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PAPER

Fluorescence and visual sensing of nitroaromatic explosives using electron rich discrete fluorophores†

Sankarasekaran Shanmugaraju,* Sachin A. Joshi and Partha Sarathi Mukherjee*

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Several π-electron rich fluorescent aromatic compounds containing trimethylsilylethynyl functionality have been synthesized by employing Sonogashira coupling reaction and they were characterized fully by NMR (^{1}H, ^{13}C)/IR spectroscopy. Incorporation of bulky trimethylsilylethynyl groups on the peripheral of the fluorophores prevents self-quenching of the initial intensity through π–π interaction and thereby maintains the spectroscopic stability in solution. These compounds showed fluorescence behavior in chloroform solution and were used as selective fluorescence sensors for the detection of electron deficient nitroaromatics. All these fluorophores showed the largest quenching response with high selectivity for nitroaromatics among the various electron deficient aromatic compounds tested. Quantitative analysis of the fluorescence titration profile of 9,10-bis(trimethylsilylethynyl)anthracene with picric acid provided evidence that this particular fluorophore detects picric acid even at ppb level. A sharp visual detection of 2,4,6-trinitrotoluene was observed upon subjecting 1,3,6,8-tetrakis (trimethylsilylethynyl)pyrene fluorophore to increasing quantities of 2,4,6-trinitrotoluene in chloroform. Furthermore, thin film of the fluorophores was made by spin coating of a solution of 1.0×10^{-3} M in chloroform or dichloromethane on a quartz plate and was used for the detection of vapors of nitroaromatics at room temperature. The vapor-phase sensing experiments suggested that the sensing process is reproducible and quite selective for nitroaromatic compounds. Selective fluorescence quenching response including a sharp visual color change for nitroaromatics makes these fluorophores as promising fluorescence sensory materials for nitroaromatic compounds (NAC) with a detection limit of even ppb level as judged with picric acid.

1. Introduction

Design of suitable chemical sensors for the detection of nitroaromatic compounds (NAC) has attracted much attention in the last decade in an effort to better combat terrorism and control environmental pollution.[1] Among various nitroaromatic compounds trinitrotoluene (TNT), dinitrotoluene (DNT) and picric acid (PA) are the primary constituents of many unexploded land mines worldwide.[2] In addition to their explosive nature, nitroaromatics are also considered as environmental contaminants and are toxic to living organisms.[3] For example, continuous exposure to one of the widely used secondary nitroaromatic explosives TNT can cause headaches, anemia and skin irritation.[4] Moreover, excess TNT may result in liver, eye and neurological damage.[3,4] A selective and highly sensitive chemosensor for the detection and elimination of unexploded nitroaromatic explosives in buried land mines is an urgent need for the protection of living organisms, environmental remediation and national security.[5] Various methods are available for sensing nitroaromatic explosives including metal detectors, which are inefficient for explosive screening in an airport due to plastic casing. Instrumental techniques available for the purpose of nitroaromatic explosive detection include GC-MS, ion mobility spectroscopy (IMS), surface-enhanced Raman spectroscopy, and various other spectroscopic techniques.[6] These instrumental techniques are selective, and some are expensive and not easy to operate in the field. Moreover, many simple techniques are inefficient for explosive detection in the field due to high cost and a lack of selectivity.[7] Thus there is an urgent need to find an efficient and more reliable detection technique which is cheap and very easy to use. Among various transduction methods used for explosive detection, the fluorescence quenching, in particular, is considered to be the most effective tool for sensing nitroaromatic explosives in recent years owing to its high sensitivity, easy visualization, and short response time for detection.[8]

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, 560 012, India. E-mail: shanmugam@ipc.iisc.ernet.in; Fax: +91-80-2360-1552; Tel: +91-80-2293-3352; psm@ipc.iisc.ernet.in

† Electronic supplementary information (ESI) available: NMR (^{1}H and ^{13}C) spectra of the fluorophores **2** and **4**. The fluorescence quenching titration profile of the fluorophores **4** and **5** with picric acid along with their corresponding Stern–Volmer plot and Cartesian coordinates of the complexes for the DFT study are available. See DOI: 10.1039/c1jm10406c

Identifying and distinguishing related (chemically or structurally) compounds by optical detection methods are challenging tasks for chemical sensing based detection.[9] One of the best detection strategies to distinguish structurally related nitroaromatics is to make a series of fluorophores which would eventually provide differential fluorescence quenching responses.[10] Recently, a family of Zn(salicylaldimine)[11] based sensors showed differential optical response to closely related nitroaromatics. Here, we report a series of discrete π-electron-rich fluorophores (Chart 1) which exhibit differential quenching responses for the structurally related nitroaromatics compounds. In addition to the available fluorophores such as conjugated organic polymers by Swager *et al.*,[12] inorganic conjugated polymers by Trogler *et al.*[13] and Zn(salicylaldimine) based small molecule by Knapp *et al.*,[14] we have recently shown that finite 3D supramolecular cages,[15] synthesized *via* a directional bonding approach, can sense nitroaromatics in solution. Despite the intensive and extensive efforts made during the past decade, the development of π-conjugated fluorophores for sensitive and selective detection of nitroaromatic explosives is still required. Two important characteristics need to be considered in designing a new small molecule-based fluorophore for sensing nitroaromatics. Firstly, the fluorophore should be π-electron rich and planar in nature. Secondly, a bulky substituent must be attached on the peripheral of the chromophore to prevent the intermolecular excimer formation through π–π interaction. Our strategies to design a new fluorophore for sensing nitroaromatics (NAC) are very simple, *i.e.*, the introduction of trimethylsilylethynyl (TMS) substituent on the peripheral of the fluorophores. This strategy produces a significant increase in fluorescence emission intensity of the fluorophores and is expected to prevent the intermolecular stacking that decreases the life of the fluorophores. It has been reported that the substitution of a bulky trimethylsilylethynyl (TMS) group on the fluorophore results in a large bathochromic shift of absorption and emission bands than that of unsubstituted fluorophores.[16] This behavior is explained in terms of the σ–π interaction between the C–Si σ and acetylene π bonds. Here, we wish to report the synthesis and characterization of a series of trimethylsilylethynyl (TMS) substituted small molecule-based fluorophores (**1–5**). Fluorophores **1–5** (Chart 1) showed fluorescence behavior in chloroform solution and were used as selective and sensitive fluorescence quenching based sensors for the detection of nitroaromatic explosives. Fluorescence quenching titration revealed that the nitroaromatic compounds (NAC) showed the largest quenching response with high selectivity among the various other electron deficient aromatic compounds. We also report that 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**5**) indicates a detectable visible color change upon subjecting to increased concentration of trinitrotoluene (TNT) in chloroform solution. In the case of fluorophore 9, 10-bis(trimethylsilylethynyl) anthracene (**4**) and 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**5**), a thin film prepared by spin coating of a chloroform/dichloromethane solution (1.0 × 10^{-3} M) over quartz plate showed significant fluorescent quenching responses upon exposure to saturated vapors of nitroaromatic explosives. The vapor phase sensing performance of these thin films showed highly selective and reproducible quenching efficiency towards nitroaromatic compounds.

