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Electron rich supramolecular polymers as fluorescent sensors for nitroaromatics

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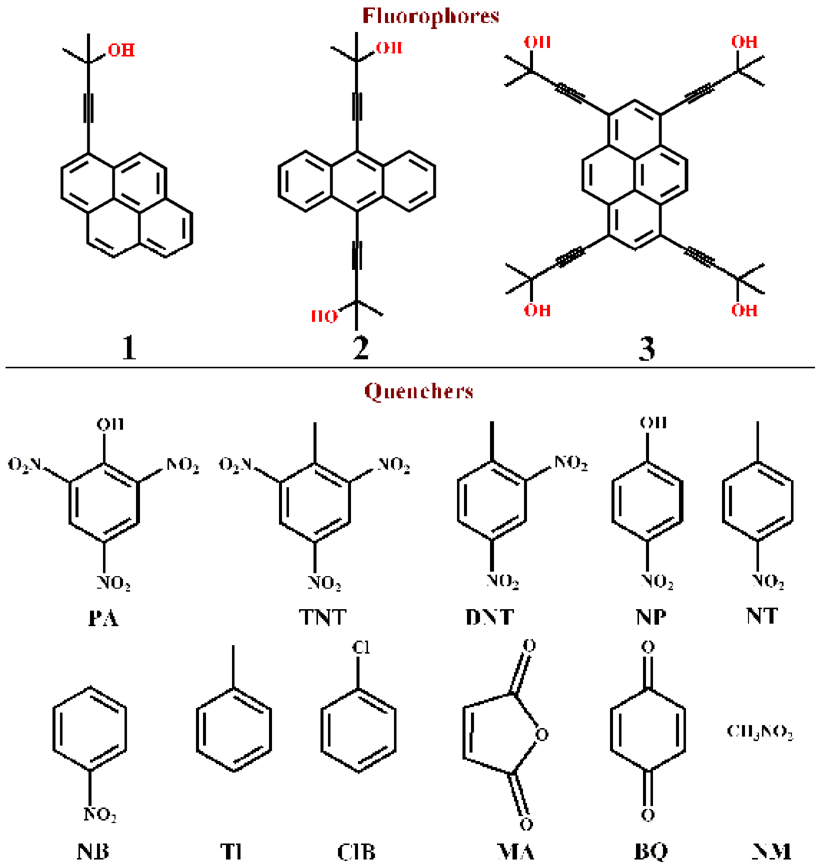
Abstract: Three π-electron rich fluorescent supramolecular polymers (**1**−**3**) have been synthesized incorporating 2-methyl-3-butyn-2-ol groups in reasonable yield by employing Sonagashira coupling. They were characterized by multinuclear NMR (^{1}H, ^{13}C), ESI-MS and single crystal X-ray diffraction analyses [**1** = 1-(2-methyl-3-butyn-2-ol)pyrene; **2** = 9,10-bis(2-methyl-3-butyn-2-ol)anthracene; **3** = 1,3,6,8-tetrakis(2-methyl-3-butyn-2-ol)pyrene]. Single crystal structures of **1**−**3** indicated that the incorporation of hydroxy (−OH) groups on the peripheral of the fluorophores helps them to self-associate into an infinite supramolecular polymeric network *via* intermolecular hydrogen bonding interactions between the adjacent discrete fluorophore units. All these compounds showed fluorescence characteristics in chloroform solution due to the extended π-conjugation and were used as selective fluorescent sensors for the detection of electron deficient nitroaromatics. The changes in photophysical properties of fluorophores (**1**−**3**) upon complex formation with electron deficient nitroaromatic explosives were studied in chloroform solution by using fluorescence spectroscopy. All these fluorophores showed the largest quenching response with moderate selectivity for nitroaromatics over various other electron deficient/rich aromatic compounds tested (Chart 1). Analysis of the fluorescence titration profile of 9,10-bis(2-methyl-3-butyn-2-ol)anthracene fluorophore (**2**) with 1,3,5-trinitrotoluene/2,4-dinitrotoluene provided evidence that this particular fluorophore detects nitroaromatic in nanomolar range [2.0 ppb for TNT, 13.7 ppb for DNT]. Moreover, sharp visual color change was observed upon mixing nitroaromatic (DNT) with fluorophores (**1**−**3**) both in solution as well as in solid phase. Furthermore, the vapor-phase sensing study of thin film of fluorophores (**1**−**3**) showed efficient quenching responses for DNT and this sensing process is reproducible. Selective fluorescence quenching response including a sharp visual color change for nitroaromatics make these tested fluorophores (**1**−**3**) as potential sensors for nitroaromatic compounds with detection limit of ppb level.

Introduction

Discovery of suitable sensor for the detection of explosives has attracted increased attention in recent time.[1] Among various known chemical explosives, nitroaromatics [picric acid (PA), trinitrotoluene (TNT) and dinitrotoluene (DNT)] are the common components in various explosives and make them as common focus in explosive detection.[2] Not only their explosive nature, these nitroaromatics have several health and safety concerns. [3] Therefore, sensitive and selective method for trace detection of nitroaromatics in soil, ground-water and buried land mines is important. Several sophisticated techniques using metal detector, canine teams, ion mobility spectrometry (IMS) and X-ray diffraction are being currently used for nitroaromatics detection.[4] Very recently fluorescence quenching based detection has attracted much attention due to their high sensitivity and selectivity.[5] Nitroaromatics like trinitrotoluene (TNT), dinitrotoluene (DNT) and picric acid are challenging for vapor based chemical sensing due to their moderate vapor pressure (VP_{TNT}=1 ppb). These electron-poor nitroaromatics can show π-stacking interaction with π electron rich chemical species.[1,2] Therefore, as a synthetic chemist the first idea one can imagine is of designing π-electron rich conjugated fluorophore which in turn binds effectively with electron deficient nitroaromatics and subsequently results in the quenching of emission intensity of fluorophore.[1c] In last several years synthetic chemists have synthesized variety of fluorophores for nitroaromatics sensing that include conjugated organic polymers[6], inorganic conjugated polymers[7] and Zn(salicylaldimine) based small molecule.[8] The most prominent of the organic conjugate polymers used for nitroaromatics detections are modified poly(phenyleneethylene) and poly(phenylenevinylene). The high sensitivity of these conjugate 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 excitons migration throughout the individual polymer chain.[9] However, the use of these polymeric materials for sensing applications is limited because of their time consuming multi-step covalent synthesis and poor molecular organization, which resist the rapid diffusion of analytes within the internal porosity and thus reduces the overall quenching efficiency.[6-9] Therefore, finding of a new sensor that can enable long-range excitons migrations and in turn exhibits high sensitivity towards nitroaromatics is indeed appealing. An alternative way by which one can intend to make a suitable sensor is to construct the so-called supramolecular polymeric sensors in which two or more molecular entities self-associate spontaneously to adopt an infinite network like structure having well defined molecular organization and large internal porosity.[10]

