} \text{ M}$ ) with different concentrations of picric acid (PA) in EtOH is shown in Figure 2.14. Upon gradual addition of PA to **57**, there was an increase in the absorption maxima at  $\lambda = 238 \text{ nm}$  and  $\lambda = 374 \text{ nm}$  with the formation of a new broad absorption peak above  $\lambda = 400 \text{ nm}$ . Since the intensity of the new absorption peak gradually increases with increase in the concentration of PA, this indicates the formation of donor-acceptor complex between the  $\pi$ -electron rich fluoranthene and electron deficient PA. Similar results were observed upon treatment of **55-57** with other NACs.



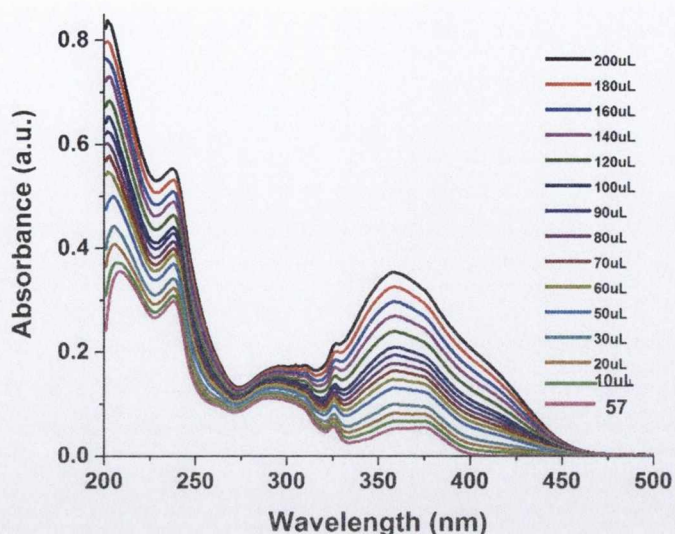


Figure 2.14: The spectrophotometric titration of **57** upon gradual addition of PA in ethanol.

### 2.7.3 Effect of TFA on Fluoranthenes **55-57**

As the highest degree of quenching appears to occur with the nitroaromatics possessing the lowest  $pK_A$  values, it was necessary to assess the degree of quenching arising purely from the protonation of the sensor. Whilst a degree of quenching is observed upon stepwise addition of trifluoroacetic acid to the fluoranthene derivatives (Figure 2.15), the degree of emission reduction is far more dramatic when the nitroaromatic analytes are employed. This, along with the close matching of the quenching behaviour observed in the “all-carbon” **55** with the N-containing compounds, supports our growing assertion that protonation is not a principal factor in the quenching mechanism and allows us to assume that the formation of a CT complex is the dominant quenching mechanism in these cases.<sup>71</sup> Also, the spectrophotometric titrations of PA (seen in Figure 2.14) is very different from titrations of TFA (shown in Figure 2.16) in confirming the formation of CT complex with **56** and **57** and PA.

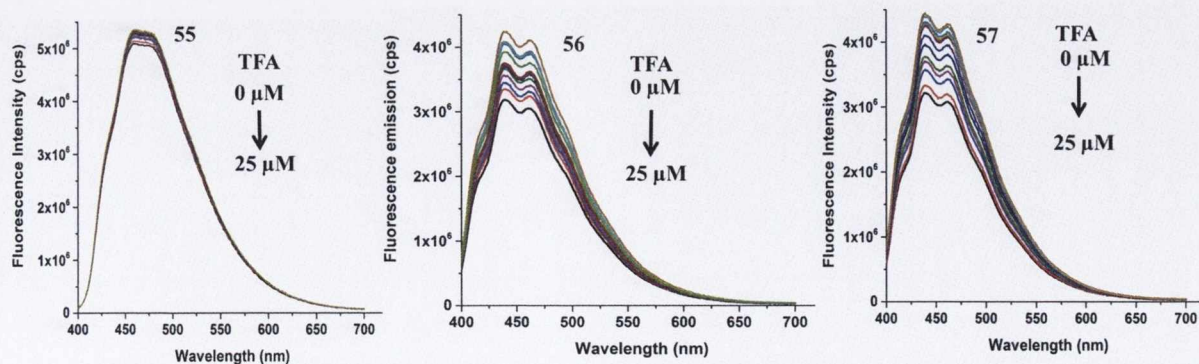


Figure 2.15: The fluorescence emission titrations of **55**, **56** and **57** upon gradual addition of  $10^{-4}$  M TFA in ethanol. Here 25  $\mu$ M corresponds to 4 equivalents to TFA.

The increased sensitivity to acidic analytes is therefore attributed to the strong electron-withdrawing power of the carboxyl groups rendering these compounds excellent acceptors in the formation of CT complexes with the fluoranthene sensor, and not as a result of a simple acid-base effect.

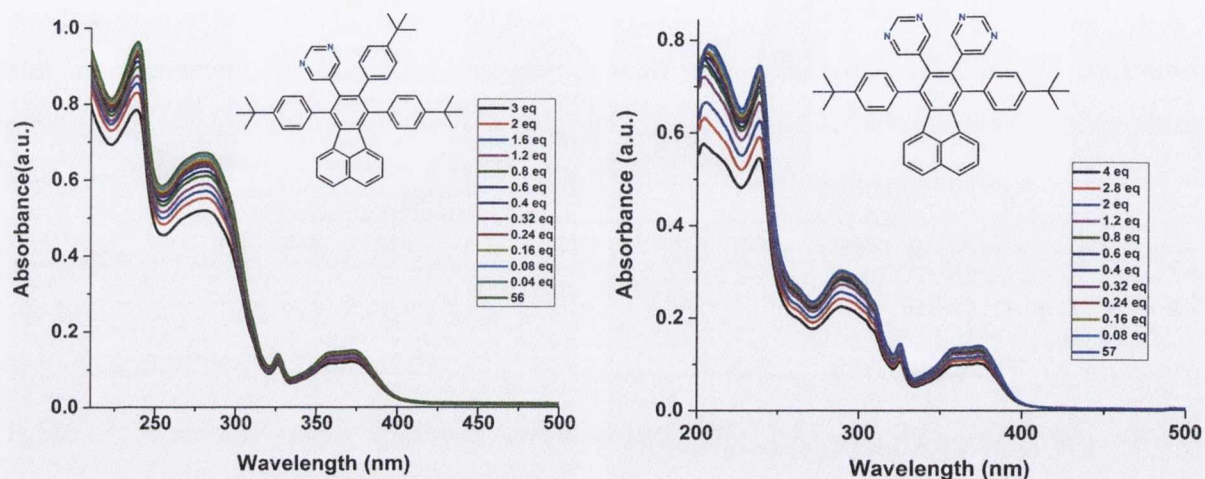


Figure 2.16: The spectrophotometric titration of **56** and **57** ( $1 \times 10^{-5}$  M) upon gradual addition of TFA ( $1 \times 10^{-4}$  M) in ethanol.

Given that the highest degree of quenching appeared to occur with the nitroaromatics possessing the lowest pKa values, the experiments were carried out in buffered solutions (H<sub>2</sub>O-EtOH (6:4) HEPES buffer solution (pH  $\sim$  7) with the buffered titrant adjusted to pH  $\sim$  7 using base).<sup>130</sup> The excitation wavelength was chosen in order to ensure reasonably constant excitation of the sample throughout the experiment. While solubility issues precluded the study of **56**, linear fits for **55** and **57** (Figure 2.17) yielded Stern-Volmer constants of  $K_{sv} = 1.14 \times 10^4$ ,  $K_{sv} = 1.2 \times 10^5 \text{ M}^{-1}$  respectively. The calculated  $K_{sv}$  value of **57** for PA was found to be higher compared to other fluorescent sensors for PA.



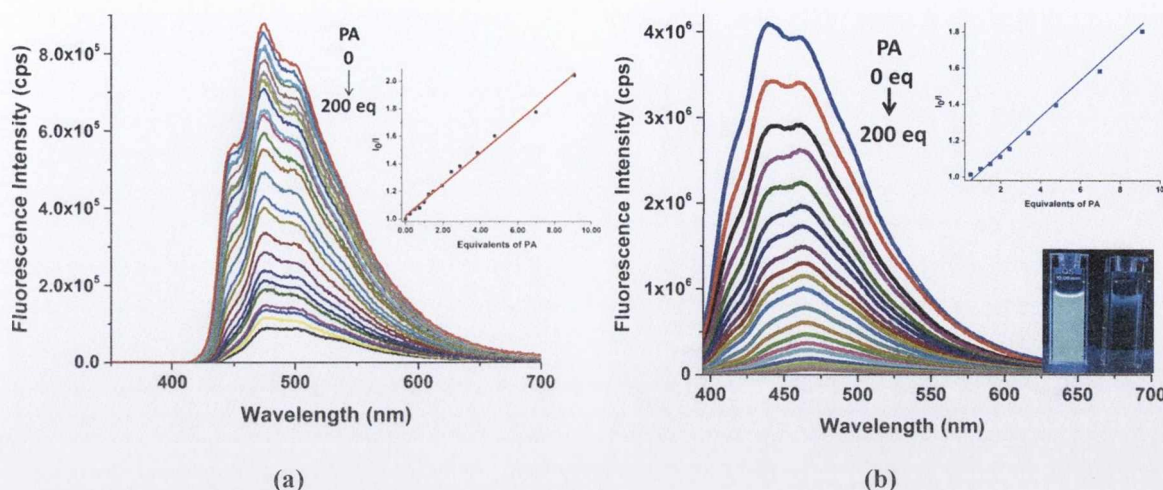


Figure 2.17: Fluorescence quenching of (a) **55** and (b) **57** ( $10^{-6}$  M) upon addition of PA ( $10^{-3}$  M) taken in  $\text{H}_2\text{O}$ : EtOH (6:4) HEPES buffer (pH  $\sim 7$ ) ( $\lambda_{\text{ex}} = 270$  nm). The top inset shows the corresponding Stern-Volmer plot. The lower inset photograph in (b) shows the visual colour change observed before and after the addition of a  $10^{-4}$  M solution of PA to a  $10^{-5}$  M solution of **57** under long wave UV light.

In order to further understand the mode of interaction between the fluoranthenes and the analytes, and to support the observed order in the fluorescence quenching, geometry optimisation of the *tert*-butyl fluoranthene derivatives **55-57** and the nitroaromatics in their ground state were carried out. This was followed by the calculation of the electron density distribution of their frontier molecular orbitals (Figure 2.18). DFT was performed using the B3LYP hybrid functional with 6-31g\* basis set in EtOH, using a polarisable continuum solvent model (PCM). The substituents are non-planar with respect to the fluoranthene core. It is found that the HOMO wave functions are predominantly localised on the fluoranthene, whereas the LUMO wave functions are localised on the analytes. The energy of the LUMOs increase with the number of pyrimidyl groups i.e.  $-1.9880$  eV (**55**)  $<$   $-1.8990$  eV (**56**)  $<$   $-1.8180$  eV (**57**). This shows the favouring of electron donation to the LUMO of the analytes ( $-3.492$  eV for PA), and giving rise to better quenching in case of **57** as shown in Figure 2.17. Also the LUMO energy of PA is lower than that of DNP and NP, making PA a better fluorescence quencher. The size of the energy gap between the LUMO of the fluorophore and the LUMO of the electron acceptor is generally the driving force for this oxidative electron transfer process, with the quenching efficiency being directly proportional to the ease of electron transfer.<sup>18, 44</sup>



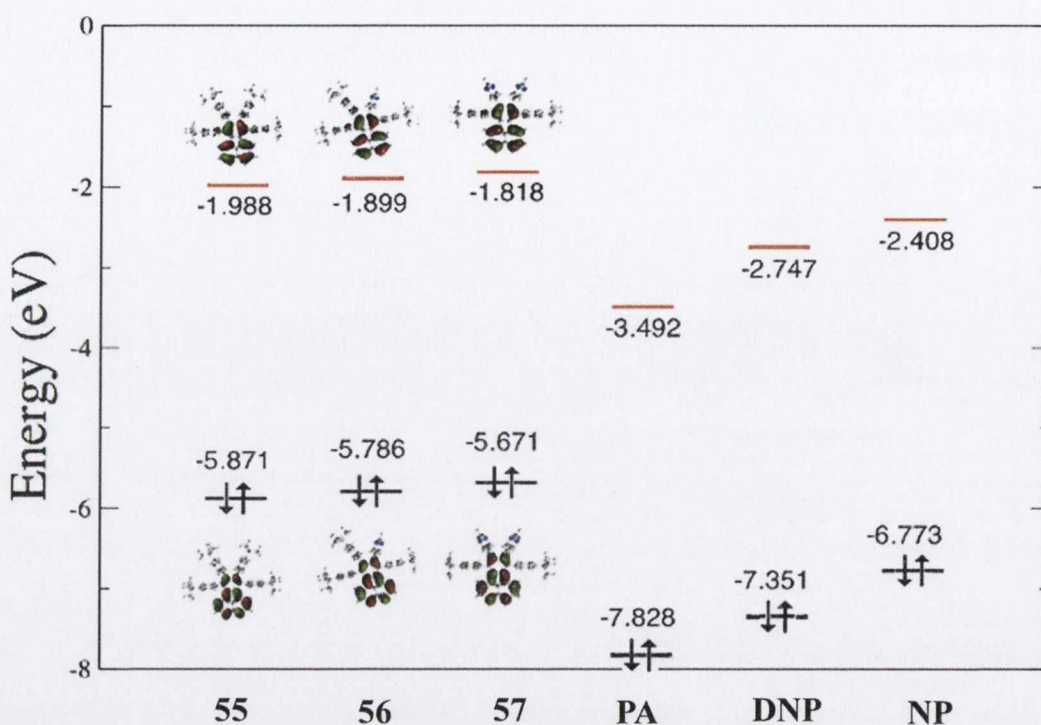


Figure 2.18: The energy level diagram showing HOMO-LUMO of fluoranthene derivatives 55-57 and the different nitroaromatics.

To understand the effect of association between the fluoranthene and the analyte (PA), optimisation of the geometry of each pair was carried out. The PA molecule was positioned on the planar five membered rings of **57** at a distance of 2 Å from the surface in two opposite orientations (Type 1 and Type 2). The final configurations show that the PA forms co-facial stacked geometry, and is involved in strong intermolecular  $\pi$ - $\pi$  interactions with the fluoranthene moiety. The energy difference between the two configurations is less than 1eV in magnitude, with a slight preference for Type 1. The electron density is localised on the fluoranthene core in the HOMO state, and on PA in the LUMO state. Also, the additional nitro groups keeps the electron density localised on the fluoranthene core in the HOMO state, which might lead to higher electron density on the PA in the LUMO state, as shown in Figure 2.19.

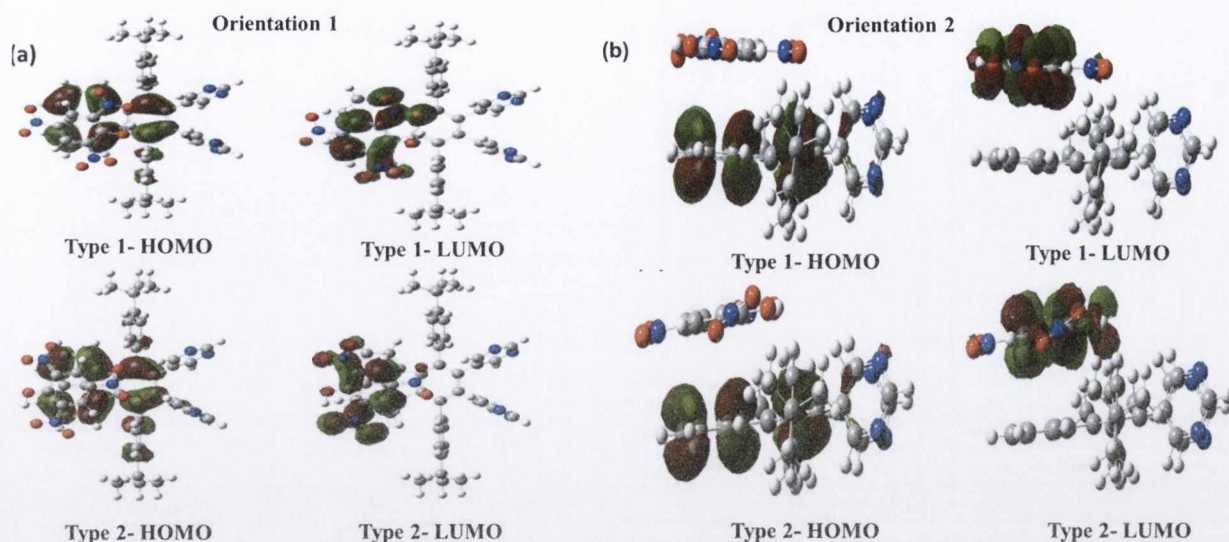


Figure 2.19: The electron density superimposed on the optimised geometry with B3LYP/6-31g\* basis set for system **57** in presence of PA in two orientations.

Similar studies to observe the effect of association between **55** and **56** with PA were performed in one orientation by placing PA on the planar five membered rings of **55-56** at a distance of 2 Å from the surface (Figure 2.20). The final optimized geometries for each pair show that the PA forms a co-facial stacked geometry and strong intermolecular  $\pi$ - $\pi$  interactions with these fluoranthene moieties.

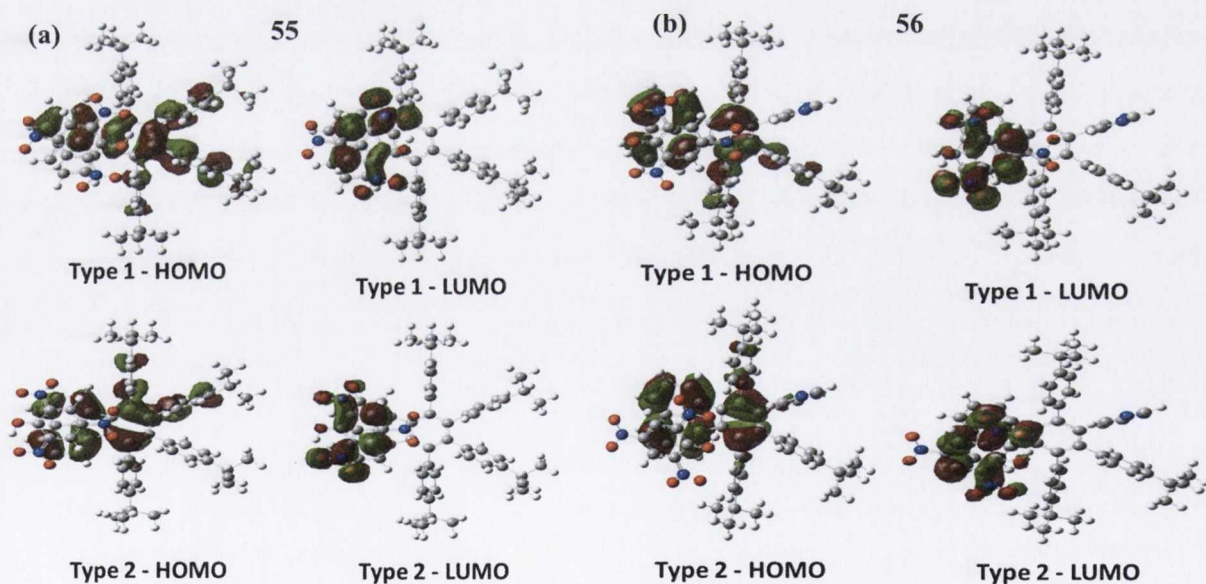


Figure 2.20: The electron density superimposed on the optimised geometry with B3LYP/6-31g\* basis set for system (a) **55** and (b) **56** in presence of PA in one orientation (Type 1 and Type 2).



### 2.7.4 Fluorescence Quenching Titrations of 55-57 with Different NACs in EtOH

As investigated earlier, the SV plots indicate a static quenching behaviour and this was further confirmed by titrations of **55-57** with different concentrations of electron deficient nitroaromatic analytes. These confirmed that sensors **55-57** are highly selective and sensitive towards the detection of nitroaromatics. The quenching behaviour of other electron deficient aromatic compounds was also studied. Figure 2.21 (a, b, c) shows the fluorescence quenching of **55**, **56** and **57** respectively with different nitroaromatics.

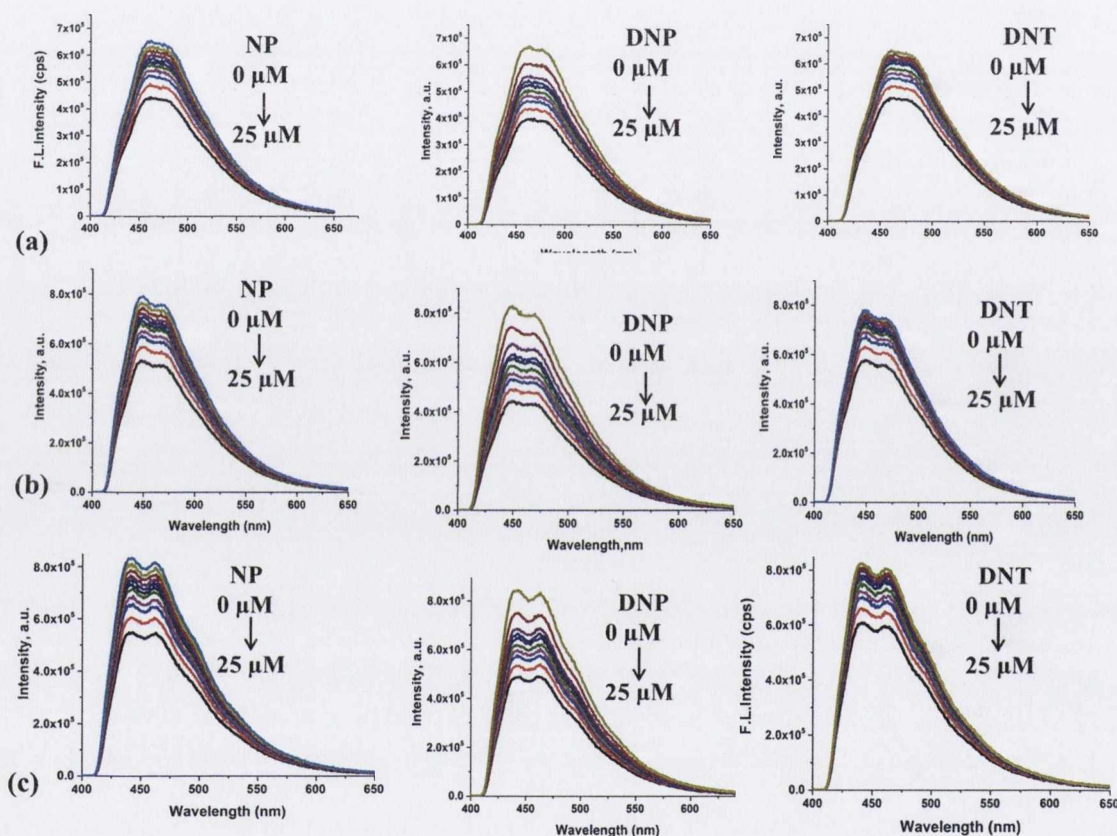


Figure 2.21: Fluorescence quenching upon addition of nitrophenol (NP), Dinitrophenol (DNP), Nitrotoluene (NT) and Dinitrotoluene (DNT) ( $\sim 10^{-4}$  M) to (a) **55**, (b) **56**, (c) **57** ( $1 \times 10^{-6}$  M) in EtOH at 25 °C, RT

### 2.7.5 Visual Detection of Nitroaromatics

The visual detection of explosives is very appealing owing to the ease of interpretation, simple material handling, rapid detection, and as a more suitable method to practice in the field. Coloured complex formation<sup>15, 89, 131</sup> develops a new chromophore which shows a different photo-physical behaviour from its starting components, including a sharp visual intensity change. In this study, we have observed a noticeable intensity change upon



subjecting the fluorophores **55-57** to PA under different experimental conditions. Due to the strong binding affinity of fluorophore **57** with nitroaromatics, the high luminescent characteristics of **57** are quenched.

Moreover, to further validate the use of these fluorophores for sensing applications, a test strip was made by the dip coating of a TLC strip into a solution of **57**, and subsequently dried in air (Figure 2.22a). Dipping this freshly made test strip into a dilute EtOH solution of PA results in the complete quenching of emission intensity of **57** in the regions exposed to PA, and is observed upon illumination with a hand-held UV lamp. In another experiment, gradual visual colour changes were noticed upon mixing of a  $\sim 10^{-5}$  M solution of fluoranthene **57** with a  $\sim 10^{-4}$  M solution of PA in EtOH under a UV lamp (Figure 2.22b).

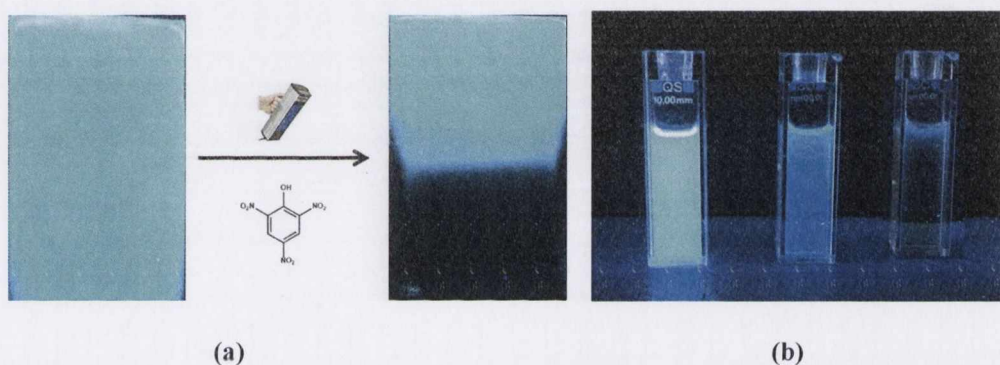


Figure 2.22: (a) Photograph of silica strip coated with **57**, before and after dipping into a solution of PA, (b) Gradual visual colour changes observed upon the mixing of a  $\sim 10^{-5}$  M solution of fluoranthene **57** with a  $\sim 10^{-4}$  M solution of PA in EtOH under a UV lamp.

### 2.7.6 Conclusion

In this work, the fluoranthene derivatives are generated *via* the Diels-Alder [4+2] cycloaddition of the desired alkynes, and the corresponding cyclopentadienone compound, establishing an efficient method for the preparation of heteroatom-substituted fluoranthenes. The characterisation undertaken suggests that these compounds display useful photophysical properties in the context of organic electronics and OLEDs, as they are relatively efficient emitters and display suitable fluorescence lifetimes. The single crystal XRD of **55** shows slipped stacking packing, and the presence of C-H $\cdots\pi$  and C-H $\cdots$ N interactions is seen in the supramolecular arrangement of the fluoranthene molecules.

The photophysical and DFT studies demonstrated that the tuning of the optical band gap with an increase in pyrimidyl groups enhances the sensitivity towards NACs. The fluorescence lifetimes followed the trend, **57**>**56**>**55**. Also, these sensors **55-57** are found to be highly

sensitive, and are capable of detecting picric acid at the ppb level. With increasing numbers of pyrimidyl rings, the fluorescence quenching efficiency increased, following the trend **57>56>55**, indicating enhanced formation of  $\pi$ -donor-acceptor complexes. Thus, we have demonstrated the use of novel nitrogen-substituted *tert*-butyl fluoranthenes as fluorescent chemosensors for the selective detection of picric acid.

**3. 2N Substituted Functionalised Fluoranthenes**





### 3.1 Introduction

We have shown in Chapter 1, that the incorporation of nitrogen atoms into the fluoranthene system increases the sensitivity of these systems towards NAC compounds, particularly that of picric acid, where the effect of fluorescence quenching increases with the increasing of nitrogen atoms. The work of this current chapter is to study the effect of the inclusion of different functional groups on the fluoranthene core, and the consequential effect on further nitroaromatic sensing studies. These studies are carried out while keeping the nitrogen loading constant.

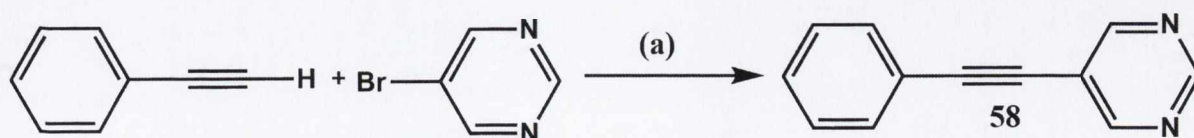
This chapter comprises of (i) the synthesis of 2N-substituted fluoranthenes *via* the [2+4]-Diels-Alder route, along with their spectroscopic characterisation, (ii) their structural & photophysical characterisation, and consequently (iii) their nitroaromatic sensing studies and their effect with varying functional groups around the periphery of 2N-substituted fluoranthenes.

### 3.2 Synthesis of 2N-Substituted Fluoranthenes

A series of 2N-substituted fluoranthenes, **65-68**, with varying substituents have been designed and synthesised. Both electron-donating and electron withdrawing groups have been incorporated to allow control over the optical properties of the generated fluoranthene-type compounds.

#### 3.2.1 Preparation of Synthetic Precursors

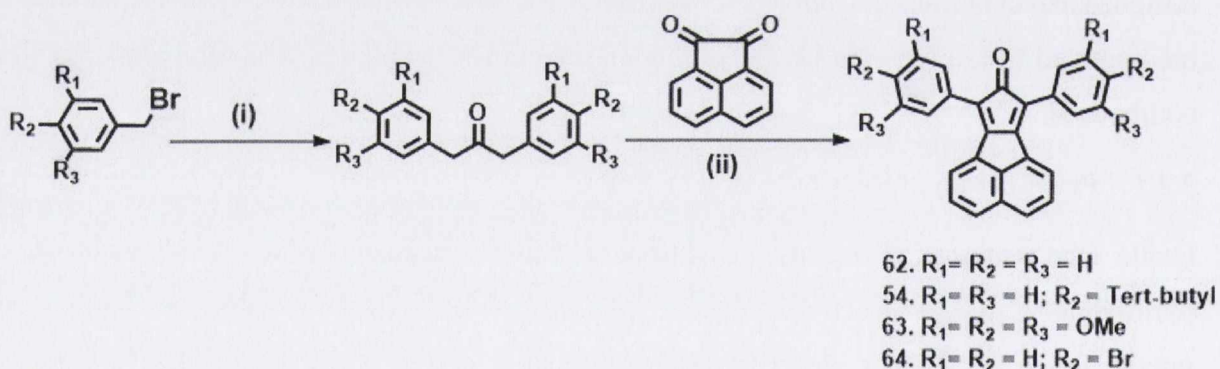
Facile incorporation of the nitrogen atoms to the fluoranthene core was achieved *via* a pyrimidine-substituted phenylacetylene. 5-(phenylethynyl)pyrimidine **58** was synthesised previously in the Draper group by the modification of a reported procedure,<sup>116</sup> and was generated *via* a Sonogashira cross-coupling between two commercially available reagents, phenylacetylene and 5-bromopyrimidine. The reaction was assisted with microwave heating.<sup>117</sup> **58** was extracted into methylene chloride, concentrated, and precipitated with cold methanol in 92% yield.



*Scheme 3.1: Synthesis of asymmetric 2N aryl acetylene, **58**; (a)  $\text{Pd}(\text{PPh}_3)_4$  (1.6 mol%),  $\text{CuI}$  (2 mol%),  $\text{DMF:DIPA}$  (1:3),  $\mu\text{w}150\text{ W}$ ,  $115\text{ }^\circ\text{C}$ , 23 min, 92%*

For the preparation of 2N fluoranthene-type derivatives, **65-68**, the initial assembly of the synthetic precursors, the fluoranthene-derived cyclopentadienones **54**, **62-64**, is a key step. These compounds provide suitably functionalised sites to which the 5-(phenylethynyl) pyrimidine was cross-coupled.

The cyclopentadienones **54** and **62-64** were obtained from a two-fold Knoevenagel condensation between varying the 1,3-diaryl propanone reagents with the commercially available acenaphthenequinone (Scheme 3.2). A modified literature procedure was used to generate the desired cyclopentadienones using refluxing EtOH as the reaction solvent.<sup>119</sup> Use of refluxing EtOH compared to the room temperature MeOH conditions, allowed for the reaction time to be considerably shortened. After cooling of the reaction mixture to room temperature, the desired products were filtered directly, and required no further purification. The desired dark purple products obtained from these reactions conditions were 7,9-diphenylcyclopenta[*a*]acenaphthylen-8-one **62**, 7,9-bis(4-*tert*-butylphenyl)-8Hcyclopenta[*I*]acenaphthylen-8-one **54** and 7,9-bis[3,4,5-(trimethoxy)phenyl]-8Hcyclopenta[*I*]acenaphthylen-8-one **63** and 7,9-bis(4-bromo)-8Hcyclopenta[*I*]acenaphthylen-8-one **64**.



Scheme 3.2: Synthetic route to cyclopentadienones (**54**, **62-64**); (i)  $\text{Ca}(\text{OH})_2$ ,  ${}^t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$  (1:1 v/v), RT (ii)  $\text{KOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , 80 °C.

The substituted 1,3-diaryl propanones, hereafter referred to as monoketones, have been synthesised previously in the Draper group.<sup>112</sup> These are obtained *via* a liquid-liquid phase-transfer carbonylation reaction, with  $\text{Fe}(\text{CO})_5$  as the source of CO and  ${}^t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$  as the phase transfer catalyst.<sup>132</sup> The reaction was carried out for 5-6 h at room temperature under  $\text{N}_2$ . On completion and cooling of the reaction mixture, it was oxidized by bubbling with air for 1 h. The mixture was finally acidified with a 10% HCl solution. Each monoketone reaction solutions was extracted into methylene chloride, dried over  $\text{MgSO}_4$  and concentrated



*in vacuo*. Each precursor was recrystallised from methylene chloride with cold methanol, and collected as white solids in >70 % yield (Figure 3.1).

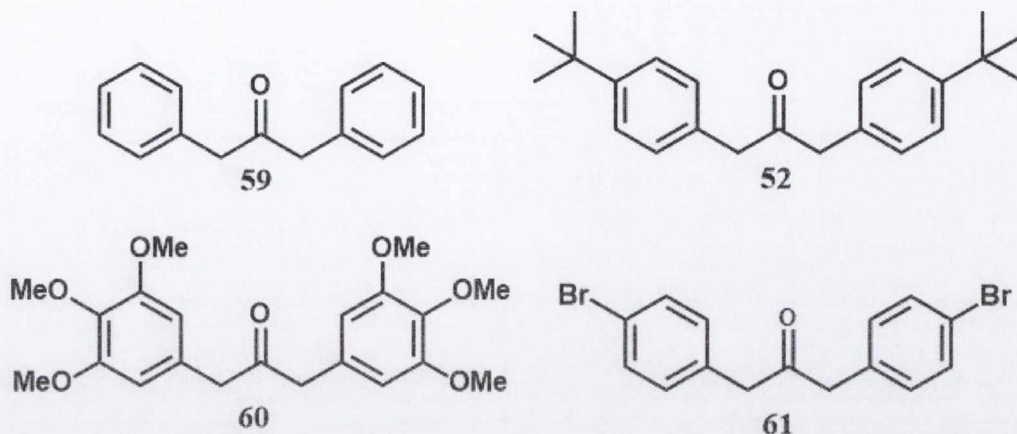


Figure 3.1: Substituted 1,3-diaryl-propanones precursors **52**, **59-61** used to prepare 2N fluoranthenes.

### 3.2.2 Synthesis of Target 2N Fluoranthenes

The target substituted 2N fluoranthene derivatives **65-68** were synthesised *via* the widely used Diels Alder [2+4] cycloaddition of 5-(phenylethynyl)pyrimidine and generated substituted cyclopentadienones in a benzophenone melt, under an argon atmosphere.<sup>120</sup> As per Chapter 1, the utility of these concerted reactions has increased dramatically since their discovery by Diels and Alder in 1950, and continue to be one of the more favourable reaction types for the generation of aromatic rings.

Typically, the Alder rule describes the rate of the reaction as the “normal electron demand” where the electron donating groups (EDG) are located on the diene (HOMO), and the electron withdrawing groups (EWG) on the dienophile (LUMO). This pathway is associated with a decrease in the energy barrier as the EDGs on the diene raise the energy of the HOMO orbitals, while the EWGs on the dienophile lower the energy of LUMO orbitals. The interaction between the diene HOMO and dienophile LUMO is very important in Diels-Alder reactions and are often controlled by the HOMO-LUMO pair closest in energy. In contrast to this, Bachmann and Deno proposed an “inverse electron demand” pathway, where an electron-rich dienophile and an electron-poor diene are favoured, as it is a diene LUMO-dienophile HOMO controlled reaction.

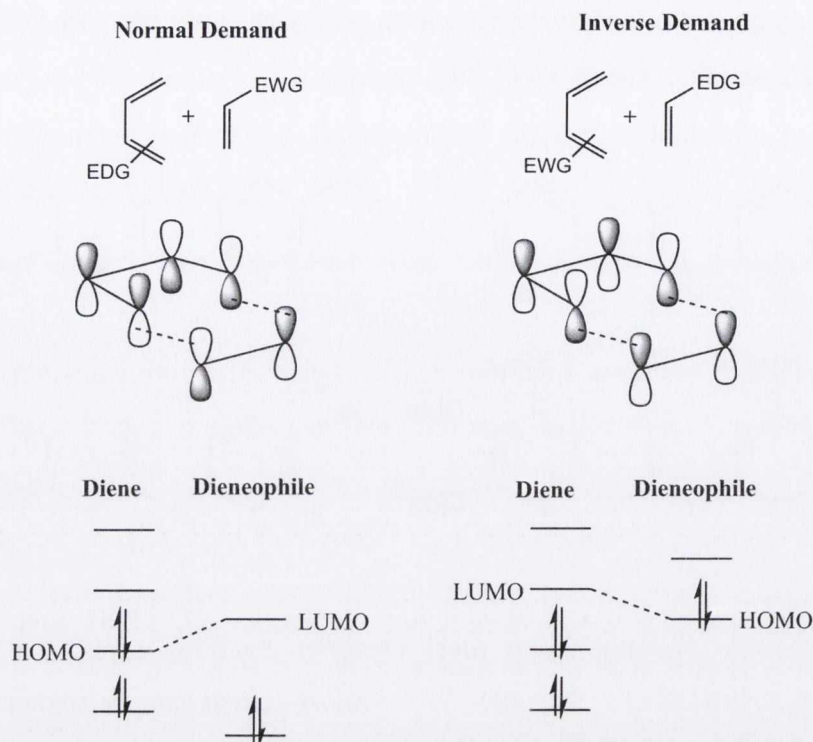
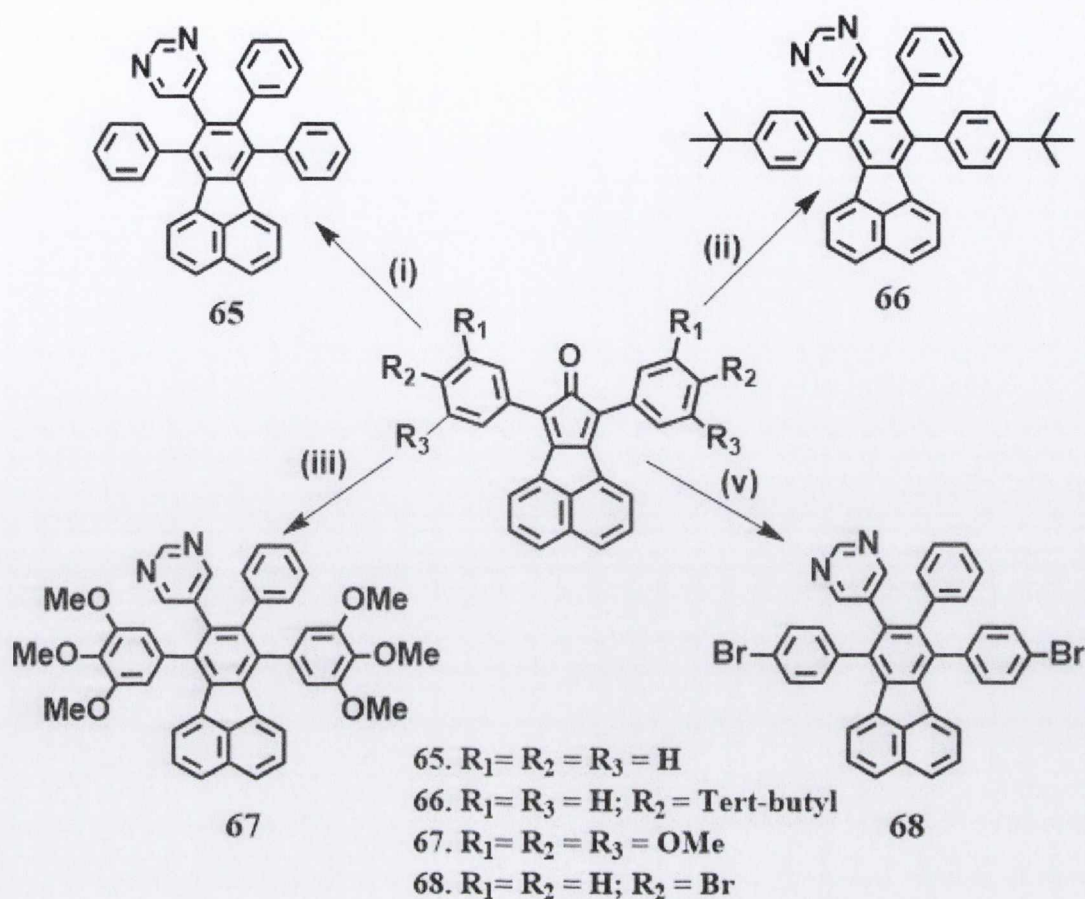


Figure 3.2: Schematic representation showing orbital interactions between diene and dienophile in Diels-Alder reaction. Normal and inverse electron demand cases are demonstrated.

From the above mechanistic pathway, the desired 2N substituted-fluoranthene derivatives *i.e.* 5-(7,9,10-triphenylfluoranthene-8-yl)pyrimidine **65**, 5-(7,10-bis(4-*tert*-butyl)phenyl)-9phenylfluoranthene-8-yl)pyrimidine **66**, 5-(9-phenyl-7,10-bis(3,4,5-trimethoxyphenyl)fluoranthene-8-yl)pyrimidine **67** and 5-(7,10-bis(4-bromophenyl)-9-phenylfluoranthene-8-yl)pyrimidine **68** were synthesised as shown in Scheme 3.3.



Scheme 3.3: Synthesis of 2N Fluoranthene by Diels-Alder reaction in a benzophenone melt.

(i) 280 °C, 8 h, 76 %, (ii) 280 °C, 6 h, 74 %, (iii) 300 °C, 5 h, 71 %, (iv) 275 °C, 8 h, 75 %

### 3.3 Structural Characterisation of 65-68

The full spectral characterisation of each 2N fluoranthene, **65-68** was carried out by multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and HSQC, HMBC), high resolution mass spectrometry, elemental analysis and infrared spectroscopy (See Chapter 7). The NMR data of the known reactants were in good agreement with the literature. Due to a  $C_2$ -plane of symmetry, the  $^1\text{H}$ -NMR spectra of each cyclopentadienone is relatively simple. The  $^1\text{H}$ -NMR spectra of **65-68** show a doublet-pseudotriplet-doublet system characteristic of the naphthyl moiety. The protons at positions **1** and **2** of the 5-pyrimidyl substituents are also magnetically equivalent.

The electrospray mass spectra of these derivatives, **65-68** reveal the major peak in each spectrum corresponds to the  $[\text{M}+\text{H}]^+$  molecular ion. These values are in excellent agreement with the values calculated. The mass spectral data is summarised in Table 3.1.



Table 3.1: Electrospray Mass spectral data for novel 2N fluoranthene derivatives **65-68** (recorded in  $\text{CH}_2\text{Cl}_2$ ,  $m/z$  in m.u.)

| Compound  | Molecular Ion           | Formula                                           | Calculated $m/z$ | Found $m/z$ (%) |
|-----------|-------------------------|---------------------------------------------------|------------------|-----------------|
| <b>65</b> | $[\text{M}+\text{H}]^+$ | $\text{C}_{38}\text{H}_{25}\text{N}_2$            | 509.2018         | 509.2026        |
| <b>66</b> | $[\text{M}+\text{H}]^+$ | $\text{C}_{46}\text{H}_{41}\text{N}_2$            | 621.3270         | 621.3269        |
| <b>67</b> | $[\text{M}+\text{H}]^+$ | $\text{C}_{44}\text{H}_{37}\text{N}_2\text{O}_6$  | 689.2652         | 689.2659        |
| <b>68</b> | $[\text{M}+\text{H}]^+$ | $\text{C}_{38}\text{H}_{23}\text{N}_2\text{Br}_2$ | 665.0228         | 665.0219        |

### 3.3.1 NMR Study of **65-68**

The pyridyl region of the spectrum is typical of the series, but the presence of the  $\text{sp}^2$  nitrogen atoms in only one ring system remove the molecule's plane of symmetry, resulting in each ring appearing as a separate spin systems. Characterisation of these asymmetric 2N fluoranthenes **65-68** proved more complex, owing to the more convoluted nature of their signals. The aromatic region of the asymmetric fluoranthenes is shown in Figure 3.3. Use of selective TOCSY experiments allowed for the full assignment of each proton signal, and when coupled with the HSQC spectrum, the assignment of all of the carbon signals was achieved.

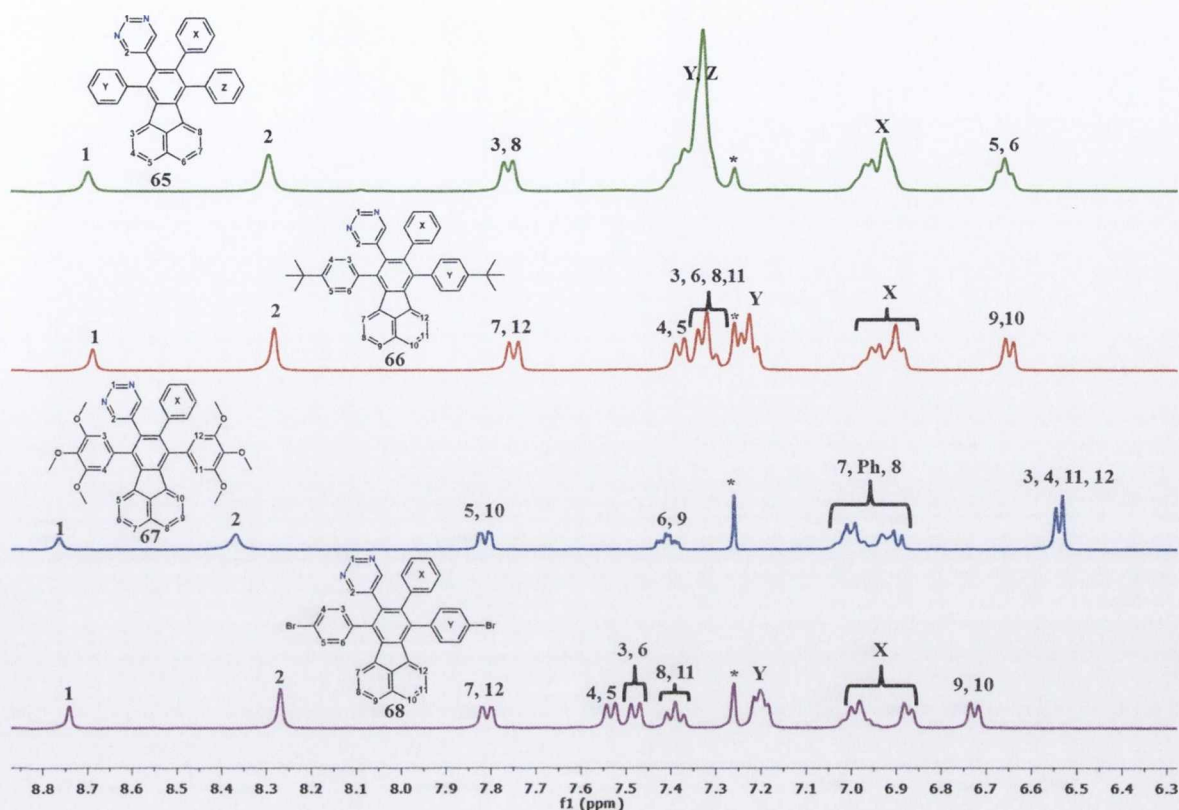


Figure 3.3: Overlaid aromatic region of 2N fluoranthenes **65-68** at RT. Asterisk denotes solvent ( $\text{CDCl}_3$ ) peak.

All the four spectra showed a similar pattern with the most downfield aromatic singlet signal around  $\delta \sim 8.6$  ppm attributed to  $\text{H}_1$ , with the second most downfield signal  $\delta \sim 8.2$  ppm owing to  $\text{H}_2$ , which are protons directly adjacent to the pyrimidyl ring in the asymmetric molecules. The pyrimidyl protons are the most deshielded due to the electron withdrawing nature of the nitrogen atoms. The resonances of the phenyl ring (X) protons appear as a multiplet signal around the  $\delta \sim 6.9$  ppm region, and the resonances of phenyl, *tert*-butyl, methoxy and bromo-containing aromatic ring protons appear as a series of overlapping signals in the region between  $\delta$  7.3 – 7.6 ppm.

A 2D TOCSY analysis, shown in Figure 3.4, proved a useful tool for assessing the nature of the systems. The spectrum shows the presence of two three spin systems in each asymmetric molecule as highlighted in the coloured boxes. The two different three spin systems arise due to the asymmetric nature of the molecule and are attributed from the fluoranthene unit.

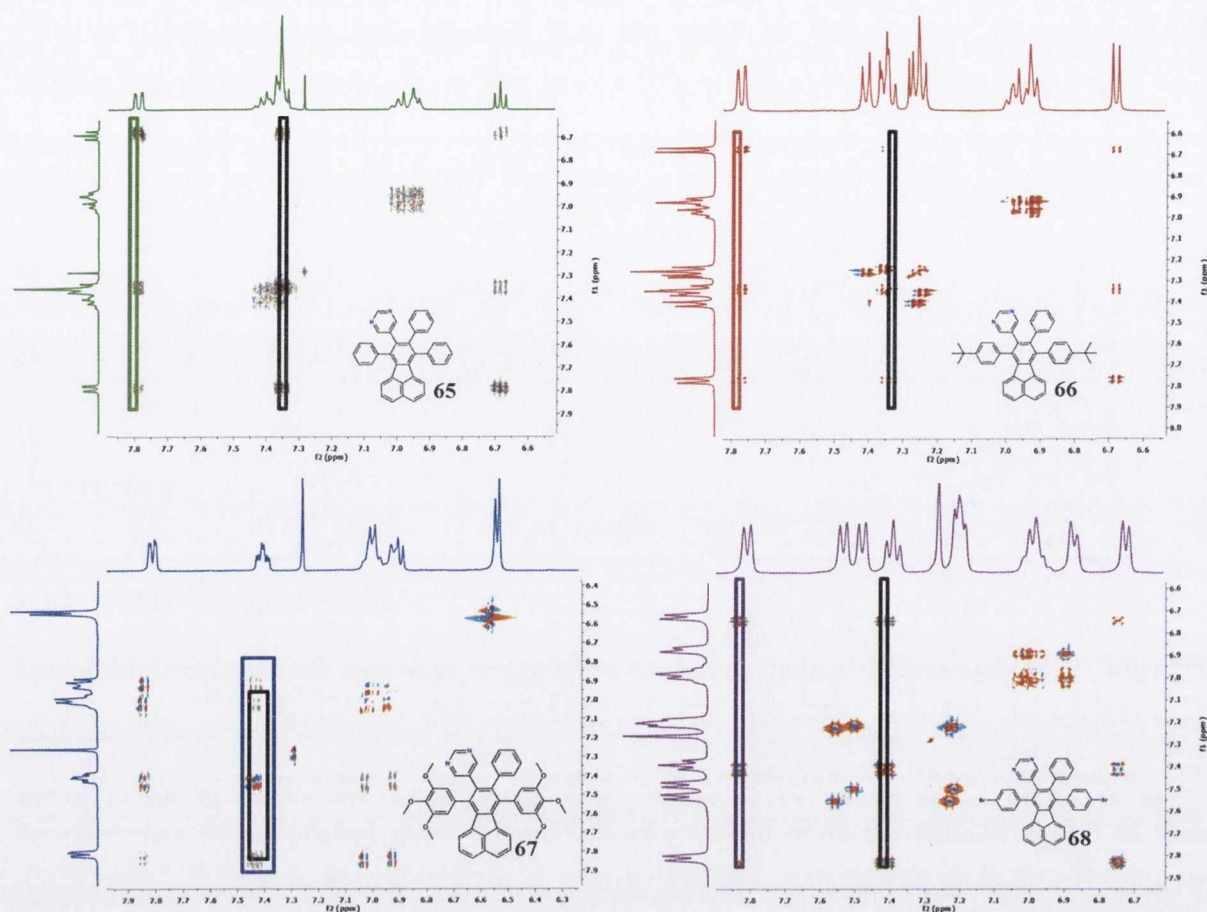


Figure 3.4: TOCSY analysis of **65**–**68**: colours represent two different 3-spin systems.

### 3.3.2 Crystallographic Study of **67**

Crystals of **67** suitable for single crystal X-ray diffraction analysis were grown from the slow evaporation of a methylene chloride/methanol solution. The single crystal X-ray analysis of **67** provides some insight into the interaction in solid state. **67** crystallises in the monoclinic  $P2_1/c$  space group with eight molecules per unit cell, and two molecules in the asymmetric unit. The fluoranthene moiety shows a planar arrangement (Figure 3.5), with the pyrimidyl (B) and phenyl rings (C) showing twists of  $89.49^\circ$  and  $65.71^\circ$  from the plane of the central aryl ring (X) respectively. The methoxy-containing aryl rings (A) show a twist of  $78.89^\circ$ , and (D) shows a twist of  $81.74^\circ$  with respect to the central aryl ring (X).



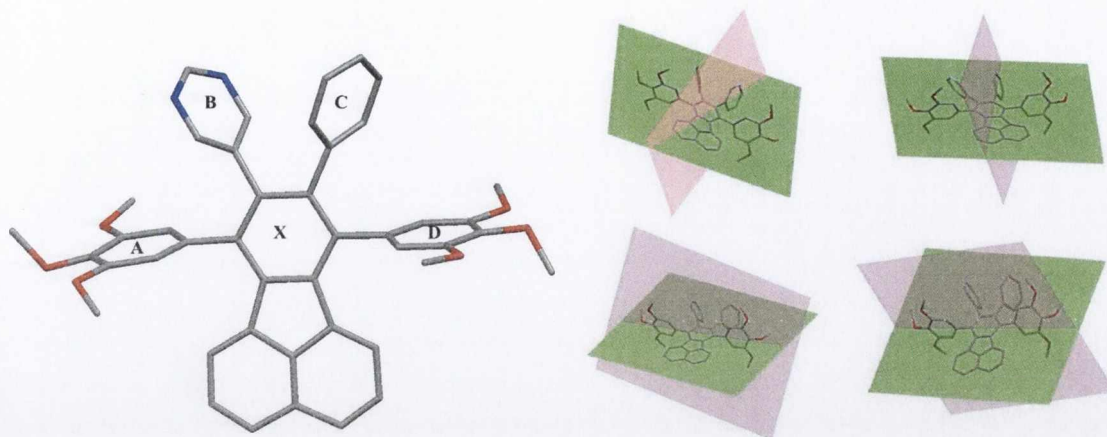


Figure 3.5: (a) Capped stick representation of **67** (carbon atoms in grey, nitrogen atoms in blue and oxygen atoms in red). (b) Graphical representation of the central ring plane and each of the pendant pyrimidyl/ phenyl / methoxy containing ring planes.

Molecules of **67** are mainly connected through  $\text{N1} \cdots \text{C1-H}$  [3.114 Å] intermolecular interactions of the adjacent pyrimidyl rings. In addition, methoxy groups shows interactions *i.e.*  $\text{O1} \cdots \text{C2-H}$  [3.386 Å] and  $\text{O1} \cdots \text{C3-H}$  [3.202 Å] with the neighbouring methoxy and phenyl ring respectively as illustrated in Figure 3.6a. Further, weak intermolecular  $\text{C} \cdots \text{H}$  interactions arising from the fluoranthene unit contribute to form a self-assembled close packed arrangement. When viewed along the 'c' axis the pyrimidine rings on adjacent molecules tend to be aligned facing one other.

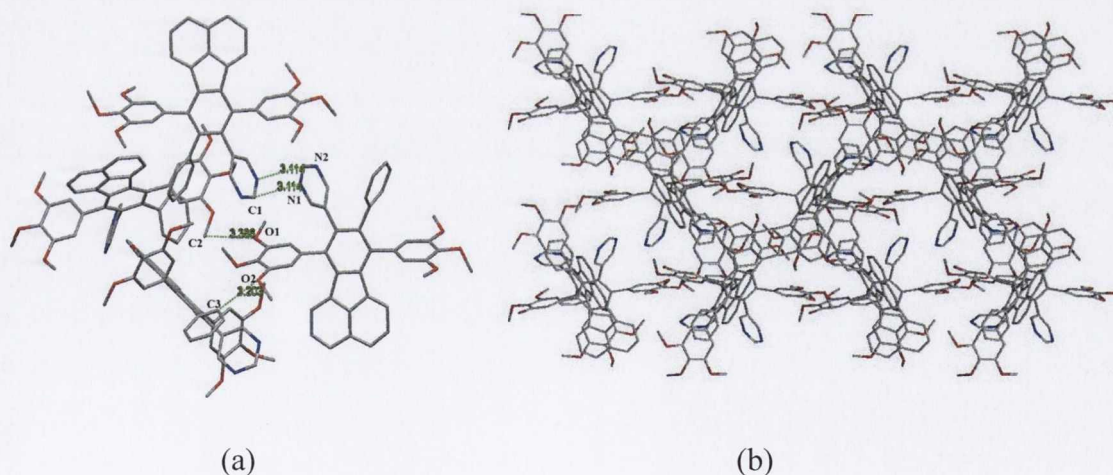


Figure 3.6: (a) Representation of the lattice stabilising interactions in **67** (distances marked in Å) using the Mercury program.<sup>133</sup> H atoms are omitted for clarity of **67**; (b) Crystal packing arrangement of **67** viewed along the c-axis.

### 3.4 Photophysical Studies of 65-68

The optical absorption spectra of different 2N fluoranthenes in EtOH are shown in Figure 3.7. All of the compounds exhibit four well resolved major intense absorption bands which arise due to  $\pi \rightarrow \pi^*$  transitions. The maximum absorption peaks for the compounds appear at similar wavelengths, with **67** as an exception showing a very slightly blue-shifted absorption peak. It suggests that outer phenyl rings and the functional groups do not extend the conjugation of the core dramatically.

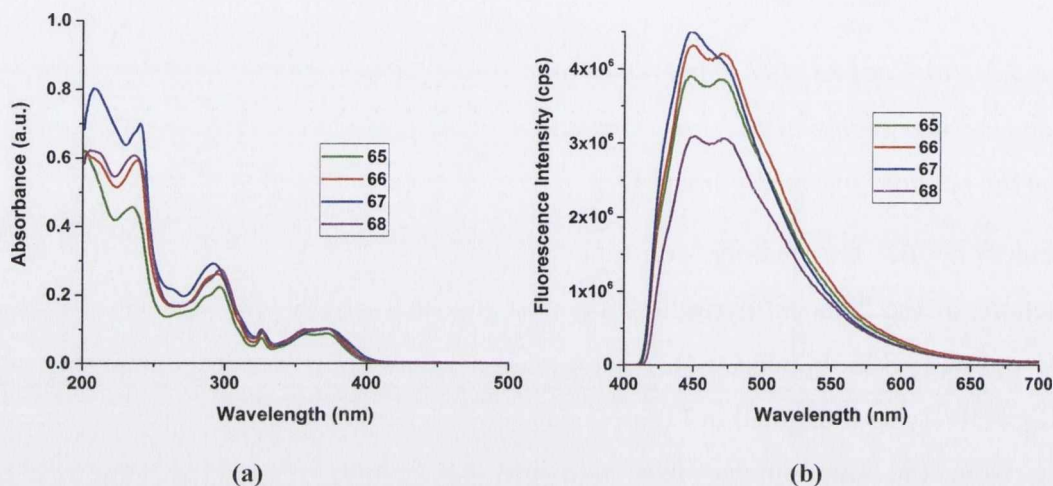


Figure 3.7: The optical (a) absorption and (b) emission spectra of 2N fluoranthenes **65-68** in EtOH at room temperature.

From the low energy onset of the absorption bands, the optical band gaps were calculated and presented in Table 3.2. It is evident from the data listed in Table 3.2, that the energy gap of these materials can be fine-tuned by appropriate substitution. The optical band gaps were found to be in the range 3.32–3.35 eV in solution.

Each fluoranthene derivative exhibits a strong blue emission (Figure 3.7b) at ~445 nm, with a Stokes' shift of 4200–4500 cm<sup>-1</sup>. The emission spectrum of **67** is slightly red-shifted in comparison to the other fluoranthene derivatives. The relative emission intensity of **68** is found to be significantly less, and this is proposed to be due to the presence of bromine groups, causing the heavy atom effect. The variations in the spectral pattern arise due to the change in the conformational relaxation occurring in the excited state process before emission takes place.



Table 3.2: Summary of photophysical data of each 2N fluoranthenes **65- 68** ( $\sim 10^{-5}$  M) in EtOH at RT.

| Compound  | $\lambda_{\text{abs}}$ [nm] | $\lambda_{\text{em}}$ [nm] | Stoke's<br>shift ( $\text{cm}^{-1}$ ) | $\Phi_f$ | Optical<br>band<br>gap (eV) | HOMO-<br>LUMO gap<br>(eV) | $\tau$ /ns |
|-----------|-----------------------------|----------------------------|---------------------------------------|----------|-----------------------------|---------------------------|------------|
| <b>65</b> | 234, 296,<br>326, 373       | 444                        | 4287                                  | 37%      | 3.32                        | 3.89                      | 26         |
| <b>66</b> | 238,295,<br>326, 372        | 445                        | 4409                                  | 41%      | 3.33                        | 3.87                      | 27         |
| <b>67</b> | 240, 292,<br>327, 371       | 446                        | 4532                                  | 15%      | 3.34                        | 3.86                      | 28         |
| <b>68</b> | 236,297,<br>326, 370        | 443                        | 4453                                  | 36%      | 3.35                        | 3.91                      | 23         |

The fluorescence quantum yield ( $\Phi$ ), collected using the integration sphere method, followed by analysis with the PQLY (Horiba, Version 4), shows a range of 35–41% for the fluoranthenes in EtOH, with **67** showing the lowest QY. The fluorescence excited state lifetimes of **65-68** in EtOH are found to be in the range of 23-28 ns; calculated using a time correlated single photon counting (TCSPC) method. The results of the photophysical and fluorescence lifetime data, affected by the relative substituents, were analysed and summarized in Table 3.2.