2. Results and discussion

2.1 Synthesis of fluorophores (1–5)

π-Electron rich aromatic compounds like pyrene and anthracene have been used extensively as fluorescence probes in several applications such as pyrene-labeled oligonucleotides as probes to study DNA hybridization.[17,18] In spite of extensive use as fluorescence sensors, electron rich aromatic compounds have two significant drawbacks as fluorescence probe. Most of the aromatic monomers show absorption and emission characteristics in the UV region and form excimers at higher concentration.[19] As our aim is to sense nitroaromatic explosives by fluorescence quenching of electron-rich aromatic fluorophores, it is desirable to have fluorophores that absorb and emit in the visible region in order to minimize the spectral overlap of the

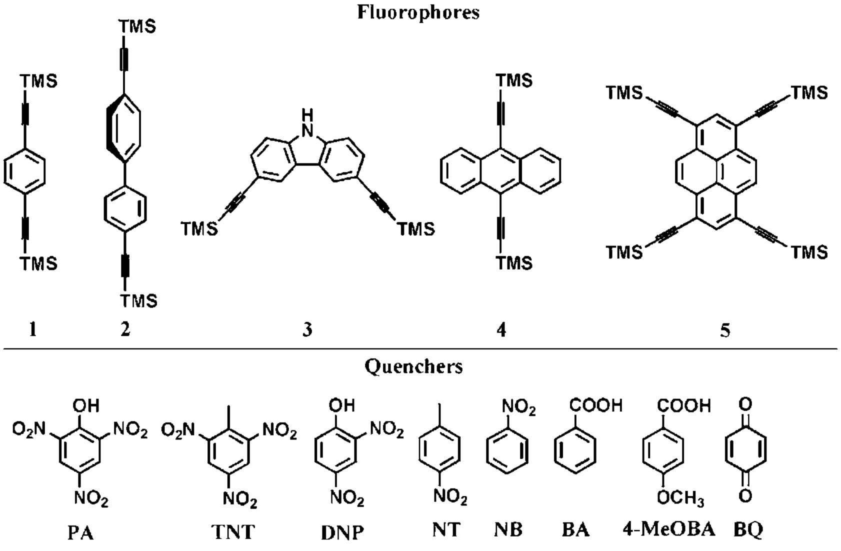


Chart 1

intrinsic fluorescence of nitroaromatics that occurs in the UV region. The well known method to bathochromically shift the emission peak is to increase the conjugation of the fluorophores by substituting unsaturated functional groups. We selected the trimethylsilylethynyl-group as a suitable substituent to increase the conjugation of fluorophores. Interestingly, the trimethylsilylethynyl functional group plays a dual role: its incorporation to pyrene/anthracene fluorophores increases the conjugation through σ–π interaction between the C–Si σ and ethynyl π bonds[16] and it prevents the intermolecular excimer formation (by π–π stacking) to maintain the spectroscopic stability of the fluorophores in solution.

The trimethylsilylethynyl (TMS) substituted fluorophores (**1–5**) were synthesized by employing palladium-catalyzed Sonogashira coupling of corresponding aryl halides and trimethylsilylacetylene under a stream of nitrogen atmosphere (Scheme 1).

