Chapter 1
Fluorescent Small Organic Molecules for Detection of Nitroaromatic Explosives – A Review

Nitro aromatic compounds (NACs) are continuously released into the environment during their commercial production in the industry or as raw materials in other industrial processes, during practical use in the laboratories, leaching from military waste sites, mining activity, space experiments etc. The degradation of these NACs leads to generation of both reactive nitrogen oxide species, which readily reacts with biological macromolecules and cause formation of potent genotoxic and mutagenic metabolites. The number of NACs such as trinitrotoluene (TNT), dinitrotoluene (DNT), 1,3,5-trinitro-perhydro-1,3,5-triazine (RDX) or 2,4,6-trinitrophenol (picric acid, PA) are the main ingredients used in the explosives and in the fabrication of landmines. So, the detection of NACs (or explosive material) in ultra low level has become an urgent issue in the interest of both global security and environmental protection. In this context, fluorescence based assays provide advantages due to their high sensitivity, specificity, potential for portability and real time monitoring with fast response time.

Various approaches have been used for the development of fluorescent materials for the detection of NACs e.g. conjugated polymers, metal organic frameworks (MOF), nanomaterials, metallmacrocycles, small organic molecules etc. Each of these approaches have their own advantages and disadvantages. For example, the conjugated polymers though have the advantage of exciton transfer along the conjugated chain resulting in multiple fluorophore quenching by a single molecule of NAC. This results in amplification of the fluorescence quenching. On the other hand, the synthesis requires special efforts and the yield of the desired product is usually low. A small decomposition can disrupt the exciton transfer and sensitivity can be lost. MOFs usually have poor solubility in normal solvents and can not be transformed into films etc. for their film based applications. The small organic molecules provide many advantages over the other methods in terms of (i) their ease in synthesis that leads to their low costs, (ii) the versatility in their design to control their redox
potentials, (iii) ease in their incorporation to presynthesized polymers and to transform them as monoliths, fibers etc., (iv) self-aggregation to different morphologies depending on the choice of solvent or other process conditions etc.

In the present research programme, we have synthesized fluorescent small organic molecules for their applications in detection of nitroaromatic derivatives especially PA, TNT, 2,4-DNP and Cl-DNB etc. The present account of literature gives the advances in the development of small organic molecules for fluorescence based detection of nitroaromatic compounds (NACs). These advances have been classified into different categories (I-VI) to highlight the various approaches used for achieving
the optimal selectivity and sensitivity. The structures of the nitroaromatic compounds along with their abbreviations used in the text have been given in scheme 1.

I. Fluorophores as their monolayers or films in polymers
II. Fluorophores in molecular state
III. Fluorophores as their aggregates
IV. Fluorophores as supramolecular polymers
V. Tweezer, cyclophane and cage shaped fluorophores
VI. NACs induced aggregation and fluorescence enhancement

I. Fluorophores as their monolayers or films in polymers

Pyrene is the smallest and first to be used fluorophore for the detection of nitroaromatic compounds. Scaiano et al in 2005 reported\(^{30}\) that ethanolic solution of pyrene (3 mM) gave emission due to both monomer and excimer which was quenched with 1,4-DNB, 1,3-DNB, NB and 5-nitro-m-xylene with nearly equal ease and with \(K_{sv}\) values between 572-618 M\(^{-1}\).

![Figure 1](image1.png)

![Figure 2](image2.png)

![Figure 3](image3.png)

Lei et al\(^{31}\) for the first time (2012) performed electro spinning of pyrene with polystyrene in the presence of tetrabutylammonium hexafluorophosphate to fabricate nano-fibers with diameter 120 ± 20 nm and length of few micrometers. These fibers on exposure to vapour of 2,4-DNT (~193 ppb) exhibited ~ 46% fluorescence quenching at 470 nm within 36 seconds and more than 90% was achieved within 6 minutes. A wide spectrum of nitro explosives, in particular, TNT, Tetryl, RDX, PETN and HMX could be “visually” detected at their subequilibrium vapours (less than 10 ppb, 74 ppt, 5 ppt, 7 ppt and 0.1 ppt, respectively) released from 1 ng explosive residues. Such outstanding
sensing performance could be attributed to the proposed “sandwich-like” conformation between pyrene and phenyl pendants of polystyrene (Figure 1) which allowed efficient long-range energy migration similar to “molecular wire”, thus achieving amplified fluorescence quenching. The films were used for the detection of buried explosives in soil by naked eye and indicated their potential application for landmine mapping.

Bayindir et al \(^3\) prepared worm-like structured thin film (Figure 2) from pyrene doped polyether sulfone solution in THF for the detection of nitroaromatic explosive vapour. \(\pi-\pi\) stacking of NAC with pyrene molecule in the thin fluorescent film allowed highly sensitive fluorescence quenching which was detectable by the naked eye in a response time of a few seconds. The quenching performance of films followed the order of 2,4-DNT > TNT > NB. The authors did not make any comment on the sensitivity of these films towards PA.

Lie et al \(^3\) later on (2015) found that electro spinning of DMF-THF (4:6) solution of polyether sulfone 6 \% and pyrene (0.1 M) gave more uniform films (Figure 3) with relatively smaller diameter (44.2 ± 15.9 nm) and length of few \(\mu\)M. The Stern–Volmer (S–V) plot for pyrene excimer fluorescence quenching by PA showed two linear regions at low (0–1 \(\mu\)M) and high concentration range (>1 \(\mu\)M) with a quenching constant of 1.26 \(\times 10^6\) \(\text{M}^{-1}\) and 5.08 \(\times 10^4\) \(\text{M}^{-1}\), respectively. The calculated \(K_{sv}\) values for other NACs were 1.80 \(\times 10^5\) \(\text{M}^{-1}\) for TNT, 7.52 \(\times 10^4\) \(\text{M}^{-1}\) for 2,4-DNT and 3.26 \(\times 10^4\) \(\text{M}^{-1}\) for RDX. LOD for PA, TNT, DNT and RDX in aqueous phase were \((S/N = 3)\) 23, 160, 400, and 980 nM, respectively. The films were used multiple times for detection of 10 \(\mu\)M TNT and then regenerating by rinsing in water.

Bayindir et al \(^4\) also prepared mesoporous thin films with bright pyrene excimer emission and studied their application in visual and rapid detection of nitroaromatic explosive vapour. The fluorescent films were produced by physically encapsulating pyrene molecules in the organically modified silica (ormosil) networks. Excimer emission was significantly brighter and excimer formation ability was more stable in porous films compared to nonporous films. Rapid and selective quenching was observed in the excimer emission against vapors of nitroaromatic molecules; TNT, 2,4-DNT, and NB. Fluorescence quenching of the films could be observed under UV light, enabling the naked-eye detection of nitro-explosives. Furthermore, excimer emission signal was
recovered after quenching simply by washing with water and the films could be reused at least five times.