### 3.4.1 Solvent Dependency Studies of 2N-Fluoranthenes

The UV-Vis absorption and emission spectra for the 2N fluoranthene derivatives were recorded in four solvent systems of increasing polarity. The UV-Vis absorption spectra show marginal shifts with changes in solvent polarity. This indicates that the ground state properties of each system are insensitive to nature of the solvent. According to the Frank-Condon principle, electronic absorptions occur faster (less than  $10^{-15}$  s) than molecular rearrangement, and thus only solvent molecules can affect the absorption spectrum of the absorbing species.<sup>43</sup> The fluoranthenes show four distinct peaks in EtOH, methylene chloride



and acetonitrile, whereas in the non-polar solvent toluene, only three distinct peaks were present in the spectra.

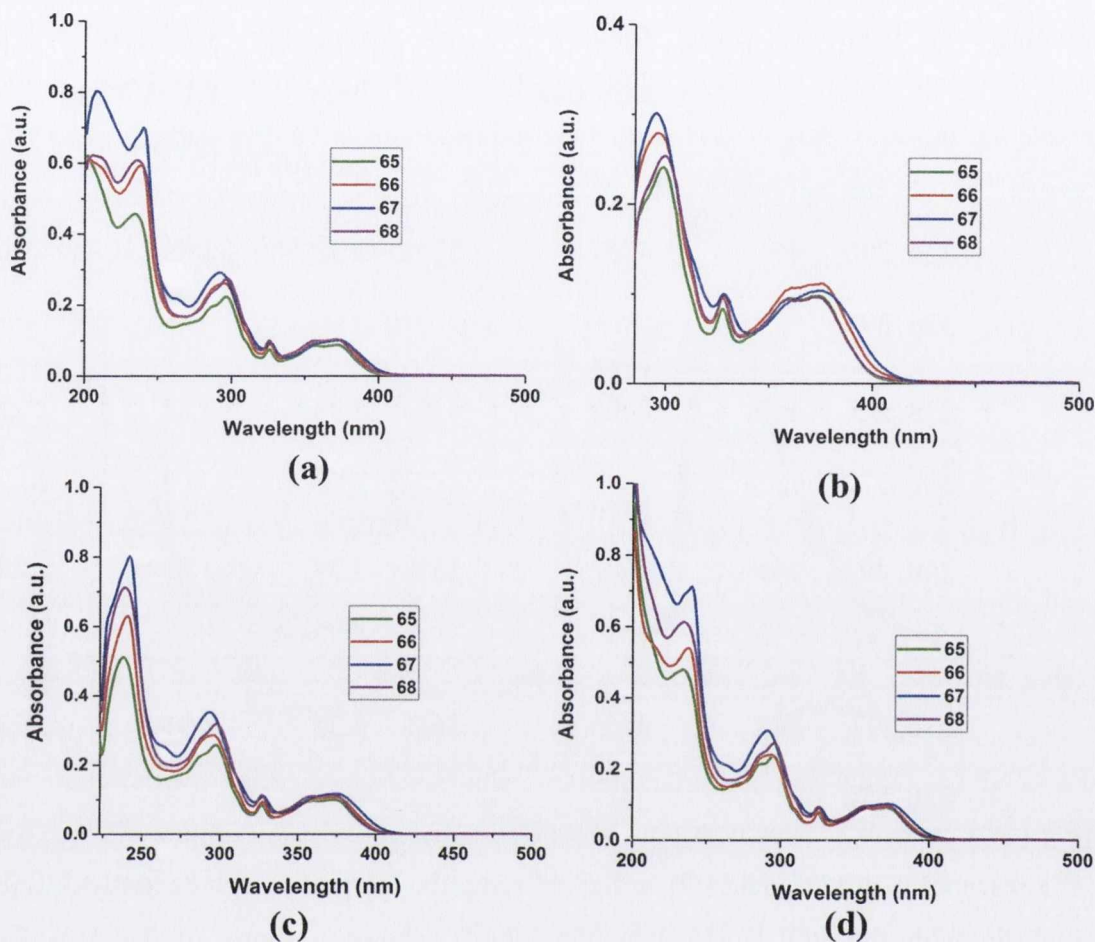


Figure 3.8: Absorption studies of 2N fluoranthenes **65-68** ( $\sim 10^{-5}$  M) in (a) Ethanol (b) Toluene (c) Methylene Chloride and (d) Acetonitrile.

In contrast to absorption spectra, the emission spectra of each fluoranthene show a pronounced shift in their  $\lambda_{\text{em}}^{\text{max}}$  with changes in solvent polarity. This indicates that the excited state is susceptible to changes in solvent polarity. Fluoranthene **67** and its emission data (Figure 3.9) will now be discussed further.

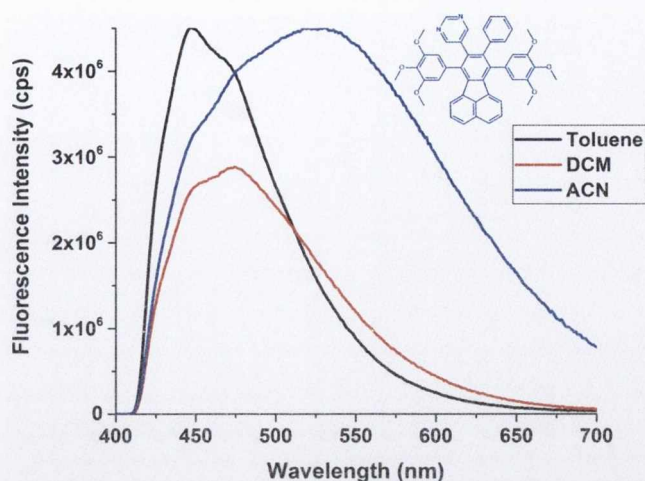


Figure 3.9: Solvent dependency emission studies of **67** ( $\sim 10^{-5}$  M), RT.

The red-shift emission observed in high polarity solvents for **67** is indicative of the greater stabilisation of the excited state by polar solvent molecules.<sup>134</sup> In comparison with the absorption, emission occurs over a longer period of time (fluorescence  $\sim 10^{-7}$  x  $10^{-9}$  s), and thus provides the opportunity for the excited state molecules to interact with surrounding solvent molecules.<sup>134, 135</sup> In particular, **67** show a significant bathochromic shift of  $\lambda_{\text{max em}}$  of  $3950 \text{ cm}^{-1}$ , transitioning from toluene to acetonitrile. This trend occurs in polar molecules that are likely to have enlarged dipoles and charge-transfer character in their excited state.<sup>136</sup> Furthermore, the solvent dependency study carried out here suggest that the emissive excited state of **67** has  $\pi$ - $\pi^*$  (ICT) character, shown by the red shifting of the peak with increasing solvent polarity.<sup>137</sup>

### 3.5 Nitroaromatic Sensing Studies

From Chapter 2, the high stability and electron rich environment of these fluoranthene derivatives make them ideal candidates to probe the potential sensing of explosive NACs. This would be achieved by the fluorescence quenching mechanism *via* donor-acceptor charge-transfer (CT) complex formation, through  $\pi$ - $\pi$  interactions. In this current work, we have employed the four fluoranthene-based sensors **65-68** to detect common NACs. As explored in other chapters, these NACs are known to be high electron deficient molecules, and undergo strong interactions with nearby excited fluorescent fluoranthene species.

All 2N-fluoranthene derivatives **65-68** were treated with different NACs including picric acid (PA), 2,4,6- trinitrotoluene (TNT), 2,4-dinitrotoulene (DNT), 2,4-dinitrophenol (DNP), nitrophenol (NP), nitrotoluene (NT), dinitrobenzene (DNB), and common interfering electron deficient molecules including benzoquinone (BQ), iodophenol (IP), phenol (P), 2,3-dichloro-



5,6-dicyanobenzoquinone (DDQ), and toluene (T). The fluorescence quenching experiments were carried out by titration of fluoranthene derivative solutions ( $1.0 \times 10^{-6}$  M) with known concentrations of explosive NACs. Due to the electron transfer process between the fluoranthene and the explosive NACs molecules, the fluorescence intensity is readily quenched upon gradual addition.

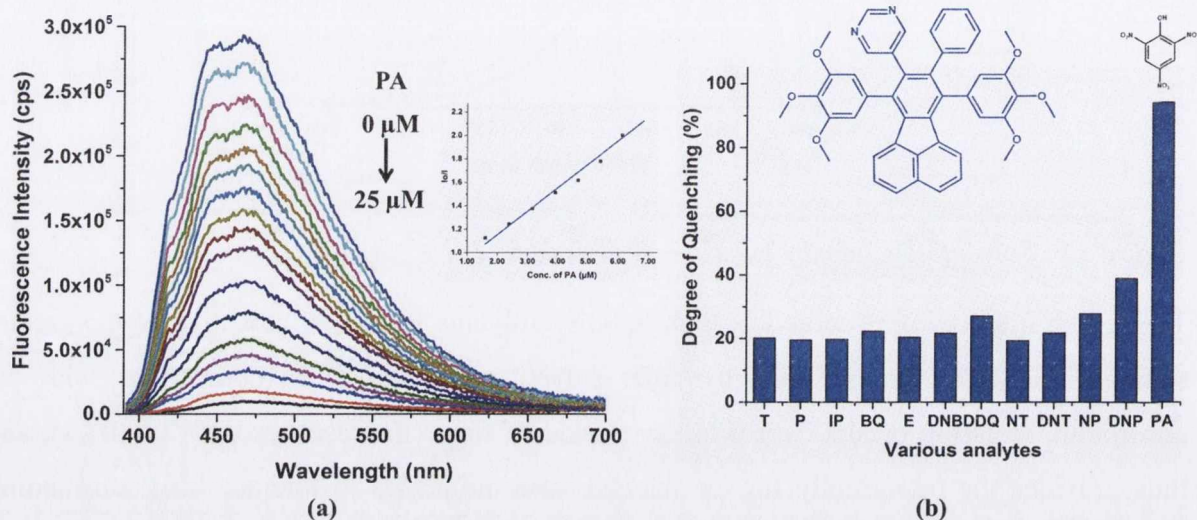


Figure 3.10: (a) Fluorescence quenching behavior of **67** ( $\sim 10^{-6}$  M) with gradual addition of PA in EtOH. The inset shows the Stern–Volmer plot of **67** with different concentrations of PA. (b) Degree of fluorescence quenching of **67** with different analytes. The inset image is the structure of **67**.

Figure 3.10a shows the fluorescence quenching behavior of **67**, upon gradual addition of 25  $\mu$ M of a  $1 \times 10^{-4}$  M solution of PA. Figure 3.10b shows the degree of fluorescence quenching with different analytes. The quenching behavior of **67** with some other NACs is shown in Figure 3.11. Upon gradual addition of different concentrations of PA to the solution of **67**, the fluorescence intensity measured at  $\sim 446$  nm is dramatically decreased, and shows 94% quenching for 25  $\mu$ M of PA. The quenching behavior was analysed by the Stern–Volmer (SV) equation,  $I_0/I = 1 + K_{SV}[Q]$ , where  $I_0$  and  $I$  are the fluorescence intensities in the absence and presence of the quencher  $[Q]$ , and  $K_{SV}$  is the Stern–Volmer rate constant. The decrease in the fluorescence intensity could be an electron transfer process, and on the basis of thermodynamic considerations, may be defined as static or dynamic quenching. The inset shown in Figure 3.10 shows a linear SV plot for **67** treated with different concentrations of PA. A similar linear behavior of each SV plot for **67** was observed with other NAC analytes. This indicates that quenching is achieved *via* a static quenching mechanism through the formation of a one-to-one non-fluorescent ground state complex.<sup>74</sup>



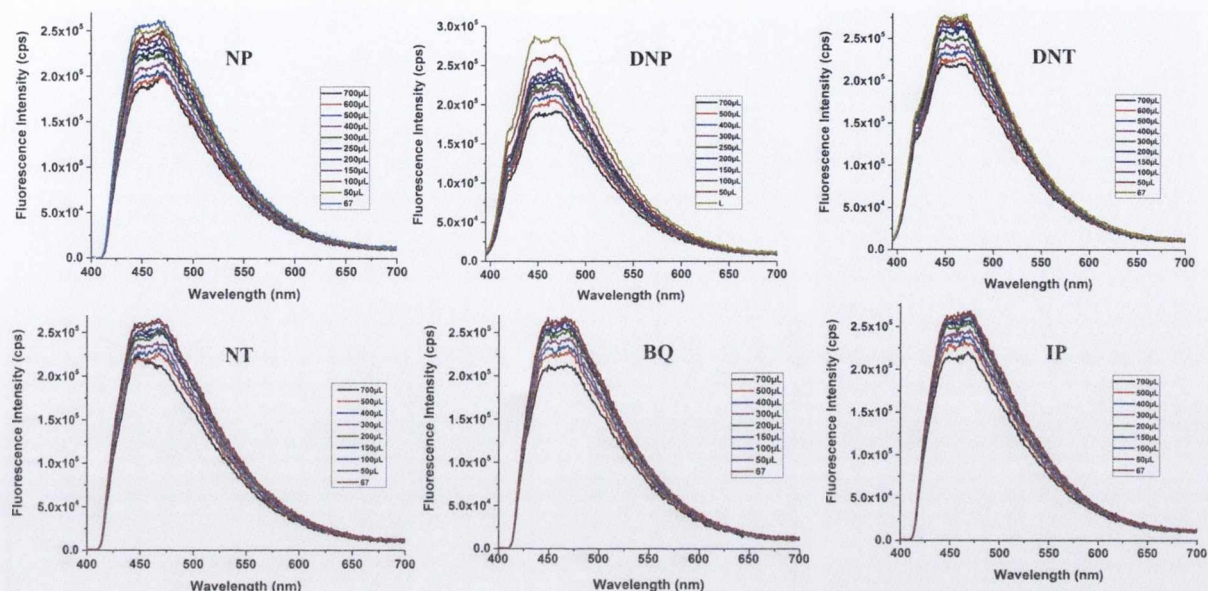


Figure 3.11: Fluorescence quenching behavior of **67** ( $\sim 10^{-6}$  M) with the gradual addition of various analytes in EtOH.

Similar results were observed for the other fluoranthene derivatives treated with different nitroaromatic analytes. The dilution effect caused by adding analyte solution altered the fluorophore concentration affecting the emission intensity at higher additions of analyte. The fluorescence quenching behavior of **65**, **66** and **68**, upon the gradual addition of 25  $\mu$ M of  $1 \times 10^{-4}$  M solution PA is shown in Figure 3.12.

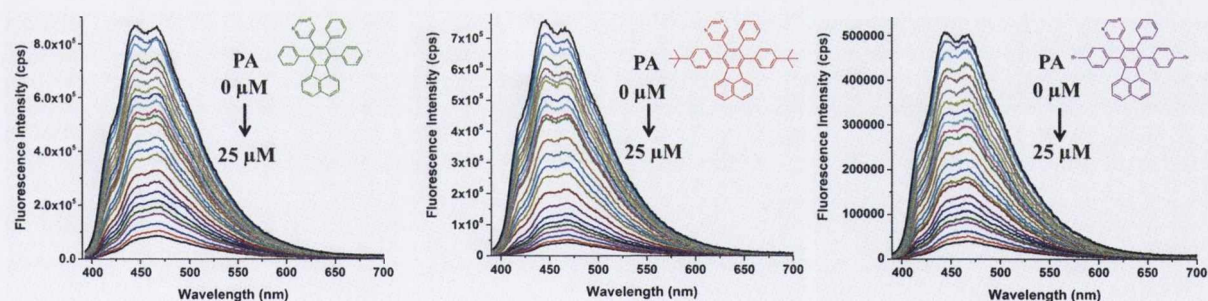


Figure 3.12: The fluorescence quenching behaviour of other 2N-fluoranthene derivatives **65**, **66** and **68** ( $\sim 10^{-6}$  M) with different concentrations of PA.

PA exhibits the highest quenching response at a parts per billion level (5–25 ppb), while DNT and NT show  $\sim 1.5$  ppm level of detection in solution. The quenching rate constants were found to be high for picric acid  $5.48 \times 10^5 \text{ M}^{-1}$  for **67**, and follow the order **67** > **66** > **68** > **65**. Figure 3.13 shows the degree of fluorescence quenching of various 2N-fluoranthenes with 25  $\mu$ M of PA.

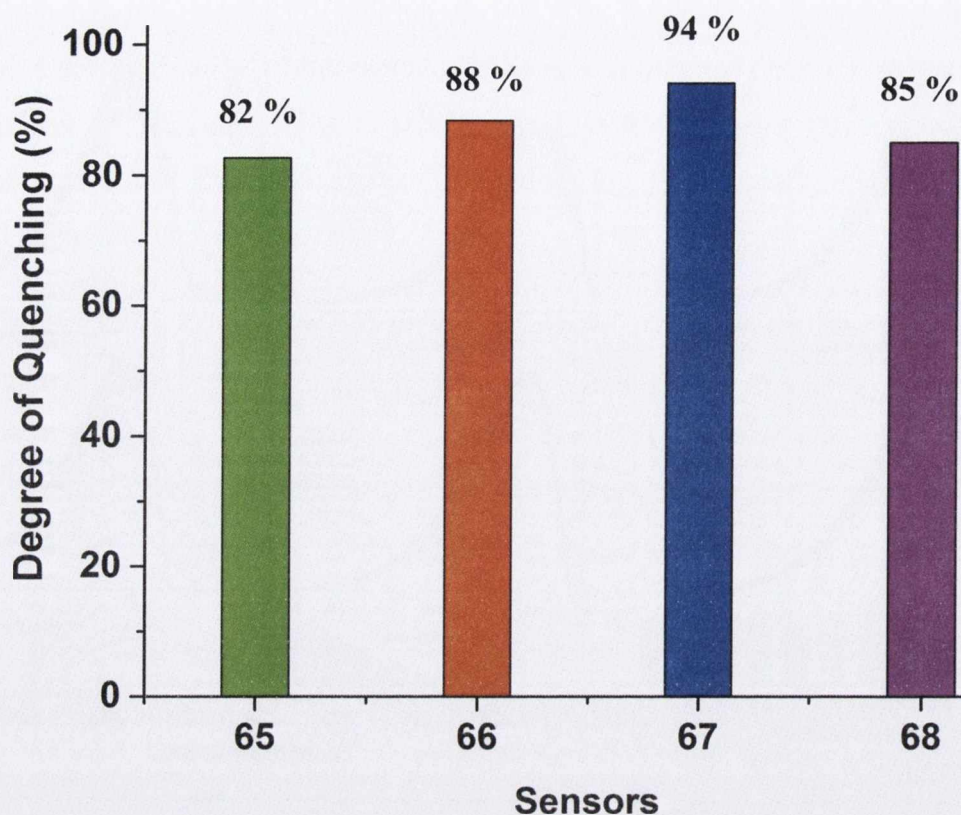


Figure 3.13: Degree of fluorescence quenching of various 2N-fluoranthenes **65-68** ( $\sim 10^{-6}$  M) with PA ( $\sim 10^{-4}$  M) in EtOH.

Interestingly, a significant decrease in the fluorescence intensity with the other electron deficient analytes is not observed, suggesting that the fluoranthene derivatives are sensitive and selective for the detection of NACs. The formation of a ground state complex between the fluoranthene derivatives and NACs is further confirmed by the invariant fluorescence life-times (Table 3.3.) Also, the spectrophotometric titration suggests the formation of a ground state complex between **67** and PA (Figure 3.14).



Table 3.3: The fluorescence life-time measurements of 2N-fluoranthenes **65-68** ( $\sim 10^{-6}$  M) with various concentrations of PA ( $\sim 10^{-4}$  M).

| Compound         |           | Life time ( $\tau$ ) (ns) |           |           |  |
|------------------|-----------|---------------------------|-----------|-----------|--|
| Fluoranthene (F) | <b>65</b> | <b>66</b>                 | <b>67</b> | <b>69</b> |  |
| F                | 28 ns     | 27 ns                     | 20 ns     | 23 ns     |  |
| F + 0.2 eq of PA | 28.21     | 27.06                     | 20.01     | 18.04     |  |
| F + 0.5 eq of PA | 28.16     | 27.08                     | 19.95     | 18.04     |  |
| F + 1.0 eq of PA | 28.18     | 27.02                     | 19.91     | 18.03     |  |
| F + 2.0 eq of PA | 28.26     | 27.02                     | 20.07     | 18.01     |  |

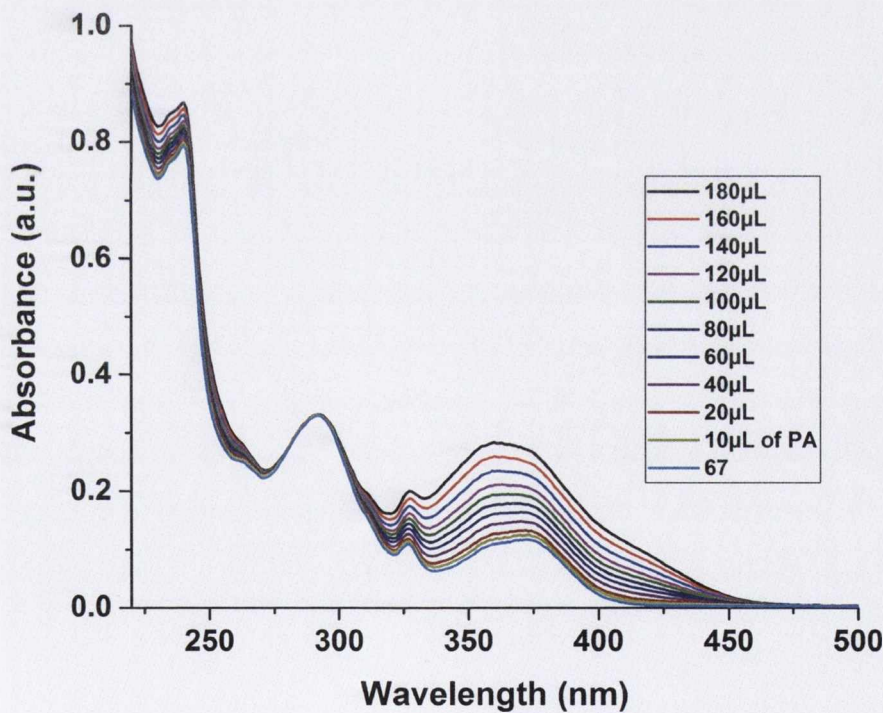


Figure 3.14: The spectrophotometric titration of **67** ( $1 \times 10^{-5}$  M) upon gradual addition of PA ( $1 \times 10^{-4}$  M) in EtOH.

The spectrophotometric titration of various fluoranthene derivatives with different concentrations of PA in EtOH was performed. With the gradual addition of PA to **67**, a slight increase in the absorption maxima at  $\lambda = 303$  nm is observed with the formation of a new broad absorption peak at  $\lambda > 400$  nm. The intensity of the new absorption peak gradually



increases with an increase in the concentration of PA. All of the compounds exhibit similar absorption patterns and show similar spectral variations, indicating the formation of donor–acceptor complexes between the  $\pi$ -electron rich fluoranthene derivatives and picric acid.

### 3.6 Theoretical Studies of 65-68

As described earlier, the ability for facile electron transfer based fluorescence quenching requires that the lowest unoccupied molecular orbital (LUMO) levels of the fluorophores and the quencher play a crucial role in this process. As such, the frontier molecular orbitals of the fluoranthene derivatives were calculated, and the results are presented in Figure 3.15.

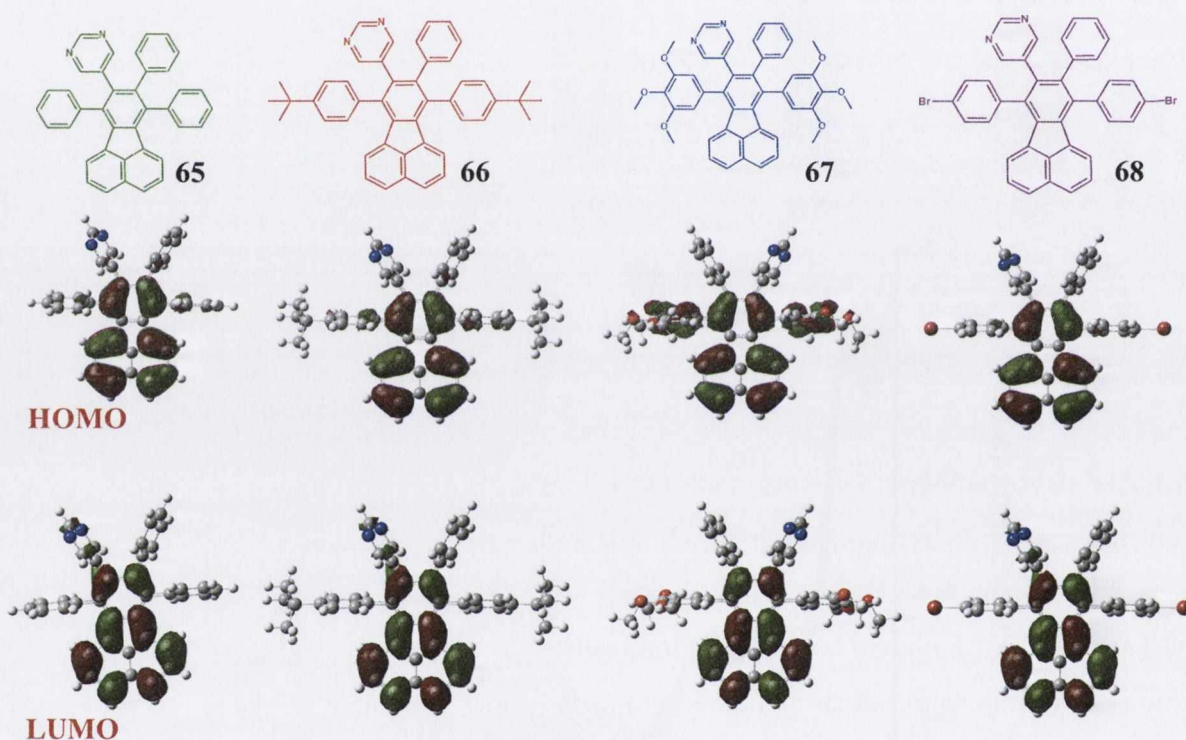


Figure 3.15: Electron density superimposed on the optimised geometry of **65-68** with the B3LYP/6-31g\* basis set.

The geometrical optimization of each derivatives was carried out with using the Gaussian 03 program, with the B3LYP and 6-31g\* basis sets. For compound **67**, the HOMO orbital is largely delocalized over the methoxy-substituted phenyl rings attached to fluoranthene, and the LUMO orbital is delocalized over the fluoranthene backbone. For **65**, **66** and **68**, the HOMO and LUMO orbitals are  $\pi$ -type, and are mainly localized over the fluoranthene core, suggesting the energy transitions originate from  $\pi \rightarrow \pi^*$  transitions.

Fluorescence quenching *via* the formation of a charge transfer complex, involves an electron transfer process from the LUMO of the excited state fluoranthene, to the LUMO of the chosen NAC. Detection limits are based on the efficiency of this process, which can be improved by carefully increasing the analyte–fluorophore binding interactions, and by matching the frontier molecular orbital energies of the fluorophore with the LUMO of the NACs.

In the previous chapter, it has been shown that analyte–fluoranthene binding interactions are stabilised by strong intermolecular, and  $\pi$ – $\pi$  interactions, resulting in complex formation. From the energy level diagram shown in Figure 3.16, it is observed that the optical band gaps are within the range of 3.85–3.91 eV, and show small variations depending upon the type of substituents present on the fluoranthene unit.

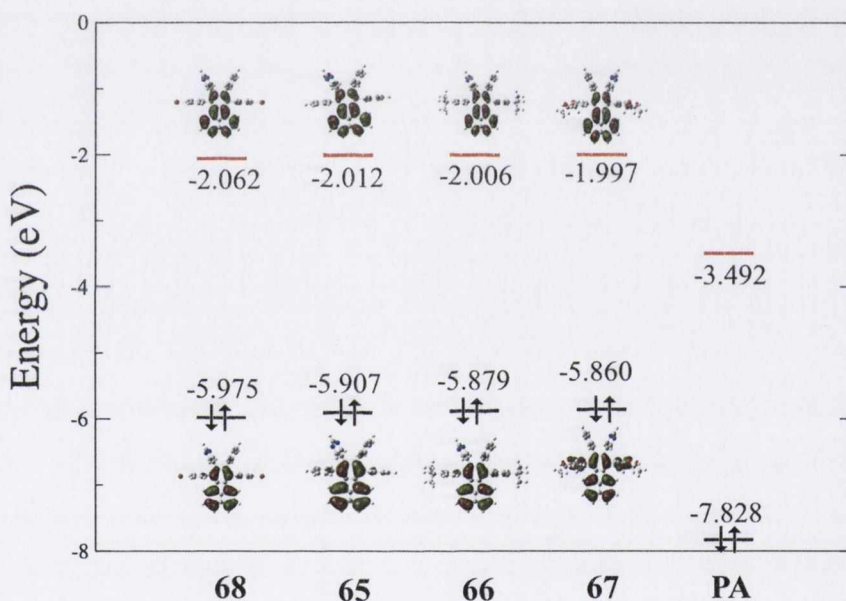


Figure 3.16: An energy level diagram showing the HOMO-LUMO distribution profiles of various 2N-fluoranthene derivatives **65–68** and PA optimized with the B3LYP/6-31g\* basis sets.

On comparison of the optical band gap values, determined both experimentally and theoretically, the values were found to be in good agreement, and support the generated theoretical molecular geometries. The optical band gap of **67** is found to be smaller when compared to the other derivatives, which is proposed as due to an increase in electron donating methoxy groups. The difference in LUMO energy values between that of **67** and PA is more pronounced when compared to the other derivatives, and this acts as the driving force for the high sensitivity of the electron transfer process when compared to other fluoranthenes.



The effect of association between **67** and the desired analyte, PA, was further investigated by carrying out the geometrical optimization of the pair. A molecule was positioned over the planar five membered ring of **67** at a distance of 2 Å, and the final optimised configurations show that the PA molecule forms a co-facial stacked geometry with the fluoranthene. The electron density is found to be localised over the fluoranthene core in the HOMO state, and over the PA molecule in the LUMO state (Figure 3.17).

This geometry of the pair facilitates a facile electron transfer from the excited state of **67** to the PA molecule, resulting in the quenching of the fluoranthene's fluorescence achieved by strong intermolecular  $\pi$ - $\pi$  interactions with the fluoranthene moiety.

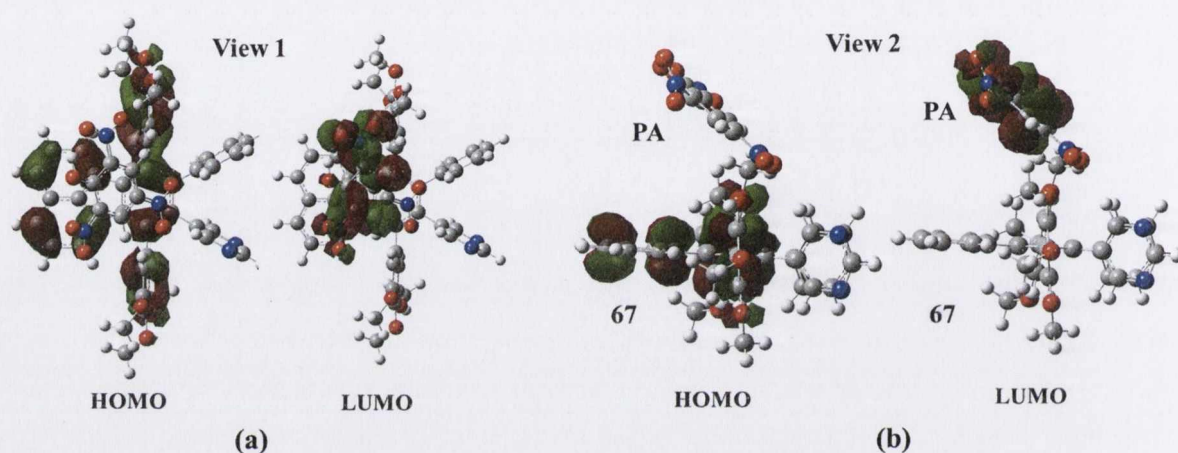


Figure 3.17: Electron-density profiles of **67**-PA charge transfer complexes with the B3LYP/6-31g\* basis set showing two orientations.

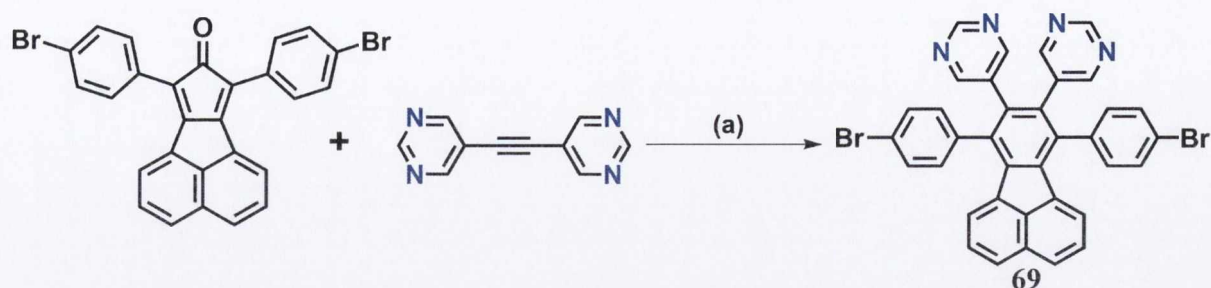
### 3.7 Readily Modifiable 4N-Dibromo-Fluoranthene, **69**

Whilst the highest selectivity and sensitivity to PA was found with compound **67**, the trimethoxy substitution prevents further modification of the compounds structure. Due to the dibromo-substitution of compound **68**, which would readily allow for the diverse functionalisation of these positions, an increase in the nitrogen loading was performed in an attempt to increase the desired selectivity and sensitivity. For this purpose, compound, **69**, was prepared.

#### 3.7.1 Synthesis of **69**

5,5'-(7,10-bis(4-bromophenyl)fluoranthene-8,9-diyl)dipyrimidine **69** was obtained by the Diels-Alder reaction between 7,9-bis(4-bromo)-8Hcyclopenta[*l*]acenaphthylen-8-one, **61**, and 1, 2-di(pyrimidin-5-yl)ethyne.





Scheme 3.4: Synthesis of **69** by Diels-Alder reaction in a benzophenone melt; (a) 300 °C, 3 h, 71 %

### 3.7.2 Structural Studies of **69**

The full structural characterisation of **69** was undertaken by multinuclear NMR techniques, and was complemented by single crystal X-ray studies. The mass spectrum of **69** was recorded with an ESI mass spectrometer. The major peak centred at  $m/z$  667.0133 m.u. corresponding to the molecular ion  $[M+H]^+$ , with a calculated value of 667.0135 m.u. for  $[C_{36}H_{21}N_4Br_2]^+$ .

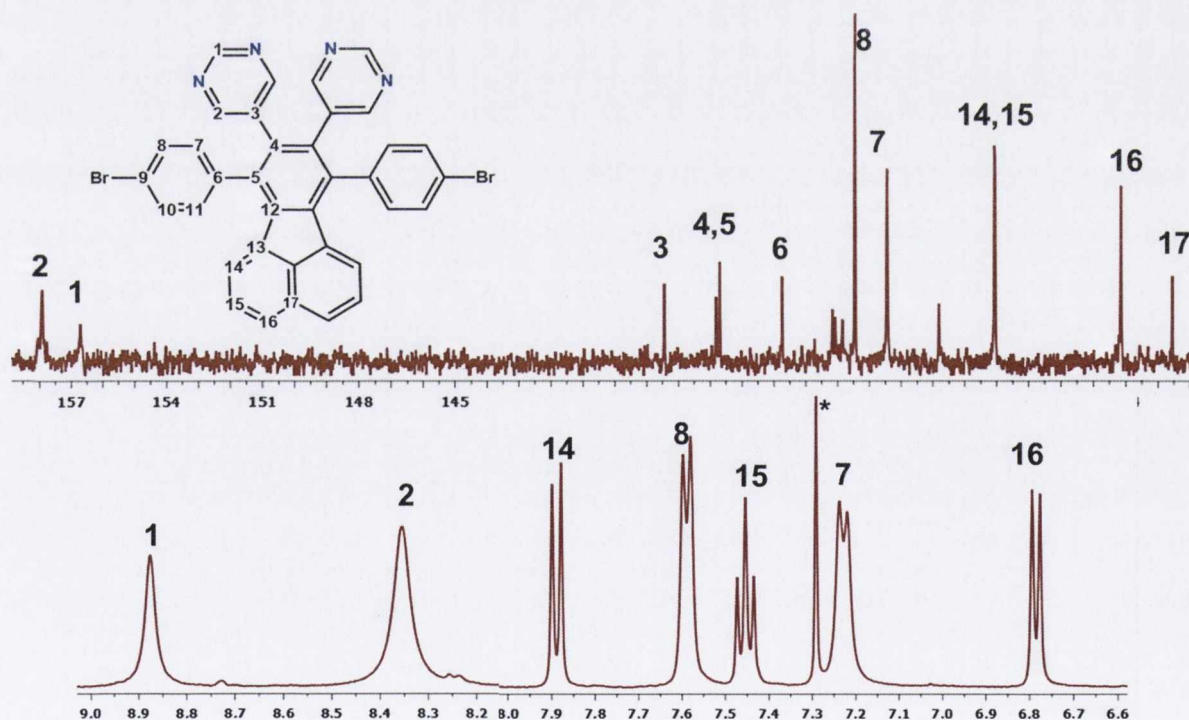


Figure 3.18:  $^{13}C$  NMR and  $^1H$  NMR assignment of **69**. (Asterisk denotes  $CDCl_3$  solvent peak, RT, 151 MHz, 400 MHz).

Analysis of the HSQC spectrum of **69** shows the presence of two distinct spin systems. Here, the most downfield signals at  $\delta \sim 8.82$  ppm and  $\delta \sim 8.36$  ppm do not show any correlations with any other aromatic signals, confirming their assignment as pyrimidyl protons. The overall structure of **69** consists of two, three spin systems, and two, two spin systems, as highlighted in the coloured regions in Figure 3.19a. The three spin systems are attributed to fluoranthene unit, while the two spin systems are attributed to the free bromo-substituted aryl rings. A HMBC spectrum was collected (Figure 3.19b), and complemented the HSQC spectrum allowing the simple assignment of these signals. The collected splitting patterns were also useful in differentiating the origin of each signal. Apart from those signals originating from the pyrimidyl rings, the molecule shows a series of doublets in the region  $\delta = 6.7 - 7.9$  ppm well separated with  $^3J$  splitting of  $\sim 8.0$  Hz.

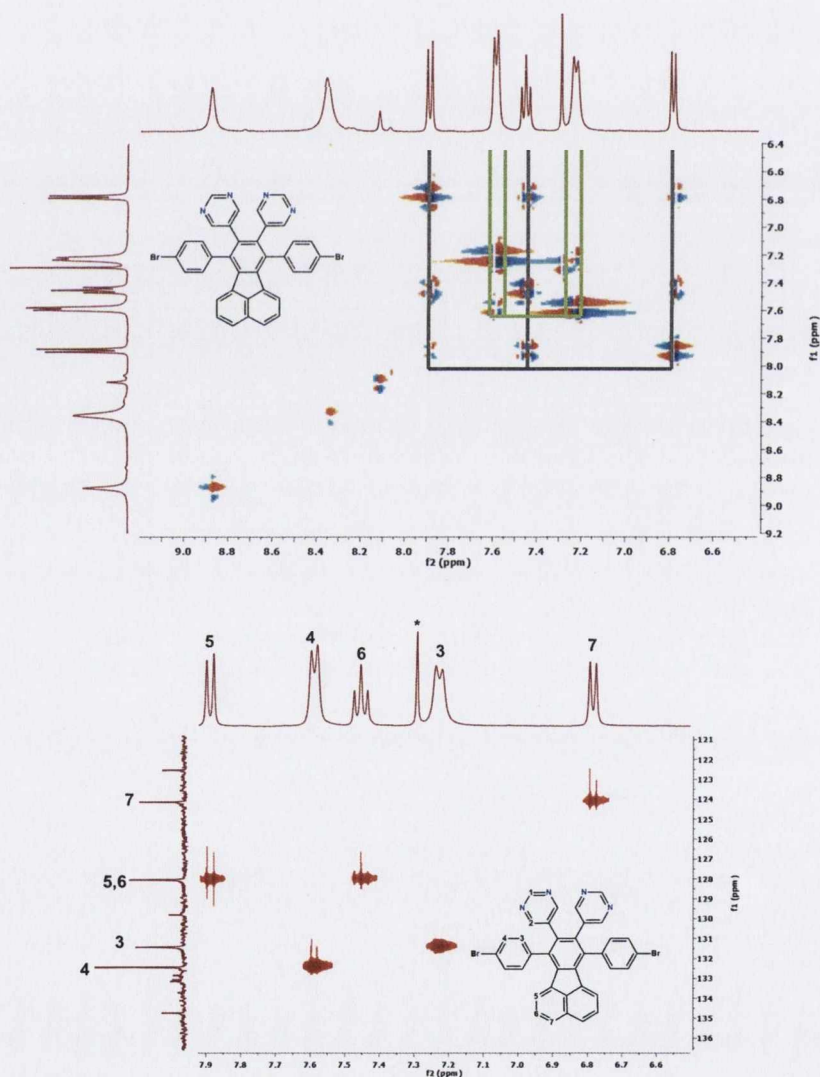


Figure 3.19: 2D NMR of **69** showing (a) HSQC showing distinct spin systems, and (b) HMBC showing C-H bond correlations.

### 3.7.3 Crystallographic Study of 69

Colourless needle shaped crystals, suitable for single-crystal X-ray diffraction studies were obtained for **69**, and were grown *via* the slow evaporation of methylene chloride from methanol. The molecules crystallised in the monoclinic with Cc space group. The unit cell consists of 8 molecules (Figure 3.20). The diffraction data collected for **69** showed data of a reasonable quality, with an  $R1 = 4.46\%$  (observed data), and a  $wR2 = 8.48\%$  (all data). The goodness-of-fit was 1.042. The pyrimidyl groups are observed to lie almost perpendicular to the fluoranthene plane at an angle of  $89.49^\circ$ . The bromo-substituted phenyl rings are twisted by an angle of  $69.71^\circ$  from the central core. The molecules pack in a head-to-tail fashion, with  $\pi$ - $\pi$  interactions between the aromatic cores.

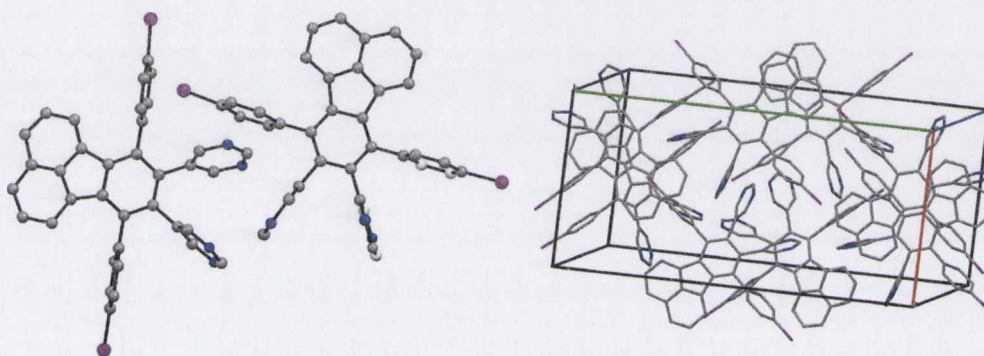


Figure 3.20: (a) Ball and stick representation of two asymmetric units of **69** (carbon atoms in grey, nitrogen atoms in blue and bromine atoms in pink). (b) Graphical representation of unit cell consisting of 8 molecules of **69**.

These interactions contribute to form a self-assembled close packed arrangement in **69**, and the crystal packing structure is shown in Figure 3.21. Molecules of **69** are mainly connected through  $\text{Br1} \cdots \text{C1}$  [ $3.434 \text{ \AA}$ ] intermolecular interactions of the adjacent pyrimidyl rings and  $\text{Br2} \cdots \text{C3}$  [ $3.682 \text{ \AA}$ ] interactions of the fluoranthene moiety. In addition, pyrimidyl rings show short contacts i.e.  $\text{C2} \cdots \text{C4}$  [ $3.482 \text{ \AA}$ ] with the neighbouring pyrimidyl ring as illustrated in Figure 3.21a.



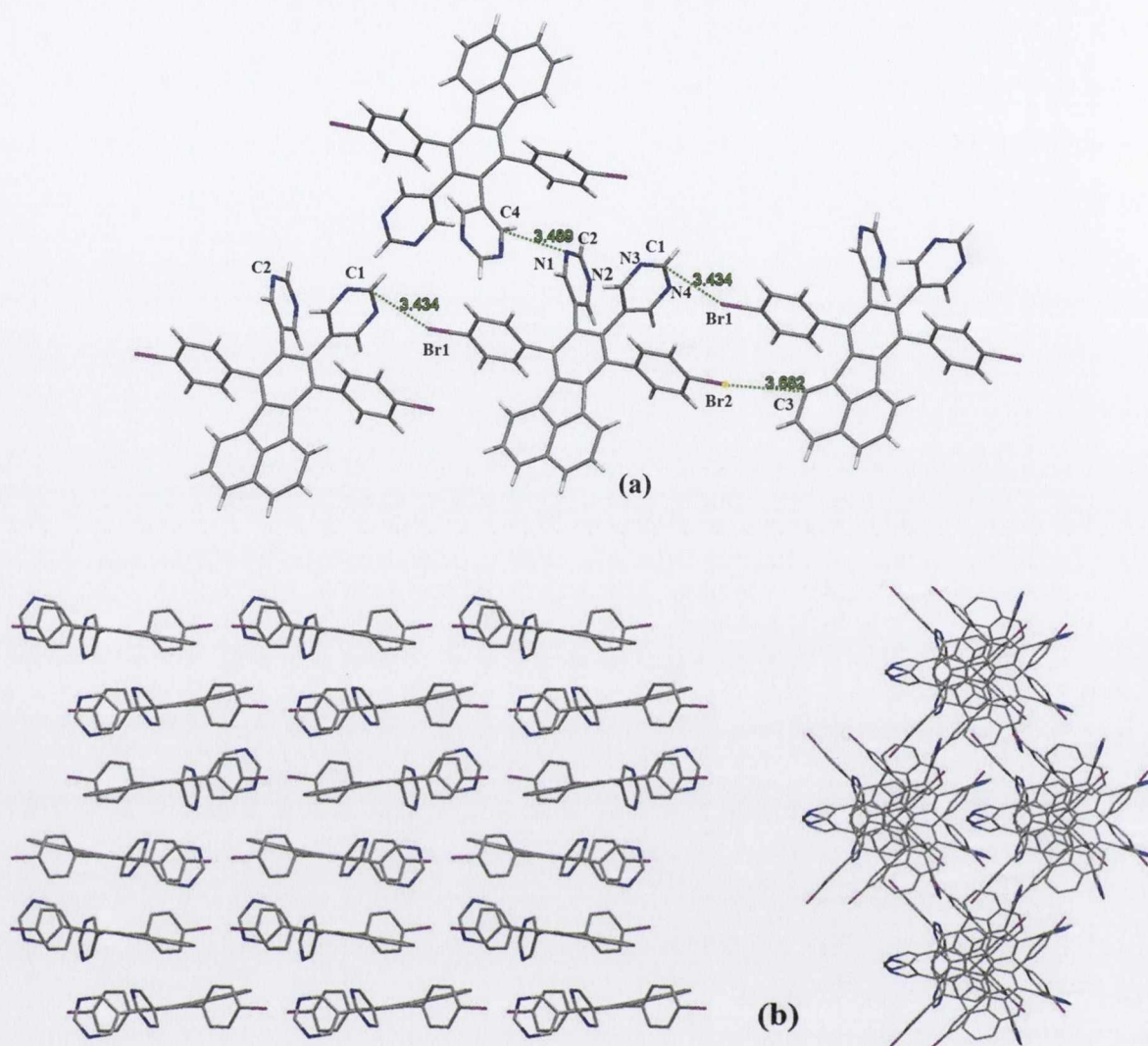


Figure 3.21: (a) Interactions of molecules of **69** (b) Crystal packing structure as viewed along the *b*-axis, and *c*-axis showing the stacking of the dimers.

### 3.7.4 Photophysical Studies of **69**

The optical absorption and fluorescence emission spectra of the bromo-substituted 4N-fluoranthene, **69**, in EtOH are shown in Figure 3.22. It exhibits four well resolved major intense absorption bands listed in Table 3.4. These arise due to  $\pi \rightarrow \pi^*$  transitions. The  $\pi$ -conjugated nature of **69** gives rise to a strong blue fluorescence emission in EtOH at  $\lambda_{\text{em}} = 440$  nm for **55** with a Stoke shift of  $4082.38 \text{ cm}^{-1}$ . The quantum yield of fluorescence of **69** is 39%, higher than that of **68** ( $\Phi_f = 36\%$ ), suggesting a correlation between nitrogen loading and quantum yields.

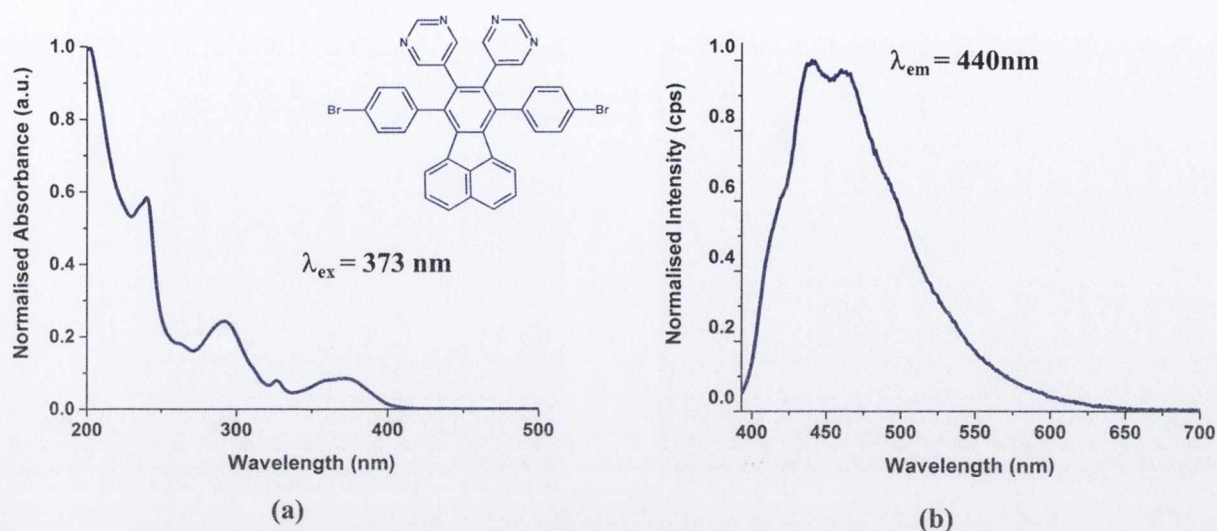


Figure 3.22: UV-Vis absorption and fluorescence emission of **69** ( $1 \times 10^{-5}$  M) in EtOH.

Table 3.4: The absorption maxima observed in the UV-Vis absorption spectra of **69**.

| $\lambda_{\text{max}}$ [nm] | $\epsilon \times 10^4/\text{M}^{-1} \text{cm}^{-1}$ |
|-----------------------------|-----------------------------------------------------|
| 238                         | 5.62                                                |
| 297                         | 2.43                                                |
| 325                         | 0.95                                                |
| 373                         | 0.12                                                |

### 3.7.5 Nitroaromatic Sensing Studies of **69**

The solution based interactions between **69** with varying NAC compounds, as well as other electron deficient acceptors, were investigated *via* their fluorescence spectra in EtOH. Figure 3.23 shows a histogram of the fluorescence quenching behaviour of **68** and **69** with different analytes. Similar to results seen in Chapter 1, strong  $\pi$ - $\pi$  interactions, and the high polarizability of PA, may be a major factor contributing to the high sensitivity of quenching compared to other analytes.

A linear SV plot was obtained with a rate constant of  $K_{\text{SV}} = 2.9 \times 10^5 \text{ M}^{-1}$  for **69**, with  $K_{\text{SV}} = 1.95 \times 10^5 \text{ M}^{-1}$  for **68**. As can be seen, the rate constant is increasing with an increasing number of pyrimidyl substituents. Further to this, the degree of fluorescence quenching of **69** by different analytes in EtOH is shown in Figure 3.24.



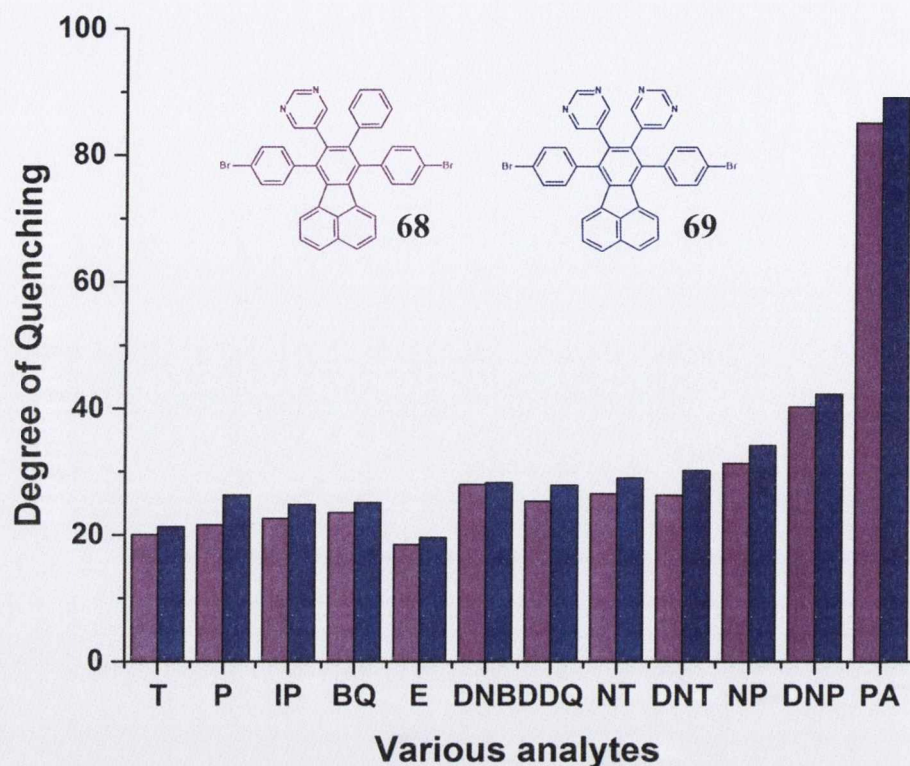


Figure 3.23: Degree of fluorescence quenching behavior of **68** and **69** with different analytes in EtOH. The inset images show the structures of **68** and **69**.

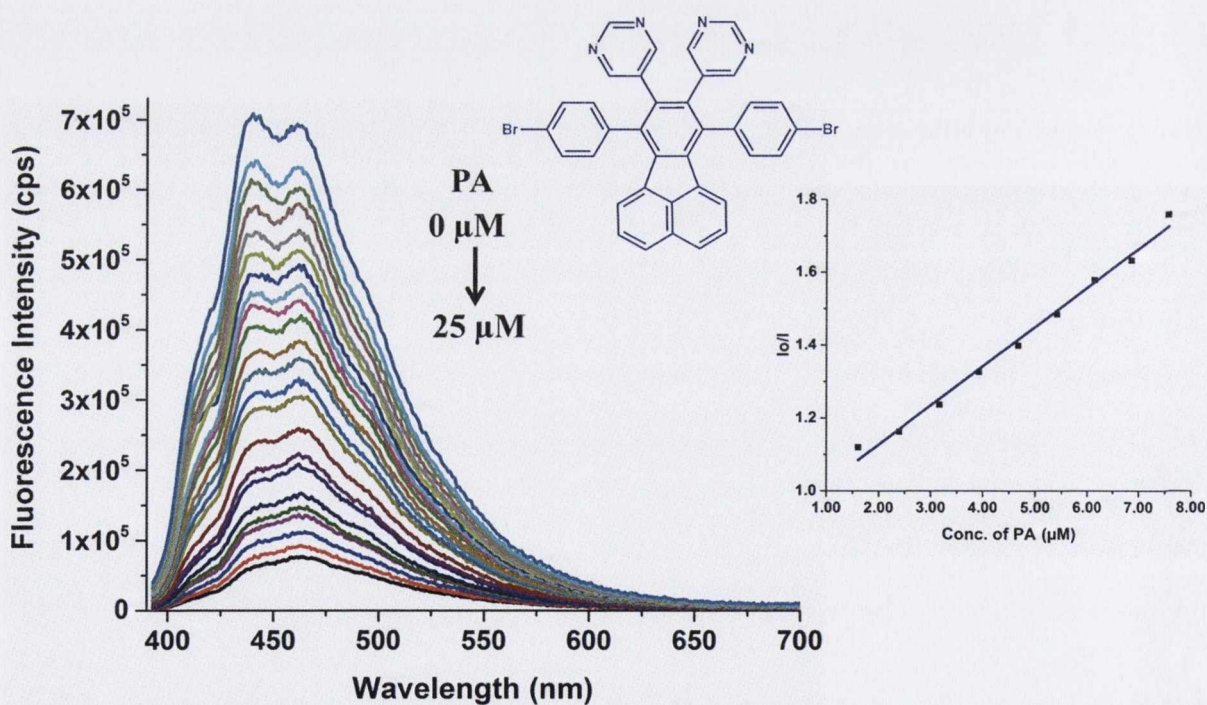


Figure 3.24: Fluorescence quenching behavior of **69** with gradual addition of PA in ethanol. The first inset image is the structure of **69**. A second inset shows the Stern–Volmer plot of **69** with different concentrations of PA.



### 3.7.6 Theoretical Studies of **69**

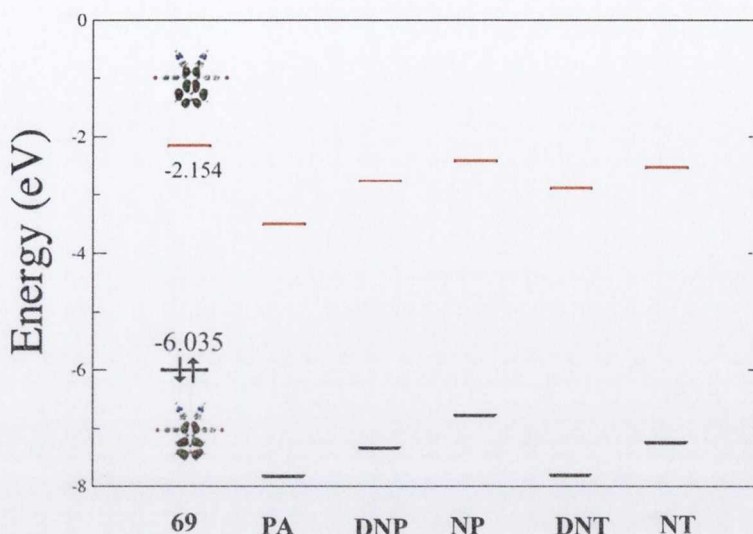


Figure 3.25: The energy level diagram showing the HOMO-LUMO energies of **69**, and the same for different nitroaromatics.

Similar to the results of theoretical studies observed earlier, in order to understand the mode of interaction between **69** and the NACs, geometrical optimization of **69** was carried out using the B3LYP hybrid functional, with the 6-31g\* basis set. As seen in **68** and **69**, the HOMO and LUMO orbitals are  $\pi$ -type, and mainly localized over the fluoranthene core. This suggests that the electronic transitions originate from  $\pi \rightarrow \pi^*$  transitions. This shows the favouring of electron donation to the LUMO of the analytes (-0.07836 eV for PA) as shown in Figure 3.25. As the LUMO energy of PA is significantly lower than that of DNP or NP, it is proposed that this results in the striking selectivity for the bromo-substituted fluoranthene over other analytes. The size of the energy gap between the LUMO of the fluorophore, and the LUMO of the electron acceptor, is generally accepted as the driving force for this oxidative electron transfer process, with the quenching efficiency being directly proportional to the ease of electron transfer.<sup>18,44</sup>

### 3.7.7 Spectroscopic Studies of **69** with PA and TFA

The spectrophotometric titration of **69** with different concentrations of PA and TFA in EtOH was performed. With the gradual addition of PA to **69**, an increase in the absorption maxima at  $\lambda = 303$  nm was observed. The formation of a new broad absorption also appeared at  $> 400$  nm. The intensity and width of the new absorption peak gradually increases with an increase in the concentration of PA added, indicating the formation of coloured donor-acceptor complex between the  $\pi$ -electron rich fluoranthene derivatives and PA. This behavior was not

seen for the addition of TFA to **69**, confirming that the quenching effect of PA on **69** is not mediated by the protonation of the nitrogen-containing pyrimidyl rings.