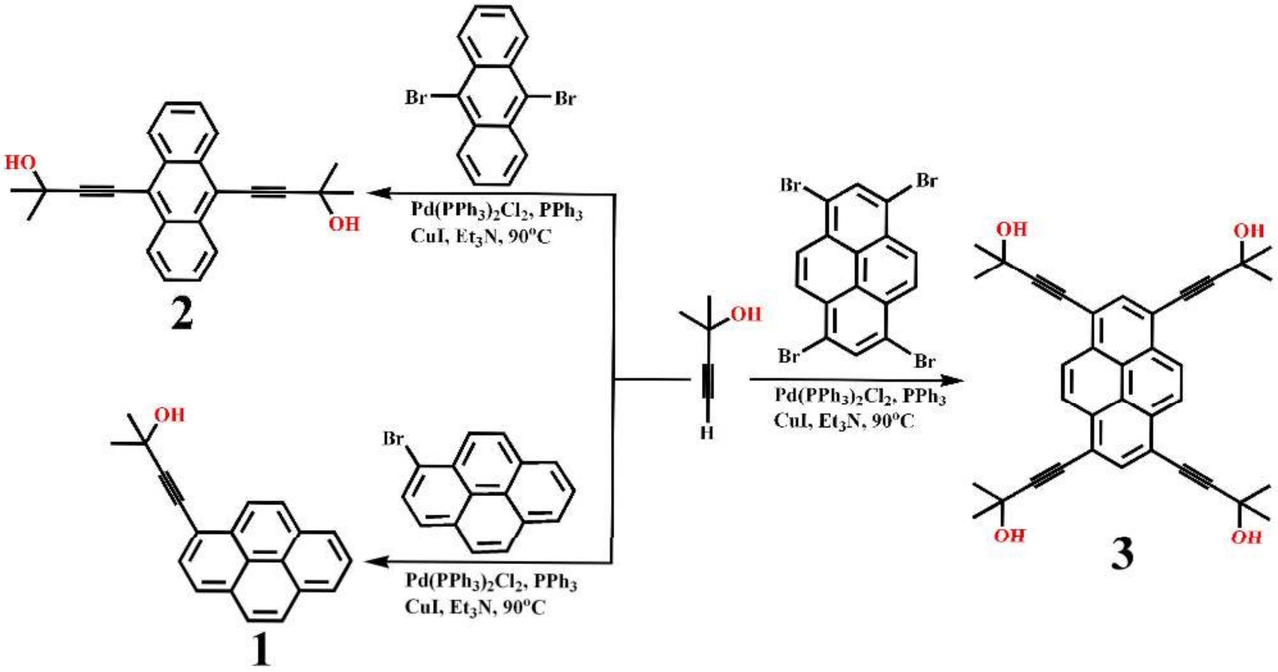
Chart I



Compared to conjugate organic polymers, supramolecular polymers are generally easy to construct from judiciously pre-designed molecular building units. We have recently shown a carboxylate (-COOH) functionalized anthracene-based supramolecular polymer as an efficient sensor for nitroaromatics detection with high sensitivity.[11] In continuation of this recent communication, we report here the synthesis, characterization of three π-electron rich supramolecular polymers (**1**–**3**) as new type of supramolecular chemosensors for the sensing of nitroaromatic explosives both in solution as well as in thin-film (Chart 1).

Results and discussion

Synthesis of fluorophores (1−3): All the three fluorophores (**1−3**) were synthesized[12] in quantitative yields by employing Sonagashira coupling between their corresponding aryl-halide and 2-methyl-3-butyn-2-ol under nitrogen atmosphere (Scheme 1). They were fully characterized by various spectroscopic methods such as multinuclear NMR (^{1}H and ^{13}C) and electrospray ionization mass spectrometry (ESI-MS). Finally, the molecular structures of **1−3** were confirmed by single crystal X-ray diffraction study.



Scheme 1. Synthesis of the fluorophores (**1−3**) via Sonagashira coupling between their corresponding halides and 2-methyl-3-butyn-2-ol under N_2 atmosphere.

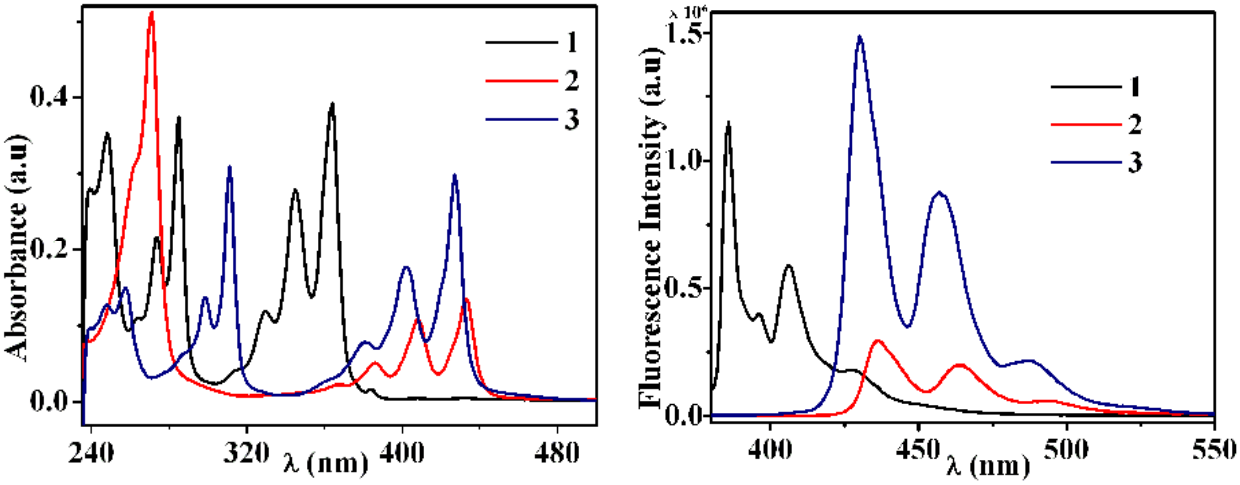


Fig. 1. Electronic absorption (left) and fluorescence emission (right) spectra of the fluorophores (**1−3**) recorded in aerated chloroform solution.

Photo-physical characteristics. The electronic absorption maxima (λ_{abs}) along with their molar extinction co-efficient (ε), and fluorescence emission maxima (λ_{em}) of the fluorophores (**1−3**) are summarized in Table 1. The absorption spectra of fluorophores **1–3** in chloroform (5.0×10^{-6} M) show the expected typical absorption peaks of pyrene or anthracene at λ = 248, 263, 274, 285, 330, 345, 364 nm for **1**; λ = 271, 386, 408, 433 nm for **2**; λ = 248, 258, 299, 311, 380, 402, 427 nm for **3** (Fig. 1). These observed peaks are tentatively ascribed to the intra/intermolecular π-π^* transitions. Due to the extended π-conjugation, all the three synthesized fluorophores show high fluorescence emissions in chloroform solution at λ = 386, 396, 406, 429 nm for **1**; λ = 436, 464, 494 nm for **2**; λ = 430, 457, 488 for **3** and their high luminescence behavior is basically attributed to the presence of unsaturated ethynyl functionality and extended π-conjugation (Fig. 1).[12]

Table 1. Photophysical data of the fluorophores (**1−3**) taken in aerated chloroform.

Fluorophores	Absorption maxima λ_{max}(nm)	Molar extinction co-efficient $\varepsilon \times 10^3$ M^{-1} cm^{-1} [λ_{max}(nm)]	Fluorescence emission maxima λ_{max}(nm)	Fluorescence emission maxima of thin-film λ_{max}(nm)
1	248, 263, 274, 285, 330, 345, **364**	78 (364)	**386**, 396, 406, 429 (sh)	458, 418 (sh)
2	**271**, 386, 408, 433	102 (271)	**436**, 464, 494 (sh)	510, 561 (sh)
3	248, 258, 299, **311**, 380, 402, 427	62 (311)	**430**, 457, 488	537

Values marked in bold represent the highest absorption (λ_{abs}) and emission (λ_{em}) maxima.

