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Supramolecular polymer for explosives sensing: role of H-bonding in enhancement of sensitivity in the solid state†‡

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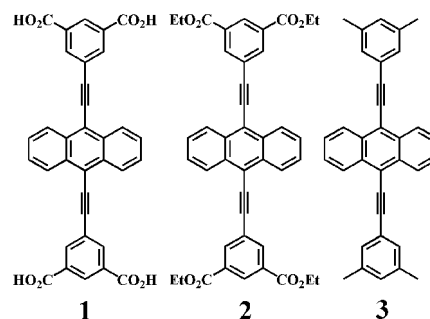
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A π -electron rich supramolecular polymer as an efficient fluorescent sensor for electron deficient nitroaromatic explosives has been synthesized, and the role of H-bonding in dramatic amplification of sensitivity/fluorescence quenching efficiency in the solid state has been established.

Research on suitable chemical sensors with high sensitivity for the detection of explosives has attracted much attention in recent time for wide applications in security screening and environment monitoring.¹ Currently, a wide range of instrumental techniques are being employed to detect explosives such as TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene) and PA (picric acid), which are the primary constituents of many unexploded land mines worldwide.² Among these competing methods, fluorescence quenching based detection of explosives has grown enormously owing to its high sensitivity, easy visualization and real-time monitoring with fast response time.³ Nitroaromatics (NAC) often act as good electron acceptors due to the presence of electron withdrawing nitro ($-\text{NO}_2$) group/s. Several π -electron rich conjugated covalent polymers have been used greatly as promising candidates for explosives sensing.¹ The high sensitivity of these conjugated polymers, often, comes from the so-called signal amplification effect, where the polymer backbone acts as a molecular wire to enable the rapid long-range exciton migration.^{1,4} However, the real time utilization of these polymeric materials is limited for several issues. Firstly, the traditional covalent synthesis of organic polymers involves multi-step synthesis, is time consuming and usually ends in low yield of the target products. Secondly, the control of molecular organization or structure determination is not easy for their non-crystalline nature/poor solubility.⁵ Therefore, development of new kinds of sensors that can overcome these problems but still enable the long-range exciton migration for better sensitivity is an ever increasing demand. An alternative way would be

the use of supramolecular polymers in which two or more molecular entities self-associate to adopt an infinite network having well defined molecular organization and large internal porosity.⁶ Compared to covalent organic polymers, supramolecular polymers are easy to synthesize from judiciously pre-designed molecular building units. Moreover, they are soluble in common solvents, and are crystalline in nature. Can supramolecular polymers substitute the traditional covalent polymers in sensing explosives? Can non-covalent interaction like H-bond influence the sensitivity/efficiency of such kind of sensors? Herein we report a π -electron rich supramolecular polymer 9,10-bis(1,3-dicarboxylicphenyl-5-ethynyl)anthracene **1** as a new type of chemosensor and its discrete analogues (**2** and **3**, Chart 1) for selective detection of nitroaromatic explosives such as TNT and PA both in solution as well as in thin-film. Solution phase sensing study gives an idea about the sensing capability of the sensors, while for infield practical application solid state sensing is most appealing. Advantages of solid sensors over solution sensors are reusability and ease/possibility of making into devices. We report here that indeed supramolecular interaction like H-bond can influence dramatic change in sensitivity/efficiency of the sensor in the solid state.

The sensors (**2–3**) were synthesized from 9,10-dibromoanthracene in one step by employing the Sonogashira coupling reaction in good yields ($<90^\circ$). Subsequent base hydrolysis of **2** was carried out to obtain **1**. All the compounds (**1–3**) were fully characterized by various spectroscopic techniques [NMR (^1H , ^{13}C) and IR] and finally, the molecular structures of **1** and **2** were determined by X-ray diffraction analysis (ESI†). Suitable single crystals of **1** and **2** were obtained

Chart 1 Chemical structures of the sensors (**1–3**).