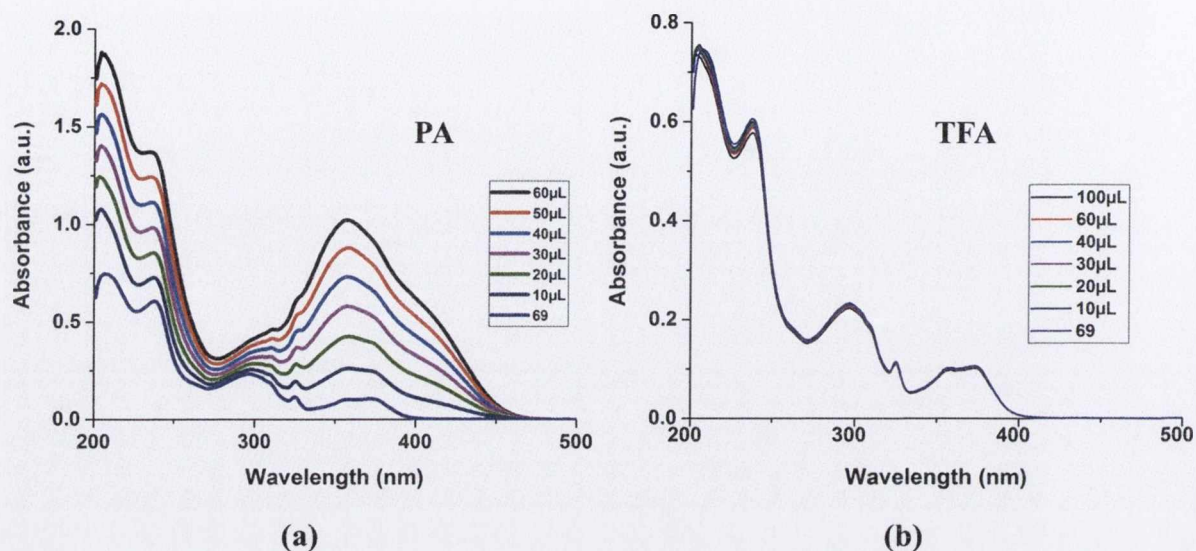


Figure 3.26: The spectrophotometric titrations of **69** ( $\sim 10^{-6}$  M) upon the gradual addition of (a) PA or (b) TFA in EtOH ( $\sim 10^{-4}$  M), indicating the formation of a charge transfer complex between the fluoranthenes and PA.

### 3.8 Visual Detection of NACs by **65-69**

In order to demonstrate the practical use of fluoranthene derivatives for NAC detection, quenching studies were carried out in the solid state by making thin films of fluoranthene derivatives using commercially available aluminum TLC plates.

This method allows a rapid visual change in fluorescence intensity and will allow for instant detection of explosives in a real world setting. To demonstrate this, solutions of the respective fluoranthene derivatives in EtOH ( $\sim 10^{-5}$  M) were prepared, and spread over the silica plate by the drop casting method. A 10  $\mu$ L portion of different concentrations of various NACs ( $10^{-3}$ – $10^{-13}$  M concentration range) were spotted on the generated coated silica plate, to give a spot area of  $\sim 0.1$  cm<sup>2</sup>. The visual fluorescence response for different analytes at different concentration levels upon exposure to UV light at 365 nm (commercial black light lamp) is shown in Figure 3.27.



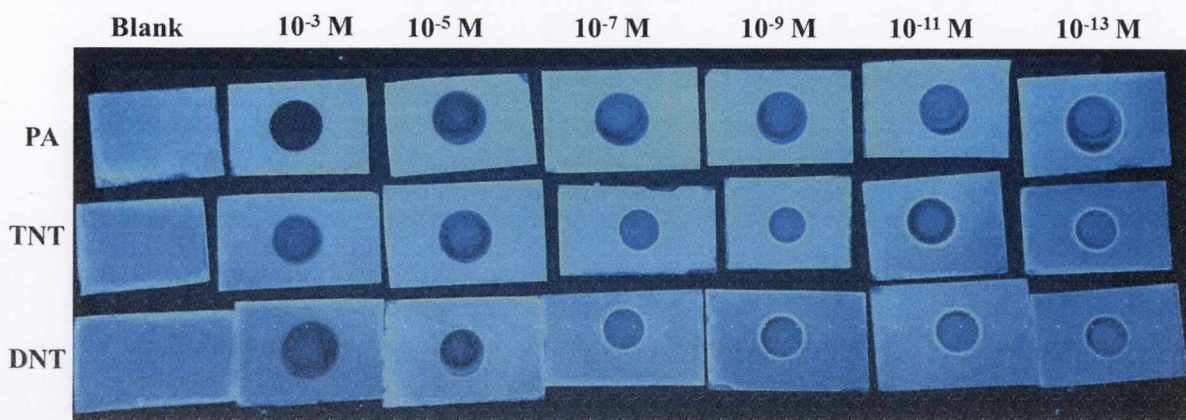


Figure 3.27: Photograph of **67** coated on the TLC plates before and after the addition of different concentrations of PA, TNT and DNT by the contact mode method with a spot area of approximately  $0.1\text{ cm}^2$  upon exposure to the UV lamp at 365 nm

The experiments were repeated for all fluoranthene derivatives for different NACs. A comparison of the fluorescence quenching efficiency for PA, TNT and DNT is shown in Figure 3.27. The quenching effect is found to be higher for PA, TNT and DNT when compared with the other NACs, with **67** showing the highest decrease in the visual fluorescence intensity.

### 3.9 Conclusion

In conclusion, a series of novel 2N-fluoranthene fluorophores were successfully synthesised with varying substituents on the free phenyl rings. The photophysical and computational studies demonstrate that by tuning the optical gap *via* an increase in electron donating groups enhances the sensitivity towards NACs. Fluorescence quenching studies reveal that these fluorophores exhibit static quenching with a 5–25 ppb level of detection for PA. The sensing of NACs towards PA are found to be in the order **67** > **66** > **68** > **65**, while 4N fluoranthene **69** > 2N-fluoranthene **68**.

A femtogram detection level for PA was achieved by the contact mode approach on thin layer silica chromatographic plates. The intense blue light emitting nature of the generated fluoranthene derivatives in solution, coupled with their high photostability, has allowed work towards the development of switchable turn off/on optoelectronic devices to be undertaken.





**4. 4N Substituted Methoxy Fluoranthenes**





## 4.1 Introduction

This chapter describes the synthesis, structural and photophysical characterisation, and the explosives sensing studies of a series of methoxy-functionalised 4N substituted fluoranthenes. This chapter consists of three main sections; (i) the synthesis of 4N-doped fluoranthenes *via* the [2+4]-Diels-Alder reaction, coupled with comprehensive spectroscopic characterisation, (ii) studies of their photophysical characteristics, and (iii) detailed explosive sensing studies which are supported with DFT calculations.

In Chapter 2, it has been shown that the incorporation of nitrogen atoms onto the fluoranthene system dramatically increases the sensitivity of these systems towards nitroaromatic-containing explosives, with particular sensitivity to picric acid. In Chapter 3, it has been further shown that by varying the substituents on the fluoranthene core, while keeping the nitrogen loading static, it is clear that methoxy-containing fluoranthene compound show the maximum amount of sensitivity. In this current chapter, a series of methoxy-functionalised nitrogen-substituted fluoranthenes have been prepared, by systematically increasing the methoxy groups with fine synthetic control.

## 4.2 Synthesis of 4N Substituted Fluoranthenes

A series of novel methoxy functionalized 4N-substituted fluoranthenes were prepared by varying the number of methoxy groups in their precursors.

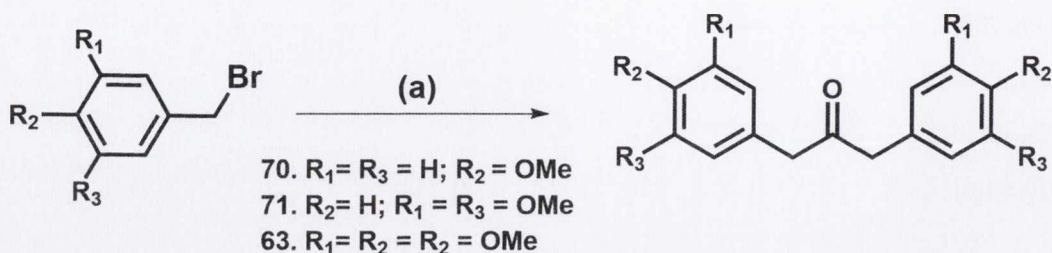
### 4.2.1 Preparation of Methoxy Functionalised 1,3-diaryl-2-Propanones

A series of three methoxy-functionalised 1,3-diaryl-2-propanones utilised in the necessary Knoevenagel condensation step, 1,3-bis-(4-methoxyphenyl)-propan-2-one **70**, 1,3-bis-(3,5-dimethoxyphenyl)-propan-2-one **71**, and 1,3-bis-(3,4,5-trimethoxyphenyl)-propan-2-one **63**, were synthesised using a modified synthetic literature preparation.<sup>138-141</sup>

The starting material, 1,3-diphenyl-2 propanone **59**, is commercially available and was used without modification.

Each 1,3-diaryl propanone was prepared *via* a biphasic phase transfer carbonylation, with  $\text{tBu}_4\text{N}^+(\text{HSO}_4)^-$ , as the phase transfer catalyst, and  $\text{Fe}(\text{CO})_5$  as the *in-situ* source of CO.<sup>132</sup> The reagents were stirred at room temperature for 6 h under  $\text{N}_2$  (Scheme 4.1). The reaction mixture was then further stirred in air for an hour in an oxidation step, after which a 10% HCl solution was added dropwise to afford the desired ketone product. Each monoketone was then extracted into dichloromethane, dried over  $\text{MgSO}_4$ , and concentrated *in vacuo*. The products

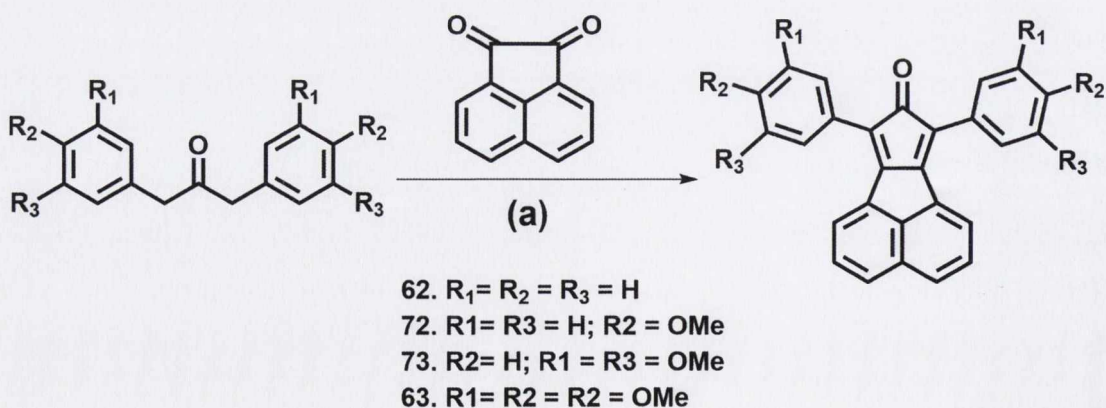
were recrystallised *via* a slow addition of MeOH to CH<sub>2</sub>Cl<sub>2</sub>. The products were collected as solids varying in colour from pale yellow to white, in yields >75 %. Significantly higher yields were found at the shorter reaction times of 5-6 h *versus* that of 16-20 h.



Scheme 4.1: Synthesis of desired 1,3-diaryl propanones (a) : (Bu<sub>4</sub>N<sup>+</sup>(HSO<sub>4</sub>)<sup>-</sup>, Fe(CO)<sub>5</sub>, Ca(OH)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>:H<sub>2</sub>O (1:1 v/v), RT, 6 h)

#### 4.2.2 Preparation of Methoxy Functionalised Cyclopentadienones

The methoxy- containing cyclopentadienones, **62-63** and **72-73**, were synthesised *via* a double Knoevenagel condensation reaction between the commercially available acenaphthenequinone, and the previously discussed methoxy-containing 1,3-diaryl propanones. A modified literature procedure was used to generate the desired cyclopentadienones using refluxing EtOH as the reaction solvent.<sup>138</sup> After cooling of the reaction mixture to room temperature, the desired products were filtered directly, and required no further purification. Four cyclopentadienones were prepared *via* this method, 7,9-bis-(phenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one, **62**, 7,9-bis-(4-dimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one,<sup>138</sup> **72**, 7,9-bis-(3,5-dimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one, **73**, and 7,9-bis-(3,4,5-trimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one, **63**.



Scheme 4.2: Synthesis of the desired cyclopentadienones. (a) KOH, EtOH, reflux, 45min.



## 4.2.2.1 Spectroscopic Characterisation of 73 and 63

Due to the symmetrical nature of **73**, the  $^1\text{H}$ -NMR spectrum of the dimethoxy-substituted cyclopentadienone was conveniently simple, and the full structural characterisation was easily achieved.

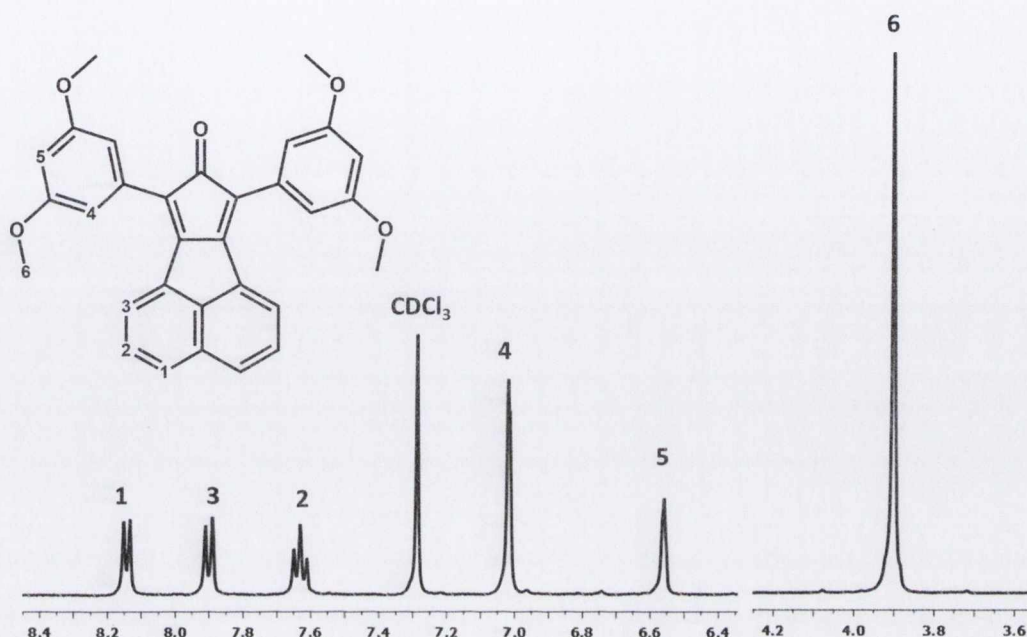


Figure 4.1: Full structural assignment of **73** via  $^1\text{H}$  NMR spectrum.  $\text{CDCl}_3$  denotes the solvent peak. (RT, 400 MHz).

The most deshielded signals in the region  $\delta = 8.13$  ppm (H<sub>1</sub>),  $\delta = 7.89$  ppm (H<sub>3</sub>) and  $\delta = 7.63$  ppm (H<sub>2</sub>) belong to the naphthyl moiety and integrate for 2 protons each (Figure 4.1). These appear in the expected region for fluoranthene-containing cyclopentadienones.<sup>112</sup> Secondary to these, the most downfield signals, at  $\delta = 7.01$  ppm and  $\delta = 6.56$  ppm, are attributed to H<sub>4</sub> and H<sub>5</sub>, integrating to 4 and 2 protons respectively. The methoxy proton signal appears as a singlet at  $\delta = 3.90$  ppm, integrating for a total of 12 protons.



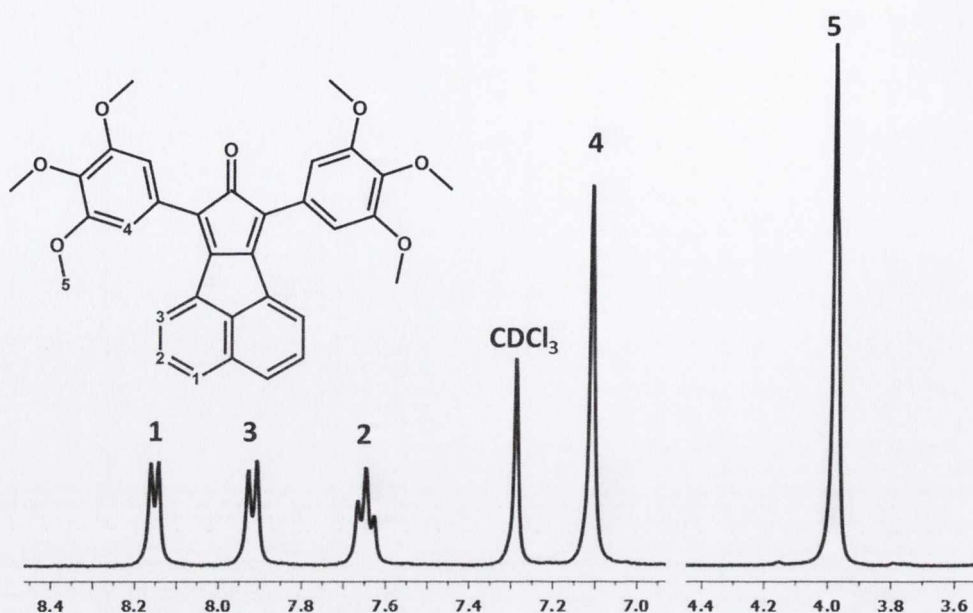


Figure 4.2: Full structural assignment of **63** via  $^1\text{H}$  NMR spectrum.  $\text{CDCl}_3$  denotes the solvent peak. (RT, 400 MHz).

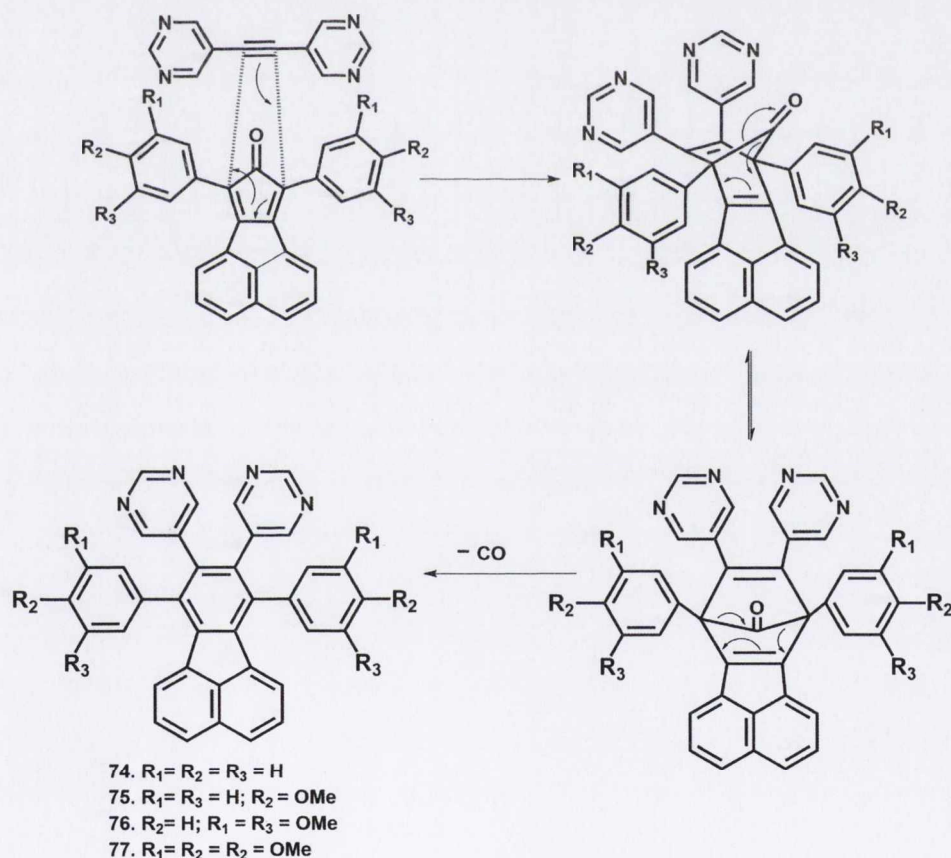
Similar to **73**, the  $^1\text{H}$ -NMR spectrum of **74** allowed for a facile structural characterisation due to the symmetric nature of the hexa-methoxy-substituted cyclopentadienone. The most downfield signals in the region  $\delta = 8.16$  ppm ( $\text{H}_1$ ),  $\delta = 7.91$  ppm ( $\text{H}_3$ ) and  $\delta = 7.65$  ppm ( $\text{H}_2$ ) belong to the naphthyl moiety, and integrate for 2 protons each (Figure 4.2). The next downfield signal, at  $\delta = 7.11$  ppm, is attributed to  $\text{H}_4$ , and integrates to 4 protons. The methoxy protons appear as a singlet at  $\delta = 3.98$  ppm, integrating for a total of 18 protons.

#### 4.2.3 Diels-Alder [2+4] Cycloaddition

The 4N methoxy-substituted fluoranthene derivatives, **74-77**, were synthesised *via* a single Diels-Alder [2+4] cycloaddition. As discussed in previous chapters, the necessary Diels-Alder cycloaddition reaction occurs between the methoxy-substituted cyclopentadienone (diene), and the desired heterocyclic-containing alkyne (dienophile), to form a substituted 6-membered aromatic ring following the extrusion of CO. Each target methoxy-substituted compound was synthesised in this manner from the necessary starting materials in a benzophenone melt (Scheme 4.3). The pyrimidyl groups are introduced into the fluoranthene *via* the 1,2-di(pyrimidin-5-yl)ethyne reagent, which was previously developed by Draper *et al.*<sup>118</sup> By synthetically varying the methoxy combinations in the monoketone reagent, a library of fluoranthene compounds, 7, 10-diphenyl-8,9-dipyrimidin-3,5-yl-fluoranthene **74**, 7,10-bis(4-methoxyphenyl)-8,9-dipyrimidin-3,5-yl-fluoranthene **75**, 7,10-bis-(3,5-

dimethoxyphenyl)-8,9-dipyrimidin-3,5-ylfluoranthene **76** and 7,10-bis-(3,4,5-trimethoxyphenyl)-8,9-dipyrimidin-3,5-ylfluoranthene **77** were prepared.

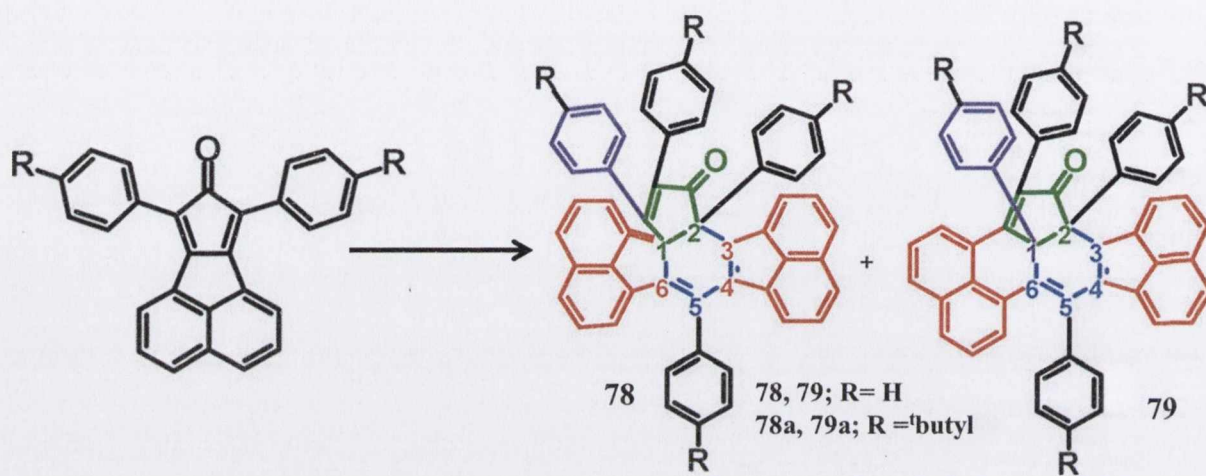
The synthesis of **74** proved facile, and was achieved in 4 h by the heating the reaction mixture to 280 °C under N<sub>2</sub>. Upon cooling, the reaction mixture was purified using column chromatography with diethyl ether as the eluent, yielding a pure sample of **74** in an 81% yield. The mono methoxy-substituted fluoranthene, **75**, required heating of the reaction mixture to 300 °C overnight (~12 h), and subsequent column chromatography yielded a pure sample in a 54% yield. In a similar fashion to **75** over **74**, **76** required heating of the reaction mixture to 330 °C with overnight stirring, yielded a 84 % yield upon purification. **77** proved difficult to synthesise and required heating of the reaction mixture to 350 °C. Temperatures of this magnitude generated an increase in undesired side products, and thus resulted in a lower yield. With careful monitoring of the reaction by TLC, **77** was obtained as a pure sample upon purification in a yield of 54 %, with a reaction time of 6 h.



*Scheme 4.3: Proposed reaction mechanism of the [2+4] Diels-Alder cycloaddition between the desired cyclopentadienones, and 1,2-di(pyrimidin-5-yl)ethyne 51. The extrusion of CO generates the aromatic core of the 4N fluoranthene.*



As a result of the high temperature nature of the reaction conditions, two fluorescent side products were obtained. These have been previously characterised as the self-dimerization product of the cyclopentadienone, and a second thermally favored rearrangement of the self-dimer. These products were identified by NMR analysis and X-ray crystallography by Draper *et al.*, and are shown in Scheme 4.4. The major structural difference between side-products **78** and **79** is the arrangement of the pendant phenyl rings on their fused cyclopentadienone. The phenyl ring outlined in purple (in Scheme 4.4), protrudes from the fused aromatic platform of **2** in position '1' of the central ring.<sup>142</sup>



Scheme 4.4: Formation of **78** and **79** (product yield of 15% and 10% respectively, using a benzophenone melt at 200 °C).

Column chromatography on silica, using diethyl ether the eluent, allowed the removal of these unwanted side products. A more polar eluent, in this case, dichloromethane:ethyl acetate (1:2 v/v), was also used. The lower yields are therefore proposed as a direct consequence of this competing self-dimerisation process. This competing process was even more prominent with azafluoranthene-derived systems, resulting in very low yields, and this will be observed in the subsequent chapter.

### 4.3 Structural Characterisation of 4N-Fluoranthenes

Full structural characterisation of **74-77** was carried out using multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, HSQC and HMBC), ESI high resolution mass spectrometry, elemental analysis, and infrared spectroscopy (see Experimental; Chapter 7).



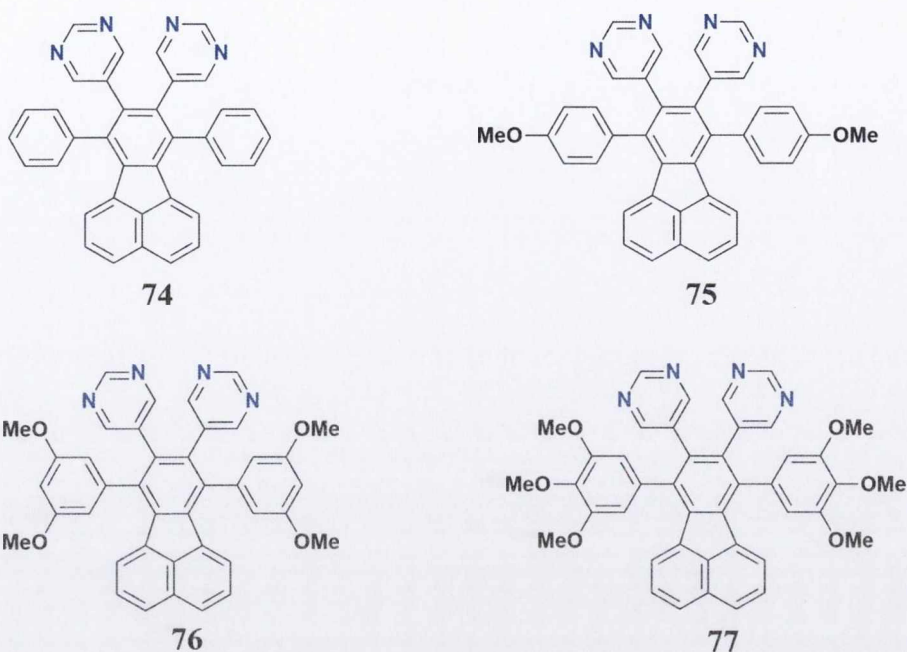


Figure 4.3: Target methoxy-substituted 4N Fluoranthenes of this study.

#### 4.3.1 Mass Spectrometry Studies of 74-77

The electrospray ionisation mass spectra of the three fluoranthenes **74**, **75** and **76**, recorded in dichloromethane, reveal the major peak in each spectrum as the  $[M+H]^+$  molecular ion. These values are in good agreement with the calculated values for the  $[M+H]^+$  molecular ion peak. Due to its size, the mass spectrum of **77** was recorded using a MALDI-TOF mass spectrometer. The major peak centred at  $m/z$  690.2466 a.m.u., favourably corresponding to the calculated molecular ion  $[M]^+$  value of 690.2478 a.m.u. for  $[C_{42}H_{34}N_4O_6]^+$ . The summary of mass spectral data is tabulated in Table 4.1.

Table 4.1: Mass spectral data for the novel 4N fluoranthenes **74-77** (recorded in CH<sub>2</sub>Cl<sub>2</sub>, m/z in a.m.u.).

| Compound  | Molecular Ion      | Formula                                                       | Calculated m/z | Found m/z (%) |
|-----------|--------------------|---------------------------------------------------------------|----------------|---------------|
| <b>74</b> | [M+H] <sup>+</sup> | C <sub>36</sub> H <sub>23</sub> N <sub>4</sub>                | 511.1923       | 511.1928      |
| <b>75</b> | [M+H] <sup>+</sup> | C <sub>38</sub> H <sub>27</sub> N <sub>4</sub> O <sub>2</sub> | 571.2056       | 571.2032      |
| <b>76</b> | [M+H] <sup>+</sup> | C <sub>40</sub> H <sub>31</sub> N <sub>4</sub> O <sub>4</sub> | 631.2345       | 631.2325      |
| <b>77</b> | [M] <sup>+</sup>   | C <sub>42</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> | 690.2478       | 690.2466      |

#### 4.3.2 <sup>1</sup>H NMR Studies of **74-77**

Due to the C<sub>2</sub>-plane of symmetry, the <sup>1</sup>H-NMR spectra of **74-77** in CDCl<sub>3</sub> are relatively simple to assign, and show very little variance between spectra (Figure 4.4). The aromatic region of the <sup>1</sup>H NMR spectra of **74-77**, shows two prominent downfield singlet peaks which are attributed to the pyrimidyl protons. In the four spectra, the pyrimidyl peaks appear around  $\delta = 8.8$  and  $\delta = 8.3$  ppm, integrating to two and four protons respectively. A similar pattern was observed for the N-doped fluoranthenes in earlier chapters, and is comparable with the other N-doped HBC polyphenylenes in the literature.<sup>143</sup> The collected spectra follow a doublet-pseudotriplet-doublet system characteristic of the naphthyl moiety, with the phenyl rings at seen at the 7, 8 positions of the fluoranthenes.

With an increase in methoxy groups, changes in the aliphatic region of each spectrum change. From no methoxy peak in **74**, two distinct methoxy peaks in **77** are seen at  $\delta = 3.92$  and  $3.75$  ppm, integrating to six and twelve protons respectively. In the systems, **75** and **76**, two singlet methoxy peaks are seen at  $\delta = 3.87$  and  $3.72$  ppm, corresponding to six and twelve protons respectively. As expected, the free rotation of the aryl rings at positions 7-10 of the fluoranthenes generates proton signals which are equivalent on the NMR timescale, thus further assisting the structural characterisation.

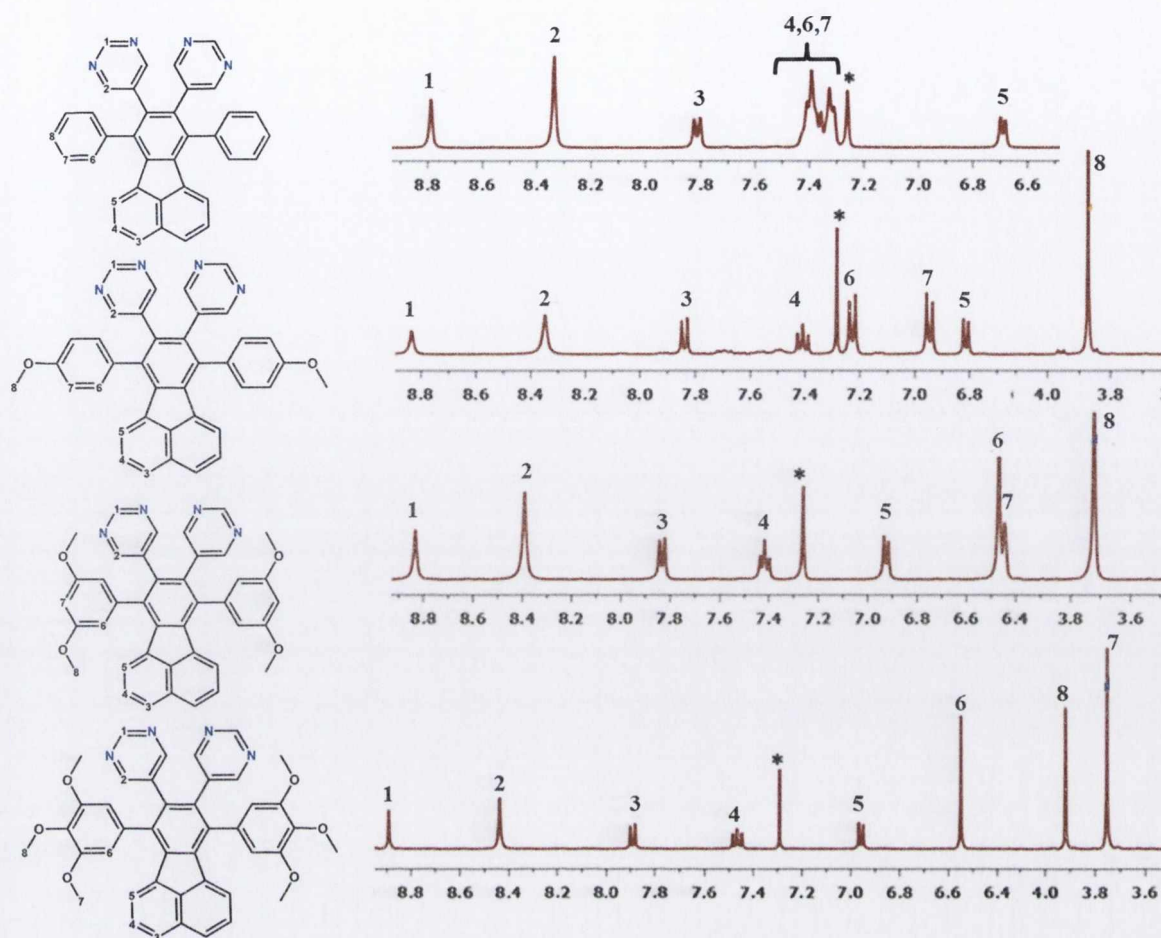


Figure 4.4: The full structural assignment of fluoranthene derivatives 74-77 with their respective  $^1\text{H}$  NMR spectra, showing their consistent aromatic and varying aliphatic regions. Asterisk denotes solvent peak ( $\text{CDCl}_3$ , RT, 400 MHz).

All of the structural determination shown in the above spectra was assisted with a comprehensive series of HSQC, HMBC, and TOCSY experiments. As the strategies employed for the assignment of all these 4N fluoranthenes were similar, only the assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of 77 by 2D NMR is shown below (Figure 4.5).

The HSQC (Heteronuclear Single Quantum Coherence) spectrum shows  $^{13}\text{C}$ - $^1\text{H}$  correlations, and facilitates the direct assignment of each  $^{13}\text{C}$  signal to their respective proton signal.



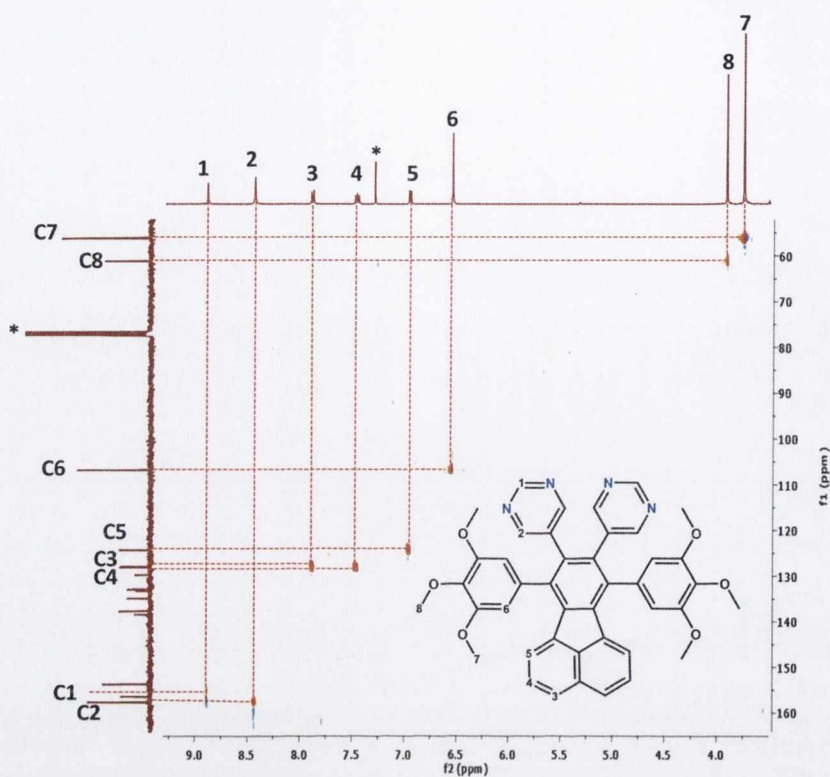


Figure 4.5: HSQC spectrum of **77** (atom labelling as per inset figure). Asterisk denotes solvent peak ( $\text{CDCl}_3$ , RT, 400 MHz).

#### 4.3.3 Single Crystal X-ray Analysis of **74-77**

Colourless needle-shaped crystals suitable for single-crystal X-ray diffraction were obtained for all the four methoxy substituted 4N fluoranthenes **74-77** which were grown from the slow evaporation of dichloromethane from methanol. The molecules **74-76** crystallised in the monoclinic space group  $\text{C2/c}$  with four molecules per unit cell whereas **77** crystallised in monoclinic space group  $\text{P2}_1/\text{n}$  with eight molecules per unit cell. The molecules showed reasonably good data which can be seen in Table 4.2.

Table 4.2: Crystallography data showing goodness-of-fit and R values for **74-77**

| Compound  | Goodness-of-fit | Variables | R1    | wR2    |
|-----------|-----------------|-----------|-------|--------|
| <b>74</b> | 1.029           | 205       | 4.98% | 11.61% |
| <b>75</b> | 1.021           | 201       | 5.57% | 14.47% |
| <b>76</b> | 1.083           | 225       | 4.79% | 15.16% |
| <b>77</b> | 1.021           | 953       | 5.40% | 13.76% |

#### 4.3.3.1 Crystallography Analysis of **74**

The molecular structure of **74** and its packing nature are shown in Figure 4.6. The pyrimidyl and phenyl groups are observed to lie almost perpendicular to the fluoranthene plane. The molecules pack in a head-to-tail fashion, with  $\pi$ - $\pi$  interactions between the aromatic cores resulting in intermolecular distance of 4.085 Å.

Molecules of **74** are mainly connected through N $\cdots$ H-C [3.506 Å] intermolecular interactions of one of the pyrimidyl ring and fluoranthene unit. In addition, strong hydrogen bonding between pyrimidyl ring N and CH of solvent molecule (methanol) was observed contributing to form a self-assembled close packed arrangement.

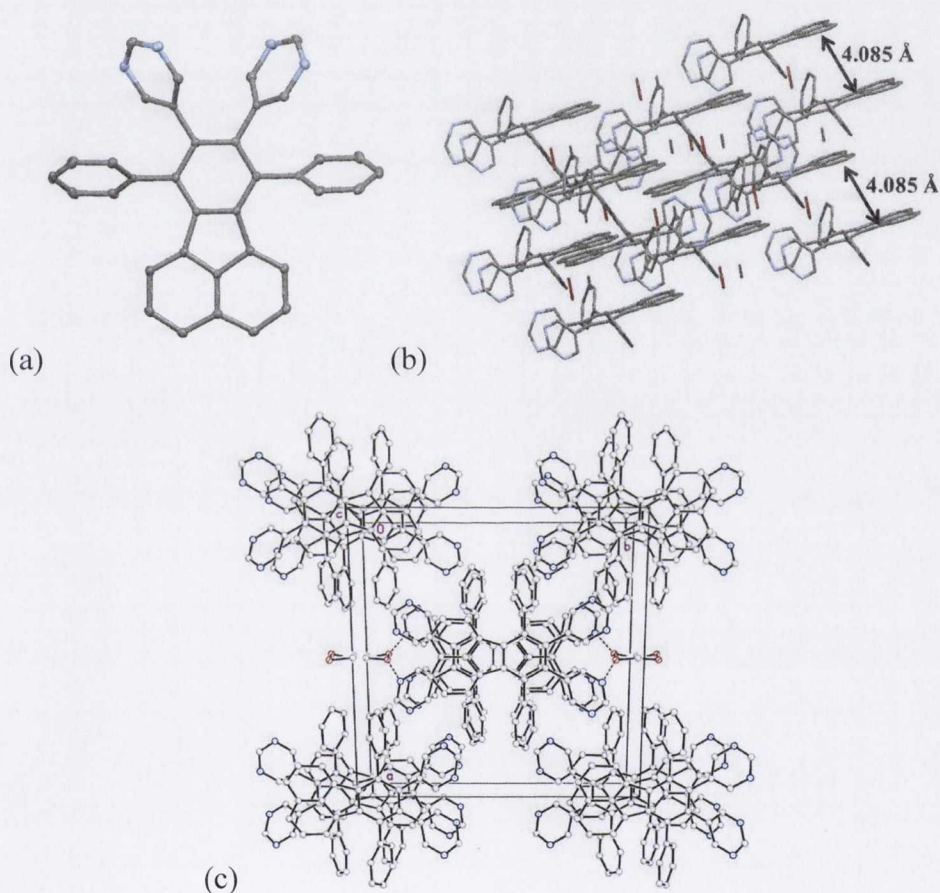


Figure 4.6: (a) Ellipsoid representation of crystal structure **74** shown at 50% probability (carbon atoms in grey and nitrogen atoms in blue). (b) Crystal packing structure as viewed along the b-axis showing the staggered stacking of the dimers with a distance of 4.085 Å between the planar aromatic cores of the molecules. (c) Packing diagram of **74** viewed down the c-axis. Dashed lines indicate strong hydrogen bonding. Hydrogen atoms omitted for clarity.



### 4.3.3.2 Crystallography Analysis of 75

The analysis of the single-crystal **75** shows that the presence of methoxy groups result in only minimal changes to the molecular structure. As observed in **74**, the pyrimidyl are observed to lie almost perpendicular to the fluoranthene plane. In **75**, the intermolecular distances between the molecules increases with the addition of methoxy groups as shown in Figure 4.7.

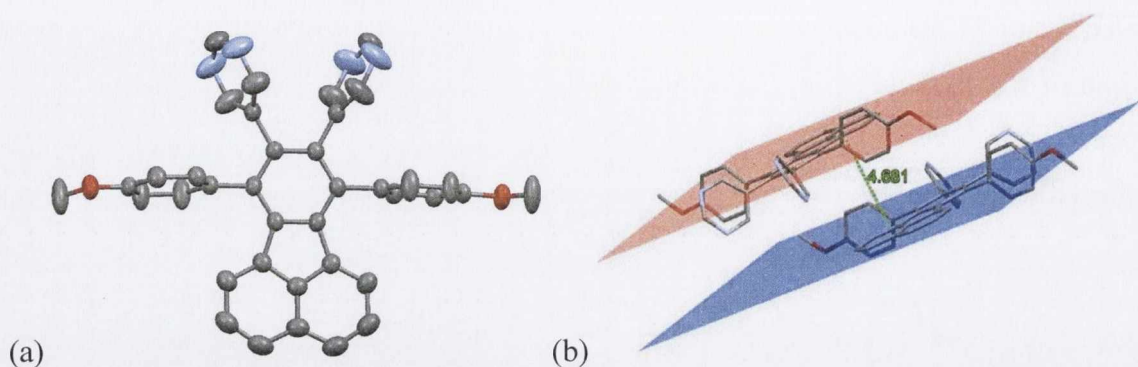


Figure 4.7: (a) Ellipsoid representation of crystal structure **75** (carbon atoms in grey, oxygen atoms in red and nitrogen atoms in blue) Thermal ellipsoids shown at 50% probability. (b) Crystal packing structure as viewed along the *b*-axis showing the interplanar distance of 4.681 Å between the planar aromatic cores of the molecules.

Molecules of **75** are mainly connected through O $\cdots$ CH intermolecular interactions. Figure 4.8 illustrates some of the interactions responsible for the self-assembled close packing arrangement in **75**. Further, weak intermolecular C $\cdots$ H interactions arising from the fluoranthene unit contribute to form a self-assembled close packed arrangement. When viewed along the '*c*' axis the pyrimidine rings on adjacent molecules tend to be aligned facing one another.

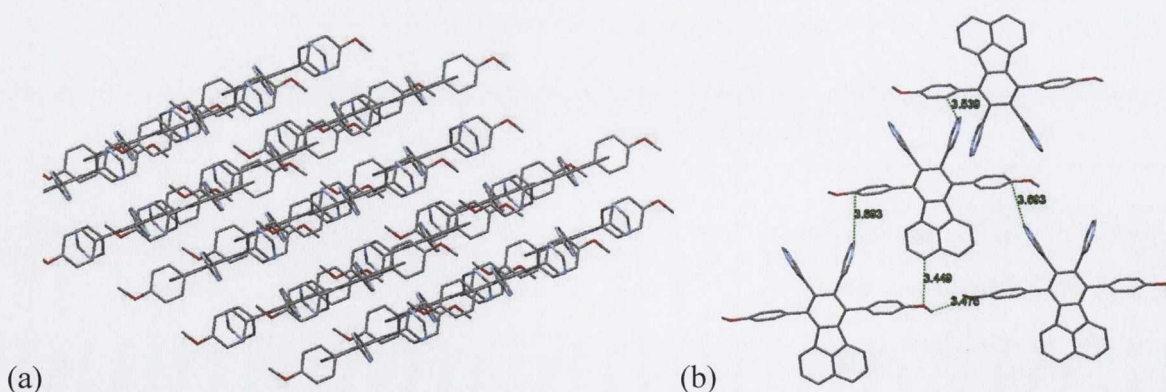


Figure 4.8: (a) Packing diagram of **75** viewed down the *b*-axis. Hydrogen atoms omitted for clarity. (b) Representation of some of the lattice stabilising interactions in **67** (distances marked in Å).



## 4.3.3.3 Crystallography Analysis of 76

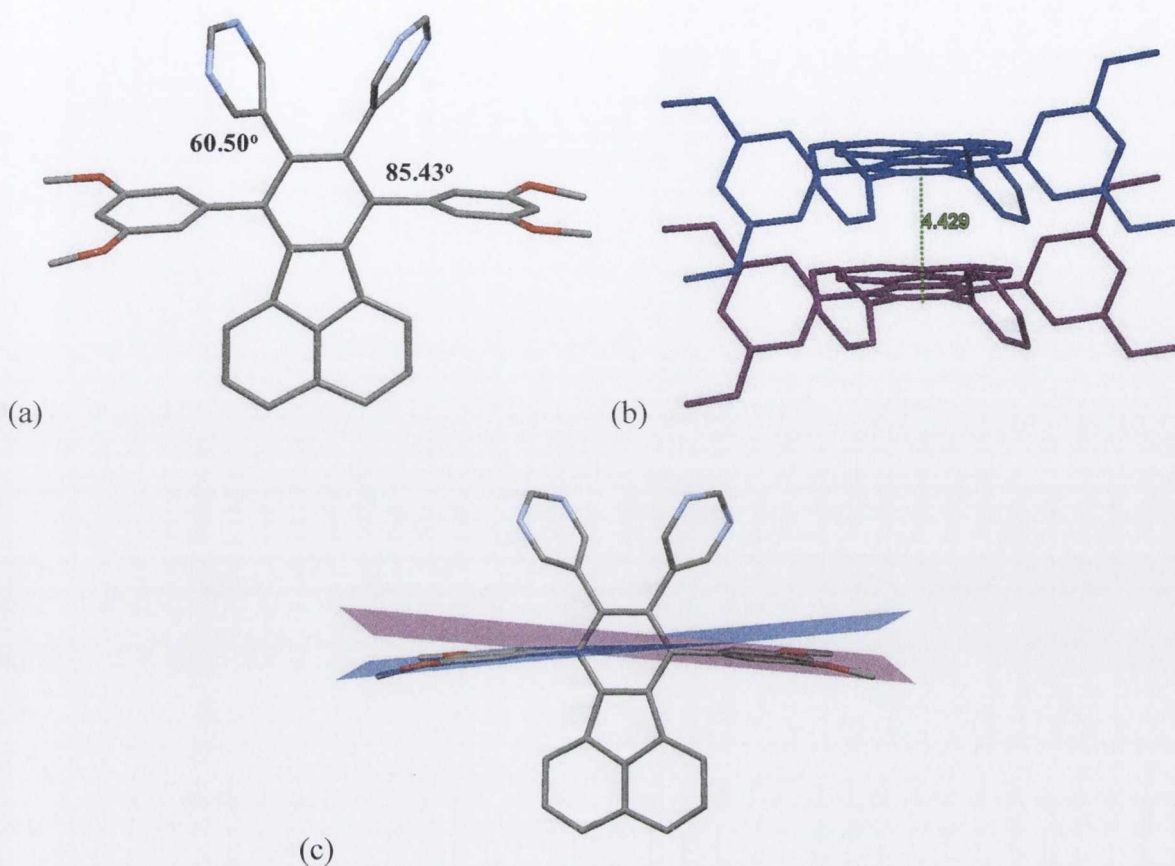


Figure 4.9: (a) Capped stick representation of crystal structure **76** (carbon atoms in grey, oxygen atoms in red and nitrogen atoms in blue) showing the angles of twist from the central aromatic ring plane of the pyrimidyl rings. (b) Crystal packing structure as viewed along the *b*-axis showing the interplanar distance of 4.429 Å between the planar aromatic cores of the molecules. (c) Graphical representation of central ring with the two di-methoxy phenyl ring planes. Hydrogen atoms omitted for clarity.

Similar to **74** and **75**, the interactions between the central ring of one molecule and the central pendant phenyl ring of its perpendicular counterpart ensure that this orientation is maintained. Hydrogen bonding from the pyrimidyl nitrogen atoms to the protons on neighbouring phenyl rings results in head-to-tail packing, with an intermolecular distance of 4.429 Å between molecules in the central fluoranthene moiety. The pyrimidyl and phenyl rings adjacent to the central core are twisted out of the average plane of the central ring by 60.50° and 85.43° respectively.

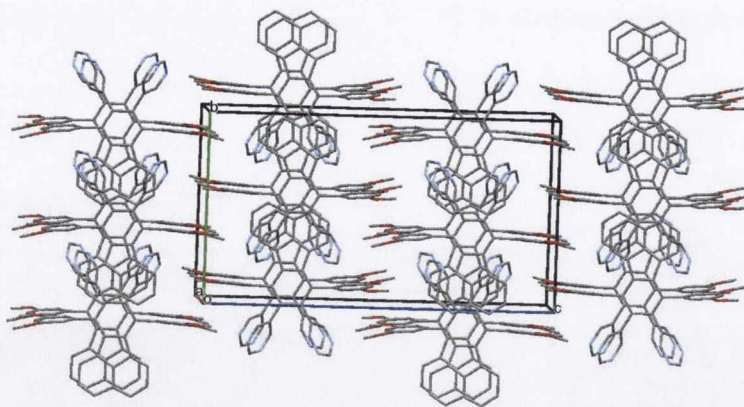


Figure 4.10: Packing diagram of **76** viewed down the *b*-axis. Hydrogen atoms omitted for clarity.

#### 4.3.3.4 Crystallography Analysis of **77**

Recrystallisation of **77** from deuterated  $\text{CH}_2\text{Cl}_2$  yielded the product as extremely thin crystalline fibres in NMR tube, which were suitable for single crystal X-ray diffraction studies. The presence of six methoxy groups in **77** results in only minimal changes to the molecular structure. The crystallographic data was refined using PLATON and HKLF 5 programmes and was successfully integrated using a monoclinic unit cell. One pyrimidine ring disordered in two positions (53:47% occupied) modelled with restraints (DFIX) and constraints (EADP). One methoxy group was disordered in three positions (ca. 74.5:13.5:12% occupancy) and was modelled with restraints (SADI) and constraints (EADP, SUMP). The intermolecular distance between the molecules increases with the addition of these methoxy groups *i.e.* was observed in the order **77** > **76** > **75**.

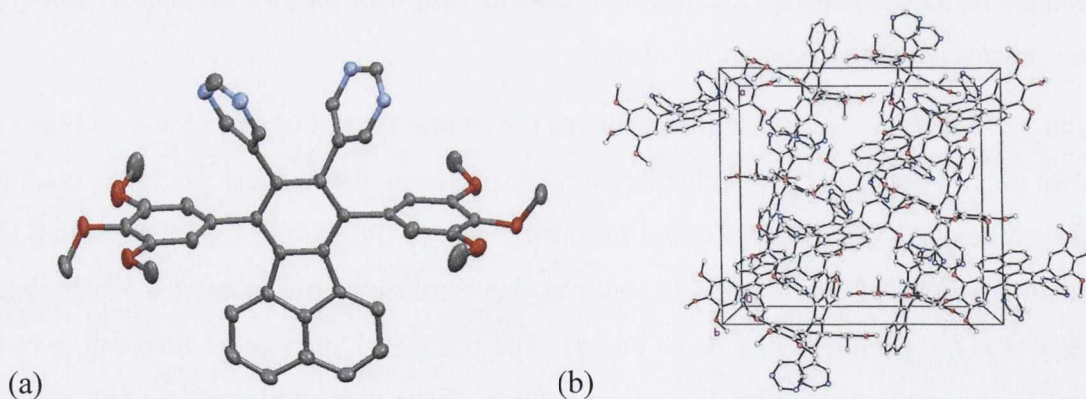


Figure 4.11: (a) Ellipsoid representation of crystal structure **77** shown at 50% probability (carbon atoms in grey, nitrogen atoms in blue and oxygen atoms in red). (b) Packing diagram of **77** (major disordered moiety only) viewed normal to the *b*-axis. Hydrogen atoms omitted for clarity.



#### 4.4 Photophysical Studies of 74-77

The UV-Vis absorption spectra and fluorescence emission spectra of **74-77** were measured in EtOH ( $\sim 10^{-5}$  M), and are shown in Table 4.3. The absorption spectra of the four 2N fluoranthenes feature strong absorption bands each in the near UV-region of the spectrum as shown in Figure 4.11. The absorption spectra of 2N fluoranthenes **74-77** consist of  $\pi$ - $\pi^*$  transitions. The strong absorption bands in the near UV region and high molar extinction coefficients of these bands further suggest  $\pi$ - $\pi^*$  nature of the absorption bands which typically display  $\varepsilon = 10^3 - 10^5 \text{ M}^{-1}\text{cm}^{-1}$ . The 4N fluoranthene **74** exhibits an electronic spectrum with an absorption maximum showing bathochromic shift.

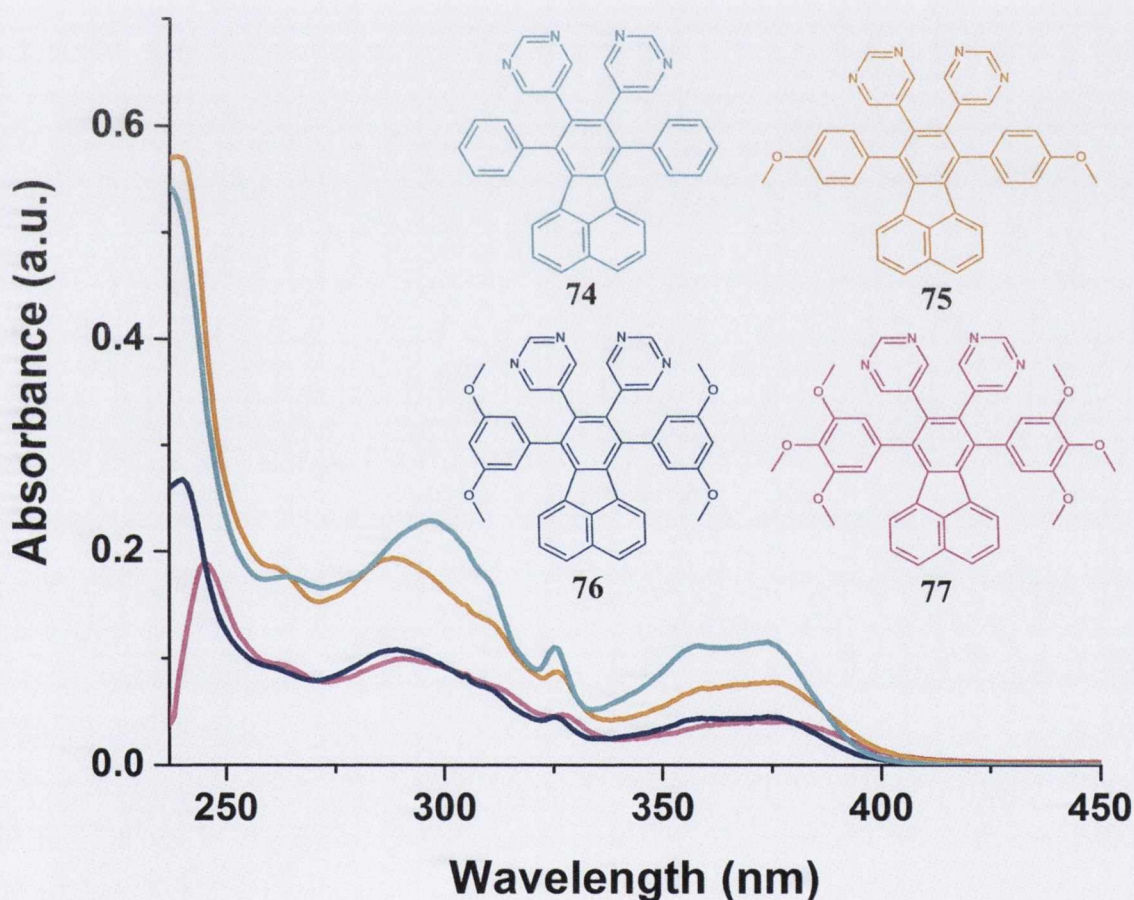


Figure 4.12: The overlaid UV-Vis spectra of 2N fluoranthenes **74-77** in ethanol ( $\sim 10^{-5}$  M).

The presence of electron withdrawing nitrogens in nitrogen substituted fluoranthenes induces a permanent dipole moment along the plane of the molecule. The permanent dipole moment on N-doped fluoranthenes can be varied by changing the substituents on the peripheral aryl rings. Upon substitution, the dipole moment of the ground state and/or first excited state is changed and thus alters the spectroscopic characteristics. The position of electron donating



methoxy substituents has significant effect on the dipole moment of the molecules. When methoxy groups are substituted on the phenyl group *i.e.* *para* with respect to the pyrimidyl rings the absorption spectra shows a greater bathochromic shift than their *ortho* substituted counterparts.<sup>116</sup> As expected, methoxy functionalisation of fluoranthenes **75-77** at the *ortho* position phenyl groups wrt pyrimidyl rings did not affect the absorption spectra significantly.

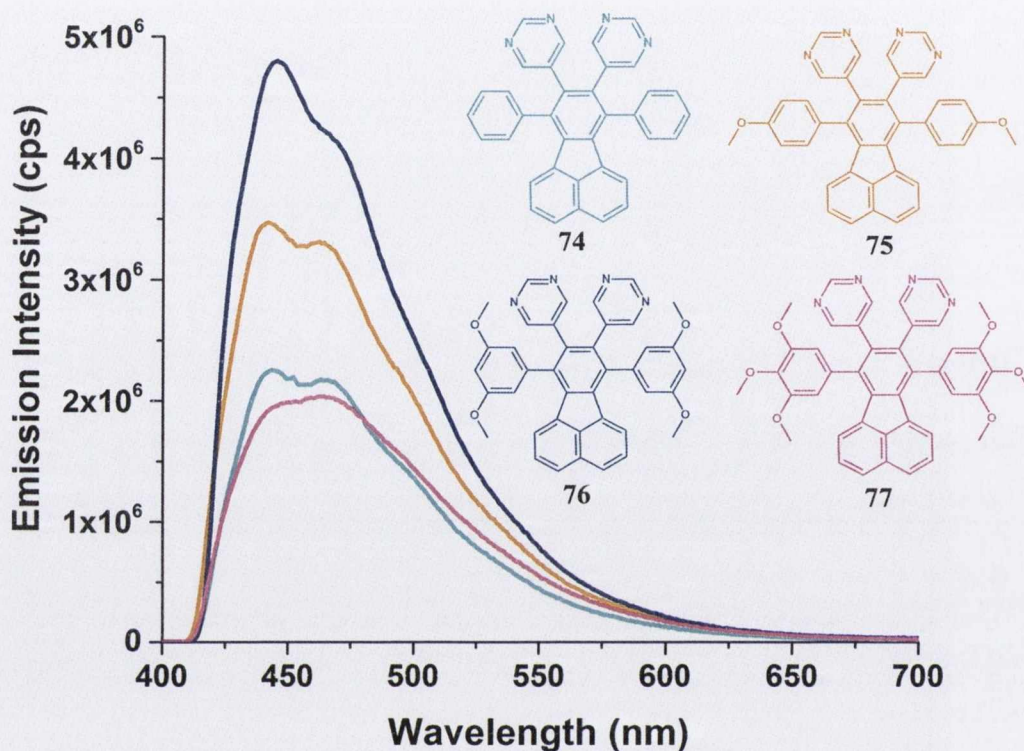


Figure 4.13: The overlaid fluorescence spectrum of fluoranthene derivatives **74-77** in EtOH solution ( $\sim 10^{-5}$  M).

