

Detection of explosive vapors with a charge transfer molecule: self-assembly assisted morphology tuning and enhancement in sensing efficiency†

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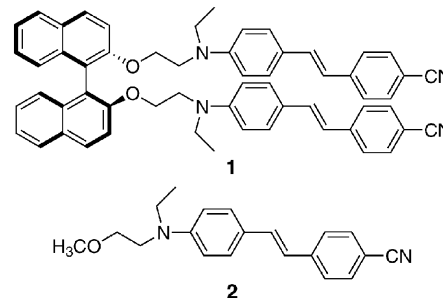
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Use of a fluorescent organic molecule consisting of binaphthyl functionalized with donor–acceptor substituted stilbenes for the detection of dinitrotoluene (DNT) and trinitrotoluene (TNT) vapors and enhancement in its sensing efficiency via self-assembly assisted morphology tuning are described.

Self-assembly of organic molecules with functional properties is an active area of research, aimed at creating novel materials with potential applications in nanosciences and nanotechnology.¹ The functionalities of such materials are significantly dependent on the supramolecular organization of the molecules and morphology of the resulting nanostructures. Through the control and modulation of molecular interactions, various kinds of self-assembled organic nanostructures with different morphologies such as fibers, tapes, wires, rods, tubes and particles have been reported.² However, self-assembly of rationally designed molecular components into a prerequisite nanostructure, which enhances its functional properties, still remains a great challenge. Here we report such a system (**1**) which is potentially useful for the detection of explosive vapors^{3–5} (DNT and TNT) through fluorescence quenching in the film state. A nearly 9-fold increase in the explosive vapor detection efficiency was achieved through self-assembly assisted morphology tuning.

The molecule under study (**1**) consists of an (*S*)-binaphthyl moiety functionalized with donor–acceptor substituted stilbenes in the 2,2′-positions. The binaphthyl group, which is chiral in nature due to the restricted rotation of the naphthalene rings, can induce its chirality in the attached chromophores in the self-assembled state resulting in helical organization of the attached chromophores.⁶ Donor–acceptor substituted stilbenes act as the functional chromophore often showing intense absorbance and fluorescence through the charge transfer interaction between the dialkyl amine (donor) and cyano (acceptor) groups.⁷ We chose this design strategy because the helical organization of the stilbene chromophores induced by the binaphthyl group may help to prevent

fluorescence quenching in the self-assembled state thereby making it possible to utilize this material for sensing applications.⁸ It is anticipated that the presence of analytes with enhanced electron acceptor properties compared to those of cyano (such as nitro derivatives like DNT and TNT) can effectively switch off the charge transfer fluorescence *via* a photoinduced electron transfer process; this process would result in the detection of those particular analytes. The stilbene part was synthesized by using known methods in the literature. A modified Mitsunobu reaction was used for functionalizing the binaphthyl group with stilbene moieties through ether linkages.⁹ A molecule without the binaphthyl unit (**2**) was also synthesized and studied for comparison. Both derivatives were characterized by various analytical techniques.¹⁰



Absorption and emission studies of **1** and **2** in various solvents (1×10^{-6} M) with different polarity were conducted. The absorption spectra of these derivatives were fairly insensitive to the solvent polarity, whereas the emission spectra exhibited a significant red-shift in the emission maximum with increasing solvent polarity, indicating an intramolecular charge transfer interaction between the amino and cyano groups. Both derivatives were weakly fluorescent in solution and exhibited quantum yields below 10%.¹⁰ However, they showed bright yellowish-green fluorescence with relatively high quantum yield in the film state. For instance, drop casted films of **1** and **2** from chloroform solution showed quantum yields of 33% and 24%, respectively. Films prepared from other solvents and solvent mixtures also showed similar values.¹⁰ The observed enhancement in quantum yields could be in general due to a more planar conformation of *trans*-stilbene in the film state. The pronounced enhancement for **1** can be attributed to the presence of the chiral binaphthyl group. This is an added advantage for these molecules for sensor applications in the film state. The sensing ability of these molecules was studied in the film state by exposing films to DNT and TNT

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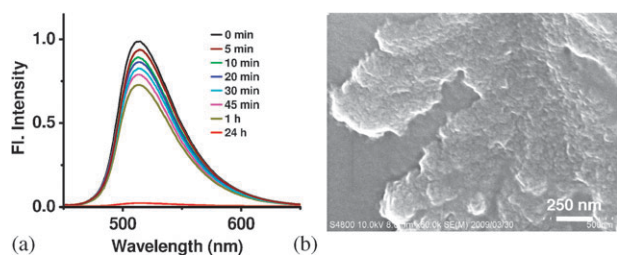