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‡ This work is dedicated to Prof. Peter J. Stang on the occasion of his 70th birthday.

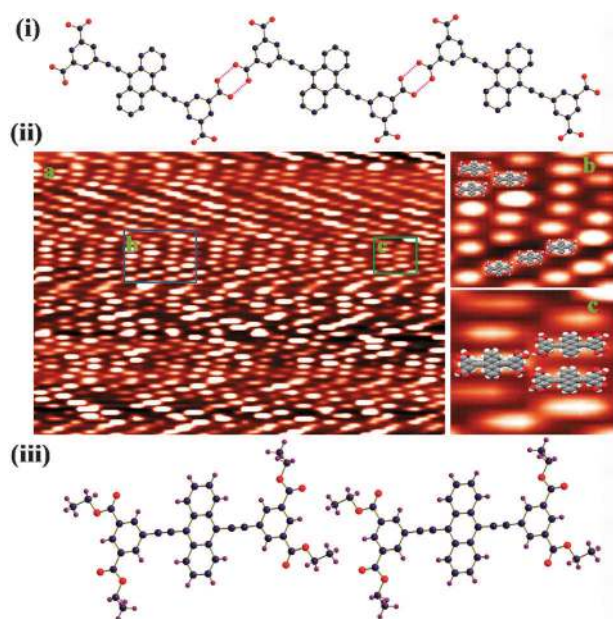


Fig. 1 (i) Solid-state packing diagram of **1** exhibiting a pair-wise infinite 1D-supramolecular polymeric chain. (ii) STM image of thin film of **1** taken on an HOPG surface with highlighted sections (b and c) showing the polymeric pattern as expected from X-ray structures. (iii) View of the molecular structure of **2** (colour code: red = oxygen; blue = carbon).

by slow evaporation of respective saturated solution in dimethylacetamide (DMA) and CHCl_3 , respectively. The crystal structure of **1** revealed that the 9, 10 positions of anthracene are connected to two 5-ethynylisophthalic acids. One of the carboxylic acid groups of each 5-ethynylisophthalic acid moiety involves in intermolecular hydrogen bonding with a carboxylic acid group of the neighbouring molecule to form an infinite 1D supramolecular chain (Fig. 1). On the other hand, X-ray structure analysis of compound **2** reveals that it does not form such supramolecular assembly due to lack of required hydrogen bonding interaction (ESI^\dagger). The carboxylic acid groups ($-\text{COOH}$) are introduced to the aromatic core moiety with a hope to generate the extended supramolecular polymer basically driven by intermolecular hydrogen-bonding interaction between adjacent building units.⁷

The UV-vis absorption spectra of **1–3** recorded in DMA or CH_2Cl_2 are almost identical and they display characteristic visible absorption bands in the range $\lambda = 274 \text{ nm}–465 \text{ nm}$ ascribed to typical $\pi-\pi^*$ transition (ESI^\dagger). Moreover, the incorporation of ethynyl groups enriches π -conjugation in **1–3** and thereby they exhibit strong fluorescence emission characteristics in the solution phase. The luminescence quantum yield ($\Phi = 0.21$) of **1** is determined to be lower than that of sensors **2** ($\Phi = 0.23$) and **3** ($\Phi = 0.47$). The reason behind such lower quantum yield of **1** could be due to excited state electronic coupling between the neighbouring fluorophore units in the polymeric chain.

To demonstrate the ability of sensor **1** to detect the trace quantity of nitroaromatic explosives, we first performed a fluorescence quenching titration experiment with picric acid (PA) in solution. The initial emission intensity of **1** quenched rapidly upon gradual addition of picric acid (Fig. 2 and ESI^\dagger).