The overlaid luminescence spectra of polyphenylenes **74-77** in ethanol are shown in Figure 4.12. The  $\pi$ -conjugated nature of these fluoranthenes gives rise to strong blue fluorescent emission in an EtOH solution. The variation in substituents shows a slight trend in the emission profile in comparison with the absorption profile. The methoxy substituted polyphenylenes **75-77** undergo a more significant bathochromic shift in their emission spectra with  $\lambda_{\text{em}}^{\text{max}}$  at 441 nm and 464 nm respectively. This trend has also been observed in other 4N methoxy substituted polyphenylenes synthesised within the group.<sup>116</sup>

Table 4.3: Summary of photophysical data of **74-77**( $\sim 10^{-5}$  M) in ethanol at RT.

| Compound  | $\lambda_{\text{abs}}$ [nm] | $\lambda_{\text{em}}$ [nm] | Stoke's shift<br>( $\text{cm}^{-1}$ ) | $\Phi_f$<br>( $\lambda_{\text{ex}}=375\text{nm}$ ) | $\tau$ /ns |
|-----------|-----------------------------|----------------------------|---------------------------------------|----------------------------------------------------|------------|
| <b>74</b> | 245 ,299,<br>327, 376       | 441                        | 3920                                  | 42%                                                | 27         |
| <b>75</b> | 236 , 297<br>325, 374       | 442                        | 4113                                  | 46%                                                | 24         |
| <b>76</b> | 244,290<br>327, 377         | 443                        | 3952                                  | 50%                                                | 28         |
| <b>77</b> | 245, 290,<br>328, 372       | 464                        | 5330                                  | 9%                                                 | 13         |

The fluorescence quantum yield ( $\Phi$ ) obtained using integrating sphere for all the 4N derivatives exhibits in the range 40–50 % in ethanol, demonstrating that the fluorescence process was quite efficient in each system. Interestingly, **77** showed the smallest quantum yield value, bucking the trend seen when increasing the number of methoxy-substitution. The relevant data of quantum yields are summarised in Table 4.3. The fluorescence lifetime obtained by time correlated single photon counting (TCSPC) method of **74-76** in ethanol is found to be in the range 24-28 ns whereas **77** again showed unusual behavior by demonstrating low lifetime of 13 ns.

#### 4.5 Theoretical Studies of **74-77**

In order to understand the absorption characteristics of the fluoranthenes, concurrent theoretical calculations were performed for the fluoranthenes **74-77**, using density functional theory with the B3LYP functional and 6-31g\* basis set. The HOMO and LUMO orbitals of **74-77** are  $\pi$  type, and are majorly localised on the fluoranthene moiety as expected. This demonstrates that the low energy transitions noted for these compounds originate from the planar fluoranthene core based  $\pi$ - $\pi^*$  transitions. The calculations show that with the increase in methoxy-substitution, the electron density is increasingly localised towards the methoxy-containing rings, showing the trend, **77** > **76** > **75** > **74** (Figure 4.13).



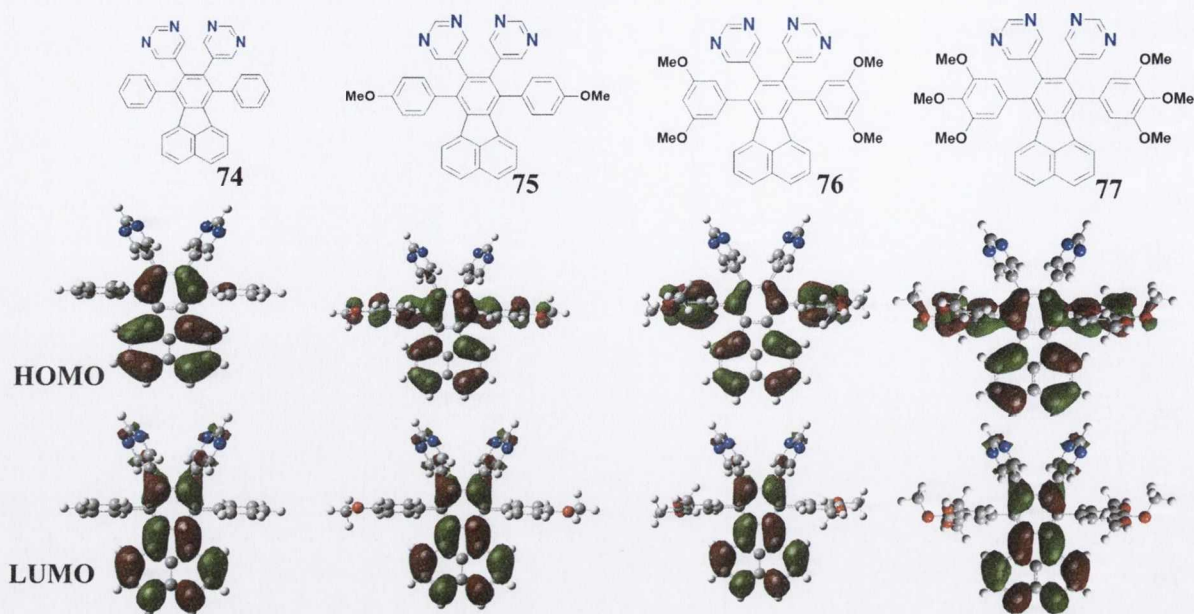


Figure 4.14: HOMO and LUMO states shown via the optimized geometries of **74-77** generated from the B3LYP functional and 6-31g\* basis set.

#### 4.6 Nitroaromatic Sensing Studies of **74-77**

The solution based interactions of **74-77** with different nitroaromatic compounds (NACs), and other electron deficient acceptors were investigated *via* their fluorescence spectra in EtOH. Figure 4.14 shows a histogram of fluorescence quenching behaviour of **74-77** with different analytes. The electron deficient NACs generally showed very high fluorescence quenching, with the quenching efficiency further varying based upon the amount of nitro-substitution of the toluenic or phenolic system. Picric acid (PA) showed the highest quenching response for all the four fluoranthene systems at a ppb concentration level of 2- 20 ppb. Other NACs such as TNT, Dinitrotoluene (DNT), and nitrotoluene (NT) showed lower levels of detection in EtOH. The strong  $\pi$ - $\pi$  interactions and high polarizability of PA might be a major factor contributing to this high sensitivity. Their common electron deficient analytes (EDA) such as benzoquinone (BQ), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), iodophenol (IP), phenol (P) and toluene (T), showed little effect on the fluorescence intensity of each fluoranthene, demonstrating that all the four systems show a strong selective quenching response with NACs, *versus* that of other EDAs.



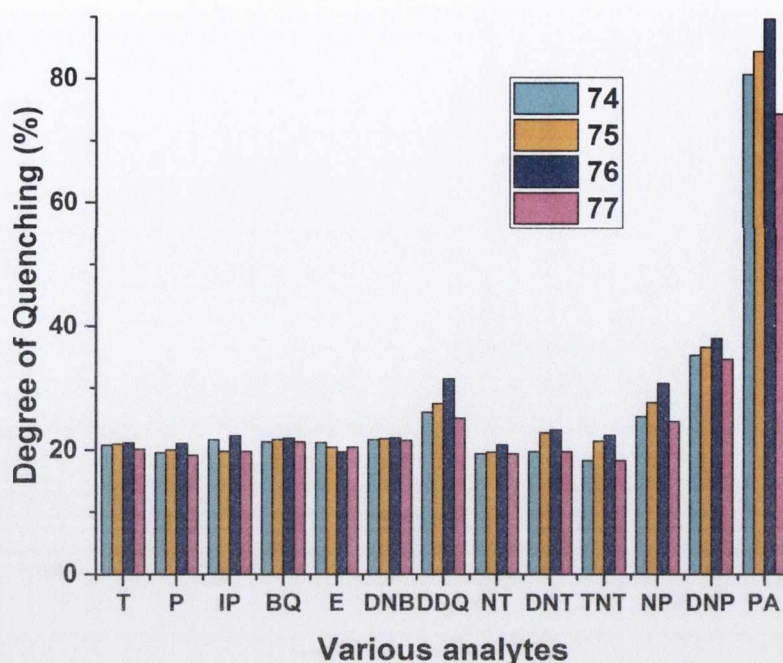


Figure 4.15: The degree of fluorescence quenching of methoxy 4N-fluoranthene derivatives **74-77** different analytes.

Among the various fluoranthenes, **76** showed the highest quenching efficiency, and the trend was observed as **76**>**75**>**74**>**77**. Furthermore, fluorescence titration studies using **76** and the optimal quencher PA were undertaken, and showed that with the gradual increase of PA concentration, there was decrease in the fluorescence intensity (Figure 4.15a). **76** showed an 89% quenching efficiency for 25  $\mu\text{M}$  of PA. The corresponding Figure 4.15b shows the normal naked eye fluorescence intensity of **76** and the lack of such fluorescence in a sample of PA. Upon the addition of 25  $\mu\text{M}$  of PA to **76**, the quenching of this system's fluorescence intensity can be witnessed. This real time, naked eye visualisation, demonstrates the potential of these systems to be utilised quickly in practical applications in the field.

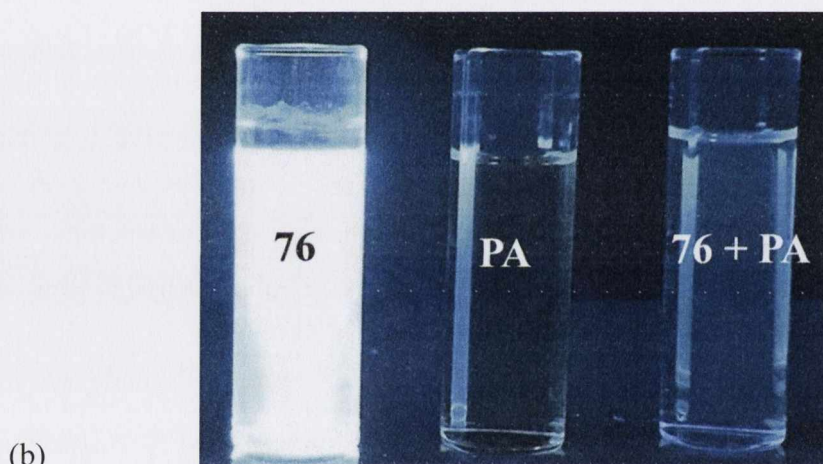
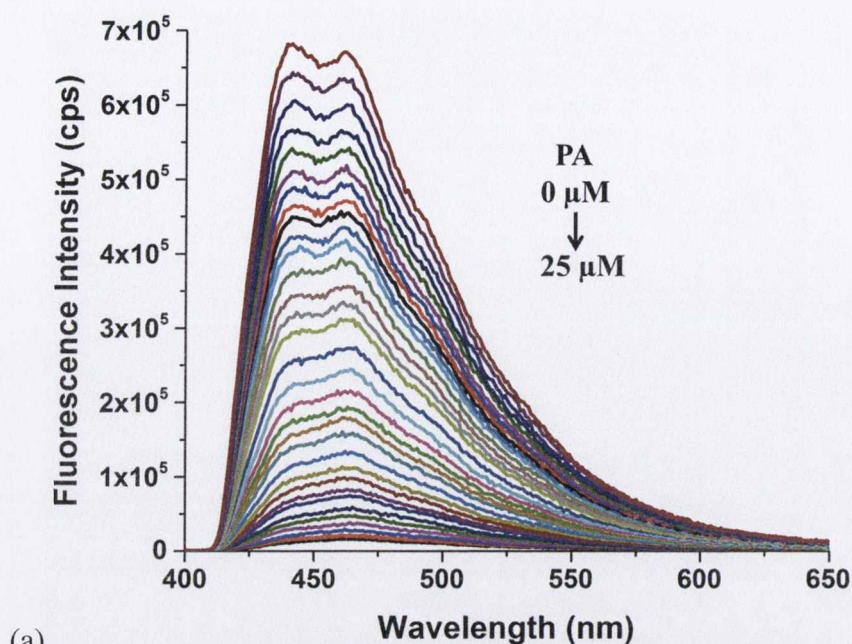


Figure 4.16: (a) Fluorescence quenching of **76** ( $\sim 10^{-5}$  M) upon addition of PA ( $\sim 10^{-4}$  M) in EtOH ( $\lambda_{ex} = 377$  nm), (b) photograph showing the fluorescence intensity of **76**, PA, and quenching of fluorescence intensity upon addition of 25  $\mu$ M PA to **76**.

As mentioned previously, all the 4N fluoranthenes of this chapter were found to be selective to PA. Thus, titration studies of **74**, **75** and **76** with PA were undertaken, and can be found in the Figure 4.16. Utilisation of the data generated by these titrations allowed for the calculation of the degree of fluorescence quenching, upon the gradual total addition of 25  $\mu$ M of PA as 84 % for **74**, 82 % for **75** and 74 % for **77**.



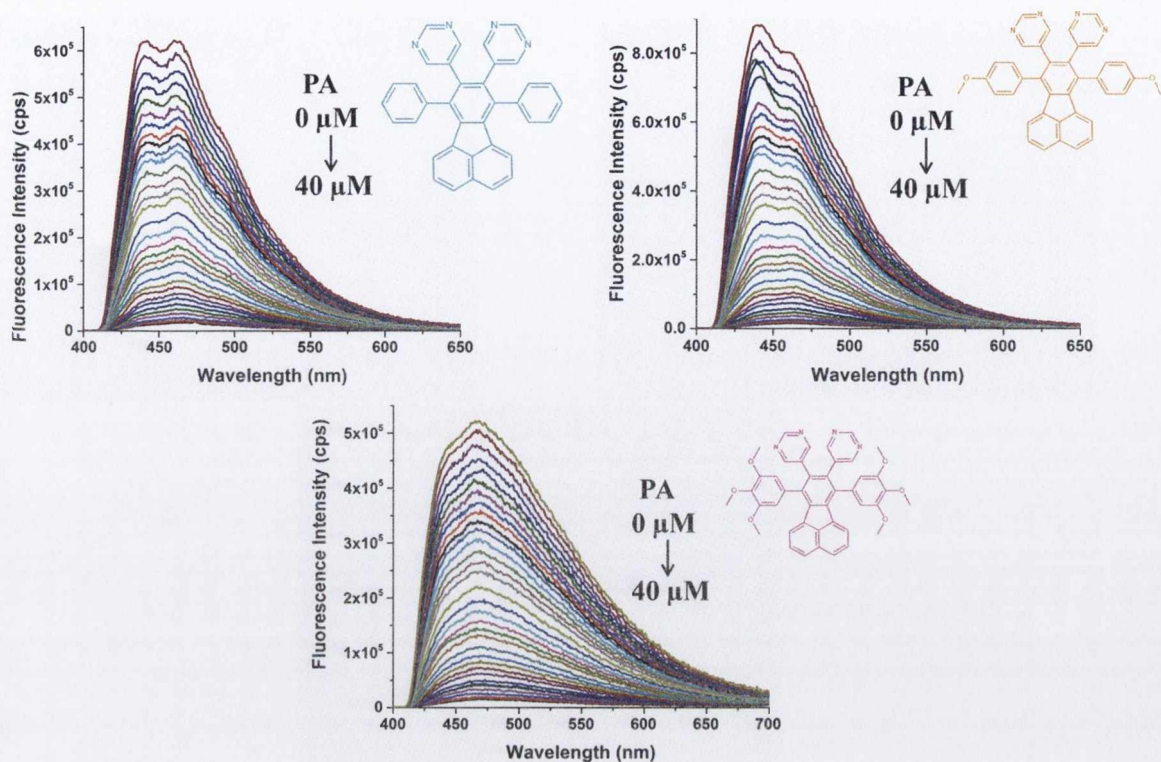
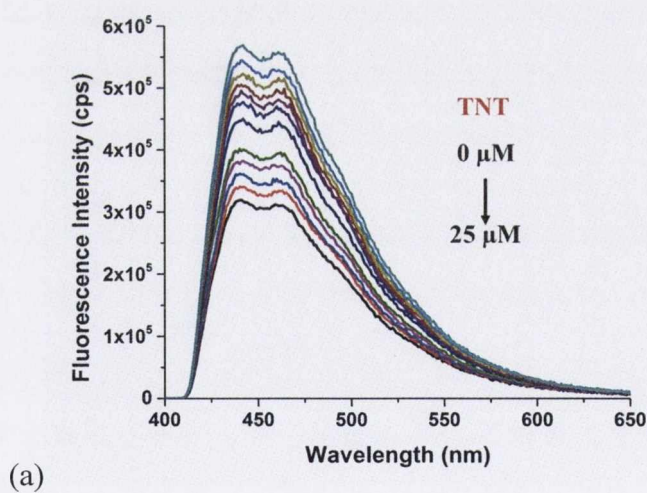
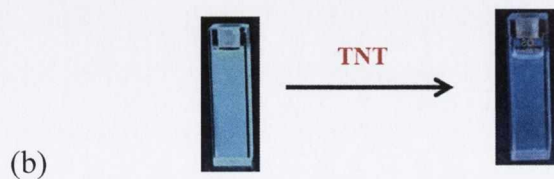


Figure 4.17: Titration studies showing the fluorescence quenching of **74** ( $\lambda_{\text{ex}} = 376 \text{ nm}$ ), **75** ( $\lambda_{\text{ex}} = 374 \text{ nm}$ ) and **77** ( $\lambda_{\text{ex}} = 372 \text{ nm}$ ) [fluoranthene concentration for all =  $\sim 10^{-5} \text{ M}$ ], upon addition of different concentrations of PA ( $\sim 10^{-4} \text{ M}$ ) in an EtOH solution.



(a)



(b)



Figure 4.18: (a) Titration study of the fluorescence quenching of **76** ( $\sim 10^{-5}$  M) upon the addition of TNT ( $10^{-4}$  M) to **76** in EtOH at 25°C. (b) Naked eye visual detection of fluorescence quenching of **76** in the presence of TNT.

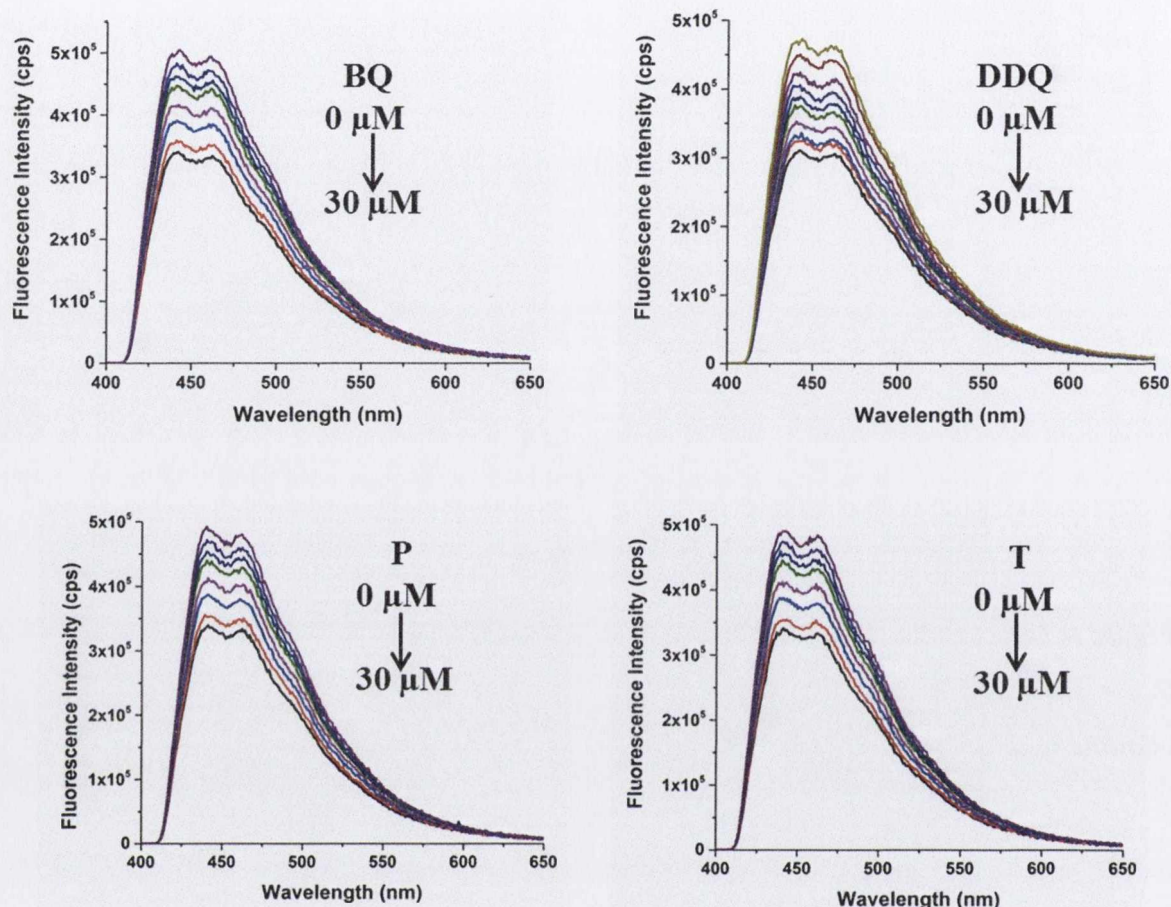


Figure 4.19: Titration studies of the fluorescence quenching of **76** ( $\sim 10^{-5}$  M) upon the addition of benzoquinone (**BQ**), 2,3-dichloro-5,6-dicyanobenzoquinone (**DDQ**), phenol (**P**) and toluene (**T**) [all EDA concentrations =  $\sim 10^{-4}$  M] to **76** in EtOH at 25°C.

To understand the quenching process between fluoranthene derivatives and NACs further, Stern-Volmer (SV) plots were calculated, and found a linear relationship, strongly indicating the presence of a static quenching mechanism. The SV follows the trend, **76**>**75**>**74**>**77**. The dilution effect altered the fluorophore concentration affecting the emission intensity at higher additions of analyte. The fluorescence lifetimes of **74-77** after titration with increasing concentrations of PA do not change, confirming that the static quenching mechanism is present for these systems (Table 4.4). This indicates the formation of a ground state complex, allowing non-radiative relaxation of the fluoranthene systems to their ground states. Also, the spectrophotometric titration of **76** with PA shows the formation of a broad peak above 400

nm, further suggesting the generation of a donor-acceptor (D-A) charge transfer complex (Figure 4.19).

Table 4.4: Excited state lifetime measurements of 74-77, with and without the addition of PA (~10<sup>-5</sup> M). Measurements carried out in EtOH at 25 °C.

| Compound         |       | Life time (τ) (ns) |       |       |  |
|------------------|-------|--------------------|-------|-------|--|
| Fluoranthene (F) | 74    | 75                 | 76    | 77    |  |
| F                | 27 ns | 24 ns              | 28 ns | 18 ns |  |
| F + 0.2 eq of PA | 27.02 | 24.06              | 28.01 | 18.04 |  |
| F + 0.5 eq of PA | 27.07 | 24.08              | 28.05 | 18.04 |  |
| F + 1 eq of PA   | 27.01 | 24.02              | 28.02 | 18.03 |  |
| F + 2 eq of PA   | 27.03 | 24.02              | 28.07 | 18.01 |  |

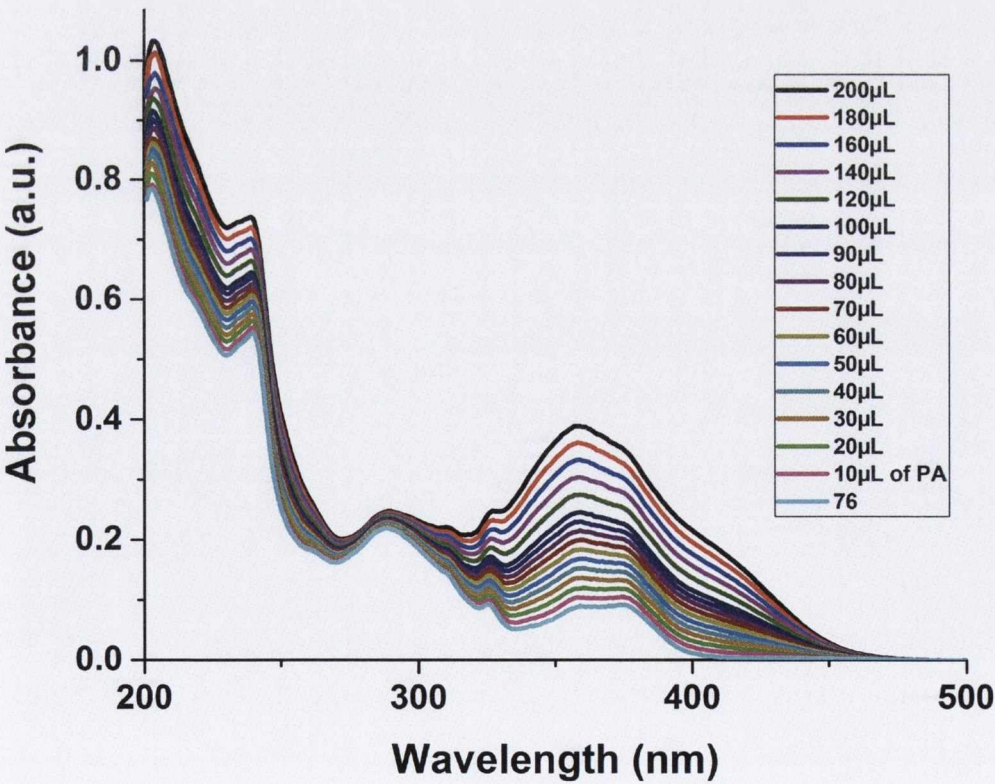


Figure 4.20: The spectrophotometric titration study of 76, upon gradual addition of PA in EtOH.



#### 4.7 DFT Studies of 76 and 77 supporting Nitroaromatic Sensing results

To complement the experimental results, the confirmation of a D-A charge transfer complex was sought with DFT based energy minimization studies, where the effect of association between the D-A was optimized for each pair. For each fluoranthene system, the electron density is localised on the fluoranthene core in the HOMO state, and on PA in the LUMO state (Figure 4.20).

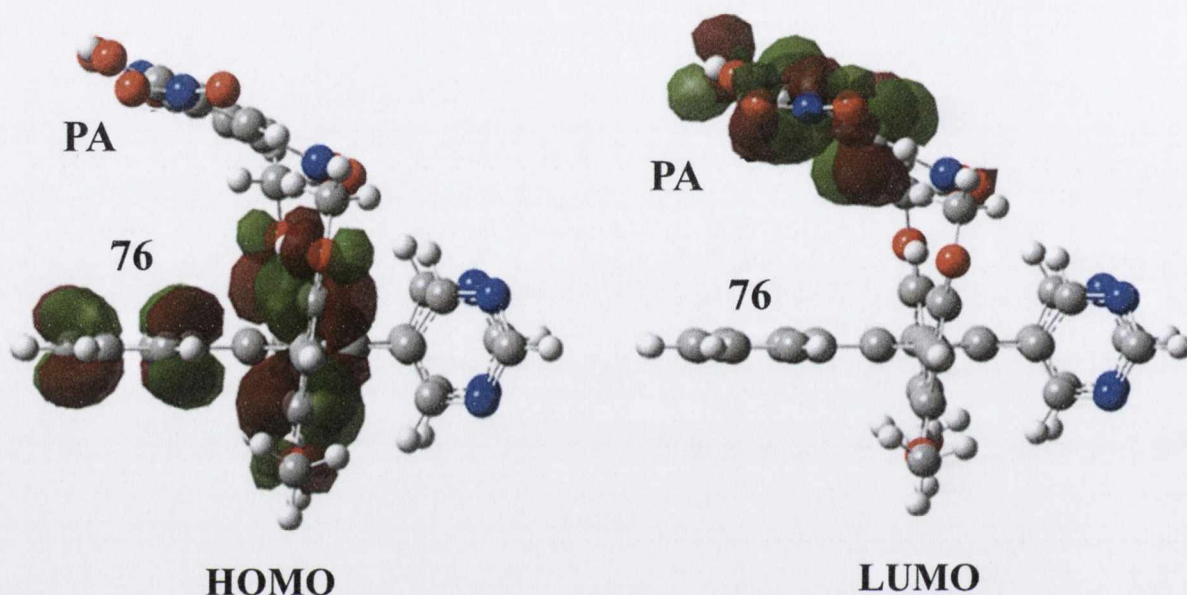


Figure 4.21: Calculated HOMO and LUMO electron density for the D-A charge transfer complex, optimized with B3LYP/6-31g\* basis set for system 76 in presence of PA.

On the basis of purely electronic consideration,  $\pi$ -electron rich tri-methoxy 4N-fluoranthene might show maximum fluorescence quenching response to the electron deficient nitroaromatic compounds. However, it was observed that electron rich 77 shows poor quenching response towards nitroaromatics than other 4N fluoranthenes tested (Figure. 4.14). This poor quenching response may be due to the steric effect of bulky tri- methoxy groups. The substitution of six bulky methoxy groups on the peripheral of the fluoranthene fluorophore may be too sterically demanding to permit an optimal interaction between the fluorophore and the electron deficient nitroaromatics which in turn results in poor fluorescence quenching response.

On the other hand, 76 was expected to have slightly weaker interaction with electron deficient nitroaromatics compared to 77, but experimental observation showed that fluoranthene 76 exhibits highest quenching response towards nitroaromatics. The reason for



this observed anomaly in quenching response is attributed to the less-steric hindrance of methoxy substituents on **76** due to their position on phenyl rings and in turn, it increases the effective binding of nitroaromatic quenchers with fluorophore **76** compared to fluorophore **77**. In order to understand the nature of interaction of fluoranthenes with analytes and to provide further support to the observed fluorescence quenching response, density functional theory (DFT) calculation was carried out using the Gaussian 03 program and 6-31G\* basis set to optimize the structure of fluorophore–analyte complexes. The electron deficient PA was optimized with **76** and **77** in view to obtain the firm evidence for the observed fluorescence quenching response.

The optimized structure of the complexes **76**-PA and **77**-PA are given in Figure 4.21. As can be seen from Figure 4.20 both the fluoranthenes (**76** and **77**) show strong intermolecular  $\pi$ – $\pi$  interaction and maintained a co-facial stacked geometry with PA. The calculated intermolecular distances between the fluorophore molecular plane and that of picric acid are 6.1 Å for **76**-PA and 8.9 Å for **77**-PA. Moreover, the estimated interaction energy for the complex **76**-PA was found to be higher than that of complex **77**-PA; this reflects the fact that fluorophore **77** forms a weak excited charge transfer complex with picric acid.

The possible reason for the observed weak complexation of **77** with picric acid could be attributed to the propinquity of electron- density from the methyl groups on OMe to the plane of picric acid and that decreases the efficiency of electron transfer from the  $\pi$ -electron rich discrete **77** to the electron deficient PA and therefore shows poor fluorescence quenching response towards nitroaromatics in solution.

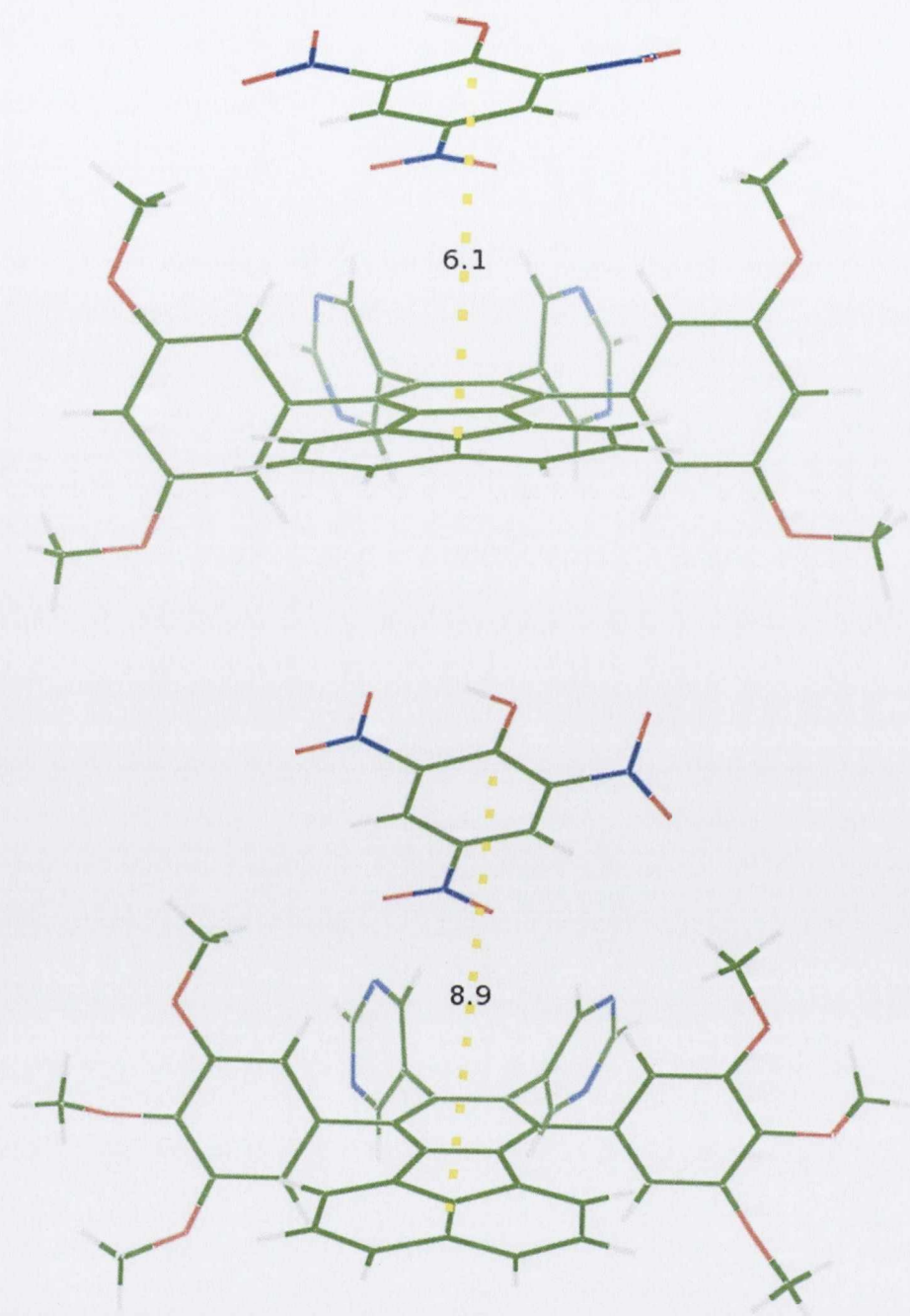


Figure 4.21: Optimised geometries of **76-PA** and **77-PA** complexes.

In addition to solution state studies, PA detection in the solid state was also carried out. **76** was adsorbed onto TLC strips, and dried under vacuum. By dip-coating solutions of PA onto the strip at random locations, fluorescence quenching was observed under UV irradiation, and is shown in Figure 4.22. The formation of non-emissive spots demonstrates the use of test strips for instant visualization of traces amounts of PA. Of the many fluorescent sensors

available for explosive detection, **76** show high selectivity and sensitivity for PA over other common explosives.<sup>74, 144</sup>

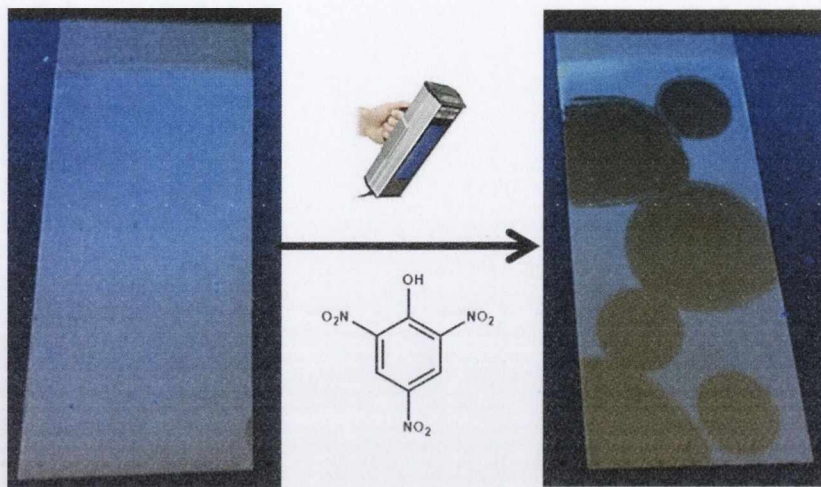


Figure 4.22: Photograph showing the dramatic loss of fluorescence observed, before and after the addition of a  $\sim 10^{-4}$  M solution of PA to a dip-coated TLC silica plate ( $\sim 10^{-5}$  M) of **76** in EtOH under UV light.

#### 4.8 Conclusion

In conclusion, the novel nitrogen-substituted methoxy-containing fluoranthenes **74-77** were synthesized *via* the Diels-Alder [2+4] cycloaddition of 1,2-di(pyrimidin-5-yl)ethyne, and appropriate cyclopentadienones. Three systems have been demonstrated as effective sensors for the detection of nitroaromatic explosives, in particular PA. The quantum yields, fluorescence lifetimes, and the nitroaromatic sensing studies followed the trend, **76**>**75**>**74**, indicating that with increasing electron rich methoxy groups, the fluorescence quenching efficiency was increased. **77**, the system with the maximum number of methoxy groups possible did not follow this trend, and may be explained *via* its respective DFT calculations. The quenching ability of these novel heterocyclic- and methoxy-containing fluoranthenes as highly selective chemosensors for the detection of PA is proposed as through a static fluorescence quenching mechanism. Experimental and theoretical studies are used to confirm this assignment.





## **5. Functionalised Azafluoranthenes**





## 5.1 Introduction

This chapter gives a brief introduction to azafluoranthenes, and then discusses the synthetic approach to prepare them. A series of novel azafluoranthenes were synthesised *via* the [4+2] Diels-Alder route and their structural characterisation was explored. The chapter will therefore be concerned with the preparation of a series of nitrogen-containing azafluoranthenes, with three aryl rings at their periphery, and their use as potential chemosensors towards the sensing of NAC compounds.

As per Chapter 1, the incorporation of nitrogen atoms into the fluoranthene core increases the sensitivity of the system towards picric acid. In Chapter 2, the nitrogen loading is maintained as a constant, and the substituents on the fluoranthene core are varied. It was observed from this study that the hexa-methoxy containing fluoranthene compound showed the maximum sensitivity of its series. By combining these two trends, in Chapter 4, the synthesis of a series of methoxy-substituted 4N-fluoranthenes was achieved by systematically increasing the number of methoxy groups, with the assumption that the hexa-methoxy substituted 4N fluoranthene would be the best chemosensor. However, through analysis of the optoelectronic properties, and the NAC sensing results, it was observed that tetra-methoxy substituted 4N fluoranthene gave the optimal sensing ability.

A combination of all of these trends was therefore used to optimize the next series of compounds generated as part of this work, substituted azafluoranthenes. By keeping the above trends and results in mind, the design and synthesis of asymmetric azafluoranthenes with phenyl, tert-butyl, tetra-methoxy and bromo substituents was performed. Utilising this approach, the behavior of asymmetric systems, and effect of methoxy-substituted azafluoranthenes with PA was monitored.

## 5.2 Azafluoranthenes

Azafluoranthenes are fluoranthenes-based compounds with nitrogen atoms incorporated directly into the fused ring system. Deriving inspiration from the nitroaromatic sensing ability of triphenyl-containing fluoranthenes *i.e.* fluoranthenes with three aryl groups, we have designed tri aryl substituted azafluoranthenes. The parent azafluoranthenes, **80**, is found as a component of coal tar, and is thus an air pollutant. They are also widely found in many natural products, including alkaloids.

As an example, some unusual alkaloids including imelutiene, rufescine, triclisine, telitoxine, norrufescine, and norimeluteine, have been extracted from natural products.<sup>145</sup> These azafluoranthenes are derivatives of indeno[1,2,3-*ij*]isoquinolines, **81** and **82** (Figure 5.1).<sup>146</sup>

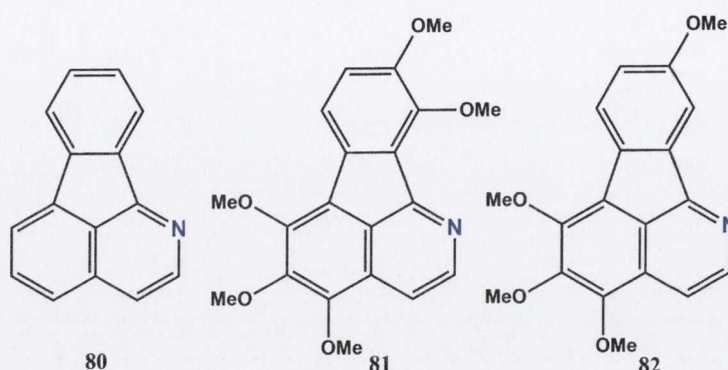


Figure 5.1: (a) 1-azafluoranthene **80**, (b) imelutine **81**, (c) rufescine **82**

The location of the nitrogen atom(s) within the core aromatic structure of the azafluoranthene can vary, and a wide variety of examples of these compounds with the nitrogen atom incorporated into the indene unit can be found in the literature.<sup>147</sup> Beginning in 1974, Sasaki *et al.* reported the synthesis of a diazafluoranthene derivative, 7,10-diphenyl-8,9-diazafluoranthene *via* a cycloaddition-type reaction.<sup>148</sup> This method was later modified by Siegel *et al* in 2009 to yield a range of 3,4,7,10-tetrasubstituted-diazafluoranthenes.<sup>149</sup> More recently, in 2013, Harding *et al.* successfully synthesised a series of azafluoranthene alkaloids for the first time using microwave-assisted direct arylation reactions.<sup>150</sup> Techasakul *et al.* then presented a facile divergent synthetic approach to prepare a library of azafluoranthenes and aporphine alkaloids.<sup>151</sup> Despite this research interest in the development of these molecules, to date, there are no examples of 7,9,10-triphenyl-8-azafluoranthenes in the literature.



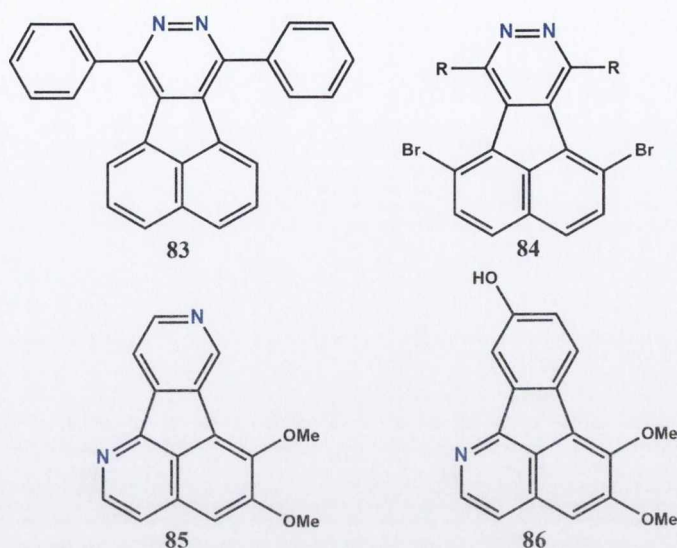


Figure 5.2: Some of the azafluoranthene derivatives in the literature

This work details the preparation of a series novel 8-azafluoranthene compounds. By treating this 8-azafluoranthene core as a molecular scaffold it was possible to add substituents in the 7 and 10 positions. The inclusion of a pyridine ring in the 9 position of the azafluoranthene core imparts N<sup>N</sup> bidentate ligand capability to the compounds, resulting in endless potential coordination with a variety of transition metals. The electron-donating and electron withdrawing substituents on the phenyl rings in the 7 and 10 positions of the azafluoranthene core have further been incorporated to tune the optical properties and study their effects on sensing application.

### 5.3 Synthesis of Azafluoranthenes

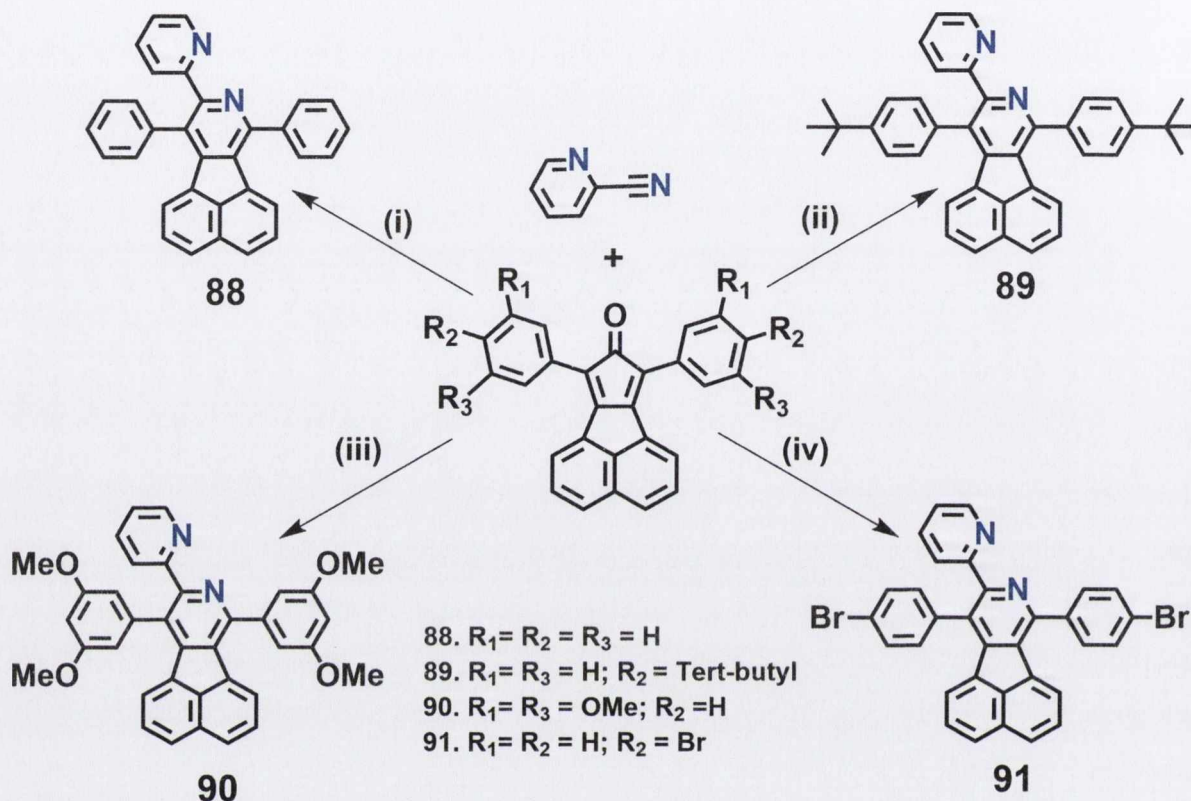
A family of novel 7,9,10-triaryl-8-azafluoranthenes ligands **88-91** were prepared. These target compounds were synthesised *via* [4+2] Diels-Alder cycloaddition between commercially available 2-pyridinecarbonitrile, and the substituted cyclopentadienone. Within the Draper group, a series of 7,9,10-triaryl-8-azafluoranthenes were prepared towards their application in organic electronics. As part of this work, a much more extensive library of compounds was generated, primarily designed to study their effects for nitroaromatic sensing.

The precursor cyclopentadienone derivatives were obtained *via* a double Knoevenagel condensation reaction between the commercially available acenaphthenequinone, and a series of 1, 3-diarylpropan-2-ones.

The substituted cyclopentadienone derivatives **54**, **62**, **64** **73**, when reacted with 2-pyridinecarbonitrile, gave the novel azafluoranthenes **88-91** *i.e.* 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthene **88**, 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene **89**, 7,10-



di(3,5-methoxyphenyl)-9-(2-pyridyl)-8-azafluoranthene **90** and 7,10-di(4-bromophenyl)-9-(2-pyridyl)-8-azafluoranthene **91** (Scheme 6.1). The [4+2] Diels-Alder cycloaddition here uses the cyclopentadienone as the diene, with 2-pyridinecarbonitrile as the dienophile. Extrusion of CO generates the heterocyclic centre ring.



Scheme 5.1: Synthesis of Azafluoranthenes **88-91**. (i) 295 °C, 12 h, 59% (ii) 300 °C, 10 h, 48% (iii) 330 °C, 6 h, 45% (iv) 300 °C, 7 h, 40%

### 5.3.1 Synthesis of 7,10-di(3,5-methoxyphenyl)-9-(2-pyridyl)-8-azafluoranthene **90**

7,10-di(3,5-methoxyphenyl)-9-(2-pyridyl)-8-azafluoranthene, **90**, was synthesized *via* a [4+2] Diels-Alder reaction with 2-pyridinecarbonitrile and 7,9-bis-(3,5-dimethoxyphenyl)-8H-cyclopenta[a]acenaphthylen-8-one, **73**. Unlike the Diels-Alder reactions carried out in earlier chapters, no benzophenone was used as the solvent. Due to the high boiling point of 2-pyridinecarbonitrile, it was added in excess (tenfold), and as a result no solvent was required. The reaction was carried out under an argon atmosphere at 310 °C for 15 h, with monitoring of completion of the reaction by TLC. Due to the generation of a large amount of undesired side products at this high temperature, purification first required removal of an insoluble black precipitate by filtration using methylene chloride as the solvent. Complete purification

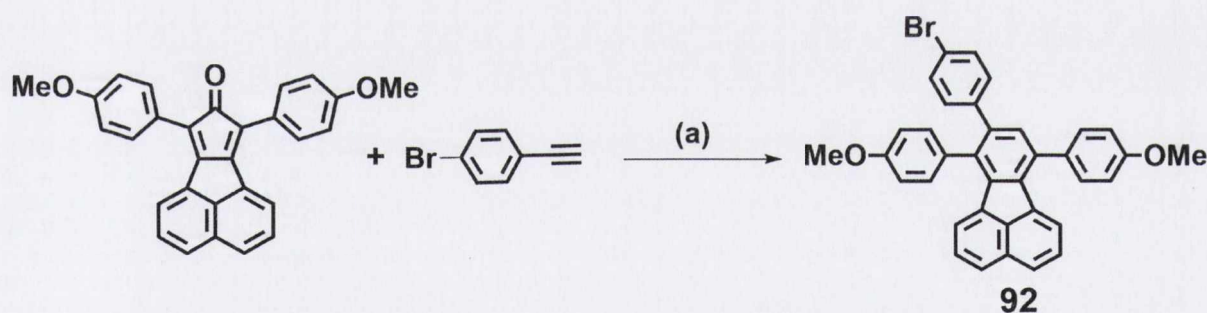
was then achieved *via* column chromatography using ethylacetate:dichloromethane (2:1) to elute the desired products.

### 5.3.2 Synthesis of 7,10-di(4-bromophenyl)-9-(2-pyridyl)-8-azafluoranthene **91**

7,10-di(4-bromophenyl)-9-(2-pyridyl)-8-azafluoranthene, **91**, was synthesised *via* a [4+2] Diels-Alder reaction with 2-pyridinecarbonitrile, and 7,9-bis-(4-bromophenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one, **64**, using the nitrile reagent as the reaction solvent at 280 °C under argon atmosphere for 12 h. This synthesis suffered the same undesired side product formation but was successfully purified following the same steps as above. However, for this compound, a reduction in yield was seen, which may be explained by the consumption of the starting materials in the generation of the side products.

### 5.3.3 Synthesis of Methoxy bromo fluoranthene **92**

Unlike the above azafluoranthenes where excess 2-pyridinecarbonitrile acts as a solvent, 8-(4-bromophenyl)-7,10-bis(4-methoxyphenyl)fluoranthene **92** was prepared *via* [2+4] Diels-Alder reaction from 1-bromo-4-ethynylbenzene and 7,9-bis-(4-dimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one **72** in benzophenone at 310 °C for 10 h.



Scheme 5.2: Synthesis of Fluoranthene **92**. (a) Benzophenone, 310 °C, 10 h, 65 %.

## 5.4 Structural Characterisation of Azafluoranthenes

The complete structural and spectral characterization of azafluoranthenes **88-91** was carried out using multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , HSQC and HMBC), ESI and MALDI high resolution mass spectrometry, elemental analysis, and infrared spectroscopy.

### 5.4.1 NMR Spectroscopic Analysis

The NMR data of the known azafluoranthenes was in good agreement with the literature. Similar to the other fluoranthenes studied in earlier chapters, the  $^1\text{H}$ -NMR spectra of **88-91** show a doublet-pseudotriplet-doublet system characteristic of the naphthyl moiety.



Due to the asymmetry of all the compounds, characterisation of these azafluoranthene proved difficult to analyse. Selective TOCSY and HMBC experiments allowed for the full assignment of the proton and carbon signals for all the compounds. The assignment of **90** is discussed in detail, and the fully assigned proton NMR of **90** is shown in Figure 5.3.

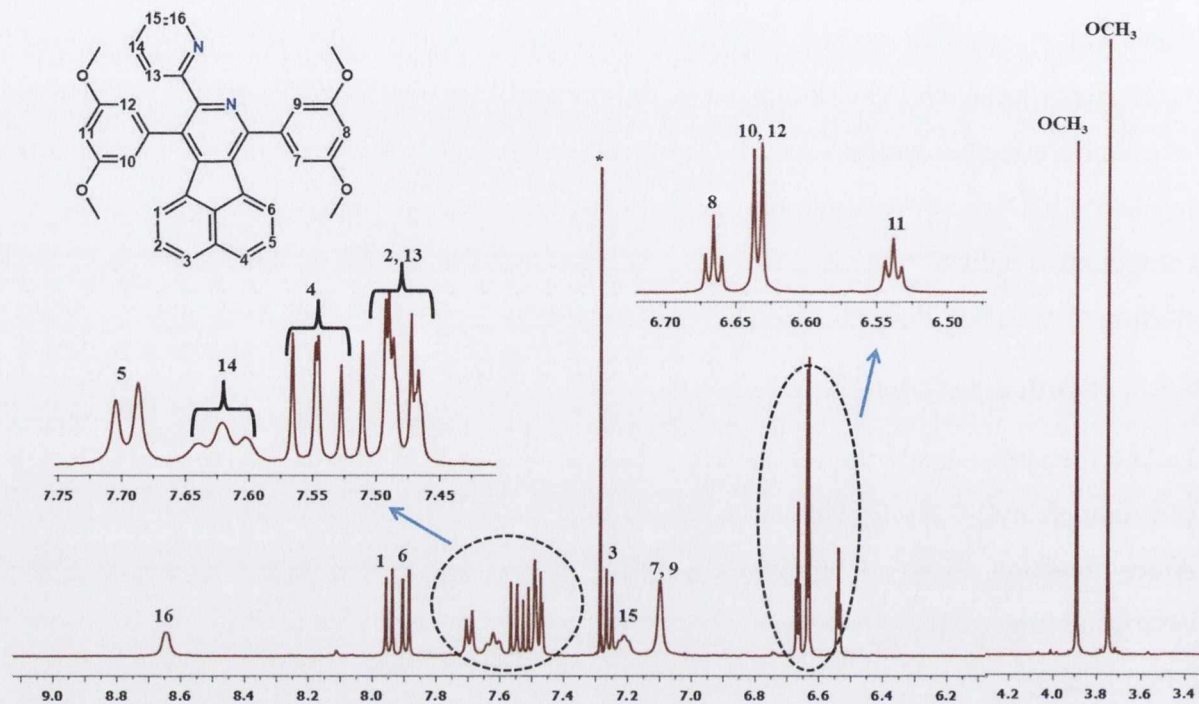


Figure 5.3:  $^1\text{H}$  NMR spectrum of **90** at RT. Asterisk denotes solvent ( $\text{CDCl}_3$ ) peak.

Identification of the proton signals belonging to the same spin system were identified by TOCSY experiments as shown in Figure 5.4. There are two distinct naphthyl 3-spin systems due to the asymmetric nature of the azafluoranthene. There are also two phenyl 3-spin systems and one 4-spin system attributed to the pyridyl ring protons, which are easily identified due to their characteristic d-t-t-d multiplicity. The most deshielded broad signal appears at  $\delta$  8.65 ppm, and belongs to  $\text{H}_{16}$ , due to its proximity to the nitrogen atom of the pyridine ring. HSQC experiments allowed for the very accurate assignment for all the carbon signals.



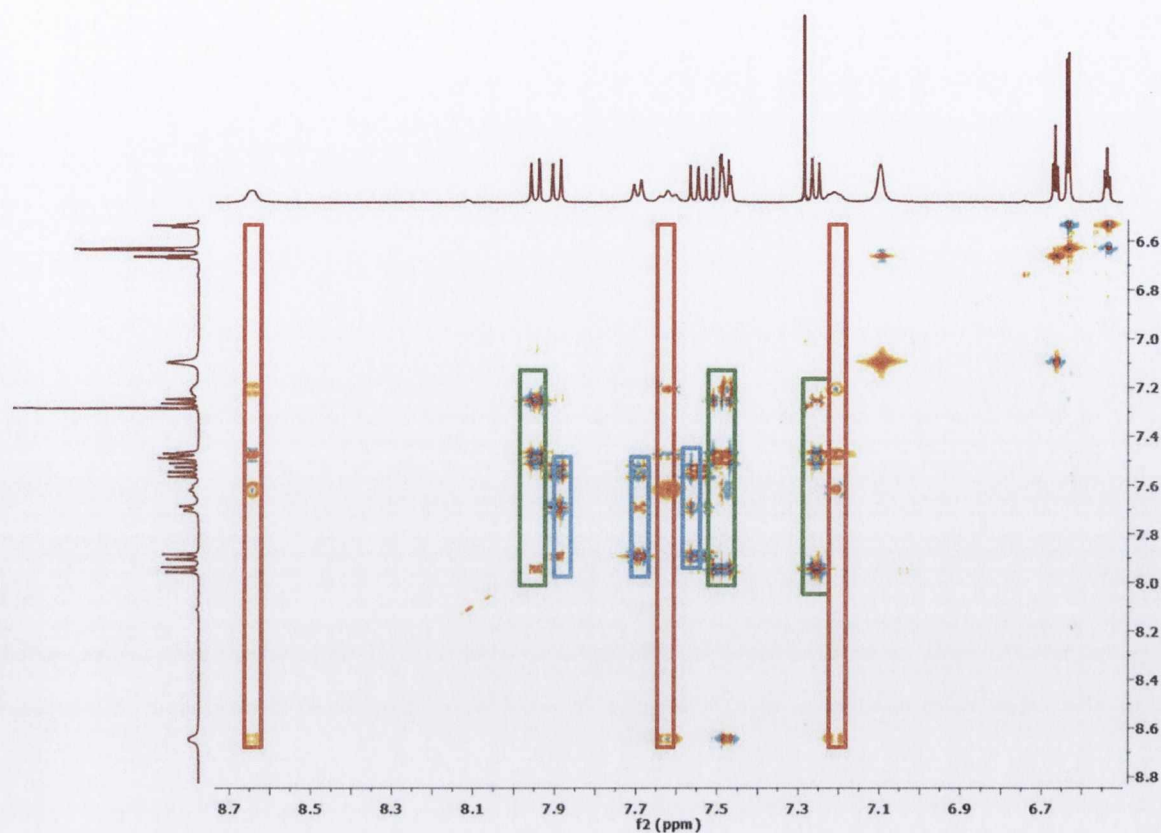


Figure 5.4: Global TOCSY analysis of **90**: colours represent three different spin systems.

#### 5.4.2 Mass Spectrometry

The high resolution mass spectra of the five fluoranthenes **88-92**, recorded in acetonitrile, reveal the major peak in each spectrum corresponds to the  $[M+H]^+$  molecular ion. These values are in good agreement with the calculated values for the molecular ion. The mass spectrum of **90** was recorded on a MALDI-TOF mass spectrometer. The summary of the mass spectral data is shown in Table 5.1

Table 5.1: Mass spectral data for novel Azafluoranthenes (recorded in  $CH_3CN$ ,  $m/z$  in *m.u.*).

| Compound  | Molecular Ion | Formula               | Calculated $m/z$ | Found $m/z$ (%) |
|-----------|---------------|-----------------------|------------------|-----------------|
| <b>88</b> | $[M+H]^+$     | $C_{32}H_{21}N_2$     | 433.1705         | 433.1706        |
| <b>89</b> | $[M+H]^+$     | $C_{40}H_{37}N_2$     | 545.2957         | 545.2966        |
| <b>90</b> | $[M+H]^+$     | $C_{36}H_{29}N_2O_4$  | 553.2127         | 553.2136        |
| <b>91</b> | $[M+H]^+$     | $C_{32}H_{19}N_2Br_2$ | 588.9915         | 588.9913        |
| <b>92</b> | $[M]^+$       | $C_{36}H_{25}O_2Br$   | 568.1038         | 568.1059        |

## 5.5 Crystallographic Study of **88** and **92**

### 5.5.1 Crystallographic Study of **88**

Colourless needle-shaped crystals, suitable for single-crystal X-ray diffraction analysis, were obtained for **88**, and grown from the slow evaporation of methylene chloride from MeOH. The molecules crystallised in the monoclinic space group  $C2/c$ , with eight molecules per unit cell. The molecular structure of **88** (asymmetric unit), and its packing nature are shown in Figure 5.5. The pyrimidyl and phenyl groups are observed to lie almost perpendicular to the fluoranthene plane. The molecules pack in a head-to-tail fashion with pyridyl rings in the same plane, and are oriented towards one another, resulting in strong hydrogen bonding interactions between the nitrogen atom of the pyridyl ring of one molecule, and the hydrogen atom of the other molecule's pyridyl ring,  $N\cdots C$  [3.619 Å]. Also  $\pi$ - $\pi$  interactions between the aromatic cores result in intermolecular distance of 3.256 Å. The diffraction data collected for **88** showed data of reasonable quality with an  $R1 = 8.43\%$ , for the observed data and  $wR2 = 25.08\%$  for all data. The goodness-of-fit was 0.989.

