New Technology for the Extraction of Energy Critical Metals from WEEE and Removal of PFOA from Water

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By

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Declaration

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Harrison Omorodion
Summary

Electrical and electronic equipment contains a plethora of energy critical metals including precious metals and lanthanides which eventually concentrates in the annual 20-50 million metric tonnes of e-wastes produced globally. This has been identified as a threat to the development of sustainable technology and to the environment. In an attempt to reclaim some of these metals, a series of fluorinated extractants with different donors, based on the Tris-(2-Aminoethyl)-Amine (Tren), cone and partial cone (PC) calix[4]arene, Triothiacyclononane (9-ane-S3 or TTCN) and Propylenediaminetetraacetic acid (PDTA) scaffolds have been synthesised. These ligands have been employed in extraction of Au$^{3+}$, Pt$^{2+}$, Pd$^{2+}$, Nd$^{3+}$, Eu$^{3+}$ and Er$^{3+}$ from aqueous solutions. For all the amido ligands tested, Au(III) was the most extracted. > 96% extraction efficiency achieved for Au(III) with the partial cone calixarene ligand. Poorer efficiency in Pt, Pd and Eu extractions points to selectivity of both ligands toward Au(III). The binding constants show that the cone calixarene eventually forms the most stable complexes. The metal-ligand interaction in the Au(III) complexes have be thoroughly investigated using spectroscopic methods including small angle X-ray scattering (SAXS). The amide derivative of the cone calix[4]arene ligand was the most perturbed in terms of size and speciation in solution. The hard donor calixaryl phosphine oxide ligand was tested in Ln$^{3+}$ extraction from the aqueous phase. 84, 90, and 80% extractions were obtained for Nd$^{3+}$, Eu$^{3+}$ and Er$^{3+}$ respectively.

The synthesis of fluorinated compounds also led to interesting observations in fluorine chemistry. Fluorine possesses low polarisability and this makes the interatomic dispersive forces rather low according to Paulings principle. However, some compounds wherein fluorine-fluorine interactions are present in the solid state and are not simply due to crystal packing but were shown to be stabilizing and give a significant energy contribution to the structures. Computational studies showed that these Fluorine-Fluorine stabilization energy are collectively of the same order of magnitude as a typical hydrogen bond. Further investigation on these interactions are being conducted in the solid state, solution phase and gas phase using a wide range of techniques including SAXS, DOSY and microwave spectroscopy in the gas phase.

These non-covalent interactions have also been harnessed in extraction of Perfluorooctanoic Acid (PFOA) from water. PFOA is a persistent organic pollutant that has been associated with diseases including cancer and kidney diseases. It is has been detected in water, soil, blood
serum of animals and humans. Extraction of PFOA is engendered by incorporation of fluorous “ponytails” into our extractant/host in order to evoke C-F…F-C interaction between the fluorous groups of the ligands and PFOA. PFOA was consistently extracted quantitatively with the amide ligands. The nature of the host-guest complexes and the role of C-F…F-C interaction has also been extensively studied in solution 1D, 2D and solid state NMR spectroscopy, thermogravimetric analysis and computational studies unambiguously showed formation of weak host-guest complexes.

Fluorine-Fluorine interactions has also been extended to development of solid support. Physisorption on a modelled fluorinated surface successfully demonstrated the potential scope of the idea and conditions required to modulate the strength of physisorption. Physisorption of fluorinated compounds on a fluoropolymer was thereby carried out harnessing these stabilising C-F…F-C interaction. Easy adsorption and desorption of the fluorinated compounds has been shown and characterised by AFM, SEM, TGA-IR. The supported extractants were applied in metal extractions with superb results and minimal leaching. EXAFS analysis of the metal ligand complexes are consistent with outer sphere ligand interactions and corroborates the spectroscopic characterisations. Polymer resins functionalised with PC ligand have been shown to quantitatively extract Au(III).
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Abbreviations

Å: Angstrom
aH: Hydrodynamic radius
AIM: Atoms-in-molecules
CP/MAS: Cross Polarisation Magic Angle Spinning
D: Distribution Coefficient
DCT: Diffusion coefficient
dFT: Density functional theory
DOSY: Diffusion Ordered Spectroscopy
DSC: Differential Scanning Calorimetry
ECM: Energy Critical Metals
EDTA: Ethylenediaminetetraacetic Acid
EEE: Electrical Electronic Equipment
EXAFS: Extended X-Ray Absorption Fine Structure
FC-75: Perfluoro-(2-perfluoro-n-butyl)tetrahydrofuran
FSL: Fluoropolymer Supported Ligand
HFS: Hirschfeld Surfaces
HRMS: High Resolution Mass Spectroscopy
IRAAS: Infrared Reflectance Absorbance Spectroscopy
K: kelvin
Ln: Lanthanide
mg: milligram

MPt: Melting point
NCI: Noncovalent Interaction
NMR: Nuclear Magnetic Resonance
°C: degree Celsius
PDDF: Pair Distance Distribution Function
PFOA: Perfluorooctanoic Acid
PFSAM: Perfluorinated Self-assembled Monolayer
PGM: Platinum Group Metals
ppm: parts per million
REEs: Rare Earth Elements
REPMs: Rare Earth Permanent Magnets
Rf, Rf, Rf: CF3(CF2)n
SAXS: Small Angle X-ray Scattering
SEM: Scanning Electron Microscopy
TGA: Thermogravimetric Analysis
Tren: Tris-(2-Aminoethyl)-Amine
TTCN, 9-ane-S3: Trithiacyclononane
UV-Vis: Ultraviolet-visible
WEEE: Waste Electrical and Electronic Equipment
XRD: X-ray Diffraction
ρ_bcp: bond critical point (ρ)
Chapter 1

Introduction
1.1 OVERVIEW
Energy critical metals are indispensable in the development of emerging sustainable energy technology and new electrical electronic equipment (EEE).\(^1\) However, these EEE quickly become obsolete, and contribute to the annual 20-50 million metric tonnes of waste electrical electronic equipment (WEEE) or e-waste globally.\(^2\) The need for cheap and effective metal reclamation process is imperative. The major aim of this project is to develop fluorinated ligands able to complex and extract metals from aqueous metal wastes. The proposed fluorinated ligands and ligand features are discussed herein.

As a way of contributing to the increasing recognition of fluororous interactions present in fluorinated compounds, the theory of halogen bonds and strategies towards characterising fluororous interactions are also discussed. Lastly, applications of fluororous interaction in host-guest interactions and the principles behind development of fluoropolymer solid supports are also presented in this chapter.

1.2 WEEE – Waste or an Urban Mine?
The rapid innovation in such technology results in a massive influx of new electrical electronic equipment (EEE)\(^1\) such as biomedical devices, fluorescent light, flat screens phosphors, fibre optics and high performance Neodymium Iron Boron (NdFeB) magnet (present in hard disc drives, hybrid cars and wind turbines) catalytic converters etc.\(^3,4,5,6\)

The amount of precious metals used in the global production of mobile phones reaches up to an average of 24 mg of Au, 250 mg of Ag, 9 mg of Pd, 9 mg of Cu and 3.8 g of Co per unit. This equates to 31 tonnes of Au, 325 tonnes of Ag, 12 tonnes of Pd, 124 tonnes of Cu and 600 tonnes of Co. On average, each PC and Laptop contains 220 mg of Au, 1,000 mg of Ag, 80 mg of Pd and 500 mg of Cu. 65 mg of Co. This adds up to 66 tonnes of Au, 300 tonnes of Ag, 24 tonnes of Pd, 150,000 tonnes of Cu and 9,100 tonnes of Co.\(^7\)

The wide range of rare earth (RE) applications is due to their unique catalytic, electrical, magnetic and optical properties. Nd, Pr, Dy and Tb have found application in high performance Neodymium Iron Boron (NdFeB) magnet used in hybrid electric cars, electric cars, wind turbines, hard disc drives (HDDs) of desktop personal computers and portable devices such as tablet, mobile phones, head phone speakers.\(^5,6\) Rare earth permanent magnets (REPMs) accounts for 38% of REs use in terms of volume. Eu, Gd, Yb, Tb and Y
are used as phosphors in fluorescent light, flat screens, euro bank notes and imaging (MRI), while Er is used in erbium-doped fibre optics for signal amplification.\(^3\),\(^4\),\(^8\)

EEE is made up of 40 – 66\% metal (Figure 1.1), including precious metals and rare earth elements (REE), mixed with various plastic, glass fibre-reinforced epoxy resin and ceramics,\(^9\),\(^10\),\(^11\) serving as protective and technical roles in EEE.\(^12\),\(^13\)

![Figure 1.1. Typical Materials composition in WEEE\(^{11,13-15}\)](image)

However, these EEE quickly become obsolete, and contribute to the annual 20-50 million metric tonnes of waste electrical electronic equipment (WEEE) or e-waste generated globally.\(^2\) This poses many problem including \textit{environmental waste} issues\(^2\),\(^11\),\(^16\) and an alarming \textit{accumulation of precious and energy critical metals in e-waste}.\(^12\),\(^17\) Rare earths (REs) are also classified as energy critical metals (ECM) due to their applications in sustainable emerging technology and also due to the \textit{threat to supply} by the Chinese evidenced in the flux in prices in recent past (Figure 1.2).\(^5\),\(^18\) These issues associated with WEEE have generated a huge interest in metal reclamation from WEEE.

![Figure 1.2. The Prices of Selected Rare Earths vs the Prices of Gold and Silver\(^{19}\)](image)
1.2.1 Anthropogenic Mining

Developing a technology that can efficiently extract metals from e-waste on an industrial scale has been identified as one of the ways to alleviate the heavy reliance on virgin materials and has been termed anthropogenic mining.

In terms of advantages, analysis of metal contained in printed circuit board (PCB) revealed 250 fold of gold when compared to primary ores (10g/tonne).\textsuperscript{7, 20, 21, 22, 23} Interestingly, Pt recycling from e-waste is estimated to save 5\% energy compared to mining from primary ores.\textsuperscript{24} Moreover, 100\% of all hybrid electric vehicles, electric vehicles, desktop PCs, portable devices contain REPM and 10\% of wind turbines contain up to 700 Kg of REPMs with the potential to cover a growing 11-15\% of REs demand as more technology reaches their end-of-life stages (EoL).\textsuperscript{25, 26}

![Figure 1.3. Potential recycling supply of Nd and predicted rise in demand of REs.\textsuperscript{25} [Reprinted with permission. © 2013, American Chemical Society]](image)

1.2.2 Current methods of WEEE recycling

WEEE recycling is carried out over different stages including disassembling, mechanical processing\textsuperscript{27-34} to concentrate the metallic and non-metallic fractions.\textsuperscript{35} The Non-metallic Fraction are generally treated by Landfilling,\textsuperscript{36} Incineration,\textsuperscript{37} Supercritical fluids extractions\textsuperscript{38, 39} and Pyrolysis.\textsuperscript{10, 40} The more relevant metallic fraction involves more complex procedures such as electrometallurgical,\textsuperscript{41} hydrometallurgical,\textsuperscript{42-44} pyrometallurgical,\textsuperscript{45} Bioleaching\textsuperscript{46} and solvent extraction.\textsuperscript{47}
### Table 1.1. Common metal extraction system, advantages and disadvantages

<table>
<thead>
<tr>
<th>Extraction Systems</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic-Liquids (IL) Extraction</td>
<td>Non-volatile, non-flammable and possess wide activity temperature range. High specificity and extraction efficiency.</td>
<td>Expensive and side reactions^52^</td>
</tr>
<tr>
<td>Synergistic extraction</td>
<td>Higher selectivity^53^ and efficiency than single systems^54^-^59^</td>
<td>Low recovery yield of the extractants^60^</td>
</tr>
<tr>
<td>Ion-Exchange Resin</td>
<td>High purity,^61^ simplicity, convenience of separation, high purification^62^-^64^ selectivity and extraction efficiency of metals^65^</td>
<td>Calcium sulfate and iron fouling, adsorption of organic materials, organic contamination from resin</td>
</tr>
<tr>
<td>Microcapsule</td>
<td>Ease of recycling the extractants,^66^ recovery of various metals,^66^-^68^ ease of metal sorption unto microcapsule,^69^-^71^ high efficiency^72^ and Selectivity^73^</td>
<td>Low encapsulation and expulsion of core during processes</td>
</tr>
<tr>
<td>Reagent impregnated resins</td>
<td>Simplicity, facile extractant recovery^74^-^82^ high separation efficiency^83^ and selectivity^84^</td>
<td>Cure shrinkage, critical mixing and corrosive handling</td>
</tr>
<tr>
<td>Liquid Membrane (LM)</td>
<td>Good extraction coefficients.^85^</td>
<td>Insufficient stability i.e. elution of the LM from support pore and polymer corrosion^86^</td>
</tr>
<tr>
<td>Solvent Extraction</td>
<td>Handles large volumes of dilute pregnant liquors</td>
<td>Stripping, use of organic volatile solvents</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>Higher extraction efficiency even at lower pH.^87^</td>
<td>Leaching and emulsification at high pH and stability.^88^</td>
</tr>
<tr>
<td>Organophosphoric acids and esters</td>
<td>High extractability and stripping rate.^89^ Suitable for industrial applications.^90, 91^</td>
<td>Loss of soluble extractants through dissolution and incomplete phase separation</td>
</tr>
<tr>
<td>Ketones and β-diketones</td>
<td>High synergistic extraction.^92^</td>
<td>leaching</td>
</tr>
<tr>
<td>Amines</td>
<td>Good extraction efficiency in sulfate media,^93, 94^ and nitrate solution.^95, 96^</td>
<td>Poor extractants in chloride media,^93, 94^ Insolubility</td>
</tr>
<tr>
<td>Crown ethers</td>
<td>Efficient^97^ and selective extraction^98^</td>
<td>High solubility in water</td>
</tr>
</tbody>
</table>
1 | Introduction

<table>
<thead>
<tr>
<th>Amides</th>
<th>It can be easily destroyed by incineration and ease of recovery</th>
<th>Can form emulsion and phase separate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfides</td>
<td>High efficiency</td>
<td>Difficulty in stripping metals</td>
</tr>
</tbody>
</table>

It is noteworthy that despite the vast amount of literature on metal extraction only a few procedures have made it to industrial application. However, solvent extraction using various systems and extractants shown in Table 1.1 offer less environmentally expensive method of metal extraction. Solvent extraction is therefore the method of choice for rapid screening/testing of the extractants developed in the work.

**Solvent Extraction with co-extractants**

This technique is central to this project and it involves the use of a biphasic system with the organic extractant dissolved in the organic layer and the metals dissolved in the aqueous phase. It can be useful for quick screening of ligands before they are selected for other extraction systems. Ligands/extractants used in solvent extraction have been grouped by Ritecy and Ashbrook into cation exchanger, chelating exchanger, solvation extractants, and anion exchanger according to the type of interaction with the metals and the donor atoms they bear. Common extractants used in solvent extraction includes ligands of carboxylic acids, phosphoric acids, phosphonic acids, phosphinic acid, phosphorous ester, phosphine oxides, ketones, thiophosphates and amines. The general structure of some of these are shown in Table 1.2.

**Supercritical Fluids**

Supercritical fluids (SCF) have been adapted in the extraction of metal due to its unique ability to be in neither liquid or gas phase above certain temperature and pressure (critical point); it diffuses like a gas and dissolves materials like a liquid. Its extraction selectivity can be enhanced by tuning the temperature, pressure and solvent. The use of scCO₂ offers a number of advantages over conventional organic solvents used in traditional solvent extractions, namely it is non-flammable, non-toxic and is a renewable feedstock of low cost, low toxicity, benign environmental impact, cost, inertness to the extraction conditions and absence of residual contamination of aqueous phase by the organic phase low critical temperature and a moderate critical pressure and remarkable extraction efficiencies. scCO₂ does however possesses low dipole moment which impedes the solubility
of polar metal ions metals in it. It has been employed in some extraction systems and shown to possess good extraction efficiency (Table 1.3).

Table 1.2. General Structure of Selected Solvent Extractants (R = alkyl group)

<table>
<thead>
<tr>
<th>Extractant</th>
<th>General structure</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acids</td>
<td>HO_R</td>
<td>Y, Ce, Pr, and large rare earth elements (LREE)</td>
</tr>
</tbody>
</table>
| Organophosphoric acids and esters| \[
\begin{align*}
\text{Phosphonic acids} & : \text{HO} & \text{PO} & \text{R}_1 \\
\text{Phosphoric acids} & : \text{HO} & \text{PO} & \text{R}_1 \\
\text{Phosphine oxides} & : \text{R}_3 & \text{P} & \text{R}_2 \\
\text{Phosphinic acids} & : \text{HO} & \text{PO} & \text{R}_1 \\
\end{align*}
\] | La, Ce, Pr, Eu, Tb, Tm, Yb, Lu, Nd, Ho, Gd, Sm, Dy, Er |
| Ketones and β-diketones         | R\_1 \_O \_R\_2   | Ln                                                                     |
| Amines                          | R\_3 \_N \_R\_1 | Eu, Pr, Ce, Y, Tm                                                      |
| Quaternary amines               | Cl \_H\_5\_C \_R\_2 |                                                                        |
| Primary amines                  | H\_2\_N \_R\_2   |                                                                        |
Table 1.3. General Structures of Selected Extractants and Typical extraction efficiency in SCF

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Structure of Extractant</th>
<th>Target (% extractions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thenoyltrifluoroacetone(^{\text{111}})</td>
<td><img src="https://example.com/structure.png" alt="TTFA structure" /></td>
<td>La(^{3+}) (30), Eu(^{3+}) (38) and Lu(^{3+}) (51)</td>
</tr>
<tr>
<td>Tributyl phosphate(^{\text{111}})</td>
<td><img src="https://example.com/structure.png" alt="TBP structure" /></td>
<td>La(^{3+}) (43.6), Ce(^{3+}) (60.5), Sm(^{3+}) (85.1), and Eu(^{3+}) (86.7)</td>
</tr>
<tr>
<td>Di-(2-ethylhexyl)phosphoric acid(^{\text{112}})</td>
<td><img src="https://example.com/structure.png" alt="DEHP structure" /></td>
<td>for Gd(^{3+}) (86.9), Dy(^{3+}) (91.8), Yb(^{3+}) (71.9) and Lu(^{3+}) (69.2)(^{\text{112}})</td>
</tr>
</tbody>
</table>

1.2.3 Problems Associated with Current Metal Extraction Systems

Some of the recycling methods described earlier are either very environmentally expensive, or are still under development and not economically feasible enough to compete with informal recycling industries. For many of the extractants, the extraction efficiencies or selectivity are poor. Some of the ligands are ineffective at industrial extraction pH. The metals are sometimes too strongly bonded to the extractant making stripping of the metal from the extractant cumbersome. Also, there is also a problem of leaching of metals or the extracted species back into the aqueous phase. The factors makes even some the effective extraction system on lab scale far from commercial application.

Application of good extraction system to WEEE recycling is further hampered by the complexity of WEEE such as the presence of some certain hazardous substances such as...
brominated flame retardants and toxic metals in EEE, heterogeneity and complex nature of WEEE further adds to difficulties in WEEE recycling.\textsuperscript{32,113}

Despite the efforts of European Parliament and Council at promoting WEEE collection and recycling under the WEEE directive (2002/96/EC)\textsuperscript{114} and the EU legislations restricting the use of hazardous substances in electrical and electronic equipment (RoHS Directive 2002/95/EC),\textsuperscript{115} WEEE collection is still too low and this hampers the enthusiasm to develop effective reclamation technology.\textsuperscript{16,116}

An example of an ideal commercial recycling facility is Umicore’s metal recycling plant in Holland but set ups like these are highly capital intensive and cannot be afforded in developing countries. Moreover, in applications where rare earths are used, the recycling rate is less than 1\% and there are no commercial methods for doing this, as the rare earths typically slag in smelter plants. This impedes the recycling in WEEE smelting plants. Obviously, a “green effective cheaper” method would be an attractive alternative. To achieve this, effective organic extractant needs to be developed for environmentally benign process such as Supercritical fluids (SCF) extractions.

1.3 LIGAND SYNTHESIS

The key physical property that enhances the solubility of compounds in \textit{scCO$_2$} or FC-72 appears to be the amount of fluorous groups present and high temperature.\textsuperscript{117} All ligands therefore needs to include various amounts and lengths of fluorinated chains attached to a scaffold like the calixarene or assembled into macrocyclic systems resulting in tri-, tetra-, penta-, hexadentate and octadentate ligands. However, donor atoms/groups on the ligand is determined by the metal of interest and general consideration of metal-ligand interactions. Coordination of these compounds to metals would be carried out through the intentional synthesis and characterisation of the compounds.\textsuperscript{118} From this, additional ligand fine-tuning would be carried out, such as varying the number of CF$_2$ groups and position of the fluorous pony tails and sizes of the compounds in order to tune solubility, reactivity and hydrophobicity of the ligands. The goal therefore is to harness the complexation properties of these ligands for the extraction of metals from WEEE and PFOA from water.

The important chemical factors in devising efficient extractants are:
1.3.1 Ligand metal interaction

*Hard-Soft Acid-Base:* Hard ions are small, highly charged, and polarising while soft ions are large with low charge density and are easily polarisable. Metals such as Fe$^{2+}$, Zn$^{2+}$ and Ln$^{3+}$ are termed hard cation and as such they form highly stable complexes with hard ligands such as phosphine oxides and acetates. Au$^{3+}$, Ag$^+$, Pt$^{2+}$ and other platinum group metals are soft metals and will complex readily with soft donor ligands such as phosphines, thiols, and amides as these are larger bases with polarisable donor atoms and are able to stabilise large polarisable cation in low charge state.

*Sigma (σ) and (π) interactions:* A sigma bond is defined as one where electron density is enhanced in a direct line joining the two atom centre whereas the sideways-on overlap of the p or the π orbital results in a π interaction. For example, a ligand such as NH$_3$ have lone pair of electron that can be directed to the σ-bonding with a metal. However, NH$_3$ cannot undertake any further π bonding. Similarly, CO can donate electrons to a metal through σ-bonding between the carbon based lobes of the σ-bonding orbital and acceptor orbital of the metal (Figure 1.4).

![Figure 1.4. Molecular orbitals showing sigma bonding](image1)

CO can also be involved in π bonding by accepting electron through back donation from the metal $t_{2g}$ set into its π$^*$ orbital (Figure 1.5) – these are π acceptors or π-acids ligands. The highest occupied molecular orbital HOMO in such ligands is used for σ-bonding while their lowest unoccupied molecular orbital LUMO are used as π acceptor. The ligand π$^*$ are higher in energy than the metal $t_{2g}$ levels. In this situation, interaction of the two therefore increases in Δo and lowers the metal $t_{2g}$ set.

![Figure 1.5. Molecular orbitals showing sigma bonding (red arrows) and back bonding (black arrows) to the ligand π* orbitals](image2)
Electrons can also flow from the filled π ligand based orbital to the empty $t_{2g}$ metal based orbital such as in halide or $O^{2-}$ anions with extra lone pair of electrons (after a $\sigma$-bonding) which they can use for repulsive interaction with the filled metal orbital and cause lowering of $\Delta_o$. These are known as $\pi$ donor ligands (Figure 1.6).

**Figure 1.6.** (Left) The $\pi$-acceptor concept in metal–ligand bonding, and its influence on energy levels. Unoccupied ligand $\pi^*$ orbitals are less stable than the metal nonbonding $t_{2g}$ orbitals. A repulsive-type interaction between these orbitals leads to a fall (stabilization) of the $t_{2g}$ and a rise in energy of the ligand $\pi$ orbitals, and a related increase in the size of $\Delta_o$. An orbital interaction view of the process in terms of overlap of a metal $d_\pi$ and empty ligand $\pi^*$ orbital. (Right) The $\pi$-donor concept in metal–ligand bonding, and its influence on energy levels. Occupied lone pair ($\pi$) orbitals on the ligand are more stable than the metal nonbonding $t_{2g}$ orbitals. A repulsive-type interaction between these orbitals leads to a rise (destabilization) of the $t_{2g}$ and a fall in energy of the ligand lone pair orbitals, and a related fall in the size of $\Delta_o$. [Reprinted with permission from reference.\textsuperscript{119} © 2010, WILEY]

Back donation from metal to $\pi$-acceptor ligand can be observed spectroscopically, typically using IR spectroscopy as the C-O stretching vibration can give an indication of the strength of the C-O bond. Co-ordination to metal weakens the C-O bond and causing in a shift to lower energy due to electrons being pushed back into the $\pi^*$ antibonding orbital.

The notion of $\pi$ donors and acceptors is related to the *Spectrochemical Series* as the $\pi$-donor are arranged on the left while the $\pi$ acceptors are arranged to the right.

$I^- < Br^- < SCN^- < CI^- < S^{2-} < NO_3^- < F^- < HO^- < OH_2 < NCS^- < NH_3 < NO_2^- < PR_3 < CN^- < CO$.
Chelate and Macrocyclic effect: Some ligands possess more than one donor group that can bind to a metal ion – polydenticity. The chelate effect is due to entropic considerations and pre-organisation of the ligand on the metal. Although the donor groups present in a polydentate ligand may not always be in a position to bind to the metal but in situations where they are suitably positioned to all bind to the metal, this forms a chelate. This affects the thermodynamic and kinetic stability of the complex formed as chelating ligands are known to form stronger complexes than the corresponding monodentate ligands (Table 1.4).\textsuperscript{120,121}

This is due to pre-organisation effects – bonding of one arm of the ligand means the other is in the outer co-ordination sphere and can readily bind to the metal. The second reason for this comes from entropic considerations.

\[
\text{Ni(NH}_3)_6 + 3\text{en} \rightleftharpoons \text{Ni(en)}_3 + 6\text{NH}_3
\]

From the reaction, the number of species on right hand side is 7 while there are 4 on the left hand side. \(\Delta H\) in the equation, \(\Delta G = \Delta H - T\Delta S\), is unchanged since the species on both sides contain four M-N bonds but there is increase in entropy (\(T\Delta S\)).

For effective chelate effect, the chelate ring size must be considered. While 5-membered rings form the most enhanced stable complexes, most of the chelate effect features becomes modest with smaller or larger (except unsaturated ligands) chelate ring.

**Table 1.4.** Stability constants of selected complexes reflecting Chelate and Macrocyclic effect

Comparison of formation constants with monodentate and related multidentate chelate ligands.

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Log (\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Ni(NH}_3\text{)}^{2+}</td>
<td>8.7</td>
</tr>
<tr>
<td>\text{[Ni(en)}_3\text{]}^{2+}</td>
<td>18.1</td>
</tr>
<tr>
<td>\text{[Cd(H}_2\text{NCH}_3\text{)\text{)}_4]}^{2+}</td>
<td>6.5</td>
</tr>
<tr>
<td>\text{[Cd(en)}_4\text{]}^{2+}</td>
<td>10.5</td>
</tr>
<tr>
<td>\text{[Zn(cyclam)}_2\text{]}^{2+}</td>
<td>15.3</td>
</tr>
<tr>
<td>\text{[Ni(tren)}\text{]}^{2+}</td>
<td>19.1</td>
</tr>
</tbody>
</table>
The macrocyclic effect occurs when there are several heteroatoms present in a ring and thus increases the metal binding capacity. Macrocyclic ligands form more stable complexes than chelate ligands again due to entropy and enthalpy. Pre-organisation effects play more significant role as the donors are all presented to the metal in a pre-defined arrangement (Figure 1.7). Matching of the cavity hole size of the ligand with the metal ion is highly important as a stronger complex can result from a good fit. It is also crucial to have sufficient donor groups present in the ligand to fill up the coordination sphere and completely wrap the metal ion (Figure 1.7).

![Figure 1.7 Comparison of the stability constants for (at left) a linear and a cyclic polyether binding to potassium ion and (at right) a linear and cyclic polyamine binding to zinc ion, illustrating the macrocyclic effect in action.](image)

*Template effect:* This is when the metal ion behaves like an ‘organiser’ of ligands around it in a way that most suits desired reactions. To this end, metal ion *lability* which is the capability of metal ion to exchange its ligand rapidly must be maximised. Slow exchange impinges ligand substitution and limits reactions. However, a functional template system can result in chirality and enantiomer discrimination.

### 1.3.2 Ligands for Precious Metals Extraction

Platinum group metals (PGMs) are typically soft metals which prefer soft and neutral donor ligands including phosphine, thioether, and amido- donor ligands. To achieve polydenticity, ligands can be appended on molecular scaffolds such as Tren, calix[4]arenes, and propylenediaminetetraacetic acid or involve macrocycles such as Trithiacyclononane (9-ane-S$_3$).
**Amides:** the coordination chemistry of amides has been well reviewed. Amides have also been shown to possess notable advantages over a number of extractants in terms of selectivity and benign decomposition products. Being a neutral sigma donor, they are known to interact with metals through the amide oxygen or nitrogen or through non-covalent interactions e.g. hydrogen bonding. Amide and related donors including thioglycoamides, hydroxy acetamide, alkylcyanamides, alkyl- and arylamides and picolinamide possess remarkable metal complexation ability which makes them very valuable to luminescence, catalysis, and extraction of f-block elements and precious metals. Extraction of gold(III) in hydrochloric acid solution using monoamide compounds has been described. Polydentate amide ligands such as Calixaryl amides are most attractive because of their excellent precious metal extraction properties than their monomeric analogues due to the presence of pre-organised ionophoric cavity.

**Phosphines:** Organophosphorus compounds are ubiquitous in coordination chemistry in the P(III) and P(V) oxidation states (phosphine and phosphine oxides respectively). Metal extractions with organophosphorus compounds relies on P(V) oxidation states. Phosphorus compounds are also extensively used in industrial chemistry, pest control, generation of abzymes, and medicinal chemistry. Involvement of organophosphorus compounds in coordination chemistry is largely because of their catalytic activity and are thus used in a number of highly active catalysts including Grubb’s, Wilkinson’s and Keim’s catalysts are based on phosphines. Some of these catalysts are very useful in organic synthesis such as Rauhut–Currier and Morita–Baylis–Hillman Reactions, Mitsunobu reaction, Wittig reaction and Appel reaction due to their ability to stabilise metals in low oxidation states and unusual geometries. Tertiary phosphines and phosphine oxides have been widely used in metal complexation, and metal extractions. These features benefit complexes with interesting reactivity and valuable applications and as such, continues to generate research interest. Fluorous phosphines have also featured in metal extraction with remarkable results. Fluorous ligands are superhydrophobic and are attractive ligands as they allow high distribution co-efficient and recycling of extractants. However, the strong electron-withdrawing effect of the fluorous group decreases electron density from the phosphorus centre and reduces its coordination capability. To mitigate this effect, it is important to have at least two or more methylene spacers between the phosphorus centre and the fluorous groups which is almost as effective as using nine methylene spacers to completely overcome the electron withdrawing effect of the fluorous groups.
The geometric arrangement and steric effect of organic groups (R) bonded to the phosphorus in respect to the metal can be described by Tolman’s cone angle where the metal occupies the apex position and the R groups are folded back. It is employed in accounting quantitatively for steric effects in a physiochemical processes as the size of the ligand (congestion of substituents around the phosphorus atom) affects the reactivity at the metal centre. The lability of the phosphine can be explained by the cone angle.\textsuperscript{151}

**Sulfide:** Phosphines and sulfides have a lone pair of electrons that can be donated to a metal to form a $\sigma$-bond. They also participate in back-bonding due to their relatively low lying d-orbital which can accept electron density into the $\sigma^*$ orbital making them very useful in coordination chemistry. In this case, the P-R and S-R bond weakens (lengthens) due to increased occupancy and in the $\sigma^*$ orbital.\textsuperscript{151-153}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure18.png}
\caption{Donation of electrons from the $\pi$ bonding of the metal to the phosphine ligand $\sigma^*$ orbital}
\end{figure}

Moreover, some metal-sulfur bonds is known to possess a great deal of ionic character with some degree of covalency which varies depending on the metal. This could be of significance to selectivity for softer cations whose chemistry is expected to be covalent.\textsuperscript{154} It is therefore reasonable that sulfur donor and sulfur containing ligands are conspicuous in metal precipitation and extraction studies.\textsuperscript{155} There are a number of commercially available sulfur ligands such as thiosubstituted organophosphinic acid extractants including Cyanex 301 and Cyanex 302 (Figure 1.9) which has featured in remarkable metal extractions.\textsuperscript{156} Sulfur containing extractants have also been shown to possess remarkable precious metal extractions\textsuperscript{157} and macrocyclic thioethers are even more efficient in this regard\textsuperscript{158,159} due to macrocyclic effect but has been less explored for many reasons including the difficulty of ligand synthesis, cost, and limited possibility of functionalisation.
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**Figure 1.9.** Selected commercial sulfur and phosphorus containing solvent extractants

### 1.3.3 Ligand for Rare Earth Elements Extraction

These are typically oxophilic metals that require chelating hard donor ligands to form stable compounds. Various hard fluorous ligands such as phosphine oxides and acetates are required in the complexation of rare earths metals.

**Acetates:** Carboxylic acids have been well investigated in extraction studies. They are regarded as cation exchangers. Low molecular weight carboxylic acids such as cekanoic (6-Methylheptanoic acid), napthenic (cyclohex-3-ene-1-carboxylic acid), neo-heptanoic (4,4-Dimethylpentanoic acid) and versatic acids (neo-decanoic) have been investigated in the extraction of RE by Singh et al. and Zheng et al. with similar conclusions. Yttrium was found to have extraction behaviour of heavy rare earth elements (HREE) with sterically hindered acids (neo-decanoic and versatic acids) and also to that of light rare earth elements (LREE) such as Ce and Pr with sterically less hindered acids (cekanolic, napthenic).  

Other carboxylic acids such as sec-nonylphenoxy acetic acid (CA-100) and sec-octylphenoxy acetic acid (CA-12) has also been employed in the extraction of RE. Results showed that sec-nonylphenoxy acetic acid (CA-100) shows better extraction of RE than neo-decanoic acid at lower pH. The use of multi-dentate extractants including calix[n]arene with carboxylate systems have been shown to exhibit a better extraction efficiency than the monodentate analogues of acetate extractants.

**Phosphine Oxides:** While the basicity of these ligands are largely determined by the solvent media, the nature of the phosphorus oxygen bond in R₃PO, are generally written as P=O – albeit the subject of some debate. Although some descriptions favoured a formal double bond between the phosphorus and oxygen atoms as the best description, the bond is said to have a strong ionic component and is best represented as R₃P⁺-O⁻. Based on
theoretical studies and supported by $^{17}$O solid state NMR studies on two polymorphs of Ph$_3$PO where the $^{17}$O quadrupolar coupling constant and the chemical shielding tensor are consistent with its strongly ionic $\sigma$-bonded nature. This is significant to bonding in lanthanide complexes which is expected to be predominantly electrostatic in nature between the Ln$^{3+}$ and the negatively charged oxygen atom. The repulsion between the positively charged P and metal centres is also of huge significance as such repulsion would be expected to make the Ln-O-P angle approach 180° in the absence of geometrical constrain brought upon by the ligand.

Fluoroalkyl phosphine oxides are known to extract metal and have been found to possess high extraction efficiency of trivalent lanthanides while calixaryl phosphine oxides have also been shown to effectively extract alkali earth metals and trivalent lanthanides due to chelate and pre-organisation effects. In keeping with the same idea of polydentivity and the use of a pre-organised scaffold, the goal is to develop a fluorinated calixarene with phosphine and phosphine oxide donor. Functionalization of all the phenolic oxygen with phosphine oxides will result in an octadentate ligand suitable for lanthanide co-ordination.

1.3.4 Ligand Scaffolds

While the donor groups on the ligand are determined by the metal of interest, one way to achieve polydentivity is to append the ligands on molecular scaffolds such as Tren, calix[4]arenes and PDTA frameworks or involve macrocycles such as trithiacyclononane (9-ane-S$_3$). Following the functionalisation of the cone and partial cone calixarenes, Tren, 9-ane-S$_3$ and EDTA with fluorinated donor groups, the ligands synthesised will then be tested in solvent extractions. Its pre-organisation effect and the influence of the size of the ionophoric cavity on extraction can be better understood through extraction of soft and hard metal ions of various sizes including Au, Ag, Pd, Pt, Nd, Eu, and Er using ligands of different degree of flexibility and cavity size.

Calixarenes: The calixarenes are metacyclophanes annulated by methylene groups. The series constitutes five members ranging from the relatively rigid tetrameric calix[4]arene to the 32 membered ring. They offer a convenient molecular scaffold with a pre-organised cavity that when functionalised, can reveal a selective ionophoric receptor capable of forming more stable species than their corresponding monomeric analogues; making these frameworks rather popular in host guest interactions with lanthanides and precious
metals. They have been regarded as the third generation of host molecule in Supramolecular chemistry after crown ethers and cyclodextrins. The ease of functionalising the methylene spacers, the upper and lower rims, the tuneable size and distinctive concave structure makes these molecular “baskets” or “crater” very attractive for chemical transport of metal ions or neutral molecules. They have found applications in catalysis (as calixarene rare earth metal complex), polymer synthesis, cyanoacrylate adhesives (super glue), host guest interactions, lanthanide and precious elements extractions, magnetic resonance imaging (MRI) contrast agent, luminescence and sensing.

Calixarenes have been involved in host-guest interaction and metal ion complexation or extraction by a number of groups using its phenolic oxygen atoms or other donor groups attached to the calixarene. The earliest work on calixarenes were carried out by Adolf von Baeyer in 1872 when he obtained a hard resinous product from treatment of aqueous formaldehyde with phenol. Leo Baekland marketed this product as Bakelite in 1905–1909. Alois Zinke, investigated the various possibilities of reacting different p-alkyl phenols with aqueous formaldehyde and sodium hydroxide, and assigned the products of the treatment as cyclic tetrameric structures. Although this class of cyclooligomers have a defined upper and lower rim with a central annulus (Figure 1.10), Cornforth was first to point out that due to the ease of rotation of the methylene spacers between the aromatic groups, the calixarenes can through flipping of the phenolic group through the annulus, assume different conformers viz, cone, partial cone, 1,3 alternate and 1,2 alternate.

C. D. Gutsche studied the optimum amount of base necessary to obtain the cyclic tetramers and hexamer by base induced condensation of phenol and formaldehyde. Recognising the resemblance of the shape of the tetrameric structures and a type of Greek vase known as the calix crater (Figure 1.10) Gutsche also introduced the term “calixarene” due to the chalice-like appearance of the smallest member of the series. Although the calixarene is known to be fluxional at room temperature in solution, the cone conformation is however preferred at low temperature and in the solid state. Part of Gutsche’s contribution includes the demonstrating that certain functional groups made the ring inversion more difficult and resulted in a more stable conformation in solution and at room temperature.