Liu et al\textsuperscript{35} prepared fluorescent electro-spun nanofibrous films from fluorophore tetrakis(4-methoxyphenyl)-porphyrin and polystyrene with uniform diameters of 300–400 nm. The electrospun nanofibrous films exhibited much stronger emission than simple drop cast films. The sensitivity of electrospun films was further enhanced by using TX-100 as a porogen to create secondary porous structure. The nanofiber films pre-treated with 2,4-DNT vapours regained the fluorescence intensity on heating at 60°C for 20 min and lost only 10% fluorescence intensity after six quenching-regeneration cycles. After 40 min exposure, the percentage of fluorescence quenching was 38%, 17%, 4%, and 2% for 2,4-DNT, 2,4-DNP, TNT and PA vapours, respectively. Thus these electro-spun nanofibrous films revealed the potential to sensitively detect down to several parts-per-billion of TNT vapour or several parts-per-trillion of PA vapour in the atmosphere.

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The number of research groups has exploited the fluorescence quencher behaviour of pyrene moieties with NACs by designing the pyrene based organic molecules attached on the glass surface or on silicon polymers for the detection of aromatic compounds. Fang et al\textsuperscript{36} chemically immobilized molecules of 1 onto a glass wafer surface via a flexible spacer by employing a single-layer chemistry technique. The respective film proved sensitive to the presence of trace amounts of NACs both in the vapor phase and in aqueous solution. For vapor phase sensing, the vapor pressure of the NACs was a predominant factor to affect the film’s response time and the quenching efficiency and followed the order NB > 2,4-DNT > TNT > PA. For aqueous phase sensing, however, the fast and efficient response of the films to PA was attributed to the specific affinity of the
films to PA due to possible proton transfer from the quencher to the film surface. The quenching process was reversible, both in the vapor phase and in aqueous solution. The detection limit by thin film was $2.08 \times 10^{-7}$ M for PA and reversibility of the sensing process was almost perfect when evaluated at PA concentration of 30 µM.

Elliott et al.\textsuperscript{37} modified the gold quartz crystal microbalance (QCM) surface with dithiol-functionalized pyrene derivative 2 to create a π-electron rich surface, which was able to interact with electron poor aromatic compounds. For example, exposure of the modified QCM surface to 2,4-DNT in solution resulted in a reduction in the resonant frequency of the QCM as a result of supramolecular interactions between the electron-rich pyrenyl surface layer and the electron-poor DNT molecules. The formation of a face-to-face π-stack between pyrenyl derivative 2 and 2,4-DNT was verified through \textsuperscript{1}H NMR spectroscopy.

Fang et al.\textsuperscript{38} also attached pyrene moieties on the glass surface via a long flexible spacer based on self-assembled monolayer technique. These surface-attached pyrene moieties 3 exhibited both monomer and excimer emission. NACs such as TNT, 2,4-DNT and PA efficiently quenched the emission of this film. The excimer emission of these surface-confined pyrene moieties at 505 nm was more sensitive to the presence of NACs than the monomer emission at 380 nm and the quenching efficiencies were in the order PA > TNT > 2,4-DNT. The fluorescence lifetime measurement revealed that the quenching was static in nature and could be caused by electron transfer from the polycyclic aromatics to the NACs. Furthermore, the response of the film to NACs was reversible, and showed promising potentials in detecting explosives in aqueous environment.

Jeppesen, Martinez-Manez and co-workers\textsuperscript{39} prepared three new hybrid gated mesoporous silica (MPS) materials loaded with the dye [Ru(bipyridine)$_3$]$^{2+}$ and capped with different tetrathiafulvalene (TTF) derivatives 4-6 with different sizes and shapes and incorporating different numbers of sulfur atoms. Suspensions of these solids in acetonitrile showed “zero release” of dye [Ru(bipyridine)$_3$]$^{2+}$, most likely because of the formation of dense TTF networks around the pore outlets. The release of the entrapped [Ru(bipyridine)$_3$]$^{2+}$ dye from MPS derivatives 4-6 was studied in the presence of tetryl, TNT, TNB, 2,4-DNT, RDX, PETN, PA, and TATP. The derivative 6 showed a fairly
selective response to Tetryl, whereas derivatives 4 and 5 released dye with tetryl, TNT, and TNB. The uncapping process in these MPS materials could be ascribed to the formation of charge transfer complex between the electron-donating TTF units and the electron-accepting nitroaromatic explosives. Derivatives 4 and 6 were used for tetryl detection in soil.

Stein et al\textsuperscript{40} prepared 1,3,6,8-tetraphenyl substituted pyrene compound 8 and mesoporous silica thin films by spin-coating mixtures of TEOS, P123 surfactant and derivative on a quartz substrate under defined conditions. They also prepared bridged MPS films derived from derivative 7 as sensors for 2,4-DNT on the basis of fluorescence quenching rates and efficiencies. In solution, 8 showed good interactions with 2,4-DNT with a quenching constant $K_{sv} = 2195$ M\textsuperscript{-1}. The sensing performance of the films toward 2,4-DNT in the gas phase depended on both film structure and film composition. Surfactant-free, derivative 7-bridged films with wormlike mesopores showed the best performance, comparable to the most advanced fluorescence sensors based on conjugated polymers. The fluorescence of surfactant-containing, derivative 8 doped mesoporous silica films were also effectively and quickly quenched by 2,4-DNT, with detection limits of the order of $10^{-8}$ M or better.
Tang, Yu and coworkers\textsuperscript{41} prepared mesoporous SBA-15 functionalized with aggregation-induced emission (AIE) luminogens tetr phenylethene (represented as 9) as a supersensitive fluorescent sensor for the detection of PA, with a $K_{sv}$ up to $2.5 \times 10^5 \text{ M}^{-1}$ in a water solution which was better than linear conjugated polysiloles reported in the literature\textsuperscript{42} ($2 \times 10^4 \text{ M}^{-1}$). The high pore volume and large surface area of the material enhanced efficient mass transport and strong interactions with the adsorbed explosive molecules. A very rapid fluorescence quenching response was observed due to the efficient photoinduced electron transfer and/or energy transfer quenching process within the nanopore. The results show that more TPE loading could lead to higher sensing performance with the detection limit being up to 0.4 ppm. The mesoporous material was reused after washing with acidic THF and alkaline aqueous solution.

Serein-Spirau, Viau and coworkers\textsuperscript{43} obtained ionogels of compound 10 and similar polymer 11 under non-aqueous sol–gel conditions by mixing them with [C4mim][NTf\(_2\)], formic acid (FA), tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS). Ionogels derived from 10 and 11 showed very slow fluorescence quenching (50\% emission decay in 16 h) when exposed to 2,4-DNT vapour which was ascribed to the slow diffusion of 2,4-DNT in to the pores of ionogels.
Tonga, Donga and coworkers fabricated layer by layer self-assembled films by alternately depositing 4,4’-biphenyldiazonium (BPD) salts and nanoaggregates of 12 on quartz slides. Derivative 12 which was non-emissive in water turned into strongly emissive in the water/THF (1:9) owing to AIE effect. The nano-aggregates of 12 with BPD salts were covalently linked after UV-irradiation. The bilayer film was found to be emissive and responded sensitively to volatile solid nitroaromatics, including nitroanilines and TNT but took ~10 minutes to provide evidential difference.
Shaw, Burn, Meredith and coworkers\textsuperscript{45,46} synthesized three generations of fluorescent carbazole dendrimers with spirobifluorene cores for the detection of nitroaromatic explosives via fluorescence quenching. Each dendrimer was tested with the five analytes: 2,4-DNT, 1,3-DNB, 4-NT, DMNB, and BP. In solution studies, for each analyte there was a significant increase in the Stern–Volmer constant between first generation (13) and second generation (14) dendrimers but with only a small difference between the values for second (14) and third (15) generation dendrimers. In solid state, three generations of dendrimers gave same response to each analyte and pointed that the synthesis of higher generation dendrimers was not beneficial for detection of NACs. In solid state, in the presence of saturated DNT vapour, ~ 30% fluorescence quenching was observed in 10 s. Heating of the analyte-exposed dendrimer films at temperatures > 60 °C under N\textsubscript{2} was essential for recovery of fluorescence.