Fluorescence quenching-based detection of nitroaromatics in solution

The general mechanism of fluorescence quenching-based detection basically involves the formation of a donor-acceptor charge-transfer (CT) complex between the π-electron rich donors (fluorophore) and electron deficient acceptors (nitroaromatics) via π-π interactions.[1,6-8]

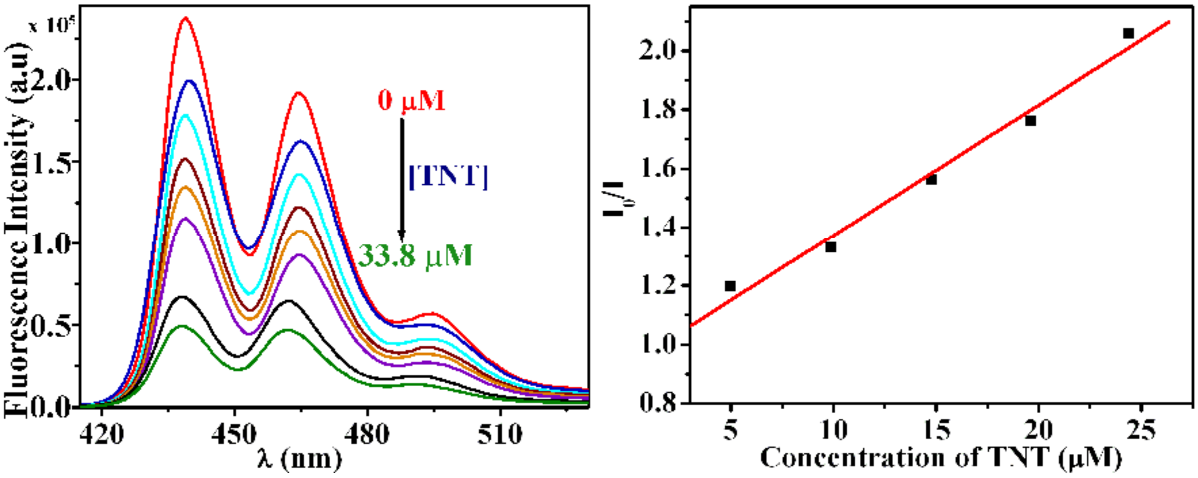


Fig. 2. Fluorescence quenching (left) of the fluorophore **2** (5.0 µM) with TNT in chloroform solution and its corresponding Stern-Volmer plot (right).

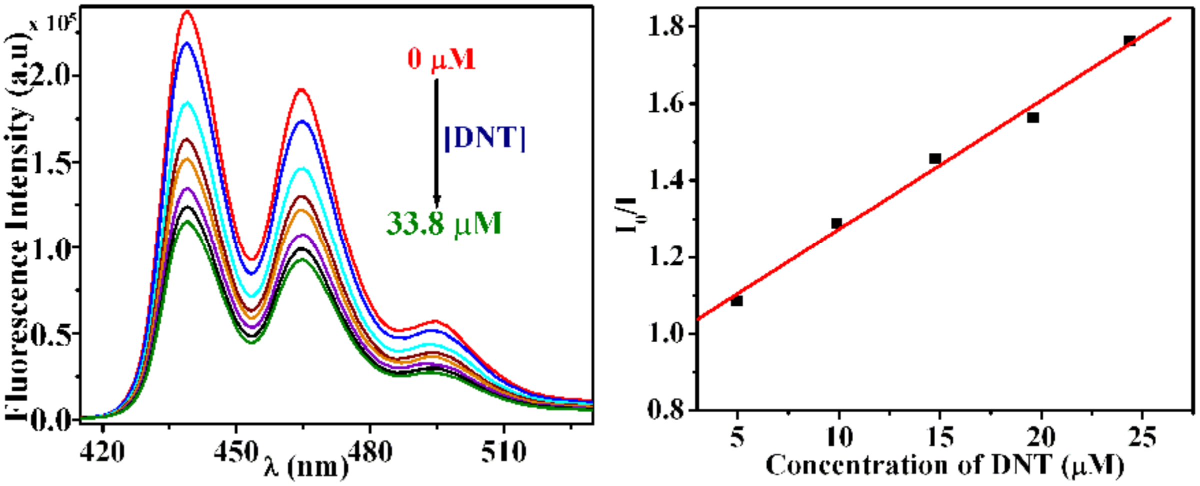


Fig. 3. Fluorescence quenching (left) of the fluorophore **2** (5.0 μM) with DNT in chloroform solution and its corresponding Stern-Volmer plot (right).

Accordingly, in this study we employed three 2-methyl-3-butyn-2-ol substituted π-electron-rich aromatic fluorophores (**1−3**) to sense nitroaromatics (NAC) based on the proposed quenching mechanism. To demonstrate the ability of fluorophores (**1**−**3**) for detection of nitroaromatics, we first performed fluorescence quenching titration study of fluorophores **1−3** with 1,3,5-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) in chloroform solution. As expected, the initial emission intensity of fluorophores (**1**−**3**) depleted upon the gradual addition of chloroform solution of TNT or DNT to a chloroform solution of the fluorophores (Figs. 2-3 and Figs. S10-13, ESI). Linear Stern-Volmer plots were obtained from the fluorescence quenching titration profiles and calculated Stern-Volmer binding constants (K_{SV}) were [1.9×10^2 M^{-1} for **1** with TNT, 8.7×10^4 M^{-1} for **2** with TNT, 6.4×10^3 M^{-1} for **3** with TNT; 1.3×10^2 M^{-1} for **1** with DNT, 8.5×10^4 M^{-1} for **2** with DNT, 3.9×10^3 M^{-1} for **3** with DNT (Figs. 2-3 and Figs. S10-13, ESI)].

The obtained quenching constants (K_{SV}) from the titration experiment for TNT and DNT are comparable with previously reported values of analogues fluorophores.[13]

On the basis of purely electronic consideration, π-electron rich 1,3,6,8-tetrakis(2-methyl-3-butyn-2-ol)pyrene (**3**) is expected to show maximum fluorescence quenching response towards electron deficient nitroaromatics than fluorophore **2**. However, a reverse order was noticed from Figs. 2−3 and Figs. S11, S13 (ESI). We think that the poor quenching response of **3** may be due to the steric effect of substituted bulky 2-methyl-3-butyn-2-ol groups. The substitution of four bulky 2-methyl-3-butyn-2-ol groups on the periphery of the pyrene chromophore may be too sterically demanding to permit an optimal interaction between the fluorophore and the electron deficient nitroaromatics which in turn results in poor fluorescence quenching response. On the other hand, because of the less π-conjugation, 1-(2-methyl-3-butyn-2-ol)pyrene (**1**) fluorophore is anticipated to have weak binding affinity for electron deficient nitroaromatics, and in turn expected to shows poor fluorescence quenching response than the other more π-electron-rich fluorophores (**2**−**3**). Indeed, fluorescence quenching titration study showed that fluorophore **1** has weak quenching response towards nitroaromatics compared to fluorophores **2** and **3**. Moreover, the propensity of fluorescence quenching of anthracene-based fluorophore **2** is much higher in comparison to fluorophore **3** and the reason for the observed efficient quenching response is attributed to the less-steric hindrance of **2**, which might results in an effective binding of **2** with nitroaromatic quenchers than that of fluorophore **3**. Overall, a significant fluorescence quenching was observed only for nitroaromatic compounds.