Further modifications have since been carried on the calixarenes including substituting the methylene group for a sulfide and modification of the upper and lower rim. The easy of removing or replacing the tert-butyl group at the upper rim facilitates the modification at the upper rim. Such modifications have resulted in compounds applicable to host-guest studies.
However, encapsulation of organic molecules, metals and ions have been achieved after lower rim modification at the phenoxy oxygen with groups such as ester, ketones ethers, amides, and other nitrogen, sulfur and phosphorus containing groups.\textsuperscript{167, 182, 188-191} Ungaro \textit{et al} reportedly alkylated phenolic oxygens of the lower rim with various ligating groups to obtain a partial cone and cone conformers in order to invoke ionophoric properties in the calixarenes.\textsuperscript{192} Shinkai and Iwamoto \textit{et al} worked out the selective synthesis of the calixarene conformational isomers.\textsuperscript{193} They showed that when tetra-O-alkylated with large groups, the Calix[4]arene three dimensional structures can be locked into four conformers namely: cone, partial cone, 1,3 alternate and 1,2 alternate depending on the base used in the alkylation and each conformer possesses selectivity for different metals.\textsuperscript{189, 194-196} This selectivity may be attributed to the sizes difference of the conformers\textsuperscript{197} for example, the cone is far more efficient in alkali metal extraction\textsuperscript{193} while the larger partial cone and 1,3 alternate have been shown to better accommodate larger cations including alkaline earths.
and the soft PGMs. Amide derivatives including thioglycoamides, hydroxy acetamide, alkylecyanamides, alkyl- and arylamides and picolinamide have been shown to possess remarkable advantages over a lot of extractants including selectivity and benign decomposition products.

\[ N,N\text{-}bis(2\text{-}aminoethyl)ethane\text{-}1,2\text{-}diamine (tren) \]

Tren ligand belongs in the class of tripodal tetrabidentate ligands. These tetrabidentate tripodal tetraamine ligands contain one tertiary N atom with three N bearing arms attached to it. When all the arms have the same conformations about the C–C and C–N bonds the ligand bears \( C_3v \) symmetry. “Splayed” arrangement of the three arms is also known in the solid state but protonated salts of the ligands can display an internally H-bonded structures in which the three arms are folded to form a cavity into which an anion can bind. Although four-coordinate displaying either a much distorted tetrahedral geometry, or a trigonal pyramidal geometry is possible, trigonal bipyramidal geometries with the tertiary N atom at an apical position are far more common in five-coordinate complexes. They are conformationally less rigid than the calixarene ligands. It therefore offers flexibility of size of metal ion it can encapsulate.

\[ 1,4,7\text{-}trithiacyclononane (ttcn or 9\text{-}ane\text{-}S_3) \]

9-ane-S\(_3\) belongs to a class of nine membered ring tridentate macrocyclic ligands with the triaza- azadithia- and trioxo- analogues which have been shown to complex various metals by a number of groups. They exhibit more thermodynamic stability in 1:1 complexes than their open ring forms dues to the macrocyclic effect. The ring size further adds more thermodynamic stability compared to the larger macrocycles. 9-ane-S\(_3\) have been shown to complex soft metals such as Pt through short Pt-S bonds to two sulfur atoms while the third sulfur adopts a variable longer Pt···S distance in distorted square planar
structures. The length of the apical Pt···S distance has been associated with the nature of ancillary ligands as phosphine and halide ancillary ligands have been shown to exhibit distances that differ widely (2.64 – 3.26 Å)\textsuperscript{202, 204-210} while bipyridyl complexes are somewhat in the middle (2.84 – 2.97 Å).\textsuperscript{211} They have featured in interesting Mo\textsubscript{2} complexes with unusual co-ordination geometry brought on by the interaction of their steric and electronic properties.\textsuperscript{212} It has also been described in complexes involved in charge transfer.\textsuperscript{213}

**Ethylenediaminetetraacetic acid**

![EDTA structure](image)

EDTA is known to form highly stable hexadentate complexes with d- and f-block metals through 2 nitrogen atoms and 3 or four acetate oxygen atoms once deprotonated. This outstanding chelating ability has led to a wide range of applications in chelation therapy,\textsuperscript{214} analytical chemistry,\textsuperscript{215} biomedical applications\textsuperscript{216} and metal extractions.\textsuperscript{217} Amine and acetate ligands are sigma donors. The coordination number of the complexes of [M(H\textsubscript{2}O)\textsubscript{n}(EDTA)]\textsuperscript{n} composition is dependent on the formal ionic radii of the metal, the average metal donor bond distance (M - O\textsubscript{ac}) and the difference $\Delta = (M-N) - (M-O\textsubscript{ac})$. For example, while many transition metal-EDTA complexes with average distance of 2.03 - 2.30 Å form 6 or 7 coordination complexes with EDTA, lanthanide are able to accommodate up to 3 H\textsubscript{2}O molecules when coordinated to hexadentate EDTA forming 9 coordination complexes.\textsuperscript{218} Up to 10 coordination number are known for dimeric lanthanide with bigger ionic radii such as La\textsuperscript{3+} and Ce\textsuperscript{3+} (1.04 and 1.02 Å).\textsuperscript{219} While most of the proposed scaffold and donor groups have been identified in some remarkable metal extractions, leaching of the extractant and/or the extracted species, low hydrophobicity, selectivity and slow extraction is a major drawback to solvent extraction.\textsuperscript{220, 221}
1.4 Exploring Non-Covalent Interactions in Fluorinated Structures

There are a profusion of non-covalent interactions that chemists can use to design supramolecular structures. Whilst hydrogen bonding continues to be a mainstay of non-covalent interactions, there is a growing realization that halogens-halogen interactions possess useful applications. Consequently there is now a growing interest in the halogen bond (XB), defined recently by IUPAC, in fields as diverse as crystal engineering, molecular recognition agents, molecular conductors, liquid crystals, catalysis, biology, material science, and medicinal chemistry. Halogen bonds have also proved useful for design of materials for applications in smart devices, bio- and nanotechnologies. The origin of XB is described in detail in Chapter 3. Although the existence of XB holds much contention, this work aims to add to the growing recognition of XB through experimental and computational characterisation of stabilisation energy contribution by such interactions. Maybe of most surprise is that F···F non-covalent interactions are known to be stabilizing and can offer a significant energy contribution to the structures, as Pauling’s principle state that the attractive interatomic dispersion forces would be low due to the low polarizability of fluorine. However, a number of studies in recent years have revealed that these sorts of interactions do exist and are not merely due to crystal packing. There are now a mounting number of examples of F···F interactions being exploited as drivers in crystal packing, pharmacotherapeutics, supramolecular chemistry, developing magnetic, conducting, elastic photoresponsive materials and gels.

There are three recognized types of F···F interactions (Chart 1); Type I are the most contentious in terms of delineating between crystal packing and stabilizing; Pseudo type I/II and Type II interactions has been described in the structure of (CF₃(CF₂)₅CH₂CH₂)₃P=O whilst Type III have recently been described in restricted geometries afforded by cyclohexane or naphthalene frameworks. Given the importance and potential use of C—
F···F—C interactions, it is imperative to ascertain the conditions where these have a stabilizing interaction and situations where these are due only to packing forces. C—H···F—C hydrogen bonds\textsuperscript{317} have only recently been recognized and are developing a strong research interest by both theory and experiment but C···F—C interactions are not so well developed. A number of C—H···F—C interactions have been noted in the structure of the carboxylic acid, CF\textsubscript{3}(CF\textsubscript{2})\textsubscript{5}CH(Me)CO\textsubscript{2}H but only C···F—C interactions were present in the alkane CF\textsubscript{3}(CF\textsubscript{2})\textsubscript{6}(CH\textsubscript{2})\textsubscript{4}(CF\textsubscript{2})\textsubscript{5}CF\textsubscript{3}.\textsuperscript{234} This preference for C—H···F—C interactions over C···F—C interactions have also been identified in the structure of 1,2,3,4-tetrafluorobenzene. This poses an interesting question as to which are the more stabilizing interaction. It is possible that more or stronger dipole-dipole interactions between non-fluorous neighbours, leads to segregation of the fluorous domains (a form of molecular xenophobia) or a steric dominated interaction, specifically the larger radius of F vs. H determines the interactions. Due to the importance of NCIs in diverse applications, it would be useful to shed light on this subject.

In addition to the information obtained from the solid state, investigations into fluorous interactions in the solution phase using Diffusion Ordered Spectroscopy (DOSY) and small angle X-ray scattering (SAXS) while in the gas phase, microwave spectroscopy can help to establish the nature of these interactions in the gas phase.

1.5 Application of F-F interactions in PFOA/Ligands Host-guest complexes

Perfluorinated compounds have a multitude of uses, partly due to their unique hydrophobic and lipophilic character. In the past 60 years, they have found applications in pharmaceuticals, stain, grease and water repellents or in the manufacture of products as diverse as emulsifying agents in polymer synthesis, paints, polishes, herbicides, insecticide, adhesives, firefighting foams and in food contact coatings such as those used in some brands of microwave popcorn bags.\textsuperscript{173,236-241} However the very strong C—F bond (485 kJ mol\textsuperscript{-1}) is resistant to hydrolysis, photolysis, biodegradation, metabolism, thermally treatments and their natural degradation pathway is unknown resulting in environmental persistence.\textsuperscript{242} Recent concern over the toxicity\textsuperscript{155, 243-246} and bioaccumulation\textsuperscript{242} has forced the reclassification as persistent organic pollutants (POPs).\textsuperscript{247} Some of the major pollutants include perfluorosulfonate (PFHS), perfluorobutane (PFBS) perfluorononanoic acid
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(PFNA) and perfluorooctanoic acid (PFOA). PFOA has been found in oceans and rivers across the world, in the blood serum of numerous animal species and occupationally exposed workers and the general public. Perfluorinated compounds are ubiquitous in the Arctic regions, which points to complex transport mechanisms, and indicates these POPs are globally distributed, with some evidence of vaporization of neutral PFOA from water. Although this has been the subject of robust debate, the probable source of POPs and related compounds are thought to be from fluorinated alcoholic telomers applied to food contact paper which due to their lipophilicity, the feature in paper coating to prevent oil in foods from soaking into the paper e.g. microwave popcorn, some fast-food wrappers, candy wrappers, pizza box liners, non-stick Teflon coating on cookware. PFOA is a known carcinogen, and also associated with liver cancer, mesothelioma or chronic kidney disease, increased risk of fatality due to diabetes mellitus, thyroid disease, decrease semen quality, disruption to metabolism and the immune system, reduced fetal growth including lower birth weight and reduced fecundity (fertility).

Interestingly, DuPont, the major manufacturer of fluoropolymers conducted a study on the extraction of PFOA from commercial non-stick Teflon coated cookwares and reported PFOA levels below detection limits (100 pg cm$^{-2}$); nonetheless, other studies have shown that some polar solvent as well as water can extract PFOA from PTFE. A thermal degradation study also shows the release of PFOA at temperature from 300-500 °C. In the context of an environmental pollutant, it is not treated by current waste water technologies so can contaminate drinking water supplies. The German water supply is known to be contaminated by up to 0.5 ppb while in the US, water companies are not required to test for PFOA. Although the 3M company, voluntarily phased out production of most of PFCs-based chemicals by the end of 2002, the US EPA launched a global stewardship program 2006 to reduce PFOA emissions and its presence in products by 95% by 2010 and complete elimination by 2015, however, the alarming need for industrial remedial procedures remains unfulfilled. As the C-F bond is very strong, selective dehydrofluorination methodologies based on transition metal catalysts have not been used to a great extent, but recent results with non-metals may hold promise. More traditional methods such as sorption onto activated carbon, polyaniline nanotubes, carbon nanomaterials, and photo-degradation especially using Ga$_2$O$_3$, In$_2$O$_3$, Fe(III)$_2$O$_3$, and modified TiO$_2$ catalysts have been reported. Reaction with OH radicals is not very efficient for photo-degradation, but Fenton-like chemistry using H$_2$O$_2$ has been reported.
Persulfate oxidation under UV-conditions is also reported to be efficient.\textsuperscript{274} Coagulation techniques,\textsuperscript{275} ball milling,\textsuperscript{276} $\gamma$-irradiation\textsuperscript{277} and sonochemistry\textsuperscript{278} have also been utilized in this field, but conspicuous in its absence is a solvent extraction process. C-F$\cdots$F-C non covalent interactions (NCIs) have been shown to not only exist in the solid structures of fluorinated compounds but adds stabilisation energy to the structure collectively in the same order of magnitude as a typical hydrogen bond.\textsuperscript{279} Application of NCIs in the solvent extraction PFOA have yet to be explored.

1.6 Application of F-F interactions in Solid Support

The need to efficiently trap catalysts or reagent with the intention of recycling or facile purification has spurred research in solid supports such as polymer-bound catalysts,\textsuperscript{280} scCO$_2$,\textsuperscript{224} scavengers,\textsuperscript{281} silica supported catalysts,\textsuperscript{282} polystyrene-supported systems,\textsuperscript{283} zeolites and mesoporous molecular sieves immobilised catalytic metal fragments,\textsuperscript{284} ionic liquids,\textsuperscript{285} soluble colloidal metal nanoparticles,\textsuperscript{286} dendrimer-bound catalyst,\textsuperscript{287} polymeric membranes in catalytic reactors.\textsuperscript{288} Immobilisation of ligands on fluorous silica gel and fluorous solid supports for applications including purification and solid state synthesis\textsuperscript{289-293} is a burgeoning area of solid support.

While most solid supports are developed using covalent linkage of the molecules to the polymer, which requires an additional reaction in specific conditions, the possibility of supporting ligands without the additional step is rather desirable. This has prompted the use of fluoropolymers for catalyst reclamation through precipitation.\textsuperscript{294} The possibility of physisorption of fluorinated compounds to a fluoropolymer by weak stabilising C-F$\cdots$F-C interaction with the intention of easy adsorption and desorption of the fluorinated compounds is yet to be investigated. This has the potential to eliminate the use of organic solvents as the extraction media.

Although the feasibility of physisorption on modelled fluorinated surfaces prepared via self-assembly of $1H,1H,2H,2H$-perfluorodecanethiol on a gold surface have been established, further studies with other ligands may be necessary in order to verify the scope of the idea. This could shed light on the possibility of adsorption of fluorous ligands on other fluoropolymer and the effect of ligand structure on adsorption and desorption.

While the synthesised ligand coated fluoropolymers can be characterised by Thermogravimetric Analysis in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere; Thermogravimetric Analysis combined with an Infrared
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Spectrometer (TG-IR) can carry out an Evolved Gas Analysis (EGA) where the volatile materials released from a heated sample on the TGA are transferred to an IR cell, where the components can be identified by their characteristic IR spectra. EXAFS spectroscopy can provide structural information about a sample by way of the analysis of its X-ray absorption spectrum.

1.7 Characterisation Methods

Hirshfeld Surfaces

Computational method of viewing molecular interaction is Hirshfeld Surfaces (HFS). Using HFS to analyse crystal packing and intermolecular interactions (NCIs) present, surface features characteristic of different molecular interaction shown as colour coded from surface to the nearest atom, can be seen while maintaining a whole-of-molecule approach, thus providing striking immediate picture of types of interactions present and even reflect their relative strength from molecule to molecule. This strips away the biases inherent in focusing on a limited amount of short contacts that are deemed to be important. HFS is defined by the 0.5 isosurface of the weight function, the sum of spherical atom electron densities from the molecule of interest (the promolecule) divided by the same sum for the crystal (the procystal).

Essentially, what you get is an electron density map of the whole crystal taking into account the electron distribution around each molecule and also accounts for intermolecular interactions denoted as deformations and red spots on the surfaces.

Inside the Hirshfeld surface the electron density of the promolecule dominates the procystal. For points on the surface, distances to the nearest atoms outside, $d_e$, and inside $d_i$ are readily defined. A three-dimensional picture of intermolecular close contacts in a crystal can be obtained when distances $d_e$ and $d_i$ are mapped on the Hirshfeld surface. They are also used to create a concise two-dimensional fingerprint plots which sums up the intermolecular interactions in the crystal. The limitation of mapping of the $d_e$ and $d_i$ on the surface is that they do not take into account the relative sizes of atoms and therefore do not effectively highlight close contacts between large atoms. $d_{\text{norm}}$ is therefore used in order to account difference in the sizes of atoms and close contacts between large atoms. The $d_{\text{norm}}$ is displayed using a red–white–blue colour scheme, where the red highlights shorter contacts,
white is used for contacts around the vdW separation, and blue is for longer contacts. Focus here is of course on the shorter contacts, which become brighter and larger red spots as internuclear separations decrease.

The 2D fingerprint plots yield quantitative analysis of the contributions of each NCIs present in the structure. This makes for quick comparison between related structures. The results of further analysis using shape index can further validate the three point bifurcated interactions and hydrogen bonding in the structures which are depicted as red spots. The curvature which is typically characterised by large areas of green separated by blue edges, shows highlights of yellow and red which indicates unusually flat regions corresponding and emphasising hydrogen bonding and the C-F···F-C interactions.

**Diffusion Ordered Spectroscopy**

The diffusional and fluxional properties of the ligands and the host guest complexes will be measured by diffusion ordered spectroscopy (DOSY) and relaxation times ($T_1$ and $T_{2ρ}$). DOSY is based on the idea that molecules in liquid or solution state possess translational motion is known as Brownian molecular motion also referred to as diffusion or self-diffusion. Diffusion is influenced by factors such as size and shape of the molecule, temperature, and viscosity of the solution. From the measured diffusion coefficient, the hydrodynamic radius can be calculated via the Stokes – Einstein equation:

$$D_{CT} = \frac{K_B T}{n \pi \eta a_H}$$

Where $n$ is either 6 or 4, assuming a spherical or oblate shaped molecule; $K_B$ is the Boltzmann constant; $T$ is the temperature; $\eta$ is the viscosity of the liquid and $a_H$ is the (hydrodynamic) radius of the molecule. Pulsed field gradient NMR spectroscopy can be used to measure translational diffusion of molecules and is sometimes referred to as q-space imaging. By use of a gradient, molecules can be spatially marked depending on their position in the sample tube. A second gradient can be applied to enable decoding of their new positions if they move after such encoding during the following diffusion time $\Delta t$. The measured signal is the integral over the whole sample volume and the NMR signal intensity is attenuated depending on the diffusion time $\Delta t$ and the gradient parameters ($g$, $\delta$).

$T_1$, Spin-Lattice (longitudinal relaxation, or relaxation in the z-direction or parallel to the external magnetic field, $B_0$) relaxation is the time constant for the physical processes
required for the relaxation of the components of the nuclear spin magnetization, leading to the establishing (or re-establishing) the normal Gaussian population distribution of α and β spin states in the magnetic field.\(^{302}\) \(T_2\), Spin-Spin (transverse relaxation, or relaxation in the x-y plane or perpendicular to \(B_0\)) is the loss of phase coherence among nuclei which is usually less than or equal to \(T_1\) (\(R = \) relaxation rate, \(R_2 = 1/T_2\), \(R_2 \geq R_1\)), since return of magnetization to the z-direction inherently results in the loss of magnetization in the x-y plane. Long \(T_2\) allows adequate transfer of magnetisation to neighbouring nuclei.

Only the phases of other nuclear spins are involved in \(T_2\) relaxation. On the other hand, and of major importance to this study is the fact that \(T_1\) relaxation involves exchanging energy between the "lattice" upon interaction with the surroundings (hence, spin-lattice relaxation), causing thermal relaxation of the spin system by thermal contact between the spins and an adequate heat reservoir, modifying in some cases drastically, the spin-spin interaction. Therefore the closeness of molecular fragment to each other in a solution can influence spin-lattice relaxation. Such information can be diagnostic of the fluxional behaviour and spatial arrangement of molecules. Also, short \(T_1\) means a faster experiment can be carried out.

Small Angle X-Ray Scattering

The extracted species will be characterised using a host of spectroscopic techniques including mass spectrometry and small angle X-ray scattering (SAXS).\(^{303,304}\) SAXS is well suited to the gold complexes as compounds with high-Z, high electron density (metals) has distinct advantageous characteristics for X-ray scattering studies as high electron-density elements scatter X-rays strongly. Compounds like metal-oxo clusters are molecular by definition, solutions in which the clusters are stable are absolutely monodisperse, and their X-ray scattering data can be simulated very accurately from solid-state crystal structures. The ‘Small-angle’ is formally defined as a q-range of approximately 0.02 up to 0.7 or 1.0 Å\(^{-1}\) (depending on the detector type), and wide-angle extends the q-range to 2.5 Å\(^{-1}\) (4.9 or 7.0 and 17.8 respectively). The extended wide-angle range allows accurate characterization of size (through determination of radius of gyration, \(R_g\) and other form factors). It can also allow us to observe the oscillations that follow the primary scattering curve. Oscillations are exploited to distinguish two very similar clusters, or to characterize clusters that possess heterogeneous electron density. However, observing oscillations is oftentimes challenged because they are sometimes masked by solvent scattering peaks. Polydispersity or presence
of other small species in solution including counter ions and other electrolytes, as well as cluster fragments that contribute to non-specific scattering in the ‘high-q’ region (i.e. above 1 Å⁻¹) where oscillations are typically observed also mask these important distinguishing features.

The advantage of this technique is that crystalline sample is not required but spatial averaging in solution leads to loss of information. Size, size distribution and shapes of monodispersed macromolecules can be determined by analysing the density difference in the sample. Experimentally, X-rays beams produced in a synchrotron are focused by a number of slits and passed through a sample. The X-ray are scattered by the molecules in the sample. The scattering at a small angle (0.1-10⁰) are recorded as these contains information about the shapes of the molecules. The scattered waves are recorded in a 2D detector from which a 1D scattered curve is generated. A calculated 3D model of the molecules is then changed by a computer program until the calculated 1D curve matches the experimental curve.

Infrared Reflectance Absorption Spectroscopy

IRAAS is used to study thin films adsorbed on reflective surfaces. As reviewed by Flach et al., 305 it is based on the notion that when mid-IR radiation impinges onto a sample, a small fraction (6%) of the light is reflected from the molecular constituents of the surface. The reflected light undergoes phase change of polarised light on the metal surface is measured as change in reflectance upon absorption (reflectance-absorbance (RA) vs wavenumber). RA is defined as −log₁₀(R/R₀) where R is the reflectivity of the film-covered surface and R₀ is the reflectivity of the aqueous subphase. IRRAS measurements provide frequencies and intensities of molecular vibrations. The intensities are interpreted in terms of molecular structures which then permits determination of ordered structural elements or the orientation of functional groups by measuring intensities of different molecular vibrations. Moreover, it is performed at a grazing incidence subject to overriding selection rule stating that only those vibrations whole dipole change is perpendicular to the surface can be detected. Nonetheless, the optical properties of the interface must be considered. Other factors that determine the reflected intensities at frequencies corresponding to molecular vibrations includes, the experimental geometry (angle of incidence, state of polarization of the radiation), extinction coefficients, the optical constants (real and imaginary parts of the refractive indices of the film and subphase), and the orientation of the vibrational transition moments relative to the incident plane of illumination. 306, 307
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However, as with most techniques the major impairment to IRAAS experiments is interference from the omnipresent rotation-vibration bands from water vapour. This can be solved by a sample shuttle technique in which a reference IRRAS spectrum is acquired from a film-free surface or polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS), developed primarily by the Bordeaux group. This possesses an advantage over the conventional IRRAS mode in that the modulated reflectivity is independent of the isotropic adsorption from vapour or bulk water. In this experiment, a photoelastic modulator generates alternating linear states of polarized light. Consequently the interfering effect of water vapour and carbon dioxide can be substantially reduced.

Scanning Electron Microscopy
Deposition of ligands on fluoropolymer such as Teflon surface can be checked by optical microscopy. To confirm that the rough surfaces are due to ligand deposition, Raman mapping and SEM will be employed for surface topography and morphology studies. SEM permits non-destructive evaluation of the specimen and very short sample preparation time. To form images, various signals from the specimen can be collected and used viz Secondary Electron (SE) images, Backscattered Electron (BSE) images; Electron beam induced current (EBIC), Cathodoluminescence (CL) and Voltage-contrast imaging.

In an SEM experiment, the incident electrons (from an electron gun) typically have energies of 2-40 keV. The electron beam electromagnetic condenser lenses demagnify into a fine probe which is scanned across a selected area of the specimen surface in a raster by scan coils. The electrons penetrate the specimen with a penetration depth that is determined by the energy of the electron beam, the atomic masses of elements in the specimen and the angle at which the electron beam hits the specimen. The interaction of the electron beam with the specimen produces secondary, backscattered and Auger electrons, x-rays and perhaps light, collected by various detectors in the specimen chamber. Energy Selected Backscattered detector and Angular selected backscatter detector (for atomic number or Bragg scattering contrast) together with Secondary Electron detector are used to collect the backscattered electron and the secondary electron. The signal from each detector can be fed to a monitor, which is rastered in synchronisation with the electron beam to produce the images.

Raman mapping
Raman imaging is widely used to characterize the distribution of components within a sample using Raman scattering. Raman mapping involves sequential measurement of spectral of the adjacent regions of a sample. This is achieved by moving each region of the sample into the beam focus of the microscope after the spectrum of the previous region has been measured. The measurement is then repeated until the entire region of the sample has been measured. Raman imaging is a powerful technique for generating detailed chemical images based on a sample’s Raman spectrum. A complete spectrum is acquired at each pixel of the image, and then interrogated to generate false colour images based on material composition, phase, crystallinity and strain. In Raman scattering, the inelastic scattering of a photon when a small fraction of the scattered light (approximately 1 in $10^7$) is scattered by an excitation which leads to scattered photons with a frequency different from that of the incident photon. The scattered photon is of unique energy levels for every molecule and the frequency of light scattered from a molecule give the structural characteristics of the chemical bonds making Raman spectrum highly chemical specific. Along with elemental analysis, characterisation by TGA and TGA-FTIR, can be used in the quantitative determination of surface coverage as well as thermal behaviour of the fluoropolymer supported ligands FSL. Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. This technique is useful in characterisation of samples with diverse applications such as environmental, food, pharmaceutical, material, and petrochemical applications. It is particularly useful in this studies due to its ability to detect phase changes as a function of temperature and produce a result in form of weight change. Thermogravimetric Analysis combined with an Infrared Spectrometer (TG-IR) can carry out an Evolved Gas Analysis (EGA) where the volatile materials released from a heated sample on the TGA are transferred to an IR cell, where the components can be identified by their characteristic IR spectra.

Extended X-ray Absorption of Fine Structure (EXAFS)

EXAFS spectroscopy provides structural information about a sample by way of the analysis of its X-ray absorption spectrum. It allows determining the chemical environment of a single element in terms of the number and type of its neighbours, inter-atomic distances and structural disorders. This determination is confined to a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5 and 10 Å radius from the
element. In principle when an atom absorbs X-ray, a core electron is excited to a state significantly above the binding energy and ejected from the core its core shell leaving a “core hole”. Relaxation of less shielded elections leads to a drop down into and filling the core hole. The photoelectron leaves the exited atom by a circular wave motion and then undergoes single elastic scattering by neighbouring atoms. The original and scattered wave function then undergo constructive or destructive interference which reinforces or cancels out the amplitude. The interference depends on the number of wavelength per distance travelled, and their atomic numbers, while the interference oscillation and amplitude depends on the distance of neighbouring atoms and number of neighbouring atoms. The data is the analysed by removing the background and Fourier transforming to obtain a radial distribution function. This is an element specific technique in that X-ray absorption edges occur for each shell of core electrons taken as when $E \sim$ binding energy of the core electron.

1.8 AIMS OF THE PROJECT

The objectives of this project are carried out in five phases, viz, (1) ligand design and syntheses (2) Studies of non-covalent interaction present in the fluorinated structures. (3) Application of these interactions in extraction of PFOA. (4) Metal extraction. (5) Development of fluoropolymer solid supports.

Metal extraction is a major aim of this project. Reclamation of ECM has been suggested as a way to reduce dependence of virgin materials whose future supplies is uncertain. Current metal recycling method and associated drawbacks have been extensively described earlier in this Chapter. This project aims to develop “green effective cheaper” extractants that can be added to environmentally benign extraction systems such as Supercritical fluids (SCF) in order to increase the solubility of the metals in the scCO$_2$ (Figure 1.12)
The rationale behind the design and synthesis of the extractants is discussed in details in Chapter 2.

Extensive characterisation of the non-covalent interactions present in the synthesised ligands will be carried out. Upon successful characterisation, potential non-covalent interactions will be harnessed in the extraction of a persistent organic pollutant – perfluorooctanoic acid (PFOA) from water using the synthesised ligands. Characterisation techniques including multinuclear NMR spectroscopy, DOSY, SAXS, and computational studies will be employed.

The metal extraction phase will be split into two themes: solution (Chapter 5) and solid state (Chapter 6) metal extractions, but the methodologies will be the same for both as shown schematically in Figure 1.12. The idea is to crush the e-waste to a powder, dissolve in acid and extract the metal salts from aqueous solutions. As a screening method for scCO$_2$ process, fluorinated solvents such as FC-72 (Fluorocarbon derivative of tetrahydrofuran) or FC-75 (Perfluorohexane) can be used as a model solvent as some fluorinated compounds have been shown to possess similar solubility profile in scCO$_2$ and in FC-72$^{316}$ making FC-72 an ideal model for scCO$_2$. This therefore requires the ligands to be fluorinated in order to promote the fluorophilicity and high distribution coefficient of metals into the model fluorinated solvent. The extraction efficiency of these extractants will be examined in metal extraction using UV spectroscopy. The distribution ratio ($D$) of metals into the fluorous/organic phase over the aqueous phase can then be extrapolated. At this point, additional fine tuning of

Figure 1.12. The Proposed Metal Extraction System
ligands by modification of various factors to increase $D$ will be carried out. While ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) has a greater sensitivity and accuracy, Electronic absorption is a good methodology for rapid screening during determination of optimum temperature, pH and ionic strength for each extractants. Study of all potentially interesting properties of the complexes will be carried out and determination of a facile method for stripping of metals from the complex will be explored. The binding constants will also be determined using UV titrations and the co-ordination modes will be shown by IR.

In addition to liquid-liquid extraction, this project aims at developing solid state extractants. Utilising characterised fluorous interactions, and the super-hydrophobicity of fluorous material, solid state sorbents based on these compounds will be prepared. Deposition of ligands on fluoropolymer such as Teflon surface can help avoid the extra reaction for supporting ligands and aid easy desorption of ligands. These ligands will be physisorbed onto Teflon tape creating solid state extractants using the fluoropolymer or a polymer resins. Such fluoropolymer supported ligands can be characterised by a host of analytical methods including Raman mapping, SEM and optical microscopy. To confirm that the rough surfaces are due to ligand deposition, SEM can be employed for surface topography and morphology studies. Along with elemental analysis, characterisation by TGA and TGA-FTIR, will be used in d quantitative determination of surface coverage as well as thermal behaviour of the fluoropolymer supported ligands FSL.

Upon successful characterisation, practical application of the FSL samples in energy critical metal extraction can give indication of ligand activity when physisorbed. Therefore, the fluoropolymer supported extractants made would be applied in solid-liquid metal extractions with the aim of facile extractant recovery. The extracted species will be characterised using EXAFS.
In conclusion, the theme this project has been introduced as the development of extractants for metal reclamation. The incorporation of fluorinated groups in the ligands design lends an interesting subject in fluorous interactions. The use of these non-covalent interactions in the extraction of PFOA and development of solid support will be discussed. The extraction of metal in solution/solution and solid/solution phase has been introduced. These concepts are discussed in details in the following chapter and the result of the studies are presented.

1.9 REFERENCES

4. V. Zepf, in *Rare Earths Industry*, Filho, Elsevier, Boston, 2016, DOI: http://dx.doi.org/10.1016/B978-0-12-802328-0.00001-2, pp. 3-17.
34. N. Mohabuth, P. Hall and N. Miles, Miner. Eng., 2007, 20, 926-932.
47. G. H. Morrison and H. Freiser, Solvent extraction in analytical chemistry, 1957.
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Chapter 2
Ligand Synthesis
2.1 OVERVIEW

The use of fluorinated extractant for solvent extraction offers the possibility of high distribution coefficients in solution extraction studies due to the hydrophobicity of fluorinated molecules.\(^1\) This hydrophobicity can be enhanced by modulating the length and/or amount of the fluorinated alkyl chain.\(^2\) Ligands with fluorous groups also display solubility in fluorinated solvents such as perfluorinated hexane (FC-72) which can be used as a model solvent for \(\text{scCO}_2\) due to similarity in the solubilising properties of the solvents.\(^3\)

The use of FC-72 allows rapid screening of ligands using liquid-liquid extraction of metals instead of \(\text{scCO}_2\) which requires high pressures. Highly fluorous co-extractants including, fluorinated ketones, phosphine oxides and sulfides have therefore been investigated in liquid-liquid extraction and their efficacy in the extraction of a number of metals into FC-72 with the aim of WEEE recycling is well documented.\(^4\)\(^-\)\(^7\) The aim is to synthesise fluorinated derivatives of well-known ligands. The presence of fluorous groups in the synthesised ligands effect properties described above. In order to obtain optimum solubility in \(\text{scCO}_2\) or FC-72 the amount and length of the fluorous groups must be well thought-out as excessive fluorination can hinder solubility in most organic or even fluorinated solvents.

The target ligands are shown in Figure 2.1. Amide functionalised tris(2-aminoethyl)amine (Tren) (1). Substitution on the lower rim of the calix[4]arene with amide functions in the cone- (2) and partial cone calix[4]arene (3) conformations or substitution with a phosphine (4) or phosphine oxide (5); Trithiacyclononane (9-ane-S\(_3\)) (6) and Propylenetetracetic acid (7) ligands will be synthesised. This chapter opens with a very brief historical account of previous synthesis of each class of ligand and is followed by the discussion about the proposed synthetic strategy and finally results.
2.1.1 N,N-tris(2-aminoethyl)-amine (tren), 1

Tren was first prepared by in 1896 by Ristenpart, as the trihydrochloride salt, from the reaction of 2-bromoethylphthalimide with dry ammonia, and subsequent deprotection of the resulting tris(2-phthalimidoethyl)amine using HCl gave the tren.3HCl salt. Exhaustive N-alkylation and acylation have been carried out on these ligands.9
2.1.2 Amide functionalised Calix[4]arene, 2 and 3

Ligands based on the calix[4]arene framework are relatively straightforward. O-alkylation of calixarene at the lower rim is a common feature in calixarenes. Such modifications usually result in a locked conformation yielding the cone 1,2-alternate, 1,3-alternate and the partial cone conformer.\textsuperscript{10-12} However, methods exist for the selective synthesis of each conformer.\textsuperscript{13, 14} The acetate can be modified to yield amide derivatives using Schotten-Baumann type reaction for the amide formation. Adaptation of the Schotten-Baumann reaction here will involve acetyl chloride derivative and a fluorous amine to generate a fluorous calixarene with an amide group between the calixarene and the fluorous groups.

2.1.3 Calixaryl-Phosphine and Calixaryl-Phosphine Oxides, 4 and 5

Fluoroalkyl phosphines and phosphine oxides are well studied in co-ordination chemistry as well as in metal extraction\textsuperscript{4, 6} Trialkylphosphines can be synthesised by a number of ways such as from metallated phosphines, halogenophosphines and organometallic reagents, addition of P–H to unsaturated compounds, reduction of phosphine oxides and related compounds,\textsuperscript{15} activation of P$_4$,\textsuperscript{16} metal-catalysed routes for C–P bond formation,\textsuperscript{17} modular formation of the phosphonium salt followed by base cleavage,\textsuperscript{18} Imine-formation from phosphinoarylaldehydes, amide- and ester-formation from phosphinoarylcarboxylic acids,\textsuperscript{19} and side-chain functional group transformations of phosphinoferrocenes.\textsuperscript{20} In this synthesis, the method adopted involved the reaction of tetratosylate derivative of the calix[4]arene with synthesised dialkylphosphide through halogenophosphines and organometallic reagents.

2.1.4 1,4,7-Trithiacyclononane (9-ane-S$_3$), 6

The related compounds of 9-ane-S3 such as DOTA,\textsuperscript{21} TACN,\textsuperscript{22} and macrocyclic phosphines\textsuperscript{23, 24} and Aza- and oxaphosphands\textsuperscript{25} and their derivatives have seen tremendous progress in terms of synthesis and co-ordination chemistry. Synthesis of the triaza- trioxo- and phosphorus ligands have been structurally modified and employed in metal chelation, to the best of our knowledge, there are no known fluorinated 9-ane-S$_3$. Since it was first reported in 1920 by Ray,\textsuperscript{26} The tritha- ligands still holds only a few synthetic routes including the Mo template synthesis and the Cs$_2$CO$_3$ procedures (Scheme 2.1 and 2.2) which yields 60 and 50% 9-ane-S$_3$ respectively.\textsuperscript{27, 28}
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2.1.5 EDTA, 7

The synthesis of EDTA by Ferdinand Munz of I. G. Farbenindustrie dates back to the early 1930s when he first recognised the compound’s valuable metal chelating or sequestering properties. He obtained nitrilotriacetic acid which he then transformed to EDTA. Early synthesis involved chloracetic acid and ethylenediamine resulting in the crude tetrasodium salt solution with sodium chloride by-products.

\[
\text{H}_2\text{N} - \text{NH}_2 + 4\text{ClCH}_2\text{COONa} + 4\text{NaOH} \rightarrow \text{NaOOCH}_2\text{C} - \text{N} - \text{CH}_2\text{COONa} + 4\text{NaCl}
\]

**Equation 2.1.** Farbenindustrie’s acid and ethylenediamine route

Other routes to EDTA involving cyanomethylation with ethylenediamine, formaldehyde, and sodium cyanide (equation 2.3) were subsequently refined to a one step cyanomethylation by the efforts of Bersworth’s and also by Geigy (equation 2.4).
Equation 2.2. Farbeinindustrie’s two step cyanomethylation\textsuperscript{30}

Equation 2.3. Bersworth’s one step cyanomethylation\textsuperscript{31}

Equation 2.4. Geigy one step cyanomethylation\textsuperscript{32}

Equation 2.5. Catalytic oxidation of tetrahydroxyethylenediamine\textsuperscript{33}

Equation 2.6. The reaction of ethylene dichloride and disodium iminodiacetate\textsuperscript{34}

Catalytic oxidation of tetrahydroxyethylenediamine has also been reported to yield the EDTA-tetrasodium salt. However, none of these routes allows the fluoro-alkylation of the ethylene spacer. Therefore a more proficient synthetic route is desired. The reaction of ethylene dichloride and disodium iminodiacetate which is another known method of EDTA synthesis and has been found to be potentially convenient as this would allow the pre-functionalisation of the ethylene dichloride or complete replacement with a more suitable electrophile.
2.2 Synthetic Strategy for the synthesis of fluorous ligands

The ligands will be synthesised with a number of considerations in order to maximise yield, purity, atom efficiency, environmentally benign chemistry, and avoid some drawbacks inherent in fluorine chemistry. Such considerations are highlighted below.

- Ligand synthesis must involve linear synthesis of some precursors and convergent assembling of the components.
- The synthesis must involve cheap, readily available and environmentally benign starting materials where possible.
- The synthetic routes employed must preferably involve the most feasible route with the least amount of reaction sequences as determined from the retrosynthesis of the ligands.
- Ligands must include one or two methylene groups before the fluorous groups to insulate the donors from the electron withdrawing nature of the attached fluorous ponytails.\(^{35}\)
- The fluorous groups must be introduced at a later stage of the synthesis where possible as the presence of a large numbers of fluorous groups could hinder the solubility of the precursor and thereby hamper the process.

2.2.1 Retrosynthetic analysis of 1

For the fluorous tren, 1, retrosynthetic analysis of the ligand is shown in scheme 2.3. In the forward sense, acylation of precursor tren using fluorinated acid chloride is expected to afford the target. The acid chloride can be readily made from the alcohol.
Scheme 2.3. Retrosynthetic analysis of Fluorous-tren
2.2.2 Retrosynthetic analysis of 2 and 3

Retrosynthesis of 2 and 3 reveals tetraacetyl chloride intermediates and amine. Amide formation reaction involving the calix[4]arene tetraacetyl chloride and a fluorinated amine is expected to yield the desired targets, 2 and 3 (Scheme 2.4). The acid chloride can be accessed through the tetraacid which is a reduced product of the tetraacetate. The tetraacetates can be made from the commercially available tetraol. It is also worth noting that the amide can also be easily assessed by reaction of the tetraacetates or the tetraacids with the amine using suitable coupling reagents such as \(N,N'\)-Dicyclohexylcarbodiimide. However, the selected route is based on available materials.

![Scheme 2.4. Retrosynthetic analysis of Fluorous-cone (2) and partial cone calix[4]arene (3)](image-url)
2.2.3 Retrosynthetic analysis of 4

A method involving the use of halogenophosphines and organometallic reagents will be adopted to synthesise the target phosphine. Phosphorus trichloride and fluoroalkylmagnesium alkylating agent would be required for this transformation.