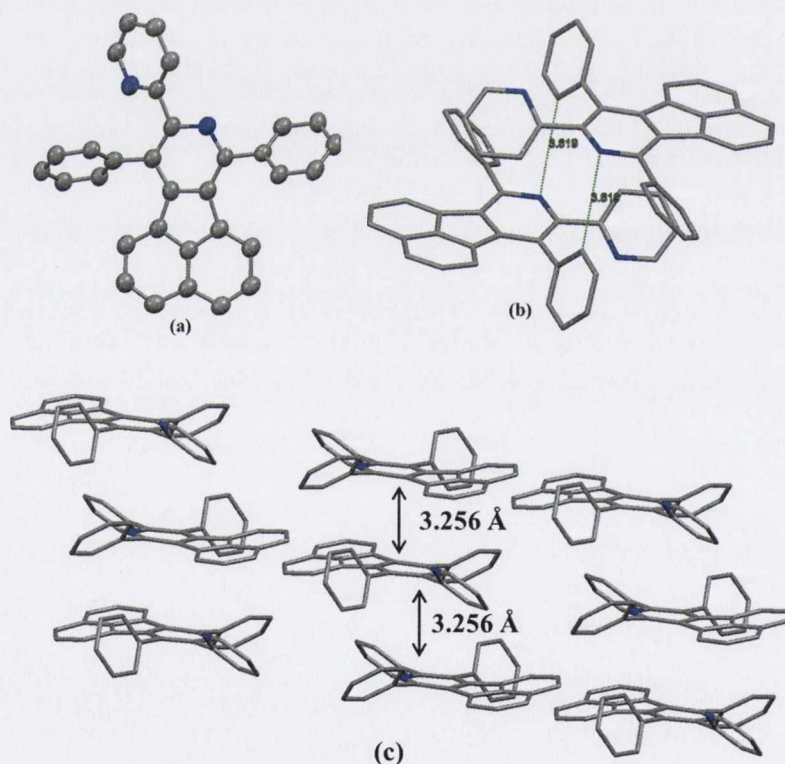


Figure 5.5: (a) Ellipsoid representation of the crystal structure of **88** (carbon atoms in grey, nitrogen atoms in blue). (b) Representation of molecular interactions within **88** (hydrogen atoms omitted for clarity). (c) Packing diagram of **88** viewed down the  $c$ -axis. Hydrogen atoms omitted for clarity.



### 5.5.2 Crystallographic Study of 92

Needle shaped crystals, suitable for single crystal X-ray diffraction analysis, were obtained from the slow concentration of **92** in evaporating methylene chloride. The molecules crystallized in the triclinic space group  $P\bar{1}$ , with two molecules per unit cell. The diffraction data collected for **92** showed data of reasonable quality at  $R1 = 3.91\%$  and  $wR2 = 9.65\%$  (all data), and the goodness-of-fit was found to be 1.011. The naphthyl moiety of the azafluoranthene is planar. The molecules arrange in a head to head fashion, with the bromo-substituted phenyl rings of both molecules in the same plane. The phenyl ring “X”, adjacent to the C-H of central core, is twisted out of the average plane of the central ring by  $57.76^\circ$ , whereas the other phenyl ring “Y”, is twisted by  $73.07^\circ$ . The phenyl ring with bromo group “Z” is twisted by  $41.01^\circ$ .

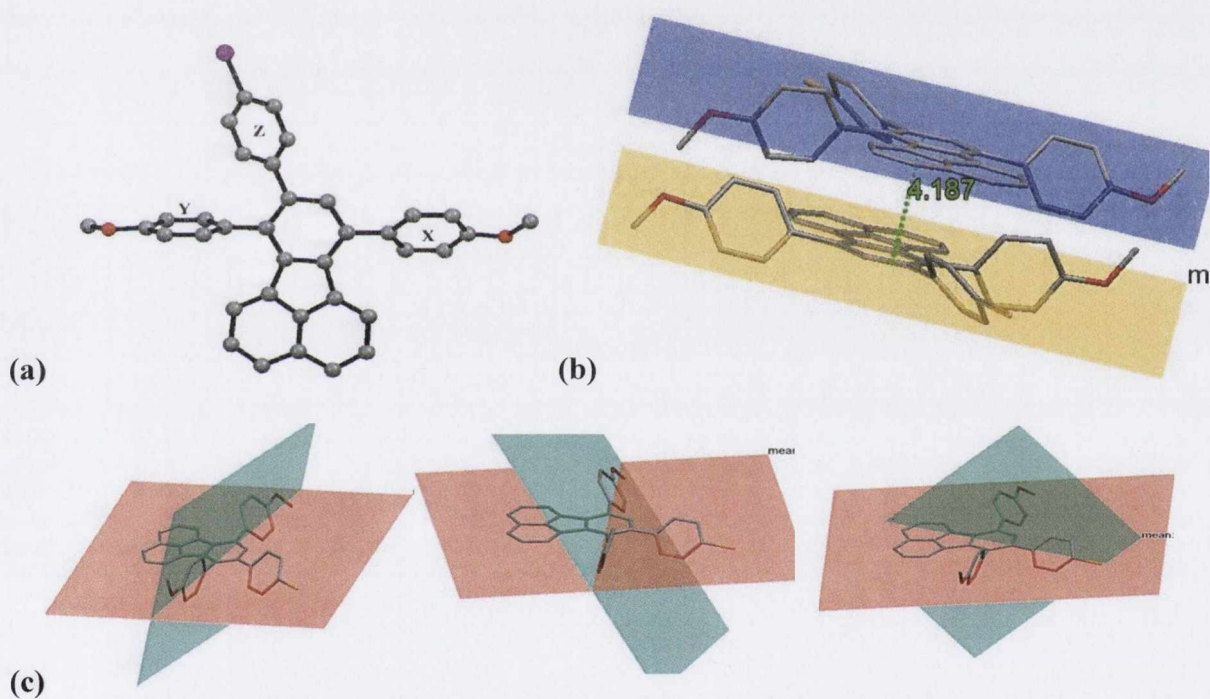


Figure 5.6: (a) Ball and stick representation of crystal structure **92** (carbon atoms in grey, oxygen atoms in red and bromine atom in pink) Thermal ellipsoids shown at 50% probability. (b) Crystal packing structure as viewed along the  $b$ -axis showing the interplanar distance of  $4.187 \text{ \AA}$  between the planar aromatic cores of the molecules. (c) Graphical representation of the central benzene ring plane and each of the X, Y and Z phenyl ring planes. Hydrogen atoms omitted for clarity



The distances between the bromo-phenyl rings of two molecules as 7.26 Å as shown in Figure 5.6. This is an important interaction as it causes the molecules to form a staggered packing arrangement.

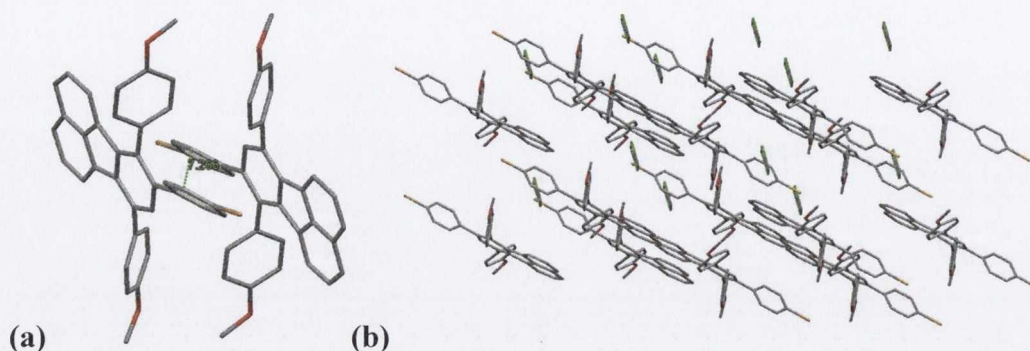


Figure 5.7: (a) Graphical representation showing the distances between the bromo-phenyl rings of two molecules (b) Packing diagram of **92** viewed down the *b*-axis. Hydrogen atoms omitted for clarity.

## 5.6 Photophysical Studies

The UV-Vis absorption spectra of the azafluoranthene systems in EtOH are shown in Figure 5.7. The absorption of **88-91** is similar to that of triphenylfluoranthene **93**, and other earlier studied systems within the Draper group, with a broad band around 350 – 400 nm, attributed to transitions within the fluoranthene ring system. Other major intense absorption bands are seen at 238, 266 and 322 nm. The intense bands at ~ 240 nm for each of the azafluoranthenes are assigned as  $\pi$ - $\pi^*$  in origin, originating from the pyridyl and phenyl rings of the compounds. The absorption coefficients are indicative of the spin allowed nature of these transitions (Table 5.2).<sup>152</sup> While, **92** shows four intense sharp bands unlike azafluoranthenes

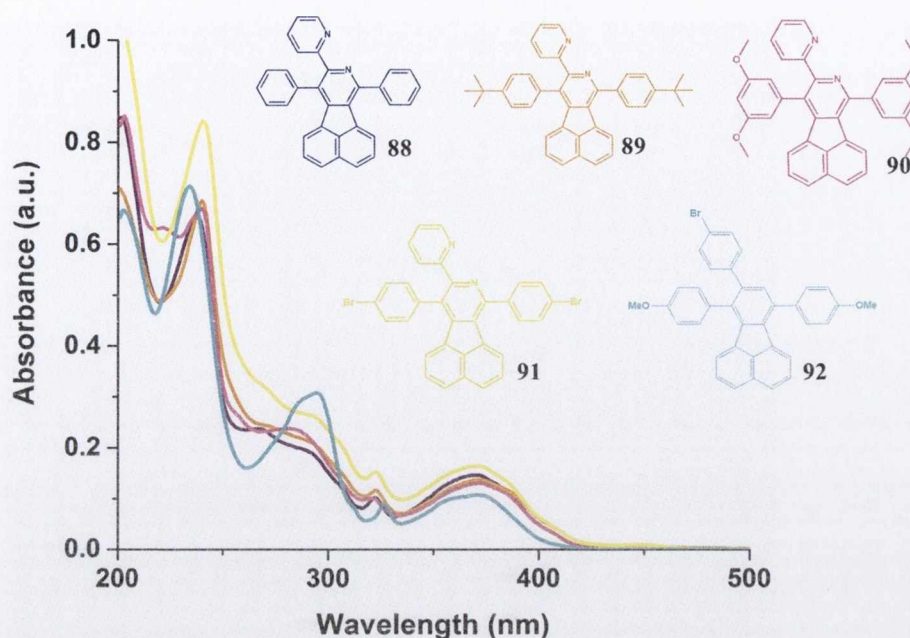


Figure 5.8: The overlaid UV-Vis absorption spectra of Azafluoranthenes **88-92** in EtOH ( $\sim 10^{-5} M$ ).

The incorporation of the nitrogen atom into the fluoranthene core structure, coupled with the replacement of a phenyl ring with a pyridine ring, appears to have an effect vs. that of the absorption spectra of **92**. The incorporation of electron donating groups to **89** and **90**, and electron withdrawing groups to **91**, appear to have little effect on the absorption spectra vs. that of **88**. Only a small difference is seen in the 270 – 295 nm regions. The addition of electron withdrawing bromo groups in the pendant phenyl rings have a significant effect of the absorption spectrum which becomes less structured with only three distinct bands.

Table 5.2: The absorption maxima observed in the UV-Vis absorption spectra of Azafluoranthenes and **92** in ethanol ( $\sim 10^{-5} M$ )

| Compound  | $\lambda_{\text{abs}}$ [nm] | $\epsilon \times 10^4 / M^{-1} \text{ cm}^{-1}$ |
|-----------|-----------------------------|-------------------------------------------------|
| <b>88</b> | 238, 266, 322, 371          | 6.40, 2.32, 1.09, 1.43                          |
| <b>89</b> | 240, 323, 372               | 6.74, 1.13, 1.35                                |
| <b>90</b> | 240, 282, 321, 372          | 6.36, 2.26, 0.96, 1.24                          |
| <b>91</b> | 240, 322, 370               | 8.24, 1.55, 1.60                                |
| <b>92</b> | 242, 292, 328, 372          | 7.10, 2.82, 0.85, 1.01                          |



The photoluminescence properties of the azafluoranthenes were studied and tabulated in Table 5.2. The emission spectra are shown in Figure 5.8. Azafluoranthene, **88**, exhibits an emission at 448 nm, with a slight shoulder at 485 nm. The emission profile of **89-91** is slightly red shifted due to the presence of EDGs in comparison to **88**, with a  $\lambda_{\text{max}}$  in the range of 451- 455 nm. Trends in the emission measurements are more predictable than that of the absorbance spectra, *i.e.* the compounds bearing electron donating groups have the highest energy emission as seen in **90**. Armaroli *et al.* have previously shown that electron-donating substituents affect the absorbance and emission spectra, and that the extent of the red-shift increases with the electron-donating properties of the substituents.<sup>153</sup>

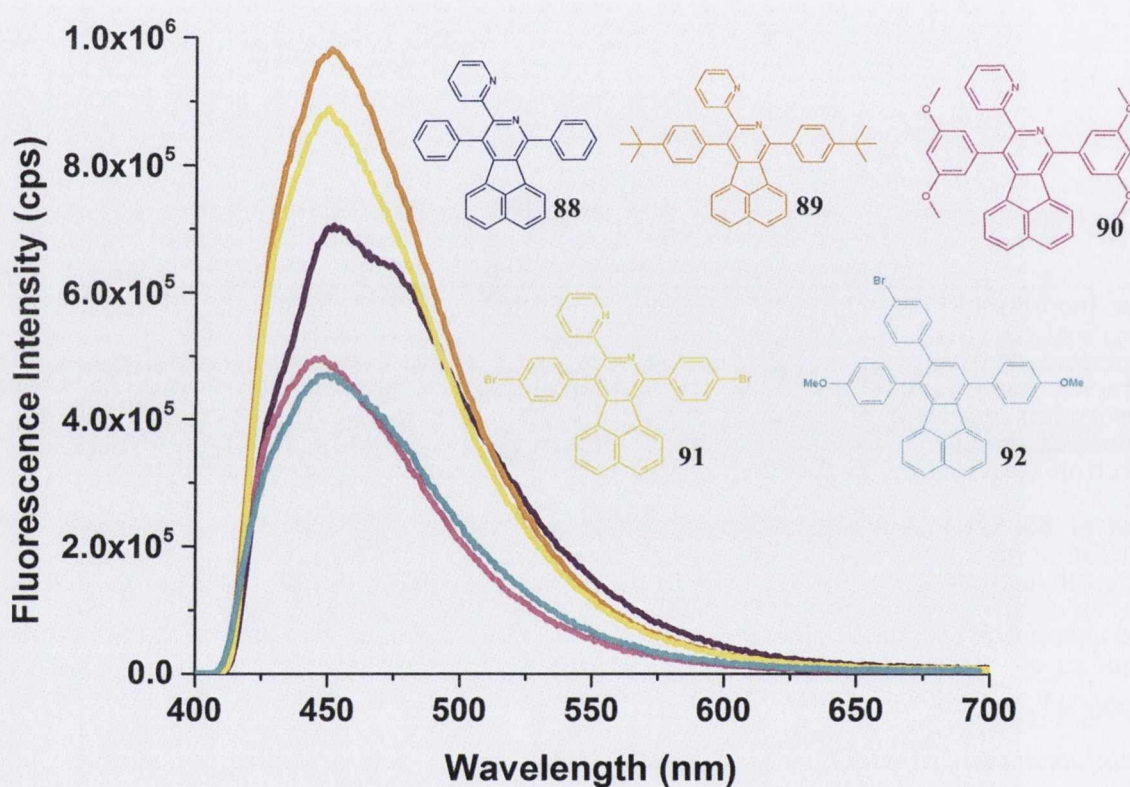


Figure 5.9: The normalised emission spectra of azafluoranthenes **86-90** in ethanol ( $\sim 10^{-5}M$ ) at  $\lambda_{\text{ex}} = 373 \text{ nm}$  at R.T.

The observed Stokes shifts between the lowest energy band of the excitation spectrum, and the onset of fluorescence are quite large, (shown in Table 5.3) suggesting a significant change in the geometry of the excited state ( $S_1$ ) and the ground state ( $S_0$ ). This large Stokes shift could also be attributed to charge transfer in the excited state.



Table 5.3: Photophysical data of **88-92** compounds.

| Compound  | $\lambda_{\text{abs}}$ [nm] | $\lambda_{\text{em}}$ [nm] | Stoke's shift ( $\text{cm}^{-1}$ ) | $\Phi_{\text{f}}$ | $\tau$ /ns |
|-----------|-----------------------------|----------------------------|------------------------------------|-------------------|------------|
| <b>88</b> | 371                         | 448                        | 4632                               | 11%               | 3          |
| <b>89</b> | 372                         | 452                        | 4757                               | 15%               | 4          |
| <b>90</b> | 372                         | 451                        | 4708                               | 4%                | 7          |
| <b>91</b> | 370                         | 452                        | 4903                               | 6%                | 6          |
| <b>92</b> | 374                         | 455                        | 4759                               | 34%               | 7          |

### 5.7 Theoretical Studies

In order to understand the absorption characteristics of the azafluoranthenes, theoretical calculations were performed for the molecules **88-91** using density functional theory. Figure 5.12 displays the optimised geometries with superimposed electron density obtained by using the B3LYP functional and the 6-31g\* basis set. The phenyl groups are significantly twisted from the fluoranthene core, and are less involved in  $\pi$ -interactions. The distribution of the HOMO and LUMO orbitals mostly located over the fluoranthene core, suggesting that the energy transitions are mainly  $\pi \rightarrow \pi^*$  in nature. From the above optimized geometries, the optical band gaps were calculated in the range 3.80–3.21 eV, and show slight variation depending upon the type of substituents present on the fluoranthene unit.

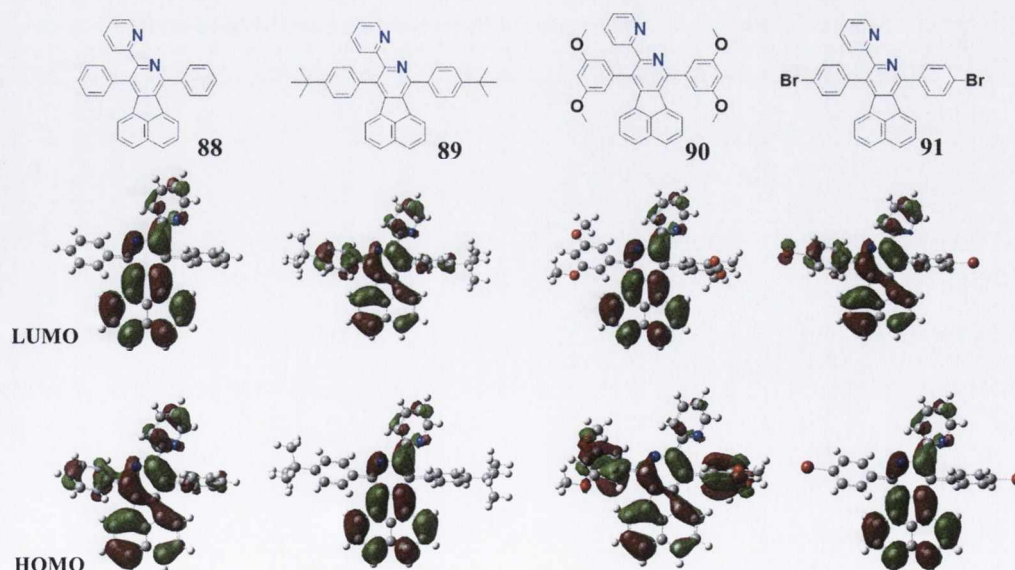


Figure 5.10: Electron density superimposed on the optimised geometry of **88-91** with B3LYP/6-31g\* basis set.

### 5.8 Nitroaromatic Sensing Studies

As mentioned in the earlier chapters, one of the most promising approaches for the sensing of nitroaromatic compounds is *via* fluorescence quenching-based detection. Once again, the mechanism of fluorescence quenching involves the formation of charge-transfer (CT) complexes between the electron rich fluorophore, and the electron deficient quencher. In this chapter, several substituted azafluoranthenes, **88-92**, have been designed to sense nitroaromatic explosives based on this proposed quenching mechanism.

To demonstrate the ability of the generated azafluoranthene compounds for the detection of nitroaromatic explosives, fluorescence quenching titration experiments were performed using the azafluoranthenes **88-92**, with NACs such as PA, TNT, and DNT. All measurements were carried out in solution. Upon gradual addition of PA to an EtOH solution of the azafluoranthene **90**, the initial fluorescence intensity was quenched efficiently as shown in Figure 5.10. A similar behaviour was observed with **91**.

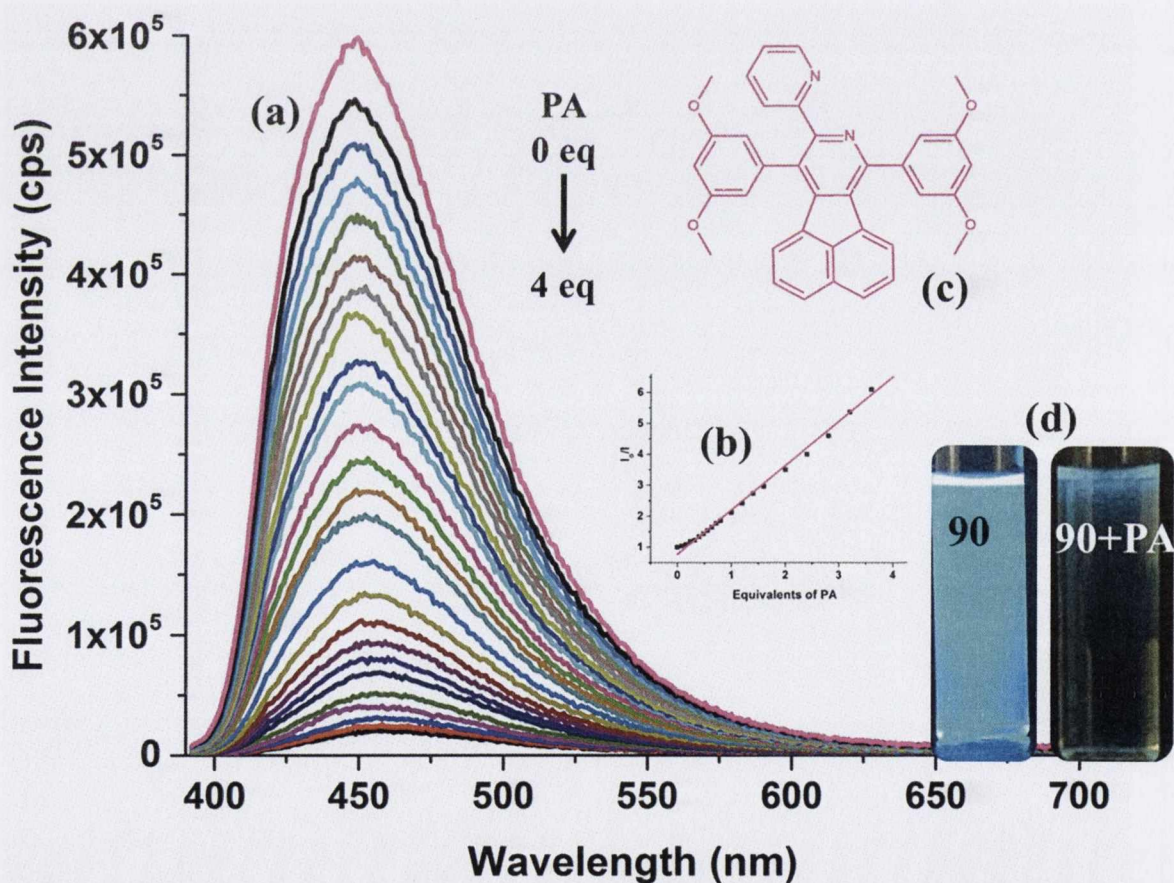


Figure 5.11: (a) Fluorescence quenching behavior of **90** ( $\sim 10^{-5}$  M) with gradual addition of PA ( $\sim 10^{-4}$  M) in ethanol. (b) The Stern-Volmer plot of **90** with different concentrations of PA.



(c) The photograph is the structure of **90** and (d) its fluorescence under UV lamp before and after addition of PA.

A linear Stern–Volmer plot was generated from the fluorescence quenching titration and the calculated Stern–Volmer binding constant,  $K_{sv}$  was  $8.35 \times 10^5 \text{ M}^{-1}$  for PA with **90**.

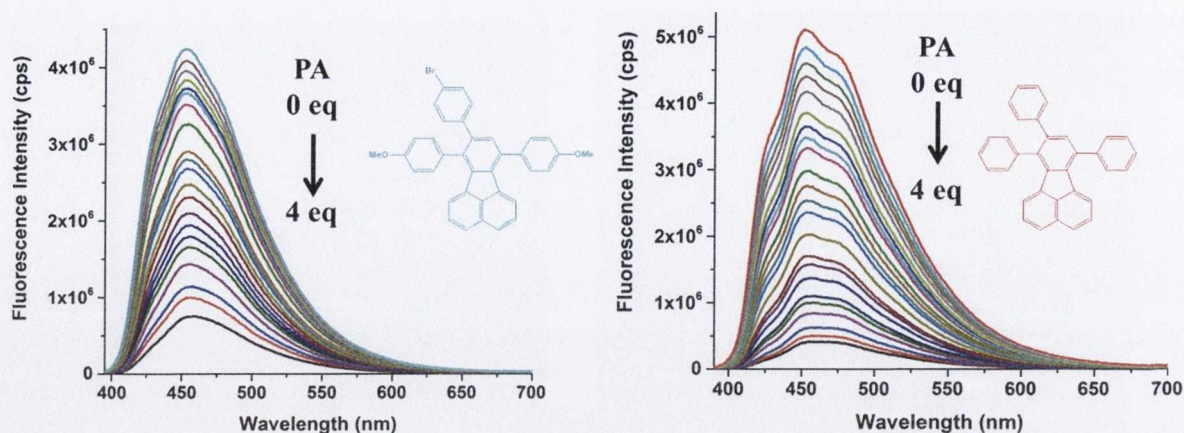
The obtained quenching constants for PA are comparable with previously reported values for other small molecules like fluorescein, and malachite green. The linear Stern–Volmer plots, coupled with the invariant lifetimes (Table 5.4), suggest that the fluorescence quenching involves a static quenching-type mechanism at lower concentration of PA addition.

Table 5.4: Excited state lifetime measurements of **88–92**, with and without the addition of PA ( $\sim 10^{-5} \text{ M}$ ). Measurements carried out in EtOH at  $25^\circ\text{C}$ .

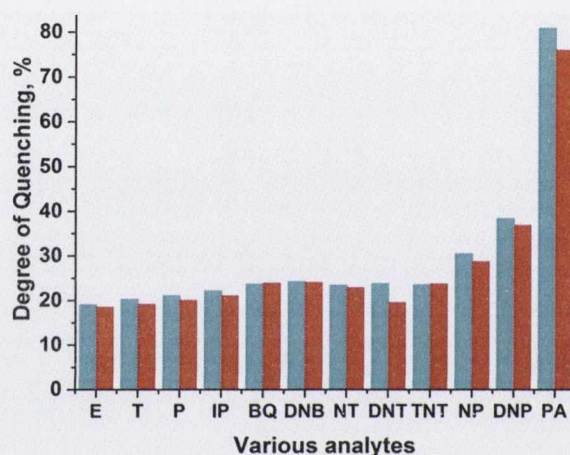
| Compound                | Life time ( $\tau$ ) (ns) |           |           |           |           |
|-------------------------|---------------------------|-----------|-----------|-----------|-----------|
| Fluoranthene (F)        | <b>88</b>                 | <b>89</b> | <b>90</b> | <b>91</b> | <b>92</b> |
| <b>F</b>                | 3 ns                      | 4 ns      | 7 ns      | 6 ns      | 7 ns      |
| <b>F + 0.2 eq of PA</b> | 3.02                      | 4.04      | 7.03      | 6.03      | 7.01      |
| <b>F + 0.5 eq of PA</b> | 3.07                      | 4.08      | 7.05      | 6.04      | 7.05      |
| <b>F + 1 eq of PA</b>   | 3.04                      | 4.05      | 7.04      | 6.04      | 7.02      |
| <b>F + 2 eq of PA</b>   | 3.02                      | 4.01      | 7.06      | 6.01      | 7.07      |

Furthermore, the sensitivity of fluoranthene **92** was explored, and compared with its counterpart, triphenylfluoranthene **93**.<sup>154</sup> The sensitivity of **92** was found to be greater than that of **93**. The presence of the electron donating groups on **92** appears to enhance the degree of fluorescence quenching, and the  $K_{sv}$  follow the trend of **92** > **93**. To explore the selectivity, we have also investigated the effect of other electron deficient aromatic compounds on the initial fluorescence intensity of the fluorophores **92** and **93** (Figure 5.11). The selected azafluoranthenes showed differential fluorescence quenching responses among the various nitroaromatic compounds, which allowed the discrimination of closely related nitroaromatic explosive compounds.





(a)



(b)

Figure 5.12: (a) Fluorescence quenching behavior of **92** and **93** ( $\sim 10^{-5}$  M) with gradual addition of PA ( $\sim 10^{-4}$  M) in ethanol. The inset photograph is the structure of **92** and **93** (b) Degree of fluorescence quenching of azafluoranthenes **92** and **93** with different analytes.

It is observed that the azafluoranthene compounds show a slightly higher degree of quenching when compared to all carbon series *i.e.*, **92** vs. **93**. The degree of quenching is demonstrated in Figure 5.12. The electron donating groups appear to have a further impact on the fluorescence quenching, suggesting that **90** is the most desirable chemosensor (Figure 5.13).

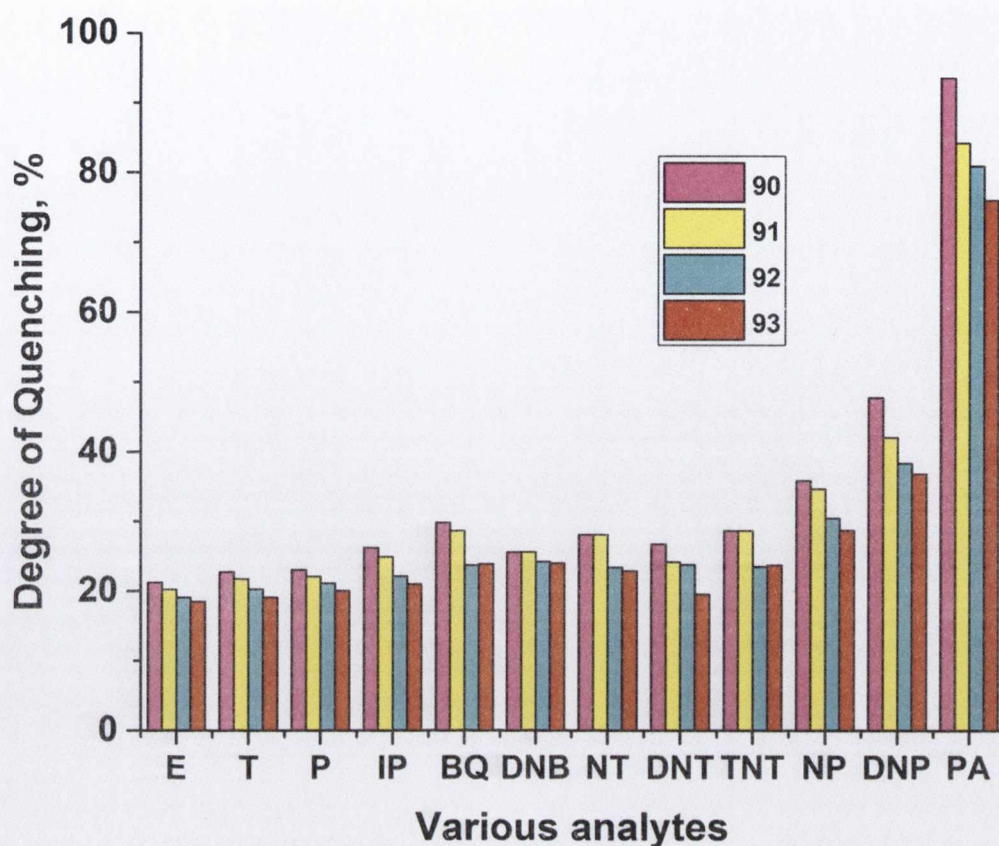


Figure 5.13: Degree of fluorescence quenching of azafluoranthenes **90-93** ( $\sim 10^{-5}$  M) with different analytes.

The obtained results are shown in Figure 5.13, which indicates that the azafluoranthene compounds show a greater quenching response for electron deficient nitroaromatic compounds, vs. that of other electron deficient non-nitroaromatics such as benzoquinone, and iodophenol. The tested non-nitroaromatic quenchers are almost non-polar in nature compared to the nitro-substituted aromatic quenchers. Since the reduction potentials of non-nitroaromatic quenchers are not significantly different from that of nitro-substituted aromatic quenchers,<sup>155</sup> it was believed that the observed higher fluorescence quenching responses of nitro-compounds are probably due to the strong dipolar or electrostatic interactions between the electron-deficient analytes with the  $\pi$ -electron rich aromatic azafluoranthenes, resulting in the formation of charge-transfer complexes between them.<sup>156</sup>

The mode of interaction and increased sensitivity of PA with **90** was further explored using density functional calculations. DFT was carried out at the B3LYP/6-31g\* level using the Gaussian 03 package. From the optimized geometry of **90**, it was observed that the HOMO orbital has a large overlap of electron density localised over the methoxy groups of the phenyl rings and the fluoranthene core, whereas the LUMO is largely localised over the



fluoranthene unit (Figure 5.13). In order to confirm that the fluorescence-quenching response and that the type of interaction is as expected, the geometries of the **90**-PA complex were optimized, and two types of orientation are presented in Figure 5.14. The complex shows a stacked geometry and  $\pi$ - $\pi$  interactions between the analyte, PA, and the fluoranthene. The fluorescence quenching involves an electron transfer process from the LUMO of the excited state fluorophore, to the LUMO of the NAC compound.

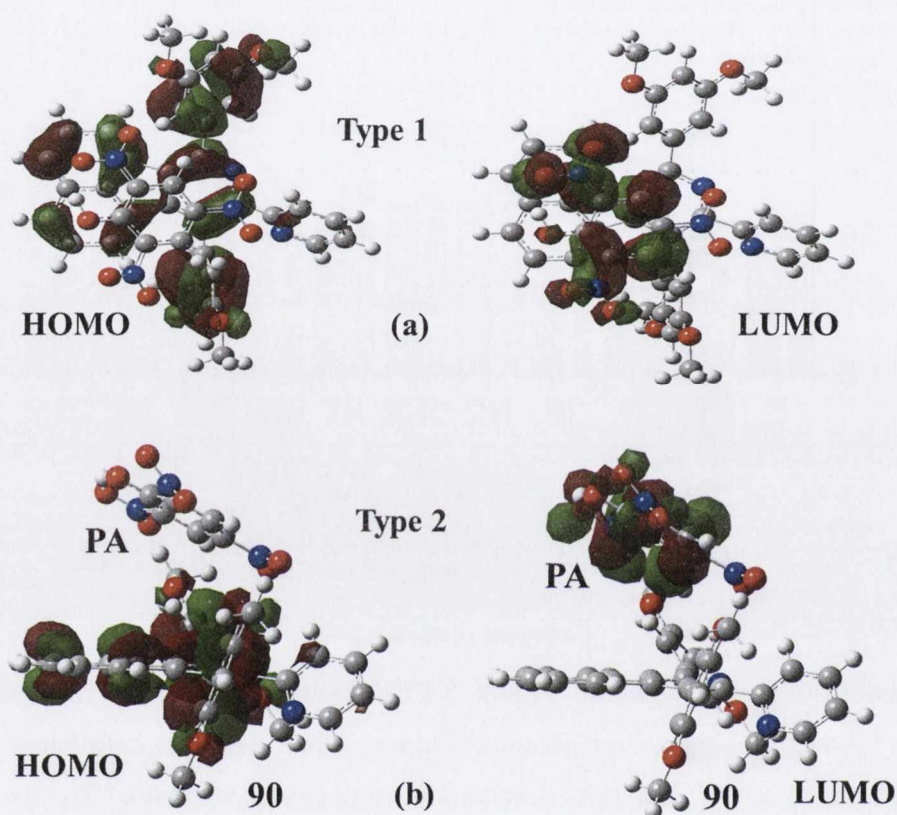


Figure 5.14: The electron density superimposed on the optimised with B3LYP/6-31g\* basis set for system **90** in presence of PA in two orientations.

It was observed that **88** and **89** show the unusual behaviour of a slight decrease in the fluorescence emission upon addition of 0.5 eq of PA, followed then by a shift in the emission wavelength. This was followed by a slight increase in intensity, with the final expected fluorescence quenching then being observed. These compounds initially undergo protonation, resulting in a shift in the emission wavelength, followed by the quenching of the protonated species. To explore the effect of acid on **88** and **89**, titrations with the strong organic acid, TFA, were carried out.



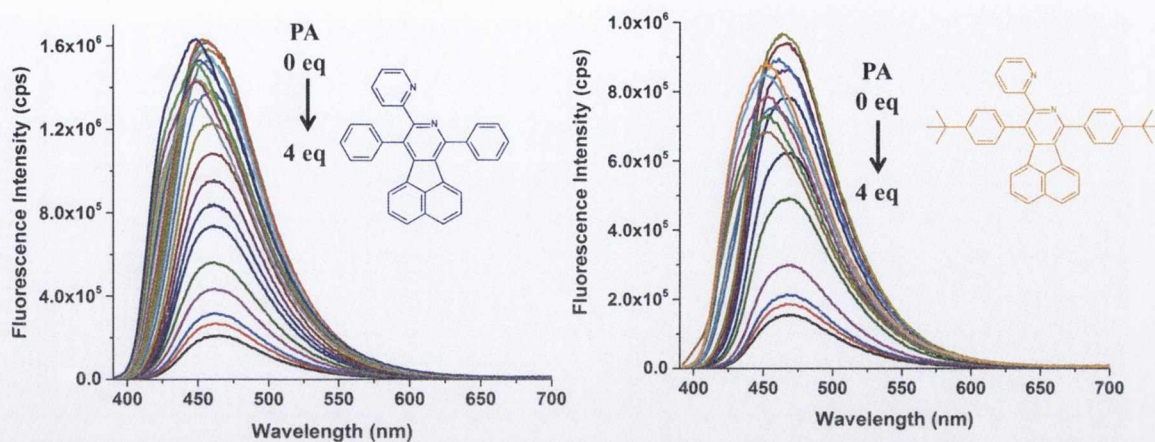


Figure 5.15: Fluorescence quenching behavior of **88** and **89** ( $\sim 10^{-5}$  M) with gradual addition of PA ( $\sim 10^{-4}$  M) in ethanol. The inset photograph is the structure of **88** and **89**.

The highest degree of quenching appears to occur with the nitroaromatic possessing the lowest pKa value, with the degree of fluorescence quenching arising purely from the protonation of the azafluoranthenes. This observation was further assessed. Titrations were carried out with TFA and it was found that the effect of TFA ( $\sim 10^{-3}$  M) on **88** is similar to that of PA ( $\sim 10^{-4}$  M). Also, the effect of TFA on **91** is also similar to that of picric acid (Figure 5.16) *i.e.*, the degree of quenching observed upon incremental addition of TFA to the azafluoranthenes was similar. Though the pKa value of TFA is greater than that of PA, the degree of emission reduction was far more dramatic when PA or other nitroaromatics were employed. Close similarities are observed in the all-carbon fluoranthenes, **92** and **93** implies that the formation of charge transfer complex is the dominant fluorescence quenching mechanism in these systems (Figure 5.12).

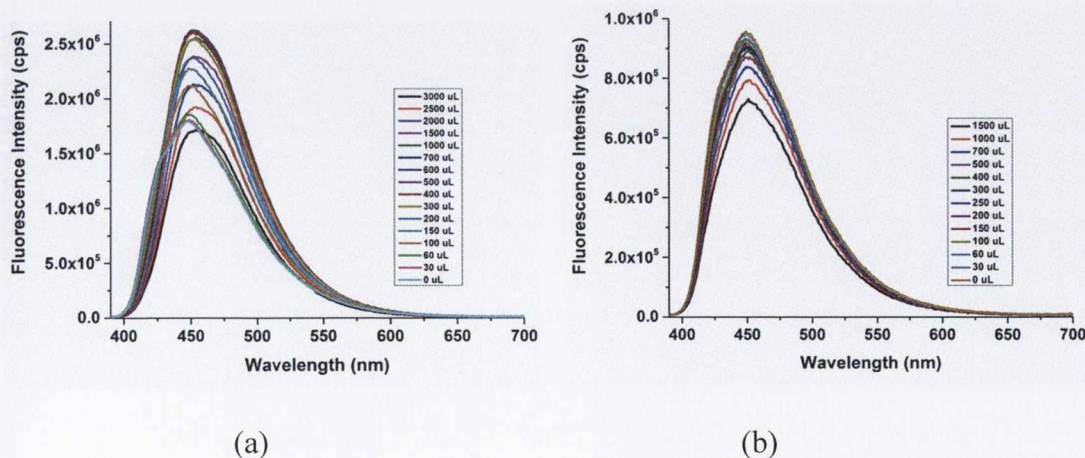


Figure 5.16: Fluorescence quenching behavior of (a) **88** and (b) **91** ( $\sim 10^{-5}$  M) with gradual addition of TFA ( $\sim 10^{-3}$  M) in ethanol.

Figure 5.17 shows some UV-Vis absorption titrations, carried out with both PA and TFA with azafluoranthene **90**, and there is a noticeable increase in the absorption intensity around  $\lambda \sim 240\text{nm}$ . The observed broad peak at  $> \lambda \sim 400\text{ nm}$ , suggests the formation of coloured CT complex.

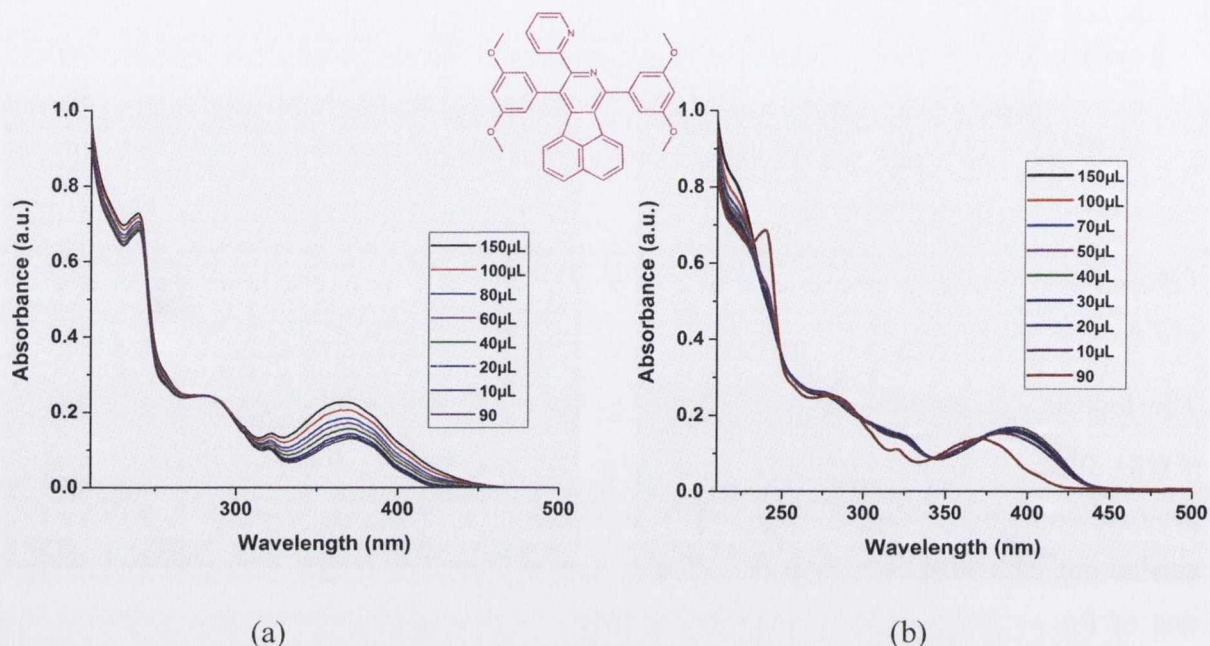


Figure 5.17: The spectrophotometric titration of **90** ( $1 \times 10^{-5}\text{ M}$ ) upon gradual addition of (a) PA and (b) TFA ( $1 \times 10^{-4}\text{ M}$ ) in ethanol

### 5.9 Visual Detection of Nitroaromatics by Azafluoranthenes

Design and development of visual sensors for the detection of nitroaromatics has been a popular field of research in the last few years owing to their ease of interpretation, simple material handling, rapid detection and suitable method to practice in the field. The formation of complex creates a new chromophore which shows totally different photo-physical characteristics from the starting explosive residue and sensor molecules including color changes.<sup>131, 157, 158</sup> Figure 5.18 shows the change in the fluorescence intensity of the best sensor, **90** upon addition of 10 μL of various analytes to it. The sharp color change is the clear identification for the presence of particular chemical explosives. In this study, we have observed a marked quenching upon subjecting **92** with PA in different concentration in ethanol solution (Figure. 5.19).



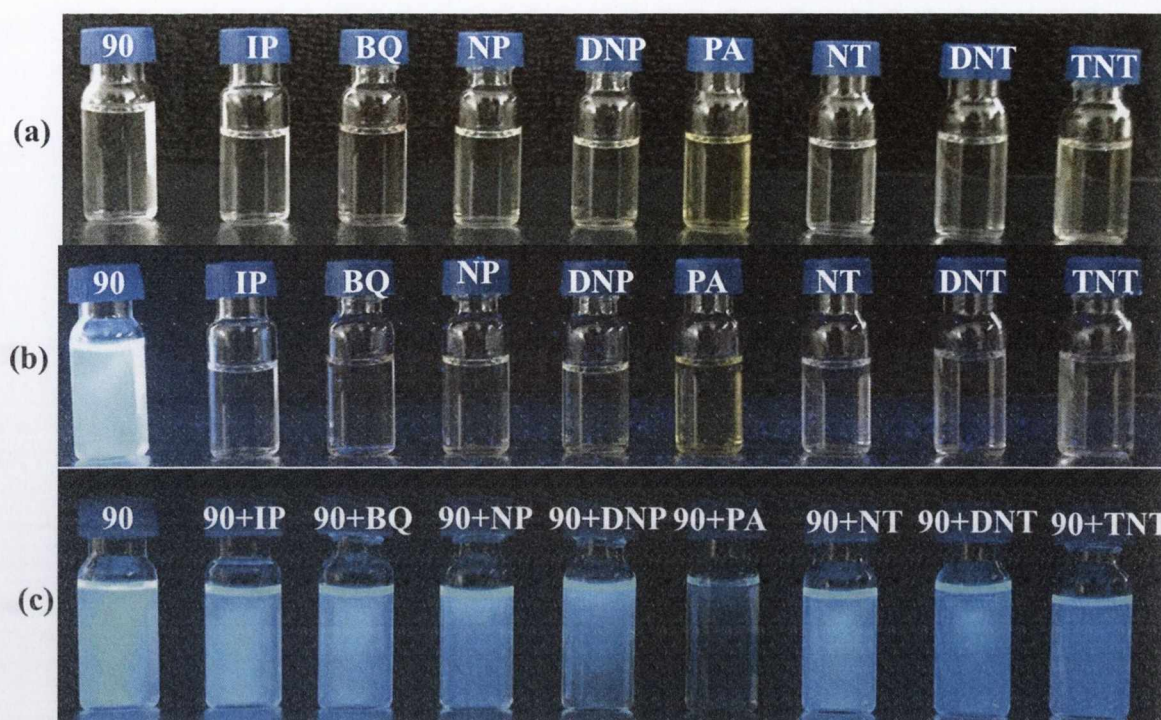


Figure 5.18: (a) Azafluoranthene **90** and various analyte solutions observed at normal light. (b) The change in the fluorescence intensity of **90** upon addition of 10  $\mu\text{L}$  of various analytes before and (c) after exposure to the UV light at 365 nm. IP (Iodophenol), BQ(benzoquinone), PA(picric acid), TNT(2,4,6-trinitrotoulene), DNP(2,4,6-trinitro phenol), DNT (2,4,-dinitrotoulene), NT (4-nitro toluene), NP(4-nitro phenol)



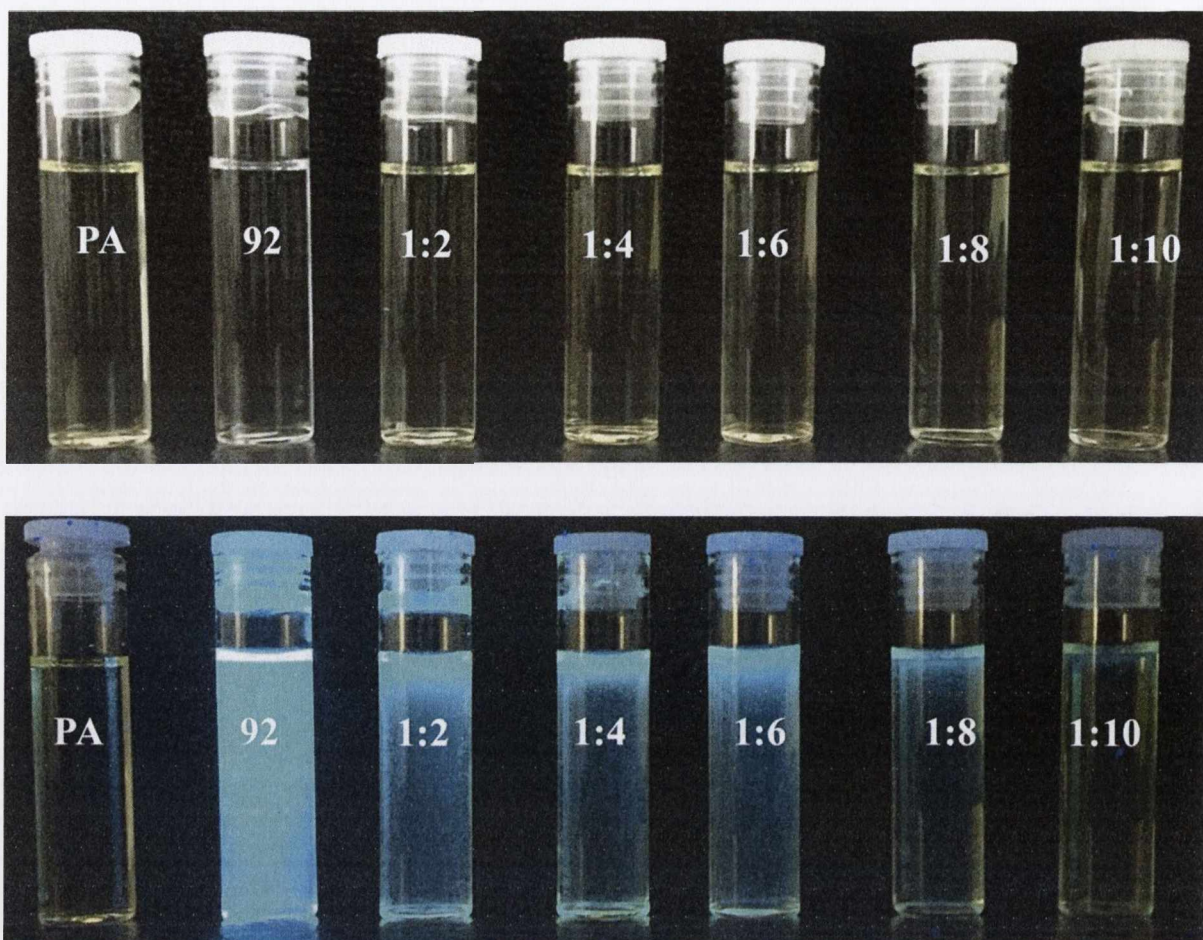


Figure 5.19: Visual colour changes observed upon subjecting 1mM solution of **92** with increasing quantity of PA in ethanol (from left to right PA, **92**, **92** with 2, 4, 6, 8 and 10 equivalents of PA) in room light (top) and under hand hold UV light (below).

### 5.10 Conclusion

In conclusion, the novel functionalised azafluoranthenes **88-92** were synthesised *via* the Diels-Alder [4+2] cycloaddition of 2-pyridinecarbonitrile, and the appropriate cyclopentadienones. These azafluoranthenes have been demonstrated as effective chemosensors for the detection of nitroaromatic explosives, in particular PA. The nitroaromatic sensing studies followed the trend, **90**>**91**>**92**>**88**, **89**, indicating that with increasing electron rich methoxy groups, the fluorescence quenching efficiency was increased. The quenching ability of these novel azafluoranthenes as highly selective chemosensors for the detection of PA is proposed as through a static fluorescence quenching mechanism. Experimental and theoretical studies are used to confirm this assignment.

**6. Future Work: Bromo-Functionalised Fluoranthenes**





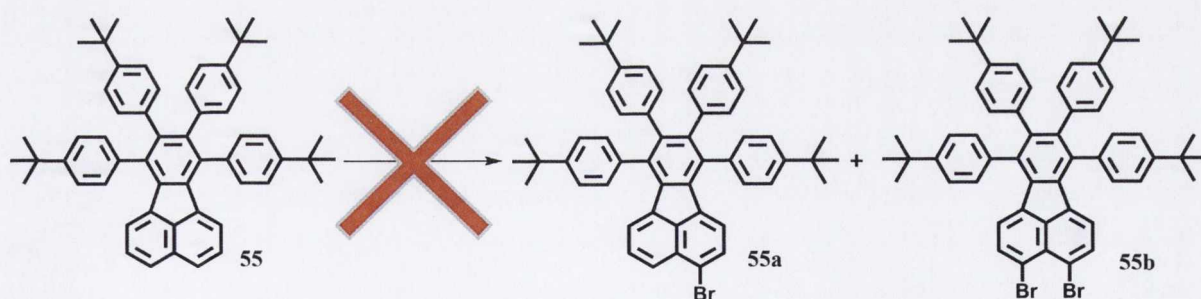
## 6.1 Introduction

This chapter discusses the scope and future prospects of expanding the family of substituted fluoranthenes. Herein, the work will show how these substituted fluoranthenes may find diverse potential in a variety of industrial applications. In addition to the NAC sensing studies, the principle focus of this thesis, fluoranthene derivatives find use as the emissive layer of OLED devices, as organic dyes in DSSC-type photoanodes, and in commercially valuable organic electronics. This is due to their high stability, and efficient fluorescence quantum yields.<sup>124, 159</sup> Therefore, it is apparent that fluoranthene derivatives with improved quantum yields are in constant demand in those industries above. As mentioned in previous chapters, bromine-substitution offers the most versatile potential for the rapid diversification of novel fluoranthene-derived compounds.

This chapter consists of following sections; (i) Synthesis of novel bromo-fluoranthenes, (ii) Future work detailing future possibilities of functionalisation of the bromo-fluoranthene systems, (iii) Commercialisation aspects of fluoranthene systems.

## 6.2 Synthesis of Bromo-Substituted Fluoranthenes

After the synthesis of a wide variety of hetero-substituted fluoranthene compounds discussed in earlier chapters, this work will be concentrated on bromo-derived fluoranthene systems. Attempts to generate the desired bromo-substituted fluoranthenes in single step were unsuccessful due to an inability to separate the mono- and di-substituted products *via* column chromatography.

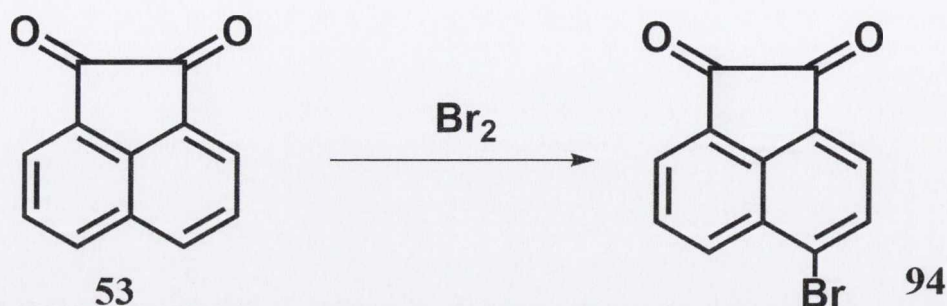


*Scheme 6.1: Bromination reaction of 55 with NBS.*

Following this failed attempt to synthesise the bromo-fluoranthene derivatives, an alternative approach was devised. In this approach, the initial precursor, acenaphthenequinone, was brominated using molecular bromine at 80 °C for 3 hours, generating the desired bromo-acenaphthenequinone, **94** (Scheme 6.2). The secondary precursor, the cyclopentadienone, was then synthesised *via* a two-fold Knoevenagel condensation, introducing two varying



types of substitution in a symmetric manner. A final [4+2] Diels-Alder cycloaddition with the desired arylacetylene was then carried out to generate the final bromo-fluoranthene compounds.



Scheme 6.2: Bromination of acenaphthenequinone via  $\text{Br}_2$ .

Besides structural characterisation with comprehensive NMR studies and high resolution mass spectrometry (Experimental; Chapter 7), high quality crystals were grown *via* the slow concentration of **94** in evaporating methylene chloride. The molecules crystallized in the monoclinic with  $\text{P2}_1/\text{n}$  space group. The unit cell consists of four molecules of **94**. Figure 6.1 shows the ellipsoid structure of **94**, and the packing arrangement. The interplanar distance is shown as 3.461 Å. The crystallographic data collected for **94** was of good quality with an  $R1 = 2.78\%$  (observed data), and  $wR2 = 7.53\%$  (all data). The goodness-of-fit was 1.069. The molecules pack in a head-to-head fashion, with close intermolecular interactions between Br and O atoms at a distance of 2.945 Å.

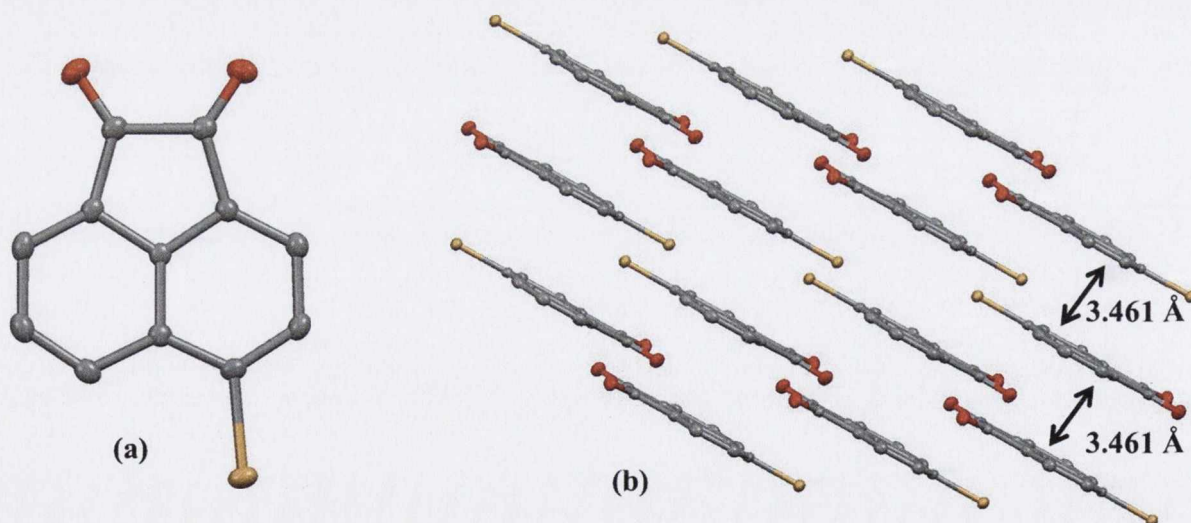


Figure 6.1: (a) Asymmetric unit of **94**. Thermal ellipsoids shown at 50% probability. (Oxygen shown in red; bromine shown in brown) (b) Crystal packing structure of **94** observed along the *b*-axis, showing an interplanar distance of 3.461 Å.

Following the successful final Diels-Alder step, a series of novel bromo-fluoranthenes were synthesized. *Tert*-butyl substitution of the polyphenylene structure was introduced to increase the solubility of each compound. As such, bromo-fluoranthenes **95-96** were each synthesised in good yield, and purified *via* column chromatography using diethyl ether as the eluent (Figure 6.2).

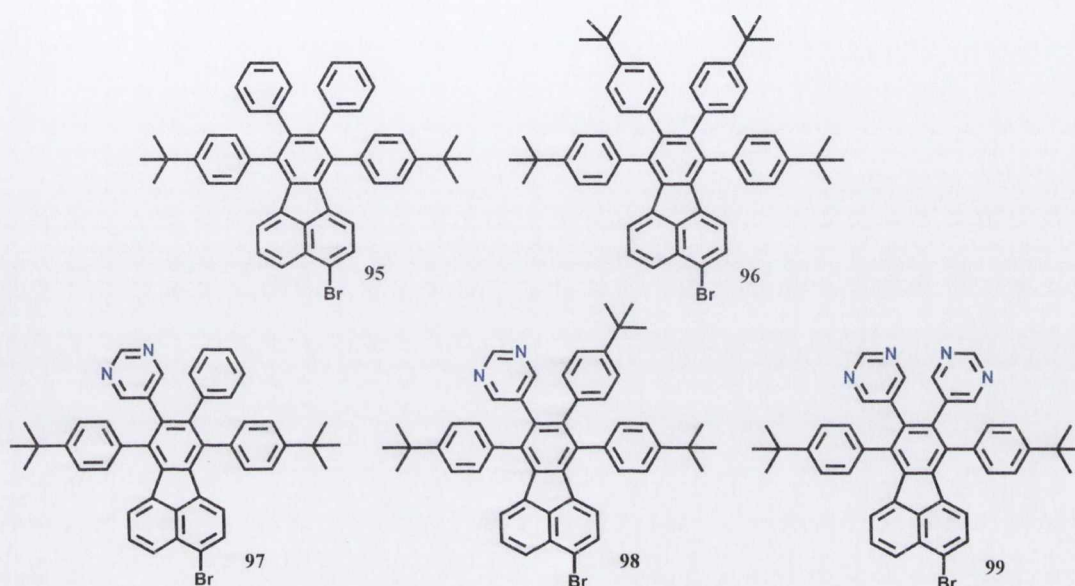


Figure 6.2: Bromo-substituted *tert*-butyl containing fluoranthenes.