2.2 Photophysical study of the fluorophores

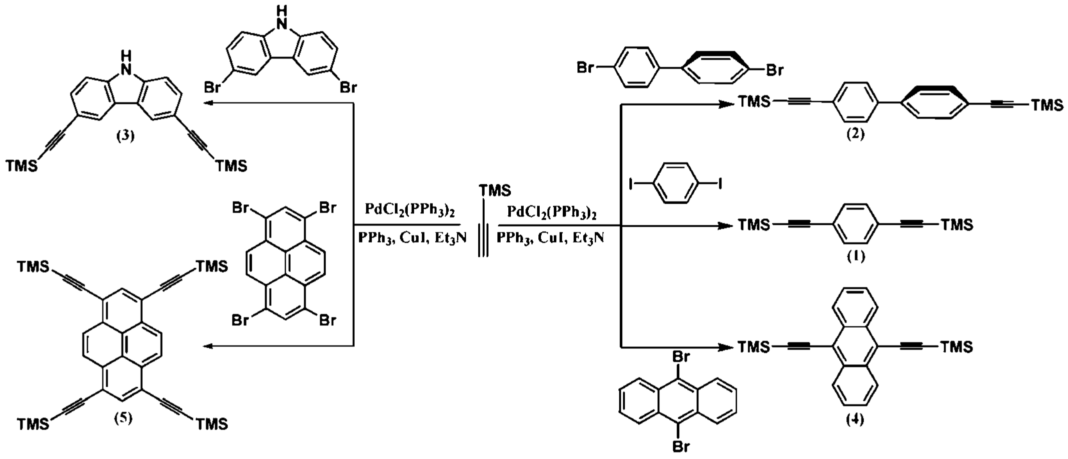
Absorption maxima (λ_{abs}) along with their molar absorptivity coefficients (ε), and fluorescence emission maxima (λ_{em}) of the fluorophores (**1–5**) including solution state fluorescence quantum yield with respect to the anthracene standard in aerated chloroform are given in Table 1. The absorption and fluorescence emission of the trimethylsilylethynyl substituted fluorophores (**1–5**) shifted to longer wavelength (bathochromic shift) in comparison to their starting aryl halides (Fig. 1). Moreover, absorption coefficients of the fluorophores increased with increased number of trimethylsilylethynyl substituents. The induced longer wavelength shift of the fluorophores after attaching the trimethylsilylethynyl group might be due to the σ–π interaction between C–Si σ and acetylene π bonds, which destabilizes the highest occupied molecular orbital (HOMO) and stabilizes the lowest unoccupied molecular orbital (LUMO) of the fluorophores.[20]

2.3 Fluorescence quenching study in solution

As mentioned above, one of the most promising approaches for sensing nitroaromatic explosives is fluorescence quenching based detection. The mechanism of fluorescence quenching involves the formation of charge-transfer (CT) complexes between the electron rich fluorophore and electron deficient quencher. In this study several trimethylsilylethynyl (TMS) substituted fluorophores (**1–5**) have been selected to sense nitroaromatic compounds (NAC) based on the proposed quenching mechanism.

To demonstrate the ability of the selected fluorophores for the detection of nitroaromatic explosives, we first performed fluorescence quenching titration experiments using the fluorophores **4** and **5** with nitroaromatics such as 2,4,6-trinitrotoluene (TNT) and picric acid (PA) in solution. Upon gradual addition of nitroaromatics to a chloroform solution of the fluorophores **4** and **5**, the initial fluorescence intensity was quenched efficiently. A linear Stern–Volmer plot was obtained from the fluorescence quenching titration and the calculated Stern–Volmer binding constants (K_{sv}) were 1.97×10^4 M^{-1} for TNT, 2.15×10^5 M^{-1} for PA (**4**); and 1.4×10^3 M^{-1} for TNT, 1.1×10^4 M^{-1} for PA (**5**) (Fig. 2, 3, S5 and S6 in the ESI†). The obtained quenching constants for TNT and PA are comparable with previously reported values for other small molecules like fluorescein, malachite green, phenol red, *etc.*[21] The linear Stern–Volmer plots suggest that fluorescence quenching involves a static-quenching mechanism at lower concentration of nitroaromatics.

To explore the selectivity, we have also investigated the effect of other electron deficient aromatic compounds on the initial fluorescence intensity of the fluorophores (**1–5**). The selected fluorophores showed differential fluorescence quenching responses among various nitroaromatics compounds, which allowed discriminating of closely related nitroaromatic explosives. The obtained results are shown in Fig. 4, which indicates that almost all the fluorophores show greater quenching response for electron deficient nitroaromatic compounds than other electron deficient non-nitroaromatics such as benzoquinone, 4-methoxybenzoic acid and benzoic acid. The tested non-nitroaromatic quenchers are almost non-polar in nature compared to the nitro-substituted aromatic quenchers. Since the reduction potential of non-nitroaromatic quenchers are not significantly different from the nitro-substituted aromatic quenchers,[2b] we believe that the observed higher fluorescence quenching



Scheme 1 Schematic representation of the synthesis of fluorophores (**1–5**) from the corresponding aryl halides.

Table 1 Photophysical data of the fluorophores (**1–5**) taken in aerated chloroform

Fluorophores	Absorption maxima λ_{max}/nm	Molar absorptivity co-efficient $\varepsilon \times 10^3$/M^{-1} cm^{-1} (λ_{max}/nm)	Fluorescence emission maxima λ_{max}/nm	Quantum yield[a] (Φ)
1	**294**, 279	34 (294)	**316**	0.003
2	**304**	48 (304)	337, **355**	0.04
3	**248**, 283	42 (248)	**375**	0.078
4	**269**, 400, 417, 440	80 (269)	**444**, 471	0.105
5	**440**, 413, 316, 304, 259, 251	76 (440)	**442**, 468	0.164

[a] Using anthracene ($\Phi_f = 0.27$) as the fluorescence standard in ethanol at room temperature. Values in bold in columns II and III represent the highest absorption (λ_{abs}) and emission (λ_{em}) maxima, respectively.

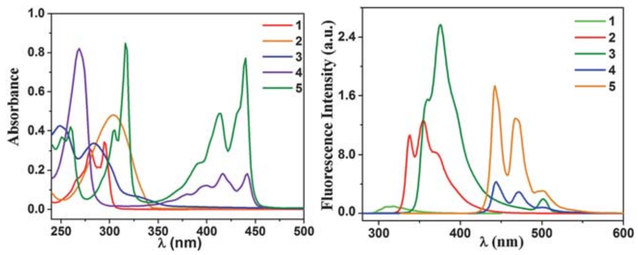


Fig. 1 Electronic absorption (left) and fluorescence emission (right) spectra of the fluorophores (**1–5**) in aerated chloroform solution.