Scheme 2.5. Retrosynthetic analysis of Fluorous-calixaryl phosphine

However, due to the tendency for phosphorus trichloride to form trialkyl product in the presence of a suitable alkylating reagent,\textsuperscript{36} this would necessitate the protection of the
phosphorus with an amine before the alkylation step while avoiding the formation of the diamido compound (Scheme 2.5). Deprotection followed by coupling of the phosphide intermediate to the Calixarene is expected to yield 4. The tetratosylate can be accessed through reduction of the corresponding tetraacetate.

### 2.2.4 Retrosynthetic analysis of 6

However, for the fluorous 9-ane-S₃, the intermediates required for the final coupling step need to be alkylated with the fluorous pony-tails so as to reveal fluorous groups on the ethylene spacers of the precursors as shown in scheme 2.6. However, unlike the nitrogen heterocycles, modification at the sulfur donor is not possible. Therefore fluoroalkylation must be at the ethylene spacers before assembling the macrocycle. Unfortunately, the electron withdrawing nature of the fluorous groups can impinge functional group interconversion to obtain the desired dithiolate precursor.

From retrosynthetic analysis, an epoxide would be a suitable starting material. Ring opening of the epoxide would generate the fluorous dialkoxy intermediate. Functional group
interconversion can yield the dibromo compound which will also be converted to the dithiol required for the final template step with fluorous dibromoethane. The fluorous dibromoethane can be obtained by brominating a fluorinated alkene.

2.2.5 Retrosynthetic analysis of 7

For the synthesis of the fluorous EDTA, there is no known ethylene diamine compound with suitable function for attaching both the fluorous and iminodiacetate groups at the methylene spacers. Therefore, like the 9-ane-S₃ synthesis, more retrosynthetic steps has to be carried out in order to reveal a fluorinated precursors that can be coupled together. The devised route would consist of a precursors fluorinated ethyl backbone that can be coupled to the iminodiacetate³⁴ (Scheme 2.7). Although the EDTA ligand can be put together by a number of procedures, none of these synthetic routes would be suitable for purpose as the ethyl backbone in the EDTA type ligand needs to be functionalised with fluorous groups. There is no known ethylene diamine compound with suitable function for attaching the fluorous groups at the ethyl backbone. Therefore the diketone shown in scheme 2.7 was therefore chosen.

Scheme 2.7. Retrosynthetic analysis of EDTA derivative
2.3 RESULTS AND DISCUSSION

2.3.1 Synthesis of Fluorous trisamidoamine

\[ \text{Scheme 2.8. Synthesis of fluorous-trisamidoamine, 1} \]

From a retrosynthetic analysis (Section 2.2.1), the synthetic route to 1 is shown in Scheme 2.8. 2H,2H-perfluoroocanoic acid, 9 was prepared by oxidation of the corresponding alcohol with Jones Reagent, as described in the literature.\(^\text{38}\) Crystallization from DCM afforded X-ray quality colorless plate-like crystals in 53% yield. Further discussion of the crystal structure is presented in Chapter 3.

Compound 9 was readily converted to the corresponding acetyl chloride, 10 using excess thionyl chloride as indicated by the \(\nu(C=O)\) at 1807 cm\(^{-1}\) in the infrared spectrum. This compound was not isolated but was used \textit{in-situ}. The target compound, 1 was obtained by the reaction of 10 with Tren eliminating HCl (overall yield of 30%). In all the fluorinated compounds, the peaks in \(^{19}\text{F} \) NMR spectra due to CF\(_3\) appear at -81 ppm and the CF\(_2\) peaks appear at -113 – 126 ppm and do not move except for the CH\(_2\)CF\(_2\) which is diagnostic of the chemical environment. Although the CF\(_2\) and CF\(_3\) groups in the \(^{19}\text{F} \) NMR of all the compounds synthesised are multiplets and triplets, but they are quoted as singlets as the best practice in the literature which is likely due to their very small coupling constants. HRMS analysis showed a molecular ion calculated as (M+H = 1227.1074). The infrared spectrum
showed ν(C=O) = 1638 cm\(^{-1}\) and \(^1\)H NMR spectrum showed overlapping peaks at δ\(_H\) = 2.62 and 3.4 ppm indicating CF\(_2\)CH\(_2\)CO, CH\(_2\)NCO and CH\(_2\)N as deduced from the HSQC analysis. The \(^{13}\)C\{\(^1\)H\} spectrum shows a resonance at δ\(_C\) = 167 ppm indicative of the amide C=O. The CH\(_2\)CF\(_2\) which is diagnostic of the chemical environment in the \(^{19}\)F NMR analysis shows a shift from δ\(_F\) = 117 ppm to δ\(_F\) = 114 ppm in the \(^{19}\)F NMR spectrum.

A small side product (yield = 28\%), 2H-perfluorooct-2-enoic acid (9c) was also isolated at the end of this reaction (Scheme 2.9). The mechanism of the reaction is rationalised as dehalogenation reaction in the presence of a base.\(^{38}\)

![Scheme 2.9. Synthesis of 2H-perfluorooct-2-enoic acid](image)

### 2.3.2 Synthesis of Fluorous Calixaryl amide

![Scheme 2.10. Synthesis of fluorous amine towards the synthesis of 2 and 3](image)
The required amine, 17 was obtained via the literature procedures, and spectroscopic data was consistent with the published data. 1H,1H,2H,2H-Perfluoroctyl iodide was converted to 15 and a triazole side product, 16 (Scheme 2.10) using NaN₃ in DMF. The azide, 15 was characterised by NMR spectroscopy. The peaks at δ_H = 2.4 ppm and δ_H = 3.6 ppm in the ¹H NMR spectrum are assigned to the CH₂CF₂ and CH₂N₃ respectively. The triazole, 16, was isolated as a minor by-product. Cooling the crude mixture to -35 °C afforded a few crystals of 16 that were structurally characterized (Chapter 3). Careful ¹H NMR spectroscopic analysis of the reaction mixture showed that 16 is consistently formed in low yield; the spectroscopic data confirmed the formulation of 16, particularly the unique CHF group at 6.1 ppm as a ddd (2_J_H-F = 25 Hz). The mechanism of formation was rather unclear but thought to involve a Huisgen 1,3-dipolar cycloaddition reaction with key features of click reaction (regioselectivity). Clearly the azide product formed reacts with the starting material which has most likely been activated in a mechanism shown in scheme 2.11. However, a number of transformation is suspected to happen to the perfluoroalkyl iodide to set up the Huisgen 1,3-dipolar cycloaddition reaction. The formation of a number of products upon dissolution of CF₃(CF₂)₃CH₂CH₂I in DMF is well known, and one of which has been identified as the dimethylammonium iodide by X-ray crystallography. Therefore a dehydrohalogenation step was thought to be involved as this is also a known feature upon reaction of the perfluoroalkyl halide with DMF, giving rise to an alkene and also accounts for the formation the unique CHF moiety. However the reaction must be more complex than this, since an alkyne must be generated otherwise an additional rearomatisation step must take place at the end of the reaction. It’s also worth noting that similar azide has been reported to form triazoles via the copper catalysed click reaction in good yield and with an intact fluorous group. A better understanding of the possible reaction mechanism comes from the reaction of 2H,2H-perfluoroctanoic acid, 9 with a base to generate perfluorooc-t-1-enoic acid, 9c as shown in Scheme 2.9, consistent with widely reported dehalogenation of perfluoroalkyl halides to generate the corresponding alkenes.

A second dehalogenation is also possible (Scheme 2.11), generating a transient allene or carbocation (as in a classic E1 reaction) – accounting for the loss of fluorine at the C3 position. An isomerisation, 1,2 or 1,3 hydride shift due to “special fluorine effect” (molecules isomerise to move a double bond to the less fluorinated carbon to relieve the destabilisation caused by the fluorine at the sp² carbon) is very likely involved. It is suspected that resulting species must then have a LUMO resembling that of a very electron
deficient alkyne, allowing the cycloaddition reaction to proceed even without a Cu(I) catalyst. Irrespective of the mechanism, an optimised synthesis of 16 involves adding small portions of NaN₃ to a solution 1H,1H,2H,2H-Perfluoroctyl iodide in DMF (yield = 67%).

![Scheme 2.11. Proposed reaction mechanism of the triazole formation](image)

The azide 15 and the triazole 16 were reduced to the amine, 17 using excess LiAlH₄ in 46% yield (Scheme 2.10). 17 was obtained as the only product as indicated by ¹H NMR spectroscopy. Although a Staudinger reduction using triphenyl phosphine is a safer method of azide reduction, the product could not be isolated due to inseparable mixture/precipitate during work-up. Using LiAlH₄, the characteristic peaks at δ_H = 3.09 ppm for CH₂NH₂, δ_H = 2.63 ppm (J_H-F = 19 Hz, J_H,H = 7 Hz for CH₂CF₂), δ_H = 1.48 for NH₂ indicating conversion of both the azide and triazole to the corresponding amine. The triazole 16 was not detected by spectroscopic analysis. Mass spectroscopy showed the calculated [M+H] molecular ion at 364.0365 as 364.0374.

In an attempt to synthesise the fully fluorinated amine with no CH₂, a reaction between CF₃(CF₂)₆CF₂I and NaN₃ in DMF was attempted to produce the corresponding CF₃(CF₂)₆CF₂N₃. This yielded a colourless, crystalline product which was shown to be CF₃(CF₂)₆CO₂H (perfluorooctanoic acid) by X-ray diffraction. The mechanism of formation is not clear but careful analysis of the crude mixture by NMR spectroscopy shows this to be the only product. Perhaps given the electron withdrawing nature of the fluororous chain this weakens the C-I bond and is thus more reactive with DMF. Interestingly, we have not been able to obtain single crystals from recrystallizing commercially available PFOA, and to the best of our knowledge this is the first time that PFOA has been structurally characterized.
The synthetic routes to the fluorous calix[4]arene amide ligands, 2 and 3 are shown in Scheme 2.12. Whilst 11 and 12 are known compounds it was found that under experimental conditions 66% of the ‘partial-cone’ conformer 12 was formed. Extraction of the crude mixture with EtOH/H₂O (20:1 v/v) resulted in a solution of 11. 12 remained as a solid. The conversion of 11 and 12 to the acid chlorides 13 and 14 was straightforward using freshly distilled SOCl₂ under an Ar atmosphere.

The reaction of the tetraacid chloride with the fluorous amine CF₃(CF₂)₅CH₂CH₂NH₂ (17) allowed a high yielding synthesis of both full (2) and partial-cone (3) calix[4]arene amide. The spectroscopic data of 2 and 3 are in accord with our formulations but despite repeated attempts, no crystals suitable for single crystal X-ray diffraction could be isolated. For compound 2, the ¹H NMR spectra shows the diastereotopic methylene protons at δ_H =3.3 and δ_H =4.2 ppm which are diagnostic of a cone conformation.¹²,¹³,⁴⁴,⁴⁵ The ¹H NMR spectra of 3 showed multiple peaks at corresponding regions and integration of tert-butyl groups gave 1:2:1 ratio suggesting a partial cone conformer. The IR spectra of compounds 2 and 3 clearly showed the presence of amide groups ν(C=O) = 1668 cm⁻¹ while mass spectrometry confirmed the presence of the products as the (M+Na⁺) ions. The NMR and vibrational data of 2 and 3 are discussed further in Chapter 4.

![Figure 2.2. ¹H NMR spectrum of 2 in CDCl₃.](image-url)
Scheme 2.12. Synthesis of 2 and 3
2.3.3 Synthesis of Fluorous Calixary phosphine

The tetratosylate derivative of calix[4]arene, 26 was obtained by literature procedures (Scheme 2.13) and the intermediates in agreement with literature. The synthesis of the dialkylchlorophosphine, 22 was more problematic. PCl₃ was treated with 2 equivalent of R₃MgI but the desired R₂PCl was not obtained. Instead, ³¹P {¹H} NMR spectroscopy showed only R₂P (δₚ = 29 ppm) in accord with the literature. Another strategy for the synthesis of the desired R₂PCl involving protection with an amine group. Compound 20 was obtained by reacting Et₂NH with PCl₃ and purified by distillation (40 – 42 °C, 760 mmHg). A single peak in ³¹P {¹H} NMR spectrum at δₚ = 162 ppm indicated a 96% pure compound 20. 21 was obtained by reacting 20 with the Grignard, 19 under an inert atmosphere (Scheme 2.14). A single peak at 46 ppm in the ³¹P {¹H} NMR spectrum showed clean formation of 21. The amino group was then removed by treating with anhydrous hydrogen chloride to obtain 22 indicated by a single peak in the ³¹P {¹H} NMR spectrum at δₚ = 105.07 ppm, indicative of ClPR₉₂. 21 was reacted with Na to generate the dialkylphosphide intermediate which was not isolated but reacted immediately with 26 to afford the perfluorodialkylphosphinous-Calix[4]arene, 4 indicated by a single peak in the ³¹P {¹H} NMR spectrum at 23.07 ppm.
Oxidation of the phosphine to the phosphine oxide 5 was achieved simply by stirring under ambient atmosphere (Scheme 2.14). The $^1$H NMR spectra of the purified compound 5 shows absence of the tosyl groups and the presence of the new multiplet at 1.36 ppm assigned to the CH$_2$P methylene groups of the phosphine oxide target compound. A single peak was found in the $^{31}$P-$^1$H NMR spectrum at 48.9 ppm. The infrared spectrum show a stretching band at 1271 and 742 cm$^{-1}$ consistent with P=O and C-P stretches respectively. The peak at $\delta_F = -114$ ppm attributable to CH$_2$CF$_2$ are also present in the $^{19}$F NMR spectrum of the
phosphine oxide, 5. The $^1$H NMR spectra showed a multiplet at 1.2 ppm indicative of CH$_2$CH$_2$P which support the formation of the target compound. The $^{13}$C {$^1$H} NMR spectrum shows the presence of two doublets ($\delta_C = 130$ and 128 ppm) in the aromatic region and a peak due to the C-P carbon at $\delta_C = 30$ ppm ($J_{P-C} = 70$ Hz).

2.3.4 Synthesis of Fluorous Trithiacyclononane

The synthesis of Fluorous 9-ane-S$_3$ have not been reported. The synthetic strategy employed involves alkylating the 9-ane-S$_3$ precursors followed by assembling of the precursor using template synthesis as shown in scheme 2.16.

3-(Perfluoroctyl)-propenoxide was ring opened to obtain the pure 1-bromo-1H,1H,2H,3H,3H-perfluoroundecan-2-ol, 29 using MgBr$_2$ in 50% yield. The IR spectrum of 29 showed the characteristic $\nu$(O-H) and $\nu$(C-Br) stretches at 3066 and 705 cm$^{-1}$ respectively. Multiplets at $\delta_H = 4.33$ and $\delta_H = 3.6$-3.5 ppm in the $^1$H NMR spectrum are assigned to CHOH and CH$_2$Br respectively. The $^{13}$C {$^1$H} NMR spectrum shows the COH and CBr at $\delta_C = 64.2$ and $\delta_C = 37.9$ ppm of the product. The HRMS analysis, m/z = 590.9024, agrees with the calculated molecular mass, 590.901742 of the product M$^+$. It is also worth noting that this ring opening at the less substituted end of the epoxide also happens with HBr (quantitatively) which is unexpected as ring opening of epoxide with acids is known to happen at the most substituted end to form a tertiary carbocation. The $^1$H NMR spectrum of the ring opening reaction using either acid or base were exactly the same. The $^{19}$F NMR
spectra also shows changes in the signal of $CF_2CH_2$ at 112-114 ppm from a doublet to doublets of doublets which is consistent with diastereotopic $CH_2$ next to the $CF_2$.

29 was converted to 30 in 68% yield by refluxing with thiourea in a basic solution. The IR spectrum shows a stretch at 3066 cm$^{-1}$ indicating an OH group and 653 cm$^{-1}$ indicating a C-S group of the compound 30. In the $^1$H NMR spectrum, resonances at $\delta_H$ = 4.33 is assigned to $CHOH$ while $\delta_H$ = 2.9 and $\delta_H$ = 2.6 ppm indicates the distereotopic $CH_2SR$. The $^{19}$F NMR spectrum shows changes in the signal of $CF_2CH_2$ at -112 to -114 ppm from doublets of doublets to triplets which is consistent with a change in chemical environment. The HRMS (ESI-) m/z = 984.994634 found for the compound agrees with the calculated value 984.994234 (M$^+$).

An alternative route involving a one-step synthesis of 30 in 51% yield was accessed by simply stirring 3-(Perfluoroctyl)-propenoxide in H$_2$O with sodium sulfide. Spectroscopic characterisation of compound 30 from either routes are in agreement.

Scheme 2.16. Adjusted route for the synthesis of fluorous 9-ane-S$_3$
Repeated attempts at a Swern oxidation for the synthesis of 1,1'-thiobis(1H,1H,2H,3H,3H-perfluoroundecan-2-one) 31 using oxalyl chloride and DMSO failed to transform compound 30 to 31 due to difficulty in stabilising the intermediate to avoid decomposition at temperatures above -40 °C at which all reactants were still frozen. Jones Oxidation involving chromic acids successfully transformed 30 to 31 evidenced by the triplet at δ_H = 3.1 ppm (J_H-F = 21 Hz) in the 1H NMR spectrum. Functional group interconversion of 31 to the thiaketone, 33 using Lawesson’s reagent failed after repeated attempts. The synthetic route (Scheme 2.16) was adjusted to include brominating the dihydroxyl compound, 30 and a reaction with thiourea to give 34. By simply stirring 30 with HBr, 32 was obtained in 87% yield. The IR spectrum of 32 shows a new band at ν = 1066 cm⁻¹ indicating C-Br group. The 1H NMR spectrum indicates the formation of CHBr at 3.22 ppm. The 13C{¹H}NMR spectrum also has a peak at δ_C = 25.9 and 28.5 indicating CF₂CBr and CBr respectively (see Appendix B).

32 was converted to 34 in a low yield (25%) by refluxing with thiourea in the presence of NaOH. High Resolution mass spectroscopy reveal a peak at m/z = 1016.9486 indicative of compound 34 and agrees with the calculated value 1016.9480 (M⁺). The 1H NMR spectrum showed multiplets at δ_H = 2.7 and δ_H = 2.8 ppm indicative of the distereotopic CH₂S and a multiplet at δ_H = 2.9 ppm assigned to the CH₂CF₂ group.

36 was obtained by heating perfluoroct-1-ene with Br₂ in 96% yield. The IR spectrum of 36 indicates its formation as a C-Br stretch is observed at 705 cm⁻¹. The 1H NMR spectrum shows a doublet of doublets at δ_H = 5.2 ppm for CF₂CHBr and δ_H = 4.2 and δ_H = 3.9 ppm for the distereotopic CH₂Br. The 13C{¹H} NMR spectrum also shows signals at δ_C = 25.9 and 28.5 indicating CF₂CBr and CBr respectively (see Appendix B).

32 was also reacted with sodium metabisulfide but 33 was not converted to 34 in appreciable amount. The brominated compound, 32 was also converted to the thiaketone compound, 33 by refluxing with lawsson’s reagent. This compound was not isolated but reduced to the bisthiol compound 34 using NaBH₄ in a very low yield. The 13C{¹H}NMR spectrum also has a peak at 64 ppm also indicating a C-S group. The 19F NMR spectrum of the bisthiol-product showed a singlet at δ_F = -114 ppm along with the other CF₂ peaks. The 1H NMR spectroscopy is in agreement with the previous procedure. The HRMS data of the bisthiol-product showed a peak at 1016.9501 which matches the calculated exact mass (1016.9580) indicating that the product is consistently formed via this route.
Using a modified literature procedure previously used for non-fluorinated compounds,\textsuperscript{28} \textbf{34} was reacted with \textbf{36} in the presence of Mo(CO)\textsubscript{3}(MeCN)\textsubscript{3} in an attempt to obtain the fluorous macrocycle, \textbf{6}. The yield of the product was very low (8\%). The scale-up of the process failed to yield compound \textbf{34} after numerous attempts probably due to the electron-withdrawing nature of the CF\textsubscript{2} groups impacting on the reactivity of compound \textbf{32}.

### 2.3.5 Synthesis of Fluorous propylenediaminetetraacetic acid (PDTA)

In the forward sense, a commercially available fluorinated diketone was reduced to the corresponding diol using LiAlH\textsubscript{4}, but the diol could not be converted to the dibromo-compound using PBr\textsubscript{3} (Scheme 2.17). The route to the target was revised as shown in scheme 2.18.
A much more facile route involving reductive amination of the iminium intermediate using NaBH₄ to obtain the tetracacetate following the Scheme 2.18. ¹H NMR spectra of the crude tetracacetate intermediate showed the presence of multiplets at δ_H = 2.1 and 3.8 ppm attributable to CH₂CHN and CHN along with the acetate peaks at δ_H = 1.2 and δ_H = 4.1 ppm.

By stirring in a solution of NaOH, the desired fluorinated tetraacid was obtained in 50% yield as indicated by the characteristic peaks at δ_H = 2.1 and 3.8 ppm due to CH₂CHN and CHN respectively on the ¹H NMR spectra. The CN peaks are also indicated in the ¹³C NMR spectrum at δ_C = 60 and 58 ppm. The diagnostic CF₂ peak in the ¹⁹F spectra is also seen to have shifted from δ_F = 120.66 in the starting material to δ_F = 121.39 ppm in the product. The infrared spectra also shows stretching bands at ν = 3379, 1716, 1234-1144, 1037 cm⁻¹ due to the O-H, C=O, C-F, and C-N groups respectively.

2.4 CONCLUSION

The synthesis of the Tren amido ligand was successful and in high yield. The synthesis of the calix[4]arene amido ligands including the cone and partial cone conformers was successful and in moderate yield. En route to the calixarene ligands, a fluororous triazole compound was isolated. This mechanism of the reaction have been hypothesised as Huisgen 1,3-Dipolar Cycloaddition with the regioselectivity feature of a Click chemistry. The synthesis of the calixaryl phosphate and calixaryl phosphate oxide ligands were in low yields. The 9-ane-S₃ ligand could not be obtained as functional group interconversion of the synthesised precursor was hampered by the electronic effect of the fluorine groups. The synthesis of PDTA ligand proved to be the most straightforward and in moderate yield,
although the relatively expensive starting material doesn’t encourage scale-up of the synthesis.

2.5 EXPERIMENTAL

Materials and Methods

$^1$H, $^{13}$C{$^1$H} and $^{19}$F NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400.23 MHz, 155.54 MHz and 376.55 MHz respectively, or a Bruker Avance II 600 NMR with a TCI cryoprobe spectrometer operating at 150.92 MHz ($^{13}$C) and were referenced to the residual $^1$H and $^{13}$C resonances of the solvent used or external CFCl$_3$. $^{19}$F NMR assignments were confirmed using COSY experiments. This gives the next nearest neighbour and not the adjacent fluorine. IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer with attenuated total reflectance (ATR) accessory. Mass spectra were measured on a MALDI QTOF Premier MS system. All compounds and solvents were obtained from commercial sources and used as received. All solvents were dried and distilled before use where necessary.

2.5.1 Fluorous trisamidoamine

\[ 2H,2H\text{-Perfluorooctanoic acid 51} \]

Compound 9 was prepared according to a method by Achilefu.$^{38}$ (0.9 g, 53%, Mpt: 55 °C). $^1$H NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ 3.4 (t, 2H, $^3$J$_{HF}$ = 17.8 Hz, CH$_2$); $^{13}$C NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ 166.6 (s, CO); 118.7 (tt, $^1$J$_{C-F}$ = 257 Hz, $^2$J$_{C-F}$ = 32.9 Hz, CF$_2$); 117.8 (tt, $^1$J$_{C-F}$ = 288 Hz, $^2$J$_{C-F}$ = 32.9 Hz, CF$_2$CF$_2$CH$_2$); 116.9 (tt, $^1$J$_{C-F}$ = 257 Hz, $^2$J$_{C-F}$ = 32.9 Hz, CF$_2$CF$_2$CH$_2$); 111.7 (tt, $^1$J$_{C-F}$ = 270 Hz, $^2$J$_{C-F}$ = 32.9 Hz, CF$_3$CF$_2$CF$_2$CF$_2$); 110.9 (tt, $^1$J$_{C-F}$ =
2 | Ligand Synthesis

270 Hz, $^{3}J_{C-F} = 32.9$ Hz, CF$_3$CF$_2$CF$_2$); 109.9 (tt, $^{1}J_{C-H} = 270$ Hz, $^{2}J_{C-F} = 32.9$ Hz, CF$_3$CF$_2$); 36.5 (tt, $^{3}J_{C-F} = 22.8$ Hz, $^{1}J_{C-H} = 21.5$ Hz; CH$_2$); $^{19}$F NMR [376.6 MHz, C$_6$D$_6$]: $\delta$ -80.9 (CF$_3$); -111.7 (CF$_2$CH$_2$); -121.9 (CF$_3$CF$_2$CF$_2$); 122.8 (CF$_3$CF$_2$CF$_2$CF$_2$, CF$_2$CF$_2$CH$_2$); 126.1 (CF$_3$CF$_2$); IR (cm$^{-1}$) $\tilde{\nu}$: 2994 (w, OH), 1714 (s, C=O), 1433, 1409 (w), 1364 (s), 1317 (s), 1240 (s, C–F), 1183 (w, C–F), 1138 (s, C–F), 1117 (s, C–F), 1066 (s, C–F), 917 (w C–F), 876 (s), 706 (s), 618 (m), 606 (m). MS (ESI-) m/z: 391.1 [M-H, 100%]; HRMS (ESI-) calculated for C$_8$H$_{12}$F$_{13}$O$_2$: 376.985739, found: 376.985270.

2H,2H-Perfluorooctanoyl chloride 10

2H,2H-Perfluorooctanoic acid (0.70g, 1.8 mmol) was refluxed with freshly distilled thionyl chloride (1 mL) for 40 h. The excess thionyl chloride along with the HCl and SO$_2$ gases produced were evaporated under reduced pressure. IR $\tilde{\nu}$ (cm$^{-1}$) $\tilde{\nu}$: 2963 (w, C–H), 1807 (s, C=O, Acetyl chloride), 1681 (s, C=C), 1363, 1388, 1317 (w, C–H), 1232, 1186, 1142, 1121 (s, C–F), 1068, 1077 (w, C–F), 979, 897, 848, 810, 708 (w, C–H), 628, 614 (m, C–H).

$N,N',N''$-(Nitrilotris(ethane-2,1-diy))tris(3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide), 1

10 (0.4 g, 2.8 mmol) was refluxed with tris-(2-aminoethyl)-amine (0.13 g, 0.8 mmol) and triethylamine (0.15 mL, 3 mmol) in THF (10 ml) for 24 h and then diluted with 0.1 M HC1 (20 ml). The product was extracted with ether (3 x10 ml) and saturated aqueous NaHCO$_3$ (10 ml) was added. The combined ether extracts were separated, dried over Na$_2$SO$_4$ and concentrated to obtain the syrupy crude product which was purified by column...
chromatography (Hexane/ethyl acetate, 5:1) to afford 1 as a brown viscous liquid. (0.7 g, 57%). $^1$H NMR [600 MHz, C$_2$D$_6$CO]: δ (ppm) 8.03 (s, 3 H, HN); 3.34 (m, 6H, CH$_2$NHCO); 2.65 (m, 12 H, NCH$_2$CH$_2$ and CH$_2$CF$_2$ overlap). $^{13}$C NMR [600 MHz, C$_2$D$_6$CO]: δ 166.6 (NCO); 118.7 (m, CF$_2$); 117.8 (m, CF$_3$CF$_2$CH$_2$); 116.9 (m, CF$_3$CF$_2$CH$_2$); 111.7 (m, CF$_3$CF$_2$CF$_2$CF$_2$); 110.9 (m, CF$_3$CF$_2$CF$_2$); 109.9 (m, CF$_3$CF$_2$); 82.1 (CH$_2$N); 55.2 (CH$_2$NHCO); 39.8 (CH$_2$). $^{19}$F NMR [376.6 MHz, C$_6$D$_6$]: δ -81.93 (s, CF$_3$); -119.07, 119.84 (s, CF$_2$CH$_2$); 123.22, -123.59 (s, CF$_2$CF$_2$); -126.11 (CF$_3$CF$_2$). IR $\tilde{\nu}$ (cm$^{-1}$) 3253 (b, N-H), 2962 (w, C-H), 1638 (s, C=O, Amide), 1461 (s, C-N), 1353 (s, C-N), 1231, 1195, 1140, 1112 (s, C-F), 1085, 1061 (w, C-F), 863 (m, C-N), 805, 746, 721, 708 (m, C-H), 643 (m, C-H). MS (ESI-) m/z: 1226.0991 [M+H, 100%]; HRMS (ESI+) calculated for C$_{30}$H$_{22}$N$_4$O$_3$F$_{39}$: 1227.1069, found: 1227.1074.

2.5.2 Fluorous Calixaryl Amide (Cone)

[Chemical structures and reactions]

Compounds 11 and 12, were prepared using the common procedure and the results were in agreement with the literature. A solution of NaOH (4.00 g, 100 mmol) in ethanol (60 mL) and H$_2$O (40 mL) was added to 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetracarboxymethoxycalix[4]arene (6 g, 6 mmol) and refluxed for 24 h. The cooled solution was acidified with 50% sulfuric acid to pH 1 and the resulting precipitate was isolated and...
dissolved (partially soluble) in ethanol-water (1:1 v/v) for recrystallization yielding 11 as colourless needles. Spectroscopic data of 11 are in accord with the literature. The undissolved precipitate was collected, washed with water and dried at 40 °C to afford the pure 12 (5g, 94%). 1H NMR (400MHz, CDCl3) δ (ppm) 8.04 (s, O\text{H}); 7.13, 7.19, 6.64, 6.60 (s each, 2 H each, ArH); 4.54 (bs, 8 H, ArOCH2); 4.41, 3.47 and 3.34 (d, 2 H, 2 H, 4 H, J = 13, ArCHAr); 1.35, 1.28 and 0.89 (s, 9 H, 9 H, 18 H, t-Bu). 13C{1H} NMR (400MHz, CDCl3) δ (ppm) 149.9 (COOH); 125.7 (ArC), 53.2 (ArOC), 30.0 (CH3); 31.0 (ArCH2Ar). IR ʋ (cm\(^{-1}\)) = 3610 (b, OH), 2994 (m, C-H), 1730 (s, C=O, carboxylic acid), 1479 (m, C-H), 1392 (w), 1362 1259 (w, C-H), 1191, 1127, 1053 (s, C-O), 870 (m, C-H), 800, 753 (s, C–H), 634 (w, C-H). MS (MALDI) m/z: 880.4398 [M+Na, 100%]; HRMS (MALDI) calculated for C\(_{52}\)H\(_{64}\)O\(_{12}\)Na: 903.4295 Found: 903.4299.

2,2',2'',2''''-((15,35,55,75-Tetra-tert-butyl-1,3,5(1,3)-tribenzena-7(1,3)-cyclohexanacyclooctaphane-73,75-diene-12,32,52,72-tetrayl)tetrakis(oxy))tetraacetyl chloride, 13

\[ \text{H,1H,2H,2H-perfluorooctane, 15} \]

\[ \text{1H,1H,2H,2H-Perfluoroctyl iodide (5.82 g, 12 mmol) was refluxed with NaN}_3 (1.6 g, 25 mmol) in DMF (60 ml) for 12 h. The mixture was filtered and the filtrate was extracted with} \]
ether (3 x 40 ml). The combined organic extracts was dried with MgSO₄ and concentrated to afford a brown oil. (3.2 g, 67%). 1-Azido-1H,1H,2H,2H-perfluoroctane, 15 obtained as the major product was spectroscopically characterised. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 3.62 (t, 2 H, J_H-H = 7 Hz, CH₂N₃); 2.40 (m, 2 H, J_H-F = 19 Hz, J_H-H = 7 Hz, CH₂CF₂). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ (ppm) 118.8 (2C, CF₃); 116.8, 115.3, 110.2, 107.9, (10 C, CF₂); 38.9 (1 C, CN₃); 36.4 (1 C, CH₂CF₂). ¹⁹F NMR [377 MHz, CDCl₃]: δ -81.45 (s, CF₃); -114.59 (s, CF₂CH₂); 122.45 (s, CF₃CF₂CF₂CF₂); 123.48 (s, CF₃CF₂CF₂CF₂CF₂); 124.14 (s, CF₃CF₂CF₂CF₂CF₂); 126.81 (CF₃CF₂). IR ν (cm⁻¹) = 2949 (w, C-H), 1681 (s, C-C), 1363, 1388, 1317 (w, C-H), 1317 (s, C-N), 1232, 1189, 1142, 1121 (s, C-F), 1091, 1077 (w, C-F), 809, 746, 732, 707 (w, C-H), 698 (m, C-H).

4-(1,2,2,3,3,4,4,5,5,6,6,6-Dodecafluorohexyl)-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-1H-1,2,3-triazole 16

1H,1H,2H,2H-Perfluoroctyl iodide (5.82 g, 12 mmol) was dissolved in DMF (60 ml). NaN₃ (1.6 g, 25 mmol) was added and refluxed for 12 h. The mixture was filtered and the filtrate was extracted with ether (3 x 40 ml). The organic extracts were combined and dried with MgSO₄ and concentrated to afford a brown oil. Recrystallization from DMF resulted in X-ray quality crystals of 16 as a side product. (1.20 g, 15 %). M.Pt. = 90-92 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.91 (s, 1H, H=C); 6.20 (ddd, 2J_H-F = 25 Hz, 3J_H-F = 18 Hz, J_H-H = 7 Hz, CHF); 4.77 (t, 2 H, J_H-H = 7 Hz, CH₂CH₂N); 2.88 (m, 2 H, J_H-F = 19 Hz, J_H-H = 7 Hz, CH₂CF₂) ¹³C {¹H} NMR (100 MHz, CDCl₃) δ (ppm) 137.8 (1C, NC=C); 124.6 (1C, NC=C); 118.8 (2C, CF₃) 116.8, 115.3, 110.2, 107.9, (10C, CF₂); 83.2-81.3 (1C, CHF); 43.0 (1 C, CH₂N); 32.5 (CH₂CF₂); 31.3 (CH₂CF₂). ¹⁹F NMR [377 MHz, CDCl₃]: δ -81.45 (s, CF₃); -114.59 (s, CF₂CH₂); -120.3 (s, CF₂CHF); -121.1 (s, CF₂CHF); -122.60 (m, CF₃CF₂CF₂); -123.54 (m, CF₃CF₂CF₂CF₂); 124.11 (s, CF₃CF₂CF₂CF₂CF₂); 125.76 (s, CHF); 126.74 (m, CF₃CF₂). IR ν (cm⁻¹) = 3121 (s, C=C); 2920 (w, C-H), 1553 (s, N-H), 1468, 1363 (w, C-H), 1320 (s, C-N), 1230, 1187, 1139, 1107 (s, C-F), 1080, 1047, 1028, 991, (m, C-F), 870, 816, 723, (w, C-H), 692 646 (m, C-H). MS (ESI-) m/z: 715.0163 [M+H, 100%]; HRMS (ESI+) calculated for C₁₆H₆F₂₅N₃: 715.0163, found: 716.0240
1H,1H,2H,2H-Perfluorooctyl-1-amine, 17

15 and 16 (2.9 g, 7.4 mmol) were dissolved in ether (20 ml), slowly added to a stirred slurry of LiAlH₄ (1.09 g, 30 mmol) in ether (50 ml) and at rt for 24 h. The mixture was quenched by adding to ice water and then extracted with ether (3 x 30 ml). The combined extract was dried with MgSO₄ and concentrated to afford the corresponding amine, 17 as a brown oil. (1.8 g, 46%). ¹H NMR (400MHz, CDCl₃) δ (ppm) 3.09 (t, 2 H, J₉,₁H = 7 Hz, CH₂NH₂); 2.48 (m, 2 H, J₉,F = 19 Hz, J₉,₁H = 7 Hz, CH₂CF₂); 1.8 (bs, 2 H, NH₂). ¹³C {¹H} NMR (100MHz, CDCl₃) δ (ppm) 119.3, 118.2, 116.8, 115.3, 110.2, 107.9, (5C, CF₂ and 1C, CF₃); 42.9 (1 C, CH₂NH₂); 30.3 (1 C, CH₂CF₂). ¹⁹F NMR [377 MHz, CDCl₃]: δ -82.15 (s, CF₃); -114.65 (s, CF₂CH₂); 122.53 (s, CF₃CF₂CF₂); 123.54 (s, CF₃CF₂CF₂CF₂); 124.27 (s, CF₃CF₂CF₂CF₂CF₂); 126.78 (CF₃CF₂). IR v (cm⁻¹) = 2963 (w, C-H), 1641 (w, N-H), 1350 (w, C-H), 1317 (s, C-N), 1232, 1190, 1142, 1121 (s, C-F), 1091, 1077 (w, C-F), 910 (m, C-N), 839, 808, 746, 732, 707 (w, C-H), 695 (m, C-H). MS (ESI+) m/z: 363.0293 [M+H, 100%]; HRMS (ESI+) calculated for C₈H₆F₁₃N: 364.0365, found 364.0374.

[2,2',2'',2'''-((15,35,55,75-Tetra-tert-butyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-12,32,52,72-tetrayl)tetrakis(oxy))tetrakis(N-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)acetamide)], 2
1-Amino-1H,1H,2H,2H-perfluorooctane (1.6 g, 4.4 mmol) was added to a solution of tetraacetyl chloride, 13 (0.8 g, 0.80 mmol) dissolved in THF. Et3N (10 ml) was added to the reaction mixture and refluxed for 24 h. The solvent was removed in vacuo and the brown solid was taken up in DCM (80 cm³) and washed with H2O (3 x 60 ml), dilute HCl (3 x 60 ml) and brine (60 ml). The combined organic phases was dried with MgSO4, and the solvent was removed under reduced pressure to obtain the crude brown solid which was purified by column chromatography (Hexane/ethyl acetate, 5:2) to afford 2. Yield 1.3 g, (45%; Mpt: 190-193 °C). 1H NMR (CDCl3) δ (ppm) 7.71 (s, 4 H, NH); 6.82 (s, 8 H, ArH); 4.9 (s, 8 H, ArOCH2); 4.44, 3.28 (s, 8H, ArCHAr); 3.56 (t, 8 H, J = 7 Hz, NHCH2); 2.43 (m, 8H, CH2CF2); 1.12 (s, 36 H, CH3). 13C{1H} NMR (CDCl3) δ (ppm) 170.1 (OCNH); 152.3, 148.1 (ArC); 118.7 (m, CF2); 117.8 (m, CF2CF2CH2); 116.9 (m, CF2CF2CH2); 111.7 (m, CF3CF2CF2CF2); 110.9 (m, CF3CF2CF2); 109.9 (m, CF3CF2); 74 (ArOC); 36.8 (ArCH2Ar); 34.0 (CNH); 30.4 (CH3); 29.8 (CCF2). 19F NMR (CDCl3) δ (ppm) -80.79 (s, CF3); -113.89 (s, CF2CH2); -121.68 (s, CF2); -122.68 (s, CF2); -123.24 (s, CF2); -125.98 (s, CF2). IR ν (cm⁻¹): 3210 (b, N-H), 2970 (w, C-H), 1668 (s, C=O, Amide), 1480 (s, C-H), 1365 (s, C-N), 1233, 1189, 1143, 1121 (s, C-F), 1075, 1016 (w, C-F), 803 (m, C-N), 732, 707 (m, C-H), 696 (m, C-H). MS (MALDI) m/z: 2260.5146 [M+Na, 100%]; HRMS (MALDI) calculated for C84H80N4O8F52Na: 2283.5044, found 2283.5063.
2,2',2'',2''''-(15,35,55,75-Tetra-tert-butyl-1,3,5(1,3)-tribenzena-7(1,3)-cyclohexanacyclooctaphane-73,75-diene-12,32,52,72-tetrayl)tetrakis(N-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl)acetamide), 3 (Partial Cone)

1-Amino-1H,1H,2H,2H-perfluorooctane (3 g, 8 mmol) was added to a stirred solution of 14 (2 g, 2 mmol) in the THF (80 mL). Et₃N (10 mL) was added to the reaction mixture and refluxed for 24 h. The solvent was removed in-vacuo and extracted with DCM (3 x 60 mL). The organic phase was washed with H₂O (3 x 60 mL), dilute HCl (3 x 60 mL) and brine (60 mL). The combined organic phases was dried with MgSO₄, and the solvent was removed under reduced pressure to obtain the crude brown solid which was purified by column chromatography (Hexane/ethyl acetate, 5:2) to afford 3 as a brown solid. Yield 1.3 g (67%).