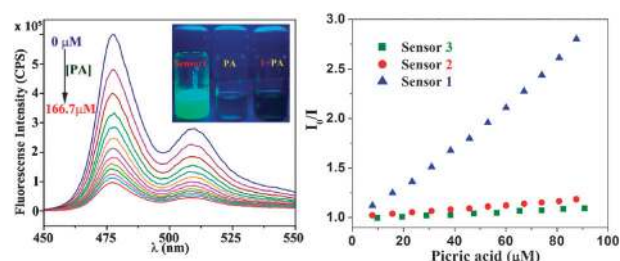


Fig. 2 Reduction in the emission intensity of sensor **1** (left) upon gradual addition of PA (inset: visual colour change of **1** before and after titrating with PA under UV-light) and corresponding Stern–Volmer plots for the titration of sensors (**1–3**) with PA at room temperature (right).

This reduction in emission intensity of **1** is ascribed to the formation of a non-fluorescent charge-transfer (CT) complex between the electron donor (fluorophore) and the electron acceptor (quencher).¹

To investigate the role of substituents on quenching efficiency, we replaced the $-\text{COOH}$ groups in sensor **1** with $-\text{COOEt}$ (**2**) and $-\text{CH}_3$ (**3**). The initial fluorescence quenching titration study of sensors (**1–3**) with picric acid (PA) demonstrated that, indeed, sensor **1** is more efficient than sensors **2** and **3** and quenching efficiency follows the order $1 < 2 < 3$. A linear Stern–Volmer relationship was obtained from the fluorescence quenching titration of **1–3** using PA as quencher (Fig. 2). The Stern–Volmer binding constants were calculated to be $K_{\text{sv}} = 2100 \text{ M}^{-1}$ (**1**), $K_{\text{sv}} = 200 \text{ M}^{-1}$ (**2**) and $K_{\text{sv}} = 130 \text{ M}^{-1}$ (**3**). High K_{sv} of **1** compared to discrete analogues **2** and **3** reflects that the quencher concentration required for quenching of **1** is less compared to the other two (higher sensitivity of **1**). As **1** is expected to be the least electron rich among **1–3** due to electron withdrawing effect of $-\text{COOH}$, this order would have been reversed if the analyte-receptor charge transfer interaction was the only mechanism.

Moreover, investigation with a series of electron deficient aromatic compounds indicated that nitroaromatic explosives (TNT and PA) show the largest quenching responses (Fig. 3). Whereas, other electron deficient compounds such as benzoquinone (BQ) and benzoic acid (BA) induce little quenching due to different electrostatic interaction with **1** compared to NAC. Notably, sensor **1** can result in detectable response with the solution of PA at parts per billion (ppb) concentration

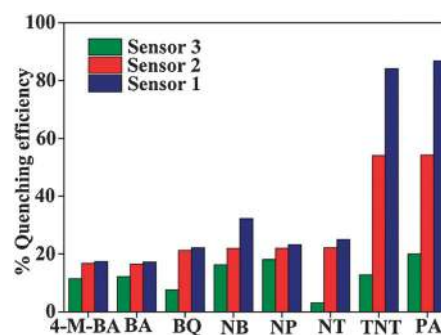


Fig. 3 Reduction in fluorescence intensity (plotted as quenching efficiency) observed upon the addition of quencher molecules. 4-M-BA = 4-methoxy benzoic acid, BA = benzoic acid, BQ = benzoquinone, NB = nitrobenzene, NP = nitrophenol, NT = nitrotoluene, TNT = 2,4,6-trinitrotoluene and PA = picric acid.

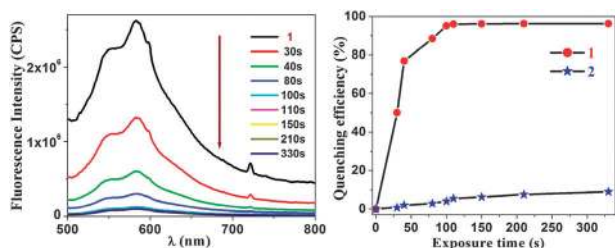


Fig. 4 Time dependent emission intensity of the thin film of **1** upon exposure to the saturated vapour of nitrobenzene (left) and quenching efficiency of **1** and **2** as a function of exposure time (right).