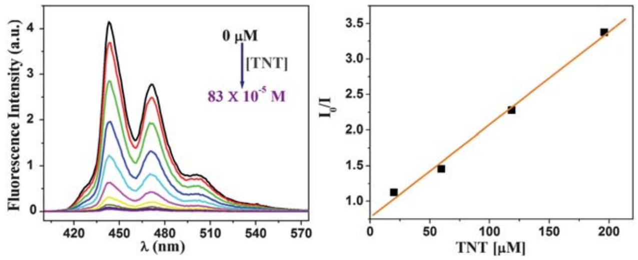


Fig. 2 Fluorescence quenching (left) of the fluorophore **4** (10 μM) with TNT in chloroform solution (λ_{ex} = 270 nm, excitation and emission slit width is 1 nm) and Stern–Volmer plot (right).

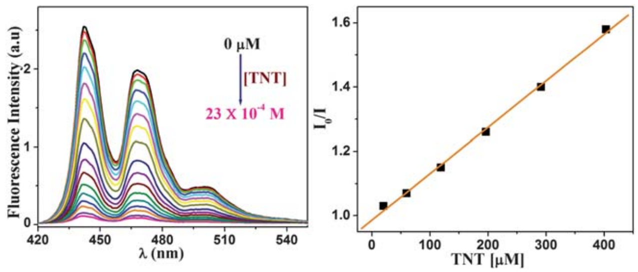


Fig. 3 Fluorescence quenching (left) of the fluorophore **5** (10 μM) with TNT in chloroform solution (λ_{ex} = 316 nm, excitation and emission slit width is 1 nm) and obtained Stern–Volmer plot (right).

responses of nitro-compounds is probably due to the strong dipolar or electrostatic interaction between the electron-deficient analytes 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.

On the basis of purely electronic consideration, π-electron rich 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**5**) might show maximum fluorescence quenching response to the electron deficient nitroaromatic compounds. However, it was observed that electron rich pyrene fluorophore shows poor quenching response towards nitroaromatics than other fluorophores tested (Fig. 4). We ascribe that this poor quenching response may be due to the steric effect of bulky trimethylsilyl groups. The substitution of four bulky trimethylsilyl groups on the peripheral 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, due to the non-planar nature, 4,4′-bis(trimethylsilylethynyl)biphenyl (**2**) fluorophore is expected to have weak interaction with electron deficient nitroaromatics, and in turn, shows poor fluorescence quenching response. Indeed, experimental observation showed that fluorophore **2** exhibits moderate quenching response towards nitroaromatics. But the fluorescence quenching of non-planar fluorophore **2** is much higher in comparison to the π-electron rich planar fluorophore **5**. The reason for this observed anomaly in quenching response is attributed to the less-steric hindrance of trimethylsilyl substituents on **2** and in turn, it increases the effective binding of nitroaromatic quenchers with fluorophore **2** compared to fluorophore **5**. In order to understand the nature of interaction of fluorophore with analytes and to provide further support to the observed fluorescence quenching response, density functional theory (DFT) calculation was carried out using the Gaussian 03 program. We used the MPWB1K hybrid meta density functional developed by Zhao and Truhlar[22] and 6-31G* basis set to optimize the structure of fluorophore–analyte complexes. The electron deficient picric acid (PA) was optimized with 1,8-bis(trimethylsilylethynyl)anthracene (**4**) and 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**5**) in view to obtain the firm evidence for the observed fluorescence quenching response. The optimized structure of the complexes **4·PA** and **5·PA** are given in Fig. 5. As can be seen from Fig. 5 both the fluorophores (**4** and **5**) show strong intermolecular π–π interaction and maintained a co-facial stacked geometry with picric acid (PA). The calculated intermolecular distances between the fluorophore molecular plane and that of picric acid are almost the same (3.17 Å for **4·PA** and 3.30 Å for **5·PA**).