The authors studied diffusion behaviour\textsuperscript{47} of 4-NT towards these dendrimers using a quartz crystal micro balance (QCM) and neutron reflectivity (NR) measurements. The studies revealed that 4-NT molecules were absorbed into the film in molecular ratio of 4-NT to dendrimer 1.67 ± 0.05 and were evenly distributed throughout the bulk of the films at saturation. The sorption process was found to be thermodynamically controlled and independent of film thickness. The films based on 15 exhibited full recovery of emission on heating at 40-60°C despite the presence of residual 4-NT which could be ascribed to large decrease of exciton diffusion coefficient with 15, preventing migration of the excitation to the remaining bound 4-NT.

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Anzenbacher et al synthesized\textsuperscript{48,49} iptycene derivatives 16a-f with different fluorogenic moieties attached to the benzene core of the iptycene. Dichloromethane
solutions of 16a-e underwent efficient fluorescence quenching with TNT and 2,4-DNT which was comparable to, if not better than, the iptycene-based amplifying polymers or polysilole sensors. The formation of non-emissive excited state by PET from LUMO of the receptor to LUMO of the NAC was responsible for fluorescence quenching. As expected the lowering in energy of LUMO in receptor 16f due to increased conjugation resulted in lower $K_{sv}$ values than that observed for 16a-e. The polyurethane nanofibres (300-400 nm diameter) electrospun from a solution of 16e (0.03%) and polyurethane (10%), underwent observable fluorescence quenching within 2-3 min and fluorescence was recovered upon re-equilibration in pure air. The encapsulation of NB through edge to face mode between the aromatic guests and electron-rich faces of the pentyptcene aromatic cavity was confirmed by X-ray crystal structures of complexes of 16b, 16c and 16e.

McLean, McHugh and coworkers have reported that the solid state vapour response towards derivatives 17 and 18 films was strongly influenced by the solid state structure and morphology of the thin film environment. Seeded thin films of derivative 18 required 756 minutes to achieve 50% reduction of emission intensity in comparison to 200 minutes taken by amorphous films of 17 and reflected the greater accessibility of fluorescent species to 2,4-DNT vapour in the amorphous film versus the more ordered seeded film environment. Seeded 100 nm thick films of derivative 18 gave 30% and 15% reduction of the total emission intensity within 2 minutes of exposure to NB and 2,4-DNT vapour, respectively. However, with 2,4-DNT, a greater degree of overall quenching was observed (45% at saturation). The difference in total fluorescence quenching was ascribed to the increased reduction potential and enhanced electron transfer rate constant of 2,4-DNT versus NB with seeded film of derivative 18.
Montméat et al\textsuperscript{52} have described a portable detector based on a specific fluorescent derivative \textsuperscript{19} for the detection of NACs. The thin film was deposited on a glass substrate that acted as a wave-guide and the developed sensor was able to detect explosives in ambient air or on objects tainted with explosives. In the presence of nitroaromatic vapors, the fluorescence of the material decreased due to the adsorption of NACs on its specific adsorption sites. The sensor could detect as low as 0.75 and 148 ppb of TNT and 2,4-DNT, respectively. Moreover, the detector demonstrated no loss of performance in the presence of humidity or interfering compounds.

\section*{II Fluorophores in molecular state}

Shaw et al\textsuperscript{53} also prepared a series of fluorescent tripodal systems that exhibited fluorescence quenching by both nitroaromatics and the plastic explosives taggant DMNB. Time-resolved measurements of fluorescence demonstrated that in contrast to conjugated polymers, quenching was dominated by collisional interactions between the tripod and the analytes with a minor static component which was also supported by low (< 100) $K_{sv}$ values for steady state fluorescence quenching.

Zhang et al\textsuperscript{54} reported a 3D nanographene \textsuperscript{22}, with three hexa-peri-hexabenzocoronenes units arraying in the 3D triptycene scaffold which displayed strong intrinsic fluorescence properties and could be used as a detector for TNP with quenching efficiency $K_{sv}$ of 1.8 x
and sensitivity of 2.4 ng/mm². The quenching efficiency was in order TNP > 2,4-DNP > 4-NP which is in consistent with the mechanism of charge–transfer process.

Murugavel et al.⁵⁵ have reported supramolecular fluorophores 23 and 24 which selectively sensed PA over other NACs viz. TNT, 2,4-DNT, 1,3-DNB and 1,4-DNB. Steady-state and time resolved fluorescence measurements indicated predominantly static quenching of these fluorophores with NACs. On replacing NH₂ groups with dimethylamino groups, $K_{sv}$ value was increased from $1.2 \times 10^5$ to $3.87 \times 10^5$ M⁻¹ which is in parallel with increased electron donating ability of derivative 24 in comparison with derivative 23. Acetonitrile solution of 23 exhibited fluorescence emission at 405 nm, which was shifted to 480 nm due to the emissive nature of the 23-PA complex. Films derived from 23 and 24 could also be utilized to detect TNT and 2,4-DNT vapour.

Xu et al.⁵⁶ constructed first "off–on" and ratiometric fluorescent probe based on ICT mechanism for PA recognition in the NIR region. The authors proposed that on
protonation of dimethylamine group of dansyl moiety through acid-base interaction, the sulfone linkage in 25 prevented the spread of the ICT interaction to squaraine backbone, thereby minimizing its fluorescence quenching effect. Furthermore, the twisted dimethylamine naphthyl unit prevented the squaraine plane from its \( \pi-\pi \) interaction with PA, reducing the efficiency of electron and energy transfer. The limited influence of PA on the squaraine backbone shifted the fluorescence signal without quenching, thereby enabling the ratiometric detection of PA. Upon addition of PA, the absorption at 663 nm gradually decreased, whereas a new absorption peak appeared at 627 nm associated with change in color of the solution from blue to green-yellow. On excitation at 620 nm, the maximum emission of 25 at 684 nm decreased and a new emission peak at 644 nm appeared, which evidently increased in intensity upon successive additions of PA. The detection limit for PA determination was 70 nM.