Fig. 1 (a) Fluorescence spectra of **1** drop casted from chloroform solution on exposure to saturated DNT vapors at different times and (b) SEM image of the corresponding film.

vapors. Film of **1** drop casted from chloroform showed 12% fluorescence quenching on exposure to saturated DNT vapors for 10 min (Fig. 1a). Nearly 98% quenching was observed on continuous exposure for 24 h. However, the rate of quenching at the initial time scale was poor compared to that of the systems reported in the literature.^{4,5} This might be due to slow diffusion of the explosive vapors in the film. SEM analysis confirmed this possibility, showing no definite morphology for **1** when it was drop casted from chloroform (Fig. 1b). In such a film, the available surface area for the interaction with quencher molecules is a minimum resulting in slow fluorescence quenching.

It is known that entangled fibrous or porous structures are ideal morphologies for detection of gaseous analytes with high efficiency. These morphologies can increase the total surface area and enhance the diffusion of the gaseous adsorbents, thereby enhancing the sensing efficiency. For organic molecules, self-assembly can be used as a tool for the realization of such morphologies. Self-assembly of **1** was studied in chloroform–toluene mixtures. Circular dichroism (CD) spectroscopic studies of **1** in chloroform–toluene mixtures showed an induced CD signal in the absorption range of stilbene which is enhanced with an increase in the vol% of toluene (Fig. 2a). This clearly indicates the self-assembly process leading to the formation of hierarchical helical assemblies. Self-assembly of **1** could be mainly due to the dipole interactions between the stilbene groups assisted by the solvophobic environment provided by toluene, which is a poor solvent for **1**. The presence of chiral binaphthyl groups biases the organization of the stilbene chromophore in a helical way. The CD intensity reached a maximum when the vol% of toluene reached 75% and then started to decrease with increasing amounts of toluene. This could be an indication that high vol% toluene destabilizes the self-assembled nanostructures resulting in less ordered structures. Interestingly, the solution of **1** in 75 vol% of toluene formed a gel type material which is highly thixotropic in nature. SEM analysis of this material showed the formation of entangled networks of fibres 50–100 nm in diameter and several micrometres in length (Fig. 2b). As expected, this film exhibited enhanced response towards DNT vapors. It showed fluorescence quenching of 91% on exposure to saturated DNT vapors for 10 min (Fig. 2c). Using fluorescence microscopy, detection of explosive vapors *via* fluorescence quenching was clearly visible (Fig. 2c inset). The bright yellowish-green fluorescence of the pristine film showed remarkable quenching on exposure to saturated DNT vapors.

In accordance with the CD studies, when the ratio of toluene increased above 75%, the fibrous morphology started to deform, consequently a significant decrease in the fluorescence quenching

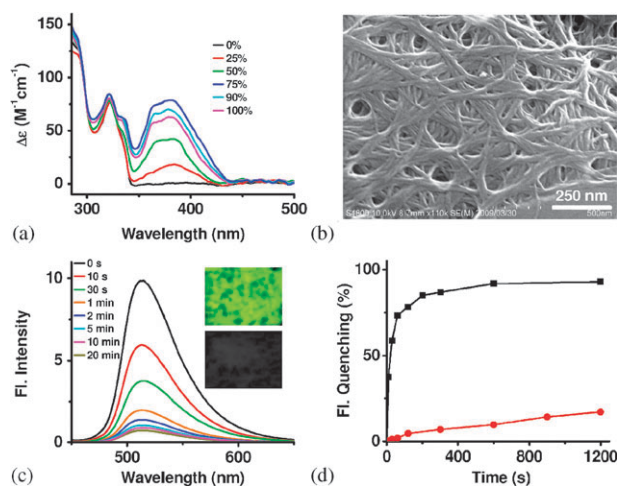


Fig. 2 (a) Change in CD spectra of **1** in chloroform with increasing volume of toluene. (b) SEM images of **1** drop casted from 1:3 (v/v) chloroform–toluene mixture and (c) the corresponding fluorescence spectra of the film on exposure to saturated vapor of DNT at different times. Inset shows the fluorescence microscope images of the same film before (top) and after (bottom) exposure to DNT vapors for 10 min. (d) Relative fluorescence quenching of films drop casted from chloroform (red) and 1:3 (v/v) chloroform–toluene mixture (black) on exposure to DNT vapors.

efficiency on exposure to DNT vapors was observed. The film drop casted from a 1:9 (v/v) chloroform–toluene mixture formed globular type structures (Fig. 3a) which showed 54% fluorescence quenching on exposure to DNT vapors for 10 min. When 100% toluene was used as the solvent, **1** formed well defined spherical objects with a nanoporous surface (Fig. 3b). Since the nanoporous structures were also ideal for vapor detection, as in the case of fibrous morphology, they showed efficient fluorescence quenching in the presence of DNT vapors (81% quenching on exposure for 10 min). The change in morphology with increasing vol% of toluene could be due to the change in polarity of the solvent mixture modulating the dipole–dipole interactions between the molecules during the self-assembly process. A stilbene derivative without the binaphthyl unit (**2**) was also studied under similar conditions. **2** was unable to self-assemble in chloroform–toluene mixture at any composition and exhibited flake like morphology in the drop casted films (Fig. 3c). The fluorescence quenching efficiency for the molecule in the film state was found to be around 14%.