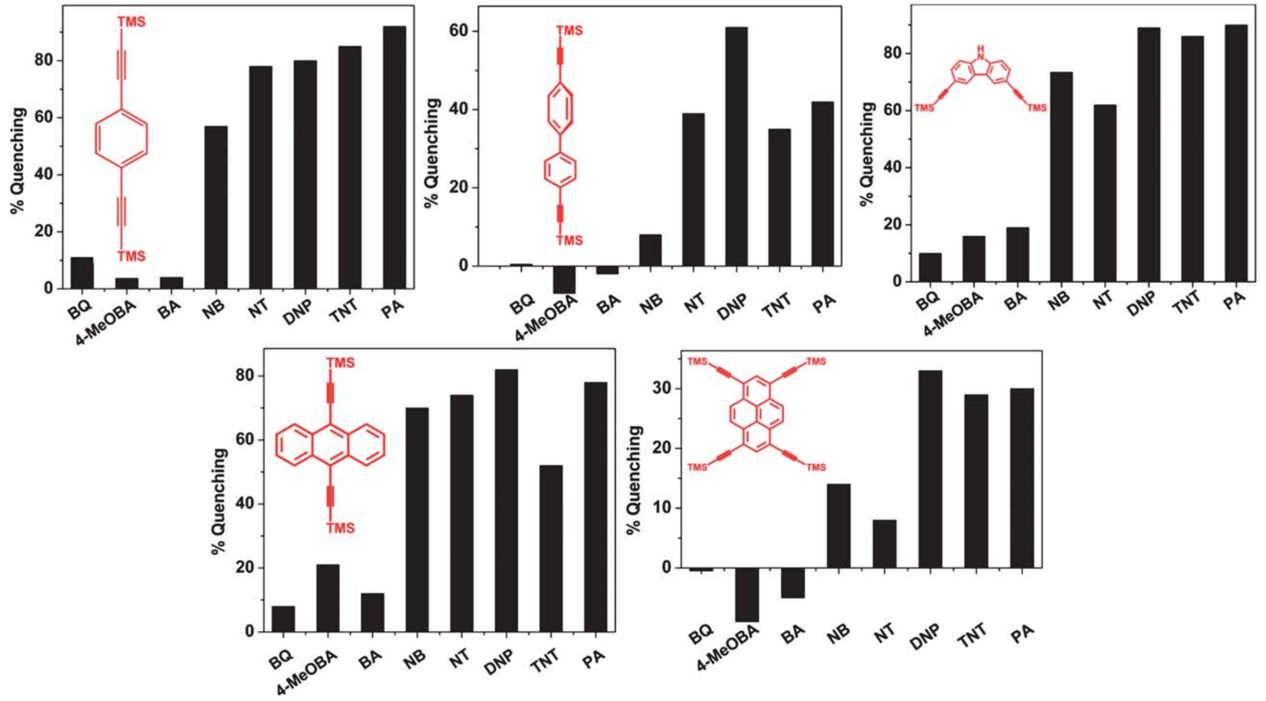


Fig. 4 Changes in fluorescence intensity of the fluorophores (**1–5**) (plotted as quenching efficiency) observed upon the addition of various analytes. BQ = benzoquinone, 4-MeOBA = 4-methoxybenzoic acid, BA = benzoic acid, NB = nitrobenzene, NT = nitrotoluene, DNP = dinitrophenol, TNT = 2,4,6-trinitrotoluene and PA = picric acid.

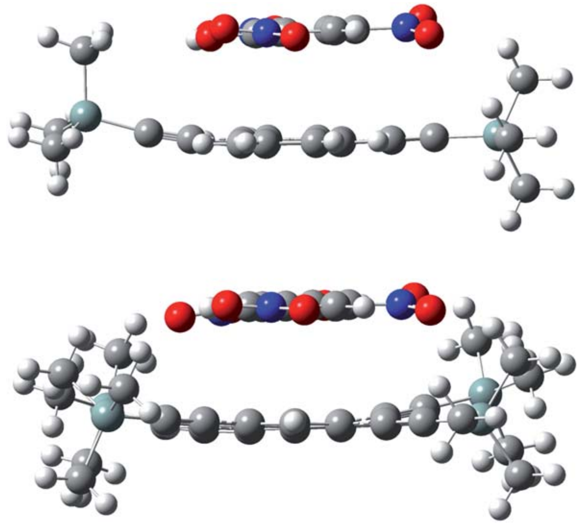


Fig. 5 Optimized geometry of complex **4**·**PA** (top) and complex **5**·**PA** (bottom) (color codes: red = oxygen, blue = nitrogen, grey = carbon, white = hydrogen and light green = silicon).

Moreover, the estimated interaction energy for the complex **4**·**PA** is 16.32 kcal mol^{-1}, which is higher than that of complex **5**·**PA** (14.09 kcal mol^{-1}); this reflects the fact that fluorophore **5** forms a weak excited charge transfer complex with picric acid. The possible reason for the observed weak complexation of **5** with picric acid could be attributed to the propinquity of electron-density from the methyl groups on TMS to the plane of picric acid and that decreases the efficiency of electron transfer from the π-electron rich discrete fluorophore **5** to the electron-deficient picric acid and therefore shows poor fluorescence quenching response towards nitroaromatics in solution.

2.4 Sensitivity

To find the sensitivity of the fluorophores towards nitroaromatics, fluorescence quenching titration was performed using fluorophore **4** with picric acid (PA) at parts per billion (ppb) concentrations. The quantitative analysis of the fluorescence titration profile (Fig. 6) shows that this particular fluorescence sensor can respond to the presence of picric acid as low as ppb level in solution. This level of sensitivity comes under the

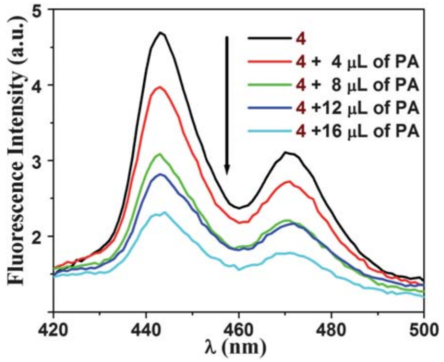


Fig. 6 Changes in initial fluorescence intensity of the fluorophore **4** (0.005 μM in CHCl$_3$) upon gradual addition of PA (0–8 ppb in methanol). (The excitation wavelength λ_{ex} = 270 nm, excitation and emission slit width = 5 nm.)

permissible limit of nitroaromatic explosives such as TNT in drinking water established by the US EPA.[23]

2.5 Visual detection of nitroaromatics

Design of visual sensors for the detection of explosives has been a popular field of research in last two decades owing to their ease of interpretation, simple material handling, rapid detection and more suitable method to practice in the field. The formation of a colored complex[24] creates a new chromophore which shows totally different photo-physical characteristics from the starting explosive residue and sensor molecules including color changes. The sharp color change is the clear identification for the presence of particular chemical explosives. In this study, we have observed a marked color change upon subjecting **5** with trinitrotoluene (TNT) in different concentration in chloroform solution (Fig. 7).

The formation of a charge transfer (CT) complex between π-electron rich fluorophore **5** and electron deficient nitroaromatic TNT was further supported by electronic absorption spectroscopic study. Slight change in the initial absorption intensity of **5** was noticed upon the gradual addition of trinitrotoluene (TNT) in methanol (1.0×10^{-3} M) to a chloroform solution (1.0×10^{-6} M) of fluorophore **5** at room temperature. The strong absorption band of **5** at 303 nm, 316 nm, 389 nm and 412 nm decreases in intensity, while a new broad band at ~342 nm gradually rises upon the addition of increasing amounts of TNT (Fig. 8). In addition to the perturbation observed in the electronic absorption spectra, the progressive appearance of two well defined isosbestic points at 321 nm and at 367 nm indicated the formation of a charge-transfer or donor–acceptor complex between π-electron rich donor **5** and electron acceptor TNT. The binding ratio of fluorophore **5** with the quencher (TNT) was calculated by stoichiometry plot analysis and it was found to be 1 : 2 (Fig. 8). Thus, one molecule of **5** complexes with two quenchers (TNT) in solution.