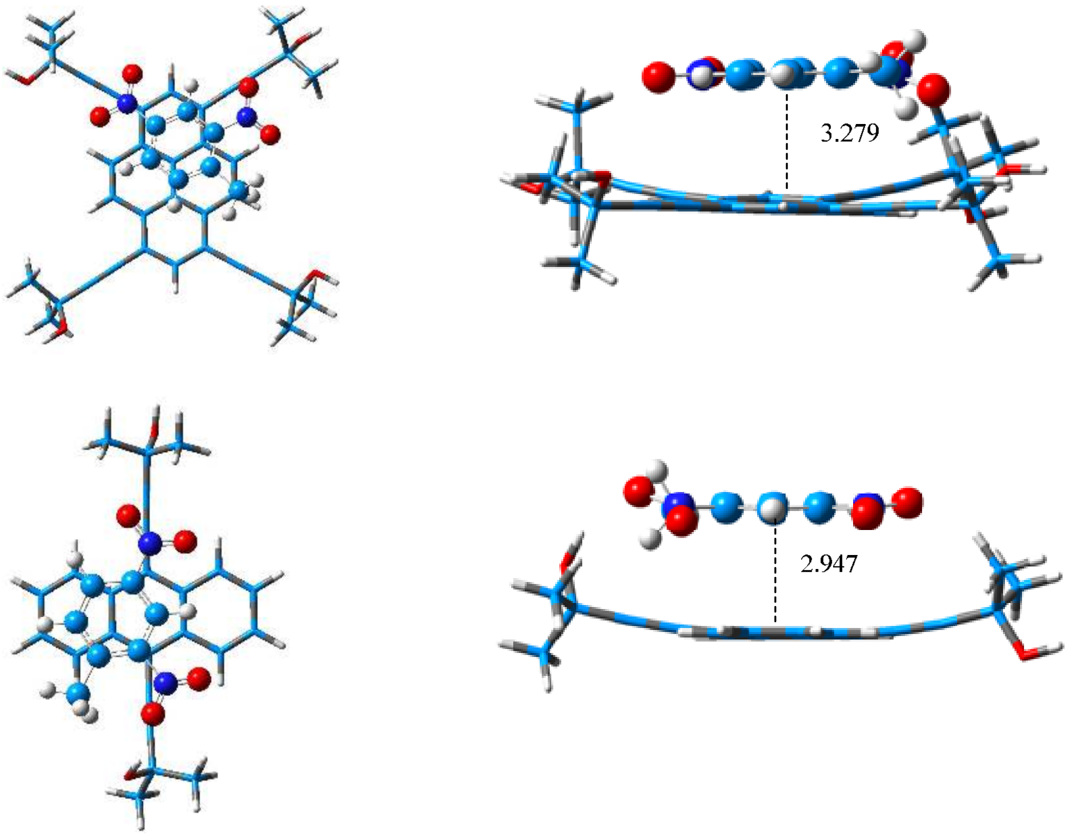


Fig. 4. Optimized geometries of **3·DNT** (top) and **2·DNT** (bottom) (color codes: red = oxygen, blue = nitrogen, cyan = carbon and white = hydrogen).

In order to understand the nature of interaction between fluorophore with analytes and to provide further support to the observed order in fluorescence quenching, density functional theory (DFT) calculation was carried out using Gaussian 09 program.[14] DFT calculation has been done at M05-2X/6-31G* level to optimize the structure of fluorophore-analyte complexes and frequency calculations were done for the optimized complexes to confirm that all the structures considered are minima on the potential energy surface. The electron deficient 2,4-dinitrotoluene (DNT) was optimized with 9,10-bis(2-methyl-3-butyn-2-ol)anthracene (**2**) and 1,3,6,8-tetrakis(2-methyl-3-butyn-2-ol)pyrene (**3**). The optimized structure of the complexes **2·DNT** and **3·DNT** are shown in Fig. 4. This demonstrates that both the fluorophores (**2** and **3**) show intermolecular π-π interaction and maintained a co-facial stacked geometry with 2,4-dinitrotoluene (DNT). In the optimized structures, the quencher molecule DNT forms a π-π stacking type of interaction at a distance of 3.279 Å (**3·DNT**) with fluorophores **3**, whereas with fluorophore **2** it is at a distance of 2.947 Å (**2·DNT**). From these calculated intermolecular distances, we can easily predict that the quenching will be more efficient for fluorophore **2** compared to **3**. Moreover, the estimated binding energy of 22.55 kcal/mol for the complex **2·DNT** is higher than that of complex **3·DNT** (17.10 kcal/mol); this in fact reflects that fluorophore **3** forms weaker charge-transfer complex with DNT compared to **2**.[15] Moreover, the observed strong binding affinity of fluorophore **2** towards DNT over fluorophore **3** was also indicated by the decrease in HOMO-LUMO energy difference of **2** and **3**, before and after binding with analyte. The calculated HOMO-LUMO energy difference of free **2** (4.97 eV) decreases significantly to 4.71 eV upon binding with DNT, whereas the HOMO-LUMO gap of **3** (4.83 eV) decreased to 4.77 eV (Fig. 6). Thus, more decrease in HOMO-LUMO energy difference of **2** pointed out that it forms stronger charge-transfer complex with DNT than fluorophore **3**, which is consistent with the fluorescence quenching experiments.

Selectivity

To corroborate the selectivity of fluorophores for detection of nitroaromatic explosives, we carried out the fluorescence titration experiments with other electron deficient/rich aromatic compounds. Interestingly, the selected fluorophores (**1**−**3**) showed differential fluorescence quenching responses among various tested analytes. The obtained results are shown in Fig. 5, which indicate that almost all the three fluorophores show modest to strong quenching response for electron-deficient nitroaromatic compounds than other aromatic compounds such as toluene

(Tl), chlorobenzene (ClB), benzoquinone (BQ) and maleic anhydride (MA). It is reported in the literature that the reduction potential of tested non-nitroaromatic quenchers are not significantly different from the nitroaromatic quenchers.[8] Therefore, we believe that the observed higher fluorescence quenching responses of nitro-compounds might, presumably, due to the strong dipolar or electrostatic interaction of electron-deficient nitroaromatics with π-electron rich aromatic fluorophores. This observation is fully consistent with the proposed quenching mechanism in which the electron-deficient nitroaromatics act as a fluorescence quencher to electron-rich fluorophores as the result of the formation of charge-transfer (CT) complex between them.

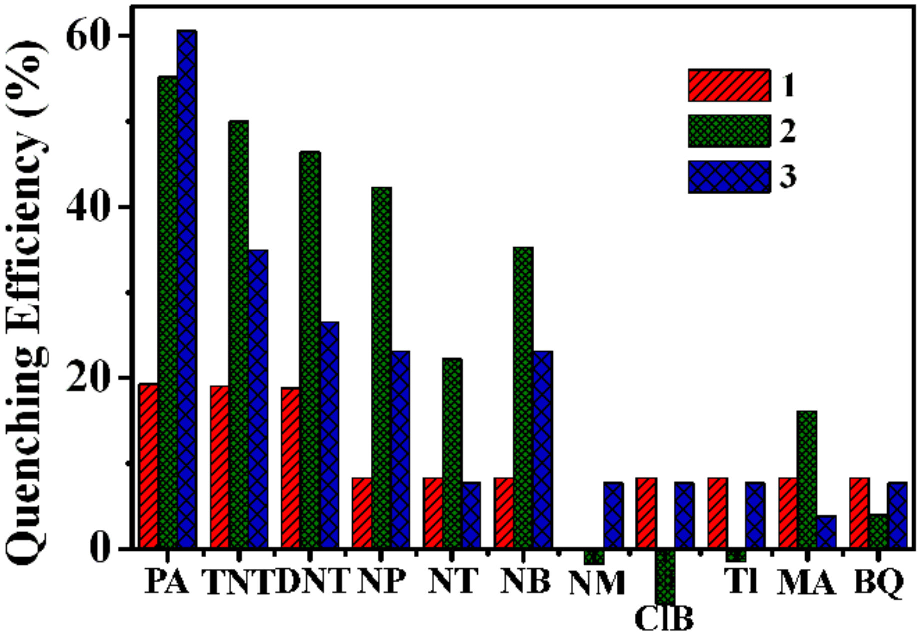


Fig. 5. Changes in fluorescence intensity of the fluorophores (**1−3**) (plotted as quenching efficiency) observed upon the addition of various analytes. PA = Picric acid, TNT = 1,3,5-trinitrotoluene, DNT = 2,4-dinitrotoluene, NP = 4-nitrophenol, NT = 4-nitrotoluene, NB = Nitrobenzene, NM = Nitromethane, ClB = Chlorobenzene, Tl = Toluene, MA = Maleic anhydride, BQ = Benzoquinone.