1H NMR (CDCl₃) δ (ppm) 8.6, 8.24, 7.9, (bs, 4 H, NH); 7.03, 6.97, 6.86, 6.64 (s, 8 H, ArH); 4.82, 4.60, 4.49 and 4.45 (s, 4 H, ArOC₂H₃); 4.39, 3.29 (d, 8 H, ArCH₂Ar); 3.70 (m, 8 H, OC₂H₂C₂); 2.45 (m, 8 H, CH₂CF₂); 1.35, 1.28, 1.09 and 0.89 (m, 36 H, t-Bu). 13C{¹H} NMR (CDCl₃) δ (ppm) 169.0 (CO₂NH); 146.2, 133.6, 130.1, 128.8, 125.2 (ArC), 118.7 (m, CF₂); 117.8 (m, CF₂CF₂CH₂); 116.9 (m, CF₂CF₂CH₂); 111.7 (m, CF₂CF₂CF₂CF₂); 110.9 (m, CF₂CF₂CF₂); 109.9 (m, CF₂CF₂); 65.4, 61.8, 57.8 (ArOC); 38.1 (ArCH₂Ar); 33.2 (CH₂NH); 32.01 (CH₂CF₂); 31.5, 29.9 (CH₃). 19F NMR (CDCl₃) δ (ppm) -80.79 (s, CF₃); -113.89 (s, CF₂CH₂); -121.68 (s, CF₂); -122.68 (s, CF₂); -123.24 (s, CF₂); -125.98 (s, CF₂). IR ṽ (cm⁻¹) 3210 (b, N-H), 2970 (w, C-H), 1668 (s, C=O, Amide), 1480 (s, C-H), 1365 (s, C-N), 1233, 1189, 1143, 1121 (s, C–F), 1075, 1016 (w, C–F), 803 (m, C-N), 732, 707 (m, C-H), 696 (m, C-F).
C-H). HRMS (MALDI) calculated for C_{84}H_{80}N_{4}O_{8}F_{52}Na [M+Na, 100%]: 2283.5044, found 2283.5132.

2.5.3 Fluorous Calixaryl-Phosphine

The previously prepared calixaryl tetraester, 24 was converted to the tetratosylate, 26 using an established procedure.\(^{46, 47}\)

\[ \text{I,1-Dichloro-N,N-diethylphosphanamine, 20} \]

\[ \begin{aligned} \text{PCL}_{3} & \quad \text{Et}_{2}\text{NH} \\ \text{Et}_{2}\text{NH} & \quad \text{PCL}_{3} \quad \text{Et}_{2}\text{NH} + \quad \text{HCl} \end{aligned} \]

Et\(_2\)NH (40 mL, 193 mmol) was slowly added to PCl\(_3\) (16.85 mL, 193 mmol) dissolved in ether (150 mL) at -78 °C and stirred for 1 h. The reaction was further stirred at room temperature overnight. The white precipitate was filtered off and the solvent was removed under reduced pressure. The crude compound was distilled at 40 °C and a pressure of 1 mbar to give as a colourless liquid, 20. 17 g, 50 % yield.\(^{31}\)P\(\{^1\text{H}\}\) NMR (400 MHz, Et\(_2\)O) δ (ppm) 162.7.

\[ (3,3,4,4,5,5,6,6,7,7,8,8,8\text{-Tridecafluoroctyl})\text{magnesium iodide, 19} \]

Mg turnings (10g), 3 drops of 1,2-dibromoethane and 2 crystals of Iodine were heated in dry Et\(_2\)O (50 mL) under Ar. Once the reaction was initiated, Et\(_2\)O (150 ml) was added and Perfluoroctyl iodide (10 mL) dissolved in Et\(_2\)O (50 ml) was added slowly over 30 mins turning the reaction mixture yellow. The mixture was refluxed at 50 °C overnight under Ar and the greyish mixture was then filtered. The concentration was checked by titrating a 1ml aliquot with water against 1 M HCl. [CF\(_3\)(CF\(_2\))\(_5\)(CH\(_2\))\(_4\)]\(_2\) was also made as a minor by-product.

\[ \text{Chlorobis(3,3,4,4,5,5,6,6,7,7,8,8,8\text{-tridecafluoroctyl})phosphane, 22} \]
The Grignard mixture was cooled to 0 °C. Diethylphosphoramidous chloride (5ml) was added slowly to the Grignard made in the previous step and stirred at r.t for 40 h. The resulting green mixture was stirred for 20 h and checked by $^{31}$P{¹H} NMR spectroscopy (400 MHz, CDCl₃): δ (ppm) +46 (Et₂NPR₂). 1 N HCl in Et₂O (100 mL) was added to the dialkylphosphinamide using a cannula at -50 °C and the reaction was stirred for 2 h at -50 °C and then at rt overnight. The solid residue was filtered off and the liquid was further concentrated to near saturation point and left at -10 °C overnight. The liquid was separated from the pasty deposit quickly under cold conditions to obtain the dialkylchlorophosphine as a liquid and dichloroalkylphosphine side product as the solid deposit. $^{31}$P NMR (400 MHz, CDCl₃): δ (ppm) 105.07 (ClPR₂)

$\text{2,2',2'',2''\prime-(15,35,55,75-Tetra-tert-butyl-1,3,5(1,3)-tribenzena-7(1,3)-cyclohexanacyclooctaphane-73,75-diene-12,32,52,72-tetrayl)tetrakis(ethylbis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphane)}, \text{ 4}$

Under Ar, Dialkylchlorophosphine, 22 (1 g, 150 % molar excess to calixarene) was dissolved in dry THF (40 ml). Freshly cut Na (0.6 g, 150 % molar excess to calixarene) were added while vigorously stirring. The mixture was refluxed for 24 h. Calix[4]arene tetratosylate, 26 (7.5 mg, 0.004 mmol) dissolved in dry THF (20 ml) was added using a dropping funnel. This was then stirred at rt for 2 days. The mixture was filtered through celite and this product was washed with dry THF. The solvent was removed in vacuo to
afford the fluorous calixaryl phosphine, 4 as a brown solid. $^{31}\text{P} \{^1\text{H} \}$ NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 23.07 (CH$_2$PR$_2$).

The fluorous phosphine compound, 4 was stirred in hydrogen peroxide solution (10 ml) over night at room temperature. Brine (40 ml) was added and extracted with DCM (4 x 40 ml). The organic phase was dried with MgSO$_4$ and concentrated to afford the crude phosphine oxide, 5 which was purified by column chromatography Hexane/EtOAc, 10:1 v/v. (0.7 g, 74.47 % yield). $^1\text{H}$ NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.73 (s, 4H; ArH), 7.54 (s, 4H; ArH); 4.33 (m, 8H, ArOC$_2$H), 1.76 (m, 8 H; CH$_2$CF$_2$), 1.38 (m, 8H; OCC$_2$H), 1.19 (m, 8 H; CH$_3$P). 0.89 (s, 36H; C(C$_3$H$_3$)$_3$). $^{13}\text{C} \{^1\text{H} \}$ NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 130.50, 128.83, (8 C, ArC), 68.1, 66.7, 65.5 (4 C, ArO), 46.1 (4C, ArCH$_2$Ar); 36.0, 28.1 (8 C, CF$_2$CF$_2$), 25.4, 19.6 (4 C, OCC), 24.6 (12 C, CH$_3$), 14.60, 11.06 (8 C, CP). $^{31}\text{P}$ NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) +51.07 (POR$_2$) $^{19}\text{F}$ NMR (400MHz, CDCl$_3$) $\delta$ (ppm) -80.79 (s, 12 F, CF$_3$); -114.89; -122.01 (s, 8 F, CF$_2$); -122.39 (s, 8 H, CF$_2$); -123.39 (s, 8H, CF$_2$); -126.18 (s, 8 F, CF$_2$).
2.5.4 Fluorous trithiacyclononane

1,2-Dibromo-1H,1H,2H-perfluorooctane 36

Perfluorooct-1-ene (3 ml, 13.2 mmol) was heated with Br₂ in a sealed tube at 120 °C for 5 days with periodic monitoring by NMR spectroscopy. The resulting mixture was distilled at 270 °C to remove the unreacted starting material. This afforded the novel 1,2-dibromoperfluorooctane, 36 as a brown liquid. 3g, 45%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.2 (m, 1 H, CF₂CHBr); 4.21 (dd, 1 H, J_H,H = 13 Hz, CH₂Br); 3.97 (dd, 2 H, J_H,H = 13 Hz, CH₂Br). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ (ppm) 125.2 – 121.5 (24 C, CF); 25.9 (1 C, CF₂CBr); 28.5 (1 C, CBr). ¹⁹F NMR [100 MHz, CDCl₃]: δ (ppm) -81.29 (s, CF₃); -110.14-120.67 (m, J_F-C = 260 Hz, J_F-F₂ = 340 Hz, CF₂CH₂; CF₃CF₂CF₂; CF₃CF₂CF₂CF₂); -123.56 (m, CF₃CF₂CF₂CF₂CF₂); -123.15 (s, CF₃CF₂CF₂CF₂CF₂CF₂); -126.75 (CF₃CF₂). IR ν (cm⁻¹) = 2966 (w, C-H), 1432, 1364 (w, C-H), 1232, 1194, 1143, 1122 (s, C-F), 1061, 1075 (s, C-F), 892, 831, 734 (w, C-H), 705 (s, C-Br).

1-Bromo-1H,1H,2H,3H,3H-perfluoroundecan-2-ol, 29

28 (0.5 ml, 4.5 mmol) was dissolved in a solution of MeOH:H₂O 8:1 (8 ml). NH₄Cl (0.51 g, 9.0 mmol) was added and stirred to dissolve. MgBr₂ (8.42 g, 45.7 mmol) was added to the mixture and refluxed for at 100 °C for 8 h. The mixture was poured into an ice water with trace amount of H₂SO₄. The mixture was extracted with Et₂O (3 x 40 ml), dried with MgSO₄ and concentrated to afford the crude product which was purified by column chromatography (CHCl₃:MeOH, 10:4) to afford the pure novel 1-Bromo-1H,1H,2H,3H,3H-perfluoroundecan-2-ol, 29 (0.5 ml, 50% yield). ¹H NMR (400MHz, CDCl₃) δ (ppm) 4.33 (m, 1 H, CHOH); 3.73 (m, 1 H, J_H,H = 5 Hz, CH₂Br); 3.63 (m, 1 H, J_H,H = 5 Hz, CH₂Br); 2.55 (m, 2 H, J_H,F = 20 Hz, J_H,H = 9 Hz, CH₂CF₂). ¹³C{¹H} NMR (100MHz, CDCl₃) δ (ppm) 64.2 (2 C, COH); 37.9 (2 C, CBr). ¹⁹F NMR [377 MHz, CDCl₃]: δ -82.15 (s, CF₃); -113.91
(dd, $J_{F-C} = 260$ Hz, $J_{F-F} = 340$ Hz, CF$_2$CH$_2$); -122.69 (s, CF$_3$CF$_2$CF$_2$); 122.95 (s, CF$_3$CF$_2$CF$_2$CF$_2$); 123.80 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CH$_2$); 124.65 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$); 127.26 (CF$_3$CF$_2$). IR $\tilde{v}$ (cm$^{-1}$) = 3066 (w, O-H), 2981 (w, C-H), 1421, 1347 (w, C-H), 1236, 1198, 1144, 1133, 1115 (s, C-F), 1056 (w, C-O), 989, 854, 810, 789 (w, C-H), 704 (s, C-Br). HRMS (ESI-) calculated for C$_{11}$H$_6$BrClF$_{17}$O [M+Cl, 100%]: 590.9017, found 590.9024.

1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecan-2-ol) 30

29 (0.5 ml, 4.6 mmol) was dissolved in a solution of EtOH (10 ml), H$_2$O (5 ml) and thiourea (0.03 g, 3.9 mmol). NaOH (0.032 g, 3.9 mmol) was added and refluxed for 18 h. The resulting mixture was taken up in Et$_2$O (40 ml) and washed with dil. HCl (3 x 40 ml), H$_2$O (3 x 30 ml) and brine (3 x 30 ml). The organic layer was dried with MgSO$_4$, concentrated and purified by column chromatography (CHCl$_3$:MeOH, 10:4) to afford the product, 30. (0.6 g, 68% yield) (0.5 ml, 50% yield). $^1$H NMR (400MHz, CDCl$_3$) $\delta$ (ppm) 4.3 (m, 2 H, CHOH); 2.89 (m, 4 H, CH$_2$S); 2.60 (m, 4 H, CH$_2$S); 2.35 (m, 4 H, $J_{H,F}$ = 17.9, $J_{H,H}$ = 7 Hz, CH$_2$CF$_2$). $^{13}$C {$^1$H} NMR (100MHz, CDCl$_3$) $\delta$ (ppm) 121.4, 120.1, 115.3, 113.5, 110.9, 108.1, 105.6 (14 C, CF$_2$); 118.1 (2 C, CF$_3$); 67.9 (2 C, COH); 44.8 (2 C, CS); 35.2 (2 C, CCF$_2$). $^{19}$F NMR [377 MHz, CDCl$_3$]: $\delta$ (ppm) = -81.30 (s, CF$_3$); -112.73 (s, CF$_2$CH$_2$); -121.99 (s, CF$_3$CF$_2$CF$_2$); 122.20 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$); 123.03 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$); 123.55 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$); 126.50 (CF$_3$CF$_2$). IR $\tilde{v}$ (cm$^{-1}$) = 3066 (w, O-H), 2981 (w, C-H), 1421, 1347 (w, C-H), 1236, 1198, 1144, 1133, 1115 (s, C-F), 1056 (w, C-O), 989, 854, 810, 789 (w, C-H), 704, 653 (s, C-S). HRMS (ESI-) calculated for C$_{22}$H$_{11}$F$_{34}$O$_2$S: [M-H, 100%]: 984.9942, found: 984.9946.

Alternative route to 1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecan-2-ol) 30
3-(Perfluorooctyl)-propenoxide, 28 (3 ml, 10.7 mmol) was added to a solution of H₂O (18 ml) and 60% sodium sulfide (3 g, 45.7 mmol) and then stirred at rt for 24 h. The resulting mixture was diluted in H₂O (50 ml) and extracted with DCM (3 x 60 ml). The combined extracts was dried with Na₂SO₄ and concentrated to yield the crude product which was purified by column chromatography (DCM:MeOH, 10:4) to yield the pure novel compound 30. (5.4 g, 51% yield).

1H NMR (400MHz, CDCl₃) δ (ppm) 4.3 (m, 2H, CHOH); 2.89 (m, 1H, CH₂Br); 2.60 (m, 1H, CH₂Br); 2.35 (m, 2H, J₆,₆ = 17.9, J₁,₁ = 7 Hz, CH₂CF₂). 13C{¹H} NMR (100MHz, CDCl₃) δ (ppm) = 124.0, 120.1, 117.4, 115.3, 112.2, 110.7, 10.8, 103.0, (16 C, CF₂ and CF₃) 70.01 (2 C, C₂OH), 44.20 (2C, CS); 34.04 (2 C, CCF₂). 19F NMR [377 MHz, CDCl₃]: δ = -82.15 (s, CF₃); -113.43 (s, CFCH₂); -122.74 (s, CF₃CF₂CF₂); 122.95 (s, CF₃CF₂CF₂CF₂); 123.80 (s, CF₃CF₂CF₂CF₂CF₂CF₂); 127.26 (CF₃CF₂). IR v (cm⁻¹) = 3066 (w, O-H), 2981 (w, C-H), 1421, 1347 (w, C-H), 1236, 1198, 1144, 1133, 1115 (s, C-F), 1056 (w, C-O), 989, 854, 810, 789 (w, C-H), 704, 653 (s, C-Br). HRMS (ESI-) calculated for C₂₂H₁₁F₃₄O₂S [M-H, 100%]: 984.9942, found: 984.9984.

Attempted synthesis of 1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecan-2-one) 32

A solution of oxalyl chloride (0.2 ml, 3 mmol) was added to dry DCM (20 ml) and cooled to -78 °C. DMSO (0.43 ml, 6 mmol) was added under inert condition and stirred for 15 min. The alcohol, 30 (0.60 ml, 0.6 mmol) in DCM (25 ml) and Et₃N (1.28 ml, 9 mmol) were added successively. The cooling bath was removed and stirred at room temperature for 2.5 h. The NMR data after extraction indicates that the desired product was not obtained.

30 (0.3 g, 0.4 mmol) was dissolved in acetone (20 ml) and diethyl ether (40 ml) and cooled in to 0 °C. Freshly prepared Jones reagent (7 ml) was added dropwise while stirring. The mixture was stirred overnight and then extracted into diethyl ether (5 x 40 ml) and the organic phase was combined and washed with water (5 x 40 ml) and brine (5 x 40 ml). The combined organic layer was dried with Na₂SO₄ and concentrated to afford the diketone, 31. (0.2 g, 67% yield). 1H NMR (400 MHz, CDCl₃) δ (ppm) 3.1 (t, 4H, J₆,₆ = 21 Hz); 2.67 (s,
Bis(1H,1H,2H,3H,3H-2-bromo-perfluoroundecyl)sulfane 33

\[
\text{HO-S-S-} \xrightarrow{\text{HBr}} \text{Br-Br}
\]

Compound 30 (3.5 g, 4.0 mmol) was dissolved in a mixture of THF (20 ml) and CHCl₃ (40 ml) and cooled to 0 °C. 6 mole excess of HBr (4 ml) was added slowly and stirred at room temperature for 14 h. The reaction was concentrated to remove the H₂O and unreacted HBr to afford the brominated compound 33 (3.8g, 87% yield). \(^1\)H NMR (400 MHz, CDCl₃) δ (ppm) 4.6 (m, 2 H, CHBr); 2.87 (t, 2 H, J₉₋₋H = 2 Hz, SCH); 2.59 (dd, 2 H, J₉₋₋H = 2 Hz, SCH); 2.42 (m, 4 H, J₉₋₋F = 19 Hz, J₉₋₋H = 7 Hz, CH₂CF₂). \(^{13}\)C\(^{\text{\text{\textsuperscript{\textsuperscript{1}}}H}}\) NMR (100 MHz, CDCl₃) δ (ppm) 118.0 (2C, CF₃), 121.0, 120.1, 115.4, 113.8, 110.8, 108.3, 105.7, (14 C, CF₂), 45.8 (2C, CS), 44.8 (2C, CBr), 25.5 (2C, CCF₂). \(^{19}\)F NMR [377 MHz, CDCl₃]: δ (ppm) -81.20 (s, CF₃); -113.39 (s, CF₂CH₂); -122.05 (s, CF₃CF₂CF₂CF₂); -122.40 (s, CF₃CF₂CF₂CF₂CF₂); -123.27 (s, CF₃CF₂CF₂CF₂CF₂CF₂); -124.05 (s, CF₃CF₂CF₂CF₂CF₂CF₂); -126.61 (CF₃CF₂). IR ν (cm⁻¹) = 2966 (w, C-H), 2866 (m, C-H), 1713 (s, C=O), 1437, 1368, 1330 (w, C–H), 1236, 1199, 1145, 1113 (s, C–F), 1066 (w, C–Br), 1025 (s, C–F), 924, 878, 804, 721 (w, C-H), 704, 654 (s, C-S).

1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecane-2-thiol) 34
33 (4 g, 3.6 mmol) and thiourea (4 g, 3.6 mmol) were stirred to dissolve in EtOH. NaOH (1.1 g, 1.5 mmol) was added and refluxed at 120 °C for 52 h. The resulting mixture was washed with dilute HCl (5 x 40 ml), H2O (3 x 30 ml) and the combined organic layer was dried with Na2SO4 and concentrated to afford the thiol, 33 (2.4 g, 65 % yield). 1H NMR (400 MHz, CDCl3) δ (ppm) 2.99 (m, 2 H, SC2H2); 2.80 (m, 4 H, SHCH2); 2.64 (m, 1 H, SC2H2) 2.33 (m, 4 H, JH,F = 20 Hz, JH,H = 7 Hz, CF2CF2). 13C{1H} NMR (100 MHz, CDCl3) δ (ppm) 118.0 (2C, CF3), 121.0, 120.1, 115.4, 113.8, 110.8, 108.3, 105.7, (14 C, CF2), 64.2 (2C, CBr), 29.7 (2C, CS), 24.8. 2(C, CS); 19F NMR [377 MHz, CDCl3]: δ (ppm) -81.20 (s, CF3); -113.39 (s, CF2CH2); -122.05 (s, CF3CF2CF2); -122.40 (s, CF3CF2CF2CF2); -123.27 (s, CF3CF2CF2CF2CF2, CF2CF2CH2); -124.05 (s, CF3CF2CF2CF2CF2CF2CF2); -126.61 (CF3CF2). IR ν (cm−1) = 2966 (w, C-H), 1437, 1368, 1330 (w, C-H), 1197, 1144, 1115 (s, C-F), 1051, 963 (m, C-F), 704 (s, C-S). HRMS (ESI-) calculated for C22H12F34S3 [M-H, 100%]: 1017.9558, found: 1016.9486.

1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecan-2-one) 32

32 (0.5 g, 0.5 mmol) and Lawesson’s reagent (0.2 g, 0.5 mmol) were stirred to dissolve in toluene and refluxed at 120 °C for 52 h. The resulting mixture was filtered to remove the unreacted reagents and then extracted with DCM (5 x 60 ml). The combined organic layer was dried with Na2SO4 and concentrated to afford the thione, 33. 19F NMR [377 MHz, CDCl3]: δ (ppm) -81.20 (s, CF3); -113.39 (s, CF2CH2); -122.05 (s, CF3CF2CF2); -122.40 (s, CF3CF2CF2CF2); -123.27 (s, CF3CF2CF2CF2CF2, CF2CF2CH2); -124.05 (s, CF3CF2CF2CF2CF2CF2CF2); -126.61 (CF3CF2). IR ν (cm−1) = 1373 (m, C=S), 1197, 1144, 1115 (s, C-F), 704 (s, C-S).
The crude 33 was dissolved in EtOH (60 ml) and NaBH₄ (4 g, 3.6 mmol) was added and stirred overnight. The resulting mixture was extracted with DCM (5 x 60 ml). The combined organic layer was dried with Na₂SO₄ and concentrated to afford the thiol, 34 (2.4 g, 65 % yield). Spectroscopic data matches the result obtained from the previous synthesis presented.

\[ \text{5,9-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-2-(perfluorohexyl)-1,4,7-trithionane 6} \]

\[
\begin{align*}
R_f' & \quad \begin{array}{c}
\text{S} \\
\text{S}
\end{array} \\
\begin{array}{c}
\text{R_f} \\
\text{R_f}
\end{array}
\end{align*}
\]

Mo(CO)₆ (2 g, 7.5 mmol) was refluxed in MeCN for 4 day and cooled to -20 °C to obtain yellow crystals of [Mo(CO)₃(MeCN)₃] (0.15 g, 0.49 mmol). The crystals were dissolved in MeCN (5 ml) and 1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecane-2-thiol) 34 (0.15 g, 0.49 mmol) was added and refluxed for 48 h. The mixture was cooled to -20 °C overnight and filtered and washed with THF. The dry crystals obtained were taken up in MeCN (25 ml) and refluxed with 1,2-Dibromo-1H,1H,2H-perfluoroctane, 37 for 48 h and concentrated. Another 1,1'-Thiobis(1H,1H,2H,3H,3H-perfluoroundecane-2-thiol), 34 (0.1 ml) was added and refluxed in DMSO (8 ml) for 20 h. H₂O (10 ml) was added to the resulting mixture, extracted with Et₂O (3 x 17 ml) and concentrated to afford the crude fluorous 9-ane-S₃ whose yield was too low to be isolated (8%).

### 2.5.5 Fluorous EDTA

\[ \text{1,3-Bromo-propylene(1,3-bisperfluorododecane)} \]

\[
\begin{align*}
\begin{array}{c}
\text{R_f} \\
\text{R_f}
\end{array} & \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \\
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\end{align*}
\]

LiAlH₄ (0.009 g, 0.2 mmol) dispersed in THF. Fluoropentadecane-7,9-dione (0.2 g, 0.2 mmol) was added to the mixture at 0 °C and stirred overnight. The resulting mixture was slowly poured in ice. The mixture was extracted with ether (3 x 25 ml), dried with MgSO₄.
and concentrated to obtain the fluorinated diol. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.81 (m, 2 H, OH); 4.32 (m, 2 H, CH$_2$); 3.32 (dd, 1 H, $J_{HH}$ = 8 Hz, CH$_2$CO); 3.12 (d, 1 H, $J_{HH}$ = 8 Hz, CH$_2$CO).

One pot synthesis of Perfluoro-propylenediaminetetraacetic acid via Reductive amination

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer and a condenser, a mixture of the required amine (0.2 g, 0.9 mmol) and the fluorinated diketone (0.4 g, 0.4 mmol) in THF (25 mL) was prepared. Then, NaBH$_4$ (0.025 g, 0.7 mmol) was added and the mixture was stirred under reflux conditions. After completion of the reaction, the mixture was filtered and the residue was washed with THF (5 mL). The crude product was further purified by column chromatography on silica gel (chloroform/hexane, 1:1 v/v). (65 % yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.02 (m, 8 H, OCH$_2$); 3.80 (m, 2 H, $J_{HF}$ = 20 Hz, $J_{HH}$ = 17 Hz, CH$_2$N); 3.42 (s, 8 H, COCH$_2$); 2.33 (m, 2 H, CF$_3$C); 1.2 (m, 12 H, CH$_3$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 164 (4 C, C=O), 118.0 (2 C, CF$_3$), 121.0, 120.1, 115.4, 113.8, 108.3, (10 C, CF$_2$), 60.2 (4 C, COCN), 58 (2 C, CNF$_3$), 48 (2 C, OCH$_2$), 26.7 (1 C, CCR$_F$), 20.7 (1 C, CH$_3$); $^{19}$F NMR [377 MHz, CDCl$_3$]: $\delta$ (ppm) -81.20 (s, CF$_3$); -121.33 (s, CF$_3$CF$_2$CF$_2$); -121.91 (s, CF$_3$CF$_2$CF$_2$CF$_2$); -122.17 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$); -122.85 (s, CF$_3$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$); -126.24 (CF$_3$CF$_2$).

Perfluoro-propylenediaminetetraacetic acid

Compound 39 was stirred in NaOH/MeOH (20% w/v) for 4 h and extracted with CH$_2$Cl$_2$ (3 x 15 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated to give a yellow oil. (60 % yield) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.51 (m, 4 H, OH); 3.80 (m, 2 H, $J_{HF}$}
\[ = 20 \text{ Hz, } J_{\text{H,H}} = 7 \text{ Hz, } CHN; 3.42 (s, 8 \text{ H, } CH_2CO) 2.33 (m, 2 \text{ H, } CH_2CR_f). \] 
\[ ^{13}\text{C} \{^1\text{H}\} \text{ NMR (100 MHz, CDCl}_3 \delta \text{ (ppm) } 152 (4 \text{ C, } C=O), 118.0 (2 \text{ C, CF}_3), 121.0, 120.1, 115.4, 113.8, 108.3, (10 \text{ C, } CF_2 \text{ and}), 60.2 (4 \text{ C, } COCN), 58 (2 \text{ C, } CNR_F) 26.7 (1 \text{ C, } CCR_F). \] 
\[ ^{19}\text{F} \text{ NMR [377 MHz, CDCl}_3 \]: } \delta \text{ (ppm) } -81.20 (s, CF_3), -121.33 (s, CF_3CF_2CF_2CF_2CH_2); -121.91 (s, CF_3CF_2CF_2CF_2); -122.17, (s, CF_3CF_2CF_2CF_2); -122.85 (s, CF_3CF_2CF_2CF_2CF_2); -126.24 (CF_3CF_2). \] 

2.6 REFERENCES

29. F. Munz, LJS. patent no 1938, 2, 130, 505.
31. F. C. Bersworth, Martin Dennis Co. patent no 1945, 2, 735.
32. H. Kroll, Dexter, Martin, patent no 1958, 2, 457.
33. G. Curme, Jr., Clark, Jared W., patent no 1945, 2, 818.


Chapter 3

Fluorous Interactions
3.1 OVERVIEW

The supramolecular chemists tool-kit encompasses a cornucopia of non-covalent interactions that can be used to design supramolecular structures.\(^1\) These includes, and not limited to, hydrogen bonding\(^2\), tetrel bonding\(^3\), pnictogen bonding\(^4\), chalcogen bonding\(^5\), halogen bonding\(^6\), van der Waals\(^7\),\(^8\) dihydrogen bonding\(^9\), dihalogen bonding\(^10\), H–H bonding\(^11\), \(\pi\)-anion/cation interaction\(^12\),\(^13\) \(\pi\)-lone pair\(^12\), \(\pi\)--CH\(^14\), \(\pi\)--\(\pi\) stacking\(^15\), cation-cation interaction.\(^16\) The interaction energy scale of some non-covalent interactions (NCIs) are presented in Table 3.1.

**Table 3.1. Noncovalent interaction and typical Interaction Energy range (\(\Delta E\) (kcal mol\(^{-1}\)))**\(^17\)

<table>
<thead>
<tr>
<th>Bonding/Interactions</th>
<th>(\Delta E) (kcal mol(^{-1}))</th>
<th>Bonding/Interactions</th>
<th>(\Delta E) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>-83</td>
<td>Ionic</td>
<td>-20</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-2 – 40</td>
<td>(\pi)--cation</td>
<td>-11 – -22</td>
</tr>
<tr>
<td>Tetrel</td>
<td>-11 – 15</td>
<td>(\pi)--anion</td>
<td>-4 – -22</td>
</tr>
<tr>
<td>Pnictogen</td>
<td>-3 – -4.7</td>
<td>(\pi)--(\pi) stacking</td>
<td>-1.9 – -3</td>
</tr>
<tr>
<td>Chalcogen</td>
<td>-2.8</td>
<td>(\pi)--CH</td>
<td>-3</td>
</tr>
<tr>
<td>Halogen</td>
<td>-0.1 – -7.8</td>
<td>(\pi)--lone pair</td>
<td>-1.7</td>
</tr>
<tr>
<td>Hydrophobic (-CH(_3)-)</td>
<td>-0.7</td>
<td>Van der Waals</td>
<td>-0.47</td>
</tr>
<tr>
<td>Dispersion</td>
<td>-0.47</td>
<td>Dipole/dipole</td>
<td>-0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dipole/induced dipole</td>
<td>-0.07</td>
</tr>
<tr>
<td>Dihalogen</td>
<td>0.47 – 3.8</td>
<td>H–H bonding</td>
<td>2.8 – 6.6</td>
</tr>
</tbody>
</table>

The increased interest in halogen interactions (XB) including F···F non-covalent interactions in diverse areas of chemistry\(^18\), biology\(^19\), material science\(^20\),\(^21\) crystal
engineering,\textsuperscript{6, 22, 23} and medicinal chemistry\textsuperscript{24, 25} has led to a growing recognition that these interactions can be energetically stabilizing albeit with some contention.

In a broad sense, in terms of the origin of XB, the electron density in halogen atoms (F, Cl, Br, and I) have been shown by Politzer and Murray\textsuperscript{17, 26-30} to be anisotropically distributed whenever the atom is covalently bound to one or more atoms.\textsuperscript{27, 29} In compounds where the halogen atom is involved in the formation of one covalent bond, “polar flattening” occurs which is a change of the halogen shape to oblate with a shorter radius along the covalent bond (Figure 3.1). Conversely, there exists a region of higher electron density, where the electrostatic potential is negative in almost all cases, which results in a belt orthogonal to the covalent bond, and the region of lower electron density (the σ-hole) where the electrostatic potential is frequently positive. A cap of depleted electron density is generated on the elongation of the covalent bond (usually smaller effective atomic radius). This region is capable of forming attractive interactions with electron-rich sites. The general ability of halogen atoms to attractively interact with electron donor sites (nucleophiles) has only recently been systematically understood, fully recognized and defined as the halogen bond (XB or R–X···X–R where X = halogen atom, R = alkyl group).\textsuperscript{31} XB donor ability changes in the order I > Br > Cl > F due to the positive character of the corresponding σ-holes, which increases with the polarizability, and decreases with the electronegativity\textsuperscript{32, 33} making F the least prone to XB.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Schematic representation of the anisotropic distribution of the electron density around covalently bound halogen atoms and the pattern of the resulting interactions.\textsuperscript{34} (adapted with permission from reference. 34. Copyright 2016 ACS)}
\end{figure}

The effect of polarizability and electronegativity of the halogen is determined by the size of the area where the electrostatic potential is frequently positive (\(V_{S,\text{max}}\)). It has been
demonstrated several times, for complexes of halides with a given negative site, that $\Delta E$ correlates well with the $V_{S,max}$ of the halogen $\sigma$-hole (Table 3.2);\textsuperscript{17, 27, 35, 36} $\Delta E$ becomes more negative as $V_{S,max}$ is more positive. The $V_{S,max}$ therefore helps to rationalize the increase in $\Delta E$ down the halogen group (Table 3.3).

**Table 3.2.** Scale of Typical Interaction Energy of selected NCIs\textsuperscript{17} and Computed $\sigma$-hole $V_{S,max}$ interaction energies $\Delta E$ for forming gas phase complexes with NH$_3$.

<table>
<thead>
<tr>
<th>X···NH$_3$</th>
<th>$\Delta E$ (kcal mol$^{-1}$)</th>
<th>$V_{S,max}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF···NH$_3$</td>
<td>-1.5</td>
<td>11</td>
</tr>
<tr>
<td>CF$_3$F···NH$_3$</td>
<td>-1.9\textsuperscript{37}</td>
<td></td>
</tr>
<tr>
<td>CF$_3$Cl···NH$_3$</td>
<td>-2.3</td>
<td>20</td>
</tr>
<tr>
<td>CF$_3$Br···NH$_3$</td>
<td>-4.7</td>
<td>25</td>
</tr>
<tr>
<td>CF$_3$I···NH$_3$</td>
<td>-6.4</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.3.** Most Positive ($V_{S,max}$) and Most Negative ($V_{S,min}$) Electrostatic Potentials (V) on the 0.001 au Surfaces of the Indicated Halogen Atoms using a Computational method (M06-2X/6-311G).\textsuperscript{38}

<table>
<thead>
<tr>
<th>Bond producing a $\sigma$-hole in CF$_3$</th>
<th>$V_{S,max}$</th>
<th>$V_{S,min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F···F</td>
<td>-0.06</td>
<td>-0.12</td>
</tr>
<tr>
<td>Cl···Cl</td>
<td>0.86</td>
<td>-0.03</td>
</tr>
<tr>
<td>Br···Br</td>
<td>1.10</td>
<td>-0.09</td>
</tr>
<tr>
<td>I···I</td>
<td>1.38</td>
<td>-0.08</td>
</tr>
</tbody>
</table>
Moreover, R–X···X–R contacts preferentially adopt two different geometries classified by G. R. Desiraju and R. Parthasarathy as Type I (symmetrical interactions where $\theta_1 = \theta_2$) and type II (bent interactions where $\theta_1 \approx 180^\circ$ and $\theta_2 \approx 90^\circ$) shown in Figure 3.2. Type I interactions are said to be geometry based contacts that arise from close packing requirements, found for all halogens, and are not XBs according to the IUPAC definition. Type II interactions occur from the pairing between the electrophilic area on one halogen atom and the electrophilic area on the other and are referred to as true XBs. There are also pseudo Type I/II contacts which are defined by a geometry in-between Type I and Type II.

\[
\begin{align*}
\text{Type I} & : \quad C-X_1 \quad \theta_1 \\
\text{Pseudo Type I/II} & : \quad C-X_1 \quad \theta_2 \quad X-C \\
\text{Type II} & : \quad C-X_1 \quad \theta_1 \quad X-C \\
\text{Type III} & : \quad X-C \quad \theta_2 \quad C \\
|\theta_2 - \theta_1| & < 15^\circ \\
|\theta_2 - \theta_1| & = 15 - 30^\circ \\
|\theta_2 - \theta_1| & > 30^\circ \\
\theta_1 & \approx \theta_2 \approx 90^\circ
\end{align*}
\]

**Figure 3.2.** Types of halogen interactions based on the direction of contacting fragments

In terms of length and strength, analyses of the Type I and Type II I···I contacts in the CSD as a function of the interaction distance showed that at distances shorter than the van der Waals contacts (2.94 or 1.40 Å as radius), the Type I interactions were more frequent at the shortest distances, while XB were more frequent closer to the van der Waals limit. This behavior has been explained as a direct consequence of the electrostatic nature of the XB, which allowed I···I contacts to be formed at longer distances, while Type I contacts, being dispersive, operated preferentially at shorter distances. Short and strong XBs are more directional than the long and weak ones, and by reducing the polarizability of the XB donor, the linearity slightly drops (mean values for the C–X···N angle are 171.4° for I, 164.1° for Br, and 154.6° for Cl).

Desiraju and co-workers reanalysed a larger data set for the occurrence of halogen···halogen ($X_1$···$X_2$) contacts in the solid state by a CSD search. It was found that Type II contacts are most favoured in iodinated derivatives, less in brominated derivatives, and the least in chlorinated derivatives. It is therefore not surprising that Type II contacts...
are very rare in fluorinated structures. Fluorine has a low polarizability which makes the interatomic dispersive forces (which favour Type I contacts) rather low according to Pauling’s Principle. Based on this notion and the discussion in the preceding paragraphs, there exist a large number of structures where the packing together of the fluorous and non-fluorous domains are simply attributed to packing forces. On the other hand, theoretical analysis on many structures have found stabilizing C–F⋯F–C interactions (predominantly type I) which can be explained by the presence of a positive σ-hole found when fluorine is bound to another fluorine atom and sometimes when it is linked to O, N, C, or other atoms bearing particularly strong electron-withdrawing substituents. Similarly, the presence of a σ-hole on fluorine atoms and consequently, XB contacts of two fluorine atoms was also experimentally observed by electron density studies of the homometric crystal of pentafluorophenyl-2,2′-bistiazole.

The solid state structure of several synthesized fluorinated compounds prepared during the course of the project will be analysed for C–F⋯F–C contacts closer than the sum of van der Waal’s radii and other NCIs in the supramolecular structures with the aims of determining which are stabilizing and the order of stabilization energy. To answer this:

(a) A series of carboxylic acids, CF₃(CH₂)ₓCH₂CO₂H with at least four CF₂ units and a CF₃ will be examined. The steric demand due to substitution of a methyl group on the methylene carbon, in terms of how this affects the packing of the fluorous chains would also be examined. This hopefully would show what interactions are present under various conditions.