The formation of charge-transfer complex was further verified by ^{1}H NMR spectroscopic analysis. In a typical ^{1}H NMR titration experiment, a pale yellow solution of picric acid was mixed with fluorophore **5** in 2 : 1 molar ratio in 500 μL of $CDCl_3$. Upon complexation, a significant upfield shifting of the proton resonance corresponding to both the fluorophore **5** and picric acid was observed and subsequent progressive dilution of the NMR sample solution resulted in a gradual downfield shifting of proton resonances (Fig. S7, ESI†). The downfield shifts of resonances attributed to the shifting of equilibrium position from the bound charge transfer state to unbound state of analytes. Based on the electronic absorption and ^{1}H NMR titration experiments, we think that the marked visual color change of fluorophore upon mixing with nitroaromatic quencher is due to the charge transfer complex formation between π-electron donor fluorophores and electron-acceptor nitroaromatic analytes in solution.

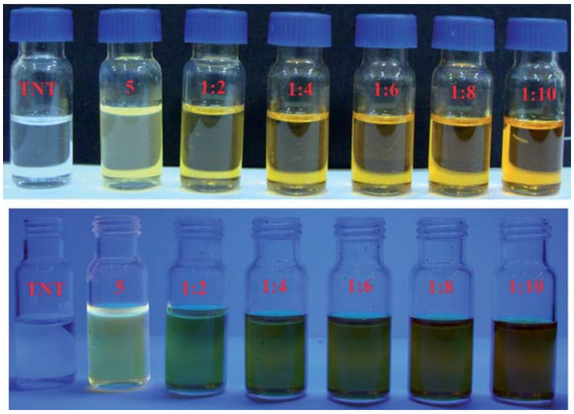


Fig. 7 Visual color changes observed upon subjecting 17 mM solution of **5** in chloroform with increasing quantity of TNT in chloroform (from left to right TNT, fluorophore, 2, 4, 6, 8 and 10 equivalents of TNT) in room light (top) and under hand hold UV light (below).

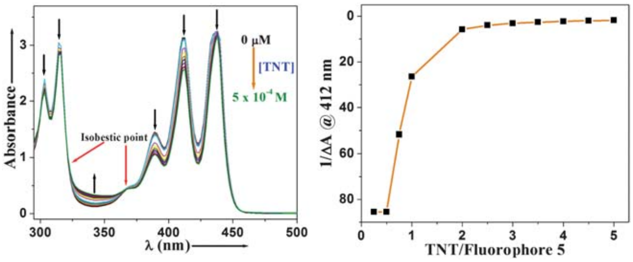


Fig. 8 Absorption spectral changes (left) of fluorophore **5** in chloroform (5.0×10^{-5} M) upon titrating with TNT in methanol ($0–5 \times 10^{-4}$ M) at 25 °C and its corresponding stoichiometry plot (right) monitored at 412 nm.

2.6 Solid-state fluorescence quenching study

Although, sensors in solution are simple and more selective towards nitroaromatic explosives, from the viewpoint of practical use, thin-film sensors are more suitable for field test. Advantages of film sensors over solution sensors are reusability and easy possibility of making into devices. Therefore, the design and preparation of fluorescent film for nitroaromatic explosives detection have become the main focus of material scientists.[25] The solid state fluorescence quenching experiment was performed for the vapor of 4-nitrotoluene (NT) with thin film of the fluorophores **4** and **5**. The thin film of the fluorophore **4** showed strong fluorescence and upon exposure to saturated vapor of 4-nitrotoluene, the initial fluorescence intensity of the film quenched dramatically (Fig. 9). Fig. 9 clearly indicates that the thin film of **4** is sensitive to the vapor of 4-nitrotoluene (NT). Exposure of the film to the saturated vapor of 4-nitrotoluene for 300 s causes nearly 18% quenching of the fluorescence and the

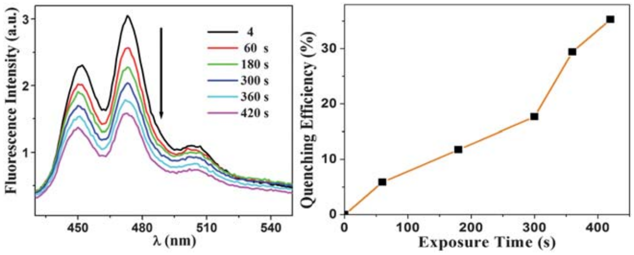


Fig. 9 Fluorescence spectra (left) of the thin film of **4** upon exposure to the saturated vapor of 4-nitrotoluene (NT) at different time and quenching efficiency (right) against time.

efficiency of fluorescence quenching increased further with increasing exposure time. Nearly 40% quenching efficiency was observed after 7 min exposure of the film to NT vapor. On the other hand, the thin film of fluorophore **5** exhibits nearly 40% reduction in the initial fluorescence intensity for 360 s exposure of film to a saturated vapor of 4-nitrotoluene (Fig. 10). Hence, fluorophore **5** looks to be more efficient and faster in response towards nitroaromatics compared to fluorophore **4** in solid state. Conversely, the fluorophore **4** exhibits more quenching efficiency towards nitroaromatics than fluorophore **5** in solution phase and the observed higher quenching performance of **5** in solid phase may be attributed to the rapid vapor diffusion of analytes into the film, which can increase the efficiency of binding while this may be more difficult in solution-phase due to the steric hindrance of methyl groups on TMS. 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 fluorophore and electron-deficient nitroaromatics. It is noteworthy that the film of fluorophore **5** is not only responsive to the vapor of nitrotoluene (NT), but also shows the differential quenching responses to the vapor of other nitroaromatic compounds like nitrobenzene (NB) and nitrophenol (NP). On comparison, the quenching efficiency of the film is more sensitive to the nitrobenzene vapor than that of nitrotoluene and nitrophenol (Fig. 11). 120 s exposure of the film of **5** to the saturated vapor of nitrobenzene results in nearly 50% reduction in the initial emission intensity.