Anzenbacher et al\(^5\) designed probes 26-28 to differentiate between TNT and RDX by turn on response with RDX and turn off response with TNT. RDX, known to undergo base catalyzed cleavage to 4-nitro-2,4-diazabutanal, HCHO, and N\(_2\)O, on interaction with probe 28 formed imine on the terminal \(-\text{NH}_2\) groups and rendered the PET from the nitrogen atoms to the pyrene unfavorable resulting in turn on fluorescence response. TNT, 2,4-DNT and 2,6-DNT caused fluorescence quenching of probes 26-28 owing to Förster resonance energy transfer (FRET) mechanism in TNT–amine Meisenheimer complex. 2,3-Dimethyl-2,3-dinitrobutane (DMDNB) showed extremely high affinity for probes 27 and 28 with \( K_{sv} \) values > 10\(^4\) M\(^{-1}\) which was assigned to the formation of a loosely bound complex held together by hydrogen-bonding interactions between the NH groups of the probe and NO\(_2\) groups of DMDNB.
Peng, Wang and coworkers\textsuperscript{58} reported that the solution of probe 29 in DMF displayed only an excimer emission band at 483 nm ($\lambda_{ex}$ 419 nm) which was completely quenched in the presence of 1 equiv. of PA. A single-crystal X-ray diffraction analysis of 1 : 1 host–guest complex 29-PA revealed that the nitrogen of the pyridine group of derivative 29 is protonated to form a cation while picric acid is deprotonated to form the anion. The cations of 29 and picate anions are self-assembled to form a supramolecular structure via multiple hydrogen-bond and $\pi$–$\pi$ interactions.

Mukherjee et al\textsuperscript{59} synthesized five $\pi$-electron rich fluorescent aromatic derivatives 30-34 where incorporation of bulky trimethylsilylethynyl groups on the peripheral of the fluorophores prevented self-quenching of the initial intensity through $\pi$–$\pi$ interaction and thereby maintained the spectroscopic stability in solution. Amongst these fluorophores, derivative 33 exhibited largest $K_{sv}$ values toward NACs and amongst NACs, it detected PA even at ppb level in chloroform solution. The presence of four bulky trimethylsilyl groups on the periphery of the pyrene chromophore resulted in poor fluorescence quenching response toward NACs owing to sterically demanding situation.
Siegel, Sukwattanasinitt and coworkers synthesized triphenyl amine derivatives for detection of TNT. Despite having the same number of fluorogenic units, displayed significantly lower quenching efficiencies \( K_{sv} = 8.4 \times 10^2 \) and \( 7.2 \times 10^2 \ \text{M}^{-1} \) than those of \( K_{sv} = 1.7 \times 10^4 \) and \( 6.4 \times 10^3 \ \text{M}^{-1} \). \(^1\)H NMR studies confirmed that the hydrogen bonding of nitro oxygen with triazole CH played an important role in enhancing quenching. The lower sensitivity of the corannulene (B) was attributed to its bowl shape geometry, which probably could not well accommodate the interaction with TNT. The paper strips allowed visual detection of 0.58 ng /m² TNT.

The analyte mediated ring opening of various xanthene derivatives has been quite frequently used as a tool for the qualitative and quantitative determination of cations and anions in organic and aqueous media. Sivaraman, Chellappa and coworkers reported a rhodamine based chemosensor 39, which in the presence of PA resulted in appearance of absorption bands at 535 nm and 425 nm and increase in fluorescence intensity at 557 nm. The addition of TFA and HCl caused increase in absorbance at 527 nm and fluorescence at 547 nm and points to their interference in the estimation of PA. The respective detection limit (LOD) and binding constant of PA with 39 was found to be 45 nM and 5.64x10⁷ M⁻¹, respectively. The authors on the basis of \(^1\)H NMR studies of 39 with PA suggested that the ring opening of the ring by PA mediated protonation of dimethylamino nitrogen was responsible for the observed color and fluorescence changes.

Bhalla, Kumar and coworkers have designed a hexaphenylbenzene (HPB) based derivative 40 having rhodamine moiety connected to it through a phenyl spacer. The emission of HPB moiety at 430 nm and absorption of rhodamine at 554 nm allowed minimum overlap of emission and absorption spectra restricting FRET phenomenon and thus allowed through bond energy transfer from HPB to rhodamine. The presence of rotor
in HPB around its own axis could affect the electron conjugation between donor and acceptor moieties to allow TBET. The addition of PA (0-30 equiv.) to the solution of receptor 40 in methanol resulted in appearance of two new absorption bands at 348 (due to PA) and at 554 nm (due to ring opened rhodamine) and an emission band at 578 nm (Φ = 0.82, λex 314 nm). The LOD for PA by derivative 38, in solution and by contact mode, respectively was 35 nM and 104.9 pg cm⁻². The addition of other NACs viz. 4-NP, 2,4-DNP, 2,4-DNT, 2-NT, 1,4-DNB to the solution of 40 did not affect the absorbance or fluorescence of the probe 40.

Ravikanth et al.⁶³ reported a BODIPY based chemosensor 41 which was weakly emissive in CH₃CN-water (9:1) because of the PET from the acetal oxygen to the BODIPY core. On addition of PA, PET process was arrested due to hydrolysis of the acetal groups to aldehydes and the fluorescence intensity was 6-fold increased. This was associated with increase in Φ from 0.08 to 0.48 and singlet state lifetime increase from 0.42 to 5.8 ns. The LOD and binding constant values were respectively 162±13 ppb and 9.2 x 10⁶ M⁻¹. Thin films prepared by spin coating of CHCl₃ solution of 41 on quartz substrate exhibited red-shifted emission band at 612 nm (red fluorescence) as compared to at 534 nm in solution state. The emission intensity of these films was reduced by 26% (120 s); 52% (300 s), 83% (500 s) on exposure to saturated vapour of PA.

Ajavakom et al.⁶⁴ synthesized glucopyranosyl-1,4-dihydropyridine derivative 42 as a fluorescent chemosensor providing an accurate quantitative determination of PA, 2,4-DNP and 4-NP in real water samples. The solution of 42 gave blue emission centred at ~450 nm (Φ = 29%) which was gradually quenched on addition of aliquots of PA with LOD 0.94 μM. Fluorescent paper sensor was fabricated for the on-site convenient,
sensitive and selective naked-eye detection of trace amounts of PA vapour down to 0.06 ppb.

Bayazit et al\textsuperscript{65} presented the direct use of indolizine derivative 43 as a photochemical sensor for the solution phase detection of nitroaromatics. Fluorescent quenching experiments depicted that nitroaromatics, particularly nitrophenol derivatives, could be detected by diester 1 with a detection limit of $6.66 \times 10^{-8}$ M. The fluorescent quenching probably occurred \textit{via} electron transfer from electron-rich indolizine to electron deficient nitrophenolics through H-bonding interaction between carbonyl/amine groups and hydroxyl as supported by $^1$H NMR and FTIR studies.

Paz, Tomé and coworkers have developed phosphonate pyrene motifs\textsuperscript{66} as chemosensors for NACs. The formation of a porous and fibril-type layer of thin films of 44 and 45 opened the possibility of fabricating highly responsive materials towards the detection of NACs. This system acts as a dual chemosensor for the fast detection of TNT as a monomer in solution and as a stable excimer in the solid state. The solutions of 44 and 45 in methanol exhibited gradual decrease in fluorescence intensity on addition of TNT, showing 91\% and 82\% quenching effect for 44 and 45 with a limit of detection (LOD) in the range of 2–14 ppb. The higher quenching efficiency of 44 than that for 45 with the addition of TNT has been attributed to strong $\pi$-$\pi$ and hydrogen bonding interactions between the quencher and 44 which was evident from $^1$H NMR studies.