Sensing mechanism

In general, the fluorescence quenching of any sensor upon binding with analyte can follow two different mechanisms such as static and dynamic quenching. Quenching via static mechanism is expected not to affect the excited-state life-time of fluorophore and in contrast, dynamic quenching does affect the life-time of fluorophore.[16] Life-time of **3** was measured as function of DNT concentration in chloroform solution and the obtained results are shown in Fig. 6. It is clear that the fluorescence life-time of **3** (2.78 ns) does not change much with increasing the concentration of DNT and thus the observed fluorescence quenching of **3** follows the static-quenching mechanism via ground-state charge-transfer complex formation with DNT.[16b]

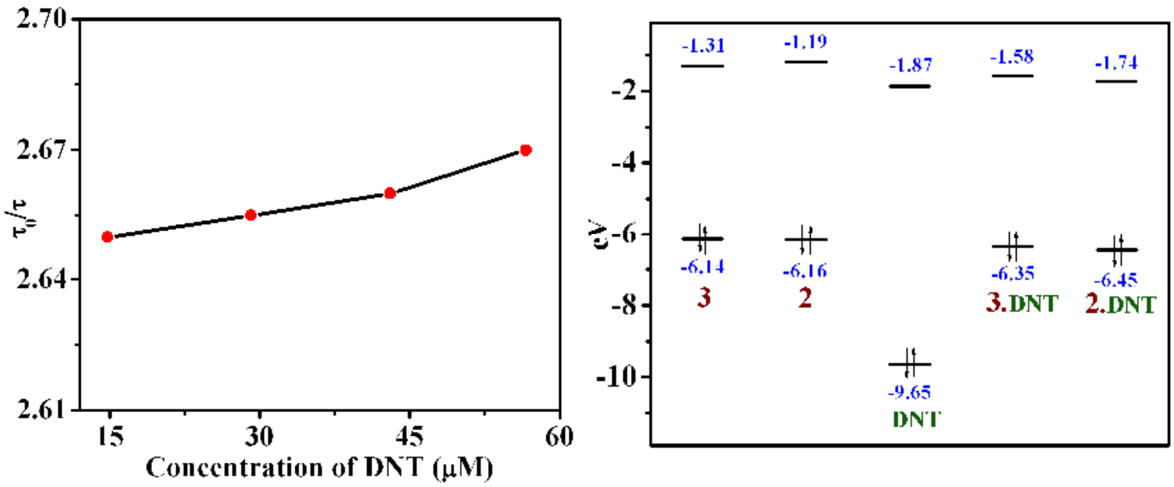


Fig. 6. Plot of ratios of **τ_0/τ** of fluorophore **3** against the concentration of DNT in chloroform solution at room temperature (left) and frontier orbital energy correlation diagram (right). Bottom line represents the HOMO energy level and top lines represent the LUMO energy level.

In addition, the formation of ground-state charge transfer (CT) complex between π-electron rich fluorophore **3** and electron-deficient nitroaromatic DNT was further supported by electronic absorption spectroscopic study. A significant increase in the initial absorption intensity of **3** was noticed upon the gradual addition of dinitrotoluene (DNT) in chloroform (1.0×10^{-3} M) to a chloroform solution (5.0×10^{-6} M) of fluorophore **3** at room temperature, which indicated the formation of a stable charge-transfer or donor-acceptor ground-state complex between π-electron-rich donor **3** and electron acceptor DNT (Fig. 7).[17] The binding constant for the charge-transfer complex formation was evaluated using Benesi-Hilderbrand relationship. A reciprocal plot of changes in the initial absorption intensity of **3** with change in the concentration of the DNT yields a linear correlation and the binding constant $K_a = 14.6 \times 10^3$ M^{-1} was obtained from the slope and intercept of the plot.

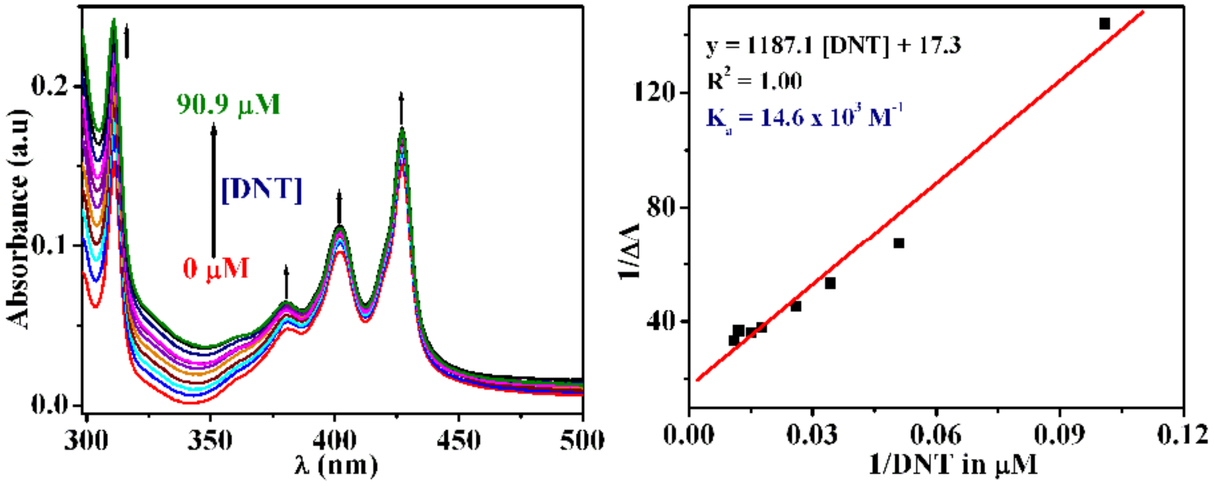


Fig. 7. Absorption spectral change (left) of fluorophore **3** in chloroform (5.0×10^{-6} M) upon titrating with DNT in chloroform ($0 - 90.9 \times 10^{-6}$ M) at 25°C and its corresponding Benesi-Hilderbrand plot monitored at 427 nm (right).

Sensitivity

To find the sensitivity (detection limit) of the fluorophores towards nitroaromatics, fluorescence quenching titration was performed using fluorophore **2** with TNT and DNT at parts per billion (ppb) concentrations. The quantitative analysis of fluorescence titration profile showed that this particular fluorophore can response the presence of nitroaromatics as low as 2.0 ppb for TNT and 13.7 ppb for DNT in solution (Fig. 8 and Fig. S14, Supporting Information). [18]

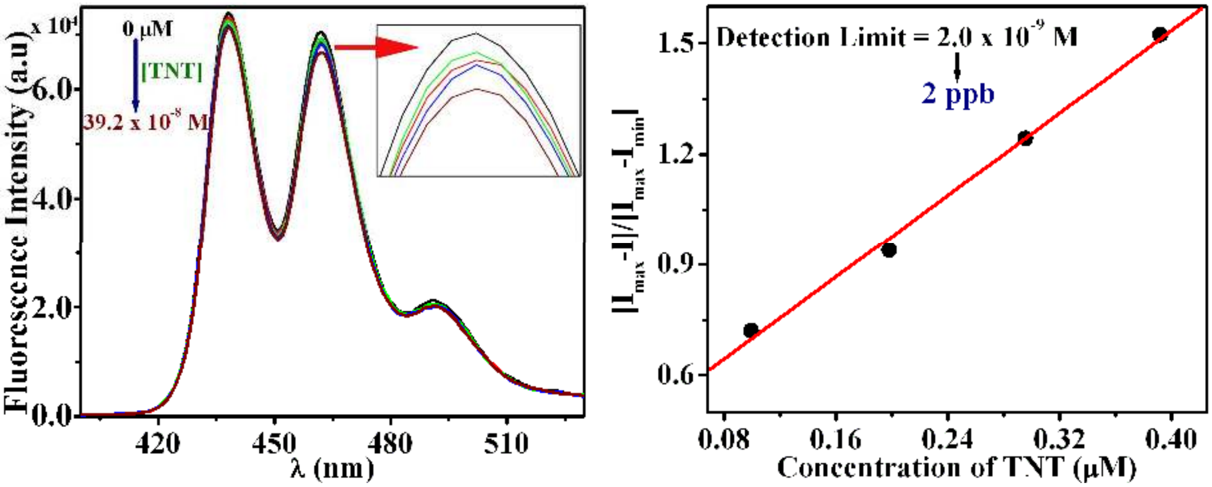


Fig. 8. Changes in initial fluorescence intensity of the fluorophore **2** upon gradual addition of TNT (0−39.2 × 10^{-8} M in chloroform) and its corresponding detection limit plot.

Visual detection of nitroaromatics

Visual detection of explosives has been much appealing owing to their ease of interpretation, simple material handling, rapid detection and more suitable method to practice in field. Colored complex formation[19] develops a new chromophore which shows a different photo-physical behavior from the starting components, including sharp visual color change. In this study, we have observed a noticeable color change upon subjecting the fluorophores **1−3** with DNT under different experimental conditions (Fig. 9-10). Due to the strong binding affinity of fluorophore **2** and **3** for nitroaromatics, the high luminescent characteristics of **2** and **3** are quenched, whereas fluorophore **1** does not show such marked changes due to its poor binding affinity.