(b) Investigation will be carried out to determine what happens when the strongly hydrogen bonded carboxylic acid in any of the perfluorinated acids such as 9 is substituted for a functional group with less tendency of being involved in hydrogen bonding such as a triazole function, 1,4-bis(perfluoroalkyl)triazole, the 1,4-diphenyl-1,2,3-triazole fragment has been used as a scaffold to explore halogen substitution in the ortho- and para-position of the phenyl group to investigate the relative strengths of the C—X⋯H bonding and it was concluded that the C—F⋯H interactions are stronger than the more popular C—Cl⋯H interaction. It may be possible to shed light on the factors that influence C—F⋯F—C and C—F⋯H—C interactions, which would be useful in the multitude of applications of these interactions.
The selected fluorinated structures present copious potential for hydrogen and halogen bond viz, \( \text{CF}_3(\text{CF}_2)_6\text{CO}_2\text{H} \) (41), \( \text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CO}_2\text{H} \) (42), \( \text{CF}_3(\text{CF}_2)_3\text{CH(Me)}\text{CO}_2\text{H} \) (43)\(^{47}\)
\( \text{CF}_3(\text{CF}_2)_4\text{CFCHCO}_2\text{H} \) (44), a fluorous triazole (45) and \( \text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3 \) (46)\(^{47}\). The series of fluorinated carboxylic acids have been chosen based on the number of hydrogen atoms present on the perfluorinated chain and steric effects. The findings from such analysis can be correlated with the analysis of fluorinated compounds with less tendency to hydrogen bonds such as the triazole, 45 and perfluorinated alkane, 46 in order to ascertain which is more stabilizing and conditions that promote these non-covalent interactions. Using Hirschfeld Surfaces (HFS) intermolecular interactions can be analysed while maintaining a whole-of molecule approach without the biases inherent in focusing on a limited amount of short contacts that are deemed to be important (Section 1.5). Such analysis have been performed for chlorinated compounds and close \( \text{C}−\text{Cl}⋯\text{Cl}−\text{C} \) and \( \text{C}−\text{Cl}⋯\text{H}−\text{C} \) contacts were highlighted on the Hirschfeld surfaces\(^{48, 49}\). Surface features characteristic of different molecular interactions are shown as colour coded regions from the surface to the nearest atom. This affords striking immediate pictures of types of interactions present and could give some idea of their relative strength from molecule to molecule.

DFT analysis can be useful in determining interaction energy between molecules by analysing the interatomic interactions. Atoms-in-Molecules (AIM) (basis-set independent) as well as other spectroscopic analysis can be used to corroborate the HFS and DFT analysis by analysing the bond critical points between the \( \text{C}−\text{F}⋯\text{F}−\text{C} \) interactions as well as \( \text{C}−\text{F}⋯\text{H}−\text{C} \) interactions that are not recognized when only using the van der Waals distances.
3.2 RESULTS AND DISCUSSIONS

Analysis of the NCIs present in the supramolecular structure were carried out in the solid and solution phase using a number of complimentary techniques.

3.2.1 Characterization in the Solid State

3.2.1.1 X-ray Crystallography

All compounds were synthesized by methods described in Chapter 2. Slow evaporation of DCM afforded clear plate-like crystals of all the compounds 41, 42, 44, 45 and 46 suitable for diffraction. The collection and refinement of data was done by Dr Brendan Twamley.
Solid State Structure of perfluorooctanoic acid, 41

Figure 3.3. X-ray structure of 41 with atomic displacement shown at 50% probability. Hydrogen atom is omitted for clarity.

Figure 3.4. Packing of 41 as viewed along the b-axis. (1) Hydrogen bonding; (2) 3-point bifurcated interaction; (3) Type I interaction.

It should be noted that the crystals were twinned and were modelled as such. The molecular structure of Perfluorooctanoic acid and its packing along the b-axis are shown in Figure 3.4.
3 | Fluorine-fluorine Interactions

The C-F bond lengths range from 1.309(14) – 1.371(10) Å, whilst the C-C bonds are within the range for previously observed for perfluorinated compounds (1.510(16) - 1.576(14) Å). A twisting of the chain is observed so that the F-C-F torsion angles are lower compared to hydrocarbon chains. This relieves the electrostatic interactions between two fluorine groups, amidst other possible factors, and results in a slight twist of the fluorocarbon chain. Dimerisation via hydrogen bonding (d_O···O = 2.928 Å (as the H are calculated), \( \angle C-O-O = 114^\circ \)) is indicated as interaction 1 on Figure 3.4. As has been noted in several structures there is a multitude of C—F···F—C interactions that segregate the fluorous and non fluorous domains: type I interactions (interaction 3 on Figure 3.4) between the CF₃ groups (d_F..F = 2.888 Å, \(|\theta_2 - \theta_1| = 12^\circ\)), and bifurcated “three-point interactions” (d_F..F = 2.869 and 2.874 Å; \( \angle F···F···F = 100^\circ \)) exists between the ‘ponytails’ (interaction 2).

Solid State Structure of 2H,2H-perfluorooctanoic acid, 42

![Figure 3.5. X-ray structure of 2H,2H-Perfluorooctanoic acid, (42) with atomic displacement shown at 50% probability. Hydrogen atoms are omitted for clarity.](image)
**Figure 3.6.** Packing diagram of 42 viewed down the b-axis. (1) Hydrogen bonding; (2) 3-point bifurcated interaction; (3) Type 1 interaction.

42 also exists as the typical hydrogen bonded dimer \( d_{O-O} = 2.665 \, \text{Å} \) (as the hydrogen atoms are calculated), \( \angle C-O-O = 119.8^\circ \) and there are a number of C—F···F—C contacts that are shorter than the sum of the van der Waals radii (2.94 Å). There are type I interactions between the CF₃ groups on the chains which extend in the c plane \( (d_{F,F} = 2.803 \) and 2.903 Å, \( |\theta_2 - \theta_1| = 0^\circ \)). Also present between the ponytails are bifurcated “three-point interactions” \( (d_{F,F} = 2.908 \) and 2.923; \( \angle F\cdots F\cdots F = 54^\circ \)). There are no short C—F···H—C interactions \( (d_{F,H} < 2.66 \, \text{Å}) \) in this complex as the hydrogens are involved in C—H···O hydrogen bonding to a carboxylate group. This observation suggests that the C—H···O interaction is stronger than a C—H···F—C interaction, and in accord with other examples in the literature. The commonly observed twisting of perfluorinated chain so that the F-C-C-F torsion angles are lower compared to hydrocarbon chains is not present in 42 as the fluorine atoms are in an eclipsed conformation. The only other example in the database that has eclipsed F atoms is the structure of heptyl 2-(perfluorohexyl)ethyl ketone, although no comment was made about this in the paper.

Solid State Structure of 2H-Perfluorooct-1-enoic acid, 44

**Figure 3.7.** X-ray structure of 2H-Perfluorooct-1-enoic acid, 44 as viewed along the c-axis with atomic displacement shown at 50% probability. Hydrogen atoms are omitted for clarity.
Figure 3.8. Packing of Perfluorooct-1-enoic acid, 44 as viewed along the b-axis. (1) Hydrogen bonding; (2) 3-point bifurcated interaction; (3) Type 1 interaction and (4) C-F···H-C interactions.

The molecular structure of Perfluorooct-1-enoic acid, 44 and its packing along the b-axis are shown in Figure 3.7 and 3.8. The C-F bond lengths range from 1.324(5) – 1.356(4) Å with the C—F bond of the CHF group, in the mid-range at 1.332(5) Å. The C-C bonds lengths are between 1.517(5) - 1.560(5) Å with shortest bond length of 1.317(6) belonging to the C=C group. The commonly observed twisting of the chain is also observed so that the F-C-C-F torsion angles are lower compared to hydrocarbon chains. The complex is also dimerised via hydrogen bonding – interaction 1 (dO···O = 2.632 Å (as the H are calculated), ∠C-O-O = 116.6°). There is also a multitude of C—F···F—C interactions: type II interactions between the CF₃ groups (dF···F = 2.879 Å, |θ₂ - θ₁| = 30.7°), and bifurcated 3-points interaction (2) between the CF₂ groups” (dF···F = 2.939 Å; ∠F···F···F = 42°) exists between the ponytails. There are also C—F···H—C interactions (4) present from the fluorine of CF of the alkene fragment to another neighbouring hydrogen (dH···F = 2.463 and 2.503 Å, ∠C···F···H = 154°) of the alkene fragment resulting in a chain along the a-axis.
Solid State Structure of 1,4-bis(perfluoroalkyl)triazole, 45

**Figure 3.9.** X-ray structure of 45 with atomic displacement shown at 50% probability. Hydrogen atoms are omitted for clarity.

**Figure 3.10.** Packing diagram of 45 viewed down the ab plane. (1) Hydrogen bonding; (2) 3-point bifurcated interaction; (3) Type 1 interaction and (4) C-F···H-C interactions.

The structure and packing of 16 is shown in Figure 3.9 and 3.10, and a plethora of non-covalent interactions are clearly evident. The most noteworthy feature from the structure of 45 is the replacement of one C—F bond for a C—H bond in one of the R_F chains. The bond lengths within the ponytails are also normal, apart from the CHF group, where the C—F bond is the longest at 1.401(6) Å and the metric parameters within the heterocyclic ring (d_{C=N} = 1.334; d_{C,N} = 1.361; d_{C-C} = 1.366; d_{N=N} = 1.305; d_{N,N} = 1.354 Å) are as expected from a survey of the Cambridge Structural Database. The F—C—C—F torsion angles are as expected for a fluorous chain, imparting a twist to the chain. The ends of the molecule
3 | Fluorine-fluorine Interactions

possesses long contacts ($d_{F\ldots F} = 2.915 \, \text{Å}$; $|\theta_2 - \theta_1| = 23.9^o$) between the chains (interaction 3) and bifurcated “three-point interactions” ($d_{F\ldots F} = 2.679$ and $2.781 \, \text{Å}$; $\angle F\ldots F\ldots F = 54^o$) that connect the chains (interaction 2). There are also $\text{C}--\text{F}\ldots \text{H}--\text{C}$ interactions present from the CHF carbon ($d_{\text{H}\ldots \text{F}} = 2.463$ and $2.503 \, \text{Å}$) which unusually exist in a bifurcated arrangement between three chains (interaction 4). Also present is a $\text{C}--\text{H}\ldots \text{N}$ hydrogen bonds between the C(13) of the triazole backbone and the N(10) of a second triazole ($d_{\text{CH}, \text{N}} = 3.235 \, \text{Å}$); it has been noted that this $\text{C}--\text{H}$ bond is highly polarized and can be as strong as amides bonds.\textsuperscript{60} The CH$_2$ groups on the ‘normal’ R$_F$ chain are also involved in hydrogen bonding to the other triazole nitrogen ($d_{\text{C}, \text{N}} = 3.662$) resulting in chains perpendicular to the plane depicted in Figure 3.10.

Solid State Structure of perfluoroalkane, 46

![Figure 3.11](image). X-ray structure of 46 viewed along the b-axis. Hydrogen atoms are omitted for clarity.
The structure of 46 was obtained although this has been previously characterised by the Baker group.\textsuperscript{47} It is presented here for the purpose of comparing with the other structures presented in this study.

\subsection{Hirshfeld Surface Analysis}

Whilst these weak interactions can be understood using DFT and AIM, this can be rather time-consuming. Hirshfeld surfaces\textsuperscript{61} is another methodology to quantify intermolecular interactions. Surprisingly fluorous interactions have rarely been analysed by this method.\textsuperscript{57} So this approach has been employed here to explore and compare the interactions in the synthesised compounds to a non-fluorous octanoic acid.\textsuperscript{58}

The results of this analysis are shown in Figure 3.13. When the d\textsubscript{norm} parameter is mapped onto the Hirshfeld surface the expected hydrogen bonding in the carboxylic acid functions are visibly observed as red spots. More subtle information on weak interactions and C-F···F-C, and the bifurcated F···F interactions are also obvious for all structures studied where such interactions are present (Figure 3.14 – 3.20).
Figure 3.13. Map of the property $d_{norm}$ of (a) 41 (b) 42 (c) 43 (d) 44 (e) 45 and (f) 46 onto the Hirsh surface (plotted at -0.1-1.0) showing Hydrogen bonds and F···F contacts as red spots.

These $d_{norm}$ plots are in agreement with the x-ray crystallographic analysis and they highlight subtle information such as the three point bifurcated interactions.

The results of further analysis by Shape index and Curvature of the structures selected are shown as b and c in Figure 3.14 - 3.20. Shape index shows highlights of yellow and red eclipses which indicates self-complimentary regions. Furthermore, the curvature which is
typically characterised by large areas of green separated by blue edges, shows unusually flat regions corresponding and emphasising hydrogen bonding and the C-F···F-C interactions. These results are in agreement with previous HFS analysis of chlorinated structures. Close Cl···Cl contacts have been noted in heavily or fully chlorinated hydrocarbons\textsuperscript{39} with features such as linear and bent configurations,\textsuperscript{48,62-64} double and triple contacts which were clearly visible in the HFS analysis.\textsuperscript{62} Conversely, the triple contacts were absent in studied fluorinated compounds and this can be explained by chlorine being more polarisable and therefore found to exhibit more XB interaction.

\textbf{Figure 3.14}. Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0), (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (d) fingerprint plot showing the H···H interactions for CH$_3$(CH$_2$)$_6$CO$_2$H (octanoic acid)
**Figure 3.15.** Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0) (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (c) fingerprint plot showing the F···F interactions for PFOA (41).

**Figure 3.16.** Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0) (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (c) fingerprint plot showing the F···F interactions for CF$_3$(CF$_2$)$_5$CH$_2$CO$_2$H. (42).
3 | Fluorine-fluorine Interactions

Figure 3.17. Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0) (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (c) fingerprint plot showing the F···F interactions for CF$_3$(CF$_2$)$_3$CH(Me)CO$_2$H (43).

Figure 3.18. Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0), (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (d) fingerprint plot showing the H···H interactions for CH$_3$(CH$_2$)$_3$CHFCH$_2$CO$_2$H (44).
Figure 3.19. Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0), (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (d) fingerprint plot showing the F···F interactions for Fluorous triazole (45).

Figure 3.20. Map of (a) $d_{\text{norm}}$ (-0.1 to 1.0), (b) shape index (-1 to +1), (c) curvedness (-4 to 0.4) and (d) fingerprint plot showing the H···H interactions for [CF$_3$(CF$_2$)$_5$(CH$_2$)$_2$]$_2$ (46)
A plot of the quantitative information on the NCIs based on the mapped 2D fingerprint plot of $d_{\text{norm}}$ shown in Figure 3.14 - 3.20 (right) summarizes the major intermolecular contacts of the entire crystal structure in a single two-dimensional colour picture. The differences in molecular interaction amongst crystals are more clearly seen. This can be used to generate quantitative data on the amount of different interactions present in the structures as shown in Figure 3.21. Comparing such information with the fingerprint analysis of previously reported structures,$^{65-70}$ it is clearly evident that the long chain perfluorinated structures are heavily dominated by $\text{F} \cdots \text{F}$ and $\text{F} \cdots \text{H}$ interactions while the short chain fluorinated structure are dominated by $\text{F} \cdots \text{H}$, $\text{F} \cdots \text{O}$ and $\text{H} \cdots \text{H}$ interactions.

![Figure 3.21](image)

**Figure 3.21.** Quantitative analysis of NCIs present in synthesised structures and selected comparable structures from the CCD.$^{65-70}$

### 3.2.1.3 Vibrational spectroscopy

It has been described that $\text{C} - \cdots \text{F} - \cdots \text{C}$ interactions can be observed by small shifts in the infrared spectrum.$^{71}$ Being the most unique amongst the perfluorinated acids in terms of structural feature described earlier, compound 42 was selected along with the fluorinated
triazole for vibrational spectroscopy but the infrared and Raman spectra of the compounds analyzed were identical in the C—F stretching and bending regions.

Among all the structures studied, the bond lengths within the fluorous domain are identical, but the C=O and C—O bonds of the acid fragment are slightly different {C—C: \(41 - 1.541(14) \text{ Å} \); \(42 - 1.510(3) \text{ Å} \); \(44 - 1.486(5) \text{ Å} \); C=O: \(41 - 1.229(11) \text{ Å} \); \(42 - 1.235(2) \text{ Å} \); \(44 - 1.268(5) \text{ Å} \); C—OH: \(41 - 1.330(12) \text{ Å} \); \(42 - 1.293(2) \text{ Å} \); \(44 - 1.262(5) \text{ Å} \);} and this difference is also reflected in the changes in the C=O stretch in the infrared spectra (\(41: 1692 \text{ cm}^{-1} \); \(44: 1709 \text{ cm}^{-1} \); \(42: 1714 \text{ cm}^{-1} \)). Compared to the non-fluorinated octanoic acid, the C=O bond length (1.240 Å)\(^72\) is longer than the fully fluorinated structure and is also reflected in the infrared spectra (1711 cm\(^{-1}\))\(^73\)

![Figure 3.22. Infrared (top) and Raman (bottom) spectra of 42.](image-url)
3.2.1.4 Thermal analysis

As expected there are more C—F···F—C interactions in 41 but the major differences are number of C—H present in the other acids. It is perhaps coincidental that the amount of H···H interactions in octanoic acid and the F···F interactions in 41 are essentially identical based on the HFS analysis and therefore requires further probing by thermal method. The melting point of 41 (58.4 °C) compares interestingly to the corresponding non-fluorinated octanoic acid (16-17 °C). this not surprising as halogenated compounds are known to possess higher thermal stability than their corresponding non-halogenated analogues. Similar trend has been observed in fluorinated structure where the thermal stability increased with increasing number of CF₂ units. The same trend holds true for a set of structures of similar number of Carbon atoms and a varied amount of H atoms. Herein a correlation between the number of H present in highly fluorinated structure and their melting points (Table 3.4) is observed in structures with increasing number of H atoms. The melting points of the structures, as determined by DSC, decreased with increasing number of H in the structures.
### Table 3.4. Key crystallographic and infrared features in the studies structure and relationship between the number of hydrogen and the melting point

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of H in (CH)n units</th>
<th>Bond Length (Å)</th>
<th>IR Stretch (cm⁻¹)</th>
<th>Melting points (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA (41)</td>
<td>0</td>
<td>1.541(14); 1.229(11); 1.330(12)</td>
<td>1692</td>
<td>60</td>
</tr>
<tr>
<td>2H-Perfluorooct-1-enoic acid (44)</td>
<td>1</td>
<td>1.486(5); 1.268(5); 1.262(5)</td>
<td>1709</td>
<td>79.2a</td>
</tr>
<tr>
<td>2H,2H-Perfluorooctanoic acid (42)</td>
<td>2</td>
<td>1.510(3); 1.235(2); 1.293(2)</td>
<td>1714</td>
<td>5575</td>
</tr>
<tr>
<td>Fluorous-triazole (45)</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>96.21a</td>
</tr>
<tr>
<td>[CF₃(CF₂)₅(CH₂)₂]₂ (46)</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>54.4</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>17</td>
<td>1.499; 1.240; 1.287 /²²</td>
<td>1711 /²²</td>
<td>18.20</td>
</tr>
</tbody>
</table>

a Does not follow trend due to the presence of an alkene and a triazole group present.

### 3.2.1.5 Solid state NMR spectroscopy

The unusual nature of the structure of 42 compared to the other fluorous structures led to the measurement of possible differences in the solid state ¹⁹F NMR spectra that may be correlated to the C—F···F—C interactions. The spectrum recorded for all compounds were very broad (Figure 3.24), possibly due to extensive dipolar couplings.⁷⁶
Moreover, peak broadening of the resonances in solid state NMR spectra has also been attributed to reduced motional dynamics. To investigate the extent of the reduced motional dynamics and aggregation in the peak broadening, the samples were diluted to 10% using an NMR inert compound, KBr. In theory, broadening related to reduced motional dynamics and aggregation should decrease and the peaks should become sharp as the motional dynamic increases due to less aggregation. However, dilution to 10% gave a spectrum whose peaks were too weak and inconclusive. 50% dilution experiment are gave broad resonance peaks which were more broad than the 100% sample most likely due to poor resolution than aggregation (Figure 3.24a).

![Figure 3.24a. CP-MAS $^{13}$C{H} NMR Spectra showing resonances in solid state NMR spectra of 41 (yellow), 42 (purple), 44 (green), 45 (red) and 46 (blue) (top to bottom).]
Figure 3.25b. CP-MAS $^{13}$C{H} NMR Spectra showing resonances in solid state NMR spectra of 10% (blue), 50% (red) and 100% (green) of 42 in KBr.

Furthermore, non-covalent interactions have been associated with “aggregation shift” which is defined as the difference between the chemical shift in the aggregate (in the solid state) and in the monomer (in solution). As shown in Figure 3.25, the carbonyl and triazole peaks of the fluorinated compounds, 41, 42, and 45 shifted downfield (by $\Delta\delta = 7, 6$ and 4 ppm respectively) due to aggregation although such clear distinction could not be made for the very broad CF peaks. The collative solid state NMR shows that non-covalent interaction is observed as peak broadening and aggregation shift. However, as reported previously, further work is required to achieve a level of accuracy on a par with NMR crystallography.
Figure 3.26. CP-MAS $^{13}\text{C}\{\text{H}\}$ NMR Spectra (red) and solution phase $^{13}\text{C}\{\text{H}\}$ NMR Spectra (blue) showing the peak shift of the acidic carbonyl in 41 (a) and 42 (b) and the triazole group in 45 (c).

3.2.2 Characterization in Solution Phase

**SAXS Analysis**

Chart 1. Ligands 1, 2 and 3

The SAXS analysis were carried out in collaboration with Prof. May Nyman, Oregon State University. Analysis of the concentrated samples (50 mmolar solutions) of three ligands based on the tren, 1 cone calix[4]arene, 2 and partial cone calix[4]arene, 3 (Chart 1) dissolved in methanol showed one population for 2 of 20 Å while 1 and 3 each have two
populations (13, 24 and 12, 23 Å) possibly due to changing conformation in solution and supports the notion that 2 is held in a rigid conformer\textsuperscript{40} resulting in a similar size of the extended structure obtained from computation calculations (20.4 Å). The size of 1 and 3 are complimentary to the sizes obtained from DOSY analysis (\textit{vide infra}) in Section 4.2.2.2.

Table 3.5. SAXS and PDDF analysis of the ligands 1, 2 and 3

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Size Distribution (diameter)</th>
<th>PDDF Modelling II (radius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 populations (relative volume): 13 Å (6), 24 (1.4) Å</td>
<td>Max extent: 26.8 Å Rg: 9.8 Å</td>
</tr>
<tr>
<td>2</td>
<td>1 population: 20 Å</td>
<td>Max extent: 33.6 Å Rg: 11.6 Å</td>
</tr>
<tr>
<td>3</td>
<td>2 populations: 12 Å (4.6), 23 (0.9) Å</td>
<td>Max extent: 29.5 Å Rg: 10.2 Å</td>
</tr>
</tbody>
</table>

In effect, except for ligand 2 which is held together in a rigid conformation in solution, the sizes of the ligands in solution are smaller or much larger than the sizes in the expected sizes in the solid state structures. This is attributed to coiling up or interdigitation of the fluorous domain resulting in the smaller or larger structures (Chart 2). This was confirmed by selective \(^{19}\text{F} \text{nOe} \text{experiments}. Coupling of the CF\textsubscript{3} to all the CF\textsubscript{2} was observed when the CF\textsubscript{3} of 2 was irradiated (Figure 3.26).
DOSY Analysis

The diffusion properties of the fluorinated compounds warrants a number of comments. In general the sizes of the molecules at the same concentration, are smaller than the measured sizes of the extended solid state structures (Figure 3.27). This may be attributed to the coiling up of the fluorous domains and is consistent with the SAXS measurements. The sizes of perfluorinated acids, 41, 42, and 44 are larger than the perfluoroalkane, 46. This is possibly due to dimerization of the acids through hydrogen bonding which is consistent with dimerisation of some acids seen in mass spectrometry (Figure 3.28). The diffusion coefficient of 41 is closer to that of the much larger triazole. This suggests that the acid is strongly dimerised as also observed in the mass spectrometry. The perfluoroalkane, 46 has the highest diffusion coefficient and is thus the smallest in solution amongst the compounds. This also suggests that in the absence of a strong hydrogen bonding, smaller (monomeric) species of the perfluoroalkane was observed. However, 41 is the largest of all the structures most likely in solution which suggests a multimeric structure due to non-covalent interactions.
Figure 3.28. Overlay of 2D DOSY spectra of 41 (top blue), 45 (red), 42 (pink), 44 (purple) and 46 (bottom blue) in acetone-$d_6$.

Figure 3.29. Mass Spectroscopy showing the dimeric species of 42 in gas phase.

Table 3.6. Sizes of studied structures based on their diffusion co-efficient $D_{CT}$ and diameter of their solid state structures

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D_{CT}$ (ms$^2$)</th>
<th>Radius (au)</th>
<th>Diameter from (Å) DOSY</th>
<th>Diameter from (Å) X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA (41)</td>
<td>$2.85 \times 10^{-9}$</td>
<td>4.2</td>
<td>10.64</td>
<td></td>
</tr>
<tr>
<td>2H,2H-Perfluorooctanoic acid (42)</td>
<td>$4.22 \times 10^{-9}$</td>
<td>2.5</td>
<td>10.31</td>
<td></td>
</tr>
</tbody>
</table>
3.2.3 Computational studies on 42 and 45

In collaboration with Dr. James Platts, Cardiff University, computational studies were carried out on representative compounds 42 and 45 due to the unusual structure of 42 and the interesting features of 45. DFT calculations of 42 suggest that the twisted, that is experimentally not observed conformation, is indeed the most stable, with the ‘untwisted’ conformer at 96 kJ mol⁻¹ higher in energy. This is most likely related to C-F···F-C interactions. Further computational analysis using a combination of DFT and Atoms-In-Molecules (vide infra) have been employed to explore the weak interactions given the unusual nature of this compound and the non-covalent interaction present in structure of 42 and the triazole, 45.

Calculation of the interaction energies between individual molecules is one of the methods of quantifying the interactions in the solid state. A series of dimers was extracted from the crystal structures of 42 and 45 and reported in Tables 3.7 and 3.8. Using this approach, five dimers were extracted from the crystal structure of 42. In the first, 42a, there exists two hydrogen bonds between the carboxylic acid groups with no close C—F···F—C contacts. 42b has only C—H···O hydrogen bonds between the carboxylic acid and the methylene group. C—F···F—C contacts of length 2.854, 2.922, and 2.861 Å, were however found in 42c. Lastly, just one C—F···F—C contact at 2.913 Å and 2.803 Å are present in 42d and 42e respectively. As expected the hydrogen bonded dimer 42a is very strongly stabilised compared to the interaction energy for the same dimer to a methyl substituted carboxylic acid CF₅(CF₂)₃CH(CH₃)CO₂H, 43⁴⁷ = -13.23 kcal mol⁻¹. 42c is only weakly stabilised despite its numerous close contacts, although this confirms the stability of the three-point interaction motif discussed above; the comparable energies for 43 was -1.69 kcal/mol. Indeed, a weak binding energy was obtained for 42d and 42e and is close to that which was previously calculated for (CF₄)₂.⁴⁷
Topological analysis have likewise been conducted utilizing Atoms-in-molecules approach and the results are shown in Table 3.6. Strictly speaking, since the considered dimers are not at their optimal geometry, associated atomic interaction line and the presence of a bond critical point cannot be used as proof of bonding. However, this approach is preferred as the interactions present in the solid state should be better preserved. Only the hydrogen bonds of the acid function are displayed in dimer 42a and the electron density at the bond critical point $\rho_{\text{bcp}}$ which is in agreement with the smaller interaction energy than that seen in compound 43 (0.048 au). Dimer 42c also exhibits C—F···F—C interactions, and again the electron density at the bond critical point $\rho_{\text{bcp}}$ is of the same order of magnitude as in compound 43, indicating that these interactions do have an important contribution to the stabilization of the dimers and are not due to crystal packing effects. Though rather weak, (c.f. $\rho_{\text{bcp}} = 0.0045$ in compound 43), AIM analysis finds one C—H···F—C interaction that was not observed by consideration of the van der Waals radii analysis. On the other hand, dimers 42d and 42e are possibly due to Type I interactions.

However, since dimers 42d and 42e are predicted to be weakly bound and contain only F···F contacts between molecules, this suggest that the intermolecular F···F contacts seen here are stabilizing. Further detail on the basis of this stabilization comes from data reported in Appendix C1 showed the contribution of dispersion to the overall interaction energy. The dispersion contribution is larger than the overall interaction energy for the purely F···F contacts found in 42d and 42e, and as such, accounts for all stabilization: electrostatic and exchange effects are possibly weakly repulsive in the crystal geometry. Dimers 42b and 42c shows identical pattern, and dispersion contribution smaller in magnitude than the overall interaction energy is only observed in the hydrogen bonded dimer 42a.

Table 3.7. Interaction energies (kcal mol$^{-1}$) and $\rho_{\text{bcp}}$ values (au) of dimers of 42 taken from the crystal structure
<table>
<thead>
<tr>
<th>Image</th>
<th>Description</th>
</tr>
</thead>
</table>
| 42b   | ![Image] IE = -2.9  
C-H···O: 0.008  
H···H: 0.003  
F···O: 0.003 |
| 42c   | ![Image] IE = -4.0  
F···F: 0.006  
0.005 (x5)  
C-H···F: 0.002  
F···O: 0.002 (x2) |
| 42d   | ![Image] IE = -0.6  
F···F: 0.004 |
| 42e   | ![Image] IE = -1.5  
F···F: 0.006 |

5 dimers of 45 were similarly generated by symmetry operations: interaction energy and $\rho_{\text{bcp}}$ values for each are reported in Table 3.8. Dimer 45a clearly displays a C—H···N hydrogen
bond between triazole rings and is almost as strongly stabilized as the dimer \textit{42a}, which has two classical O—H···O H-bonds. Substantial electron density is displayed on the C—H···N as shown by Topological analysis. Numerous other interactions including a weaker C—H···N contact between methylene and triazole, two C—H···F contacts and 12 F···F ones contributes to the large stabilization of this dimer. Together, \( \rho_{bcp} \) values of all contacts sum to 0.050 au, less than that in \textit{42a} but of similar magnitude.

Dimer \textit{45b} has one F···F contact, and its interaction energy of just 1.1 kcal/mol echoes this fact. In contrast, \textit{45c} is strongly stabilized, although there is little contribution of stacking interactions to the overall interaction despite the short distance between and parallel orientation of triazole rings. C—H···F and especially F···F contacts dominate \textit{45c}. Two C···C contacts are also present, nonetheless these link methylene with triazole and display small \( \rho_{bcp} \) values. Instead. It is notable that using the default setting of Mercury, analysis based on the geometry of the crystal structure, select only two F···F contacts in this structure, and stacking assigned as C—H···π interactions, and shows no evidence for C—H···F contacts. \textit{45d} and \textit{45e} are also strongly stabilized, through a mixture of π-stacking, C—H···F and F···F interactions in both cases. The former contains numerous F···F and F···N contacts, while the latter is the only dimer that has the pattern of critical points expected of π-stacking common in the benzene dimer and related complexes.\cite{82} Dispersion, once again, dominates these dimers, as this is larger in magnitude than the overall interaction energy in each dimer.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{45a} & \textbf{IE} = -14.2 & \textbf{C-H···N}: 0.013 & 0.006 & \textbf{C-H···F}: 0.005, 0.003 \\
\hline
\end{tabular}
\caption{Interaction energies (kcal mol\(^{-1}\)) and \( \rho_{bcp} \) values (au) of dimers of \textit{45} taken from the crystal structure.}
\end{table}
Fluorine-fluorine Interactions

45b

IE = -1.11
F···F: 0.005

45c

IE = -7.8
C···C: 0.001 (x2)
C-H···F: 0.002 (x2)
F···F: 0.008 (x2)
3.3 CONCLUSION

In conclusion, examples of compounds that feature fluorinated ponytails have been isolated and structurally characterized to explore non-covalent interactions. Interaction of the nature C=O···H—O, C—F···F—C, C—F···H—C, C—F···O and 3-point interactions were predominant in all the fluorinated structures studied. The Hirshfeld surface analysis provided instant visual representation of short contacts such as the 3-point bifurcated
interactions. Direct comparison in terms of the strength and number of non-covalent interactions present between molecular structures of a series of perfluorinated acids has been shown. While a typical hydrogen bond is stronger than the C—F···F—C, there is a profusion of fluorous interactions, shown in the quantitative Hirshfeld analysis. Solid state NMR spectroscopy showed an aggregation shift in the carbonyl resonance peak and extensive peak broadening throughout the entire spectra which could be due to a number of factors including reduced motional dynamics and dipolar coupling. Dilution experiment has been carried out to support this reasoning. However, loss in resolution upon dilution makes it difficult to attribute broadening to dipolar coupling. Further spectroscopic analysis in solution showed unexpectedly larger molecular sizes of the fully fluorinated compounds which may be due to aggregation and give further weight to the idea of C—F···F—C. Computational data show that these interactions are collectively stabilizing in the order of magnitude as a typical hydrogen bond. An unusual ‘untwisting’ of the perfluoroalkyl chain that has not been previously commented upon was found in \( \text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CO}_2\text{H} \), and this untwisting is deemed to perhaps increase the number of C—F···F—C interactions at the expense of C—F···H—C electrostatic interactions; but the energies of these interactions could be of the same order of magnitude. The structure of a triazole, 45, shows a profusion of weak interactions in the normal twisted perfluorinated chain. Computational studies reinforce previous reports that the C—F···F—C interactions are present and stabilizing adding some credence to the idea that steric interactions do play a role in the non-covalent interactions present in these compounds.

3.4 EXPERIMENTAL

Solid state NMR spectra were recorded on a Bruker 400 HD at 100.61 MHz (\(^{13}\text{C}\)), 376.50 MHz (\(^{19}\text{F}\)). X-ray crystallography data were measured on a Rikagu Saturn and on a Bruker Apex diffractometer. The collection and refinement of data was done by Dr Brendan Twamley. The structure was solved by direct methods and refined by least squares method.
on F² using the SHELXTL program package.\textsuperscript{83} Crystal data, details of data collections and refinement are given in Table 3.9. All compounds and solvents were obtained from commercial sources and used as received.

DFT calculations were carried out in Gaussian09\textsuperscript{84} with the dispersion corrected B97D functional\textsuperscript{85} and def2-TZVP basis set\textsuperscript{86} used in previous work, and taking advantage of density fitting to make larger calculations viable where possible. All calculations of interaction energy used the counterpoise method to account for basis set superposition energy.\textsuperscript{87} Converged molecular orbitals were obtained from these calculations and used for topological analysis of the resulting electron density using the AIMAll package.\textsuperscript{88}

X-ray crystallography data were measured on a Bruker Apex diffractometer. The structures were solved by direct methods and refined by least squares method on F² using the SHELXTL program package.\textsuperscript{62} The structure 41 was refined as a 2 component rotational twin (twin law: -1 -0.001 0 0 1 0 0 -0.505 -1) with a refined fractional twin volume of 19.78%. The structure was refined with restraints (RIGU, ISOR) and to convergence. The high residuals may be twinning artefacts.

<table>
<thead>
<tr>
<th>Table 3.9. Crystal Data and Refinement Parameters for Crystal structures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
</tr>
<tr>
<td>4S</td>
</tr>
<tr>
<td>44</td>
</tr>
<tr>
<td>42</td>
</tr>
<tr>
<td>41</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Temperature (K)</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space Group</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
</tr>
<tr>
<td>V (Å(^3))</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m(^3))</td>
</tr>
<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
</tr>
<tr>
<td>Completeness to theta (%)</td>
</tr>
</tbody>
</table>
### 3.5 REFERENCES


3. Fluorine-fluorine Interactions


3 | Fluorine-fluorine Interactions


81. CCDC, *Mercury 3.3*, http://www.ccdc.cam.ac.uk/mercury/


Chapter 4

Application of Non-covalent Interactions in the Extraction of PFOA
4.1 OVERVIEW

Studies on non-covalent interactions are extended to application of fluorous ligands as hosts in the extraction of a persistent organic pollutant – Perfluorooctanoic acid (PFOA) from water. There is a wealth of documented toxicity and global distribution studies on PFOA (Section 1.5), making the need to find effective remediation strategy crucial but not well studied.

Extraction of POP from water using the synthesized fluorous ligands is carried out as a way of harnessing and extending the idea of C—F···F—C interactions. On the basis of structural and theoretical investigations (Chapter 3), C—F···F—C interactions have been shown to be stabilizing in the solid state, and collectively can add the same amount of stabilizing energy as a hydrogen bond.¹ There are now a growing number of examples of F···F interactions being utilized in crystal engineering for applications in materials chemistry² or in catalysis.³ Interest in weak C—H···F—C bonding is also burgeoning.⁴ Bearing in mind the extensive use of non-covalent interactions in sensing anions,⁵ it is reasonable that with a suitably designed ligand we could extract PFOA from aqueous media, thus offering a remediation strategy. For this aim to be realized a number of features need to be incorporated into the ligand system.

- A conformationally rigid ligand would be thermodynamically favourable in forming stable host-guest complexes; a system based on a calix[4]arene would be useful as this has been used prodigiously in supramolecular chemistry.⁶
- Hydrogen bonding will be the primary non-covalent interaction,⁷ and to increase the propensity for this to occur, electron withdrawing groups near the donor atoms are required.⁸ It is also known that the fluorous acid is a strong acid, so hydrogen bonding strategies using both of these inductive effects have been described.⁹ It should be noted that the measurement of pKa’s has been controversial, with a range <0.1–3.8 reported, depending upon the conditions of the measurement and the concentration of PFOA.¹⁰ “Dipole engineering”¹¹ also lends itself to this topic as adding a fluorous chain to the amides reverses the dipole compared to a hydrocarbon framework that can then match the dipole of the fluorous acid.
Furthermore the presence of a long fluorous chain on the host will also allow a fluorophilic cavity to engender F···F interactions and add a further stabilizing non-covalent interaction.

It should be noted that host-guest complexes with PFOA and its derivatives have not been studied in detail, although some success has been seen with cyclodextrin hosts and a tripodal fluorous amide has been used to form host-guest complexes with the related perfluorooctane sulfonate (Scheme 4.1). The extraction efficiency will be monitored by spectrophotometric analysis. Thermal, vibrational and multinuclear NMR spectroscopic analysis in both solution and solid state, will be useful in elucidating the nature of interaction in the host guest structures. The stoichiometry of the host:guest species and the binding constants will be measured by $^1$H and $^{19}$F NMR titration. A computational study will be employed in order to gain further insight into the lowest energy state of the complexes which is expected to corroborate the spectroscopic measurements. To further probe the effect of the non-covalent interactions on PFOA extraction, two guests with the ability to either participate in hydrogen bonding or F···F interactions will be tested. Perfluoroalkane ($\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$) and octanoic acid possessing the potential to only participate in halogen and/or hydrogen bonding respectively will be titrated against a complementary host as PFOA in hopes of corroborating the computational studies.

$$K_2 = 4 \times 10^5 \text{ M}^{-2}$$
$$K_1 = 7 \times 10^4 \text{ M}^{-1}$$
$$K_2 = 9 \times 10^2 \text{ M}^{-2}$$

**Scheme 4.1.** Examples of host featured in host-guest complexes with PFOA and their corresponding binding constants.
4.2 RESULTS AND DISCUSSION

4.2.1 Extraction of PFOA from water using the tren (1), cone-(2) and partial cone calix[4]arene (3) ligands

Chart 4.1. Structures of tren (1), cone-(2) and partial cone calix[4]arene (3) ligands

Given that PFOA is a widespread persistent organic pollutant, the first aim was to find a system that would allow the removal of PFOA from water. The hosts have solubility in common organic solvents but the partition coefficient (P) of PFOA which is the ratio of the concentration of a compound in two immiscible or slightly immiscible liquids including a number of common organic solvents and water at equilibrium had to be first determined.\textsuperscript{14} Interestingly, at higher concentrations of PFOA foaming and the formation of a third phase was observed. The results are shown in Table 4.1. Inspection of the partition coefficients suggests that in the few solvents in which the ligand is soluble, could act as a co-extractant, but under experimental conditions they did not extract PFOA into the organic phase without the addition of the ligand. Screening of the solvents showed that the amphiphilic 1,3-bistrifluoromethylbenzene (BTFMB) had the greatest extraction ability, so this was chosen for more detailed studies. It should be noted that this solvent would not be useful for large scale applications and some ligand redesign or change of solvent is necessary.
Table 4.1. Partition coefficient of PFOA in water:solvent measured by $^{19}$F NMR spectroscopy.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>FC-72</th>
<th>BTFMB</th>
<th>Chloroform</th>
<th>DCM</th>
<th>Toluene</th>
</tr>
</thead>
</table>

Figure 4.1. Results of the extraction of PFOA from water using 1 equivalent of the hosts in BTFMB and monitored by UV-vis spectroscopy 23 °C.