Chen, Wang and coworkers\textsuperscript{67} synthesized sixteen tris(benzimidazole) based compounds, amongst which derivative 46 exhibited the best capability for detection of PA, having good selectivity and high sensitivity. The sensitivity of 46 towards NACs decreased in the order PA $>$ 2,4-DNP $>$ 4-NP $>$ TNT $>$ 2,4-DNT. The Ksv of 46 for PA
was $1.115 \times 10^5 \text{ M}^{-1}$. The observed fluorescence quenching for PA was attributed to the energy transfer from photo excited $\pi$-electron rich 46 to ground state of electron-deficient PA. The hydrogen bond interaction of OH groups with benzimidazole of 46 in case of PA, 2,4-DNP, and 4-NP could also enhance the energy transfer ability to quench the fluorescence of 46. Paper strips coated with solution of 46 could detect 11.45 pg·cm$^{-2}$ PA.

### III Fluorophores as their Aggregates

The number of polyaromatic hydrocarbons based systems have been developed which remain by and large in molecular state in organic solvents but in partially aqueous media these derivatives undergo self-aggregation usually associated with aggregation induced emission enhancement (AIEE). Therefore, the aggregates being having larger quantum yield than in their molecular state, in principle exhibit more change in fluorescence intensity on interaction with any NAC. Also, if any NAC molecule is absorbed or adsorbed by the aggregate, it can cause fluorescence quenching of multiple fluorophores through exciton migration or more efficient energy transfer due to proximity of donor-acceptor moieties. Consequently, number of research groups have synthesized molecular probes based on triphenylene, athracene, pyrene, fluoranthene, $p$-phenylvinylene etc. fluorophores and have studies their NAC detection abilities in aggregate state.

Bhalla et al$^{68}$ developed triphenylene-based discotic liquid crystals 47 bearing 1,2,3-triazole groups which resulted in stabilization of columnar mesophases down to room temperature and formed organogels in cyclohexane and hexane - dichloromethane mixture (4:1) as observed from POM, SEM and TEM analysis. The emission band of 47 (DMSO, $\lambda_{\text{max}}$ 383 nm) was completely quenched upon addition of PA (270 equiv), 2,4-DNT (520 equiv), 2,4-DNB (500 equiv) and 4-NT (650 equiv). The organogel of 47 in cyclohexane was transformed to solution on exposure to saturated vapours of PA for 8h and was associated with complete disruption of supramolecular assembly.
Derivative 48, with increased chain length, showed greater tendency to aggregate in non-polar solvents resulting in non-emissive aggregates in cyclohexane. In THF-water (95:5) mixture, weak π–π interactions between the molecules resulted in aggregates with $\Phi = 0.22$. In presence of 50 equivalents of NACs, the order of quenching efficiency of aggregates of 48 was PA > 2,4-DNT > 4-NT > 1,4-DNB > NB > TNT. Derivative 49, having carbazole moieties, exhibited high emission intensity due to extended conjugation. Despite the high emission intensity of derivative 49, it exhibited a less sensitive response towards nitroaromatic derivatives, which was attributed to the poor organization of derivative 49. Hence, the detection limit of derivative 49 and 48 for picric acid were in the order of 400 nM and 50 nM, respectively though $K_{sv}$ values of both 48 and 49 were very close $(2.92\pm0.01 \times 10^5 \text{ M}^{-1})$ for PA. Furthermore, the gel coated paper strips of derivative 48 revealed LOD 14 pg cm$^{-2}$ for PA in contact mode.

Triphenylene derivatives 50 and 51, reported by Bhalla and Kumar et al., formed fluorescent aggregates in semi-aqueous media due to the synergetic effect of slipped packing of molecules and intramolecular restriction of rotation. The aggregates of these discotic molecules 50 and 51 underwent fluorescence quenching in the presence of PA and could respectively detect 35 and 40 nM PA with $K_{sv}$ values $1.11\times10^5 \text{ M}^{-1}$ and $1.95\times10^5 \text{ M}^{-1}$. In case of 50, the flake like morphology of aggregates provided the large number of channels for the migration of excitons which resulted in enhanced sensitivity towards PA. The electrostatic interactions between aggregates of protonated form of 51
with picrate anions resulted in fluorescence quenching. Further, the solution coated test strips of derivative 51 detected up to $2.29 \times 10^{-14} \text{ g/cm}^2$ of PA.

Pentacenequinone derivative 52, reported by Bhalla et al.\textsuperscript{71} in THF gave emission maxima at 460 nm which was shifted to 492 nm and 560 nm in solutions containing water fraction 10\% and $>60\%$, respectively. The appearance of a $\sim 100$ nm red-shifted emission band suggested the formation of aggregates of 52 in H$_2$O/THF (9:1) mixture. Nanoaggregates of 52 offered diffusion channels for the excitons to migrate, thus allowing them to be more quickly annihilated by PA with a LOD 500 ppb and $K_{sv}$ 4.3x10$^3$ M$^{-1}$. The main quenching mechanism for PA was the energy transfer.

Bhalla et al.\textsuperscript{72} studied luminescent supramolecular aggregates of derivative 53 both in bulk as well as in solution phase. $\pi-\pi$ interactions between the pentacenequinone molecules resulted in columnar assembly. In addition, the presence of lone-pair electrons on heteroatoms in 1,2,3-triazole groups introduced a transverse dipole moment and triazole groups formed a pseudo network by their dipole–dipole and $\pi-\pi$ interactions, which stabilized the columnar assembly of pentacenequinone moiety. Polarized optical
microscopy (POM) analysis and powder X-ray diffraction studies of derivative 53 showed presence of isotropic phase at 233 °C and columnar mesophase in the temperature range 187 to 206 °C. Nitroaromatic analyte acted as fluorescence quencher as the result of an electron-transfer event. The gel of 53 in toluene/DCM (8:2) showed complete quenching of emission band at 515 nm with the addition of 30 equiv. of PA and resulted in $K_{sv} = 1.55 \times 10^4$ M$^{-1}$. LOD was $3.5 \times 10^{-7}$ M PA. Gel-coated paper strips detected PA at nanomolar level and provide a method for detection of PA in aqueous solution, vapour phase, and in contact mode. After exposure to PA vapour, the appearance of band at 485 nm supported the formation of ground-state complex between PA and organogel.

Bhalla et al$^{73}$, synthesized pentacenequinone derivatives 54a-e by a Suzuki–Miyaura coupling protocol. These derivatives formed fluorescent aggregates in mixed aqueous media due to their AIEE attributes. Amongst pyridine based derivatives 54a-c, the aggregates of 54c (H$_2$O / DMSO 1:1) attained most regular flake like morphology and could detect 600 nM PA in comparison to 720 and 650 nM detection limits for 54a and 54b, respectively. Derivatives 54d and 54e having electron rich phenyl groups behaved as donor–acceptor–donor type systems and formed fluorescent aggregates in mixed aqueous media (THF / H$_2$O 1:9) and could detect 250 and 290 nM PA, respectively. Paper strips coated with compound 54d could detect 3 μl of 10$^{-8}$ M PA.