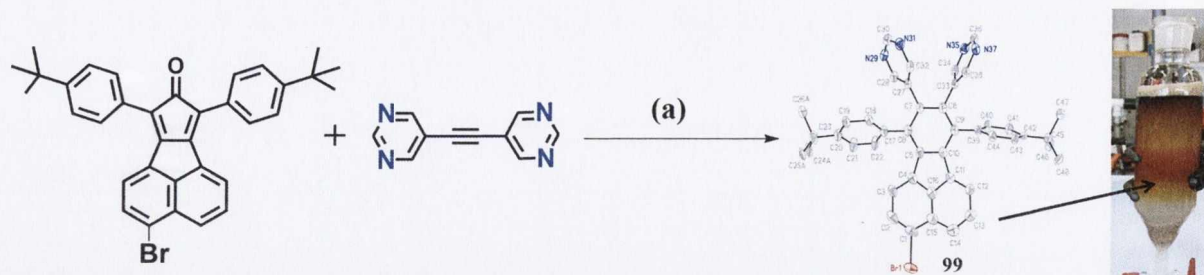
The mass spectra of **95-97** were recorded on a MALDI-TOF mass spectrometer, while **98** and **99** were recorded using the ESI method, confirming the major peak in each spectrum to be the  $[M+H]^+$  molecular ion. These values are in good agreement with the calculated values for the molecular ion. The summary of spectral data is shown in Table 6.1

Table 6-1: Mass spectral data of **95-99** (recorded in  $CH_2Cl_2$ ,  $m/z$  in *m.u.*).

| Compound  | Molecular Ion | Formula             | Calculated $m/z$ | Found $m/z$ (%) |
|-----------|---------------|---------------------|------------------|-----------------|
| <b>95</b> | $[M]^+$       | $C_{48}H_{41}Br$    | 696.2392         | 696.2426        |
| <b>96</b> | $[M]^+$       | $C_{56}H_{57}Br$    | 808.3644         | 808.3638        |
| <b>97</b> | $[M]^+$       | $C_{46}H_{39}N_2Br$ | 698.2297         | 698.2285        |
| <b>98</b> | $[M+H]^+$     | $C_{50}H_{48}N_2Br$ | 755.298835       | 755.299538      |
| <b>99</b> | $[M+H]^+$     | $C_{44}H_{38}N_4Br$ | 701.225713       | 701.227436      |

The synthesis and characterization of **99** will now be discussed in detail.





Scheme 6.3: Diels-Alder reaction generating compound **99**. (a) 300 °C, 5 h, 81%. The crystal structure of **99** is shown in the product side and the insert shows the yellow product on a flash column.

The complete structural characterisation of the **99** was carried out via  $^1\text{H}$  NMR studies (Figure 6.3). The bromination, as expected, results in a desymmetrisation of the molecule, generating five signals which exhibit a marginal shift due to the electronegative effect of the halogen substitution.

The most downfield singlet at  $\delta = 8.82$  ppm (integrating to two protons), and second most downfield signal  $\delta = 8.36$  ppm (integrating to four protons), are signals originating from hydrogens adjacent to the pyrimidyl nitrogens in the fluoranthene compound. As seen in **57**, the pyrimidyl protons are found to be the most deshielded signals due to the electron withdrawing ability of the nitrogen atoms. The resonances of the *tert*-butyl functionalised aromatic ring protons appear as two doublet signals integrating for four protons each. The doublet-pseudotriplet-doublet signals characteristic of the naphthyl moiety, are shown in Figure 6.2. The *tert*-butyl signals appear in the aliphatic region as two singlet peaks at  $\delta = 1.35$  ppm and at  $\delta = 1.36$  ppm, integrating to 18 protons in total.

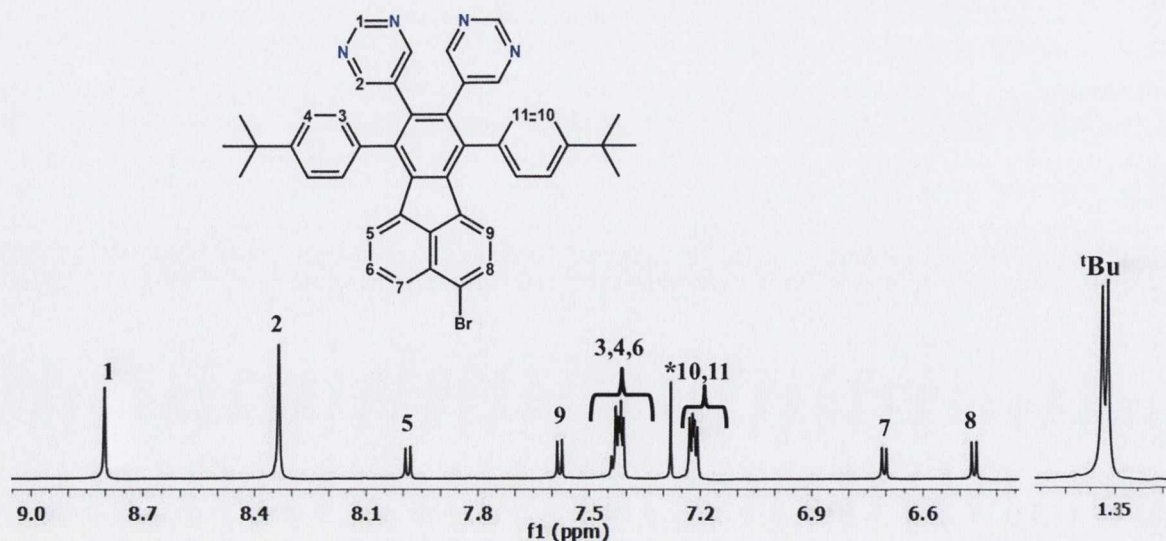
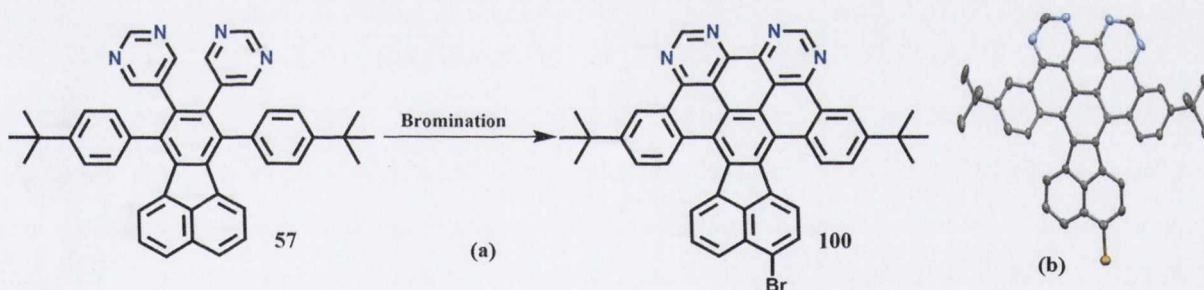


Figure 6.3:  $^1\text{H}$  NMR spectrum of **99**. Asterisk denotes solvent peak,  $\text{CDCl}_3$ .

### 6.3 Cyclodehydrogenation *via* Bromination

The generation of new C-C bonds *via* the oxidative coupling of benzenes and its derivatives has been investigated over the years. Intramolecular oxidative cyclodehydrogenation-type reactions have been extensively used in the synthesis of  $\pi$ -conjugated systems, with extended aromatic frameworks starting from polyphenylene precursors *via* surface-assisted processes, Scholl reactions, or solution-based radical or arenium cation processes.

Further to attempts above of the direct bromination of the polyphenylene fluoranthene, attempts with the corresponding pyrimidyl-containing systems, successful direct bromination was achieved. However, in an unexpected process, a secondary unexpected cyclodehydrogenation step was observed. Due to the geometry and reactive nature of pyrimidyl rings, the molecular bromine is seen to catalyse this intramolecular oxidative coupling, leading to complex extended polyaromatic systems. Previous work carried out by Draper *et al.* found that intramolecular coupling could not be achieved in isolation, using a range of different cyclodehydrogenation conditions.<sup>160</sup> As such, in this instance, the bromine-catalysed cyclodehydrogenation, carried out with Br<sub>2</sub> in toluene, resulted in the tandem cyclisation and monobromination, generating the fused fluoranthene **100**.<sup>160</sup>



Scheme 6.4: (a) In-situ cyclodehydrogenation via bromination of **57** with Br<sub>2</sub> in toluene. (b) Insert shows the crystal structure of **100**.

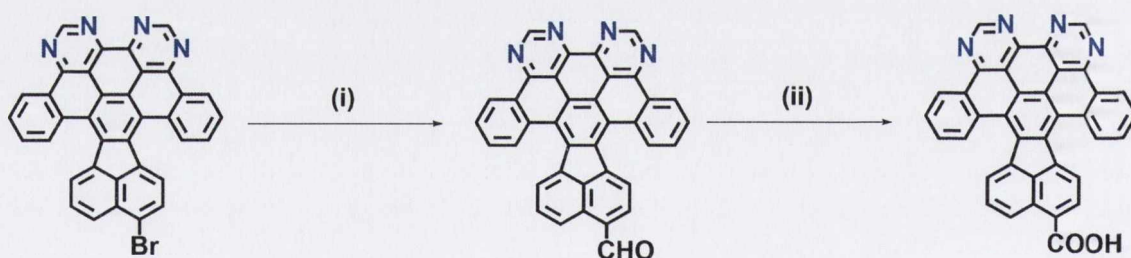
### 6.4 Future Work

As alluded to earlier, fluorescent organic dyes have been shown to have applications in biomedical imaging, light harvesting systems, semiconductors, and optoelectronic devices.<sup>161-164</sup> Modulation of the optical properties of these luminescent materials is increasingly important for the generation of the desired functional properties. Lately, many different design strategies including the incorporation of two or more fluorescent chromophores (dyads, triads and polyads) in a single molecular unit, has attracted significant attention. This synthetic strategy allows the individual proficiencies to be harnessed in a single platform, and



thus creates new opportunities.<sup>165</sup> However, acceptable control over the luminescence in these composite molecular systems is a challenging task, as even trivial alterations in the molecular structure may result in vastly different emission properties. This problem arises from the different extent of interchromophoric interactions, and small changes in molecular environments.<sup>166</sup>

Dye-sensitized solar cells (DSSCs) have attracted massive attention in previous decades because of their relatively high efficiency, but more so due to their low cost compared with conventional inorganic panels. Several organic dyes have been put forward in the literature whose efficiencies are in the range of 5-9%, which suggest that pure organic dyes may be a promising type of sensitizers for dye-sensitized solar cells.<sup>167</sup> Due to the extended  $\pi$ -electron system, and high quantum yields, fluoranthene containing structural motifs are slowly being exploited for DSSC-type applications.<sup>168, 169</sup> A necessary “anchoring” carboxylic acid group is introduced to allow functionalisation of the nanocrystalline  $\text{TiO}_2$  surface. Should metalation be required to enhance the light harvesting ability of the system, the presence of nitrogen atoms in the structure allows for this. In this current subsection, a variety of proposed substituted fluoranthenes could be designed by the incorporation of intense light-absorbing moieties like BODIPY or porphyrins.<sup>170-172</sup>



Scheme 6.5: Proposed synthetic route of 4N-fluoranthene showing carboxylic acid substitution.

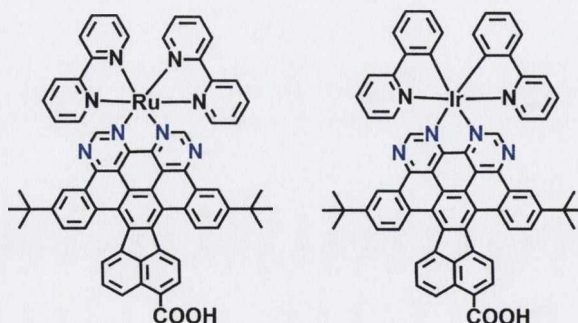
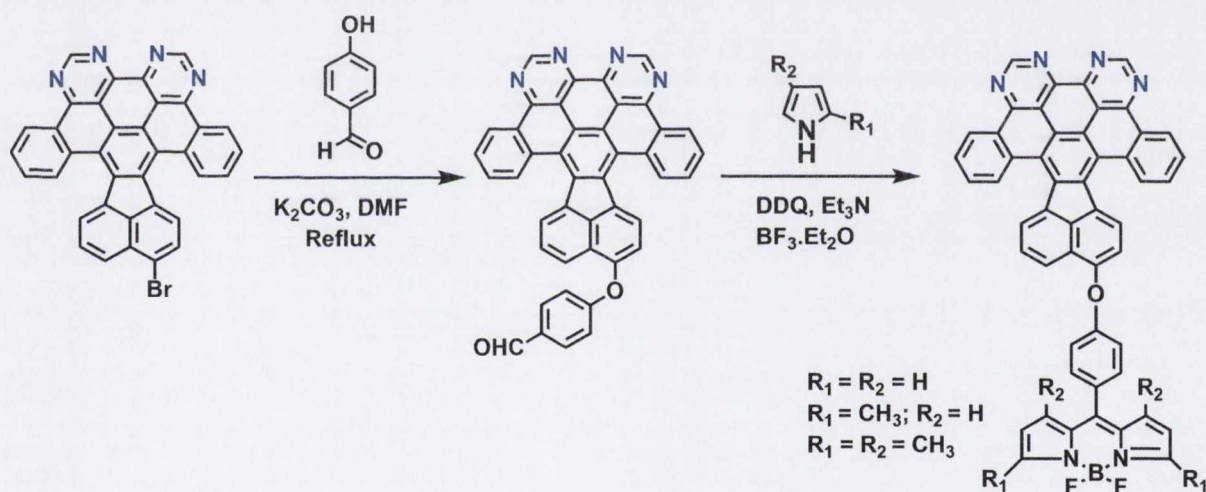


Figure 6.4: Possible Ir(III) or Ru(II) coordination to carboxylic acid containing 4N-fluoranthenes.

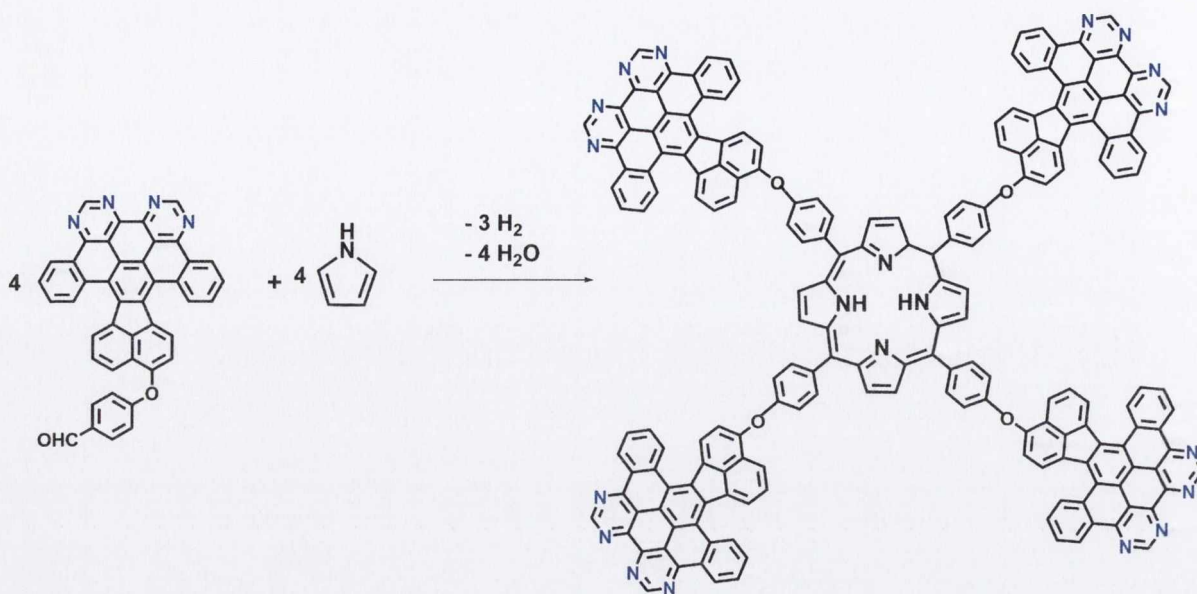
Among the most widely studied organic dyes, the 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacenes (BODIPY) class, have emerged as one of the most versatile classes of organic fluorophores.<sup>171</sup> Despite being initially commercialized as fluorescent tags for bio-imaging and as laser dyes, their use may span over nearly all areas of materials chemistry.<sup>173, 174</sup> BODIPY-derived systems generally show sharp emission bands due to their structural rigidity.<sup>175</sup> However, while BODIPYs are excellent emitters in the solution state, they are often poor emitters in aggregated or condensed states, which limit their potential as materials for solid-state applications.<sup>176</sup> Recently, exceptions to the above-mentioned features of BODIPY systems have appeared in the literature, where multiple emission wavelengths are seen from single molecular entities.<sup>177</sup> Synthetic strategies using bulky substituents exhibiting aggregation-induced emission have been utilized to govern efficient emission from BODIPYs in aggregated states.<sup>178</sup> A beneficial addition to the literature would be to combine these desirable properties in a single molecular entity.



Scheme 6.6: Proposed synthetic route for 4N fluoranthene-BODIPY complexes.

As porphyrins have both several peripheral positions for selective modulation, and a choice of metal centre, manipulation of their coordination behavior and absorption properties may be achieved. Therefore, inclusion of 4N-fluorathenes at the peripheral positions of a porphyrin may generate interesting systems for applications-based testing in both DSSC-type systems, and NAC sensing.





Scheme 6.7: Proposed synthetic route for porphyrin systems with 4N-fluoranthene substitution.

## 6.5 Commercialisation Potential

The end objective of the work of this thesis is to use the generated systems in an actual device for the sensing of nitroaromatic explosive-based threats. In this volume of work, the design of a wide variety of fluorophores for solution-based sensing could be converted to the solid state by the coating of a surface with these systems, generating a thin reactive film for a chip. A swab could then be used to sample the surrounding air, water or surface for potential threats. A device could internally vaporize the content of the swab, and pass the vapour over the generated sensor-coated chip, allowing selective binding of the nitroaromatic compound. These chips have the potential to be incorporated into small, hand-held electronic devices which can already effectively measure the differential emission caused by the presence or absence of the target compounds. Ideally, inclusion of multiple chips, each sensitive to a particular nitroaromatic, would allow this hand-held devices to be able to detect multiple types of explosive.

The detailed swab technique has already been shown to be extremely effective. This is possible because when someone touches an explosive, either while packaging or transporting, extremely minute quantities can adhere to the body, or clothing of the individual. Designing fluorescence quenching-based portable systems for the on-field non-contact detection of explosives is therefore a readily realizable goal. It is no surprise then that the design and

development of re-usable fluorescent films has become the main focus of material scientists in this area.

The most widely used device is called “FIDO” and was designed and developed by Swager *et al.*. FIDO began as a research project for the Defense Advanced Research Projects Agency (DARPA), to offer comparable explosive detection similar to that of trained canines. FIDO is comprised of a small glass capillary known as the sensing element, which is coated with a patented amplifying fluorescent polymer (AFP).<sup>26</sup> Ambient air is drawn into the sensing element, and vapours are passed over the coating of the AFP; a process not dissimilar to that of inhaled air passing over a dog’s olfactory epithelium towards their embedded sensory receptors. When the AFP molecules are activated by a carefully chosen wavelength, the polymer fluoresces. However, when explosive molecules enter the tube and bind to the chromophores, they become rigid and bind to the surrounding chromophores, forming a “molecular wire.” This process reduces, or quenches, the AFP’s fluorescence by suppressing its light-emitting state. Other electronic “sniffers” use similar fluorescent polymers to detect odours or explosives, but are less indicative of the presence of a target explosive material, because only a single fluorescent molecule is quenched by the explosive molecule. With the FIDO device, when a single repeating molecule of AFP is bound by the target molecule, a chain reaction occurs, resulting in the joining of several chromophores to form a rigid “wire”, which no longer produce visible fluorescence.<sup>26</sup> Thus, the number of repeating molecules in the FIDO sensing element that can be quenched by one explosive molecule is greatly amplified.<sup>179</sup> This reduction of fluorescence, then causes a response within the device’s photonic detector, and alerts the user to the presence of the target molecule. Though the original goal of this technology was to detect explosives chemically similar to that of TNT, studies have shown that FIDO can also recognize other dangerous compounds, including the often difficult to detect chemical pentaerythritol tetranitrate (PETN). Overall, FIDO has provided a cost-effective method for landmine detection, as a tool for the screening of people and vehicles for explosive chemicals, and has even been adapted for underwater detection in the device called the FIDO SeaPup. The detection of the FIDO device has been shown to be as low as 1 part per quadrillion of the target molecule.



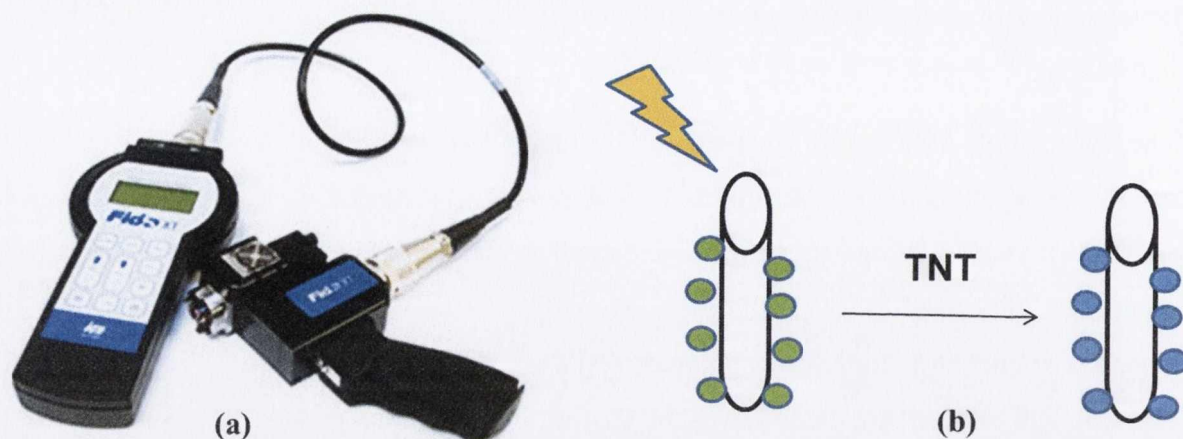


Figure 6.5: (a) The FIDO device, (b) Schematic demonstration of the working of FIDO.

Apart from FIDO, a variety of hand-held multi-threat devices for the detection of explosives and narcotics, are being designed and are constantly under revision. For example, Duoscan is a portable narcotics and contraband detector currently on the market, and is capable of detecting and identifying a much broader range of narcotics, while still maintaining the high levels of sensitivity and selectivity. Another device is that of the QS-H150 explosive trace detector, which employs a patented vortex collector for the simultaneous detection of explosive particulates, and vapour, with or without physical contact. This simultaneous approach is also conducted in real time.



**Duoscan**



**QS-H150**

Figure 6.6: Examples of commercially available devices: Duoscan and QS-H150

While historically, to take a molecular sensor like the ones described above from the lab to market would take several years of engineering, development and testing, with the advent of internet of things (IoT), it is now possible to reduce the entire prototyping and testing process to less than a year. This dramatic reduction in lab-to-market time will allow this work to be included in a device going forward, and it is the intention to build such a device to further study the robustness of these molecules in real-world applications.

7. Experimental





## 7.1 General Experimental Methods

Unless otherwise stated, all reactions were performed under an inert atmosphere of either nitrogen or argon using standard Schlenk techniques. All solvents were dried using appropriate drying agents and distilled under nitrogen atmosphere. Dichloromethane, diisopropylamine, triethylamine distilled over  $\text{CaH}_2$  and tetrahydrofuran over sodium/benzophenone. Flash chromatography was performed using silica gel (Fluka 60) particle size 0.04-0.063 mm as the stationary phase and all separations were carried out in air. All chemicals were purchased from commercial sources (Sigma-Aldrich Ltd) and were used without further purification.

The known compounds 1,3-bis-(4-*tert*-butylphenyl)propan-2-one, 1,3-bis-(bromophenyl)propan-2-one, 1,3-bis-(4-methoxyphenyl)propan-2-one, 5-ethynylpyrimidine, di(pyrimid-3,5-yl)acetylene, 5-((4-(*tert*-butyl)phenyl)ethynyl)pyrimidine, 7,9-bis(4-bromophenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one, 7,9-bis(4-methoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one, 3-bromo-7,9-diphenyl-8H-cyclopenta[*a*]acenaphthylen-8-one, were synthesised according to literature procedures.<sup>118, 137, 160</sup>

Microwave reactions were carried out in a CEM Discover 300 W multimode reactor at constant power. All reactions were performed under pressure in 35mL specialised sealed 'snap-cap' vessels.

IR spectra (reported in  $\text{cm}^{-1}$ ) were recorded in solid form on a Perkin-Elmer Spectrum 100 FT-IR spectrometer equipped with a Universal-ATR sampling accessory.

Electrospray mass spectra (ESI-MS) were recorded on a micromass LCT TOF electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer using a  $\alpha$ -cyano-4-hydroxy cinnamic acid or trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malonitrile (DCTB) matrix. Accurate mass spectra were referenced against Leucine Enkephalin ( $555.6 \text{ g mol}^{-1}$ ) or [Glu<sup>1</sup>]-Fibrinopeptide B ( $1570.6 \text{ g mol}^{-1}$ ) and reported to within 5 ppm.

Elemental analyses were performed on a Carlo Erba 1006 automatic analyser in the Microanalytical Laboratory, University College Dublin. Melting points are given uncorrected and were determined in capillary tubes using a Griffin Melting Point apparatus.

Nuclear magnetic resonance (NMR) spectra were recorded in  $\text{CDCl}_3$  with (i) Bruker Avance DPX-400 MHz spectrometer operating at frequencies 400.13MHz for  $^1\text{H}$  and 100.6 MHz for  $^{13}\text{C}$  (ii) Bruker AV-400 MHz spectrometer operating at 400.23 MHz for  $^1\text{H}$  and 100.6 MHz



for  $^{13}\text{C}$  or (iii) Bruker AV-600 MHz spectrometer at 600.13 MHz for  $^1\text{H}$ , 150.9 MHz for  $^{13}\text{C}$ . The signals for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced relative to TMS ( $\delta$  0.00 ppm).  $^{13}\text{C}$  NMR spectra were proton decoupled. Chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) in Hertz. All 2-D  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded using a Bruker Avance 400 MHz spectrometer or an AV-600 MHz spectrometer and were employed to assign  $^1\text{H}$  and  $^{13}\text{C}$  peaks. Homonuclear correlation spectroscopy was performed using TOCSY or  $^1\text{H}$ - $^1\text{H}$  COSY experiments and heteronuclear correlation spectroscopy was performed using HSQC, HMQC or HMBC (long-range experiments).

**X-ray crystallography:** Crystal and structural experimental data are summarised in tables in the Annex. The single crystal analysis was performed by Dr. Brendan Twamley in Trinity College with a Bruker SMART APEX CCD diffractometer and a Rigaku Saturn-724 diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) source at the temperature given in the tables. Data integration and reduction was performed using Bruker Saint Shelxtl\* version 6.14 software. Intensities were corrected for Lorentz and polarization effects and for absorption using SADABS. Space group were determined from systematic absences and checked for higher symmetry. The structures were solved by direct methods using SHELXS and refined on  $F^2$  using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons.

All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were fixed from the residual electron density using appropriate HFIX commands. Intermolecular interactions were computed using the PLATON program. Absolute structure determinations were based on the Flack parameter. The functions minimised were  $\Sigma w(F_o^2 - F_c^2)^2$ , with  $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ , where  $P = [\max(F_o^2) + 2(F_c^2)]/3$ . In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions.

**Photophysical measurements:** All photophysical measurements were carried out with optically dilute solutions ( $10^{-5} - 10^{-6}$  M) containing in  $1 \times 1 \text{ cm}^2$  quartz cuvettes in HPLC grade solvents. UV-Visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Emission and excitation spectra were obtained on a Perkin-Elmer LS55 fluorimeter or on a Horiba-Jobin-Yvon Fluorolog FL-3-11 spectrophotometer with double grating emission and excitation monochromators. Emission lifetime measurements were performed with an IBH Datastation HUB 5000F using NanoLED pulsed diode laser

excitation sources of appropriate wavelength. Appropriate excitation repetition rates were chosen in order to ensure that no re-excitation of the sample occurred until the decay has reached the baseline. TAC (time to amplitude convertor) ranges were set at approximately twenty times the expected average decay time, and were less than the reciprocal of the source repetition rate. To prevent pile-up, the start-stop ratio ( $\alpha$ ) was maintained at less than 2%. If the repetition rates required were  $> 100$  kHz, the experiments were carried out in reverse mode. Data was fit using monoexponential decays where possible, while attempting to maintain a  $\chi^2$  statistic of  $\sim 1$ , a Durbin-Watson statistic of  $\sim 2$ , a random spread of residuals with approximately 60 % of residuals within one standard deviation of the fitted parameter, and over 99 % of the residuals within 3 standard deviations. When these parameters could not be satisfied (particularly where non-random behaviour was observed in the residuals plot), biexponential fits were obtained instead. The same criteria as above were applied to these residuals/fits. For shorter lifetimes (in the nanosecond range), the instrument response factor (IRF) was estimated through running a scattering solution with the detector set to the excitation wavelength. When reconvolution failed, this IRF estimate was used to aid analysis through tail fitting. The optical density of the solutions at the excitation wavelength was less than 0.15 when recorded in a 1 cm pathlength cuvette.

Emission quantum yields of the solutions were measured using integrating sphere from Horiba. TBX-04-D picosecond photo detection module was used as a detector. For data analysis, PLQY calculator version 4 (excel spread sheet) was used along with DAS version 6.3 software from Horiba.

**Electrochemistry:** Cyclic voltammetry was carried out using a CH instruments Electrochemical Analyser Model 600B. Cyclic voltammograms were measured on 1 mM solutions of ligands in  $\text{CH}_2\text{Cl}_2$  using tetra-*n*-butylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , 0.1 M) as supporting electrolyte. A standard three-electrode cell was used with a glassy carbon working electrode, a Pt wire counter electrode, and an SCE or Ag/AgCl electrode as the reference electrode. Potentials are quoted vs. the ferrocene/ferrocenium couple (0.0 V), and all potentials were referenced against the ferrocene internal standard which was added at the end of each experiment. Solutions were degassed for several minutes by nitrogen bubbling before the experiments were performed, and a constant stream of nitrogen gas over the solution was maintained for the duration of the experiment.



**Experimental details of Nitroaromatic Sensing techniques**

To determine the detection limit, fluorescence titration of fluoranthene compounds with picric acid was carried out by adding aliquots of a picric acid solution of micromolar concentration and plotting the fluorescence intensity as a function of picric acid. From this graph, the concentration at which there was a sharp change in the fluorescence intensity multiplied by the concentration of receptor gave the detection limit.

**Preparation of TLC strips**

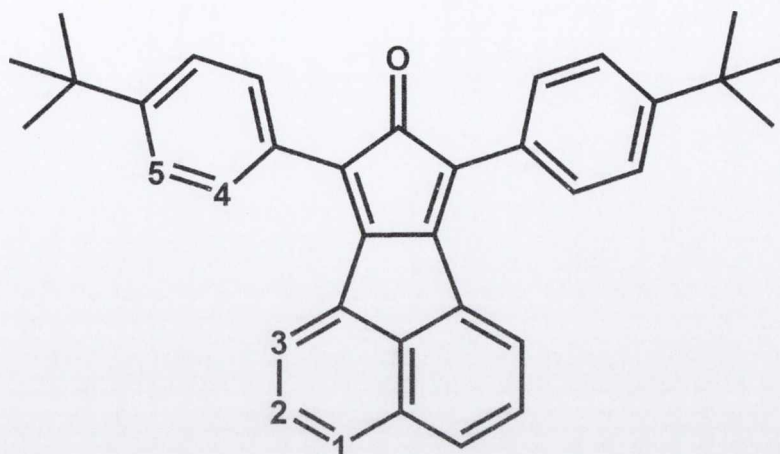
TLC strips (5 cm x 2 cm) were prepared by coating with fluoranthenes ( $1 \times 10^{-5}$  M), followed by removal of solvent in a vacuum at room temperature. The ensemble-coated strips were then used as the test strips for the detection of explosives.

**Contact mode visual detection of PA**

Aqueous samples were prepared by dissolving PA in ethanol. The explosive solutions were spotted onto the TLC strips at the desired concentration using a micropipette. A solvent blank was spotted near the spot of each explosive. In order to ensure consistent analysis, all depositions were prepared from a 20  $\mu$ L volume, thereby producing a spot  $\sim$  1.0 cm in diameter. After solvent evaporation, the TLC strip was illuminated with 365 nm UV light. The blue-coloured spots (under UV light) were identified by an independent observer, and each set of experiments was repeated three times for consistency. The detection limits were calculated from the lowest concentration of the explosive that enabled an independent observer to detect the quenching visually.

## 7.2 Experimental Procedures

### 7.2.1 7,9-bis(4-*tert*-butylphenyl)-8H-cyclopenta[a]acenaphthylen-8-one (54)



Acenaphthenequinone (400 mg, 2.19 mmol, 1 eq), 1,3-bis(4-*tert*-butylphenyl)propan-2-one (700 mg, 2.2 mmol, 1 eq) and KOH (61.71 mg; 1.1 mmol, 0.5 eq) were refluxed in ~ 20 mL ethanol for 1 h. The resulting purple/black precipitate **54** was cooled in ice, filtered, washed with cold ethanol and dried in vacuum. An analytical sample was crystallised from a mixture of dichloromethane and methanol.

**Yield:** 882 mg, 86 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.13 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, H<sub>3</sub>), 7.89 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, H<sub>1</sub>), 7.81 (d, 4H, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, H<sub>4</sub>), 7.62 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 6.0 Hz, H<sub>2</sub>), 7.58 (d, 4H, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, H<sub>5</sub>) and 1.42 (s, 18H, <sup>t</sup>butyl).

**<sup>13</sup>C NMR** (100 MHz CDCl<sub>3</sub>, δ in ppm): 202.5 (C = O), 153.6 (C<sub>quat</sub>), 151.4 (C<sub>quat</sub>), 144.7 (C<sub>quat</sub>), 132.1 (C<sub>quat</sub>), 131.7 (C<sub>quat</sub>), 128.7 (2C, C<sub>Ar</sub>), 128.5 (C<sub>Ar</sub>), 128.3 (C<sub>Ar</sub>), 127.9 (C<sub>Ar</sub>), 125.5 (C<sub>Ar</sub>), 121.5 (C<sub>quat</sub>), 120.8 (1C, C<sub>Ar</sub>), 34.8 (CMe<sub>3</sub>) and 31.3 (CMe<sub>3</sub>).

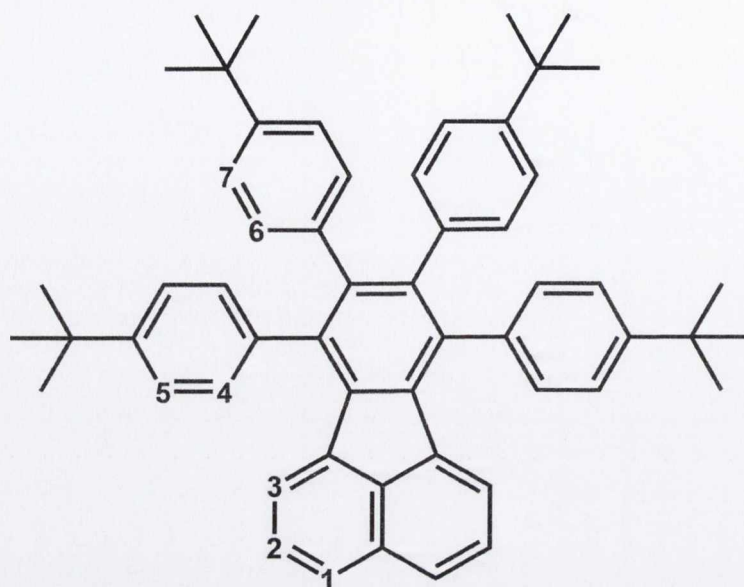
**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>35</sub>H<sub>33</sub>O [M+H]<sup>+</sup> *m/z* 469.2531, found 469.2534.

**Elemental analysis** (C<sub>35</sub>H<sub>32</sub>O): Calcd (%): C, 89.70; H, 6.88. Found (%): C, 88.69; H, 6.58.

**IR** (neat) cm<sup>-1</sup>: 2958 (-CH<sub>methyl</sub>), 1701 (C=O), 1507 (C<sub>aromatic</sub>), 1360, 1271, 1131, 846, 826 and 773

**m.p.:** 310 °C



7.2.2 7, 8, 9, 10-tetra(4-*tert*-butylphenyl)-fluoranthene (55)

1,2-bis(4-(*tert*-butyl)phenyl)ethyne (272.69 mg, 0.939 mmol, 1.1 eq) and 7,9-bis(4-*tert*-butylphenyl)-8H-cyclopenta [a]acenaphthylen-8-one (400 mg, 0.853 mmol, 1 eq) and benzophenone (900 mg, 4.931 mmol) were taken in a 10 mL round-bottomed flask and to heated at 280 °C under argon for 8 h. The mixture was cooled and then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (~5 mL). The product was precipitated from excess methanol (~30 mL), filtered and washed with cold methanol to remove any traces of benzophenone. The desired compound was obtained as an off-white powder.

**Yield:** 415 mg; 76 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): δ 7.73 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.14, H<sub>1</sub>), 7.34(m, 2H, H<sub>6</sub>), 7.32 (m, 4H, H<sub>2</sub>), 7.24 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 8.26, H<sub>7</sub>), 6.89 (d, 4H, J = 8.31, H<sub>5</sub>), 6.795 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 3.6, H<sub>4</sub>), 6.78 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 2.33Hz, H<sub>3</sub>), 1.36 (s, 18H, -CH<sub>3</sub>), 1.14 (s, 18H, -CH<sub>3</sub>)

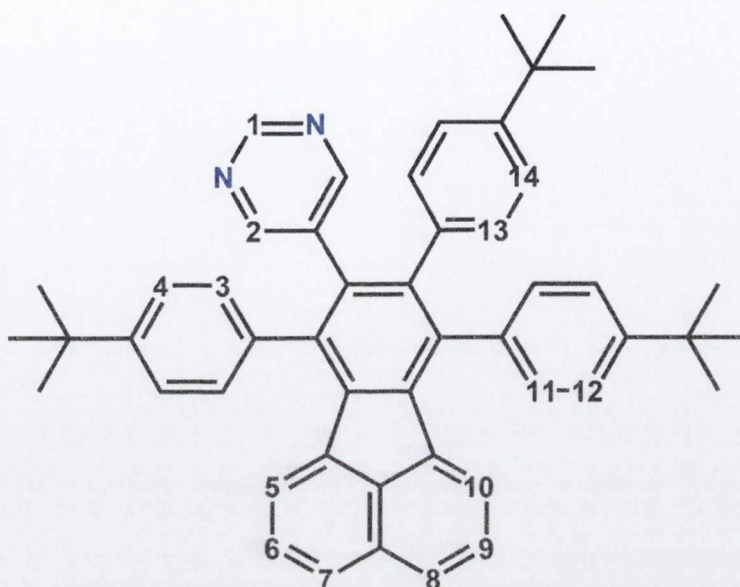
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm) 149.4(C<sub>quat</sub>), 147.6(C<sub>quat</sub>), 141.4(C<sub>quat</sub>), 137.3(C<sub>quat</sub>), 137.1(C<sub>Ar</sub>), 136.9(C<sub>quat</sub>), 136.8(C<sub>quat</sub>), 136.2(C<sub>quat</sub>), 133.3(C<sub>Ar</sub>), 130.9(C<sub>quat</sub>), 129.7(C<sub>quat</sub>), 127.8(C<sub>Ar</sub>), 126.4(C<sub>Ar</sub>), 126.2(C<sub>Ar</sub>), 124.7(C<sub>quat</sub>), 123.1(C<sub>quat</sub>), 34.4(C<sub>t-butyl</sub>), 34.0(C<sub>t-butyl</sub>), 31.5(CH<sub>3</sub>), 31.2(CH<sub>3</sub>).

**Elemental analysis** (C<sub>56</sub>H<sub>58</sub>): Calcd (%): C, 92.00; H, 8.00. Found (%): C, 91.85; H, 8.03.

**ESI-MS** (CH<sub>3</sub>CN): calculated for C<sub>56</sub>H<sub>58</sub> [M+H]<sup>+</sup> *m/z* 730.4539, found 730.4531.

**IR** (neat) cm<sup>-1</sup>: 2958 (-CH<sub>3</sub> methyl), 1602 (C<sub>aromatic</sub>), 1511, 1459, 1424, 824, 797, 773, 699.

**m.p.:** 279 °C

7.2.3 7,9,10-tri(4-*tert*-butylphenyl)-8-(5-pyrimidyl)fluoranthene (56)

5-((4-*tert*-butyl)phenyl)ethynyl)pyrimidine (138.5 mg, 0.586 mmol, 1.1 eq), 7,9-bis(4-*tert*-butylphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (250 mg, 0.533 mmol, 1 eq) and benzophenone (700 mg, 3.841 mmol) were heated at 280 °C under argon for 6 h. The resulting brown residue was crystallised from dichloromethane/methanol to yield the desired product as white needles.

**Yield:** 252 mg, 74 %.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): δ 8.70 (s, 1H, H<sub>1</sub>), 8.31 (s, 2H, H<sub>2</sub>), 7.74 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0; H<sub>8,10</sub>), 7.38 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0; H<sub>4</sub>), 7.33-7.25 (m, 6H, H<sub>12,9,6</sub> and H<sub>3</sub>), 7.20 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0; H<sub>11</sub>), 6.92 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0; H<sub>14</sub>), 6.81 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0; H<sub>5</sub>), 6.76 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.0; H<sub>13</sub>), 6.64 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0, H<sub>7</sub>), 1.31 (d, 18H, <sup>3</sup>J<sub>HH</sub> = 12.0; -CMe<sub>3</sub>), 1.11 (s, 9H, -CMe<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): δ 157.8 (2C, C<sub>Pym</sub>), 154.8 (1C, C<sub>Pym</sub>), 150.3 (C<sub>quat</sub>), 149.9 (C<sub>quat</sub>), 148.7 (C<sub>quat</sub>), 141.7 (C<sub>quat</sub>), 137.8 (C<sub>quat</sub>), 137.7 (C<sub>quat</sub>), 137.1 (C<sub>quat</sub>), 136.8 (C<sub>quat</sub>), 136.2 (C<sub>quat</sub>), 135.5 (C<sub>quat</sub>), 135.5 (C<sub>quat</sub>), 135.1 (C<sub>quat</sub>), 135.0 (C<sub>quat</sub>), 134.1 (C<sub>quat</sub>), 132.9 (C<sub>quat</sub>), 132.4 (C<sub>quat</sub>), 130.8 (C<sub>Ar</sub>), 129.1 (C<sub>quat</sub>), 129.5 (C<sub>Ar</sub>), 127.7 (C<sub>Np</sub>), 126.9 (C<sub>Ar</sub>), 126.7 (C<sub>Ar</sub>), 125.6 (C<sub>Ar</sub>), 124.8 (C<sub>Ar</sub>), 124.0 (C<sub>Ar</sub>), 123.7 (C<sub>Ar</sub>), 123.3 (C<sub>Ar</sub>), 34.6 (C<sub>t-butyl</sub>), 34.5 (C<sub>t-butyl</sub>), 34.0 (C<sub>t-butyl</sub>), 31.3 (CMe<sub>3</sub>), 31.1 (CMe<sub>3</sub>).

**Elemental analysis (C<sub>50</sub>H<sub>48</sub>N<sub>2</sub>):** Calcd (%): C, 88.71; H, 7.15; N, 4.14. Found (%): C, 86.77; H, 7.00; N, 4.05.

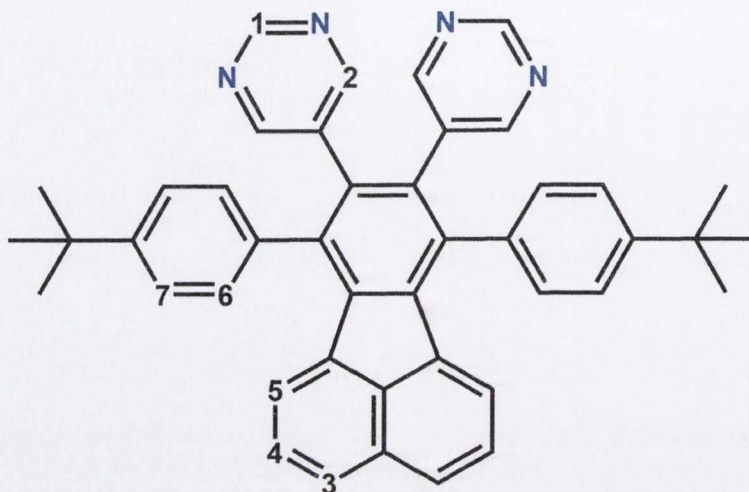


**ESI-MS** (CH<sub>3</sub>CN): calculated for C<sub>50</sub>H<sub>49</sub>N<sub>2</sub> [M+H]<sup>+</sup> *m/z* 677.3896, found 677.3876.

**IR** (neat) cm<sup>-1</sup>: 2962(-CH<sub>methyl</sub>), 1548(C<sub>aromatic</sub>), 1421, 1118, 835, 825, 778, 730.

**m.p.:** > 300 °C

#### 7.2.4 7,10-di-(4-*tert*-butylphenyl)-8,9-dipyrimidin-3,5-ylfluoranthene (57)



1,2-di(pyrimidin-5-yl)ethyne (106.76 mg, 0.586 mmol, 1.1 eq), 7,9-bis(4-*tert*-butylphenyl)-8H-cyclopenta[a]acenaphthylen-8-one (250 mg, 0.533 mmol, 1 eq) and benzophenone (700 mg, 3.841 mmol) were heated at 300 °C under argon for 3 h. After cooling, the reaction mixture was purified by chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a white solid.

**Yield:** 201.20 mg; 71 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): δ 8.81 (s, 2H; H<sub>1</sub>), 8.35 (s, 4H; H<sub>2</sub>), 7.82 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.0; H<sub>3</sub>), 7.42 (d, 4H, <sup>3</sup>*J*<sub>HH</sub> = 8.0; H<sub>6</sub>), 7.38 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.0; H<sub>4</sub>), 7.22 (d, 4H, <sup>3</sup>*J*<sub>HH</sub> = 12.0; H<sub>7</sub>), 6.72 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.0; H<sub>5</sub>), 1.36 (s, 18H; -CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 157.5 (C<sub>Pym</sub>), 155.7 (C<sub>Pym</sub>), 150.6 (C<sub>quat</sub>), 138.0 (C<sub>quat</sub>), 137.3 (C<sub>quat</sub>), 135.0 (C<sub>quat</sub>), 134.3 (C<sub>quat</sub>), 134.2 (C<sub>quat</sub>), 132.8 (C<sub>quat</sub>), 132.7 (C<sub>quat</sub>), 129.2 (C<sub>quat</sub>), 128.9 (C<sub>Ar</sub>), 127.4 (C<sub>Ar</sub>), 127.0 (C<sub>Ar</sub>), 125.4 (C<sub>Ar</sub>), 123.6 (C<sub>Ar</sub>), 34.2 (C<sub>t-butyl</sub>), 31.3 (CH<sub>3</sub>).

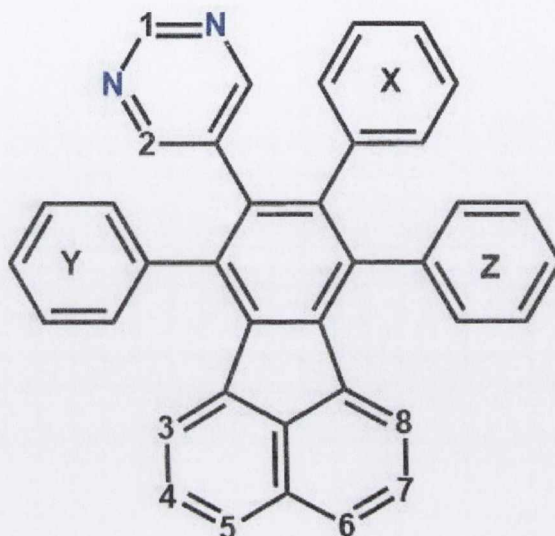
**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>44</sub>H<sub>38</sub>N<sub>4</sub> [M+H]<sup>+</sup> *m/z* 623.3175, found 623.3164.

**Elemental analysis** (C<sub>44</sub>H<sub>38</sub>N<sub>4</sub>): Calcd (%): C, 84.85.; H, 6.15; N, 9.00. Found (%): C, 84.92; H, 6.22; N, 8.80.

**IR** (neat)  $\text{cm}^{-1}$  : 2954( $-\text{CH}_{\text{methyl}}$ ), 1579( $\text{C}_{\text{aromatic}}$ ), 1548, 1513, 1462, 1402, 1362, 1267, 1185, 1118, 1014, 916, 827, 775 and  $730\text{ cm}^{-1}$ .

**m.p.:**  $> 300^{\circ}\text{C}$

#### 7.2.5 5-(7,9,10-triphenylfluoranthene-8-yl)pyrimidine (65)



5-(phenylethynyl)pyrimidine (55 mg, 0.306 mmol, 1 eq), and 7,9-diphenyl-8H-cyclopenta[*l*]acenaphthylen-8-one (120 mg, 0.336 mmol, 1.1 eq) and benzophenone (600 mg, 3.230 mmol) were heated at  $280^{\circ}\text{C}$  for 8 h. Chromatography ( $\text{SiO}_2$ , diethyl ether) gave the product as a white solid.

**Yield:** 118.28 mg, 76 %.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.73 (s, 1H;  $\text{H}_1$ ), 8.33 (s, 2H;  $\text{H}_2$ ), 7.80 (d, 2H,  $^3J_{\text{HH}}=8.10$ ;  $\text{H}_{3,8}$ ), 7.02-6.93 (m, 5H,  $\text{H}_x$ ), 7.42-7.33(m, 12H,  $\text{H}_{y,z,4,7}$ ), 6.88 (t, 2H,  $^3J_{\text{HH}}=6.70$ ;  $\text{H}_{4,7}$ ).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 157.8( $\text{C}_{\text{Pym}}$ ), 155.8( $\text{C}_{\text{Pym}}$ ), 141.0( $\text{C}_{\text{quat}}$ ), 139.0( $\text{C}_{\text{quat}}$ ), 138.6 ( $\text{C}_{\text{quat}}$ ), 138.5( $\text{C}_{\text{quat}}$ ), 138.0( $\text{C}_{\text{quat}}$ ), 137.5( $\text{C}_{\text{quat}}$ ), 137.2( $\text{C}_{\text{quat}}$ ), 136.91( $\text{C}_{\text{quat}}$ ), 135.8( $\text{C}_{\text{quat}}$ ), 135.7( $\text{C}_{\text{quat}}$ ), 133.2( $\text{C}_{\text{quat}}$ ), 131.1( $\text{C}_{\text{Ar}}$ ), 129.9( $\text{C}_{\text{Ar}}$ ), 129.8( $\text{C}_{\text{Ar}}$ ), 129.6( $\text{C}_{\text{quat}}$ ), 128.9( $\text{C}_{\text{Ar}}$ ), 128.3( $\text{C}_{\text{Ar}}$ ), 128.2( $\text{C}_{\text{quat}}$ ), 127.85( $\text{C}_{\text{quat}}$ ), 127.8( $\text{C}_{\text{Ar}}$ ), 127.7( $\text{C}_{\text{Ar}}$ ), 127.4( $\text{C}_{\text{Ar}}$ ), 127.3( $\text{C}_{\text{Ar}}$ ), 127.1( $\text{C}_{\text{Ar}}$ ), 127.05( $\text{C}_{\text{Ar}}$ ), 126.4( $\text{C}_{\text{Ar}}$ ), 123.8( $\text{C}_{\text{Ar}}$ ), 123.4( $\text{C}_{\text{Ar}}$ ).

**ESI-MS** ( $\text{CH}_2\text{Cl}_2$ ): calculated for  $\text{C}_{38}\text{H}_{25}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^{+}$   $m/z$  509.2018, found 509.2026.

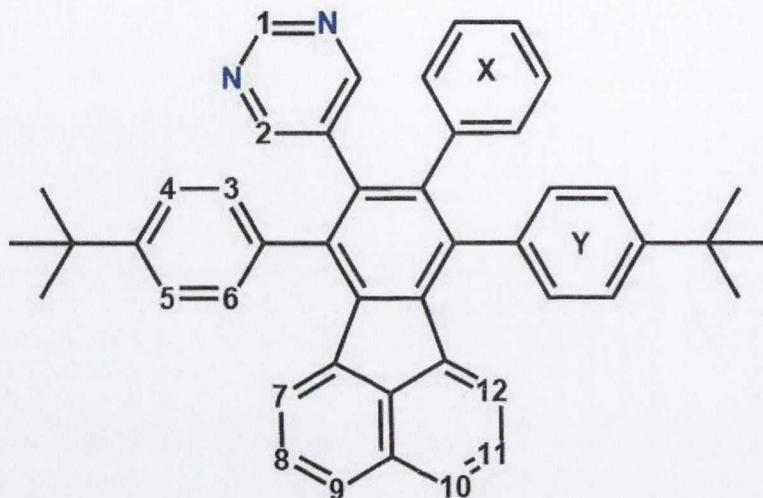
**Elemental analysis** calc (%) for  $\text{C}_{38}\text{H}_{24}\text{N}_2$ : C, 89.74; H, 4.76; N, 5.51; found: C, 86.00; H, 4.58; N, 5.18.



**IR** (neat):  $\nu = 2970, 1717, 1547, 1492, 1372, 1225, 1092, 1010$  and  $821\text{ cm}^{-1}$ .

**m.p.:**  $> 300\text{ }^{\circ}\text{C}$

#### 7.2.6 5-(7, 10-bis(4-(*tert*-butyl)phenyl)-9-phenylfluoranthene-8-yl)pyrimidine (66)



5-(phenylethynyl)pyrimidine (42 mg, 0.232 mmol, 1 eq), 7,9-bis(4-*tert*-butylphenyl)-8H-cyclopenta [a]acenaphthylen-8-one (120 mg, 0.256 mmol, 1.1 eq) and benzophenone (650 mg, 3.567 mmol) were heated at  $280\text{ }^{\circ}\text{C}$  for 6 h. Chromatography ( $\text{SiO}_2$ , diethyl ether) gave the product as a white solid.

**Yield:** 106.6 mg, 74 %

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.72 (s, 1H;  $\text{H}_1$ ), 8.31 (s, 2H;  $\text{H}_2$ ), 7.76(d, 2H,  $^3J_{\text{HH}}=8.12$ ;  $\text{H}_{7,12}$ ), 7.42 (d, 2H,  $^3J_{\text{HH}}=7.62$ ;  $\text{H}_{4,5}$ ), 7.37-7.32 (m, 4H,  $\text{H}_{3,6,8,11}$ ), 7.27-7.23 (m, 4H,  $\text{H}_Y$ ), 7.0-6.91 (m, 5H,  $\text{H}_X$ ), 1.37 (s, 9H;  $^t\text{Bu}$ ), 1.36 (s, 9H;  $^t\text{Bu}$ ).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 157.4 ( $\text{C}_{\text{Pym}}$ ), 155.8 ( $\text{C}_{\text{Pym}}$ ), 150.2 ( $\text{C}_{\text{quat}}$ ), 149.5 ( $\text{C}_{\text{quat}}$ ), 140.7 ( $\text{C}_{\text{quat}}$ ), 138.3 ( $\text{C}_{\text{quat}}$ ), 137.6 ( $\text{C}_{\text{quat}}$ ), 136.8 ( $\text{C}_{\text{quat}}$ ), 136.7 ( $\text{C}_{\text{quat}}$ ), 136.5 ( $\text{C}_{\text{quat}}$ ), 135.5 ( $\text{C}_{\text{quat}}$ ), 134.9 ( $\text{C}_{\text{quat}}$ ), 134.0 ( $\text{C}_{\text{quat}}$ ), 132.7, 132.4, 130.7( $\text{C}_{\text{Ar}}$ ), 129.0( $\text{C}_{\text{Ar}}$ ), 128.9 ( $\text{C}_{\text{Ar}}$ ), 127.2( $\text{C}_{\text{Ar}}$ ), 126.8( $\text{C}_{\text{Ar}}$ ), 126.5( $\text{C}_{\text{Ar}}$ ), 126.3( $\text{C}_{\text{Ar}}$ ), 125.6( $\text{C}_{\text{Ar}}$ ), 125.2, 124.64( $\text{C}_{\text{Ar}}$ ), 123.6( $\text{C}_{\text{Ar}}$ ), 122.9( $\text{C}_{\text{Ar}}$ ), 34.4( $\text{C}_{\text{t-butyl}}$ ), 30.9( $\text{C}_{\text{t-butyl}}$ ).

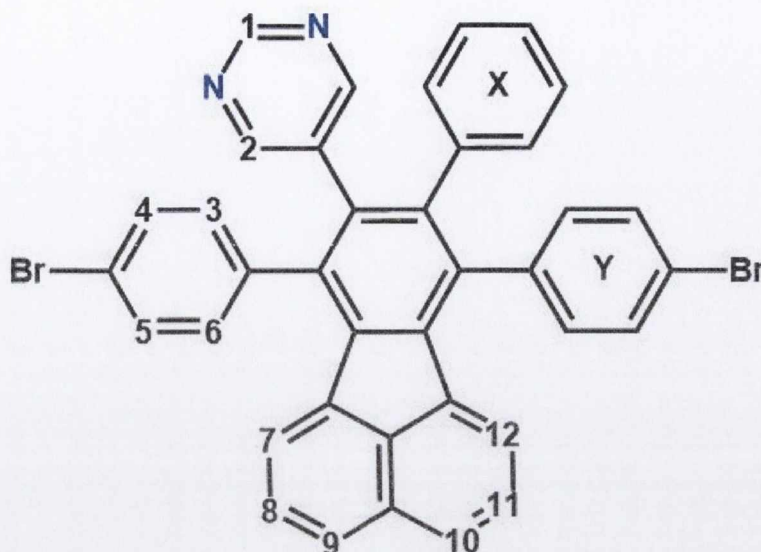
**ESI-MS** ( $\text{CH}_2\text{Cl}_2$ ): calculated for  $\text{C}_{46}\text{H}_{41}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^+$   $m/z$  621.3270, found 621.3269.

**Elemental analysis** calc (%) for  $\text{C}_{46}\text{H}_{40}\text{N}_2$ : C, 88.99; H, 6.49; N, 4.51 found: C, 86.94; H, 6.36; N, 4.34.

**IR** (neat):  $\nu = 2958, 1602, 1548, 1421, 1361, 1265, 1112, 1014$  and  $826\text{ cm}^{-1}$ .

**m.p.:**  $>300\text{ }^{\circ}\text{C}$

## 7.2.7 5-(7,10-bis(4-bromophenyl)-9-phenylfluoranthene-8-yl)pyrimidine (68)



5-(phenylethynyl)pyrimidine (48 mg, 0.265 mmol, 1 eq), and 7,9-bis(4-bromophenyl)-8H-cyclopenta[a]acenaphthylen-8-one (150 mg, 0.291 mmol, 1.1 eq) and benzophenone (700 mg, 3.841 mmol) were heated to reflux for 8 h. Chromatography ( $\text{SiO}_2$ , diethyl ether) gave the product as a off-white solid.

**Yield:** 132.45 mg, 75 %.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.74 (s, 1H;  $\text{H}_1$ ), 8.27 (s, 2H;  $\text{H}_2$ ), 7.80 (d, 2H,  $^3J_{\text{HH}}=8.09$ ;  $\text{H}_{7,12}$ ), 7.52 (d, 2H,  $^3J_{\text{HH}}=7.80$ ;  $\text{H}_{3,6}$ ), 7.47 (d, 2H,  $^3J_{\text{HH}}=7.72$ ;  $\text{H}_{4,5}$ ), 7.39 (t, 2H,  $^3J_{\text{HH}}=7.67$ ;  $\text{H}_{8,11}$ ), 7.20 (m, 4H,  $\text{H}_Y$ ), 6.98-6.88 (m, 5H,  $\text{H}_X$ ), 6.73 (d, 2H,  $^3J_{\text{HH}}=6.99$ ;  $\text{H}_{9,10}$ ).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 157.3 ( $\text{C}_{\text{Pym}}$ ), 155.4 ( $\text{C}_{\text{Pym}}$ ), 140.6 ( $\text{C}_{\text{quat}}$ ), 137.6 ( $\text{C}_{\text{quat}}$ ), 137.4 ( $\text{C}_{\text{quat}}$ ), 136.9 ( $\text{C}_{\text{quat}}$ ), 136.5 ( $\text{C}_{\text{quat}}$ ), 136.4 ( $\text{C}_{\text{quat}}$ ), 135.9 ( $\text{C}_{\text{quat/Ar}}$ ), 135.6 ( $\text{C}_{\text{quat}}$ ), 134.9 ( $\text{C}_{\text{quat}}$ ), 134.8 ( $\text{C}_{\text{quat}}$ ), 133.4 ( $\text{C}_{\text{quat}}$ ), 132.6 ( $\text{C}_{\text{quat}}$ ), 132.3 ( $\text{C}_{\text{Ar}}$ ), 131.7 ( $\text{C}_{\text{Ar}}$ ), 131.1 ( $\text{C}_{\text{Ar}}$ ), 131.1 ( $\text{C}_{\text{Ar}}$ ), 131.1 ( $\text{C}_{\text{Ar}}$ ), 130.4 ( $\text{C}_{\text{quat}}$ ), 129.2 ( $\text{C}_{\text{quat}}$ ), 127.4 ( $\text{C}_{\text{Ar}}$ ), 127.2 ( $\text{C}_{\text{Ar}}$ ), 127.0 ( $\text{C}_{\text{Ar}}$ ), 126.9 ( $\text{C}_{\text{Ar}}$ ), 126.2 ( $\text{C}_{\text{Ar}}$ ), 123.4 ( $\text{C}_{\text{Ar}}$ ), 123.3 ( $\text{C}_{\text{Ar}}$ ), 123.0 ( $\text{C}_{\text{Ar}}$ ), 121.69 ( $\text{C}_{\text{quat}}$ ), 121.1 ( $\text{C}_{\text{quat}}$ ).