The extraction of PFOA (0.8 mM solution) from water into the fluorous solvent containing the extractants was carried out by a maintained slow stirring of the biphasic solution at 400 rpm to avoid solvent mixing and allow the reaction to happen at the interface. The extraction was monitored by UV-vis spectroscopy, as PFOA has an absorption band at 206 nm in water. Experiments involving variation of PFOA concentration while keeping the same ligand concentration and vice-versa have also been carried out with similar results. The averaged results of the 1:1 (ligand/PFOA) extractions repeated four times with the three hosts are shown in Figure 4.1. It can be seen that the removal of PFOA from water is effective for all hosts, with the more rigid full cone conformer 2 being the most effective. The host 1 is the slowest at extracting, suggesting that conformational rigidity might be a key factor. UV-vis absorption and $^{19}$F NMR spectroscopy for host 2 shows that no PFOA is detectable in the aqueous phase at the end of the experiment. The shape of the curves warrants some discussions. There is an equilibration phase at the start of the experiment which can be attributed to the solubilizing and rearrangement of the ligands. In 2 and 3, this is followed by PFOA extractions until maximum extraction is reached. The extraction efficiency then drops, suggesting leaching of PFOA back into the aqueous phase through the formation of a...
meta-stable micro-emulsion which breaks down and leaches back into the aqueous phase at the end of the reactions. This is not the case with ligand 1 wherein after 40% extraction, the extraction stopped for some time and then continued again until maximum extraction is attained. The reason for this is rather unclear but may suggests that an intermediate is formed which then goes on to finish the reaction. Whilst these results are pleasing, it is also worth noting that the PFOA does slowly leach back into the water phase if these phases are contacted overnight. The implications from these results are that the host-guest complex is not very stable over long periods of time. This could be due to the stronger hydrogen bonding in water over the hydrogen bonding system in the hosts.

4.2.2 PFOA interactions with Hosts

In order to understand the host-guest species present during the extraction, a number of experiments have been carried out to determine the stoichiometry and probe the nature of the bonding. These conclusions have been supported by computational investigations.

4.2.2.1 Determination of the Stoichiometry

In order to determine the number of PFOA guests that fit into the hosts 1, 2 and 3 a simple acid-base titration and two solution based methods, namely absorbance spectroscopy via a continuous variations plot\(^1\) and \(^{1}H\) and \(^{19}F\) NMR titration experiments\(^2\) have been utilized. For the host 2, free PFOA is only detected by titration with 0.010 M NaOH after the addition of 2 equivalents of PFOA, suggesting a 1:1 stoichiometry. Host 1 is more complex as a higher stoichiometry species of ~6 appears to be favored. Continuous variations plots confirm this stoichiometry (Figure 4.2).
**NMR Titrations:** Analysis of the $^1$H and $^{19}$F NMR titrations (Figure 4.3-6) using WINEQNM R2\textsuperscript{18} gave the best fit to a 1:1 complex with a log$\beta$ = 2.66 ± 0.35 from the $^1$H NMR data. Host 3 also displays a 1:1 stoichiometry from titration and continuous variations plots and the $^1$H NMR titration gives a log$\beta$ = 1.90 ± 0.21 (log$\beta$ = 1.14 ± 0.20 from $^{19}$F NMR titrations). Given that the major difference between 2 and 3 is the reduced number of fluorous ponytails, and thus the less fluorophilic cavity in 3, the trends in the binding constant can be readily rationalized.
Figure 4.3. Partial spectra of $^1$H NMR titration of 1 (top), 2 (middle) and 3 (bottom) with varying amounts of PFOA (0 – 20 eq., bottom to top) showing the OH of the guest in d$_6$-acetone at 300 K
Figure 4.4. Plot of $\Delta\delta_{\text{ppm}}$ changes upon addition of 0-20 equivalents of PFOA
Figure 4.5. Partial spectra of $^{19}$F NMR titration of 1 (top), 2 (middle) and 3 (bottom) with varying amounts of PFOA (0 – 20 eq., bottom to top) showing the CF$_2$ of the guest in d$_6$-acetone at 300 K
4.2.2.2 Characterization of the host-guest complexes

Given the stoichiometric ratios determined from the experiments described above, the 1:1 and 2:1 complexes were selected for further studies as these were the most stable species formed. Standard characterization methods were employed to explore the formation of these species, and any intermediates that could be formed. Thermal methods are useful in the characterization of host-guest complexes. DSC and TGA measurements were carried out on the hosts and the 1:1 and 2:1 compounds. In the thermal analysis, PFOA shows two endothermic transitions at 60 °C, ascribed to melting and 170 °C associated with vaporization (Figure 4.7). DSC thermograms show the loss of thermal transitions associated to the PFOA guest but no other phase transitions in the hosts 1, 2 and 3 (Appendix D5 – D7); only a small increase in the thermal stability of the ligand is observed.

Figure 4.6. Plot of $\Delta \delta_F$ changes upon addition of 0-20 equivalents of PFOA
Figure 4.7. DSC thermogram showing the thermal transitions associated to the PFOA guest

Thermogravimetry adds further weight to the proposition of an inclusion complex with the same small increase in thermal stability of the ligands is observed. A plot of the derivative weight % vs temperature shows evidence of the vaporization of the guest at 197 °C for host 1, along with decomposition of the ligand at 225 °C (Figure 4.8). The behavior of 2 and 3 are essentially the same and shown in Figure 4.9-10; this thermal behavior is similar to that observed where β-cyclodextrin is the host.¹²

Figure 4.8 TGA (Derivative weight) of 1 and its 1:1 and 2:1 host:guest complexes
The infrared spectra of the host-guest complexes from complex 1, 2 and 3 are shown in Figure 4.11-4.13. A number of points warrant discussion. Firstly the host is likely to have strong intramolecular C=O···H—N hydrogen bonding between the chains, as observed in the non-fluorous analogue (amide I band at 1654 cm$^{-1}$ and amide II band at 1545 cm$^{-1}$) and the shifts in 2, discussed below are comparable. The OH stretching frequency of the guest shifts to lower wavenumbers upon addition of one equivalent of PFOA and does not change.
in position after more equivalents, consistent with the 1:1 stoichiometry determined in solution. The C=O stretching frequencies of 2 (1667 cm\(^{-1}\); amide I band) and PFOA (1692 cm\(^{-1}\)) broaden but only shift slightly upon addition of 1 equivalent of PFOA (1643 cm\(^{-1}\)) and shift to slightly higher wavenumbers upon addition of 2 equivalents of PFOA (1659 cm\(^{-1}\)), whilst the amide II band (1547 cm\(^{-1}\)) is not affected. The infrared spectra of 1 and the corresponding 1:1 and 2:1 complexes are shown in Figure 4.11 and follow a different trend. The band at 1613 cm\(^{-1}\) does not change in position but now appears almost as a shoulder but the band at 1661 cm\(^{-1}\) shifts to 1666 in the 1:1 and 2:1 complexes and the band at 1691 cm\(^{-1}\) shifts to 1681 cm\(^{-1}\); the amide II bands are not affected. This is consistent with the host acting as a hydrogen bond acceptor. Interestingly the OH peak of the acid is not observable in the IR spectra of the 1:guest complexes, but the infrared spectra do not support a proton transfer mechanism, as the ionized carboxylate show a C=O stretch at ~1650 cm\(^{-1}\).

![Graph](image-url)

**Figure 4.11.** Partial Infrared spectra of PFOA, 1:1, 2:1 inclusion complexes and hosts 1.
Figure 4.12. Partial Infrared spectra of PFOA, 1:1, 2:1 inclusion complexes and hosts 2.

Figure 4.13. Partial Infrared spectra of PFOA, 1:1, 2:1 inclusion complexes and hosts 3.

Conductivity measurements show that solutions of 1 and PFOA are non-conductive. Therefore the thermal characterization methods and infrared spectroscopy support the stoichiometry developed above that both 2 and 3 are 1:1 host-guest complexes whilst 1 is more complex. Moreover the C=O⋯H-N hydrogen bonding network in hosts 2 and 3 do not
appear to be significantly disrupted upon addition of the guest, indicating either weak
binding or a different mechanism.

**Solution Phase NMR Spectroscopy.** Multinuclear NMR spectroscopy has been used to
explore the solution conformers of the hosts and the Spin-Lattice relaxation (T₁)
measurements to shed further light on the inclusion complexes.²¹ Diffusion Ordered
Spectroscopy (DOSY) NMR techniques is useful for measuring the translational diffusion
of molecules and thus gives indication of the sizes of the ligands and the host guest
complexes.²² DOSY have been increasingly utilized in supramolecular host-guest
complexes.²³ As shown in the NMR titration experiments (Figure 4.3-6), there is a shift of
the CF₂CH₂ fluorine nucleus on the host (δF ≈ -118 or -114 ppm) and the CF₂CO₂H fluorine
nucleus on the guest (δF ≈ -120 ppm) which is diagnostic of an inclusion complex; the other
peaks in the ¹⁹F NMR spectrum are not significantly shifted. The ¹H NMR spectra are also
informative as the OH peak of the guest shifts upon encapsulation.

¹⁹F DOSY spectra of the host, guest and the 1:1 and 2:1 complexes have been measured and
the diffusion coefficient, D_CT, recorded in Table 4.2 (selected spectra are shown in Figure
4.14-16); for the measurements D_CT for the CF₃ groups at δF = -81 ppm have been used,
although it is noted that D_CT for the CH₂CF₂ nuclei are slightly different as these are sensitive
to their chemical environment.

![Figure 4.14. ¹⁹F DOSY spectra of PFOA (purple), host 1 (red) the 1:1 complex (blue) 2:1 complex (pink) and in d₆-Acetone at 300 K.](image)
Figure 4.15. Overlaid $^{19}$F DOSY spectra of 2 (red) the 1:1 complex (blue) and PFOA (purple) in $d_6$-Acetone at 300 K.

Figure 4.16. Overlaid $^{19}$F DOSY spectra of 3 (red) the 1:1 complex (blue) and PFOA (purple) in $d_6$-Acetone at 300 K.
Table 4.2. Diffusion Coefficient, calculated hydrodynamic radius and T_1 for selected fluorous nuclei in host and 1:1 and 2:1 host:guest complexes in d_6-acetone at 300 K.

<table>
<thead>
<tr>
<th>Host</th>
<th>D_{CT}</th>
<th>a_H</th>
<th>Host CF_2</th>
<th>Host CF_3</th>
<th>Guest CF_2</th>
<th>Guest CF_3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ms^2)</td>
<td>(nm)</td>
<td>(s)</td>
<td>(s)</td>
<td>(s)</td>
<td>(s)</td>
</tr>
<tr>
<td>PFOA</td>
<td>2.51x10^{-9}</td>
<td>0.43</td>
<td>-</td>
<td>-</td>
<td>0.30 ± 0.007</td>
<td>2.37 ± 0.04</td>
</tr>
<tr>
<td>1</td>
<td>2.13x10^{-9}</td>
<td>5.1</td>
<td>1.56 ± 0.05</td>
<td>1.71 ± 0.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1:1PFOA</td>
<td>1.35x10^{-9}</td>
<td>0.79</td>
<td>0.71 ± 0.07</td>
<td>1.75 ± 0.06</td>
<td>0.87 ± 0.03</td>
<td>1.62 ± 0.05</td>
</tr>
<tr>
<td>1:2PFOA</td>
<td>4.85x10^{-10}</td>
<td>22.2</td>
<td>0.97 ± 0.3</td>
<td>1.60 ± 0.05</td>
<td>0.69 ± 0.12</td>
<td>1.6 ± 0.05</td>
</tr>
<tr>
<td>2</td>
<td>1.60x10^{-9}</td>
<td>0.67</td>
<td>0.47 ± 0.02</td>
<td>1.70 ± 0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2:1PFOA</td>
<td>1.29x10^{-9}</td>
<td>0.83</td>
<td>0.09 ± 0.05</td>
<td>1.54 ± 0.03</td>
<td>0.65 ± 0.04</td>
<td>1.45 ± 0.05</td>
</tr>
<tr>
<td>3</td>
<td>1.86x10^{-9}</td>
<td>0.58</td>
<td>0.65 ± 0.05</td>
<td>2.02 ± 0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3:1PFOA</td>
<td>2.10x10^{-9}</td>
<td>0.51</td>
<td>0.62 ± 0.05</td>
<td>1.91 ± 0.3</td>
<td>0.69 ± 0.04</td>
<td>1.86 ± 0.04</td>
</tr>
</tbody>
</table>

From the measured diffusion coefficient, the hydrodynamic radius can be calculated via the Stokes–Einstein equation:

\[ D_{CT} = \frac{K_B T}{n \pi \eta a_H} \]

Here n is either 6 or 4 assuming a spherical or oblate shaped molecule. \( K_B \) is the Boltzmann constant, \( T \) is the temperature, \( \eta \) is the viscosity of the liquid and \( a_H \) is the (hydrodynamic) radius of the molecule. In the examples shown the molecules are likely to be more prolate than spherical, so the modified Stokes-Einstein equation where \( n = 4 \) have been used. Interestingly the hydrodynamic radius of 2 and 3 are similar, but the 1D \(^1\)H NMR spectra confirm the asymmetric nature of host 3, and variable temperature \(^1\)H and \(^19\)F NMR spectroscopy show no sign of conformational isomerization (i.e cone – partial cone), as expected. Furthermore the 2:1 complexes of 2 and 3 were essentially the same as the 1:1 complexes. Host 2 is the least conformationally labile and the small hydrodynamic radius suggests that intramolecular hydrogen bonding holds this host in a relatively rigid C_3
symmetry. From the $^{19}$F DOSY spectra of the host-guest complexes, there is an increase in the size of 2 with the guest whilst small changes are observed in 3. However, the small changes in D$_{CT}$ and the corresponding hydrodynamic radius of hosts 2 and 3 support the formation of a compact inclusion complex. In contrast, host 1 has a large hydrodynamic radius, suggesting that it does not have a C$_3$ rigid structure in solution. Upon addition of one equivalent of guest, the hydrodynamic radius significantly shrinks indicating a conformational change to encapsulate the guest. A further addition of a guest forces a much larger structure. T$_1$ measurements of the individual $^{19}$F nuclei were also measured as there are unique $^{19}$F signals to the host ($\delta_F \approx -118$ ppm) and guest ($\delta_F \approx -120$ ppm); the data is reported in Table 4.2. The fluorine nuclei of the host and guest decreases throughout the series, indicative of reduced motion, apart from the T$_1$ of the host CF$_2$ in 2. Therefore both 1D & DOSY NMR spectroscopy and T$_1$ measurements indicates the formation of a host-guest complex that is stable in solution.

**Solid State NMR Spectroscopy.** To further probe the solid-state structures of the inclusion complexes $^{13}$C and $^{19}$F solid-state MAS NMR spectroscopy and CP-MAS spectroscopy have been utilized. The $^{13}$C and $^{19}$F MAS NMR spectra for the guest are relatively sharp and consistent with previous results (Appendix D14 – D15). The hosts show spectra that are relatively broad but can be assigned on the basis of their solution NMR spectra (Appendix B25 – B26). Variable spin rate $^{19}$F MAS NMR spectroscopy are essentially identical at all spin rates, indicating that there is only one phase present (Appendix D32 – D34). In the MAS $^{13}$C{$^1$H} NMR spectra of the hosts the amide carbon can be clearly observed at 169 ppm in both 2 and 3, whilst the carbons of the fluorous chain resonate at ~127 ppm. Finally the 'butyl peaks are observed at 30 ppm, but there is a shoulder at 37 ppm due to the CH$_2$O and CH$_2$CH$_2$CF$_2$ carbons. The $^{19}$F{$^{13}$C} MAS NMR spectra are well resolved but rather broad and suggest slow dynamics in the fluorous chain; deconvolution of the CF$_3$ peak using Gaussian functions (Figure 8) shows three peaks at $\delta_F = -81.26$ (Peak 1, relative area = 0.40), -81.64 (Peak 2, relative area = 1) and -81.92 (Peak 3, relative area = 0.62). The 1:1 host guest complexes of 2 were examined and whilst the $^{13}$C{$^1$H} spectrum is generally very similar to the host, the shoulder at 37 ppm is more pronounced, or alternatively the 'Bu resonance has sharpened in the host:guest complex, whilst the guest C=O resonance is likely to overlap with the host C=O amide resonance. In the $^{19}$F{$^{13}$C} MAS NMR spectrum of this
1:1 complex the only discernable difference is in the linewidths and position of the CF$_3$ group at ~ -81 ppm; these could be deconvoluted (Figure 4.17) to give two components at $\delta_F = -81.43$ (Peak 1, relative area = 0.52) and -81.64 (Peak 2, relative area = 1). Whilst it is not possible to fully assign these peaks, it is clear that there are multiple CF$_3$ environments in the host that are reduced in the host:guest complex, possibly due to the reorganization of the fluorous cavity to accommodate the guest. The linewidths are narrower in the complex than the free host indicating an increase in dynamic behavior, at least of this group. For the 1:1 complex with host 3 the same spectral features are observed, but the spectra are broader and in keeping with the less conformationally rigid structure of the host (Appendix D25). However in the $^{19}$F{$^{13}$C} MAS NMR spectrum a more pronounced shift occurs and deconvolution of the peak (Figure 4.17) reveals only two components in both the host (Peak 1: $\delta_F = -81.75$ relative area = 0.96; Peak 2: $\delta_F = -82.06$ relative area = 1) and host:guest complex (Peak 1: $\delta_F = -83.23$ relative area = 0.73; Peak 2: $\delta_F = -82.75$, relative area = 1). The linewidths increase in this complex compared to the host, indicating that there is a different dynamic mechanism to the complex formed from host 2.
Further evidence of support for this hypothesis comes from inspection of the $^{19}\text{F} T_1\rho$ relaxation times of the CF$_3$ ($\delta_F \sim -82$ ppm), CF$_3$CF$_2$ ($\delta_F \sim -126$ ppm), CH$_2$CF$_2$ ($\delta_F \sim -113$ ppm) and the remaining CF$_2$ groups ($\delta_F \sim -122$ ppm), which are listed in Table 4.3. $T_1\rho$ describes the spin-lattice relaxation in the rotation frame at the presence of an external RF pulse in the transverse plane. The relaxation time of $T_1\rho$ is longer than the relaxation time of $T_2$ which were measured to be very short in the complexes. The CF$_3$ $T_1\rho$ reduces slightly
in the host:guest complexes of 2 and 1 but there is a very large decrease in the CF\textsubscript{2}CH\textsubscript{2} group. This could possibly be due to the more constrained arrangement of the latter in the host:guest complex whereas the CF\textsubscript{3} group is relatively free to rotate. This has been confirmed by the variable temperature studies on 2:1 PFOA, which show that only the CF\textsubscript{3} group is influenced by increasing the temperature (Figure 4.18).

**Table 4.3.** \textsuperscript{19}F \textit{T}_1\textsubscript{p} relaxation times (ms) of the various fluorous groups in the host and host:guest complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>CF\textsubscript{3}</th>
<th>CF\textsubscript{3}CF\textsubscript{2}</th>
<th>CF\textsubscript{2}</th>
<th>CF\textsubscript{2}CH\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>287 ± 1.3</td>
<td>260 ± 2.5</td>
<td>223 ± 1.5</td>
<td>219 ± 7.9</td>
</tr>
<tr>
<td>1</td>
<td>8 ± 0.39</td>
<td>5.1 ± 1.4</td>
<td>5 ± 1.4</td>
<td>584 ± 1.4</td>
</tr>
<tr>
<td>1:2PFOA</td>
<td>29.6 ± 3</td>
<td>18 ± 0.3</td>
<td>174 ± 0.2</td>
<td>20 ± 2.2</td>
</tr>
<tr>
<td>2</td>
<td>178 ± 0.6</td>
<td>10.1 ± 0.02</td>
<td>11.1 ± 0.02</td>
<td>403 ± 2.6</td>
</tr>
<tr>
<td>2:PFOA</td>
<td>155 ± 82</td>
<td>22 ± 0.18</td>
<td>8.1 ± 0.06</td>
<td>5.1 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>36 ± 7.8</td>
<td>24 ± 0.83</td>
<td>24 ± 0.5</td>
<td>23 ± 2.8</td>
</tr>
<tr>
<td>3:PFOA</td>
<td>42 ± 0.9</td>
<td>26 ± 0.05</td>
<td>14.9 ± 0.05</td>
<td>3.5 ± 0.009</td>
</tr>
</tbody>
</table>
Application of Non-covalent Interactions in the Extraction of PFOA

Figure 4.18. Variable temperature studies on 2:1 PFOA. Yellow (40 °C), blue (20 °C), red (0 °C) and purple (-20 °C).

$^{19}F \rightarrow ^{13}C$ CP/MAS NMR Spectroscopy. Polarization transfer techniques are useful for determining inclusion complexes as dipolar interactions between the host and guest can be probed directly. It is a high-sensitivity technique involving the polarization transfer from abundant nuclei to a neighbouring nucleus ($^{19}F \rightarrow ^{13}C$ in this case) by eliminating broadening caused by dipolar coupling and shift anisotropy. It produces highly resolved spectra and can be used to elicit spatially close groups in the molecular structure. In order to probe the orientation of the guest, the CP MAS spectra of the host, guests and the corresponding complexes have been measured at varied Hartmann-Hahn contact times (1, 2, 4, 6, 8, 10) at 10 KHz spin rate. The CP/MAS NMR spectra of PFOA shows magnetization transfer to the C=O resonance at 162 ppm as well as the CF carbon atoms (Appendix D35) possibly due to interdigitation discussed in Chapter 3. Host 2 shows the presence of a resonance at 35 ppm after a contact time of 2 ms (Figure 4.19) and increases in intensity with increasing contact time. This indicates that there is magnetization transfer to the CH$_2$O or CH$_2$CH$_2$CF$_2$ groups. Using the computationally derived structure (vide infra) this is likely to be the latter due to the strong hydrogen bonding between the amides of two chains, and consistent with the infrared data. The same resonance is observed in the host:guest complex but longer contact times are required to observe the resonance (10 ms). This indicates that the chains are now further apart and the lack of resonance of the guest acid which suggests that this group is not close to the hosts CF$_2$ groups i.e. is close to the CH$_2$ portion of the host.
Figure 4.19. $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectrum of 2 at 10 kHz spin rate and 291 K (Top); 2:PFOA $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectrum with a contact time = 10 ms (middle); 2 $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectrum with a contact time = 2 ms (bottom).

For host 1, there is no magnetization transfer observed indicating that the solid-state structure is not $C_3$ symmetric and the fluorous and non-fluorous domains are not close enough for magnetization transfer. Upon addition of the host (2 equivalents), a resonance at 163 ppm is observed even at 1 ms contact time (Figure 4.20). For host 3 there is no observable magnetization transfer (Figure 4.21) and no definitive magnetization transfer in the 1:1 complex, consistent with the less conformationally rigid structure compared to 2. Interestingly there is magnetization transfer to the peak at ~30 ppm with a contact time of 8 ms in the 2:1 complex.
Figure 4.20. $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectrum of 1 (left) 1:2PFOA (right) with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).

Figure 4.21. $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP/MAS NMR spectrum of 3 (left) 3:2PFOA (right) with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).
4.2.2.3 Computational Studies

Despite numerous efforts crystals suitable for X-ray diffraction of the hosts or the host:guest complexes could not be grown. Therefore host 2 and the corresponding 1:1 host:guest complex were examined by computational means in order to corroborate experimental observations. The computational studies were carried out by Dr. Jamie Platts, Cardiff University. An energy minimization and stochastic conformational search, resulting in a cone-shaped structure (Figure 4.22 left) containing two short C=O···H—N hydrogen bonds (dO···N = 2.627 and 2.745 Å) comparable to that seen in the structure of the calixarene ligand featuring "hexyl substituents on the amides (dO···N = 2.816(1) and 2.869(4) Å). The structure (Figure 4.22 right) retains the short C=O···H—N hydrogen bonds (O···H = 1.887 and 2.020 Å) within the host, as well as numerous contacts between host and guest. The most obvious of these is a hydrogen bond from O—H of PFOA to an ether oxygen of 2 (O···H = 2.310 Å), but in addition there are numerous close C—H···O contacts in the range 2.4 to 2.9 Å and F···F contacts in the range 2.8 to 3.3 Å. Atoms-in-molecules (AIM) has been utilized and there are a plethora of C···F—C and C···F—H—C interactions (as summarized in Table 4.4) typical for these type of interactions. The hydrogen bonding to the ether oxygen is also reproduced. The binding energy of guest to host is calculated to be -65.16 kJ mol⁻¹ (-15.57 kcal/mol) at the DFT level after counterpoise correction indicating substantial stabilization of the host-guest complex. Clearly, a significant proportion of this stabilization stems from specific interactions noted above, but additional stabilization may stem from overall dipole-dipole interactions.

Figure 4.22. Computed structure of host 2 (left) and the host:guest complex (right).
DFT-predicted dipole moments for 2 and PFOA are 10.89 and 2.76 D, respectively, while that of the host-guest complex is 12.42 D indicating parallel alignment of dipoles in the complex, and consistent with the design principle of dipole engineering.

Repeating this process with octanoic acid (OA) as the guest results in a broadly similar structure, with two C=O···H-N hydrogen bonds (1.927 and 2.085 Å) within the receptor and one O—H···O (2.490 Å) H-bond from OA to ether oxygen in 2. In addition, several C—H···O contacts (2.4 to 2.7 Å) are present, as well as “close” C—H···F contacts (2.4 to 2.9 Å). AIM analysis again shows an abundance of non-covalent interactions; the interactions are dominated by C—F···H—C but the hydrogen bonding interaction is the same magnitude as for PFOA. In keeping with this, the calculated binding energy of octanoic acid is only very slightly less than that for PFOA at -63.73 kJ mol⁻¹ (-15.23 kcal/mol).

<table>
<thead>
<tr>
<th>PFOA</th>
<th>ρ_bcp</th>
<th>Octanoic acid</th>
<th>ρ_bcp</th>
</tr>
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<td>F···F</td>
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</tr>
<tr>
<td>(27)</td>
<td>0.006x8, 0.005x5, 0.004x3,</td>
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<td></td>
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<tr>
<td></td>
<td>0.003x2, 0.002, 0.001x3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F···O</td>
<td>0.008x2, 0.002x2</td>
<td></td>
<td>F···O (4)</td>
</tr>
<tr>
<td>(4)</td>
<td></td>
<td></td>
<td>0.008x2, 0.006x2</td>
</tr>
<tr>
<td>H···F</td>
<td>0.008, 0.005, 0.004, 0.003</td>
<td>F···H (26)</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td></td>
<td>0.010, 0.009x2, 0.008, 0.007x5,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.006x3, 0.005, 0.004x2,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.003x3, 0.002x5, 0.001</td>
<td></td>
</tr>
<tr>
<td>H···O</td>
<td>0.013, 0.011, 0.008, 0.006</td>
<td>H···O (5)</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td>0.013, 0.010x3, 0.006</td>
<td></td>
</tr>
<tr>
<td>O···H</td>
<td>0.011</td>
<td>O···H (1)</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td>0.007</td>
<td></td>
</tr>
</tbody>
</table>
4.2.2.4 Reactions with other guests.

Given that the calculations suggest that the host:guest binding is through the ether oxygen and C—H···O interactions, the binding energies of octanoic acid with 2 and a fluorour guest with no capacity for hydrogen bonding have been examined to corroborate these theories. $^1$H and $^{19}$F NMR titrations were carried out in order to determine the binding constants (Figure 4.23). Octanoic acid showed no changes in the $^1$H or $^{19}$F NMR spectrum, indicating that a stable inclusion complex is not formed. Given the theory suggests that once in the cavity it should form a stable hydrogen bonded system, this inconsistency is ascribed to the fact that 2 has an intentionally designed fluorophilic cavity so the octanoic acid does not react with this cavity in solution. Using {CF$_3$(CF$_2$)$_5$CH$_2$CH$_2$}$_2$ the extent of the fluorophilic cavity without the primary hydrogen bonding were ascertained. Again no shifts in the $^1$H and $^{19}$F NMR spectra were observed upon addition of up to 20 equivalents. These two experiments show the design features worked as anticipated and suggests selectivity for a fluorinated hydrogen bond donor/acceptor.

![Figure 4.23](image)

Figure 4.23. $^1$H (left) and $^{19}$F (right) NMR titration of 2 against varying amounts of octanoic acid (0 – 10 eq.) in d$_6$-acetone at 300 K.
4.3 CONCLUSIONS

In summary, a series of hosts have been designed for the removal of a major global pollutant utilizing hydrogen bonding and a fluorophilic cavity, and excellent extraction ability is observed. The drawback is the leaching of the host out of the guest over time. The stoichiometry of the host-guest complexes have been determined and fully characterized by extensive solution and solid-state NMR spectroscopic techniques. For the calix[4]arene hosts the stoichiometry is 1:1 and the binding constant is lower in the partial cone compared to the full cone, due to the reduction in the fluorophilic cavity. The conformationally labile tren based ligand is not as effective at extracting PFOA and the stoichiometry is ~ 6 indicating that a stable host:guest species is not formed; this is corroborated by the solution DOSY experiments where large hydrodynamic radii are measured for the 2:1 complex. Solid state NMR spectroscopy, particularly cross-polarization techniques, has also been used and substantiates the solution data. A computational study lends support to the experimental observations and allows us to identify the major hydrogen bonding interactions in the full cone. These have been experimentally probed by the investigation of other guests and the fluorophilic cavity and the hydrogen bond ability of the hosts appears to be important for the formation of the inclusion complex with PFOA. The crystal structure of perfluorooctanoic acid have also, for the first time, been reported.
4.4 EXPERIMENTAL

DSC spectra were recorded on a Perkin Elmer Diamond DSC and TGA on a Perkin Elmer Pyris 1 TGA. All spectrophotometric analysis were measured on a Lambda 1050 UV-Vis NIR, using fused silica cells with a path length of 1 cm. Synthesis of compounds 1, 2 and 3 are shown in Chapter 2.

4.4.1 General Procedure for the Extraction of PFOA

The ligands (1 molar equivalent to PFOA) were dissolved in 1,3-bis(trifluoromethyl)benzene (5 cm³). Solutions of PFOA (1.8 mg, 0.004 mmol) in distilled H₂O (5 cm³) were carefully added to the ligand solutions and stirred. The concentration of PFOA in the aqueous layer was periodically monitored spectrophotometrically following the peak at 206 nm and referenced to a standard curve. Control experiments were carried out without the ligands.

4.4.2 General procedure for synthesis of the host:guest complexes

The hosts (25.0 mg, 0.02 mmol for 1; 25.0 mg, 11 mmol for 2 and 3) were dissolved in isopropanol (5 cm³) and added to a 1 and 2 molar equivalents of PFOA (3.3 mg and 6.7 mg for the 1; 4.8 mg and 9.8 mg for the 2 and 3) dissolved in H₂O (5 cm³). The solution were stirred at 80 °C for 1 hr and then at 50 °C to completely evaporate all solvents.

4.4.3 Computational Studies

The structure of host 2 was manually built using MOE, and energy minimization followed by stochastic conformational search using the MMFF94 forcefield carried out. An extended conformations of PFOA was placed manually within the cone-shaped cavity of host 2 with the acid group in proximity to host amide groups, and the resulting complex energy
minimized with MMFF94. This structure was then subjected to a short (1 ns) NVT molecular dynamics simulation to remove any artefacts of manual placement, and the final snapshot of this trajectory re-minimized. The resulting structure was optimized with molecular orbital methods, first with semi-empirical PM7 and then density functional B97-D/def2-SVP methods, both of which include empirical correction for dispersion effects, within a continuum model of aqueous solvation.

4.5 NOTES AND REFERENCES

19. The calixarene amide with a nhexyl group has been structurally characterized, see:
21. T1 measurements for PFOA have been reported and our data are similar considering the differing concentrations. Buchanan, G. W.; Munteanu, E.; Dawson, B. A.; Hodgson D. Mag. Reson. Chem. 2005, 43, 528-534.
Chapter 5

Solution Phase Metal Extractions
5.1 OVERVIEW

Energy critical metals (ECM) required for sustainable technology are known to accumulate in electronics (eventually in e-wastes).\textsuperscript{1-4} Reclaiming of the metals has been suggested as a way to reduce metal dissipation in e-waste.\textsuperscript{5} Current commercial reclamation of metals is carried out via smelting, cyanide/sulfide leaching and other hydrometallurgy processes. However, in applications where rare earths are used, the recycling rate is less than 1% and there are no commercial methods for doing this, as the rare earths typically slag in smelter plants which typically impedes the recycling of WEEE smelting plants.\textsuperscript{6, 7} Solvent extraction involving Dialkyl- and trialky-phosphines,\textsuperscript{8, 9} perfluorophosphine oxides,\textsuperscript{10} dialkyl sulfides\textsuperscript{11} dithiocarbamates\textsuperscript{12}, β-diketones,\textsuperscript{13} hydroxyoximes, carboxylic acids\textsuperscript{14} and so on have been seen in some remarkable Precious metals and Ln\textsuperscript{3+} extractions (Chapter 1). Some organophosphorus compounds including, Cyanex 301 and 302, D2EHTPA, and Cyanex 272 have been investigated as ligands in the extraction of heavy toxic metals in scCO\textsubscript{2}.\textsuperscript{15} However addition of fluoroalkyl group to extractants makes for easy extractant recovery, offers high partition coefficient of the extracted species in metal extractions and increases the solubility of extractants in scCO\textsubscript{2}. Moreover, fluorinated β-diketones and tributyl phosphate have been shown to synergistically extract Ln\textsuperscript{3+} quantitatively in supercritical fluids.\textsuperscript{16} Fluorous phosphines ligands have also featured in metal extraction with remarkable results.\textsuperscript{17} Traditional solvent extraction involving dialkyl-, trialky-phosphines\textsuperscript{8, 9} and calix-aryl phosphine oxide\textsuperscript{18} ligands have shown remarkable Precious metals and Ln\textsuperscript{3+} extractions and was therefore chosen as one of the ligand for this studies.

However, amide derivatives including thioglycoamides,\textsuperscript{19} hydroxy acetamide,\textsuperscript{20} alkylcyanamides\textsuperscript{21}, alkyl- and arylamides\textsuperscript{22, 23} and picolinamide \textsuperscript{24} have been shown to possess notable advantages over a lot of extractants including selectivity and benign decomposition products.\textsuperscript{25, 26} In an attempt to reclaim some of these critical metals, a series of fluorinated extractants \textit{viz}: Tren (1) cone-(2) and partial-cone calix[4]arene (3) acetamide and calixaryl phosphate oxide (5) ligands of different sizes and degree of flexibility imposed by their molecular scaffolds have been synthesised. These have been employed in the extraction of precious metals and lanthanides. However, leaching of the extractant and/or the extracted species, low hydrophobicity, selectivity and slow extraction is a major drawback to solvent extraction.\textsuperscript{11} The use of fluorinated extractant for solvent extraction offers the possibility of high distribution coefficients due to the hydrophobicity of
fluorinated molecules. This hydrophobicity can be enhanced by modulating the length and/or amount of the fluorinated alkyl chain.

To this end, ligand of varying degree of rigidity, size of ionophoric cavity, donor groups and amount of fluorous arms have been synthesised as described in Chapter 2. 1, 2 and 3 will then be employed in a preliminary extraction studies to determine the optimum extraction conditions for metal extractions. Once optimised, effect of factors such as concentration and pH on metal extraction will be studied by simply varying the factor while keeping everything else constant. Information gained from these studies will shed light on the effect of the ligand structure on metal extraction efficiency. Although the cone Calixarenes have been extensively used the extraction of alkali and earth metals, partial cone Calixarenes have featured in extraction of larger metal ions including Hg and Ag. Using both conformers in these studies the effect of ligand structure can be better understood.

In conjunction with other spectroscopic techniques, the extracted species will be characterised by small angle X-ray scattering (SAXS) in order to work out the speciation, assembly state, extended conformation and molecular sizes in solution. The rate of reaction will be monitored using UV-Vis absorption spectroscopy. The binding constant will determine using UV titrations and the co-ordination modes will be shown by IR spectroscopy.
5.2 RESULTS AND DISCUSSION

5.2.1 Metal extraction

The extraction efficiency of fluorous ligands 1, 2 and 3 have been examined for the influence of rigidity and size of cavitand on selectivity and efficiency in metal extraction by using ligands that possess a defined amount of flexibility. Metal extractions were carried out by dissolving the chosen ligands in DCM and a 5 cm³ aliquot was stirred with a varied amount of metal ions in water (5 cm³) for a specified time. All data presented are averages of at least three runs (metal extraction using the same conditions) using freshly prepared solution in each case. The optimum extraction time was determined by varying the extraction time whilst keeping all other variables constant. Similarly, the effect of concentration and pH on metal extractions were investigated by keeping all other factors constant. Pt complexes with 2 and 3 were found to be insoluble in both the organic and the aqueous phase thus preventing further studies with Pt. With all amide ligands, the soft metals were better extracted than the rare earths. Soft metal extractions efficiency followed the trend, Au³⁺>Pd²⁺>Ag⁺>Pt²⁺ with Au³⁺ extracted at over 98% extraction (Figure 5.1-5.3). The rare earths extraction efficiency followed the trend, Er³⁺ > Nd³⁺ > Eu³⁺ but the extraction efficiency of the amide ligands (≤ 56%) were considerably lower than that obtained for corresponding calixaryl phosphine oxide ligands (80 – 90%), which is consistent with the literature, and clearly due phosphine oxides being harder donors. As expected, fluorous calix[4]arene acetamide 2 and 3 exhibited the higher percentage extraction of precious metals compared to the fluorous tren, 1 due to pre-organisation effect brought on by the rigid calixarenes scaffolds. Amongst the calixarenes, the full cone calix[4]arene, 2 was expected to be better at extracting the metal ions but 3 does however show higher extraction efficiency than 2. These results have been rationalised as due to the difference in the sizes of the ionophoric cavity of the full cone and the partial cone. The partial cone which has been determined to be larger than the cone calix[4]arene is perhaps better at accommodating the soft cations as seen with Au³⁺ which is consistent with some previous studies where Ag⁺, Hg⁺, and alkali earth metals were better extracted with partial cone ligands bearing propyl ether, ether crown and sulfonyl carboxamides donor groups.
Figure 5.1 Percentage extraction of metals with various molar equivalent of 1 ligands at pH 2.

Figure 5.2 Percentage extraction of metals with various molar equivalent of 2 ligands at pH 2

Figure 5.3 Percentage extraction of metals with various molar equivalent of 3 ligands at pH 2
5.2.2 The effect of ligand concentration

Figure 5.1 shows the effect of ligand concentration on the percentage extraction using 0.5, 0.75, 1, 1.25, 1.5, 1.75, and 2 molar equivalents (eq) of ligands. For all ligands studied, the percentage extraction increased when the molar equivalent of ligand was increased. The extraction time also decreased with increase in ligand concentration (Table 5.1). However, Pt was only extracted with 0.5 eq of 1 due to is solubility, extraction of Pt(II) with higher molar equivalent of 1, and all molar equivalent of 2 and 3 resulted in insoluble precipitates. Ag extraction with 1 also resulted in precipitation with molar equivalents higher than 0.5. For all systems, ligand concentration had more impact on extraction time than efficiency. All molar equivalents of each ligand ultimately achieved similar percentage extractions when the extractions were allowed to run until maximum extraction in preliminary studies (Table 5.1). Precious metals %E increased by 20-40% while Ln$^{3+}$ %E increase moderately (5-30%) with increase in ligand concentration up to 2 equivalents.