Che, Zang and coworkers$^{74}$ prepared the fluorescent nanofibrils with diameter of ~30 nm and length of few microns from a 2,7-linked carbazole trimer 55. The $\pi$–$\pi$ stacking
of carbazole trimer molecules in these nano-fibrils was quite evident from short d spacings of 3.8 Å in X-ray diffraction analysis and appearance of emission maxima centered at 438 nm, red-shifted by 44 nm from the maxima recorded for the molecules dissolved in solution. The fluorescence quenching of these films reached 50% after 30 s and 10 s respectively on exposure to the saturated vapour of TNT (ca. 5 ppb) and DNT (ca. 100 ppb). The quenching of fluorescence was reversible for several cycles and was recovered simply by heating the film at 50°C in a vacuum oven for 10 min.

Moore et al\textsuperscript{75} reported the selective detection of TNT vapour using the nano-porous fibers fabricated by self-assembly of carbazole-based linear acyclic molecules. Oligomer molecules \textit{56} formed solid nanofibers and subsequently formed exterior porous films upon piling. Nanofibers of \textit{56} upon exposure to the saturated vapour of 2,4-DNT for 20 s resulted in ~ 55% fluorescence quenching which was considerably recovered upon reopening to clean air. The authors have assigned this reversibility to solid nano-fibers of \textit{56} which have near micropore size on the surface that caused desorption of NAC upon re-exposure to clean air, thus leading to recovery of fluorescence. The selective detection limit of a few tens of parts per trillion for TNT was achieved by creating nano-porosity and tuning molecular electronic structure.

Ajayaghosh et al\textsuperscript{76} reported a fluorescent organogelator \textit{57}, the gel of which on coating on paper strips detected \textit{10}\textsuperscript{-18} g (~12 ag/cm\textsuperscript{2}) TNT with a detection limit of 0.23 ppq. Fluorescence quenching could be visually detected to the level of \textit{1.37 \times 10}\textsuperscript{-18} g 2-
NT, $1.82 \times 10^{-18}$ g 2,4-DNT, $2.27 \times 10^{-18}$ g TNT, and $1.23 \times 10^{-10}$ g NB using the test strips when 10 μL of the analyte was spotted with a spread of ~ 0.2 cm$^2$ which states the selectivity order as 2-NT ~ 2,4-DNT ~ TNT. The unique molecular packing of 57 and edge-to-face π-stacking between the electron-deficient aromatic core of TNT and the electron-rich perfluoroarene moieties of 57 favored the formation of a tight complex. This stacking was also assisted by the hydrogen bonding between the nitro groups in TNT and the hydrogen atoms in the backbone of 57. The significance of organogel in detection of TNT was also highlighted by weak fluorescence quenching of solution of 57 against TNT.

![Molecular structure](image1)

Takeuchi et al$^{77}$ found that the sensing efficiency of a molecular probe can be significantly enhanced by self-assembly assisted morphology tuning. The solution of 58 in toluene-chloroform (3:1) formed a gel type material which showed the formation of entangled networks of fibres 50–100 nm in diameter and several micrometres in length. The bright yellowish-green fluorescence of the film showed 91% and 72% quenching on exposure to saturated 2,4-DNT and TNT vapour for 10 min owing to photoinduced electron transfer from 58 to 2,4-DNT/TNT. In comparison to this, non-morphological film obtained from chloroform solution of 58 by drop cast method took 24h for similar quenching. Derivative 59 without the binaphthyl unit did not self-assemble in chloroform–toluene mixture and its drop-cast film exhibited only 14% fluorescence quenching on exposure to 2,4-DNT.

![Molecular structure](image2)
Wang, Pei and coworkers added a new dimension to the material design by achieving morphology control through the self-assembly of the aromatic molecules by a solution process in different solvents. Compound 60 self-assembled in three different crystalline structures viz. microbelts in 1,4-dioxane and two different flower shaped super nanostructures from THF (flower A) and decane (flower B) solutions. The differences in the crystal structures and in the film morphologies led to dramatic enhancements of the explosive detection speed. With the evolution of structures from the networked 1D microbelts to the 3D flower B super nanostructures, the detection speed of the 2,4-DNT/TNT vapour was improved by more than 700-fold and was attributed to the larger surface areas and the more porous film morphology of the flower-like super nanostructures. The 10-fold detection speed improvements by flower B compared to flower A could be due to their different crystal conformations.

Bhattacharya et al developed p-phenylenevinylene based probes 61 and 62 for selective detection of PA in multiple media including water, micelles or in organogels as well as using test strips. The electron transfer from the electron-rich chromophoric probe to the electron deficient NACs was responsible for fluorescence quenching. The respective detection limits of compound 61 towards PA and 2,4-DNP were ~35 and ~22 nM. Probe 62 showed a lower detection limit (11.8 nM) with PA indicating that 62 is a superior probe than 61 for PA sensing. Probe 62 at higher concentration (14 mM) formed a self-supporting physical gel in THF via the intermolecular H-bonding through the acylhydrazone groups, π-stacking through the aromatic moieties and van der Waals interactions via their n-hexadecyl chains. Addition of PA in the gel state led to ~14-fold quenching of the emission intensity with ~24 nm blue shift and was associated conversion of gel to liquid.
Bhalla et al.\textsuperscript{80} have reported “no quenching” probe 63 for the detection of PA in ethanol-water (6:4). The fluorescence studies of aggregates of 63 with PA revealed two step sensing mechanism. In the first step, interaction between the aggregates of 63 and PA caused quenching of the emission band at 339 nm. In the second step, upon the light absorption, the basicity of pyridyl nitrogen was enhanced, which facilitated proton transfer from PA to pyridyl nitrogen in the excited state and resulted in emission centered at 460 nm. The similar two step interaction of compound 64 and lack of appearance of new emission band in case of 65 point to the importance of 2-pyridyl groups for “no quenching” detection of PA in aqueous media. The fluorescent TLC strips carrying aggregates of 63 could detect 2.29 femto gram PA.

Patil et al.\textsuperscript{81} designed fluoranthene derivative 66 in which the presence of an asymmetric phenyl ring on the fluoranthene moiety weakened the $\pi-\pi$ interaction leading to formation of layer-by-layer assembly of the molecules. This generated the pathway for intercalation with NACs, thereby, increasing the fluorescence quenching efficiency, especially for the detection of PA. PA exhibited quenching response for 2–20 ppb while DNT and TNT showed a 1.1 ppm level detection in ethanol solution. $K_{sv}$ value of 9.9 x 10$^4$ M$^{-1}$ for PA indicates static quenching through excited state interaction and was significantly lower for DNT (860 M$^{-1}$) and TNT (1609 M$^{-1}$). Silica films coated with 66
underwent fluorescence quenching with PA which was recovered on washing with ethanol.

Patil et al.\textsuperscript{82} synthesized five fluoranthene fluorophores varied with nature and type of substituents for the detection of NACs. X-ray crystal structure of 67e showed the presence of extended conjugation and two alkyloxy chains on phenyl rings induced flexibility to orient opposite to each other and interacted with another fluoranthene unit with weak π−π interactions and showed unique supramolecular arrangements. The photophysical and computational study revealed that tuning of the optical gap with an increase in conjugation in 67e enhanced the sensitivity towards NACs. In solution phase, these fluorophores exhibited static quenching with a 2–20 ppb level of detection for PA and \( \sim 1.1 \) ppm level of TNT. Using contact mode approach on thin layer silica chromatographic plates, \( \sim 1.15 \) fg/cm\(^2\) PA and TNT could be detected. The fast and efficient response of the film to PA was attributed to the high diffusion of PA into the porous nature of fluoranthene films and strong intermolecular interactions between PA and fluoranthene molecules.