(ESI⁺) and such level of sensitivity falls below the permissible level of TNT in drinking water established by the US EPA.⁸

Solution state fluorescence quenching of **1** was a good enough indication to explore the possibility of its use in the solid state. Solid state sensing of explosives vapour is most appealing for infield practical use. To further explore the quenching efficiency of supramolecular polymer **1** in the solid-state, we monitored the emission intensity of a freshly made thin film of **1** as a function of time before and after exposure to the saturated nitroaromatic vapour. The initial emission intensity of the film decreased significantly upon exposing the film to the saturated nitrobenzene vapour at room temperature for a certain period of time. The emission was quenched by about 77% within only 35 s exposure. Upon continuous exposure for longer time, the quenching reached its equilibrium value at 96% after just 110 s (Fig. 4), which is very high compared to just ~8% quenching in the case of **2** upon exposure for 300 s. The efficient quenching of fluorescence intensity in the case of **1** might be due to the presence of a supramolecular polymeric structure and also due to the easy passage of analytes into the intrinsic internal pores in the solid state. IR and STM images of the film indicated that it has a similar H-bonded structural pattern (ESI⁺). Supramolecular interaction (H-bonding) between the adjacent molecular entities in **1** provided great amplification of optical signals because of the long-range exciton communication along the entire supramolecular chain and thus results in very high sensitivity of **1** for the electron deficient quencher.⁹

The thin film of **1** also showed highly reversible sensing of nitroaromatic explosives. After exposing the film to a saturated nitrobenzene vapour at room temperature for certain time, initial emission intensity of the film was recovered by washing with methanol and drying in hot air. By these treatments, the thin-film quickly regains the emission intensity and thus can be re-used for a significant number of cycles (Fig. 5).

Over several numbers of cycles, the quenching efficiency of the film towards nitrobenzene decreased gradually presumably due to the occupation of the free volume of the film by solvent molecules. It is noteworthy that the efficient regaining of initial fluorescence intensity over repeated cycles implies the high photostability of the film for their long time infield explosive screening application.

In conclusion, a new type of supramolecular fluorescence sensor (**1**) has been developed from a π -electron rich fluorophore building unit for the detection of very trace amount of nitroaromatic explosives. Sensor **1** shows highly selective fluorescence quenching response upon interaction with electron deficient nitroaromatic explosives like PA and TNT. In contrast

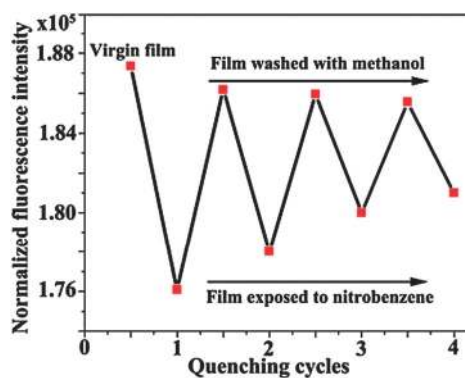


Fig. 5 Reversibility of the thin film of **1** to the saturated vapour of nitrobenzene (NB). The quenching was performed by exposing the film to NB vapour for 120 s and the fluorescence of the film was recovered by washing with methanol.

to traditional covalent polymers, the present system (**1**) represents the first example of a supramolecular polymer as an efficient chemical sensor for selective sensing of nitroaromatic explosives. The present study also reveals that the polymeric arrangement *via* H-bonding in **1** facilitates the long-range excitons migration and thus increases the overall quenching efficiency/sensitivity compared to analogous discrete systems (**2** and **3**) in the solid state. This new methodology of amplification of a fluorescence chemosensory event using supramolecular interaction may enable future development of much improved sensors for chemical explosives. Research is under progress to establish the full scope of this unique methodology.

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