Whereas 120 s exposure of the same film to the saturated vapors of nitrotoluene and nitrophenol exhibits nearly 25% and 46% quenching, respectively (Fig. 11). Overall, the quenching efficiency of the film of fluorophore **5** follows the order of NB > NP > NT (Fig. 11). The reason for the observed differences in the quenching efficiency of the film to different nitroaromatic compounds might be due to their difference in vapor pressure and redox potential. Thus, in the present case, the significantly faster quenching response of nitrobenzene (NB) than nitrophenol (NP) and nitrotoluene (NT) could be attributed to the higher vapor pressure (1.0 mm of Hg at 44.4 °C) of NB. The poor quenching response of nitrotoluene might be due to its lower redox potential (−1.2 V) compared to other nitroaromatic compounds.

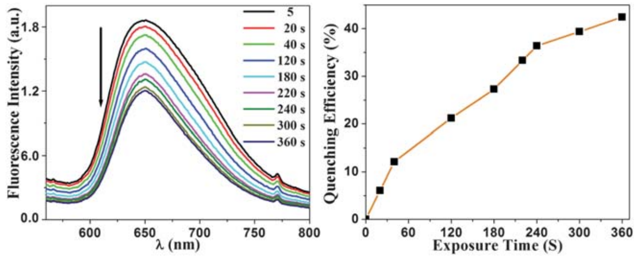


Fig. 10 Fluorescence spectra (left) of thin film of **5** upon exposure to the saturated vapor of 4-nitrotoluene (NT) at different time interval and quenching efficiency (right) against time.

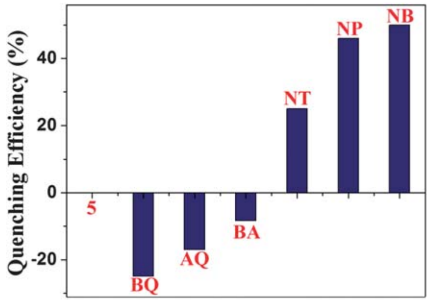


Fig. 11 The percentage quenching efficiency of the thin film of fluorophore **5** by different analytes at room temperature with the exposure time of 120 s.

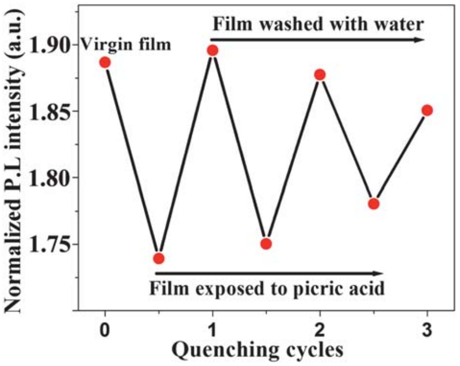


Fig. 12 Reproducibility of sensing ability of thin film **4** to the saturated vapor of picric acid (PA). The film was excited at $\lambda = 380$ nm and the corresponding emission was monitored from $\lambda = 430$ nm. The excitation and emission slit width for all the measurements is 3 nm.

Interestingly, the exposure of the film of **5** to the saturated vapors of other electron deficient aromatic compounds like benzoic acid (BA), benzoquinone (BQ) and anthraquinone (AQ) results in no reduction in intensity rather than a little enhancement of initial fluorescence intensity. Hence, all these sensing experiments revealed that the thin film of fluorophore **5** exhibits highly selective quenching response towards nitroaromatics.

2.7 Recyclability of sensing process

As far as a real-time security application is concerned, the sensing process of a sensor molecule must be a highly recyclable one. The reproducibility of the sensing process was examined using a thin film of the fluorophore **4** with picric acid (PA) at 25 °C. The film was first exposed to a saturated PA vapor at room temperature for 300 s of exposure 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 supplied by a heat gun. The emission spectrum of the film was recorded again and the whole process was repeated for three times. After three cycles the film regained 97% of the initial fluorescence intensity and thus the film can be used for significant number of sensing cycles. The obtained results are given in Fig. 12, which clearly suggests that the sensing response of the film to the PA vapor is basically reproducible.

3. Conclusion

Conjugated polymeric sensors have been widely studied for explosives sensing as several excitons can be quenched by one molecule of analyte. But there are a few drawbacks of polymers: time consuming synthesis, poor solubility in many cases and difficult to control the structure. We report here a series of trimethylsilylethynyl substituted π-electron rich aromatic fluorophores which can act as selective and sensitive fluorescence sensors for nitroaromatics explosives. Strong quenching of the initial fluorescence intensity of the fluorophores (**1–5**) was observed upon the gradual addition of the solution of electron deficient nitroaromatics. The observed fluorescence quenching is ascribed to the charge transfer 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 shows that these molecules are sensitive and able to show the marked quenching response for nitroaromatics as low as parts per billion level concentrations in solution. Vapor phase quenching study of the thin film of fluorophore **4** or **5** revealed that the sensing process is basically recyclable and selective only for nitroaromatic compounds. Sensitive and selective fluorescence response including sharp visual color changes for nitroaromatic compounds makes these fluorophores as promising fluorescence sensory materials for nitroaromatics (NAC). Thus, the present results demonstrate that small molecule fluorophores can also be viewed as a suitable class of compounds for further development of efficient sensors by introducing various substituents that can enhance the binding interaction between the sensors and explosives constituents.