Lu, Feng and coworkers\textsuperscript{83} have found that silicon-owed derivative 69 showed lower detection limit, higher sensitivity, and higher quenching efficiency in detecting NB and
1,3-DNB than derivative 68. The detection limits of 69 were 50 and 10 ppm toward NB and 1,3-DNB, respectively and were lower than those observed for fluoranthene derivatives 66 and 67. The fluorescence of thin film obtained from 69 was completely quenched after exposure to saturated NB vapour for 120 s.

![Chemical structures](image)

Tang et al. synthesized propeller-shaped molecules 70-72 which were non-emissive in good solvents, but became highly emissive when aggregated in poor solvents or in the solid state, showing the phenomenon of aggregation-induced emission (AIE). Restriction of intramolecular motion has been identified as the main cause for this effect. The emission of nanoaggregates of these luminogens in THF/H2O mixtures (1:9) was quenched exponentially by PA or selectively by Ru3+ with quenching constants up to 10^5 and ~2.0 × 10^5 M⁻¹, respectively. The fluorescence quenching was clearly discerned at 1 μg ml⁻¹ or 1 ppm of PA. Derivatives 70-72 formed electrostatic or charge transfer interactions with PA, which lead to the formation of non-emissive ground-state dark complexes but maintaining the natural lifetimes of their unbound luminogens.

![Chemical structures](image)

Li, Wang, Kaner and coworkers synthesized blue light-emitting oligotriphenylene nanofibers with 50 to 200 nm diameter by oxidation of triphenylene using ferric chloride.
Strong π–π stacking of oligotriphenylene molecules of 73 provided the driving force for growth of the nanofibers. After oligomerization, both maximum excitation and emission wavelengths of the oligotriphenylene nanofibers red-shifted by 92 and 71 nm, respectively, due to the extended conjugation length and the quantum yield was increased five times to 0.5. Oligotriphenylene 73 was well dispersed in thin films made from yellow solution of oligotriphenylene in polysulfone and underwent selective fluorescence quenching with PA with Ksv \(1.3 \times 10^5\) M\(^{-1}\) and LOD of \(1.0 \times 10^{-8}\) M. Significantly, the comparison with TNT and 2,4-DNP the other strong electron-deficient NACs is not available.

Montmeat et al.\(^86\) reported 74, a π-conjugated phenylene–ethynylene diimine, an efficient sensitive material for the detection of TNT despite its low vapour pressure. The fluorescence inhibition was contained by 28 to 6% for 150 to 10 ppb vapour of 74 with 12 ppb as the LOD.
Fang et al\textsuperscript{87} fabricated the film by the physical immobilization of the pyrene capped fluorophore 75, onto a glass plate pre-coated with chol-ph-chol a low-molecular-mass gelator. The emission maxima of the film at ~ 525 nm underwent almost 70% fluorescence quenching within 60s on exposure to NB vapour and the quenching process was fully reversible. The films on exposure to vapour of TNT and DNT did not show fluorescence quenching.

He, Cheng and coworkers prepared three fluorescent derivatives 76-78\textsuperscript{88}, amongst which derivative 78 possessing eight pyrenyl groups assembled into nanospheres composed coarse film and produced rapid and significant fluorescence quenching with a response rate of about 27% within 10 s and about 55% within 50 s upon exposure to saturated nitroglycerine (NG) vapour. The final quenching efficiency with 78 was about 81% within 300 s, which was far better than that of 56% and 32% quenching efficiency for 76 and 77, respectively. The contact-mode approach exhibited a detection limit of 0.5 fg/cm\textsuperscript{2} for NG. The film prepared from 78 showed poor response to TNT and DNT vapour.

Singh et al\textsuperscript{89} used quinoxaline derivative 79 to discriminate 2,4-DNA from other NACs. The solution of 79 in THF gave emission maxima at 487 nm due to excimer emission which was quenched by 2,4-DNA (91%) > 4-NA (89%) > 4-NP (75%) > PA (55%) > 2,4-DNP (31%). The paper strips soaked with solution of 79 could detect by the naked-eye, under illumination with UV lamp (365 nm), as low as 9.1, 13.8, 13.9, 22.9, and 92 nanograms for 2,4-DNA, 4-NA, 4-NP, PA, and 2,4-DNP, respectively.

Singh et al\textsuperscript{90} have described a pyrene based chemosensor 80 which exhibited aggregation induced excimer emission centered at ~480 nm in THF – HEPES buffer (1:9) and could detect 1.93 ppb of PA in solution and 0.46 attogram in direct contact mode. The quenching process predominantly involved static quenching mechanism, proposed on the basis of steady state and life-time fluorescence measurements.
Bhalla et al\textsuperscript{91} synthesized hexa-peri-hexabenzocoronene (HBC) based molecules 81a-b appended with two rotors to invoke aggregation induced emission enhancement (AIEE). Compounds 81a and 81b respectively formed spherical aggregates of average size 200 and 150 nm in H\textsubscript{2}O/THF (4:6), as observed from SEM images. The aggregates of both derivatives gave yellow emission and behaved as highly sensitive and selective chemosensors for PA. The protonation of NH\textsubscript{2} groups of aggregates of 81a by PA assisted the electron transfer from photoexcited HBC core to the electron deficient PA to quench the emission. The aggregates of 81a and 81b possess detection limits of 4 nM and 9 nM, and K\textsubscript{SV} of 3.2 × 10\textsuperscript{6} M\textsuperscript{−1} and 2.0 × 10\textsuperscript{6} M\textsuperscript{−1}, respectively. The fluorescent paper strips coated with aggregates of 81a-b could detect up to 23 attogram PA. At pH 4, aggregates of 81a gave only 35% quenching with 5 µM PA.