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5.2.3 Effect of pH on feed solution on $D$

The effect of pH on the extractions was examined at pH 2, 6 and 10 shown in Table 5.2 and the log of $D$ is presented in Figure 5.4. Extraction efficiency of the ligands at low pH mimics such process in industrial scale as it can provide insight into ligand performance in similar conditions. The influence of pH on the Distribution ratio, $D$ of the metal ions into the
aqueous and organic phases has been studied by adjusting the pH with HCl or NaOH solution. The solution were kept below the metal precipitation pH so the only clear solutions with the metals completely dissolved in solution were used for the extraction. For all systems, no adduct formation between the complexes and the mineral acid was observed as the extractability did not increase with increasing acidity. Increase in the acidity resulted instead in a decrease of the $D$ values and increase in pH resulted in increased extractability due to the presence of more ionised ligands at higher pH. At pH 2, Au and Pd were extracted quantitatively while the other metals were extracted to a lesser extent. However, at pH 6 there was a significantly increase in $D$ of all metals while at pH 10, all metals (except Nd and Er) were quantitatively extracted with all ligands employed. The effect of ligand structure remained all through the different pH studied. At all pH, the extraction efficiency retains the order $3>2>1$. The $D$ of Au and Pd were the highest with all ligands at 0.5 eq and at all pH. This high $D$ in Pd(II) exactions has been explained as better size matching of Pd(II) with the amide derivatives of calix[4]arenes.$^{32}$ Pd(II) (ionic radius = 0.86 Å) and Au(III) (ionic radius = 0.85 Å) are relatively similar to ionic size and thus have the highest $D$ as they both better fit the ligand cavity. The trivalent lanthanides show much lower $D$ compared to the precious metals which might be due to the preceding argument and also due to mismatch of hard metals which prefer ionic ligands. Nd(III) had the lowest $D$ (0.2 – 1.2) along with the other Ln$^{3+}$ at all pH considered. These $D$ values are considerably less than values obtained for some previous trivalent lanthanide extraction with bidentate amides such as N-methyl-N-phenyl-2-(1H-benzimidazol-2-yl)pyridine-6-carboxamide (MePhBIZA)$^{33-36}$ (1-6 at similar acid concentration) and further reiterates the suitability of these ligands for precious metal.
Figure 5.4. Dependence of Log $D$ on the pH using 1 molar equivalent of the ligand at 23 °C. All results are averages of three experiments.

Table 5.2 Dependence of $D$ on the pH using 1 molar equivalent of the ligand at optimum conditions. (Errors = ± 3%)

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### Table 5.3 Effect of mixing time on percentage extraction of studied metals. (Errors = ± 3%)

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Figure 5.5 Dependence of %E of Precious metals on extraction time using 1 molar equivalent of 1
5 | Solution Phase Metal Extraction

Figure 5.6 Dependence of %E of Precious metals on extraction time using 1 molar equivalent of 2

Figure 5.7 Dependence of %E of Precious metals on extraction time using 1 molar equivalent of 3

5.2.4 Stoichiometry of the extracted complexes

The nature of the extractable species can be explored by plotting a graph of the log of ligand concentration against the log of distribution coefficient $D$. The Log [L] vs. Log $D$ produces a straight line; a slope of which indicates the stoichiometry of the extractable species. In the metal-ligand complexes, a slope of about 1 was obtained which suggests a 1:1
complexation except with Au-1 (3.6) and Au-3 (9.9) complexes (Figure 5.8-5.13). Such deviation from an ideal slope of 1 has been previously observed with carboxylate and phosphine oxide derivatives of the calixarene and ascribed to possibility of the influence of factors such as co-extraction of the organic acid and activity coefficient effects.\textsuperscript{18, 37, 38} However, such factors were absent in this study and it is more reasonable to assume that more than one calixarene ligand could be complexing the metal.\textsuperscript{18}

**Figure 5.8** Graph of log of ligand concentration against log $D$ of Au$^{3+}$

**Figure 5.9** Graph of log of ligand concentration against log $D$ of Pd$^{2+}$
Figure 5.10 Graph of log of ligand concentration against log $D$ of Nd$^{3+}$

Figure 5.11 Graph of log of ligand concentration against log $D$ of Eu$^{3+}$
To further investigate the nature of the extracted species, the Au complexes were dissolved in MeOH and analysed by MALDI-TOF-MS. A molecular ion peak for $\text{C}_{84}\text{H}_{78}\text{AuCl}_3\text{F}_{52}\text{Na}_4\text{NaO}_8$ = 2583.3618 corresponding to the singly charged species
Na[AuCl₃(3 – 2H)]²⁻ was observed at m/z 2583.3. This result is consistent with the UV/VIS titrations (Figure. 5) indicating a 1:1 ligand to metal stoichiometry.

![Figure 5.14. MALDI-TOF mass spectrometry (isotope mode) of Au³⁺ 1:1 complex with 2 as the only specie formed in MeOH at 23 °C.](image)

5.2.5 Nature of the extracted complexes

5.2.5.1 Spectroscopic analysis

The IR of the Au and Pd complexes showed changes in the frequency of the amide I $\nu$(C=O stretching) and II (C-N-H bending) bands which suggests co-ordination of the ligand to the metals. The amide I and II bands of the complexes of 1 were found to shift to lower and higher frequencies respectively suggesting co-ordination through the NH of the amide which is consistent with some previous studies.³⁹-⁴¹ The $\nu$(C-N) of the apical nitrogen at 1078 cm⁻¹ also shifted by about 5-43 cm⁻¹ suggesting participation in metal co-ordination.⁴² There was no significant shift in the phenoxy oxygen (C-O bending) of 2 and 3 (Figure 5.13). The amide I of the 2 and 3 were shifted to lower frequency while the amide II bands of the complexes of 2 and 3 are shifted to higher frequency (Table 5.4) which is attributable to a decrease in C=O character and increase in C-N double bond suggesting co-ordination
through the amide oxygen. Also, amide donor groups are not expected to substitute the inner-sphere Cl atoms of [AuCl₄]⁻ to form direct co-ordination to Au(III). Therefore outer-sphere interactions involving hydrogen bonding which has been suggested for [AuCl₄]⁻ in weakly acidic solutions is expected as the speciation of [AuCl₄]⁻ in weakly acidic solution is [AuCl₃(OH)]⁻ or [AuCl₂(OH)₂]⁻. The [AuCl₃(OH)]⁻ species are more likely based on the mass spectrometric analysis. Nonetheless, in 3 M HCl solution, Pd(II) exists predominantly as [PdCl₄]²⁻. It has been shown that two Cl⁻ atoms are replaced by two ligating functions of the extractants in similar systems. Two amide donor groups are therefore expected to interact with Pd(II) in a 1:1 complex.

**Figure 5.15.** IR spectra of the 2, the Au and Pd complexes with 2

**Figure 5.16.** IR spectra of the 2, the Nd, Eu and Er complexes with 2
The IR of the ligand before and after complexation with the lanthanides shows small changes in the $\tilde{\nu}$(C-O) of the phenoxy oxygen and a significant shift of the amide I ($\nu$ C=O) and II ($\delta$ C-N-H) vibrations of all ligands. The amide I band in 2 and 3 are shifted to a higher frequency by about 39 and 46 cm$^{-1}$ while the amide II bands shifted to lower frequency by about 13-20 cm$^{-1}$ on complexation which suggests possible participation of amide N-H in the co-ordination (Figure 5.16). However, Ln$^{3+}$ are generally known to occupy the lower rim cavity of similar acetates calixarene derivatives and bond through phenoxy and the carbonyl oxygen atoms in amide systems.$^{20, 48}$ While the participation of N-H in the complexation is evidenced in the IR, this forms a 4-membered ring possibly in equilibrium with phenoxy C-O-Ln complex (Figure 5.18). The complex formed is therefore rationalised as a co-ordination of the Ln$^{3+}$ to eight donor oxygen atoms of phenoxy and the carbonyl oxygen atoms, completing the nine co-ordination sphere of the Ln$^{3+},^{42}$ forming a stable five membered ring. Other than the donor groups, the high stability of the precious metals with
the ligands maybe due to other factors such as size and structure of the ligands, which has also been shown in other studies, allows soft metals to reside deep inside the calixarene cavity forming an endo-complex and stabilised by non-covalent interactions whereas the \( \text{Ln}^{3+} \) complexes with the phenoxy oxygen atoms and carbonyl of the amide.\(^{14}\)

![Proposed structure of the Ln\(^{3+}\) complexes with 2](image)

**Figure 5.18.** Proposed structure of the Ln\(^{3+}\) complexes with 2

**Table 5.4.** Spectroscopic data and stability constants of the ligands and the extracted metal ligand complexes.

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<th>v(C=O)</th>
<th>δ(C-N-H)</th>
<th>v(C-N)/(C-O-C)</th>
<th>Log β</th>
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### Solution Phase Metal Extraction

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The $^1$H NMR spectra of 2 and the 2-Au complex are shown in Figure 5.19. The spectra are essentially the same except for the broadening of the peaks and a new peak at $\delta = 3.5$ ppm assigned to the $\text{C}H_2\text{NH}$ in the spectra of the complex which means that the metal ion is close to this group. It is also worth mentioning that there is no peak shift in the spectra of the complex.

![Figure 5.19. $^1$H NMR (400 MHz, CDCl$_3$) spectra of 2 (bottom) and the gold complex with 2(top)](image-url)
To further verify that the encapsulation of Au in the calixarene cavity, diffusion ordered spectroscopy (DOSY) was employed. This is useful in determining the diffusion coefficient of molecules in solution and from this, the sizes (hydrodynamic radius, $a_H$) can be calculated. The DOSY spectra of 2 and 2+Au complex is shown in Figure 5.20. The complex is found to possess smaller diffusion coefficient and thus a larger $a_H$ (0.99 nm) than the ligand (0.67 nm). This clearly suggest encapsulation of a metal ion in the host cavity.

5.2.5.2 SAXS analysis

Although crystals of the host guest complexes could not be grown despite repeated attempts, X-ray scattering allows the determination of molecular structures in solution based on a model. It provides information on the macromolecular folding, unfolding, aggregation, extended conformations, flexible linked domains, shape, conformation and assembly state. 49
Figure 5.21. SAXS analysis of 1 and its Au$^{3+}$ complex.

Figure 5.22. SAXS analysis of 2 and its Au$^{3+}$ complex.
Results of the analysis of the concentrated samples (50 mmolar solutions) of the ligands and the complexes dissolved in methanol are shown in Figure 5.21-5.23. The low, mid and high q regions in the curves denotes size, shape and inner structure (flexibility) respectively of the molecules. The sizes of ligands 1 and 3 (13 Å) change only slightly in the complexes, (13.5, 24.2 Å for 1+Au; 13.9, 23.8 Å for 3+Au). As discussed in Chapter 3, in solution, 2 showed only one specie whose size is consistent with a calculated extended structure (20.4 Å). However, the size of 2 changed significantly in the complex showing two populations (16.2, 27.6 Å) attributable to complexes with coiled up fluorous domains to reveal smaller sizes and the interdigitated form. The change in the size of 2 is consistent with gold complexation. The appearance of a corresponding smaller species in the gold complex suggests the presence of both the single and dimeric species attributable to interdigitation of the fluorous domains (which gives weight to the notion of C-F…F-C interactions discussed in Chapter 3).

Table 5.5. SAXS and PDDF analysis of the ligands and complexes.

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</table>

Figure 5.23. SAXS analysis of 3 and its Au³⁺ complex.
Radial atomic pair distance distribution function (PDDF) gives the interatomic distance distribution, or “probability” of finding atomic pairs distance $r$ apart, and therefore provides a way of analysing diffraction data in real space. Unlike XRD, there is no assumption about periodicity, evaluation of all intensities from both Bragg and diffuse scattering is carried out. PDDF of the ligands and their Au complexes have been carried out and the results are shown in Table 5.5. The experimental PDDF fits quite well with simulated PDDF and are comparable to the sizes measurements obtained from SAXS. The absence of a shoulder further adds weight to the idea that there is no core-like interactions\textsuperscript{49} with [AuCl$_4$]$^-$. Nonetheless, 2 has the highest maximum linear extent followed by 3 but in the complex, 3 has the highest maximum extent. The sizes of the ligands and complexes obtained from the SAXS, PDDF and DOSY NMR analysis suggests that the complexes are bigger than the free ligands which is indicative of ligand-gold complexes.
5.2.6 Kinetics and stability constants

Stability constants of the ligand-metal complexes of the quantitatively extracted nuclei have been determined by UV/Vis titrations of 0.1 molar equivalent of the metal against the ligand. UV/Vis titrations can provide insight into the stoichiometry of the complexes.\(^50\) For all system studied (Figure 5.24), upon addition of the metal ions, the n-π* transition band of the fluorinated systems at 322 nm undergo bathochromic shift of 6-18 nm as well as an increase in absorbance attributable to metal co-ordination. The shift in peak position was greater in the Au\(^{3+}\) reactions suggesting a stronger binding of Au. Upon reaching approximately 1 molar equivalent of metal to the ligand, the slope changes suggesting the formation of a 1:1 ligand to metal complexes (Figure 5.24 – 5.26). The plot of the binding isotherm for Au and Pd with all three ligands is shown in Figure 5.26. 1 and 3 shows change in the slope after adding approximately 1 equivalent of the metal with very little change in absorbance after upon addition of more metal. Ligand 2 however showed continued increase in absorbance until 1 equivalent wherein the absorbance was too high to give reliable results. The binding constants for the Au and Pd obtained from the analysis of the UV titrations using BindFit programme\(^51\) gave the best fit to a 1:1 complexes as shown in Table 5.4. This values are within the same order of magnitude as previously observed for Au and thiocyanide and amine complexes.\(^52\)\(^-\)\(^54\) Pd complexes with amines and amino acids have been reported to display stability constants in the same range.\(^55\)\(^,\)\(^56\) However, the higher stability of Au over Pd complexes is consistent with the selectivity of Au(III) displayed during extraction which is likely a contribution of stronger hydrogen bond interaction with the gold species.
Figure 5.24. UV/VIS spectra of serial addition of 0.2 molar equivalent of Au$^{3+}$ to 1 (a), 2 (b) and 3 (c) at 23 °C.
Figure 5.25. UV/VIS spectra of serial addition of 0.2 molar equivalent of Pd^{2+} to 1 (a), 2 (b) and 3 (c) at 23 °C.
5.2.7 Back extraction

The metals extracted from the aqueous mixtures into the organic phase can be back extracted from the extracted species in the organic phase into a fresh aqueous phase by stripping using water, acidified water, inorganic acids or thiourea. After complete extractions, the quantitatively extracted Au and Pd were back extracted from the organic phase by stirring the organic phase with a 3M HNO₃ solution and periodically monitoring by spectrophotometric analysis. Au and Pd were recovered in 92 and 97% yield respectively. The ligands were analysed by ¹H NMR spectroscopy after stripping and found to be intact.

5.2.8 Emission Spectroscopy

Enhanced luminescence or quenching effect can be achieved when ligands with the correct energy level are complexed with emissive metals. The emission studies of Eu(III) was carried out in EtOH/DCM using fluorous tren (1) and the partial cone calix[4]arene ligand
The 1:1 M-L complexes had emission lifetimes of 0.144 ± 4 and 0.188 ± 3 ms for the respective Tren and calixarene complexes. The full emission profile with the ligands were performed by adding varied amount of increasing amounts of the ligands to the metals. Although many nitrogen containing ligands have been shown to give enhanced luminescence to the complexes but in the case with chosen ligands, 1 and 3 increase in ligand concentration caused a continued decrease in emission as expected. This is due a quenching effect resulting from a radiationless de-excitation via energy transfer to the ligand O-H and N-H vibrational overtones pathway. The emission spectra resulting from the electronic relaxation from \( ^5D_0 \) to the \( ^7F \) manifolds in this way is characteristic of Eu(III). The intense peaks at 620 and 700 nm are due to emission from \( ^5D_0 – ^7F_2 \) and \( ^5D_0 – ^7F_5 \) states respectively. Changes in intensities of one of the peaks with respect to the other gives an indication of the symmetry around the Eu centre of the complex. However, general decrease in the intensity of all peaks across the spectrum is observed as the molar equivalent of the ligands increased in both complexes due to the quenching effect. While Horrock’s equation maybe used to probe the number of water molecules around the Eu centre when the experiment is performed in D\(_2\)O, the experiment was performed in EtOH/DCM.
Figure 5.27. Normalized emission spectra of Eu-Tren (left) and Eu-Calixarene ligands (right)

5.2.9 Americium extraction studies

Americium extraction has implications in the removal of long-lived, highly toxic isotopes of minor actinides (mainly americium and curium) from high-level radioactive waste (waste partitioning). This operation is accomplished by transmutation of the actinides to short-lived isotopes and removal of the harmful long-lived nuclides from liquid radioactive wastes, before their disposal; thus reducing risks connected with the final waste disposal. The extraction was carried out by Dr. Saptarshi Biswas (TCD) and Dr. Luis Leon (UCD) by measuring $^{241}\text{Am}$ activity in both phases in order to establish the distribution coefficient of
the metal in both phases and the results are included in Table 5.1. Control experiment showed that no Americium was extracted into the DCM phase. A 1:1 distribution ratio (DCM/water) was obtained with ligand 1 while 2 and 3 showed approximately 2:1 partition into the organic phase. Ligand 3 showed slightly better Am(III) extraction efficiency. The results showed poor distribution ratio of Am(III) due to the covalency of actinide-hard donor requirement which is unmet.

Of all the new ligands, the calixarene derivatives are the strongest. the amide derivative of the partial cone calixarene is just as good as the commercial hydoxyoxime, cyanide and thiourea systems for Au extraction. However it is poses less safety concerns compared to processes such as cyanide leaching. Phosphine ligand shown here was tremendously better at extracting lanthanides (80 – 90%) compared to the commonly used TOPO (Triocetylphosphine oxide) and CMPO [(N,N-diisobutylcarbamoylmethyl)octylphenylphosphine oxide] which can extract Eu$^{3+}$ at 18 and 69% respectively.\(^{37}\) Compared to other phosphine oxide ligands in the literature the extraction efficiency is slightly less as phosphate oxide derivatives of calix[4]arene have been known to extract Ln$^{3+}$ in over 95%. On the other hand,\(^{24}\) these previously reported ligands possess very long extraction time with up to 96 h for some phosphine oxides,\(^{18}\) the extraction time with the presented phosphine is only 50 h.

5.3 CONCLUSION

Fluorous acetamide derivatives of Tren, cone calix[4]arene, and partial cone calix[4]arene have been employed in the extraction studies of Au(III), Ag(I), Pt(II), Pd(II), Nd(III), Eu(III) and Er(III) from aqueous media in a typical liquid-liquid extraction to examine the influence of rigidity and size of the ligands cavity on metal extractions. The relatively bigger partial cone ligand was found to have better extraction efficiency with all metals studied. Au(III) and Pd(II) were extracted in >> 98% and to lesser amount for the other metals. Au was however extracted much faster than Pd suggesting ligand selectivity for Au(III). The Tren ligand, being less rigid and least affected by pre-organisation effects showed the least extraction efficiency which may also be due to the size of the ionophoric cavity. Increase in concentration resulted in increase in the extraction efficiency for the metals. The calixaryl phosphine oxide ligand displayed excellent Ln$^{3+}$ extraction efficiency. All ligands formed moderately stable complexes by non-covalentoutersphere interactions through the carbonyl
C=O of the amide. While the partial cone is very fast at extracting the precious metals, the binding constants suggest that the cone calix[4]arene forms the most stable metal-ligand complex. This is corroborated by the SAXS analysis of the Au complexes which showed that the cone calix[4]arene is the most perturbed upon metal complexation while the other ligands showed very little changes in sizes and speciation.

5.4 EXPERIMENTAL

All extractants/ligands were synthesised in chapter 2. All solvents were obtained from commercial sources and used as received. PGMs solutions were prepared by dissolving a weighed amount of sodium tetrachloroaurorate (Johnson Mathey Chemicals, England), palladium dichloride (BDH Chemical Ltd, England), Silver Nitrate, Sodium tetrachloroplatinate, (Aldrich) in acidified H$_2$O. The working solutions of these metals had a pH of 2. All spectrophotometric analysis were obtained using the Lambda 1050 UV-Vis NIR, using fused silica cells with a path length of 1 cm. Steady-state photoluminescence spectra were recorded on a Horiba-Jobin-Yvon Fluorolog-3 spectrofluorimeter. Luminescence lifetime data were recorded following 375-nm and 405-nm excitation, using time-correlated single-photon counting (a PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained, and the quality of fit was judged by minimization of reduced chi-squared and residuals squared. All emission spectroscopy was carried out using a Horiba Fluorolog-3 and lifetime data were obtained using a Horiba Fluoromax-4.

$^1$H, $^{13}$C{H} and $^{19}$F NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400.23 MHz, 155.54 MHz and 376.55 MHz respectively, or a Bruker Avance II 600 NMR with a TCI cryoprobe spectrometer operating at 150.92 MHz ($^{13}$C) and were referenced to the residual $^1$H and $^{13}$C resonances of the solvent used or external CFCl$_3$. IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer with attenuated total reflectance (ATR) accessory. The SAXS measurements were measured by Prof. May Nyman, Oregon State University. The Am-241 measurements were carried out by high-resolution gamma spectrometry using an n-type high-purity germanium detector (EG&G Ortec model GMX-15190) with a relative efficiency of 19% and a resolution of 1.90 keV (FWHM) at 1.33 MeV; this gives a total error of 15% in the measurements.
5.4.1 General procedure for Solution Extraction Studies of Precious metals

5 cm$^3$ Aliquots of the stock solution of the metals (1x10$^{-3}$M, 2x10$^{-4}$M, 9x10$^{-3}$M and 5x10$^{-4}$M of NaAuCl$_4$, PdCl$_2$, K$_2$PtCl$_4$, and AgNO$_3$ respectively) were added to solutions of 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 molar equivalents of the ligands in DCM. The layers were stirred together in a stoppered vial for a specified time. The concentration of the aqueous phase was periodically determined by spectrophotometric measurement and a calibration curve.

5.4.2 Solution Extraction Studies of the Rare Earth Elements

A 5 cm$^3$ solution of the Ln$^{3+}$ (2x10$^{-3}$M) were vigorously stirred with 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 molar equivalents of the ligands in DCM for 96 h and 50 h with the fluorous calixaryl phosphine oxide. The calorimetric reagent was prepared by dissolving Arsenazo-III (0.09 g) in a buffer solution of formic acid and sodium formate pH 2.5 to make a solution of 0.64 mM. The Arsenazo III solution (5 mL) was added to 1 cm$^3$ of the aqueous phase and made up to 50 cm$^3$ with the buffer solution. The concentration of Ln$^{3+}$ in the aqueous phase was determined spectrophotometrically.

The effect of pH on metal extractions was determined by repeating the above procedures at pH 2, 6, 10. The distribution ratio, $D$ was measured as a ratio between the concentration of metals in the organic and the aqueous phases, using Eq. (1);

$$D_M = \frac{[M]_{org}}{[M]_{aq}}$$

Percentage extraction (%E) of metal ion was determined by Eq. (2);

$$%E = \frac{[M]_{aq,\text{initial}} - [M]_{aq}}{[M]_{aq,\text{initial}}} \times 100$$

Where M is the investigated metal ions. Each sample was repeated, 3-4 times and uncertainties in the extraction measurements are ±3%. Cumulative error including sampling phases and other volumetric operations are uniformly taken to be ±5%.
5 | Solution Phase Metal Extraction

5.4.3 Back extraction

In the Liquid-Liquid extractions, the organic phases were separated. 3 M HNO₃ (5 ml) was added and stirred for 4 h. The concentrations of the aqueous phases were examined by spectrophotometric measurements.

5.4.4 Eu(III) Emission study

Emission spectra were recorded at a wavelength of 394 nm using a solution of ligand of equal concentration to the stock Eu(III). The ligand solution was added to the stock solution of europium in 20% v/v Ethanol/DCM. For the enhanced luminescence studies, serial addition of 1 molar eq of the ligand to Eu solution was carried out and the emission spectra were recorded.

5.4.5 Americium extraction studies

A 1 cm³ solution of the Am³⁺ (20 mM) were vigorously stirred with 1.0 molar equivalents of the ligands in DCM for 96 h. the phases were separated and each phase was analysed using high-resolution gamma spectrometry. The activities calculated as described in Table 5.1
5.5 REFERENCES


Chapter 6

Development of Fluoropolymer Solid Support
6.1 OVERVIEW

Catalysts continue to gain interest spurring growing research in areas including polymer-bound catalysts,¹ scCO₂,² scavengers,³ silica supported catalysts,⁴ polystyrene-supported systems,⁵ zeolites and mesoporous molecular sieves immobilised catalytic metal fragments,⁶ ionic liquids,⁷ soluble colloidal metal nanoparticles,⁸ dendrimer-bound catalyst,⁹ polymeric membranes in catalytic reactors¹⁰ and the use of flouorous tags. Some of the named recovery processes have therefore incorporated catalyst recovery into the catalyst design or the catalytic media. Attaching flouorous tags on catalysts induces separation of catalyst or extractants into aqueous or flouorous media that are orthogonal to the product containing media.¹¹

In line with this notion, engineering molecular structures to possess flouorous liquid phase affinity by attachment of flouorous “pony tails” of the formula, (CH₂)m(CF₂)n-1CF₃ is a common feature in flouorous biphasic systems. In other systems, the flouorous groups engenders temperature dependant solubility wherein one phase is obtain at increased temperature and the catalyst easily recovered at lower temperatures as introduced by Horvath.¹² However most recovery methods have their potential draw-backs including cumbersome recovery procedures; fluorinated solvents in particular are expensive and pose the risk of solvent leaching and environmental persistence.¹² This has led to research in fluoropolymer solid supports,¹³-¹⁸ temperature dependent precipitation¹⁹ and solvent aided precipitation onto fluoropolymer support.²⁰ Whilst most catalyst recovery processes involves covalently linking the catalyst to the solid support which may require specific reaction conditions for linking, cleaving and catalysis.²¹ Others have successful employed what is regarded as a simple precipitation where the fluoropolymer support such as Teflon is used as a locus for deposition for the flouorous catalyst during catalyst recovery – albeit with leaching concerns.¹⁸

Work discussed in Chapter 3 and by others²² have shown that C-F···F-C interactions can be energetically favourable in fluorinated molecules in the solid state. This suggests that the underlying mechanism for the catalyst recovery is possibly beyond a simple precipitation onto the fluoropolymer and understanding of this could be central to developing Teflon supports with minimal leaching. Moreover, the feasibility of physisorption on fluoropolymer surfaces have been explored using modelled fluorinated gold surfaces with a successful outcome.²³ In this chapter, previously synthesised fluorinated ligands will be physisorbed
on a model fluorinated surface prepared via self-assembly of 1H,1H,2H,2H-perfluorodecanethiol (PFSAM) on a gold surface. This PFSAM and the PFSAM with ligands can be characterised using Infrared reflectance absorption spectroscopy (IRAAS). IRRAS measurements provide frequencies and intensities of molecular vibrations. The intensities are interpreted in terms of molecular structures which then permits determination of the orientation of functional groups or ordered structural elements. The outcome of such studies will pave the way for the physisorption of fluorinated compounds onto fluorinated surfaces (fluoropolymers) such as Teflon, Gore-Tex® and Rastex® and the effect of ligand structure on adsorption and desorption.

Therefore, we aim to intentionally synthesise and characterise Fluoropolymer supported ligands (FSL) by physisorption using fluorous interactions. The chosen compounds include fluorinated Tren (1), cone (2) and partial cone calixarenes (3) ligand. The attached fluorous pony-tails (Figure 6.1) affords enhanced fluorophilicity with the aim of promoting C-F···F-C interactions with Teflon which is made up of –CF₂–CF₂- repeating units. Variation in the structure of the ligands offers insight into optimum ligand design for Teflon solid supports.

The synthesised ligand coated fluoropolymers can be characterised by Thermogravimetric Analyses (TGA) which measures the change in mass of a substance as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. In addition, TGA combined with an Infrared Spectrometer (TG-IR) can carry out an Evolved Gas Analysis (EGA) where the volatile materials released from a heated sample on the TGA are transferred to an IR cell and the components can be identified by their characteristic IR spectra.

The surface topography and morphology of the FSL samples will be characterised by Raman mapping and scanning electron microscopy (SEM).

Upon successful characterisation, practical application of the FSL samples will be carried out. Solid supported ligand has applications in metal separation and of interest is its application in energy critical metal extraction and recycling.24 Therefore, the fluoropolymer supported extractants made will be applied in solid-liquid metal extractions with the aim of facile extractant recovery. The recovery and reuse of the fluoropolymer supported extractants will also be studied. The leaching profile of the FSL will be examined. Lastly, successful desorption of ligand from the fluoropolymer support to obtain a free ligand will be demonstrated.
The ligands chosen (Figure 6.1) possess various degree of flexibility and number of fluorinated chains in order to check the influence of such factors on physisorption on fluorinated surfaces.

### 6.2 RESULTS AND DISCUSSION

**Figure 6.1** Supported fluorinated compounds

#### 6.2.1 Physisorption on modelled fluorinated surface and characterisation by Infrared reflectance absorption spectroscopy (IRAAS).

The functional groups as well as their orientation relative to the reflective surface can be determined by IRRAS. The peak intensities observed in IRRAS spectroscopy are attributable to surface coverage and orientation effects. Integrating the peak intensity can give an indication of surface coverage in the case of disordered films.\(^{25, 26}\) The IRRAS analysis was performed as described in the literature.\(^{23}\) The fluorinated extractants were physisorbed onto modelled fluorinated surfaces prepared *via* self-assembly of (PFSAM) on a gold surface and then exposed to acetone solutions of 1, 2 and 3.

Control experiments on bare gold surfaces showed significant absorption peaks for the fluorinated compounds, which were removed when sonicated for 30 mins as shown in Figure 6.2 (gold and red curves). Figure 6.3 shows the IRRAS spectra of the PFSAMs displaying C-F stretches of the -CF\(_2\) and -CF\(_3\) groups in the 1400-1000 cm\(^{-1}\) region with an integrated
area of 0.015 (0.01 (90% C.I.). Upon adsorption of fluorinated compounds, amide I and II bands in the 1640 and 1560 cm\(^{-1}\) are observed, and the integrated intensity in the region 1000-1400 cm\(^{-1}\) increases due to an increase in the surface density of the fluorinated amide compounds (trace b-d). Figure. 6.4 (a-c) show a much slower decrease in intensity of the C=O amide stretching absorbance of 1-3 on the PFSAM functionalised surfaces compared to the bare gold surface. This demonstrates that the PF-SAM is essential to the adsorption of the compounds and that a stronger interaction is present in the molecular assembly on to the PFSAM than a simple precipitation/aggregation from solution.

**Figure 6.2.** Control experiments with 1 (left) and 3 (right) on bare gold surfaces compared to 1 and 3 on PF-SAM. The solid lines indicates physisorbed compounds and broken lines indicates physisorbed compounds after sonicating for 30 mins.
Figure 6.3. IRRAS spectra in the 1800-800 cm\(^{-1}\) region of PF-SAMs (a) before and after adsorption of compound (b) 1, (c) 2 and (d) 3 at the PF-SAM layer. Spectra have been offset for clarity.

Figure 6.4. IRRAS spectra in the 1800-800 cm\(^{-1}\) region of compound (a) 1, (b) 2 and (c) 3. The solid coloured line represents the adsorption of compounds 1-3 at the PF-SAM layer. The dot lines show the compounds 1-3 at PF-SAM layer after a vigorous sonication for 120 (for compound 1) and 60 mins.

All extractant were efficiently physisorbed as shown on Figure 6.5 of the integrated absorptions graph. The largest surface coverage on the PFSAM was observed for 1 attributable to its flexible structure and being able to extend itself over a large surface area – maximising fluorous-fluorous interactions. The least absorption was observed for 3 which is due to the smaller footprints of compound 3 compared to the four pendant arms present in compound 2. The physisorbed compounds were desorbed from PFSAM surface in amounts reflective of the structure of the compounds and strength of interactions. 86.13 ± 0.02 and 92.52 ± 0.01% of the physisorbed compound 2 and 3 were desorbed from the
PFSAM surface after 60 min of sonicating, which compares very well with previous studies where fluorinated ligands with 1-3 pendant arm were physisorbed on teflon.\textsuperscript{23} However, 44.16 \pm 0.04\% of compound 1 was desorbed from the PFSAM surface after 60 min and sonicating for another 60 mins only removed another 22.49 \pm 0.08\% of compound 1. These results indicates that physisorption on fluorinated surfaces is reversible and the extent of desorption might be related to the ligand structure. While compound 2 has four pendants arms as previously discussed, compound 1 is less rigid and it is possible that this structure extends itself on the Teflon surface giving it a larger footprint than compound 2 and 3. This increases its interaction with the surface significantly making its physisorption properties a lot better but more difficult to desorb.

![Figure 6.5](image)

**Figure 6.5.** Integrated absorbance in the 1800-1430 cm\textsuperscript{-1} region of PF-SAMs after adsorption (solid bars) and desorption (dot bars) of compounds 1-3; error bars indicate 90\% C.I..
Schematic diagram of ligands interaction with the fluorinated surface. The proposed number of ligand interactions based on the ligand conformation is highlighted in red.

**Elipsometry** is a convenient technique for characterisation of surfaces and film thicknesses based on its characteristic high precision and accuracy, non-intrusive, and high temporal resolution even in the presence of various fluids, including high-pressure gases and vapours. However, characterisation of the PFSAM samples or the PFSAM with the compounds using this method failed to yield sufficient data that can be accurately modelled due to the surfaces being too thin for accurate modelling.

### 6.2.2 Synthesis and Microscopy of Teflon® supported ligands

Compounds 1, 2 and 3 were used in the synthesis of fluoropolymer supported ligands (FSL) 1, FSL 2 and FSL 3. Ligands coated Teflon® tape was synthesised by stirring the Teflon® strips in a solution of the ligand dissolved in IPA/H₂O, 1:1 v/v. Slow evaporation of the solvent precipitated the ligand on the Teflon® strips. The strips were thoroughly washed until the washes showed no ligand desorption (by analysing the last washes using \(^{19}\)F NMR spectroscopy). To avoid folding of the strips during microscopy, it was necessary to make a thick Teflon strip by simply laying and pressing 10 Teflon strips together.
The optical images at 10 µm show a change in the Teflon® substrate indicated by the bright spots on the dark Teflon background shown in Figure 6.6 (A-D). The optical image of 1 on Teflon shown in Figure 6.6B shows has bright spots on a dark background compared to the bare Teflon substrate shown in Figure 6.6A. Figure 6.6C shows more contrast compared to the Teflon substrate although this might be due to the fine nature of the powered sample while Figure 6.6D shows 3 on Teflon as relatively bigger spots and more dispersed than Figure 6.6B but with more dark background character than Figure 6.6C.

![Optical Images of Fluorinated ligand deposited Tape](image)

**Figure 6.6.** Optical Images of Fluorinated ligand deposited Tape: (A) Bare Teflon (B) Teflon coated with 1 (C) Teflon coated with 2 (D) Teflon coated 3. The scale bar is 10 µm for all images.

In order to confirm the presence of the ligand on Teflon and that the observed contrast is not due to just a rough surface, coated Teflon® tapes were analysed by scanning electron microscopy. SEM analyses of the FSL samples were performed using the in-lens detector for collecting Secondary Electron (SE) and the images formed are shown in Figure 6.7. The SE images provide the highest spatial resolution images with topographic information and compositional contrast. The micrographs of the images obtained from the collected secondary electron showed a non-uniform deposition of the fluorinated ligands on the Teflon
tape. Upon comparison, Figure 6.7A shows an expected smooth Teflon surface while Figure 6.7B-D show depositions on the Teflon surface. The surface appears smoother in image C compared to B and D. Deposition on 5D is however rougher than all surfaces with bigger clusters of the deposited material which is consistent with optical images.  

![Figure 6.7](image)

**Figure 6.7.** SEM images of Fluorinated ligand deposited Tape: A) Teflon® tape  B)  C)  D) 3. The scale bar is 20 µm for all images.

Ligands deposition Teflon® tapes were further analysed by Raman mapping technique. A spectral hypercube (a Raman spectrum from each position on the sample in a single file), was collected by point-by-point mapping method where the laser is focused to a spot and a motorised stage moves the sample under the laser. The Spectra were sequentially acquired from an array of sample points spanning the defined region of interest. The hypercube was then analysed to produce Raman images by tracing the C-F stretching bands at 1200 – 1400 cm⁻¹. The sample composition is indicated by the Raman intensity due to C-F stretching. The colour contrast in the Raman analysis can be used to deduce the surface composition of the sample. From the images obtained (Figure 6.8 and the 3D images in Figure 6.9), there is clearly ligand deposition on the Teflon indicated by a darker colour map of compounds 1-3 on the Teflon substrate suggesting effective physisorption. Raman peak intensity has been shown to be reflective of the amount of sample deposition on the substrate. The images shows a notable difference in the intensity between the bare Teflon
surface and the FSL samples. The FSL 3 sample shows the highest intensity than FSL 1 and FSL 2. FSL 1 however shows higher intensity than FSL 2 perhaps due to the structure of the ligands. While the structure of ligand 2 has four pendant arms which allows it to interact with the surface more than the ligand 1, ligand 1 conformation is likely splayed on the surface and therefore more deposited than 3.

**Figure 6.8.** Raman mapping of the intensities of characteristic Raman scattering peaks at 1200 – 1400 cm⁻¹ of (A) Bare Teflon (B) Teflon coated with 1 (C) Teflon coated with 2 (D) Teflon coated with 3 showing the difference in intensity. The scale bar is 5 µm for all images.
6.2.3 Elemental analysis

Elemental analysis was carried out using 4.5 mg of the FSL samples. Estimations based on percentage composition of nitrogen in the FSL samples suggested a loading of 0.12, 0.1 and 0.09 moles of compounds 1, 2 and 3 per gram of the Teflon tape in the FSL samples indicating a far greater loading per gram of solid support compared to other solid support developed using covalently linkage such as Calix-Pro-MN\textsuperscript{31} and calix[4]arene attached to a Tentagel S NH\textsubscript{2} resin polymer\textsuperscript{29} (Table 6.1).

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Bounded amount (mol/g)</th>
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<tr>
<td>FSL 1</td>
<td>25.01</td>
<td>0.66</td>
<td>7.81</td>
<td>0.12 x 10\textsuperscript{a}</td>
</tr>
<tr>
<td>FSL 2</td>
<td>35.76</td>
<td>1.95</td>
<td>3.48</td>
<td>0.1 x 10\textsuperscript{a}</td>
</tr>
<tr>
<td>FSL 3</td>
<td>31.15</td>
<td>1.25</td>
<td>3.21</td>
<td>0.09 x 10\textsuperscript{a}</td>
</tr>
<tr>
<td>Calix-Pro-MN\textsuperscript{31}</td>
<td>27.57</td>
<td>3.67</td>
<td>1.63</td>
<td>0.194 x 10\textsuperscript{-3a}</td>
</tr>
<tr>
<td>Tentagel-calixarene\textsuperscript{29}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.24 x 10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated according to the N content.

6.2.4 Thermal analysis

The idea is to monitor the changes in weight, onset and end points of each thermal event and the rate of phase change with increasing temperature under non-reactive atmosphere. Maintaining identical conditions while minimising the effects factors such as heating rate, sample weight, crucible shape and sample atmosphere, the percentage ligand physisorbed onto Teflon and any physio-chemical changes in the ligands or Teflon upon physisorption can be observed.

The TGA analysis of the coated FSL samples (Figure 6.10) showed weight loss during thermal analysis. There are two weight loss phases attributable to the ligand and the Teflon\textsuperscript{®}.
weight loss. The first phase (A) represents decomposition of the ligand with an on-set of 160 and 190 °C and continued into the next weight loss phase (B) with an on-set at 478 °C and an endpoint of 600 °C. These compounds have been showed to exhibit decomposition temperatures from 200 - 600 °C suggesting that ligand decomposition here may have continued into the Teflon® decomposition temperatures making it difficult to calculate the exact amount of ligand adsorptied onto the Teflon®. Estimated the percentage weight loss based on ligand decomposition onset to Teflon® decomposition onset at 470 °C shows 11 - 17% adsorption of compounds 1-3 onto the Teflon®.