**ESI-MS** ( $\text{CH}_2\text{Cl}_2$ ): calculated for  $\text{C}_{38}\text{H}_{23}\text{N}_2\text{Br}_2$  [ $\text{M}+\text{H}$ ] $^+$   $m/z$  665.0228, found 665.0219.

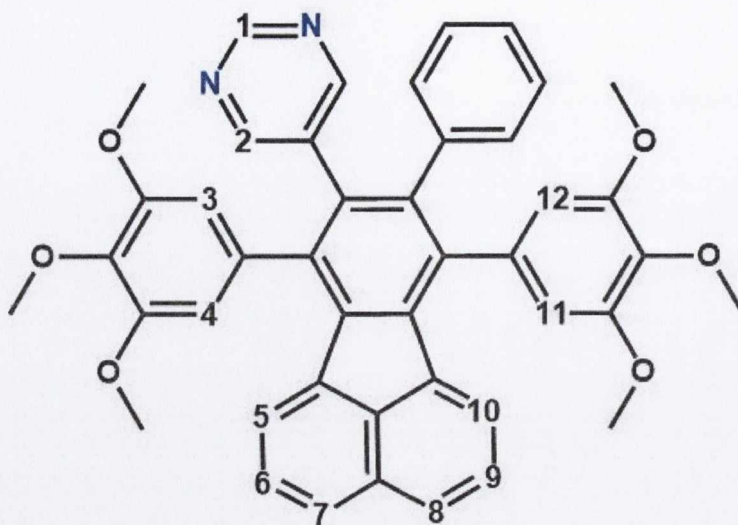
**Elemental analysis** calc (%) for  $\text{C}_{38}\text{H}_{22}\text{N}_2\text{Br}_2$ : C, 68.49; H, 3.33; N, 4.20; Br, 23.98 found: C, 67.94; H, 3.20; N, 4.23; Br, 23.44

**IR** (neat):  $\nu = 2957, 1546, 1422, 1407, 1389, 1208, 1180, 1070$  and  $821\text{ cm}^{-1}$ .

**m.p.:**  $>300^\circ\text{C}$



## 7.2.8 5-(9-phenyl-7,10-bis(3,4,5-trimethoxyphenyl)fluoranthene-8-yl)pyrimidine (67)



5-(phenylethynyl)pyrimidine (46 mg, 0.254 mmol, 1 eq), and 7,9-bis-(3,4,5-trimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (131.12 mg, 0.279 mmol, 1.1 eq) and benzophenone (800 mg, 4.390 mmol) were heated at 300 °C for 5 h. Chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a white solid.

**Yield:** 124.21 mg, 71 %.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.76 (s, 1H; H<sub>1</sub>), 8.37 (s, 2H; H<sub>2</sub>), 7.82 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.14; H<sub>5,10</sub>), 7.41 (t, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.62; H<sub>6,9</sub>), 7.01 (s, 1H, H<sub>7</sub>), 7.58 (m, 5H, H<sub>Ph</sub>), 7.69 (s, 1H, H<sub>8</sub>), 6.54 (d, 4H, <sup>3</sup>*J*<sub>HH</sub>=5.84; H<sub>3,4,11,12</sub>), 3.89 (s, 6H; -OCH<sub>3</sub>), 3.72 (s, 6; -OCH<sub>3</sub>), 3.68 (s, 6H; -OCH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 157.5 (C<sub>Pym</sub>), 155.4 (C<sub>Pym</sub>), 153.6(C<sub>quat</sub>), 153.1(C<sub>quat</sub>), 141.0(C<sub>quat</sub>), 138.6(C<sub>quat</sub>), 137.9(C<sub>quat</sub>), 137.5(C<sub>quat</sub>), 137.4(C<sub>quat</sub>), 137.3(C<sub>quat</sub>), 137.0(C<sub>quat</sub>), 137.0(C<sub>quat</sub>), 135.6(C<sub>quat</sub>), 135.4(C<sub>quat</sub>), 134.0(C<sub>quat</sub>), 133.7(C<sub>quat</sub>), 133.2(C<sub>quat</sub>), 132.5(C<sub>quat</sub>), 130.9(C<sub>Ar</sub>), 129.7(C<sub>quat</sub>), 127.6(C<sub>Ar</sub>), 127.4(C<sub>Ar</sub>), 127.2(C<sub>Ar</sub>), 126.5(C<sub>Ar</sub>), 124.0(C<sub>Ar</sub>), 123.7(C<sub>Ar</sub>), 107.3(C<sub>Ar</sub>), 107.1(C<sub>Ar</sub>), 61.1(OMe), 56.2(OMe), 56.1 (OMe).

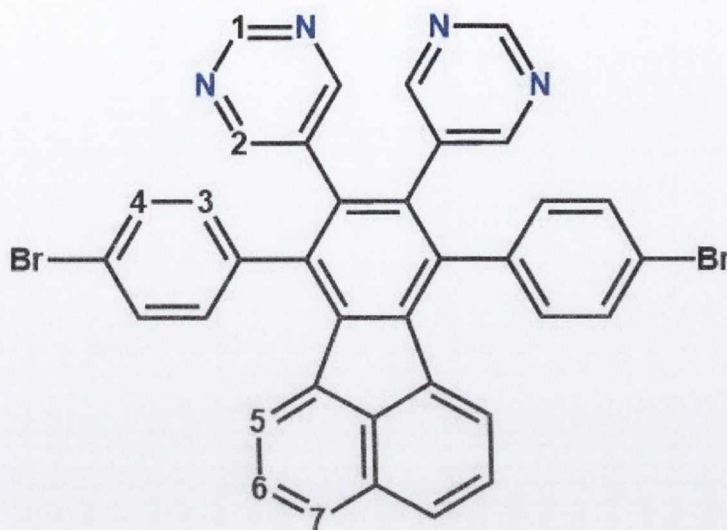
**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>44</sub>H<sub>37</sub>N<sub>2</sub>O<sub>6</sub> [M+H]<sup>+</sup> *m/z* 689.2652, found 689.2659.

**Elemental analysis** calc (%) for C<sub>44</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>: C, 76.73; H, 5.27; N, 4.07; found: C, 76.00; H, 5.21; N, 3.94

**IR** (neat): ν = 2970, 1716, 1607, 1547, 1493, 1419, 1373, 1225, 1010, 951 and 821 cm<sup>-1</sup>.

**m.p.:** > 300°C

## 7.2.9 5,5'-(7,10-bis(4-bromophenyl)fluoranthene-8,9-diyl)dipyrimidine (69)



1,2-di(pyrimidin-5-yl)ethyne **51** (54 mg, 0.295 mmol, 1 eq), 7,9-bis(4-bromophenyl)-8H-cyclopenta[a]acenaphthylen-8-one **64** (167 mg, 0.324 mmol, 1.1 eq) and benzophenone (900 mg, 4.940 mmol) were heated at 300 °C for 3 h. Chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a pale yellow solid.

**Yield:** 140 mg, 71 %.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.82 (s, 2H; H<sub>1</sub>), 8.36 (s, 4H; H<sub>2</sub>), 7.88 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8.16; H<sub>5</sub>), 7.58 (d, 4H, <sup>3</sup>J<sub>HH</sub>=7.02; H<sub>4</sub>), 7.46 (t, 2H, <sup>3</sup>J<sub>HH</sub>=7.62; H<sub>6</sub>), 7.24 (d, 4H, <sup>3</sup>J<sub>HH</sub>=7.14; H<sub>3</sub>), 6.79 (d, 2H, <sup>3</sup>J<sub>HH</sub>=7.08; H<sub>7</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 157.7 (C<sub>Pym</sub>), 156.4 (C<sub>Pym</sub>), 138.4(C<sub>quat</sub>), 136.7(C<sub>quat</sub>), 134.7(C<sub>quat</sub>), 133.1(C<sub>quat</sub>), 133.0(C<sub>quat</sub>), 132.8(C<sub>quat</sub>), 132.4(C<sub>Ar</sub>), 131.4 (C<sub>Ar</sub>), 129.8(C<sub>quat</sub>), 128.0(C<sub>Ar</sub>), 128.0(C<sub>Ar</sub>), 124.1(C<sub>Ar</sub>), 122.5(C<sub>quat</sub>).

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>36</sub>H<sub>21</sub>N<sub>4</sub>Br<sub>2</sub> [M+H]<sup>+</sup> *m/z* 667.0135, found 667.0133.

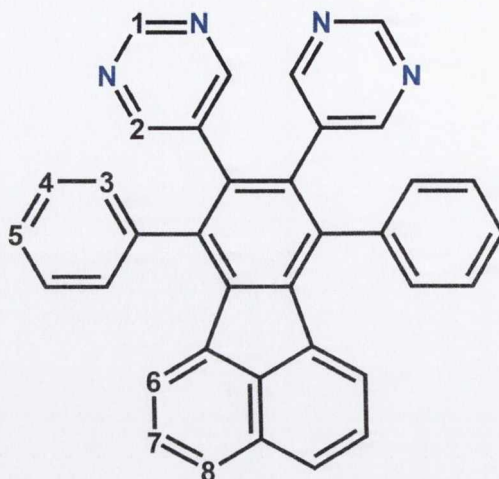
**Elemental analysis** calc (%) for C<sub>36</sub>H<sub>20</sub>N<sub>4</sub>Br<sub>2</sub>: C, 64.69; H, 3.02; N, 8.38; found: C, 63.44; H, 3.00; N, 7.55

**IR** (neat): ν = 2971, 1717, 1590, 1547, 1492, 1419, 1390, 1225, 1185, 1092 and 821 cm<sup>-1</sup>.

**m.p.:** > 300°C



## 7.2.10 5, 5'-(7,10-diphenylfluoranthene-8,9-diyl)dipyrimidine (74)



1,2-di(pyrimidin-5-yl)ethyne (70 mg, 0.382 mmol, 1 eq), 7,9-diphenyl-8H-cyclopenta[*l*]acenaphthylen-8-one (150 mg, 0.420 mmol, 1.1 eq) and benzophenone (500 mg, 2.744 mmol) were heated to reflux for 4 h. Chromatography (SiO<sub>2</sub>, diethylether) gave the product as a light yellow solid.

**Yield:** 195 mg, 81%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm):  $\delta$  8.79 (s, 2H; H<sub>1</sub>), 8.34 (s, 4H; H<sub>2</sub>), 7.81 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.0; H<sub>8</sub>), 7.37 (m, 12H; H<sub>3,4,5,7</sub>), 6.71 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.0; H<sub>6</sub>);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm):  $\delta$  = 157.5 (C<sub>Pym</sub>), 155.9 (C<sub>Pym</sub>), 143.4 (C<sub>quat</sub>), 137.9 (C<sub>quat</sub>), 137.4 (C<sub>quat</sub>), 137.3 (C<sub>quat</sub>), 134.7 (C<sub>quat</sub>), 132.7 (C<sub>quat</sub>), 132.5 (C<sub>quat</sub>), 129.3 (C<sub>Ar</sub>), 128.6 (C<sub>Ar</sub>), 127.7 (C<sub>Ar</sub>), 127.4 (C<sub>Ar</sub>), 127.2 (C<sub>Ar</sub>), 123.6 (C<sub>Ar</sub>).

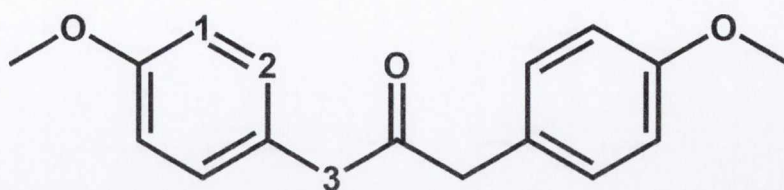
**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>36</sub>H<sub>23</sub>N<sub>4</sub> [M+H]<sup>+</sup> *m/z* 511.1923, found 511.1928.

**Elemental analysis** (C<sub>36</sub>H<sub>23</sub>N<sub>4</sub>): Calcd(%): C, 84.68; H, 4.34; N, 10.97. Found (%): C, 80.30; H, 4.41; N, 9.58

**IR** (v<sub>max</sub>/cm<sup>-1</sup>) = 3050(-CH<sub>3</sub> methyl), 1791(C<sub>aromatic</sub>), 1549, 1423, 1402, 1399, 1267, 1185, 1117, 1094, 916, 827, 779 and 733 cm<sup>-1</sup>

**m.p.:** > 300°

## 7.2.11 1,3-bis(4-methoxyphenyl)propan-2-one (70)



Ca(OH)<sub>2</sub> (2.96 g, 40.0 mmol, 4 eq) and Bu<sub>4</sub>NHSO<sub>4</sub> (1.70 g, 5.0 mmol, 0.5 eq) were dissolved in 1:1 dichloromethane:water (180 mL) and stirred. 4-Methoxybenzyl bromide (4.02 g, 20.0 mmol, 2 eq) was added followed by Fe(CO)<sub>5</sub> (1.96 g, 10.0 mmol, 1 eq) and the reaction mixture was stirred at room temperature for 7 h with a constant stream of argon circulated over the reaction. The reaction mixture was oxidized in air and acidified with 10% HCl solution. The aqueous phase was extracted with dichloromethane and the organic washings combined and reduced to yellow oil. Chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a light yellow solid.

**Yield:** 1.75 g, 65 %.

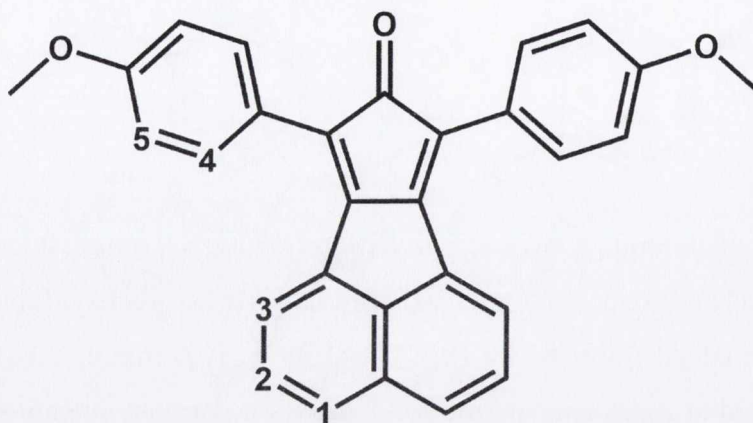
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 7.10 (d, 4H, <sup>3</sup>J<sub>HH</sub>=8.5; H<sub>2</sub>), 6.89 (d, 4H, <sup>3</sup>J<sub>HH</sub>=8.5; H<sub>1</sub>), 3.64 (s, 4H; H<sub>3</sub>), 3.78 (s, 6H; -OCH<sub>3</sub>)

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 206.1 (C=O), 158.2 (C-OMe), 130.1 (C<sub>Ar</sub>), 125.6 (C<sub>quat</sub>), 113.7 (C<sub>Ar</sub>), 47.6 (CH<sub>2</sub>), 54.8 (OCH<sub>3</sub>).

**ESI-MS** (CH<sub>3</sub>CN) calculated for C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> *m/z* 293.1154, found 293.1149.



## 7.2.12 7,9-bis(4-methoxyphenyl)-8H-cyclopenta[a]acenaphthylene-8-one (72)



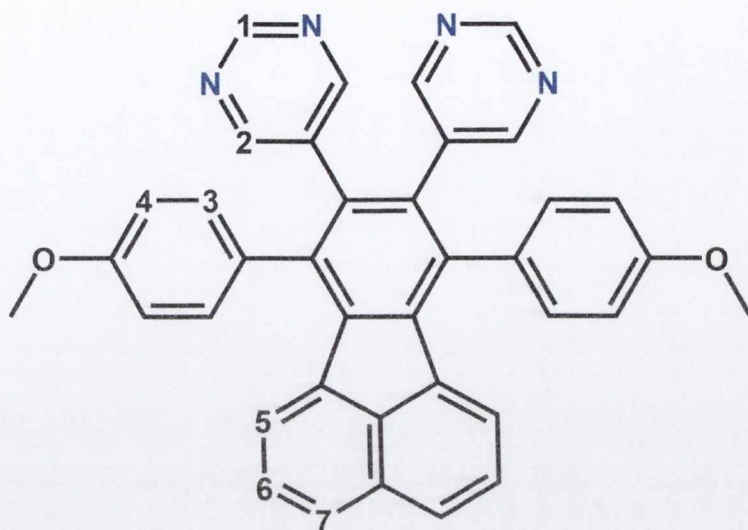
Acenaphthenequinone (455 mg, 2.50 mmol, 1 eq), 1,3-bis(4-methoxyphenyl)propan-2-one **70** (675.82 mg, 2.50 mmol, 1 eq) and KOH (70 mg, 4.50 mmol, 0.5 eq) were stirred in 180 mL of methanol for 24 h. The green precipitate was filtered off. Chromatography (SiO<sub>2</sub>, dichloromethane) gave the product as a blue solid.

**Yield:** 624.71 mg, 60 %.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm):  $\delta$  = 8.02 (d, 2H,  $^3J_{\text{HH}}=7.0$ ; H<sub>1</sub>), 7.84 (d, 2H,  $^3J_{\text{HH}}=8.0$ ; H<sub>3</sub>), 7.80 (d, 4H,  $^3J_{\text{HH}}=8.7$ ; H<sub>4</sub>), 7.58 (t, 2H,  $^3J_{\text{HH}}=8.0$ ; H<sub>2</sub>), 7.07 (d, 4H,  $^3J_{\text{HH}}=8.7$ ; H<sub>5</sub>), 3.92 (s, 6H; -OCH<sub>3</sub>);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm):  $\delta$  = 172.2 (C=O), 159.1(C<sub>quat</sub>), 152.3(C<sub>quat</sub>), 131.7 (C<sub>quat</sub>), 131.4(C<sub>quat</sub>), 129.9 (C<sub>Ar</sub>), 127.9 (C<sub>Ar</sub>), 126.8 (C<sub>Ar</sub>), 126.7 (C<sub>quat</sub>), 123.6 (C<sub>quat</sub>), 120.7 (C<sub>quat/Ar</sub>), 120.0 (C<sub>Ar</sub>), 113.7 (C<sub>Ar</sub>), 54.9 (OCH<sub>3</sub>).

## 7.2.13 5,5'-(7,10-bis(4-methoxyphenyl)fluoranthene-8,9-diyl)dipyrimidine (75)



1,2-di(pyrimidin-5-yl)ethyne (91 mg, 0.500 mmol, 1 eq), 7,9-di-(4-methoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (213 mg, 0.500 mmol, 1 eq) and benzophenone (500mg) were heated to 300 °C for 12 h. Chromatography (SiO<sub>2</sub>, 1:1 ethyl acetate:dichloromethane) gave the product as a white solid.

**Yield:** 155 mg, 54%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.83 (s, 2H; H<sub>1</sub>), 8.35 (s, 4H; H<sub>2</sub>), 7.84 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.0; H<sub>7</sub>), 7.41 (t, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.7; H<sub>6</sub>), 7.23 (d, 4H, <sup>3</sup>*J*<sub>HH</sub>=8.3; H<sub>3</sub>), 6.95 (d, 4H, <sup>3</sup>*J*<sub>HH</sub>=8.3; H<sub>4</sub>), 6.81 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.5; H<sub>5</sub>), 3.87 (s, 6H; -OCH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 158.0(C<sub>Pym</sub>), 156.2(C<sub>Pym</sub>), 138.7(C<sub>quat</sub>), 137.5 (C<sub>quat</sub>), 135.4(C<sub>quat</sub>), 133.4(C<sub>quat</sub>), 133.3(C<sub>quat</sub>), 133.2 (C<sub>quat</sub>), 130.9(C<sub>Ar</sub>), 129.9(C<sub>quat</sub>), 129.7 (C<sub>quat</sub>), 127.9(C<sub>Ar</sub>), 127.5(C<sub>Ar</sub>), 124.0(C<sub>Ar</sub>), 114.4(C<sub>Ar</sub>), 55.2(OMe).

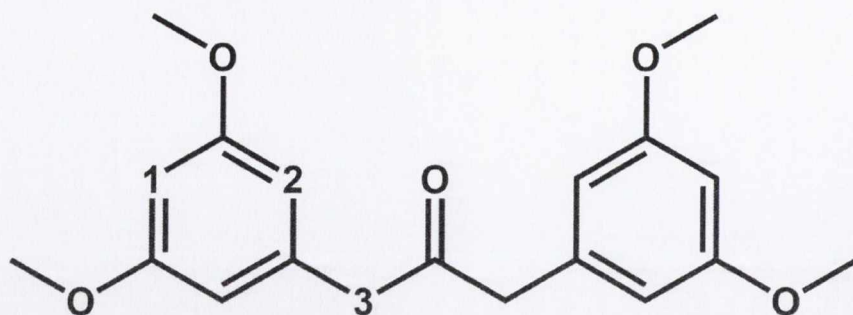
**ESI-MS** (CH<sub>3</sub>CN): calculated for C<sub>38</sub>H<sub>27</sub>N<sub>4</sub>O<sub>2</sub>, [M+Na]<sup>+</sup> *m/z* 571.2134, found 571.2155.

**Elemental analysis** (C<sub>38</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>): Calcd (%):C, 79.98; H, 4.59; N, 9.82. Found (%): C, 78.96.; H, 4.51; N, 9.00

**IR** (neat) ν = 2955(-CH<sub>methyl</sub>), 1580(C<sub>aromatic</sub>), 1547, 1510, 1461, 1402, 1362, 1267, 1181, 1117, 1014, 916, 824, 779 and 732 cm<sup>-1</sup>

**m.p.:** > 300°C

## 7.2.14 1,3-bis(3,5-dimethoxyphenyl)propan-2-one (71)



Ca(OH)<sub>2</sub> (3.20 g, 43.2 mmol, 4 eq) and Bu<sub>4</sub>NHSO<sub>4</sub> (1.83 g, 5.4 mmol, 0.5 eq) were dissolved in 1:1 dichloromethane:water (240 mL) and stirred. 3,5-dimethoxybenzyl bromide (5.00 g, 21.6 mmol, 2 eq) was added followed by Fe(CO)<sub>5</sub> (2.12 g, 10.8 mmol, 1 eq) and the reaction mixture was stirred at room temperature for 72 h with a constant stream of argon circulated over the reaction. The reaction mixture was oxidized in air and acidified with 10% HCl solution. The aqueous phase was extracted with dichloromethane and the organic washings combined and reduced to yellow oil. Chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a light yellow solid.

**Yield:** 2.53 g, 71 %.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub> δ in ppm): 6.39 (t, 2H, <sup>4</sup>J<sub>HH</sub>=2.0; H<sub>1</sub>), 6.33 (d, 4H, <sup>4</sup>J<sub>HH</sub>=2.0; H<sub>2</sub>), 3.67 (s, 4H; H<sub>3</sub>), 3.78 (s, 12H; -OCH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub> δ in ppm): 204.9 (C=O), 160.5 (C-OMe), 135.6 (C<sub>quat</sub>), 107.1 (C<sub>Ar</sub>), 98.7 (C<sub>Ar</sub>), 54.8 (OCH<sub>3</sub>), 48.8 (CH<sub>2</sub>).

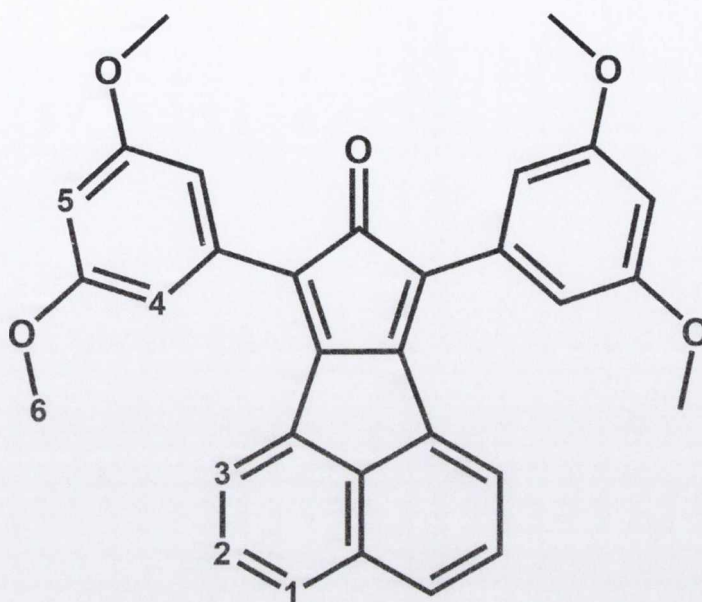
**ESI-MS** (CH<sub>3</sub>CN): calculated for C<sub>19</sub>H<sub>22</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup> *m/z* 353.1365, found 353.1376.

**Elemental analysis** calc (%) for C<sub>19</sub>H<sub>22</sub>O<sub>5</sub>: C, 69.07; H, 6.71; found: C, 68.52; H, 6.72

**IR** (neat): ν = 2941, 1712, 1607, 1587, 1431, 1306, 1208, 1148, 1054 and 818 cm<sup>-1</sup>.



## 7.2.15 7,9-bis-(3,5-dimethoxyphenyl)-8H-cyclopenta[1]acenaphthylen-8-one (72)



Acenaphthenequinone (151.5 mg, 0.823 mmol, 1 eq), 1,3-bis-(3,5-dimethoxyphenyl)-propan-2-one (**71**) (275 mg, 0.832 mmol, 1 eq) and KOH (23 mg, 0.412 mmol, 0.5 eq) were refluxed in ~ 10 mL ethanol for 45 min. The resulting purple precipitate **72** was cooled in ice, filtered, washed with cold ethanol and dried in vacuum. An analytical sample was crystallised from dichloromethane/methanol.

**Yield:** 268 mg, 62 %

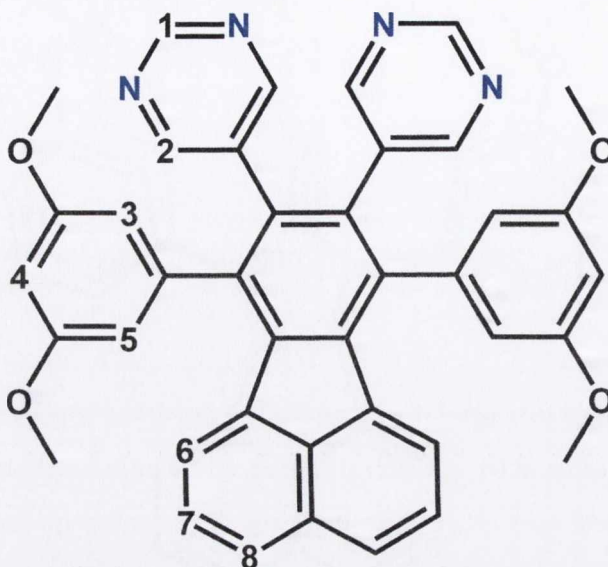
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.12 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=6.5; H<sub>1</sub>), 7.88 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.0; H<sub>3</sub>), 7.61 (t, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.2; H<sub>3</sub>), 7.01 (d, 4H, <sup>4</sup>*J*<sub>HH</sub>=2.0; H<sub>4</sub>), 6.55 (t, 2H, <sup>4</sup>*J*<sub>HH</sub>=2.0; H<sub>5</sub>), 3.89 (s, 12H; -OCH<sub>3</sub>)

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 186.6 (C=O), 160.4(C<sub>quat</sub>), 153.9(C<sub>quat</sub>), 144.4 (C<sub>quat</sub>), 132.6(C<sub>quat</sub>), 131.7(C<sub>quat</sub>), 130.9(C<sub>quat</sub>), 130.5(C<sub>Ar</sub>), 127.4(C<sub>Ar</sub>), 121.2(C<sub>quat</sub>), 120.9(C<sub>Ar</sub>), 106.6(C<sub>Ar</sub>), 100.6(C<sub>Ar</sub>), 55.1(OMe)

**IR** (neat): ν = 2958, 1697, 1590, 1447, 1419, 1260, 1192, 1148, 1060, 840, 823 and 777 cm<sup>-1</sup>.

**ESI-MS** (CH<sub>3</sub>OH): calculated for C<sub>31</sub>H<sub>25</sub>O<sub>5</sub> [M+H]<sup>+</sup> *m/z* 477.1702, found 477.1716.

## 7.2.16 5,5'-(7,10-bis(3,5-dimethoxyphenyl)fluoranthene-8,9-diyl)dipyrimidine (76)



1,2-di(pyrimidin-5-yl)ethyne (41 mg, 0.229 mmol, 1 eq), 7,9-bis-(3,5-dimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (105.45 mg, 0.229 mmol, 1 eq) and benzophenone (400 mg) were heated at 330 °C for 12 h. Chromatography (SiO<sub>2</sub>, ethyl acetate) gave the product as a white solid.

**Yield:** 121.3 mg, 84 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.83 (s, 2H; H<sub>1</sub>), 8.39 (s, 4H; H<sub>2</sub>), 7.84 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.1; H<sub>8</sub>), 7.42 (t, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.75; H<sub>7</sub>), 6.93 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.0; H<sub>6</sub>), 6.47 (d, 4H, <sup>3</sup>*J*<sub>HH</sub>=1.3; H<sub>3,5</sub>), 6.45 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=1.4; H<sub>4</sub>), 3.72 (s, 12H; -OCH<sub>3</sub>)

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 160.8(C<sub>Pym</sub>), 157.7(C<sub>Pym</sub>), 156.0(C<sub>quat/Ar</sub>), 139.2(C<sub>quat/Ar</sub>), 137.6(C<sub>quat/Ar</sub>), 137.1(C<sub>quat/Ar</sub>), 134.5(C<sub>quat/Ar</sub>), 132.1(C<sub>quat/Ar</sub>), 129.2(C<sub>quat/Ar</sub>), 127.9(C<sub>quat/Ar</sub>), 127.2(C<sub>quat/Ar</sub>), 123.9(C<sub>Ar</sub>), 107.3(C<sub>Ar</sub>), 99.5(C<sub>Ar</sub>), 55.1(OCH<sub>3</sub>).

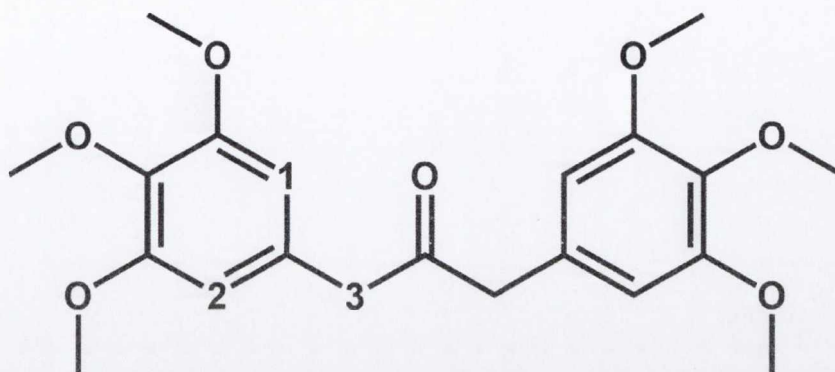
**ESI-MS** (CH<sub>3</sub>OH): calculated for C<sub>40</sub>H<sub>31</sub>N<sub>4</sub>O<sub>4</sub> [M+H]<sup>+</sup> *m/z* 631.2345, found 631.2325.

**Elemental analysis** (C<sub>40</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>): Calcd(%):C, 76.18; H, 4.79; N, 8.88; Found (%): C, 73.20; H, 4.70; N, 8.19.

**IR** (neat) ν = 2954(-CH<sub>3</sub> methyl), 1576(C<sub>aromatic</sub>), 1548, 1513, 1462, 1407, 1361, 1269, 1185, 1117, 1014, 916, 827, 775 and 756 cm<sup>-1</sup>

**m.p.:** > 300°C

## 7.2.17 1,3-bis(3,4,5-trimethoxyphenyl)propan-2-one (60)



Ca(OH)<sub>2</sub> (2.96 g, 40.0 mmol, 4 eq) and Bu<sub>4</sub>NHSO<sub>4</sub> (1.7 g, 5.0 mmol, 0.5 eq) were dissolved in 1:1 dichloromethane:water (200 mL) and stirred. 3,4,5-trimethoxybenzyl bromide (5.22 g, 20.0 mmol, 2 eq) was added followed by Fe(CO)<sub>5</sub> (1.96 g, 10.0 mmol, 1 eq) and the reaction mixture was stirred at room temperature for 6 h with a constant stream of argon circulated over the reaction. The reaction mixture was oxidized in air and acidified with 10 % HCl solution. The aqueous phase was extracted with dichloromethane and the organic washings combined and reduced to yellow oil. Chromatography (SiO<sub>2</sub>, 2:1 ethyl acetate: hexane) gave the product as a pale yellow oil which crystallises on standing.

**Yield:** 2.26 g, 58 %.

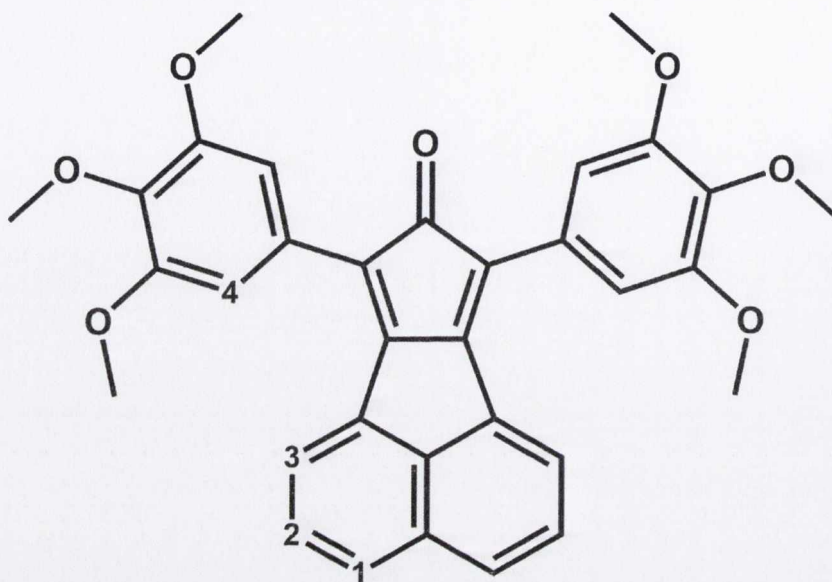
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 6.33 (s, 4H; H<sub>1,2</sub>), 3.67 (s, 4H; H<sub>3</sub>), 3.82 (s, 6H; -OCH<sub>3</sub>), 3.80 (s, 12H; -OCH<sub>3</sub>)

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 205.4(C=O), 152.9(C-OMe), 136.6(C-OMe), 128.6(C<sub>quat</sub>), 106.0(C<sub>Ar</sub>), 60.4(-OCH<sub>3</sub>), 55.6(-OCH<sub>3</sub>), 48.9(CH<sub>2</sub>).

**ESI-MS** (CH<sub>3</sub>OH): calculated for C<sub>21</sub>H<sub>27</sub>O<sub>7</sub> [M+H]<sup>+</sup> *m/z* 391.1757, found 391.1768.



## 7.2.18 7,9-bis-(3,4,5-trimethoxyphenyl)-8H-cyclopenta[l]acenaphthylen-8-one (63)



Acenaphthenequinone (536 mg, 2.940 mmol, 1 eq), 1,3-bis-(3,4,5-trimethoxyphenyl)-propan-2-one **60** (1.147 g, 2.940 mmol, 1eq) and KOH (302 mg, 5.38 mmol, 0.5 eq) were refluxed in ~10 mL ethanol for 45 min. The green precipitate was filtered off. Chromatography (SiO<sub>2</sub>, 20:1 dichloromethane: methanol) gave the product as a green solid.

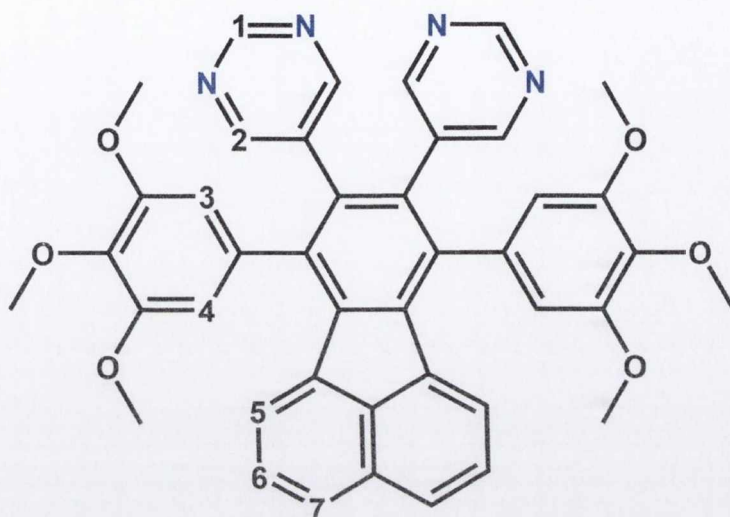
**Yield:** 897.15 g, 65 %.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.15 (d, 2H, <sup>3</sup>J<sub>HH</sub>=7.0; H<sub>1</sub>), 7.91 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8.5; H<sub>3</sub>), 7.64 (t, 2H, <sup>3</sup>J<sub>HH</sub>=7.0, <sup>3</sup>J<sub>HH</sub>=8.5; H<sub>2</sub>), 7.10 (s, 4H; H<sub>4</sub>), 3.97 (s, 12H; -OCH<sub>3</sub>), 3.96 (s, 6H; -OCH<sub>3</sub>);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 171.4 (C=O), 153.2 (C<sub>quat</sub>), 152.9 (C<sub>quat</sub>), 144.4 (C<sub>quat</sub>), 138.0 (C<sub>quat</sub>), 131.8 (C<sub>quat</sub>), 131.1 (C<sub>quat</sub>), 128.0 (C<sub>Ar</sub>), 127.3 (C<sub>Ar</sub>), 126.3 (C<sub>quat</sub>), 121.0 (C<sub>quat</sub>), 120.4 (C<sub>Ar</sub>), 105.8 (C<sub>Ar</sub>), 60.6 (OMe), 55.9 (OMe).

**ESI-MS** (CH<sub>3</sub>OH): calculated for C<sub>33</sub>H<sub>29</sub>O<sub>7</sub> [M+H]<sup>+</sup> *m/z* 537.1913, found 537.1919.

## 7.2.19 5,5'-(7,10-bis(3,4,5-trimethoxyphenyl)fluoranthene-8,9-diyl)dipyrimidine (77)



1,2-di(pyrimidin-5-yl)ethyne (39 mg, 0.216 mmol, 1 eq), 7,9-bis(3,4,5-trimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (116 mg, 0.216 mmol, 1eq) and benzophenone (600 mg) were heated at 350 °C for 6 h. Chromatography (SiO<sub>2</sub>, ethyl acetate) gave the product as a white solid.

**Yield:** 80 mg, 54 %

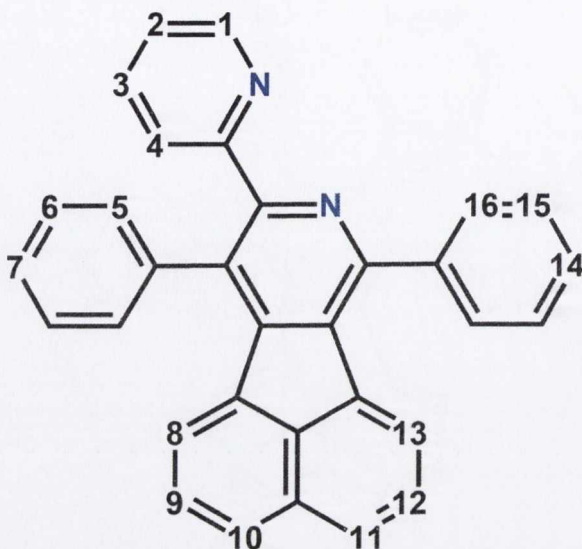
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.89 (s, 2H; H<sub>1</sub>), 8.44 (s, 4H; H<sub>2</sub>), 7.90 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.0; H<sub>7</sub>), 7.46 (t, 2H, <sup>3</sup>*J*<sub>HH</sub>=8.1; H<sub>6</sub>), 6.97 (d, 2H, <sup>3</sup>*J*<sub>HH</sub>=7.0; H<sub>5</sub>), 6.55 (s, 4H; H<sub>3,4</sub>), 3.92 (s, 6H; -OCH<sub>3</sub>), 3.75 (s, 12H; -OCH<sub>3</sub>).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>, δ in ppm): 157.6(C<sub>Pym</sub>), 156.4(C<sub>Pym</sub>), 153.7(C<sub>quat</sub>), 138.4 (C<sub>quat</sub>), 137.7(C<sub>quat</sub>), 134.9(C<sub>quat</sub>), 133.3(C<sub>quat</sub>), 133.0(C<sub>quat</sub>), 132.8(C<sub>quat</sub>), 129.7(C<sub>quat</sub>), 128.1(C<sub>Ar</sub>), 127.9(C<sub>Ar</sub>), 124.3(C<sub>Ar</sub>), 106.6(C<sub>Ar</sub>), 106.81(C<sub>Ar</sub>), 61.29(OCH<sub>3</sub>), 56.25(OCH<sub>3</sub>).

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>42</sub>H<sub>35</sub>N<sub>4</sub>O<sub>6</sub> [M+H]<sup>+</sup> *m/z* 690.2478, found 690.2466.

**m.p.:** > 300°C

## 7.2.20 7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (88)



2-pyridinecarbonitrile (1.25g, 12 mmol, 10 eq), and 7,9-diphenyl-8H-cyclopenta[1]acenaphthylen-8-one (428 mg, 1.20 mmol, 1 eq) were heated at 295 °C for 12 h under argon. The brown precipitate was purified in steps, first dichloromethane:methanol(9:1) and second diethyl ether (100%) chromatography gave the product as a pale yellow solid.

**Yield:** 306 mg, 59 %.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.54(d, 1H; <sup>3</sup>J<sub>HH</sub> = 4.68 Hz, H<sub>1</sub>), 7.96 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 6.87 Hz, H<sub>16</sub>), 7.91(d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.15 Hz, H<sub>10</sub>), 7.87 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.12 Hz, H<sub>11</sub>), 7.61-7.57 (m, 5H, H<sub>13</sub>, H<sub>14</sub>, H<sub>15</sub> and H<sub>3</sub>), 7.53-7.50(m, 2H, H<sub>12</sub> and H<sub>4</sub>), 7.46-7.41 (m, 6H, H<sub>5</sub>, H<sub>6</sub>, H<sub>7</sub> and H<sub>9</sub>), 7.14 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 5.83 Hz, H<sub>2</sub>) and 7.02 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.13 Hz, H<sub>8</sub>).

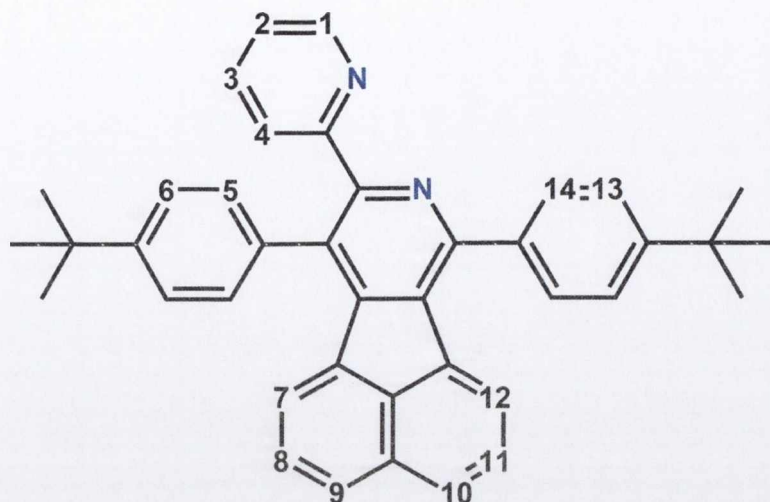
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>, δ in ppm): 158.2 (C<sub>quat</sub>), 153.9(C<sub>quat</sub>), 148.7(C<sub>quat</sub>), 146.3(C<sub>Ar</sub>), 140.3(C<sub>quat</sub>), 137.6(C<sub>quat</sub>), 135.7(C<sub>Ar</sub>), 134.6(C<sub>quat</sub>), 134.2(C<sub>quat</sub>), 133.0(C<sub>quat</sub>), 131.2(C<sub>quat</sub>), 131.0(C<sub>quat</sub>), 130.0(C<sub>quat</sub>), 129.8(C<sub>Ar</sub>), 129.2(C<sub>quat</sub>), 128.9(C<sub>Ar</sub>), 128.7 (C<sub>Ar</sub>), 128.6 (C<sub>Ar</sub>), 128.5(C<sub>Ar</sub>), 127.9(C<sub>Ar</sub>), 127.8(C<sub>Ar</sub>), 127.6 (C<sub>Ar</sub>), 127.5(C<sub>Ar</sub>), 125.3(C<sub>Ar</sub>), 125.9(C<sub>Ar</sub>), 123.9 (C<sub>Ar</sub>), 122.1(C<sub>Ar</sub>)

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>32</sub>H<sub>21</sub>N<sub>2</sub> [M+H]<sup>+</sup> *m/z* 433.1705, found 433.1706

**m.p.:** > 300°C.

**IR** (neat) ν = 3006, 1586, 1475, 1422, 1402, 1276, 1261, 828, 766, 749, 704 cm<sup>-1</sup>.



7.2.21 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (89)

2-pyridinecarbonitrile (520 mg, 5.0 mmol, 10 eq) and 7,9-bis(4-*tert*-butylphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (235 mg, 0.5 mmol, 1 eq) were heated at 300 °C, under nitrogen for 10 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using diethyl ether gave the ligand as a pale yellow solid.

**Yield:** 133 mg, 48 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.67 (br, m, 1H, H<sub>1</sub>), 8.00 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.63 Hz, H<sub>14</sub>), 7.92 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.16 Hz, H<sub>9</sub>), 7.88 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.13 Hz, H<sub>10</sub>), 7.77 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 6.88 Hz, H<sub>12</sub>), 7.62 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.12 Hz; H<sub>13</sub>), 7.55 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7.67 Hz; H<sub>3</sub> and H<sub>11</sub>), 7.49-7.45 (m, 3H, <sup>3</sup>J<sub>HH</sub> = 6.63 Hz; H<sub>6</sub> and H<sub>8</sub>), 7.41 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.26 Hz; H<sub>4</sub>), 7.39 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.22 Hz; H<sub>5</sub>), 7.22(m, 1H, H<sub>2</sub>), 7.03 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 6.14 Hz; H<sub>7</sub>), 1.45 (s, 9H, <sup>t</sup>Bu) and 1.42 (s, 9H, <sup>t</sup>Bu).

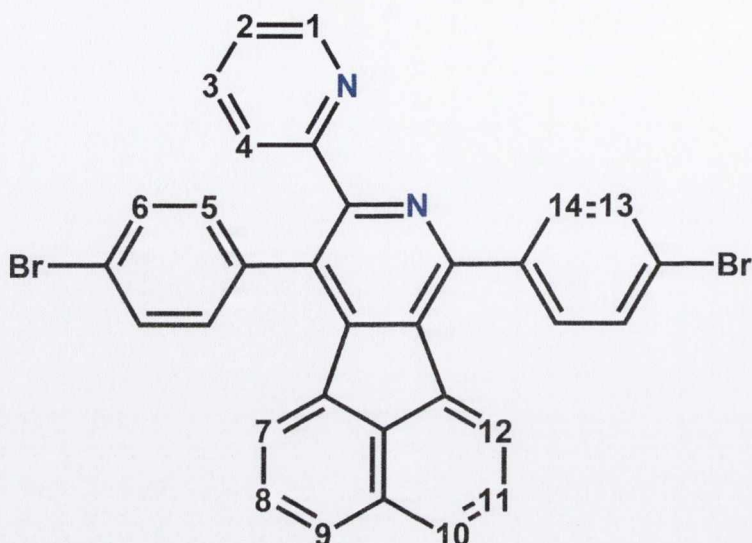
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>, δ in ppm): 158.5 (C<sub>quat</sub>), 155.1(C<sub>quat</sub>), 153.8 (C<sub>quat</sub>), 151.7(C<sub>quat</sub>), 150.6(C<sub>quat</sub>), 148.7(C<sub>Ar</sub>), 146.3(C<sub>quat</sub>), 137.4(C<sub>quat</sub>), 135.3(C<sub>Ar</sub>), 134.8(C<sub>quat</sub>), 134.5(C<sub>quat</sub>), 134.4(C<sub>quat</sub>), 133.0 (C<sub>quat</sub>), 131.0(C<sub>quat</sub>), 130.8(C<sub>quat</sub>), 129.8(C<sub>quat</sub>), 129.6(C<sub>Ar</sub>), 128.8(C<sub>Ar</sub>), 128.7(C<sub>Ar</sub>), 127.9(C<sub>Ar</sub>), 127.7(C<sub>Ar</sub>), 127.3(C<sub>Ar</sub>), 125.4(C<sub>Ar</sub>), 125.3(C<sub>Ar</sub>), 125.2(C<sub>Ar</sub>), 125.0 (C<sub>Ar</sub>), 123.8(C<sub>Ar</sub>), 121.9 (C<sub>Ar</sub>), 34.8(C<sub>t-butyl</sub>), 34.6(C<sub>t-butyl</sub>) and 31.4(C<sub>t-butyl</sub>).

**m.p.:** > 300°C.

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>40</sub>H<sub>37</sub>N<sub>2</sub>[M+H]<sup>+</sup> *m/z* 545.2957, found 545.2966

**IR** (neat): ν = 2958, 1701, 1473, 1360, 1271, 1130, 840, 825 and 773 cm<sup>-1</sup>

## 7.2.22 7,10-di(4-bromophenyl)-9-(2-pyridyl)-8-azafluoranthene (91)



2-pyridinecarbonitrile (406 mg, 3.9 mmol, 10 eq) and 7,9-bis(4-bromophenyl)-8H-cyclopenta[a]acenaphthylen-8-one (200 mg, 0.39 mmol, 1 eq) were heated at 300 °C, under nitrogen for 7 h. The brown solution was allowed to cool. Chromatography on silica using diethyl ether gave the ligand as a pale yellow solid.

**Yield:** 118 mg, 40%

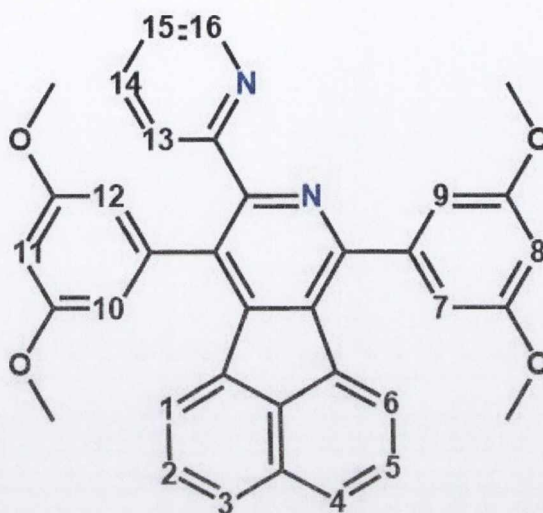
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.58 (br, m, 1H, H<sub>1</sub>), 7.99 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.03 Hz, H<sub>14</sub>), 7.94 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.10 Hz, H<sub>9</sub>), 7.89 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.22 Hz, H<sub>4</sub> and H<sub>10</sub>), 7.78 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.40 Hz, H<sub>12</sub>), 7.69 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.06 Hz; H<sub>13</sub>), 7.61 (m, 2H, H<sub>3</sub> and H<sub>11</sub>), 7.59-7.48 (m, 3H, H<sub>6</sub> and H<sub>8</sub>), 7.37 (m, 2H, H<sub>5</sub>), 7.25 (m, 1H, H<sub>2</sub>), 7.07 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.01 Hz; H<sub>7</sub>)

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>, δ in ppm): 152.1(C<sub>quat</sub>), 148.2(C<sub>quat</sub>), 146.0(C<sub>quat</sub>), 138.4(C<sub>quat</sub>), 136.0(C<sub>quat</sub>), 135.8(C<sub>quat</sub>), 133.6(C<sub>quat</sub>), 133.2(C<sub>quat</sub>), 132.5(C<sub>Ar</sub>), 131.4(C<sub>quat</sub>), 131.3(C<sub>quat</sub>), 133.2(C<sub>quat</sub>), 130.5(C<sub>quat</sub>), 129.7(C<sub>quat</sub>), 129.5(C<sub>quat</sub>), 128.9(C<sub>Ar</sub>), 127.6(C<sub>Ar</sub>), 127.4(C<sub>Ar</sub>), 124.9(C<sub>Ar</sub>), 124.6(C<sub>Ar</sub>), 123.5(C<sub>Ar</sub>), 122.8(C<sub>Ar</sub>), 121.9(C<sub>Ar</sub>), 121.5(C<sub>Ar</sub>).

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>32</sub>H<sub>19</sub>N<sub>2</sub>Br<sub>2</sub> [M+H]<sup>+</sup> *m/z* 588.9915, found 588.9913

**m.p.:** > 300°C.

## 7.2.23 7,10-Bis-(3,4,5-trimethoxyphenyl)-9-(2-pyridyl)-8-azafluoranthene (90)



2-pyridinecarbonitrile (541 mg, 5.2 mmol, 10 eq) and 7,9-bis-(3,4,5-trimethoxyphenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (250 mg, 0.52 mmol, 1 eq) were heated at 330 °C, under nitrogen for 6 h. The reddish brown solution was allowed to cool. Chromatography on silica using diethyl ether, followed by ethyl acetate: dichloromethane (8:2) gave the ligand as a pale yellow solid.

**Yield:** 130 mg, 45 %

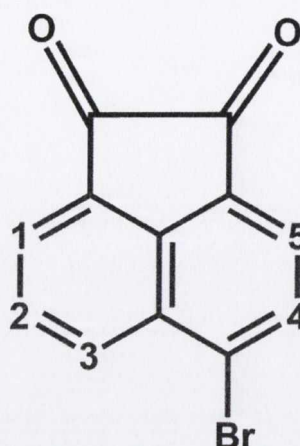
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.65 (br, 1H, H<sub>16</sub>), 7.94(d, 1H, H<sub>1</sub>), 7.88 (d, 1H, H<sub>6</sub>), 7.69 (d, 1H, H<sub>5</sub>), 7.2 (t, 1H, H<sub>14</sub>), 7.57-7.53 (m, 1H, H<sub>4</sub>), 7.51-7.47 (m, 2H, H<sub>2</sub>, H<sub>13</sub>), 7.27 (d, 1H, H<sub>3</sub>), 7.21 (t, 1H, H<sub>15</sub>), 7.10 (br, 1H, H<sub>7,9</sub>), 6.67 (t, 1H, H<sub>8</sub>), 6.63 (d, 2H, H<sub>10,11</sub>), 6.54 (t, 1H, H<sub>11</sub>), 3.89 (s, 6H, OCH<sub>3</sub>), 3.75 (s, 6H; OCH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 161.2(C<sub>quat</sub>), 160.9(C<sub>quat</sub>), 153.8(C<sub>quat</sub>), 148.9(C<sub>quat</sub>), 145.90(C<sub>quat</sub>), 142.9(C<sub>quat</sub>), 142.0(C<sub>quat</sub>), 139.2(C<sub>quat</sub>), 135.8(C<sub>quat</sub>), 134.3(C<sub>quat</sub>), 134.0(C<sub>quat</sub>), 133.0(C<sub>quat</sub>), 133.0(C<sub>quat</sub>), 131.1(C<sub>quat</sub>), 131.0(C<sub>quat</sub>), 129.8(C<sub>quat</sub>), 129.0(C<sub>Ar</sub>), 128.0(C<sub>Ar</sub>), 127.9(C<sub>Ar</sub>), 127.9(C<sub>Ar</sub>), 125.6(C<sub>Ar</sub>), 124.8(C<sub>Ar</sub>), 124.2(C<sub>Ar</sub>), 122.3(C<sub>Ar</sub>), 107.9(C<sub>Ar</sub>), 106.9(C<sub>Ar</sub>), 101.6(C<sub>Ar</sub>), 100.3, 55.4(OCH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 53.3(C<sub>quat</sub>/Ar).

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>36</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> *m/z* 553.2127, found 553.2136



## 7.2.24 5-bromoacenaphthylene-1,2-dione (94)

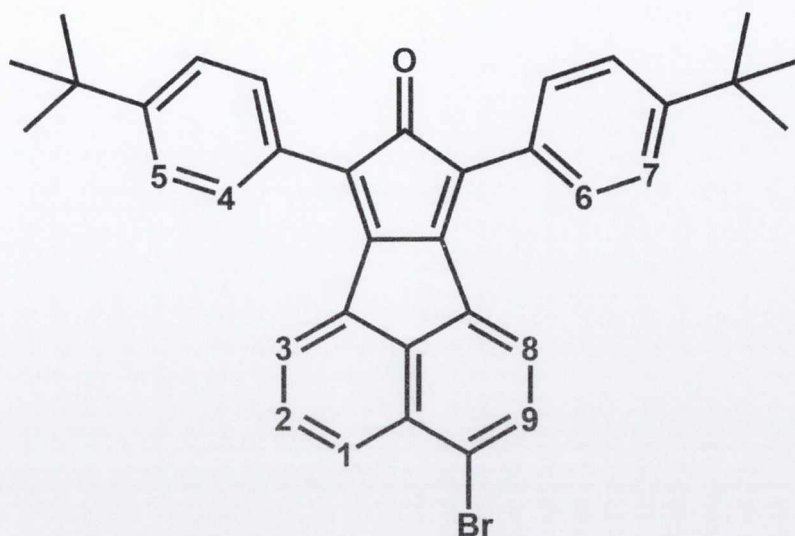


Acenaphthenequinone (1 g, 5.49 mmol, 1 eq) was taken in a 25 mL RBF and Br<sub>2</sub> (0.8 mL, 32.9 mmol, 6 eq) was added using a glass syringe at 0 °C. After connecting the water condenser, the reaction mixture was heated at 70 °C in oil bath. A “U” shaped tube was fixed on the top of condenser to let the HBr flow into the fumehood.

**Yield:** 900 mg; 63 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.52 (d, 1H, <sup>3</sup>J<sub>HH</sub>=8.44; H<sub>1</sub>), 8.19 (d, 1H, <sup>3</sup>J<sub>HH</sub>=6.89; H<sub>5</sub>), 8.13 (d, 1H, <sup>3</sup>J<sub>HH</sub>=7.31; H<sub>3</sub>), 8.00 (d, 2H, <sup>3</sup>J<sub>HH</sub>=7.54; H<sub>2,4</sub>)

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>12</sub>H<sub>6</sub>BrO<sub>2</sub> [M+H]<sup>+</sup> *m/z* 260.954568, found 260.954142

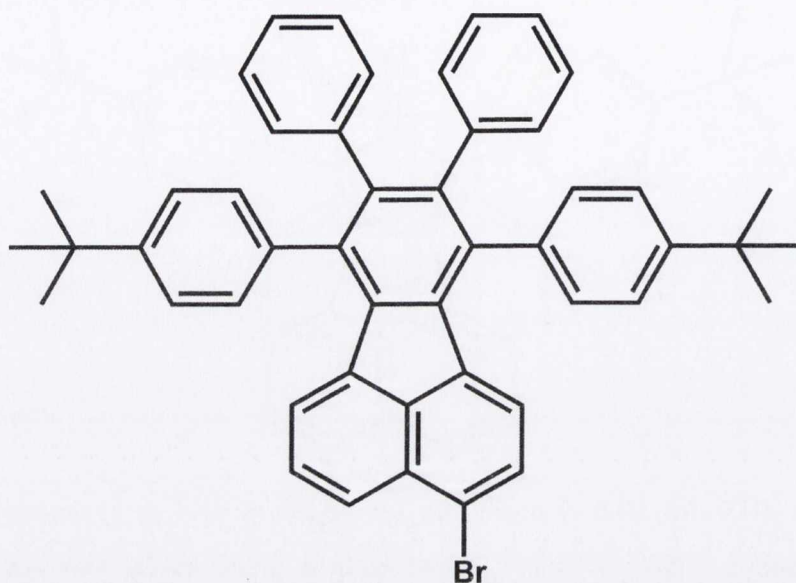
7.2.25 3-bromo-7,9-bis(4-(*tert*-butyl)phenyl)-8H-cyclopenta[a]acenaphthylen-8-one

5-bromoacenaphthylene-1,2-dione (200 mg, 0.766 mmol, 1 eq), 1,3-bis(4-*tert*-butylphenyl)propan-2-one (271.7 mg, 0.842 mmol, 1.1 eq) and NaOH (15 mg, 0.383 mmol, 0.5 eq) were refluxed in ~ 15mL ethanol for 45 min. The resulting purple precipitate was cooled in ice, filtered, washed with cold ethanol and dried in vacuum.

**Yield:** 315 mg; 753 %

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.15 (d, 1H,  $^3J_{\text{HH}} = 7.18$  Hz,  $\text{H}_3$ ), 8.06 (d, 1H,  $^3J_{\text{HH}} = 8.38$  Hz,  $\text{H}_8$ ), 7.94 (d, 1H,  $^3J_{\text{HH}} = 7.69$  Hz,  $\text{H}_1$ ), 7.85 (d, 1H,  $^3J_{\text{HH}} = 7.70$  Hz,  $\text{H}_9$ ), 7.80-7.77(m, 4H,  $\text{H}_4$  and  $\text{H}_6$ ), 7.73-7.70 (m, 2H,  $^3J_{\text{HH}} = 8.0$  Hz,  $\text{H}_2$  and  $\text{H}_9$ ), 7.98 (d, 4H,  $^3J_{\text{HH}} = 7.54$  Hz,  $\text{H}_5$  and  $\text{H}_7$ ) and 1.42 (s, 18H,  $t$ butyl).