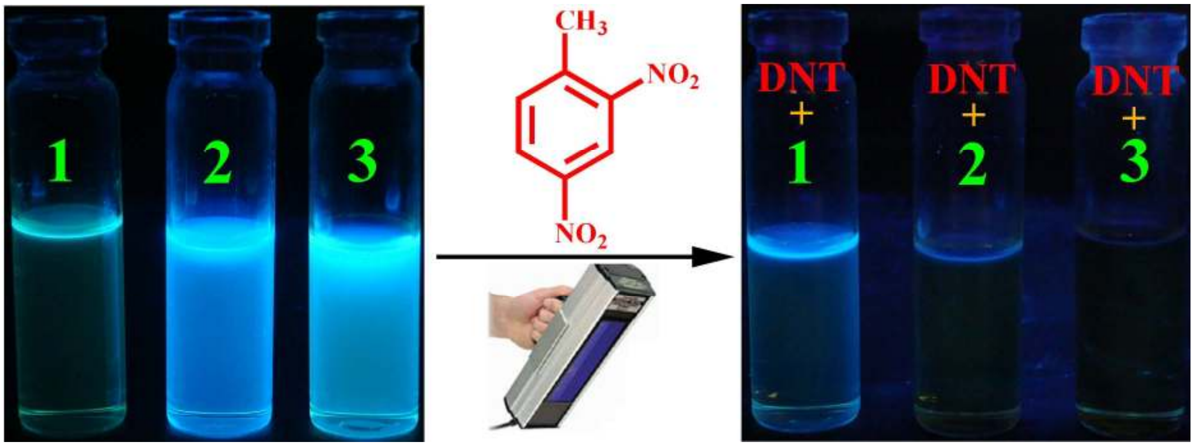


Fig. 9. Visual color changes observed upon mixing 10 mM solution of fluorophores **1−3** with 10 mM solution of DNT in chloroform under hand hold UV light.

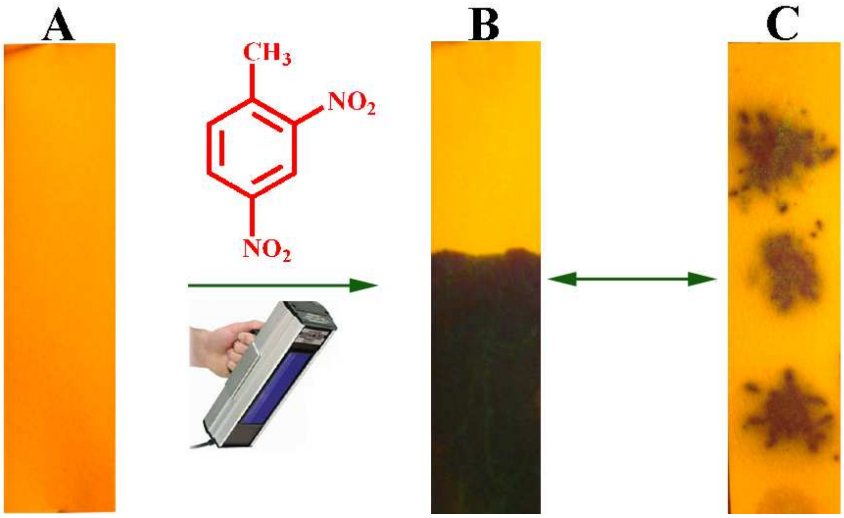


Fig. 10. Photographs of test strip coated with **3** (A), after dipping strips into a solution of DNT in chloroform (B), and after exposing the strip to the crystals of DNT for 30s (C). All photographs were taken under a hand-hold UV lamp.

Moreover, to further validate the use of these fluorophores for sensing application, a test strip was made by dip coating of solution of **3** on to a Whatman filter paper and dried in air (Fig. 10, A). Dipping this freshly made test strip into a dilute chloroform solution of DNT causes the complete quenching of emission intensity of **3** observed upon illumination with a hand-hold UV lamp (Fig. 10, B). In another experiment, to verify the visual sensing in solid-state, DNT crystals were placed over the strip for 30s and illumination with UV lamp showed black spots (Fig. 10, C). Visual color changes both in solution as well as in solid-phase illustrate the potential utility of these fluorophores as visual sensor for the infield trace detection of nitroaromatic explosives.[20]

Solid-state fluorescence quenching study

For infield application vapour phase sensing of explosives using thin-film of sensor is challenging.[21] In general, the electron deficient aromatic molecules quench initial fluorescence intensity of aromatic moiety-based fluorophores via aromatic π-π charge transfer complex formation[22] and such electron deficient analytes form stronger charge transfer complexes with more π-electron rich fluorophores.

In the present study, fluorophore **3** is more π-electron rich than **2** and **1**. As discussed earlier, computational study reveals that substituted methyl groups in **3** sterically hinder the close proximity with DNT and thus prevent formation of strong charge-transfer complex. On the other hand, DNT can form stronger charge transfer complex with **2** due to less bulkiness. Hence, fluorophore **2** is expected to exhibit better sensitivity towards DNT than **3**. While fluorophore **3** is more π-electron rich than **1** and thus the former is expected to be better sensor than the later. Though the sensing efficiencies of the fluorophores toward DNT in solution are as expected, solid state sensing study with analyte DNT showed that the fluorophore **3** is the most efficient senor followed by **2**.