4. Experimental section

4.1 Synthesis of 4,4′-bis[trimethylsilylethynyl]biphenyl (2)

In a flame dried 100 mL round bottom Schlenk flask were dissolved 4,4′-dibromobiphenyl (3.0 g, 9.6 mmol) and 4 mL trimethylsilylacetylene in freshly distilled 100 mL dry triethylamine. A mixture of 150 mg of [$(PPh_3)_2PdCl_2$] (0.21 mmol), 75 mg of triphenylphosphine (0.29 mmol) and 75 mg of CuI (0.4 mmol) was added, and the suspension was refluxed with stirring under nitrogen atmosphere for 12 h. The volatile solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using hexane as eluent to obtain the expected 4,4′-bis[trimethylsilylethynyl]biphenyl **2** as an off-white solid in 80% yield. Anal. calcd for $C_{22}H_{26}Si_2$: C, 76.23; H, 7.56. Found: C, 76.29; H, 7.61%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (s, 8H, biphenyl-H), 0.26 (s, 18H, trimethylsilyl). ^{13}C NMR ($CDCl_3$): δ 140.6, 132.9, 127.2, 122.8, 105.3, 95.7, 0.47 ppm. HRMS: calcd. for $C_{22}H_{26}Si_2$ 346.61; found 347.6 (M + H). IR (KBr): $\nu = 2154$ cm^{-1} for ethynyl group.

4.2 Synthesis of 9,10-bis[trimethylsilylethynyl]anthracene (4)

In a flame dried 100 mL round bottom Schlenk flask were dissolved 9,10-dibromoanthracene (3.0 g, 8.9 mmol) and 4 mL trimethylsilylacetylene in freshly distilled 50 mL dry triethylamine. A mixture of 150 mg of [$(PPh_3)_2PdCl_2$] (0.21 mmol), 75 mg of triphenylphosphine (0.29 mmol) and 75 mg of CuI (0.4 mmol) was added, and the suspension was refluxed with stirring under nitrogen atmosphere for 12 h. The volatile solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using hexane as eluent to obtain the expected 9,10-bis[trimethylsilylethynyl]anthracene **4** as an intense red solid in 60% yield. Anal. calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.85; H, 7.18%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, 4H, J = 10.0 Hz, anthracene-H), 7.62 (d, 4H, J = 10.0 Hz, anthracene-H), 0.42 (s, 18H, trimethylsilyl). ^{13}C NMR ($CDCl_3$): δ 132.7, 127.6, 127.3, 122.8, 118.9, 108.6, 101.9, 0.69 ppm. HRMS: calcd. for $C_{24}H_{26}Si_2$ 370.63; found 371.16 (M + H). IR (KBr): $\nu = 2124$ cm^{-1} for ethynyl group.

4.3 Fluorescence quenching titrations in solution

A 2 mL stock solution (10×10^{-6} M) of the fluorophores (**1–5**) was placed in a quartz cell of 1 cm width and analytes solution (10×10^{-3} M) was added in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated at least three times to get concordant value. For all measurements excitation wavelength (λ_{ex}) 280 nm for **1**, 305 nm for **2**, 249 nm for **3**, 270 nm for **4**, 316 nm for **5** and the corresponding emission wavelength (λ_{em}) was monitored at 290 nm for **1**, 315 nm for **2**, 260 nm for **3**, 280 nm for **4**, and 326 nm for **5**. Both excitation and emission slit widths were 1 nm for **1–5** except for **3** were at 5 nm. Relative fluorescence intensities were measured for the solution of fluorophores **1–5** in chloroform and the various analytes were used as quencher in methanol. There was no change in shape of the emission spectra except gradual quenching of the initial fluorescence emission intensity upon titration with electron deficient nitroaromatic quenchers. Analysis of the normalized fluorescence emission intensity (I_0/I) as a function of increasing quenchers concentration ([Q]) was well described by the Stern–Volmer equation $I_0/I = 1 + K_{SV}[G]$. The Stern–Volmer binding constant was calculated from the slope of the Stern–Volmer plot.

4.4 Preparation of thin films

The stock solution (1.0×10^{-3} M) of the fluorophores **4** or **5** in chloroform or dichloromethane was added drop wise over a clean surface of quartz plate and then the plate was kept under rotation at 60 rounds per second speed for 60 s. This process was repeated at least thrice to get a better film and the film was dried in air before the fluorescence quenching study.

4.5 Solid-state fluorescence quenching study

The fluorescence quenching of the fluorophores **4** and **5** with 4-nitrotoluene in solid state was performed by inserting the freshly prepared thin film into the beaker containing solid 4-nitrotoluene and cotton gauze, which prevents the direct contact of the film with 4-nitrotoluene and maintains the vapor pressure of the quencher during measurements. After a period of exposure, film was placed in the sample holder immediately and checked for the fluorescence quenching of the initial film intensity. For all measurements the excitation wavelength λ_{ex} = 380 nm and corresponding emission was monitored at 430 nm in the case of fluorophore **4**. For fluorophore **5**, the film was excited at λ = 440 nm and corresponding emission was monitored at λ = 450 nm. The excitation and emission slit width were at 5 nm for **4** and 2 nm for **5**. The observed fluorescence quenching was calculated using the following equation

$$\eta = (I_0 - I/I_0) \times 100\%$$

Where, I_0 is the initial fluorescence intensity of the fluorophore and I is the fluorescence intensity after a period of exposure time.

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