**ESI-MS** ( $\text{CH}_2\text{Cl}_2$ ): calculated for  $\text{C}_{35}\text{H}_{32}\text{BrO}$   $[\text{M}+\text{H}]^+$   $m/z$  547.163104, found 547.163871

7.2.26 3-bromo-7,10-bis(4-(*tert*-butyl)phenyl)-8,9-diphenylfluoranthene (95)

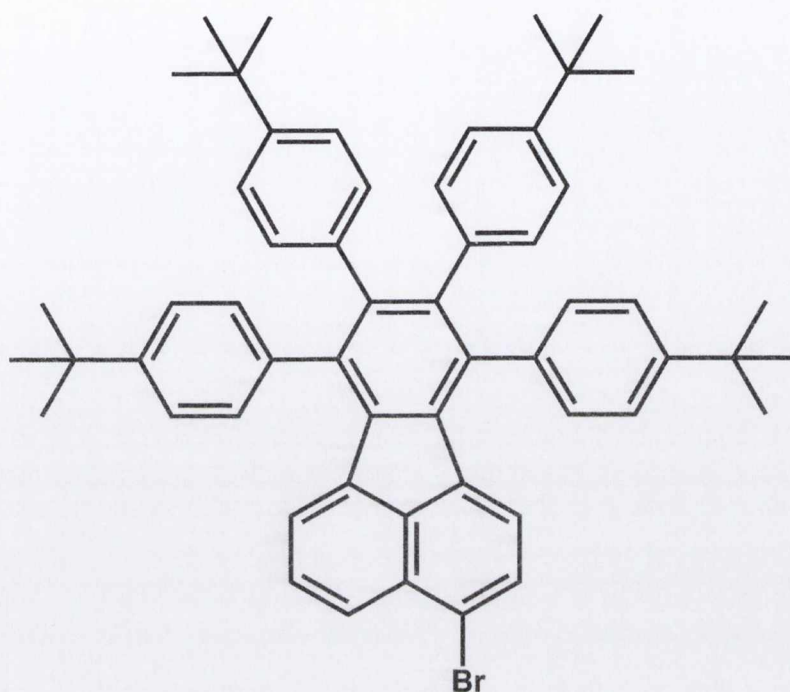
1,2-diphenylethyne (81 mg, 0.456 mmol, 1 eq), 3-bromo-7,9-bis(4-(*tert*-butyl)phenyl)-8H-cyclopenta[a]acenaphthylen-8-one (250 mg, 0.456 mmol, 1 eq) and benzophenone (900 mg) were heated at 300 °C under argon for 8h. After cooling, the reaction mixture was purified by chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a off-white solid.

**Yield:** 241 mg; 76%

**MALDI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>48</sub>H<sub>41</sub>Br [M] *m/z* 696.2392, found 696.2426

**m.p.:** >300 °C



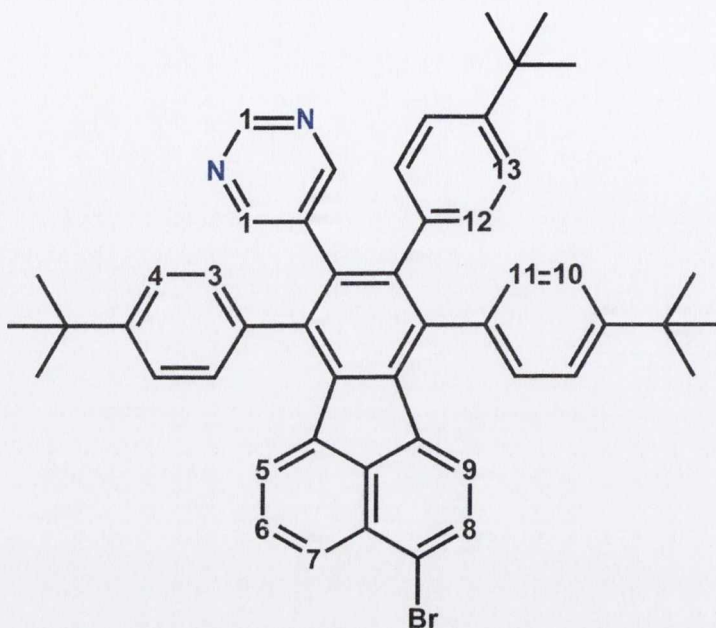
7.2.27 3-bromo-7,8,9, 10-tetrakis (4-*tert*-butylphenyl)fluoranthene (96)

1,2-Bis(4-(*tert*-butyl)phenyl)ethyne (132.6 mg, 0.456 mmol, 1 eq), 3-bromo-7,9-bis(4-(*tert*-butyl)phenyl)-8H-cyclopenta[a]acenaphthylen-8-one (250 mg, 0.456 mmol, 1 eq) and benzophenone (900 mg) were heated at 300 °C under argon for 8h. After cooling, the reaction mixture was purified by chromatography (SiO<sub>2</sub>, diethyl ether) gave the product as a off-white solid.

**Yield:** 266 mg; 72 %

**MALDI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>56</sub>H<sub>57</sub>Br [M] *m/z* 808.3644, found 808.3638

**m.p.:** > 300 °C

7.2.28 5-(3-bromo-7,9,10-tris(4-(*tert*-butyl)phenyl)fluoranthene-8-yl)pyrimidine (98)

5-((4-*tert*-butyl)phenyl)ethynyl)pyrimidine (90 mg, 0.38 mmol, 1.1 eq), 3-bromo-7,9-bis(4-(*tert*-butyl)phenyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (250 mg, 0.456 mmol, 1 eq) and benzophenone (700 mg, 3.841 mmol) were heated at 300 °C under argon for 7 h. After cooling, the reaction mixture was purified by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>:hexane – 1:1) gave the product as a off-white solid.

**Yield:** 210 mg; 61 %

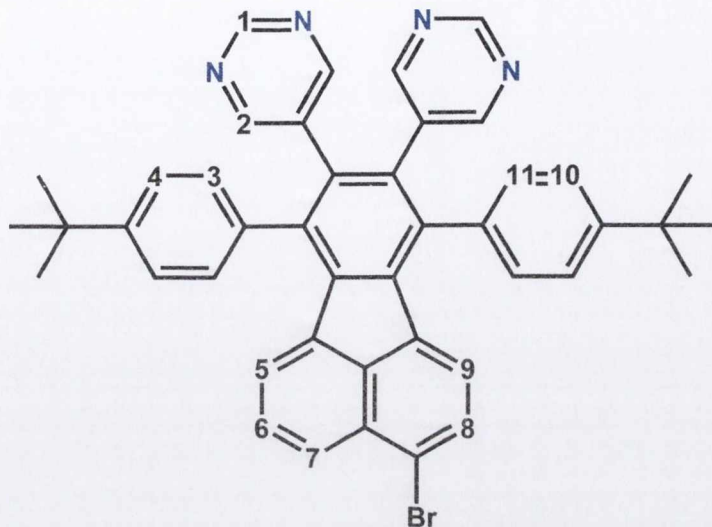
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): δ 8.74(s, 1H, H<sub>1</sub>), 8.34 (s, 2H, H<sub>2</sub>), 7.95(d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 8.0; H<sub>5</sub>), 7.57 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 8.0; H<sub>9</sub>), 7.42-7.40 (m, 5H, H<sub>3,8,11</sub>), 7.32-7.31 (m, 2H, H<sub>6</sub>), 7.25-7.17 (m, 2H, H<sub>13</sub>), 6.95 (d, 2H, H<sub>12</sub>), 6.78-6.44 (m, 5H, H<sub>4,7,10</sub>), 1.37 (s, 9H, -CMe<sub>3</sub>), 1.33 (s, 9H, -CMe<sub>3</sub>), 1.13 (s, 9H, -CMe<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 157.8(C<sub>Pym</sub>), 154.9(C<sub>Pym</sub>), 150.9(C<sub>quat</sub>), 150.1(C<sub>quat</sub>), 148.9(C<sub>quat</sub>), 141.9(C<sub>quat</sub>), 141.8(C<sub>quat</sub>), 138.0(C<sub>quat</sub>), 137.9(C<sub>quat</sub>), 137.4, 137.3(C<sub>quat</sub>), 137.2(C<sub>quat</sub>), 136.5(C<sub>quat</sub>), 136.4(C<sub>quat</sub>), 136.0(C<sub>quat</sub>), 135.9(C<sub>quat</sub>), 135.7(C<sub>quat</sub>), 135.4(C<sub>quat</sub>), 135.3(C<sub>quat</sub>), 135.1(C<sub>quat</sub>), 134.5(C<sub>quat</sub>), 134.4(C<sub>quat</sub>), 131.1(C<sub>Ar</sub>), 130.7(C<sub>Ar</sub>), 129.4(C<sub>Ar</sub>), 128.9(C<sub>Ar</sub>), 126.1(C<sub>Ar</sub>), 126.0(C<sub>Ar</sub>), 125.8(C<sub>Ar</sub>), 124.9(C<sub>Ar</sub>), 124.4(C<sub>Ar</sub>), 124.2(C<sub>Ar</sub>), 124.1(C<sub>Ar</sub>), 124.0(C<sub>Ar</sub>), 123.8(C<sub>Ar</sub>), 123.3(C<sub>quat</sub>), 122.1(C<sub>quat</sub>), 34.6(C<sub>quat</sub>), 34.5(C<sub>quat</sub>), 34.2(C<sub>quat</sub>), 31.3(C<sub>Ar</sub>), 31.0(C<sub>Ar</sub>)

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>50</sub>H<sub>48</sub>BrN<sub>2</sub>[M+H]<sup>+</sup> *m/z* 755.299538, found 755.298835

**m.p.:** > 300 °C

7.2.29 5, 5'-(3-bromo-7,10-bis(4-(*tert*-butyl)phenyl)fluoranthene-8,9-diyl)dipyrimidine  
(99)



1,2-di(pyrimidin-5-yl)ethyne (83.18 mg, 0.456 mmol, 1.1 eq), 3-bromo-7,9-bis(4-(*tert*-butyl)phenyl)-8H-cyclopenta[a]acenaphthylen-8-one (250 mg, 0.456 mmol, 1 eq) and benzophenone (700 mg, 3.841 mmol) were heated at 300 °C under argon for 3 h. After cooling, the reaction mixture was purified by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH – 19:1) gave the product as a off-white solid.

**Yield:** 252.80 mg; 79 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.80 (s, 2H; H<sub>1</sub>), 8.34 (s, 4H; H<sub>2</sub>), 7.98(d, 1H, <sup>3</sup>J<sub>HH</sub>=8.33; H<sub>5</sub>), 7.57 (d, 1H, <sup>3</sup>J<sub>HH</sub>=7.62; H<sub>9</sub>), 7.44-7.41 (m, 5H, H<sub>3,4,6</sub>), 7.23-7.21 (m, 4H, H<sub>10,11</sub>), 6.71(d, 1H, <sup>3</sup>J<sub>HH</sub>=7.62; H<sub>7</sub>), 6.47(d, 1H, <sup>3</sup>J<sub>HH</sub>=7.62; H<sub>8</sub>), 1.32 (s, 9H; <sup>t</sup>Bu).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ in ppm): 157.7(C<sub>Pym</sub>), 156.0(C<sub>Pym</sub>), 151.1(C<sub>quat</sub>), 137.9(C<sub>quat</sub>), 137.8(C<sub>quat</sub>), 137.7(C<sub>quat</sub>), 137.7(C<sub>quat</sub>), 135.6(C<sub>quat</sub>), 135.0(C<sub>quat</sub>), 134.3(C<sub>quat</sub>), 134.2(C<sub>quat</sub>), 131.1(C<sub>Ar</sub>), 129.39(C<sub>Ar</sub>), 129.1(C<sub>Ar</sub>), 129.0(C<sub>Ar</sub>), 128.8(C<sub>Ar</sub>), 126.5(C<sub>Ar</sub>), 125.8(C<sub>Ar</sub>), 124.5(C<sub>Ar</sub>), 124.3(C<sub>Ar</sub>), 122.7(C<sub>quat</sub>), 34.5, 31.1(C<sub>Ar</sub>)

**ESI-MS** (CH<sub>2</sub>Cl<sub>2</sub>): calculated for C<sub>44</sub>H<sub>38</sub>BrN<sub>4</sub>[M+H]<sup>+</sup> *m/z* 701.227436, found 701.225713

**m.p.:** > 300 °C





## 8. References

1. J.-S. Yang and T. M. Swager, *Journal of the American Chemical Society*, 1998, **120**, 11864-11873.
2. J. Yinon, *Forensic and Environmental Detection of Explosives*, Wiley, Chichester, 1999.
3. D. S. Moore, *Review of Scientific Instruments*, 2004, **75**, 2499-2512.
4. M. Nambayah and T. I. Quickenden, *Talanta*, 2004, **63**, 461-467.
5. S. Shanmugaraju and P. S. Mukherjee, *Chemistry – A European Journal*, 2015, **21**, 6656-6666.
6. Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Costero, M. Parra and S. Gil, *Chemical Society Reviews*, 2012, **41**, 1261-1296.
7. R. Schulte-Ladbeck, M. Vogel and U. Karst, *Analytical and Bioanalytical Chemistry*, 2006, **386**, 559-565.
8. L. Senesac and T. G. Thundat, *Materials Today*, 2008, **11**, 28-36.
9. J. I. Steinfeld and J. Wormhoudt, *Annual Review of Physical Chemistry*, 1998, **49**, 203-232.
10. S. Singh, *Journal of Hazardous Materials*, 2007, **144**, 15-28.
11. P. Kolla, *Angewandte Chemie International Edition in English*, 1997, **36**, 800-811.
12. R. L. Woodfin, *Trace Chemical Sensing of Explosives*, John Wiley & Sons, Hoboken, New Jersey, 2007.
13. M. J. Lefferts and M. R. Castell, *Analytical Methods*, 2015, **7**, 9005-9017.
14. M. A. Tarr, *Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications*, MARCELD EKKERIN, C., 1 edn., 2003.
15. L. M. Dorozhkin, V. A. Nefedov, A. G. Sabelnikov and V. G. Sevastjanov, *Sensors and Actuators B: Chemical*, 2004, **99**, 568-570.
16. H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, *Journal of the American Chemical Society*, 2003, **125**, 3821-3830.
17. P.-C. Zhu, L.-N. Luo, P.-Q. Cen, J.-T. Li and C. Zhang, *Tetrahedron Letters*, 2014, **55**, 6277-6280.
18. H. Nie, Y. Lv, L. Yao, Y. Pan, Y. Zhao, P. Li, G. Sun, Y. Ma and M. Zhang, *Journal of Hazardous Materials*, 2014, **264**, 474-480.
19. L. Feng, H. Li, Y. Qu and C. Lu, *Chemical Communications*, 2012, **48**, 4633-4635.
20. Z. Naal, J. H. Park, S. Bernhard, J. P. Shapleigh, C. A. Batt and H. D. Abruña, *Analytical Chemistry*, 2002, **74**, 140-148.
21. P. Cooper, *Explosive Engineering*, Wiley-VCH, New York, 1 edn., 1996.
22. J. Akhavan, *Chemistry of Explosives*, Royal Society of Chemistry, Cambridge, 2nd edn., 2004.
23. J. Shen, J. Zhang, Y. Zuo, L. Wang, X. Sun, J. Li, W. Han and R. He, *Journal of Hazardous Materials*, 2009, **163**, 1199-1206.
24. X. Yang, C.-G. Niu, G.-L. Shen and R.-Q. Yu, *Analyst*, 2001, **126**, 349-352.
25. S. J. Toal and W. C. Trogler, *Journal of Materials Chemistry*, 2006, **16**, 2871-2883.
26. J. Yinon, *Analytical Chemistry*, 2003, **75**, 98 A-105 A.
27. J. Y. J. Gardner, *Electronic Noses & Sensors for the Detection of Explosives*, Springer, Warwick, 2006.
28. V. Lopez-Avila and H. H. Hill, *Analytical Chemistry*, 1997, **69**, 289-306.
29. M. E. Walsh, *Talanta*, 2001, **54**, 427-438.



30. H. H. Hill and G. Simpson, *Field Analytical Chemistry & Technology*, 1997, **1**, 119-134.
31. H.-X. Zhang, J.-S. Hu, C.-J. Yan, L. Jiang and L.-J. Wan, *Physical Chemistry Chemical Physics*, 2006, **8**, 3567-3572.
32. Q. Lu, G. E. Collins, M. Smith and J. Wang, *Analytica Chimica Acta*, 2002, **469**, 253-260.
33. R. Yatabe, T. Onodera and K. Toko, *Frontiers in Bioengineering and Biotechnology*, 2014, **2**, 10.
34. M. E. Germain and M. J. Knapp, *Chemical Society Reviews*, 2009, **38**, 2543-2555.
35. P. T. Charles, A. A. Adams, P. B. Howell, S. A. Trammell, J. R. Deschamps and A. W. Kusterbeck, *Sensors (Basel, Switzerland)*, 2010, **10**, 876-889.
36. H. Tong, L. Wang, X. Jing and F. Wang, *Macromolecules*, 2003, **36**, 2584-2586.
37. A. Ding, L. Yang, Y. Zhang, G. Zhang, L. Kong, X. Zhang, Y. Tian, X. Tao and J. Yang, *Chemistry – A European Journal*, 2014, **20**, 12215-12222.
38. T. L. Andrew and T. M. Swager, *Journal of the American Chemical Society*, 2007, **129**, 7254-7255.
39. T. W. Bell and N. M. Hext, *Chemical Society Reviews*, 2004, **33**, 589-598.
40. E. M. Nolan and S. J. Lippard, *Chemical Reviews*, 2008, **108**, 3443-3480.
41. D. Samanta, S. Shanmugaraju, S. A. Joshi, Y. P. Patil, M. Nethaji and P. S. Mukherjee, *Chemical Communications*, 2012, **48**, 2298-2300.
42. S. Shanmugaraju, A. K. Bar, K.-W. Chi and P. S. Mukherjee, *Organometallics*, 2010, **29**, 2971-2980.
43. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, Maryland, 3rd edn., 2006.
44. G. He, N. Yan, J. Yang, H. Wang, L. Ding, S. Yin and Y. Fang, *Macromolecules*, 2011, **44**, 4759-4766.
45. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angewandte Chemie International Edition*, 2013, **52**, 2881-2885.
46. D. Dinda, A. Gupta, B. K. Shaw, S. Sadhu and S. K. Saha, *ACS Applied Materials & Interfaces*, 2014, **6**, 10722-10728.
47. E. R. Goldman, I. L. Medintz, J. L. Whitley, A. Hayhurst, A. R. Clapp, H. T. Uyeda, J. R. Deschamps, M. E. Lassman and H. Mattoussi, *Journal of the American Chemical Society*, 2005, **127**, 6744-6751.
48. J. R. Cox, P. Müller and T. M. Swager, *Journal of the American Chemical Society*, 2011, **133**, 12910-12913.
49. M. K. Seery, N. Fay, T. McCormac, E. Dempsey, R. J. Forster and T. E. Keyes, *Physical Chemistry Chemical Physics*, 2005, **7**, 3426-3433.
50. D. A. Olley, E. J. Wren, G. Vamvounis, M. J. Fernée, X. Wang, P. L. Burn, P. Meredith and P. E. Shaw, *Chemistry of Materials*, 2011, **23**, 789-794.
51. V. Bhalla, S. Kaur, V. Vij and M. Kumar, *Inorganic Chemistry*, 2013, **52**, 4860-4865.
52. Z. Ding, Q. Zhao, R. Xing, X. Wang, J. Ding, L. Wang and Y. Han, *Journal of Materials Chemistry C*, 2013, **1**, 786-792.
53. M. E. Germain and M. J. Knapp, *Journal of the American Chemical Society*, 2008, **130**, 5422-5423.
54. K. K. Kartha, S. S. Babu, S. Srinivasan and A. Ajayaghosh, *Journal of the American Chemical Society*, 2012, **134**, 4834-4841.
55. K. K. Kartha, A. Sandeep, V. C. Nair, M. Takeuchi and A. Ajayaghosh, *Physical Chemistry Chemical Physics*, 2014, **16**, 18896-18901.
56. S. K. Kim, J. M. Lim, T. Pradhan, H. S. Jung, V. M. Lynch, J. S. Kim, D. Kim and J. L. Sessler, *Journal of the American Chemical Society*, 2014, **136**, 495-505.



57. T. Naddo, Y. Che, W. Zhang, K. Balakrishnan, X. Yang, M. Yen, J. Zhao, J. S. Moore and L. Zang, *Journal of the American Chemical Society*, 2007, **129**, 6978-6979.
58. N. Niamnont, N. Kimpitak, K. Wongravee, P. Rashatasakhon, K. K. Baldrige, J. S. Siegel and M. Sukwattanasinitt, *Chemical Communications*, 2013, **49**, 780-782.
59. P. E. Shaw, S. S. Y. Chen, X. Wang, P. L. Burn and P. Meredith, *The Journal of Physical Chemistry C*, 2013, **117**, 5328-5337.
60. C. Zhang, Y. Che, X. Yang, B. R. Bunes and L. Zang, *Chemical Communications*, 2010, **46**, 5560-5562.
61. G. V. Zyryanov, M. A. Palacios and P. Anzenbacher, *Organic Letters*, 2008, **10**, 3681-3684.
62. S. Rochat and T. M. Swager, *ACS Applied Materials & Interfaces*, 2013, **5**, 4488-4502.
63. D. Zhao and T. M. Swager, *Macromolecules*, 2005, **38**, 9377-9384.
64. S. W. Thomas, G. D. Joly and T. M. Swager, *Chemical Reviews*, 2007, **107**, 1339-1386.
65. A. Dubey, A. Mishra, J. W. Min, M. H. Lee, H. Kim, P. J. Stang and K.-W. Chi, *Inorganica Chimica Acta*, 2014, **423**, Part A, 326-331.
66. S. Shanmugaraju, D. Samanta, B. Gole and P. S. Mukherjee, *Dalton Transactions*, 2011, **40**, 12333-12341.
67. P. J. Stang and B. Olenyuk, *Accounts of Chemical Research*, 1997, **30**, 502-518.
68. B. H. Northrop, Y.-R. Zheng, K.-W. Chi and P. J. Stang, *Accounts of Chemical Research*, 2009, **42**, 1554-1563.
69. D. T. McQuade, A. E. Pullen and T. M. Swager, *Chemical Reviews*, 2000, **100**, 2537-2574.
70. S. W. Thomas Iii, J. P. Amara, R. E. Bjork and T. M. Swager, *Chemical Communications*, 2005, DOI: 10.1039/B508408C, 4572-4574.
71. S. Shanmugaraju and P. S. Mukherjee, *Chemical Communications*, 2015, **51**, 16014-16032.
72. J. V. Goodpaster and V. L. McGuffin, *Analytical Chemistry*, 2001, **73**, 2004-2011.
73. W. Chen, N. B. Zuckerman, J. P. Konopelski and S. Chen, *Analytical Chemistry*, 2010, **82**, 461-465.
74. S. Shanmugaraju, S. A. Joshi and P. S. Mukherjee, *Journal of Materials Chemistry*, 2011, **21**, 9130-9138.
75. N. Venkatramaiah, S. Kumar and S. Patil, *Chemical Communications*, 2012, **48**, 5007-5009.
76. T. Liu, K. Zhao, K. Liu, L. Ding, S. Yin and Y. Fang, *Journal of Hazardous Materials*, 2013, **246-247**, 52-60.
77. D. Udhayakumari, S. Velmathi, P. Venkatesan and S.-P. Wu, *Analytical Methods*, 2015, **7**, 1161-1166.
78. S. Anbu, S. Shanmugaraju, R. Ravishankaran, A. A. Karande and P. S. Mukherjee, *Dalton Transactions*, 2012, **41**, 13330-13337.
79. M. Alfonso, A. Espinosa, A. Tárraga and P. Molina, *ChemistryOpen*, 2014, **3**, 242-249.
80. L. Wenfeng, M. Hengchang and L. Ziqiang, *RSC Advances*, 2014, **4**, 39351-39358.
81. P. B. Pati and S. S. Zade, *Tetrahedron Letters*, 2014, **55**, 5290-5293.
82. A. Chowdhury and P. S. Mukherjee, *The Journal of Organic Chemistry*, 2015, **80**, 4064-4075.
83. M. M. Haley, R. R. Tykwinski and Editors, *Carbon-Rich Compounds: From Molecules to Materials*, Wiley-VCH Verlag GmbH & Co. KGaA, 2006.

84. N. Marinov, W. Pitz, C. Westbrook, M. Castaldi and S. Senkan, *Combustion Science and Technology*, 1996, **116**, 211-287.
85. W. Pisula, X. Feng and K. Muellen, *Chem. Mater.*, 2011, **23**, 554-567.
86. J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science*, 2004, **304**, 1481-1483.
87. H. Seyler, B. Purushothaman, D. J. Jones, A. B. Holmes and W. W. H. Wong, *Pure Appl. Chem.*, 2012, **84**, 1047-1067.
88. *Carbon Rich Compounds*, Springer: Berlin, 1998.
89. K. S. Raja, S. Ramakrishnan and V. A. Raghunathan, *Chemistry of Materials*, 1997, **9**, 1630-1637.
90. V. Vij, V. Bhalla and M. Kumar, *ACS Applied Materials & Interfaces*, 2013, **5**, 5373-5380.
91. Goldschmiedt, *Berichte der Deutschen Chemischen Gesellschaft* 1877, **10**, 2022.
92. F. a. F. Gebhard, F. *Berichte der Deutschen Chemischen Gesellschaft* 1877, **10**, 2141.
93. E. Bergmann and M. Orchin, *Journal of the American Chemical Society*, 1949, **71**, 1917-1918.
94. M. Zhu and C. Yang, *Chem. Soc. Rev.*, 2013, **42**, 4963-4976.
95. Q.-X. Tong, M.-Y. Chan, S.-L. Lai, T.-W. Ng, P.-F. Wang, C.-S. Lee and S.-T. Lee, *Dyes and Pigments*, 2010, **86**, 233-237.
96. L. Wang, Y. Jiang, J. Luo, Y. Zhou, J. Zhou, J. Wang, J. Pei and Y. Cao, *Advanced Materials*, 2009, **21**, 4854-4858.
97. K. Okumoto, H. Kanno, Y. Hamaa, H. Takahashi and K. Shibata, *Applied Physics Letters*, 2006, **89**, 063504.
98. C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *Journal of Applied Physics*, 2001, **90**, 5048-5051.
99. I. Kang, J.-Y. Back, R. Kim, Y.-H. Kim and S.-K. Kwon, *Dyes and Pigments*, 2012, **92**, 588-595.
100. S. Ye, J. Chen, C.-a. Di, Y. Liu, K. Lu, W. Wu, C. Du, Y. Liu, Z. Shuai and G. Yu, *Journal of Materials Chemistry*, 2010, **20**, 3186-3194.
101. T. Qin, W. Wiedemair, S. Nau, R. Trattnig, S. Sax, S. Winkler, A. Vollmer, N. Koch, M. Baumgarten, E. J. W. List and K. Müllen, *Journal of the American Chemical Society*, 2011, **133**, 1301-1303.
102. H. Wettach, S. S. Jester, A. Colsmann, U. Lemmer, N. Rehmann, K. Meerholz and S. Höger, *Synthetic Metals*, 2010, **160**, 691-700.
103. Z. Liu, *Dyes and Pigments*, 2010, **85**, 109-116.
104. Y.-H. Lee, T.-C. Wu, C.-W. Liaw, T.-C. Wen, S.-W. Feng, J.-J. Lee, Y.-T. Wu and T.-F. Guo, *Organic Electronics*, 2013, **14**, 1064-1072.
105. J.-K. Bin and J.-I. Hong, *Organic Electronics*, 2011, **12**, 802-808.
106. J. Wu, W. Pisula and K. Müllen, *Chemical Reviews*, 2007, **107**, 718-747.
107. Y.-H. Lee, T.-C. Wu, C.-W. Liaw, T.-C. Wen, T.-F. Guo and Y.-T. Wu, *Journal of Materials Chemistry*, 2012, **22**, 11032-11038.
108. S. Kumar and S. Patil, *The Journal of Physical Chemistry C*, 2015, **119**, 19297-19304.
109. V. S. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra and K. Müllen, *Angewandte Chemie International Edition in English*, 1997, **36**, 1604-1607.
110. C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, 1952, **17**, 845-854.
111. H. Des Abbayes, J. C. Clement, P. Laurent, G. Tanguy and N. Thilmont, *Organometallics*, 1988, **7**, 2293-2299.
112. S. M. Draper, D. J. Gregg and R. Madathil, *J. Am. Chem. Soc.*, 2002, **124**, 3486-3487.



113. D. J. Gregg, E. Bothe, P. Höfer, P. Passaniti and S. M. Draper, *Inorganic Chemistry*, 2005, **44**, 5654-5660.
114. R. C. Chiechi, R. J. Tseng, F. Marchioni, Y. Yang and F. Wudl, *Advanced Materials*, 2006, **18**, 325-328.
115. D. J. Gregg, *Ph.D. Thesis, University of Dublin, Trinity College*, 2003.
116. B. S. Lankage, *Ph.D. Thesis, University of Dublin, Trinity College*, 2010.
117. S. Nagarajan, C. Barthes and A. Gourdon, *Tetrahedron*, 2009, **65**, 3767-3772.
118. S. M. Draper, D. J. Gregg and R. Madathil, *Journal of the American Chemical Society*, 2002, **124**, 3486-3487.
119. C. F. H. Allen and J. A. VanAllan, *The Journal of Organic Chemistry*, 1952, **17**, 845-854.
120. N. Venkatramaiah, S. Kumar and S. Patil, *Chemistry – A European Journal*, 2012, **18**, 14745-14751.
121. H. B. Kagan and O. Riant, *Chemical Reviews*, 1992, **92**, 1007-1019.
122. Y.-T. Wu, T. Hayama, K. K. Baldridge, A. Linden and J. S. Siegel, *Journal of the American Chemical Society*, 2006, **128**, 6870-6884.
123. S. Amin, G. Balanikas, K. Huie, N. Hussain, J. E. Geddie and S. S. Hecht, *Journal of Organic Chemistry*, 1985, **50**, 4642-4646.
124. J. D. Debad, J. C. Morris, V. Lynch, P. Magnus and A. J. Bard, *Journal of the American Chemical Society*, 1996, **118**, 2374-2379.
125. S. J. Toal, J. C. Sanchez, R. E. Dugan and W. C. Trogler, *Journal of Forensic Sciences*, 2007, **52**, 79-83.
126. M. E. Germain, T. R. Vargo, B. A. McClure, J. J. Rack, P. G. Van Patten, M. Odoi and M. J. Knapp, *Inorganic Chemistry*, 2008, **47**, 6203-6211.
127. A. Narayanan, O. P. Varnavski, T. M. Swager and T. Goodson, *The Journal of Physical Chemistry C*, 2008, **112**, 881-884.
128. X. Sun, Y. Wang and Y. Lei, *Chemical Society Reviews*, 2015, **44**, 8019-8061.
129. B. Gole, A. K. Bar and P. S. Mukherjee, *Chemical Communications*, 2011, **47**, 12137-12139.
130. V. Bhalla, A. Gupta and M. Kumar, *Organic Letters*, 2012, **14**, 3112-3115.
131. F. Terrier, *Chemical Reviews*, 1982, **82**, 77-152.
132. C. Reichardt, M. Eschner and G. Schäfer, *Journal of Physical Organic Chemistry*, 2001, **14**, 737-751.
133. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.
134. R. P. Wayne, *Photochemistry*, Elsevier, Butterworths, London, 1970.
135. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2006, **3rd edition**.
136. C. S. S. Creaser, J. R., *Perspectives in Modern Chemical Spectroscopy*, 1990, 103-136.
137. L. P. Wijesinghe, B. S. Lankage, G. M. O. Maille, S. D. Perera, D. Nolan, L. Wang and S. M. Draper, *Chemical Communications*, 2014, **50**, 10637-10640.
138. L. Ding, H.-B. Li, T. Lei, H.-Z. Ying, R.-B. Wang, Y. Zhou, Z.-M. Su and J. Pei, *Chemistry of Materials*, 2012, **24**, 1944-1949.
139. O. Verho, E. V. Johnston, E. Karlsson and J.-E. Bäckvall, *Chemistry – A European Journal*, 2011, **17**, 11216-11222.
140. S. Chiavarelli, L. V. Fennoy, G. Settimj and L. De Baran, *Journal of Medicinal and Pharmaceutical Chemistry*, 1962, **5**, 1293-1297.
141. J. Luo, X. Xu, R. Mao and Q. Miao, *Journal of the American Chemical Society*, 2012, **134**, 13796-13803.



142. C. Delaney, S. D. Perera, G. M. O. Maille and S. M. Draper, *Chemical Communications*, 2014, **50**, 1599-1601.
143. D. J. Gregg, C. M. A. Ollagnier, C. M. Fitchett and S. M. Draper, *Chemistry – A European Journal*, 2006, **12**, 3043-3052.
144. G. He, H. Peng, T. Liu, M. Yang, Y. Zhang and Y. Fang, *Journal of Materials Chemistry*, 2009, **19**, 7347-7353.
145. M. Shamma, in *The Alkaloids: Volume 6*, ed. M. F. Grundon, The Royal Society of Chemistry, 1976, vol. 6, pp. 170-188.
146. M. P. Cava, K. T. Buck and A. I. DaRocha, *Journal of the American Chemical Society*, 1972, **94**, 5931-5931.
147. D. L. Boger and C. E. Brotherton, *The Journal of Organic Chemistry*, 1984, **49**, 4050-4055.
148. T. Sasaki, K. Kanematsu and T. Hiramatsu, *Journal of the Chemical Society, Perkin Transactions 1*, 1974, DOI: 10.1039/P19740001213, 1213-1215.
149. N. Rahanyan, A. Linden, K. K. Baldridge and J. S. Siegel, *Organic & Biomolecular Chemistry*, 2009, **7**, 2082-2092.
150. S. Ponnala and W. W. Harding, *European Journal of Organic Chemistry*, 2013, **2013**, 1107-1115.
151. N. Khunnawutmanotham, P. Sahakitpichan, N. Chimnoi and S. Techasakul, *European Journal of Organic Chemistry*, 2015, **2015**, 6324-6332.
152. A. Bhattacharjee and J. K. De Brabander, *Tetrahedron Letters*, 2000, **41**, 8069-8073.
153. N. Armaroli, L. De Cola, V. Balzani, J.-P. Sauvage, C. O. Dietrich-Buchecker and J.-M. Kern, *Journal of the Chemical Society, Faraday Transactions*, 1992, **88**, 553-556.
154. N. Kapoor and K. R. J. Thomas, *New Journal of Chemistry*, 2010, **34**, 2739-2748.
155. A. L. Kanibolotsky, I. F. Perepichka and P. J. Skabara, *Chemical Society Reviews*, 2010, **39**, 2695-2728.
156. Rabih O. Al-Kaysi, G. Guirado and Edward J. Valente, *European Journal of Organic Chemistry*, 2004, **2004**, 3408-3411.
157. 2008.
158. *United States Pat.*, US007256921B2, 2007.
159. M. Wehmeier, M. Wagner and K. Müllen, *Chemistry – A European Journal*, 2001, **7**, 2197-2205.
160. C. Delaney, G. M. Ó Máille, B. Twamley and S. M. Draper, *Organic Letters*, 2016, **18**, 88-91.
161. X. Qian, Y. Xiao, Y. Xu, X. Guo, J. Qian and W. Zhu, *Chemical Communications*, 2010, **46**, 6418-6436.
162. S. K. Kim and J. L. Sessler, *Chemical Society Reviews*, 2010, **39**, 3784-3809.
163. A. Ajayaghosh, V. K. Praveen, C. Vijayakumar and S. J. George, *Angewandte Chemie International Edition*, 2007, **46**, 6260-6265.
164. R. Ziessel and A. Harriman, *Chemical Communications*, 2011, **47**, 611-631.
165. T. Weil, E. Reuther and K. Müllen, *Angewandte Chemie International Edition*, 2002, **41**, 1900-1904.
166. C. Trieflinger, H. Röhr, K. Rurack and J. Daub, *Angewandte Chemie International Edition*, 2005, **44**, 6943-6947.
167. C.-S. Chou, R.-Y. Yang, C.-K. Yeh and Y.-J. Lin, *Powder Technology*, 2009, **194**, 95-105.
168. W. Wu, F. Guo, J. Li, J. He and J. Hua, *Synthetic Metals*, 2010, **160**, 1008-1014.
169. X. Ma, W. Wu, Q. Zhang, F. Guo, F. Meng and J. Hua, *Dyes and Pigments*, 2009, **82**, 353-359.

170. Y. Liu, H. Lin, J. T. Dy, K. Tamaki, J. Nakazaki, D. Nakayama, S. Uchida, T. Kubo and H. Segawa, *Chemical Communications*, 2011, **47**, 4010-4012.
171. A. Loudet and K. Burgess, *Chemical Reviews*, 2007, **107**, 4891-4932.
172. J.-J. Lee, S.-C. Lee, D. Zhai, Y.-H. Ahn, H. Y. Yeo, Y. L. Tan and Y.-T. Chang, *Chemical Communications*, 2011, **47**, 4508-4510.
173. T. Kowada, J. Kikuta, A. Kubo, M. Ishii, H. Maeda, S. Mizukami and K. Kikuchi, *Journal of the American Chemical Society*, 2011, **133**, 17772-17776.
174. A. Vázquez-Romero, N. Kielland, M. J. Arévalo, S. Preciado, R. J. Mellanby, Y. Feng, R. Lavilla and M. Vendrell, *Journal of the American Chemical Society*, 2013, **135**, 16018-16021.
175. S. Kolemen, O. A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Gratzel and E. U. Akkaya, *Chemical Science*, 2011, **2**, 949-954.
176. T. Wang, E. F. Douglass, K. J. Fitzgerald and D. A. Spiegel, *Journal of the American Chemical Society*, 2013, **135**, 12429-12433.
177. Y. Kubo, K. Watanabe, R. Nishiyabu, R. Hata, A. Murakami, T. Shoda and H. Ota, *Organic Letters*, 2011, **13**, 4574-4577.
178. S. Madhu, D. K. Sharma, S. K. Basu, S. Jadhav, A. Chowdhury and M. Ravikanth, *Inorganic Chemistry*, 2013, **52**, 11136-11145.
179. P. U. Kurup, *Technologies for Homeland Security, 2008 IEEE Conference on*, 2008, 144-149.



## 9. Annex: Crystal data

Crystal data and structure refinement for **57**

|                                   |                                                |                           |
|-----------------------------------|------------------------------------------------|---------------------------|
| Identification code               | tcd284                                         |                           |
| Empirical formula                 | C <sub>44</sub> H <sub>38</sub> N <sub>4</sub> |                           |
| Formula weight                    | 622.78                                         |                           |
| Temperature                       | 100(2) K                                       |                           |
| Wavelength                        | 0.71073 Å                                      |                           |
| Crystal system                    | Triclinic                                      |                           |
| Space group                       | P $\bar{1}$                                    |                           |
| Unit cell dimensions              | a = 6.2047(3) Å                                | $\alpha$ = 102.3467(14)°. |
|                                   | b = 15.1159(8) Å                               | $\beta$ = 99.0964(14)°.   |
|                                   | c = 19.1649(10) Å                              | $\gamma$ = 100.9755(14)°. |
| Volume                            | 1686.33(15) Å <sup>3</sup>                     |                           |
| Z                                 | 2                                              |                           |
| Density (calculated)              | 1.227 Mg/m <sup>3</sup>                        |                           |
| Absorption coefficient            | 0.072 mm <sup>-1</sup>                         |                           |
| F(000)                            | 660                                            |                           |
| Crystal size                      | 0.500 x 0.110 x 0.040 mm <sup>3</sup>          |                           |
| Theta range for data collection   | 1.418 to 26.397°.                              |                           |
| Index ranges                      | -7 ≤ h ≤ 7, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23         |                           |
| Reflections collected             | 52929                                          |                           |
| Independent reflections           | 6890 [R(int) = 0.0436]                         |                           |
| Completeness to theta = 25.242°   | 100.0 %                                        |                           |
| Absorption correction             | Multi-scan                                     |                           |
| Max. and min. transmission        | 0.7454 and 0.6598                              |                           |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>    |                           |
| Data / restraints / parameters    | 6890 / 0 / 439                                 |                           |
| Goodness-of-fit on F <sup>2</sup> | 1.014                                          |                           |
| Final R indices [I > 2σ(I)]       | R1 = 0.0395, wR2 = 0.0913                      |                           |
| R indices (all data)              | R1 = 0.0582, wR2 = 0.1007                      |                           |
| Largest diff. peak and hole       | 0.237 and -0.202 e.Å <sup>-3</sup>             |                           |



Crystal data and structure refinement for **67**

|                                   |                                                                    |                             |
|-----------------------------------|--------------------------------------------------------------------|-----------------------------|
| Empirical formula                 | $\text{C}_{44}\text{H}_{36}\text{N}_2\text{O}_6$                   |                             |
| Formula weight                    | 688.75                                                             |                             |
| Temperature                       | 99.99 K                                                            |                             |
| Wavelength                        | 1.54178 Å                                                          |                             |
| Crystal system                    | Monoclinic                                                         |                             |
| Space group                       | $P2_1/n$                                                           |                             |
| Unit cell dimensions              | $a = 21.3648(9)$ Å                                                 | $\alpha = 90^\circ$ .       |
|                                   | $b = 15.5441(6)$ Å                                                 | $\beta = 92.698(3)^\circ$ . |
|                                   | $c = 23.5134(9)$ Å                                                 | $\gamma = 90^\circ$ .       |
| Volume                            | $7800.1(5)$ Å <sup>3</sup>                                         |                             |
| Z                                 | 8                                                                  |                             |
| Density (calculated)              | 1.173 Mg/m <sup>3</sup>                                            |                             |
| Absorption coefficient            | 0.631 mm <sup>-1</sup>                                             |                             |
| F(000)                            | 2896                                                               |                             |
| Crystal size                      | 0.27 x 0.04 x 0.04 mm <sup>3</sup>                                 |                             |
| Theta range for data collection   | 2.731 to 68.666°.                                                  |                             |
| Index ranges                      | $-25 \leq h \leq 25$ , $-18 \leq k \leq 18$ , $-26 \leq l \leq 28$ |                             |
| Reflections collected             | 120998                                                             |                             |
| Independent reflections           | 14298 [R(int) = 0.1409]                                            |                             |
| Completeness to theta = 67.679°   | 99.9 %                                                             |                             |
| Absorption correction             | Semi-empirical from equivalents                                    |                             |
| Max. and min. transmission        | 0.7531 and 0.6470                                                  |                             |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                        |                             |
| Data / restraints / parameters    | 14298 / 1 / 824                                                    |                             |
| Goodness-of-fit on F <sup>2</sup> | 1.044                                                              |                             |
| Final R indices [I > 2σ(I)]       | R1 = 0.0785, wR2 = 0.2057                                          |                             |
| R indices (all data)              | R1 = 0.1336, wR2 = 0.2487                                          |                             |
| Extinction coefficient            | 0.00066(9)                                                         |                             |
| Largest diff. peak and hole       | 0.426 and -0.384 e.Å <sup>-3</sup>                                 |                             |

Crystal data and structure refinement for **69**

|                                   |                                                                |                             |
|-----------------------------------|----------------------------------------------------------------|-----------------------------|
| Identification code               | tcd470                                                         |                             |
| Empirical formula                 | C <sub>36</sub> H <sub>20</sub> Br <sub>2</sub> N <sub>4</sub> |                             |
| Formula weight                    | 668.38                                                         |                             |
| Temperature                       | 100.0 K                                                        |                             |
| Wavelength                        | 0.71073 Å                                                      |                             |
| Crystal system                    | Monoclinic                                                     |                             |
| Space group                       | Cc                                                             |                             |
| Unit cell dimensions              | a = 12.1564(6) Å                                               | $\alpha = 90^\circ$ .       |
|                                   | b = 25.3294(12) Å                                              | $\beta = 97.450(2)^\circ$ . |
|                                   | c = 18.0970(9) Å                                               | $\gamma = 90^\circ$ .       |
| Volume                            | 5525.3(5) Å <sup>3</sup>                                       |                             |
| Z                                 | 8                                                              |                             |
| Density (calculated)              | 1.607 Mg/m <sup>3</sup>                                        |                             |
| Absorption coefficient            | 2.969 mm <sup>-1</sup>                                         |                             |
| F(000)                            | 2672                                                           |                             |
| Crystal size                      | 0.22 x 0.16 x 0.07 mm <sup>3</sup>                             |                             |
| Theta range for data collection   | 2.768 to 27.794°.                                              |                             |
| Index ranges                      | -15 ≤ h ≤ 15, -33 ≤ k ≤ 33, -23 ≤ l ≤ 23                       |                             |
| Reflections collected             | 84123                                                          |                             |
| Independent reflections           | 12942 [R(int) = 0.0932]                                        |                             |
| Completeness to theta = 26.000°   | 99.9 %                                                         |                             |
| Absorption correction             | Semi-empirical from equivalents                                |                             |
| Max. and min. transmission        | 0.7456 and 0.6235                                              |                             |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                    |                             |
| Data / restraints / parameters    | 12942 / 2 / 758                                                |                             |
| Goodness-of-fit on F <sup>2</sup> | 1.044                                                          |                             |
| Final R indices [I > 2σ(I)]       | R1 = 0.0446, wR2 = 0.0764                                      |                             |
| R indices (all data)              | R1 = 0.0759, wR2 = 0.0848                                      |                             |
| Absolute structure parameter      | 0.174(10)                                                      |                             |
| Largest diff. peak and hole       | 0.482 and -0.629 e.Å <sup>-3</sup>                             |                             |

Crystal data and structure refinement for **74**

|                                   |                                                  |                    |
|-----------------------------------|--------------------------------------------------|--------------------|
| Identification code               | tcd461                                           |                    |
| Empirical formula                 | C <sub>37</sub> H <sub>26</sub> N <sub>4</sub> O |                    |
| Formula weight                    | 542.62                                           |                    |
| Temperature                       | 99.99 K                                          |                    |
| Wavelength                        | 0.71073 Å                                        |                    |
| Crystal system                    | Monoclinic                                       |                    |
| Space group                       | C2/c                                             |                    |
| Unit cell dimensions              | a = 18.1401(8) Å                                 | α = 90°.           |
|                                   | b = 17.3206(8) Å                                 | β = 108.4224(16)°. |
|                                   | c = 9.1345(4) Å                                  | γ = 90°.           |
| Volume                            | 2723.0(2) Å <sup>3</sup>                         |                    |
| Z                                 | 4                                                |                    |
| Density (calculated)              | 1.324 Mg/m <sup>3</sup>                          |                    |
| Absorption coefficient            | 0.081 mm <sup>-1</sup>                           |                    |
| F(000)                            | 1136                                             |                    |
| Crystal size                      | 0.17 x 0.17 x 0.15 mm <sup>3</sup>               |                    |
| Theta range for data collection   | 3.173 to 29.179°.                                |                    |
| Index ranges                      | -24 ≤ h ≤ 24, -23 ≤ k ≤ 23, -12 ≤ l ≤ 12         |                    |
| Reflections collected             | 21426                                            |                    |
| Independent reflections           | 3682 [R(int) = 0.0582]                           |                    |
| Completeness to theta = 26.000°   | 99.8 %                                           |                    |
| Absorption correction             | Semi-empirical from equivalents                  |                    |
| Max. and min. transmission        | 0.7458 and 0.7053                                |                    |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>      |                    |
| Data / restraints / parameters    | 3682 / 0 / 205                                   |                    |
| Goodness-of-fit on F <sup>2</sup> | 1.029                                            |                    |
| Final R indices [I > 2σ(I)]       | R1 = 0.0498, wR2 = 0.1052                        |                    |
| R indices (all data)              | R1 = 0.0729, wR2 = 0.1161                        |                    |
| Largest diff. peak and hole       | 0.358 and -0.292 e.Å <sup>-3</sup>               |                    |



Crystal data and structure refinement for **75**

|                                   |                                                                    |                                |
|-----------------------------------|--------------------------------------------------------------------|--------------------------------|
| Identification code               | tcd413                                                             |                                |
| Empirical formula                 | $C_{38}H_{26}N_4O_2$                                               |                                |
| Formula weight                    | 570.63                                                             |                                |
| Temperature                       | 297.95 K                                                           |                                |
| Wavelength                        | 0.71073 Å                                                          |                                |
| Crystal system                    | Monoclinic                                                         |                                |
| Space group                       | C2/c                                                               |                                |
| Unit cell dimensions              | $a = 17.4876(12)$ Å                                                | $\alpha = 90^\circ$ .          |
|                                   | $b = 17.1586(12)$ Å                                                | $\beta = 126.7264(19)^\circ$ . |
|                                   | $c = 12.7392(9)$ Å                                                 | $\gamma = 90^\circ$ .          |
| Volume                            | $3063.8(4)$ Å <sup>3</sup>                                         |                                |
| Z                                 | 4                                                                  |                                |
| Density (calculated)              | 1.237 Mg/m <sup>3</sup>                                            |                                |
| Absorption coefficient            | 0.078 mm <sup>-1</sup>                                             |                                |
| F(000)                            | 1192                                                               |                                |
| Crystal size                      | 0.37 x 0.09 x 0.09 mm <sup>3</sup>                                 |                                |
| Theta range for data collection   | 2.907 to 26.431°.                                                  |                                |
| Index ranges                      | $-21 \leq h \leq 21$ , $-21 \leq k \leq 21$ , $-15 \leq l \leq 12$ |                                |
| Reflections collected             | 11761                                                              |                                |
| Independent reflections           | 3148 [R(int) = 0.0442]                                             |                                |
| Completeness to theta = 25.242°   | 99.8 %                                                             |                                |
| Absorption correction             | Semi-empirical from equivalents                                    |                                |
| Max. and min. transmission        | 0.7454 and 0.6904                                                  |                                |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                        |                                |
| Data / restraints / parameters    | 3148 / 0 / 201                                                     |                                |
| Goodness-of-fit on F <sup>2</sup> | 1.021                                                              |                                |
| Final R indices [I > 2σ(I)]       | R1 = 0.0557, wR2 = 0.1219                                          |                                |
| R indices (all data)              | R1 = 0.1008, wR2 = 0.1447                                          |                                |
| Largest diff. peak and hole       | 0.153 and -0.204 e.Å <sup>-3</sup>                                 |                                |

Crystal data and structure refinement for **76**

|                                   |                                                               |                               |
|-----------------------------------|---------------------------------------------------------------|-------------------------------|
| Identification code               | tcd517                                                        |                               |
| Empirical formula                 | C <sub>40</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub> |                               |
| Formula weight                    | 630.68                                                        |                               |
| Temperature                       | 100 K                                                         |                               |
| Wavelength                        | 1.54178 Å                                                     |                               |
| Crystal system                    | Monoclinic                                                    |                               |
| Space group                       | C2/c                                                          |                               |
| Unit cell dimensions              | a = 8.8738(4) Å                                               | $\alpha = 90^\circ$ .         |
|                                   | b = 13.5916(5) Å                                              | $\beta = 91.2861(16)^\circ$ . |
|                                   | c = 24.8708(10) Å                                             | $\gamma = 90^\circ$ .         |
| Volume                            | 2998.9(2) Å <sup>3</sup>                                      |                               |
| Z                                 | 4                                                             |                               |
| Density (calculated)              | 1.397 Mg/m <sup>3</sup>                                       |                               |
| Absorption coefficient            | 0.737 mm <sup>-1</sup>                                        |                               |
| F(000)                            | 1320                                                          |                               |
| Crystal size                      | 0.18 x 0.08 x 0.08 mm <sup>3</sup>                            |                               |
| Theta range for data collection   | 3.555 to 70.096°.                                             |                               |
| Index ranges                      | -10 ≤ h ≤ 10, -13 ≤ k ≤ 16, -27 ≤ l ≤ 29                      |                               |
| Reflections collected             | 11821                                                         |                               |
| Independent reflections           | 2809 [R(int) = 0.0347]                                        |                               |
| Completeness to theta = 67.679°   | 99.9 %                                                        |                               |
| Absorption correction             | Semi-empirical from equivalents                               |                               |
| Max. and min. transmission        | 0.7533 and 0.6353                                             |                               |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                   |                               |
| Data / restraints / parameters    | 2809 / 1 / 225                                                |                               |
| Goodness-of-fit on F <sup>2</sup> | 1.083                                                         |                               |
| Final R indices [I > 2σ(I)]       | R1 = 0.0479, wR2 = 0.1459                                     |                               |
| R indices (all data)              | R1 = 0.0527, wR2 = 0.1516                                     |                               |
| Largest diff. peak and hole       | 0.547 and -0.223 e.Å <sup>-3</sup>                            |                               |

## Crystal data and structure refinement for 77

|                                   |                                                               |                 |
|-----------------------------------|---------------------------------------------------------------|-----------------|
| Identification code               | tcd571_sq                                                     |                 |
| Empirical formula                 | C <sub>42</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> |                 |
| Formula weight                    | 690.73                                                        |                 |
| Temperature                       | 100.02 K                                                      |                 |
| Wavelength                        | 0.71073 Å                                                     |                 |
| Crystal system                    | Monoclinic                                                    |                 |
| Space group                       | P2 <sub>1</sub> /n                                            |                 |
| Unit cell dimensions              | a = 21.0577(10) Å                                             | α = 90°.        |
|                                   | b = 15.5536(8) Å                                              | β = 90.924(2)°. |
|                                   | c = 23.2223(11) Å                                             | γ = 90°.        |
| Volume                            | 7604.9(6) Å <sup>3</sup>                                      |                 |
| Z                                 | 8                                                             |                 |
| Density (calculated)              | 1.207 Mg/m <sup>3</sup>                                       |                 |
| Absorption coefficient            | 0.082 mm <sup>-1</sup>                                        |                 |
| F(000)                            | 2896                                                          |                 |
| Crystal size                      | 0.22 x 0.2 x 0.17 mm <sup>3</sup>                             |                 |
| Theta range for data collection   | 2.619 to 26.195°.                                             |                 |
| Index ranges                      | -26 ≤ h ≤ 26, -19 ≤ k ≤ 15, -28 ≤ l ≤ 28                      |                 |
| Reflections collected             | 72693                                                         |                 |
| Independent reflections           | 15200 [R(int) = 0.0571]                                       |                 |
| Completeness to theta = 26.000°   | 99.9 %                                                        |                 |
| Absorption correction             | Semi-empirical from equivalents                               |                 |
| Max. and min. transmission        | 0.7453 and 0.6990                                             |                 |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                   |                 |
| Data / restraints / parameters    | 15200 / 10 / 953                                              |                 |
| Goodness-of-fit on F <sup>2</sup> | 1.021                                                         |                 |
| Final R indices [I > 2σ(I)]       | R1 = 0.0540, wR2 = 0.1236                                     |                 |
| R indices (all data)              | R1 = 0.0842, wR2 = 0.1376                                     |                 |
| Largest diff. peak and hole       | 0.519 and -0.350 e.Å <sup>-3</sup>                            |                 |



Crystal data and structure refinement for **87**

|                                   |                                                 |                   |
|-----------------------------------|-------------------------------------------------|-------------------|
| Identification code               | tcd197                                          |                   |
| Empirical formula                 | C <sub>12</sub> H <sub>5</sub> BrO <sub>2</sub> |                   |
| Formula weight                    | 261.07                                          |                   |
| Temperature                       | 100(2) K                                        |                   |
| Wavelength                        | 0.71073 Å                                       |                   |
| Crystal system                    | Monoclinic                                      |                   |
| Space group                       | P2 <sub>1</sub> /n                              |                   |
| Unit cell dimensions              | a = 7.3397(3) Å                                 | α = 90°.          |
|                                   | b = 8.1315(4) Å                                 | β = 95.3180(10)°. |
|                                   | c = 15.5788(7) Å                                | γ = 90°.          |
| Volume                            | 925.78(7) Å <sup>3</sup>                        |                   |
| Z                                 | 4                                               |                   |
| Density (calculated)              | 1.873 Mg/m <sup>3</sup>                         |                   |
| Absorption coefficient            | 4.410 mm <sup>-1</sup>                          |                   |
| F(000)                            | 512                                             |                   |
| Crystal size                      | 0.290 x 0.070 x 0.050 mm <sup>3</sup>           |                   |
| Theta range for data collection   | 2.626 to 28.498°.                               |                   |
| Index ranges                      | -9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20          |                   |
| Reflections collected             | 21685                                           |                   |
| Independent reflections           | 2338 [R(int) = 0.0300]                          |                   |
| Completeness to theta = 25.242°   | 99.8 %                                          |                   |
| Absorption correction             | Semi-empirical from equivalents                 |                   |
| Max. and min. transmission        | 0.7459 and 0.5900                               |                   |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>     |                   |
| Data / restraints / parameters    | 2338 / 0 / 136                                  |                   |
| Goodness-of-fit on F <sup>2</sup> | 1.069                                           |                   |
| Final R indices [I > 2σ(I)]       | R1 = 0.0278, wR2 = 0.0728                       |                   |
| R indices (all data)              | R1 = 0.0344, wR2 = 0.0753                       |                   |
| Largest diff. peak and hole       | 0.934 and -0.475 e.Å <sup>-3</sup>              |                   |

Crystal data and structure refinement for **88**

|                                   |                                                                    |                              |
|-----------------------------------|--------------------------------------------------------------------|------------------------------|
| Identification code               | tcd422                                                             |                              |
| Empirical formula                 | $C_{32}H_{20.15}N_2O_{0.08}$                                       |                              |
| Formula weight                    | 433.85                                                             |                              |
| Temperature                       | 100.0 K                                                            |                              |
| Wavelength                        | 1.54178 Å                                                          |                              |
| Crystal system                    | Monoclinic                                                         |                              |
| Space group                       | C2/c                                                               |                              |
| Unit cell dimensions              | $a = 27.8245(19)$ Å                                                | $\alpha = 90^\circ$ .        |
|                                   | $b = 9.7773(6)$ Å                                                  | $\beta = 130.867(4)^\circ$ . |
|                                   | $c = 21.0172(14)$ Å                                                | $\gamma = 90^\circ$ .        |
| Volume                            | $4323.9(5)$ Å <sup>3</sup>                                         |                              |
| Z                                 | 8                                                                  |                              |
| Density (calculated)              | 1.333 Mg/m <sup>3</sup>                                            |                              |
| Absorption coefficient            | 0.603 mm <sup>-1</sup>                                             |                              |
| F(000)                            | 1814                                                               |                              |
| Crystal size                      | 0.3 x 0.07 x 0.03 mm <sup>3</sup>                                  |                              |
| Theta range for data collection   | 4.202 to 68.340°.                                                  |                              |
| Index ranges                      | $-33 \leq h \leq 33$ , $-11 \leq k \leq 11$ , $-24 \leq l \leq 25$ |                              |
| Reflections collected             | 24178                                                              |                              |
| Independent reflections           | 3963 [R(int) = 0.1185]                                             |                              |
| Completeness to theta = 67.679°   | 99.9 %                                                             |                              |
| Absorption correction             | Semi-empirical from equivalents                                    |                              |
| Max. and min. transmission        | 0.7531 and 0.5895                                                  |                              |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                        |                              |
| Data / restraints / parameters    | 3963 / 1 / 314                                                     |                              |
| Goodness-of-fit on F <sup>2</sup> | 0.989                                                              |                              |
| Final R indices [I > 2σ(I)]       | R1 = 0.0843, wR2 = 0.2076                                          |                              |
| R indices (all data)              | R1 = 0.1303, wR2 = 0.2508                                          |                              |
| Extinction coefficient            | 0.0011(2)                                                          |                              |
| Largest diff. peak and hole       | 0.334 and -0.296 e.Å <sup>-3</sup>                                 |                              |

Crystal data and structure refinement for **92**

|                                   |                                                                    |                                |
|-----------------------------------|--------------------------------------------------------------------|--------------------------------|
| Identification code               | tm3final                                                           |                                |
| Empirical formula                 | $C_{36.50}H_{26}BrClO_2$                                           |                                |
| Formula weight                    | 611.93                                                             |                                |
| Temperature                       | 100.01 K                                                           |                                |
| Wavelength                        | 0.71073 Å                                                          |                                |
| Crystal system                    | Triclinic                                                          |                                |
| Space group                       | $P\bar{1}$                                                         |                                |
| Unit cell dimensions              | $a = 9.7862(9)$ Å                                                  | $\alpha = 87.9356(14)^\circ$ . |
|                                   | $b = 11.1970(10)$ Å                                                | $\beta = 82.0541(13)^\circ$ .  |
|                                   | $c = 12.8037(12)$ Å                                                | $\gamma = 86.4553(14)^\circ$ . |
| Volume                            | $1386.3(2)$ Å <sup>3</sup>                                         |                                |
| Z                                 | 2                                                                  |                                |
| Density (calculated)              | 1.466 Mg/m <sup>3</sup>                                            |                                |
| Absorption coefficient            | 1.613 mm <sup>-1</sup>                                             |                                |
| F(000)                            | 626                                                                |                                |
| Crystal size                      | 0.2 x 0.2 x 0.15 mm <sup>3</sup>                                   |                                |
| Theta range for data collection   | 1.606 to 29.499°                                                   |                                |
| Index ranges                      | $-13 \leq h \leq 13$ , $-15 \leq k \leq 15$ , $-17 \leq l \leq 17$ |                                |
| Reflections collected             | 19718                                                              |                                |
| Independent reflections           | 7669 [R(int) = 0.0338]                                             |                                |
| Completeness to theta = 26.000°   | 99.8 %                                                             |                                |
| Absorption correction             | Semi-empirical from equivalents                                    |                                |
| Max. and min. transmission        | 0.7464 and 0.6932                                                  |                                |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                        |                                |
| Data / restraints / parameters    | 7669 / 0 / 381                                                     |                                |
| Goodness-of-fit on F <sup>2</sup> | 1.011                                                              |                                |
| Final R indices [I > 2σ(I)]       | R1 = 0.0391, wR2 = 0.0890                                          |                                |
| R indices (all data)              | R1 = 0.0615, wR2 = 0.0965                                          |                                |
| Largest diff. peak and hole       | 1.274 and -0.684 e.Å <sup>-3</sup>                                 |                                |