The use of **1** for the detection of TNT vapors was also studied. A film drop casted from 1:3 (v/v) chloroform–toluene mixture showed efficient quenching of fluorescence when exposed to saturated TNT vapors. However, the quenching efficiency was found to be less when compared to that of DNT vapors (Fig. 4a). On exposure for 10 min, only 72% quenching was observed in presence of TNT compared to that of 91% for DNT. The vapor pressure of TNT is known to be 20 times lower than that of DNT. This could be the reason for the reduced fluorescence quenching of **1** in presence of TNT compared to that of DNT. More insight into the fluorescence quenching mechanism of **1** on exposure to explosive vapors was obtained from *ab initio* calculations. Geometry optimization and energy calculation were performed with density-functional

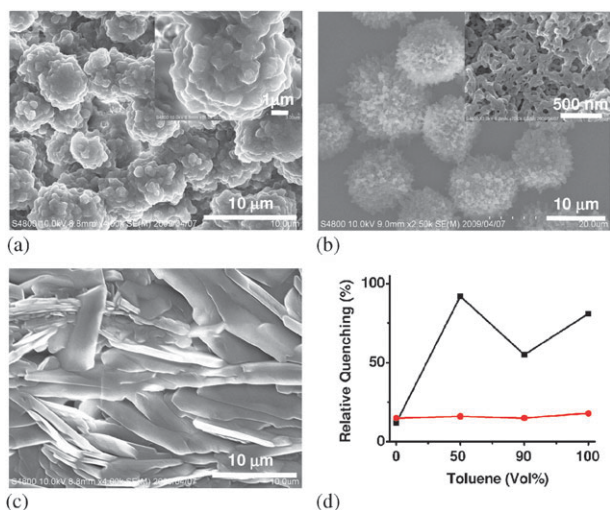


Fig. 3 SEM images of **1** drop casted from chloroform–toluene mixture containing (a) 90% and (b) 100% of toluene with zoomed images in the inset. (c) SEM image of **2** drop casted from 1:3 (v/v) chloroform–toluene mixtures. (d) Relative fluorescence quenching of **1** (black) and **2** (red) films drop casted from solutions with different vol% of toluene on exposure to saturated DNT vapors for 10 min.

theory at the B3LYP/6-31G* level and show that the HOMO and LUMO of **1** is at -5.1 and -1.7 eV, respectively (Fig. 4b). LUMO of DNT and TNT were found to be -3.3 and -3.8 eV, respectively. This indicates that photoinduced electron transfer is possible between **1** and quencher molecules resulting in fluorescence quenching of the former. The driving force for the photoinduced electron transfer between **1** and the quenchers is 1.6 and 2.1 eV for DNT and TNT, respectively.

In summary, a fluorescent charge transfer molecule consisting of binaphthyl functionalized with donor–acceptor substituted stilbenes was designed and synthesized. The charge transfer induced fluorescence of this molecule was quenched on exposure to explosive vapors such as DNT or TNT as a result of photoinduced electron transfer which allows the detection of the latter. The sensing efficiency was significantly enhanced by self-assembly assisted morphology tuning. This work illustrates the application of self-assembly for the enhancement of functional properties of organic molecules to make them suitable for useful applications.

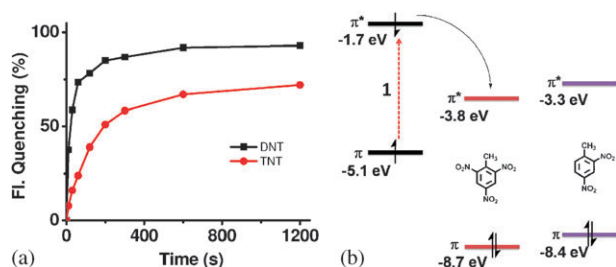


Fig. 4 (a) Fluorescence quenching of **1** when exposed to DNT (black) and TNT (red) vapors. (b) HOMO and LUMO energy levels of **1**, TNT and DNT.

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