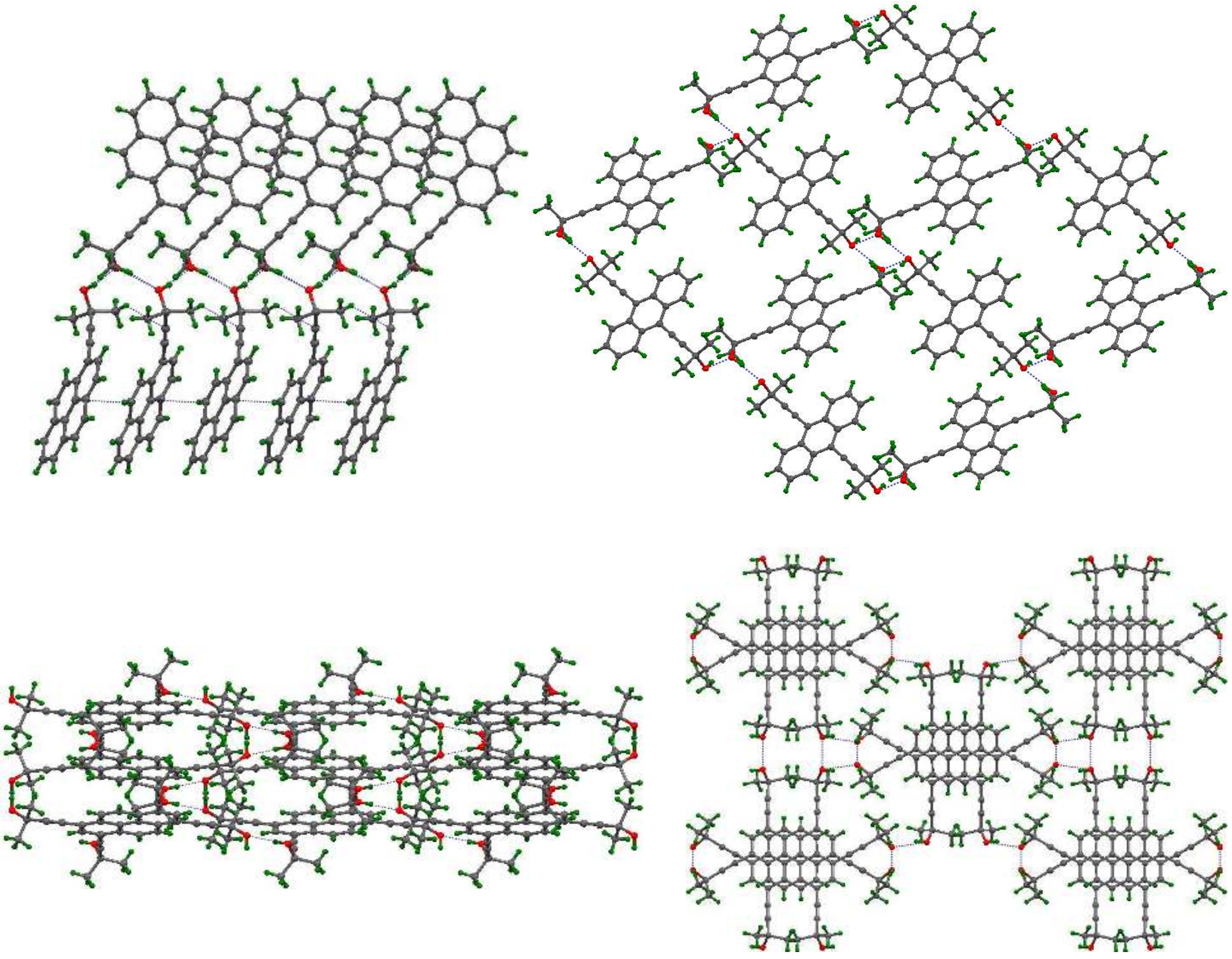


Fig. 11. Solid-state packing view of fluorophore **1** (top left) along *b*-axis, fluorophore **2**[12a] (top right) along *b*-axis and side (bottom left) and top view (bottom right) of fluorophore **3** along *c*-axis (color code; grey = carbon, green = H, red = oxygen).

Such observations can be understood from single crystal X-ray diffraction analysis and rationalized through supramolecular interactions in the solid-state. Solid state packing diagram of obtained single crystal X-ray structure of the fluorophore **1** contains two independent molecules in the asymmetric units and exhibits a H-bonded (1.97 Å) 1D chain. Neighboring chains are mutually stacked to form a Zig-Zag compact 2D network via CH-π (2.85 Å) interactions (Fig. 11

A). In the case of **2**, 2D H-bonded (1.97 Å) supramolecular polymeric layers formed a compact 3D network via π-π (3.35 Å) interactions (Fig. 11 B). The basic X-ray structure of **2** was reported earlier by Garcia-Garibay *et al*.[12a] The fluorophore **3** forms 3D supramolecular porous network via only H-bonding (1.95 Å) interactions (Fig. 11 C) and this molecule lies about an inversion centre. Such intrinsic porosity of **3** makes it as better sensor towards nitroaromatic vapour in solid-state due to easy diffusion of the explosive vapor into the porous pocket. To realize experimentally, the solid state fluorescence quenching experiment was performed using the vapor of 2,4-dinitrotoluene (DNT) with thin film of the fluorophores **1−3** [DNT was chosen because of its high vapour-pressure over other nitroaromatic explosives]. The freshly made thin film of the fluorophores **1−3** exhibit strong emission characteristics and upon exposure to saturated vapor of 2,4-dinitrotoluene, the initial fluorescence intensity of the film quenched dramatically (Fig. 12).

As can be seen from Fig. 12, the quenching efficiency of thin film of **3** is more sensitive to the DNT vapor compared to films of **2** and **1**. Exposure of the film **3** to saturated vapor of DNT for 360 s causes nearly 55 % quenching of the fluorescence intensity and the efficiency of fluorescence quenching increased further with increasing exposure time. Nearly 67 % quenching efficiency was observed after 6 min exposure of the film of **3** to DNT vapor. On the other hand, the thin films of fluorophores **1** and **2** exhibit nearly 31 % and 50 % reduction in the initial fluorescence intensity after 360 s exposure to a saturated vapor of DNT, respectively (Fig. 12). Hence, fluorophore **3** found to be more efficient and faster in response towards nitroaromatics compared to fluorophores **1** and **2** in solid-state. The reduction in fluorescence intensity of the thin-film of fluorophores upon exposure to the nitroaromatic vapor is ascribed to the charge transfer complex formation between electron-rich supramolecular polymers (**1**–**3**) and electron-deficient nitroaromatics.

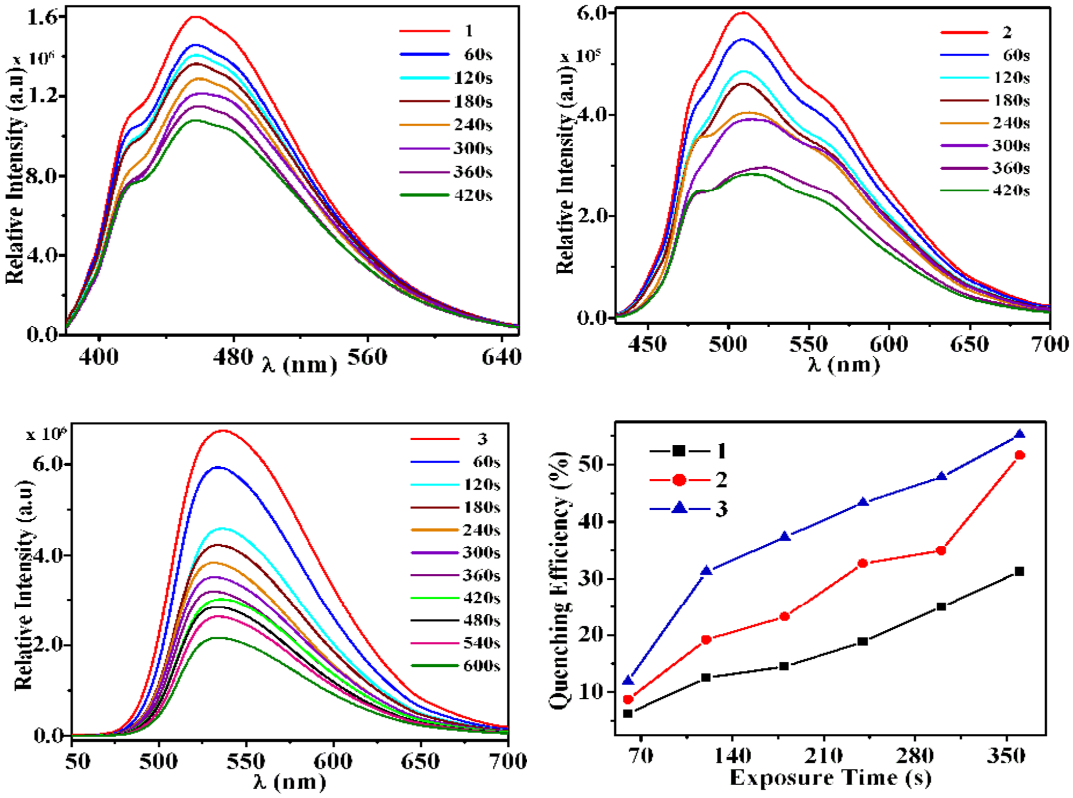


Fig. 12. Fluorescence spectra (left) of thin film of **1** (top left), **2** (top right) and **3** (bottom left) upon exposure to the saturated vapor of DNT at different time interval and their corresponding quenching efficiency plot (bottom right) against exposure time.

Moreover, to better understand the vital role of supramolecular interactions on quenching efficiency, we carried a comparative fluorescence quenching study of fluorophore **3** with its analogues non-hydroxy compounds such as 1,3,6,8-tetraethynylpyrene and pyrene in solid-state. The solid-state fluorescence quenching study of thin-film of fluorophore **3**, 1,3,6,8-tetraethynylpyrene and pyrene with DNT vapor demonstrated that, indeed, fluorophore **3** is more sensitive than that of 1,3,6,8-tetraethynylpyrene and pyrene (Fig. 13 and Fig. S15, Supporting Information). Thus, it is confirmed that the high quenching efficiency of **3** in comparison to 1,3,6,8-tetraethynylpyrene and pyrene is, presumably, due to the self-association of **3** into 3D supramolecular polymer via inter-molecular hydrogen-bonding interactions.