**Figure 6.10.** Selected TGA curves showing the endothermic processes during thermal decomposition of the bare Teflon® and ligand coated Teflon® heated at 5 °C/min under nitrogen atmosphere at a purge rate of 20 mL/minute.
Figure 6.11. Derivative TGA curves showing the endothermic processes during the thermal decomposition of the bare Teflon®, ligand and ligand coated Teflon® involving 1 (top), 2 (middle) and 3 (bottom)
The derivative weight describes all curved portions of the thermogram with an inflection at which \( \frac{dw}{dt} \) is a minimum but not zero. Simply put, the peak of the differential thermogravimetric curve corresponds to the curved portion of the thermogravimetric curve. The peak of the derivative indicates the point of the greatest rate of change and weight loss. Some measure of the stability of the intermediate can be extracted from the derivative curve where the height of the trough above the line \( \frac{dw}{dt} = 0 \). Features in the thermogravimetric curve that are not readily discerned are more clearly seen in the differential thermogravimetric curve, e.g., any change in the rate of weight loss may be seen immediately as a trough, indicating two consecutive reactions, or as a shoulder to the peak, indicating two almost overlapping reactions or as a tail to a peak, which is probably an indication of strong adsorption of the volatile product on the new solid phase.\(^3\) Figure 6.11 therefore shows the 1\(^{\text{st}}\) derivative treatment of all the TGA curve obtained in the fluoropolymer supported samples analysis are overlaid with that of the free ligands and the bare Teflon curves. Teflon decomposition curve shows a peak at 600 °C. The decomposition curve showed a faster phase change and a higher decomposition rate than bare Teflon during decomposition. Teflon decomposition point also decreases in all FSL samples by 35, 20 and 20 °C for FSL 1, 2 and 3 respectively. This is in contrast to previous studies where the thermal stability increased with radiated grafting of polystyrene sulfonic acid on PTFE membranes\(^4\) whereas immobilization of calixarenes in the sol – gel matrix does not seem to affect the stability of the material.\(^5\) In most cases, the decomposition temperature of all ligands increased significantly upon physisorption which suggests increase in the thermal stability of the structure due to non-covalent interactions.\(^6\) Compound 1 decomposes at 220 °C as a free ligand and 400 °C when physisorbed. Compound 2 decomposes at 280 °C as a free ligand and 350 – 410 °C upon physisorption which may be due to a more ordered microenvironments when physisorbed. Compound 3 decomposes at 220 °C – 350 in two thermal events as a free ligand owning to the presence of more than one microenvironment in the ligand but decomposes at 310 °C in a single thermal event indicating a more ordered state when physisorbed. FSL 1 showed the highest change in decomposition temperature (180 °C). The decomposition temperature of FSL 2 increased by 100 °C and the curve showed two peak which can also be attributed to a formation of an intermediate upon physisorption. The thermal stability for FSL 3 remains the same indicated by the decomposition temperature which remained within the range of the free ligand.
Table 6.2. Characterisation of physisorbed ligand and difference in the onset of weight loss of the ligands

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight loss onset (°C)</th>
<th>Weight loss onset (°C)</th>
<th>Difference in Weight loss onset (°C) compared to the free ligands</th>
<th>% Physisorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSL 1</td>
<td>190</td>
<td>410</td>
<td>220</td>
<td>11</td>
</tr>
<tr>
<td>FSL 2</td>
<td>160</td>
<td>400</td>
<td>240</td>
<td>12</td>
</tr>
<tr>
<td>FSL 3</td>
<td>160</td>
<td>190</td>
<td>30</td>
<td>17</td>
</tr>
<tr>
<td>Teflon</td>
<td>465</td>
<td>600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2.5 Thermal analysis coupled to infrared analysis

TGA combined with an Infrared Spectrometer (TG-IR) can carry out an Evolved Gas Analysis (EGA). This technique is applicable here as the evolved gases can be identified by the C-F stretch. This characterisation technique can help identify exact onset and end points of weight loss phases using in-situ FTIR to determine specific molecular units of the gases evolved during the thermal analysis. The corresponding IR spectra of the TGA-IR analysis of ligand 1-3 coated Teflon® (Figure 6.12-14) show the C-F stretching from 1010-1290 cm⁻¹ at temperatures up to 465 °C. In all cases, the IR spectra then changes showing stronger C-F stretching from 1000-1400 cm⁻¹ indicative of Teflon® decomposition at temperatures above 465 °C. The weight percent loss after the first phase due to 1, 2 and 3 coated Teflon® is 17.8% while Teflon® weight percent loss of 80.6-84% is observed at the second decomposition endotherm.
Figure 6.12 TGA-IR analysis of 1 coated Teflon®. (A) Normalised weight and normalised weight derivatives of the thermal analysis. (B) IR of the ligand coated at 320 – 476 °C and (C) at 479 – 600 °C.
Figure 6.13 TGA-IR analysis of 2 coated Teflon®. (A) Normalised weight and normalised weight derivatives of the thermal analysis. (B) IR of the ligand coated at 320 – 476 °C and (C) at 479 – 600 °C
Conclusive evidence have been obtained for the physisorption of the ligands on the Teflon. The optical analysis have showed changes on the surfaces of the synthesised FSL samples compared to bare Teflon. SEM analysis showed that the colour contrast observed are indeed deposition on the substrate whilst tracing the C-F stretches by Raman mapping confirmed the presence of fluorinated compounds on the surface. Quantitative analysis of the amount of compound physisorbed on the Teflon surface was achieved by CHN analysis corroborated

Figure 6.14. TGA-IR analysis of 3 coated Teflon®. (A) Normalised weight and normalised weight derivatives of the thermal analysis. (B) IR of the ligand coated at 320 – 476 °C and (C) at 479 – 600 °C
by weight percent of physisorption on Teflon determined from thermal analysis coupled with infrared spectroscopy.

### 6.2.6 Metal extraction with solid supported ligands

Metal extraction with the synthesised Teflon® supported ligands showed high extraction efficiency. Using 0.5 equivalent of the ligands, %E similar to that of the free ligands were obtained. 3 retains the highest extraction efficiency (>96%) with Au(III). The extraction times were however longer as the solid supported ligands took longer to achieve similar percentage extraction as the free ligands. Reduction in efficiency is well noted in the use of solid support as opposed to free ligands.38

Stripping of the extracted metal was achieved by washing the ligand coated Teflon® in 3 M HNO3 and Au (91%) and Pd (93%) were recovered from the solid extractants after 20 h.

**Table 6.3.** Characterisation of selected supported ligands samples and comparism between liquid-liquid and liquid-solid Extraction of Au(III) with 0.5 molar equivalent (based on % wt of ligand on FSL samples) of 1-3

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Liquid-Liquid</th>
<th>Solid-Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Extraction</td>
<td>Time (h)</td>
</tr>
<tr>
<td>1</td>
<td>54 ± 0.8</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>52 ± 1.2</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>96 ± 0.8</td>
<td>6</td>
</tr>
</tbody>
</table>

### 6.2.7 EXAFS Analysis of the Au3+ Complexes

The results of the Au L3-edge EXAFS analysis are shown in Figure 6.15 – 6.18 and Table 6.4. EXAFS of Au-amide complexes used in extractions has recently been described by Doidge *et al.*40 Fitting the EXAFS data using Feff code, only the first coordination shell was used in order to obtain the coordination number around the Au, and the bond length obtained are reasonable for [AuCl4]−.42 In all the samples, phase-shift-corrected FT-EXAFS showed one intense peak at 2 – 2.21 Å attributed to the chloride ions in all the Au-amide complexes. Using firstly a standard, Na[AuCl4], a coordination number of 4 and an Au-Cl
bond length of 2.29 Å was calculated from the fit. Fits for the three compounds on Teflon for the first shell show the best statistics for a coordination number of 4 and Cl ions; attempts to fit the data with O or N afforded poor statistics. The Au-Cl bond length of FSL 2 and FSL 3 are consistent with the Na[AuCl₄] standard and the literature. The Au-Cl bond length in the FSL 1 sample is 2.38Å which is longer than expected but the reasons for this are unknown Å. Fitting with the 2nd and 3rd shell are currently on-going. Notably, the broad peak at 4.1–4.4 Å is most likely produced by multiple scattering from the dominant Au-Cl correlation. The peak at 5.1–5.5 Å, which was absent in [AuCl₄]– may be produced by backscattering from N, O or both atoms on the ligand as it hydrogen bonds to the outer sphere of the [AuCl₄]– ion.

**Figure 6.15.** Au L₃-Edge Fourier Transformed EXAFS data for solid Na[AuCl₄] showing the fit (red) and experimental curve (black solid). k weighted and q weighted EXAFS spectra and best fits shown below.
Figure 6.16. Au L₃-Edge Fourier Transformed EXAFS data for solid FSL 1 showing the fit (red) and experimental curve (black solid). k weighted and q weighted EXAFS spectra and best fits shown below.
Figure 6.17. Au L3-Edge Fourier Transformed EXAFS data for solid FSL 2 showing the fit (red) and experimental curve (black solid). k weighted and q weighted EXAFS spectra and best fits shown below.

Figure 6.18. Au L3-Edge Fourier Transformed EXAFS data for solid FSL 3 showing the fit (red) and experimental curve (black solid). k weighted and q weighted EXAFS spectra and best fits shown below.
Recycling of the ligand coated samples and the ligands

Washing the ligand coated Teflon® with hot IPA resulted in ligand recovery. NMR spectroscopy of the desorbed ligand shows a fully intact ligand while the TGA of the previously coated Teflon® showed 0.6-2% ligand was left on the Teflon after desorption.

### Table 6.4. $k^3 \chi(k)$EXAFS data for [Na(AuCl4)] and the FSL samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>$\sigma^2 (\text{Å}^2)$</th>
<th>R factor (%)</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Na(AuCl4)]</td>
<td>4.000</td>
<td>0.00229</td>
<td>2.10000</td>
<td>2.29</td>
</tr>
<tr>
<td>FSL 1</td>
<td>4.000</td>
<td>0.00043</td>
<td>2.30000</td>
<td>2.39</td>
</tr>
<tr>
<td>FSL 2</td>
<td>4.000</td>
<td>0.00443</td>
<td>2.30000</td>
<td>2.28</td>
</tr>
<tr>
<td>FSL 3</td>
<td>4.000</td>
<td>0.00267</td>
<td>2.30000</td>
<td>2.28</td>
</tr>
</tbody>
</table>

#### 6.3 Functionalisation of Polymer Resin with Ligand 3 and Application in Metal Extractions

Polyacrylic (containing CO$_2$H and NH$_2$) resins were donated to this research by Magpie polymers. These were functionalised with ligand 3 – being the most effective at extracting precious metals. Extraction of Au(III) from aqueous solution was carried out in a column loaded with the resins. The metal solution was simply passed through the column in 2 h (resin 1) and the eluted solution analysed spectrophotometrically. 85% extraction was obtained using functionalised resins 1 and 2. Elution from resin 2 was however much slower (overnight).

Further testing of the polymer resins using a mixed metal solution was carried out in order to determine selectivity. The eluted extracted solution was clear and colourless compared to the dark yellow stock solution. ICP-MS analysis of the extracted mixed metal solution is underway.
6.4 CONCLUSION

The use of fluoropolymers as a solid support has been explored. Physisorption of fluorinated compounds on a self-assembled monolayer of fluorinated thiols on a gold surface was analysed. This showed that fluorinated surfaces such as Teflon, Gore-Tex® and Rastex® with more surface area may be used as solid support by way of physisorption. Successful physisorption was followed by desorption. The order of desorption of the extractants from the PFSAM surface was of the order 3>2>1 and this has been attributed to the size and structure of the extractants thus suggesting tuneable systems in terms of reversible and irreversible physisorption. Fluorinated extractants were therefore physisorbed on Teflon® through C-F···F-C interactions and quantitatively characterised by TGA and TGA-FTIR analysis and elemental analysis and shown to contain 11-17 %wt and 0.09-0.12 g/mol respectively of the samples. Total coverage of Teflon and a multi-layered ligand particle deposition were also observed from the Raman mapping and SEM analysis.

The non-conventional fluoropolymer-supported solid-liquid extraction featuring Au(III) showed similar extraction efficiency as in the liquid-liquid extractions although with longer extraction times. Stripping of the extracted metals from the ligand was achieved using a 3M HNO₃ from the solid supported ligands. The solid supports were reused in 4 extraction cycles and found to have minimal decrease in extraction efficiency and no significant
leaching. The extractants were desorbed off the Teflon® support to recover the free ligand which demonstrates similar reversibility as seen with PFSAM surfaces.

The nature of co-ordination sphere around the Au(III) are being studied using EXAFS.

6.5 EXPERIMENTAL

All ligands were synthesized as described in chapter 2. All solvents were obtained from commercial sources and used as received. The Teflon® tape (PTFE Thread Seal Tape BS 7786: 1995 Grade L) was obtained from commercial sources. Metal solutions were prepared by dissolving a weighed amount of Sodium Tetrachloroaurate (Johnson Mathey Chemicals, England) in acidified H₂O. The working solutions of these metals had a pH of 2. All spectrophotometric analysis were obtained using the Lambda 1050 UV-Vis NIR, using fused silica cells with a path length of 1 cm. All thermogravimetric analysis were measured on the Perkin Elmer Pyris 1 TGA heating at 10 °C/minute in Nitrogen atmosphere. Raman mapping were performed using a Witec Alpha 300R confocal Raman microscope, utilising a 532 nm laser and an 1800 lines/mm grating. A laser power of less than 1 mW was used for all measurements in order to avoid sample damage. Raman maps were obtained by measuring four discrete spectra every μm in the x and y direction. SEM Imaging of the ligands coated Teflon® was confirmed by using Carl Zeiss Ultra with an accelerating voltage of 5 kV using an in-lens detector. All IRRAS spectra were collected on a Fourier Transform Infrared (FTIR) spectrometer (Tensor 27, Bruker) equipped with a Mercury Cadmium Telluride (MCT) detector, a Zinc Selenide polarizer and a specular reflectance accessory (VeeMax II). 256 spectra were collected at 4 cm⁻¹ resolution at 80° incidence p-polarized light using a bare gold substrate as background; spectra were baseline corrected using FTIR software (WinFIRST). The elemental analyses were perform on the Exeter Analytical CE
Development of Fluoropolymer Solid Support

440 elemental analyser. $^1$H, and $^{19}$F NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400.23 MHz, 155.54 MHz and 376.55 MHz respectively, or a Bruker Advance II 600 NMR with a TCI cryoprobe spectrometer operating at 150.92 MHz ($^{13}$C) and were referenced to the residual $^1$H or external CFCl$_3$. IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer with attenuated total reflectance (ATR) accessory.

Percentage extraction (%E) of metal ion was determined by the Equation:

$$\% E = \frac{[M]_{aq, initial} - [M]_{aq}}{[M]_{aq, initial}} \times 100$$

Where M is the investigated metal ions. Each sample was repeated, 3-4 times and uncertainties in the extraction measurements are ±3%. Cumulative error including sampling phases and other volumetric operations are uniformly taken to be ±5%.

6.5.1 Preparation of Perfluorinated Self-Assembled Monolayers

PF-SAMs of $1H,1H,2H,2H$-perfluorodecanethiol were prepared according to previous reports.$^{39}$ The gold substrates were immersed in 1.0 mM solutions of $1H,1H,2H,2H$-perfluorodecanethiol in absolute ethanol for 1 h under argon flow. The surfaces were vigorously rinsed three times with absolute ethanol, sonicated for 2 min to remove any physisorbed species and dried under argon. The PF-SAM coated gold substrates were then immersed for 30 min in 1.0 mM solutions of compounds 1-3 in acetone. The substrates were rinsed three times with acetone and dried under argon prior to IRRAS characterization. Following measurements, the substrates were sonicated for 60 min in acetone to remove physisorbed species and IRRAS measurements repeated.

6.5.2 Synthesis of Teflon® supported ligands

Teflon® strips of (20 mg, 2 x 1 cm) were stirred in a solution of the ligands 1, 2 and 3 (90 mg) dissolved in IPA/H$_2$O (1:1 v/v). The mixture was heated to 70 °C for 24 h to evaporate all solvent. The strips were washed several times with H$_2$O (5 x 5 cm$^3$) to remove all non-adsorbed ligands. The last washing was examined by $^{19}$F NMR to ensure absence of the ligand in the last washings.
6.5.3 Solid-liquid metal extraction

5 cm³ Aliquots of the Au(III) stock solution (1 x 10⁻³ M,) in water was added to solutions of 0.5 molar equivalents ligand on Teflon® sample (18% ligand) and stirred for the required time. Solutions of Fe(III), Co(II) and Cr(VI) (50ppm) Were similarly treated with Teflon coated with 1 molar equivalent of 4. The concentration of the metal solutions were determined periodically by spectrophotometric analysis.

6.5.4 Back extraction

Solid-liquid stripping was achieved by collecting the solid sample and similarly treated with 3 M HNO₃ (5 cm³). The concentrations of the aqueous phases were examined by spectrophotometric measurements.

6.5.5 Functionalisation of the Polymer Resin and Metal Extractions

The polymer resins (2g) were washed twice with MeOH (10 ml) and diethyl ether (10 ml) to remove their water content. The resins were dried overnight and then slowly stirred in the ligand solution (0.2g in 10 ml DCM) until all solvent evaporated and then dried in the oven overnight at 50 °C.

The resins were poured into a burette plugged at the neck with 2-3 mm of cotton wool. The resins were washed twice with deionised water and then dried as much as possible by blowing Ar through. 10 ml of Au solution (0.02 g Au) or the mixed metal solution (0.02 g Au, Pt, Pd, Fe, Ni and Cu in 100 ml) was added and then allowed to flow out slowly (resin 1 = 2; resin 2 overnight). The Au solution was analysed using spectrophotometric analysis while the mixed metal solution was analysed by ICP-MS.
6.6 REFERENCES

Conclusion

AND FUTURE WORK
CONCLUSION

Electrical and electronic equipment contains a plethora of energy critical metals including precious metals and lanthanides. In an attempt to reclaim some of these metals, a series of fluorinated extractants with different donors, based on the calix[4]arene, Tris-(2-Aminoethyl)-Amine (Tren), Trithiacyclononane (TTCN) and Propylenediaminetetraacetic acid (PDTA) scaffolds have been synthesised.

The synthesis of the Tren amido ligand was successful and in high yield. En route to the Tren ligand, a perfluorinated acid was isolated and careful analysis shows that the commonly observed twisting of perfluorinated chain is absent in this compound. Computational analysis reveals that the non-twisted conformer is the least energetically stable conformation. The synthesis of the calix[4]arene amido ligands including the cone and partial cone conformers was successful and in high yield. En route to the calixarene ligands, a fluororous triazole compound was isolated. This mechanism of the reaction have been hypothesised as Huisgen 1,3-Dipolar Cycloaddition with the stereospecific feature of a Click chemistry. The synthesis of the calixaryl phosphine and calixaryl phosphine oxide ligands was successful but in low yields. The 9-ane-S3 ligand could not be obtained as functional group interconversion of the precursor was hampered by the electronic effect of the fluorine groups. The synthesis of PDTA ligand proved to be the most straightforward with moderate yield although the relatively expensive starting material doesn’t encourage scale-up of the synthesis.

These ligands have been employed in extraction of Au$^{3+}$, Pt$^{2+}$, Pd$^{2+}$, Nd$^{3+}$, Eu$^{3+}$ and Er$^{3+}$ from aqueous solutions. For all the amido ligands tested, Au(III) was the most extracted. > 96% extraction efficiency achieved for Au(III) with the partial cone calixarene ligand. Poorer efficiency in Pt, Pd and Eu extractions points to selectivity of both ligands toward Au(III). The metal-ligand interaction in the Au(III) complexes have be thoroughly investigated using spectroscopic methods including small angle X-ray scattering (SAXS). The amide derivative of the cone calix[4]arene ligand was the most perturbed in terms of size and speciation in solution. The hard donor calixaryl phosphine oxide ligand was tested in Ln$^{3+}$ extraction from the aqueous phase. 84, 90, and 80% extractions were obtained for Nd$^{3+}$, Eu$^{3+}$ and Er$^{3+}$ respectively.
The synthesis of fluorinated compounds also led to interesting observation in fluorine chemistry. Fluorine possesses low polarizability and this makes the interatomic dispersive forces rather low according to Paulings principle. However, perfluorinated acids wherein fluorine-fluorine interactions are present in the solid state and are not simply due to crystal packing but were shown to be stabilizing and give a significant energy contribution to the structures. Computational studies showed that these Fluorine-Fluorine stabilization energy are of the same order of magnitude as a typical hydrogen bond. Substitution of the acid group with an azide group with less propensity to be involved in hydrogen bond was also analysed in the solid states and C-F…F-C interactions were also present. Further investigation in the solid state by solid state $^{13}$C NMR shows aggregation shift when compared to the solution $^{13}$C NMR. The diffusion studies in solution revealed the presence of a multimeric species of the fully fluorinated acid which calls for further studies of these NCIs in the solution and gas phase.

These non-covalent interactions have also been harnessed in extraction of Perfluorooctanoic Acid (PFOA) from water. PFOA is a persistent organic pollutant that has been associated with diseases including cancer and kidney diseases. It is has been detected in water, soil, blood serum of animals and humans. Extraction of PFOA is engendered by incorporation of fluororous “ponytails” into our extractant/host in order to evoke C-F…F-C interaction between the fluorous groups of the ligands and PFOA. PFOA was consistently extracted in 83, 98, 83% with 1, 2 and 3 respectively. The nature of the host-guest complexes was determined to be stable 1:1 complexes with 2 and 3 while 1 is favours higher stoichiometry and the role of C-F…F-C interaction has also been extensively studied in solution 1D, 2D and solid state NMR spectroscopy, thermogravimetric analysis and computational studies unambiguous results showed formation of weak host-guest complexes. Interestingly, there was no change in the $^1$H NMR spectrum which the non-fluorinated octanoic acid is titrated against 2.

Fluorine-Fluorine interactions has also been extended to development of solid support. Physisorption on a modelled fluorinated surface successful demonstrated the potential scope of the idea and conditions required to modulate the strength of physisorption. Physisorption of fluorinated compounds on a fluoropolymer was thereby carried out harnessing these stabilising C-F…F-C interaction. Easy adsorption and desorption of the fluorinated compounds has been shown and characterised by AFM, SEM, TGA-IR. The supported extractants were applied in metal extractions with superb results and minimal leaching. EXAFS analysis of the metal ligand complexes are consistent with outer sphere ligand interactions and corroborates the spectroscopic characterisations. This has also been
extended to development of functionalised Polymer resins. The resins functionalised with 3 was tested in the extraction of Au from Au solution and a mixed metal solution. Quantitative extraction from the Au solution was achieved with the resins. The mixed metal solution analysis is currently on-going.

**FUTURE WORK**

Further investigation on fluorous interactions are being conducted. It is expected that if the line broadening is due to coupling, upon dilution, the resonance peak would become sharper. Therefore a serial dilution in the solid state using and NMR inactive compound, KBr has used in the dilution. Further solution phase characterisation using DOSY and various solvents would show the effect of polar, non-polar and fluorinated solvents on fluorous interaction. SAXS characterisation of the sizes of some simple fluorinated acids in solution compared to other solution and solid state characterisation will be useful in determining aggregation and the extent of fluororous interactions in the solution phase. The absence of the commonly observed twisting of hydrocarbon chains in 2H,2H-Perfluorooctanoic acid, 42 will be further probed using various pressure crystallographic studies. Gas phase studies of the fluorinated compounds using microwave spectroscopy with be highly useful in characterising fluorous interactions as it enables measurement under condition of effective isolation of molecules, avoiding perturbations of the ground state structure from solvent or lattice effects.

Further ligands modifications will be considered as the donor groups can be easily changed in order to change the selectivity of the ligands for other metals. Other sizes of the calixarene could give a fit with better metal ions of interest. The length and position of the fluorinated chains will also be modified to enhance solubility in fluorinated solvent. The tert-buty groups in the calixarene will be substituted with the long fluorinated chains leaving metal complex the lower rim. Other substitution may include urea function at the upper or lower rim. Less fluxional group like fluoro-phenyl groups can also be used in place of the fluorinated chains in order to obtain a more compact structure which is more likely to crystallise. The synthesised phosphine oxide ligand will be used in more metal extractions involving all the lanthanides. The synthesis of the phosphine oxide ligands will be scaled up in other to allow further studies with the ligand. Optimum Ln$^{3+}$ extractions condition for the phosphine oxide ligand will be carried out. Extraction of all Ln$^{3+}$ in order to establish any possible trend that could lead to Lanthanides/Actinides separation.
Solid support synthesis can be extended to other fluoropolymer with more surface area such as Gore-Tex and Rastex in order to maximise metal extraction. The synthesize phosphine oxide ligand will also be used in development of functionalised solid support. Ln$^{3+}$ extractions will also be explored using the fluoropolymer supported phosphine oxide. The work on the polymer resins will be extended to the phosphine oxide ligands with the aim of lanthanide extraction. Extensive process optimisation and resin characterisation is also required in order to determine loading, rate of extractions, leaching and reuse of resins.
Appendix

A – Crystallographic Data
B – Characterisation data for ligands and precursors
C – Characterisation of Fluorous-Fluorous Interactions
D – Characterisation of host guest complexes
APPENDIX A

X-Ray Crystallographic Data

Crystal data and structure refinement for 41

Identification code tcd274
Empirical formula C₈H₁₅F₁₅O₂
Formula weight 414.09
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group Pī
Unit cell dimensions
\[ a = 9.9639(17) \text{ Å} \quad \beta = 96.641(4)^\circ. \]
\[ b = 10.7932(18) \text{ Å} \quad \gamma = 90.839(4)^\circ. \]
\[ c = 23.575(4) \text{ Å} \quad \delta = 90.018(4)^\circ. \]
Volume 2518.0(7) Å³
Z 8
Density (calculated) 2.185 Mg/m³
Absorption coefficient 0.296 mm⁻¹
F(000) 1600
Crystal size 0.430 x 0.100 x 0.030 mm³
Theta range for data collection 0.870 to 25.499°.
Index ranges -9≤h≤12, -13≤k≤13, -28≤l≤28
Reflections collected 25077
Independent reflections 9338 [R(int) = 0.0630]
Completeness to theta = 25.242° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7455 and 0.6740
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 9338 / 846 / 906
Goodness-of-fit on F² 1.045
Final R indices [I>2σ(I)] R1 = 0.0971, wR2 = 0.2500
R indices (all data) R1 = 0.1549, wR2 = 0.2831
Largest diff. peak and hole 1.019 and -0.563 e.Å⁻³
Appendix

Crystal data and structure refinement for 42

Identification code  tcd72_1
Empirical formula  C8 H3 F13 O2
Formula weight  378.10
Temperature  93(2) K
Wavelength  0.71073 Å
Crystal system  Triclinic
Space group  P -1
Unit cell dimensions  
  a = 5.1220(10) Å  \( \alpha = 88.91(3)^\circ \)
  b = 6.1827(12) Å  \( \beta = 87.15(3)^\circ \)
  c = 18.005(4) Å  \( \gamma = 80.56(3)^\circ \)
Volume  561.7(2) Å³
Z  2
Density (calculated)  2.235 Mg/m³
Absorption coefficient  0.295 mm⁻¹
F(000)  368
Crystal size  0.300 x 0.240 x 0.100 mm³
Theta range for data collection  2.265 to 27.489°
Index ranges  -6<=h<=6, -6<=k<=7, -23<=l<=23
Reflections collected  8368
Independent reflections  2412 [R(int) = 0.0284]
Completeness to theta = 25.242°  95.3 %
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  1.0000 and 0.8931
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameters  2412 / 0 / 212
Goodness-of-fit on F²  1.171
Final R indices [I>2sigma(I)]  R1 = 0.0479, wR2 = 0.1398
R indices (all data)  R1 = 0.0496, wR2 = 0.1415
Extinction coefficient  n/a
Largest diff. peak and hole  0.425 and -0.307 e.Å⁻³
Appendix

Crystal data and structure refinement for 44

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<th>Value</th>
</tr>
</thead>
<tbody>
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</tr>
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APPENDIX B

Characterisation data for ligands 1 and its precursors

Appendix B 1. $^1$H NMR spectrum of 9 in acetone-d$_6$.

Appendix B 2. $^{13}$C($^1$H) NMR spectrum of 9 in acetone-d$_6$. 
Appendix B3. $^{19}$F NMR spectrum of 9 in acetone-$d_6$.

Appendix B4. $^{19}$F-$^{19}$F COSY NMR spectrum of 9 in acetone-$d_6$. 
Appendix B 1. $^1$H NMR spectrum of 10 in CDCl$_3$.

Appendix B 2. $^{13}$C NMR spectrum of 10 in CDCl$_3$.

Appendix B 3. $^{19}$F NMR spectrum of 10 in CDCl$_3$. 
Appendix B 4. HSQC spectrum of 10 in CDCl₃.

Appendix B 5. Infrared spectrum of 10
Appendix

Appendix B 6. HRMS spectrum of 10

Appendix B 7. $^1$H NMR spectrum of 1 in CDCl$_3$. 
Appendix B 8. $^{13}$C{$^{1}$H} NMR spectrum of 1 in CDCl$_3$.

Appendix B 9. $^{19}$F NMR spectrum of 1 in CDCl$_3$.

Appendix B 10. HSQC NMR spectrum of 1 in CDCl$_3$. 
Appendix B 11. Mass spectrometry and HRMS data for 1.
Appendix B 12. $^1$H NMR spectrum of 16 in CDCl$_3$. Insert shows zoom in of the peak at 6.2 ppm.
Appendix B 13. $^{13}$C($^1$H) NMR spectrum of 16 in CDCl$_3$.

Appendix B 14. $^{19}$F NMR spectrum of 16 in CDCl$_3$. 
Appendix B 15. \(^{19}\text{F}\)-\(^{19}\text{F}\) COSY NMR spectrum of 16 in acetone-d\(_6\).

Appendix B 16. \(^1\text{H}\) NMR spectrum of 2 in CDCl\(_3\).
Appendix

Appendix B 17. $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 2 in CDCl$_3$.

Appendix B 18. $^{19}$F NMR spectrum of 2 in CDCl$_3$. 
Appendix

Characterization data for ligand 3

Appendix B 20. $^1$H NMR spectrum of 3 in CDCl$_3$.

Appendix B 21. $^{13}$C{$^1$H} NMR spectrum of 3 in CDCl$_3$.

Appendix B 22. $^{19}$F NMR spectrum of 3 in CDCl$_3$. 
Appendix B 23. Mass spectrometry and HRMS data for 3.
Appendix

Characterization data for host 4 and its precursors

Appendix B 24. $^31$P NMR spectrum of 21 in CDCl$_3$.

Appendix B 25. $^31$P NMR spectrum of 21 in CDCl$_3$. 
Appendix B 26. $^{31}$P NMR spectrum of 22 in CDCl$_3$.

Appendix B 27. $^{31}$P NMR spectrum of 4 in CDCl$_3$.

Characterization data for host 5 and its precursors

Appendix B 28. $^1$H NMR spectrum of 5 in CDCl$_3$. 
Appendix

Appendix B 29. $^{31}$P NMR spectrum of 5 in CDCl₃.

Appendix B 30. $^{19}$F NMR spectrum of 5 in CDCl₃.

Appendix B 31. $^{13}$C NMR spectrum of 5 in CDCl₃.
Appendix B 32. Infrared spectrum of 5

Characterization data for host 6 and its precursors

Appendix B 33. $^1$H NMR spectrum of 36 in CDCl$_3$. 

Appendix B 34. $^{13}$C NMR spectrum of 36 in CDCl$_3$. 

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Appendix B 35. $^{19}$F NMR spectrum of 36 in CDCl$_3$.

Appendix B 36. Infrared spectrum of 36

Appendix B 37. $^1$H NMR spectrum of 29 in CDCl$_3$. 
Appendix B 38. $^{13}$C NMR spectrum of 29 in Acetone-$d_6$.

Appendix B 39. $^{19}$F NMR spectrum of 29 in CDCl$_3$.

Appendix B 40. Infrared spectrum of 29 in CDCl$_3$. 
Appendix B 41. HRMS spectrum of 30 in CDCl₃.

Appendix B 42. ¹H NMR spectrum of 30 in CDCl₃.

Appendix B 43. ¹H NMR spectrum of 30 in Acetone-d₆.
Appendix B 44. $^{13}$C NMR spectrum of 30 in Acetone-$d_6$.

Appendix B 45. $^{13}$C DEPT spectrum of 30 in Acetone-$d_6$.

Appendix B 46. $^{19}$F NMR spectrum of 30 in Acetone-$d_6$. 
Appendix

Appendix B 47. HSQC spectrum of 30 in Acetone-d₆.

Appendix B 48. Infrared spectrum of 30.

Appendix B 49. ¹H NMR spectrum of 31 in Acetone-d₆.
Appendix B 50. $^{19}$F NMR spectrum of 31 in Acetone-$d_6$.

Appendix B 51. Infrared spectrum of 31.

Appendix B 52. $^1$H NMR spectrum of 32 in Acetone-$d_6$. 
Appendix

Appendix B 53. $^{13}$C NMR spectrum of 32 in Acetone-$d_6$.

Appendix B 54. $^{19}$F NMR spectrum of 32 in Acetone-$d_6$.

Appendix B 55. Infrared spectrum of 32.
Appendix B 56. Infrared spectrum of 33.

Appendix B 57. HRMS spectrum of 34 in Acetone-d₆.
Appendix

Appendix B 58. $^{13}$C NMR spectrum of 34 in CDCl$_3$.

Appendix B 59. $^{19}$F NMR spectrum of 34 in Acetone-d$_6$.

Appendix B 60. Infrared spectrum of 34

Name | Description
---|---
HO$_3$-3-4BISTHANE | Sample 033 By omorodih Date Tuesday, January 20 2015
Appendix B 61. $^1$H NMR spectrum of 7 in CDCl$_3$.

Appendix B 62. $^{19}$F NMR spectrum of 7 in CDCl$_3$.

Appendix B 63. Infrared spectrum of 7
APPENDIX C

Characterisation of Fluorous-Fluorous Interactions

Solid State $^{13}$C{1H} NMR spectrum of 41: See Appendix C15

Solid-State $^{19}$F NMR spectrum of 41: See Appendix C16

Table C 1. Basis set superposition error and dispersion contribution to interaction energy (in kcal/mol).

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<tr>
<td>2c</td>
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<tr>
<td>2d</td>
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<tr>
<td>2e</td>
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Interaction energy calculated as $IE = E_{\text{dimer}} - E_{\text{monomer1, CP}} - E_{\text{monomer2, CP}}$, where CP indicates that the monomer energy has been counterpoise corrected. All geometries were extracted from crystal structure without further modification.
Appendix C 2. Solid-State $^{19}$F NMR spectrum of 42 (* indicates spinning side bands).

Appendix C 3. Solid-State $^{19}$F NMR spectrum of 44
Appendix C 4. Solid-State $^{19}$F NMR spectrum of 45.

Appendix C 5. Solid-State $^{19}$F NMR spectrum of 46.

APPENDIX D

Characterisation of host guest complexes.
Appendix D 1. $^1$H NMR spectrum of PFOA in CDCl$_3$.

Appendix D 2. $^{13}$C/$^1$H NMR spectrum of PFOA in CDCl$_3$.

Appendix D 3. $^{19}$F NMR spectrum of PFOA in CDCl$_3$.

Thermal characterization of hosts and host:guest complexes
Appendix

Appendix D 4. DSC Thermogram of PFOA.

Appendix D 5. DSC Thermograms of 2 (top), 1:1 complex (middle) and 2:1 complex (bottom).

Appendix D 6. DSC Thermograms of 3 (top), 1:1 complex (middle) and 2:1 complex (bottom).
Appendix D 7. DSC Thermograms of 1 (bottom), 1:1 complex (middle) and 2:1 complex (top).

Appendix D 8. TGA of 2 and its 1:1 and 2:1 host:guest complexes.

Appendix D 10. TGA of 1 and its 1:1 and 2:1 host:guest complexes.
Appendix D 11. Analysis of $\delta_H$ changes upon addition of 0-20 equivalents of PFOA.

Appendix D 12. Analysis of $\delta_H$ changes upon addition of 0-8 equivalents of PFOA.
Appendix

Appendix D 13. Analysis of $\delta_F$ changes upon addition of 0-8 equivalents of PFOA.

Solid-State NMR spectroscopy of hosts and host:guest complexes

Appendix D 14. $^{13}_C\{^{19}_F\}$ MAS NMR spectrum of PFOA at 20 kHz spin rate and 298 K.
Appendix D 15. $^{19}$F{$^{13}$C} MAS NMR spectrum of PFOA at 20 kHz spin rate and 298 K.

Appendix D 16. $^{13}$C{$^{19}$F} MAS NMR spectrum of 2 at 10 kHz spin rate and 298 K.

Appendix D 17. $^{19}$F{$^{13}$C} MAS NMR spectrum of 5 at 20 kHz spin rate and 298 K.
**Appendix D 18.** Deconvolution of CF₃ resonance from the $^{19}$F$^{13}$C MAS NMR spectrum of 2.

**Appendix D 19.** $^{13}$C ($^{19}$F) MAS NMR spectrum of 2:1PFOA at 10 kHz spin rate and 298 K.
Appendix D 20. $^{19}$F{$^{13}$C} MAS NMR spectrum of 2:1PFOA at 20 kHz spin rate and 298 K.

Appendix D 21. Deconvolution of CF$_3$ resonance from the $^{19}$F{$^{13}$C} MAS NMR spectrum of 2:1PFOA.
Appendix D 22. $^{13}C\{^{19}F\}$ MAS NMR spectrum of 3 at 10 kHz spin rate and 298 K.

Appendix D 23. $^{19}F\{^{13}C\}$ MAS NMR spectrum of 3 at 20 kHz spin rate and 298 K.
Appendix D 24. Deconvolution of CF$_3$ resonance from the $^{19}$F{$^{13}$C} MAS NMR spectrum of 3.

Appendix D 25. $^{13}$C{$^{19}$F} MAS NMR spectrum of 3:1PFOA at 10 kHz spin rate and 298 K.
Appendix D 26. $^{19}$F-{$^{13}$C} MAS NMR spectrum of 3:1PFOA at 20 kHz spin rate and 298 K (* indicates spinning side bands.

Appendix D 27. Deconvolution of CF$_3$ resonance from the $^{19}$F-{$^{13}$C} MAS NMR spectrum of 3:1PFOA.
Deconvolution analysis of the spectra of the CF$_3$ groups of the host 2, 3 and their host:guest complexes.

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Appendix D 28. $^{13}$C$\{^{19}$F$\}$ MAS NMR spectrum of 1 at 5 kHz spin rate and 298 K.

Appendix D 29. $^{19}$F$\{^{13}$C$\}$ MAS NMR spectrum of 8 at 5 kHz spin rate and 298 K (* indicates spinning side bands.)
Appendix D 30. $^{13}$C($^{19}$F) MAS NMR spectrum of 1:1PFOA at 10 kHz spin rate and 298 K.

Appendix D 31. $^{19}$F($^{13}$C) MAS NMR spectrum of 1:2PFOA at 20 kHz spin rate and 298 K.

Appendix D 32. $^{19}$F($^{13}$C) MAS NMR spectrum of 3 at variable spin rates 10, 15, 20 kHz (top to bottom) and 298 K.
Appendix

Appendix D 33. $^{19}\text{F}{}^{13}\text{C}$ MAS NMR spectrum of $3\text{PFOA}$ at variable spin rates 10, 15, 20 kHz (top to bottom) and 298 K

Appendix D 34. $^{19}\text{F}{}^{13}\text{C}$ MAS NMR spectrum of $3\text{2PFOA}$ at variable spin rates 10, 15, 20 kHz (top to bottom) and 298 K
Appendix D 35. $^{19}$F $\rightarrow$ $^{13}$C CP/MAS NMR spectrum of PFOA with a contact times 1, 2, 4, 6, 8, 10 ms (bottom to top).