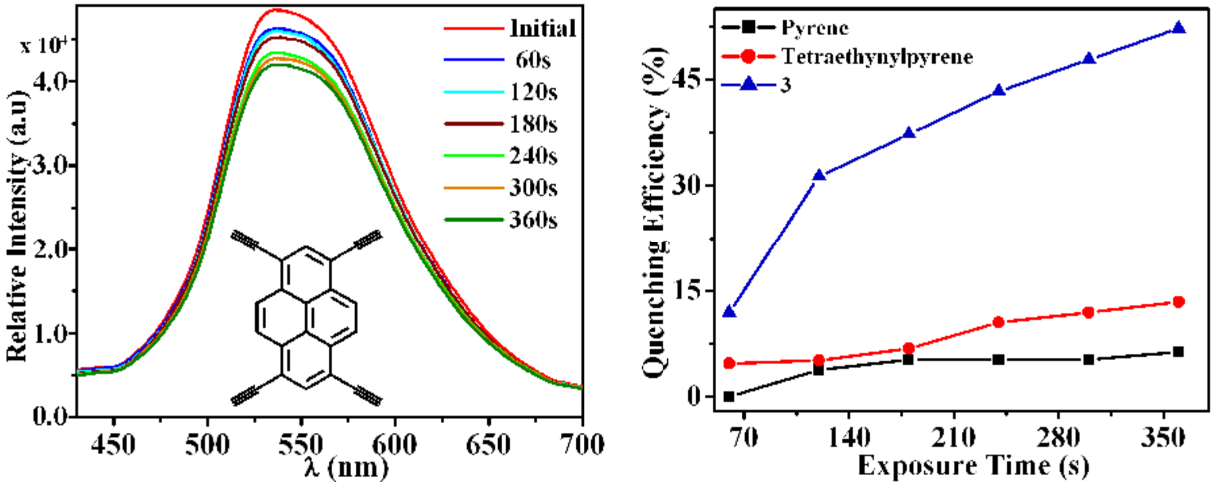


Fig. 13. Fluorescence spectra (left) of thin-film of 1,3,6,8-tetraethynylpyrene upon exposure to the saturated vapor of DNT at different time interval and comparative quenching efficiencies (right) of **3**, pyrene and tetraethynylpyrene.

Recyclability of sensing process

As far as practical application is concerned, the sensing process of any sensor must be highly recyclable one. The reproducibility of the sensing process was examined using a thin film of the fluorophore **3** with 2,4-dinitrotoluene at 25°C. The film was first exposed to a saturated DNT vapor at room temperature for 600 s and then its emission spectrum was recorded immediately. After the measurement, the film was washed several times with distilled water and dried in hot air. The emission spectrum of the film was recorded again and the whole process was repeated for three times. By these treatments, the film regains the initial emission intensity almost close to the initial fluorescence intensity and thus the film can be used for significant number of sensing cycles. The obtained results are given in Fig. 14, which clearly suggests that the sensing response of the film towards DNT vapor is basically reproducible. It is noteworthy mentioned that the efficiency of fluorescence quenching is decreases on increasing cycles, which is probably due to the occupation of free volume of the film by solvent molecules.

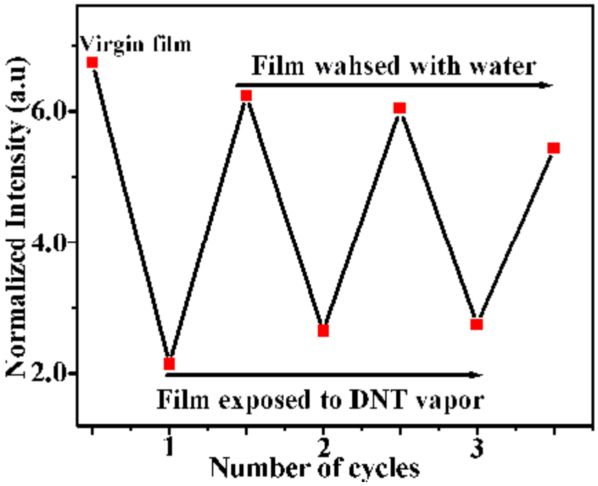


Fig. 14. Reproducibility of thin film of **3** to the saturated vapor of 2,4-dinitrotoluene (DNT). The film was excited at λ = 427 nm and the corresponding emission was monitored from λ = 450 nm. The excitation and emission slit width for all the measurement is 2 nm.

Conclusion

We have employed 2-methyl-3-butyn-2-ol substituted π-electron rich aromatic fluorophores as selective fluorescence sensors for nitroaromatics, which are the chemical signatures of many commercial explosives. Moderate to strong quenching of the initial fluorescence intensity of the fluorophores (**1−3**) was observed upon gradual addition of the solution of electron deficient nitroaromatics. The observed fluorescence quenching is ascribed to the charge-transfer complex formation between fluorophore and nitroaromatics. Moreover, the differential fluorescence quenching response of the fluorophores to closely related nitroaromatics allows the selective discrimination of the structurally related explosive species. Quantitative analysis of the fluorescence quenching profile allows that these sensor molecules are sensitive and able to show the marked quenching response for nitroaromatics as low as 2.0 ppb (TNT), 13.7 ppb (DNT) level concentration in solution. Although, the fluorophores **1−3** behave as discrete small molecule fluorogenic sensor in solution, the incorporation of peripheral hydroxy (-OH) groups makes them to self-associate into an infinite supramolecular polymeric networks through inter-molecular hydrogen bonding interactions in solid-state and exhibits efficient fluorescence quenching responses upon interacting with the electron-deficient nitroaromatic explosives. Vapor-phase quenching study of the thin-film of fluorophores **1−3** revealed that the sensing process is basically reversible and highly efficient for nitroaromatic compounds. The high sensitivity of fluorophores (**1−3**) in solid-state compared to the solution study is attributed to the rapid-diffusion of analytes within the intrinsic micro-porosity of supramolecular chains, which facilitates the long-range excitons migrations throughout the polymer backbones and thus increases the overall quenching efficiency of supramolecular polymeric sensors.

Acknowledgements: P.S.M thanks the CSIR-India and STC-IISc for the financial support.

Supporting information available: Synthesis of fluorophores (**1−3**), NMR (^{1}H & ^{13}C) and ESI-MS spectra of the fluorophores (**1−3**) including crystallographic details of **1**, **3** in CIF format [available in CCDC 883582(**1**) and 883583(**3**)], and details of fluorescence quenching titration study are available.

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TOC

Electron rich supramolecular polymers as fluorescent sensors for nitroaromatics

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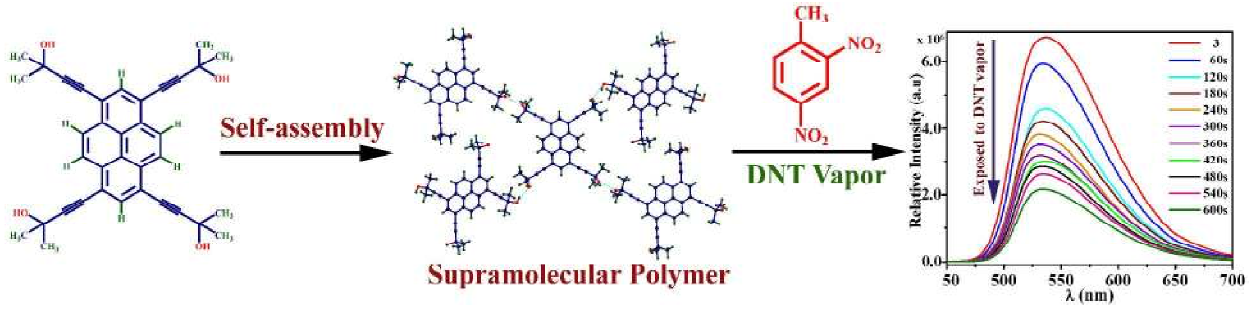

Three π-electron rich fluorescent supramolecular polymers incorporating 2-methyl-3-butyn-2-ol groups are discussed. They show selective sensing of nitroaromatics in both solution and vapour phases.