IV Fluorophores as supramolecular polymers
Mukherjee et al.\textsuperscript{92} have reported a series of anthracene, pyrene, alkyne and triphenylamine based fluorescent tetracarboxylic acids which formed supramolecular polymers as multiple molecules self-organized by noncovalent interactions like H-bonding and $\pi-\pi$ interactions to form infinite network, as evident from the X-ray diffraction study. The concentration-dependent aggregation by $\pi-\pi$ interaction was confirmed by DLS and fluorescence studies. The significance of these H-bonded polymers was evident from larger Stern–Volmer binding constant for acid 82 ($K_{sv} = 2100 \text{ M}^{-1}$) over its ester derivative 83 ($K_{sv} = 200 \text{ M}^{-1}$) and tetramethyl derivative 84 ($K_{sv} = 130 \text{ M}^{-1}$). The fluorescence quenching efficiency was also in the order $82 > 83 > 84$. TNT and PA showed largest and similar quenching response towards 82 and it could detect these NACs at ppb level. The authors also tested the solid state sensing of explosives vapour of nitrobenzene which was found to reversible. In case of pyrene based probes, $K_{sv}$ values for acids 85, 86 and 87 for PA were $2.2 \times 10^4 \text{ M}^{-1}$, $3.2 \times 10^4 \text{ M}^{-1}$ and $3.78 \times 10^4 \text{ M}^{-1}$, respectively. These values are significantly higher than those observed for 82. The lowest detectable level for PA and TNT were below 0.5 ppt for these chemosensors. Though the increase in surface area increased the sensitivity of pyrene based tetracarboxylic acids towards NACs but it was not achieved without poor selectivity amongst PA, TNT, TNB, 1,3-DNB, 4-NP etc. Triphenylamine based chemosensors 88 and 89 demonstrated limit of detection $\sim 5$ ppb and Stern–Volmer constants for PA were $5.72 \times 10^6 \text{ M}^{-1}$ for 88 and $2.9 \times 10^5 \text{ M}^{-1}$ for 89. Except 2,4-DNP, all other compounds showed insignificant quenching of the emission intensity. The quenching efficiency of 2,4-DNP was less than 40\% for both the acids, but monosubstituted nitrophenols did not exhibit any considerable quenching behavior.
Mukherjee et al\textsuperscript{93} has further extended the concept of hydrogen-bonded supramolecular polymers in 2-methyl-3-butyn-2-ol substituted pyrene and anthracene based $\pi$-electron rich fluorophores 90-92 for selective detection of NACs. In chloroform solution, the fluorescence quenching of anthracene-based fluorophore 91 was much higher in comparison to fluorophore 92, the more electron-rich derivative. The observed less efficient quenching response of 92 was attributed to the steric bulk present on the pyrene moiety. Amongst 90-92, the least electron-rich derivative 91 showed the poorest response towards NACs. Probe 91 could detect 2.0 ppb TNT, 13.7 ppb 2,4-DNT in chloroform solution. In solid-state, derivative 92 was more efficient sensor than derivative 91 towards 2,4-DNT. This could be understood as derivative 92 formed 3D supramolecular porous network via H-bonding interactions (X-ray) and allowed easy diffusion of the explosive vapour into the porous pocket.

Paz and Tomé et al\textsuperscript{94} investigated the usage of the phosphonate-appended porphyrin derivatives as efficient chemosensors for NACs in DMF. Among the free base porphyrins, 93c showed the best fluorescence quenching behavior for TNT. Upon addition of different amounts of TNT, the emission maxima of 93c at ~ 650 nm gradually decreased, exhibiting a maximum fluorescence quenching of 94% for 100 μM TNT. Other NACs showed much smaller quenching. The presence of phosphonic acid groups at the peripheral positions of the porphyrin molecule induced a pronounced decrease in the emission intensities through transfer of protons from the hydroxyl groups to the basic nitro groups, yielding hydrogen bonded adducts formed by the porphyrin and the NAC. Protonation of the pyrrole nitrogen atoms of the free base porphyrin induces a non planar distortion of the macrocycle with enhanced electron donating strength of the resulting porphyrin. As expected, protonated porphyrins 93c and 93d exhibited significantly
enhanced quenching behavior in comparison with their free base forms. 93d showed a remarkable 98% fluorescence quenching with the addition of 60 μM TNT. The quantitative analysis of fluorescence titration of 93c and 94d showed the response as low as 20 ± 3 and 5 ± 2 nM in solution. The emission intensity of the films was found to be highly reversible after several cycles indicating a high photostability of the sensing thin films.

Bhalla, Kumar and coworkers95a reported a probe-Hg²⁺ ensemble which exhibited remarkable selectivity toward PA. Spherical aggregates of hexaphenylbenzene derivative 94 underwent metal-induced modulation to form nanorods in the presence of Hg²⁺ ions, which exhibited selective and sensitive response toward PA with a detection limit of 6.87 ppb and KSV 1.92 × 10⁵ M⁻¹. Using contact mode approach, 0.229 ppb PA could be detected. The aggregates of derivative 94 in the absence of Hg²⁺ ions did not exhibit a response toward PA and indicate the importance of the Hg²⁺ ensemble of derivative 94. The transfer of proton of hydroxyl groups from PA to the basic N,N-dimethylamino group to make an electrostatic complex between host and guest has been proposed to be responsible for fluorescence quenching. Similarly, 95-Hg²⁺ supramolecular ensemble95b served as sensitive sensor for PA with Ksv 1.71 × 10⁵ M⁻¹ and LOD 50 × 10⁻¹² M. In case of aggregates of 96-Hg²⁺ ensemble lower Ksv (0.55 × 10⁵M⁻¹) and the LOD (35 × 10⁻⁹M) for PA were observed. The paper strips coated with 96-Hg²⁺ ensemble could detect PA 2.29 fg/cm². The authors attributed the high quenching efficiency of the probe 95 to increase in surface area of the ensemble on coordination of 95 with Hg²⁺.
The aggregates of derivative 97, in ethanol / water underwent reorganization to nano rods in the presence of cyanide ions. These nano-rods served as a sensitive fluorogenic sensor for the detection of TNT with a detection limit of 10.21 ppq (parts per quadrillion) in solution and ~23 ag cm$^{-2}$ in vapour phase. The aggregates of 97 in the absence of cyanide ions and CN$^-$ ions in the absence of 97 did not exhibit any response towards TNT. The solution of 97–CN$^-$ ensemble showed color change from yellow to red with enhancement in the absorption in the visible region and quenching of fluorescence in the presence of TNT. The electrostatic interaction of TNT molecules with the nanoaggregates of 97–CN$^-$ ensemble was responsible for these photophysical changes.

V Tweezer, cyclophane and cage like fluorophores

Structurally defined cleft-like molecules containing two or more parallel subunits capable of interacting with substrates, so-called molecular tweezers, have received increasing attention over the years. Such rigid molecular tweezers based on electron rich or deficient subunits can encapsulate respective electron deficient or rich guest molecules. The cyclophanes and molecular cages due to their preorganised cavity and poor dielectric constant in the cavity in comparison to that of solvent medium provide more conducive environment for encapsulation of the hydrophobic guests. In this section, the applications of tweezers (dipodal and tripodal), cyclophanes and cages (bicyclophanes) in detection of NACs has been discussed.

![Image of molecular structures](image_url)

Cho et al$^{97}$ hypothesized that simple bis-pyrenyl derivatives may effectively form an excimer by utilizing hydrophobic interactions and conformational strains, which may subsequently lead to extinction upon the addition of an electron-deficient species.
Amongst these derivatives, the order of affinity was $101 > 100 > 99 > 102 > 98$ in the semi-aqueous solution (acetone/water, 2:8). The large increase in the association constant of 99 in comparison to derivative 98 was ascribed to a relatively small energy penalty (preorganization energy) required to form a TNT chemosensor complex. Chemosensor 101 could detect $< 2$ ppb of TNT in a semi-aqueous solution.

Kim, Kim, Sessler coworkers$^{98}$ found that pyridine bridged tweezer 103 formed a supramolecular oligomer both in chloroform solution and in the solid state whereas analogue 104 did not interact in an intermolecular fashion. This supramolecular oligomer formed from 103 underwent deaggregation upon exposure to TNB or TNT to form 1:1 complexes with these nitroaromatic explosives. During this process, TNB slided into the cleft provided by the two pyrene moieties and thereby stabilized a supramolecular donor-acceptor complex, as revealed by X-ray structure analysis. However, the complexes were destroyed and the initial aggregated structure was re-formed upon the subsequent addition of methanol to chloroform solutions of 103·TNB or 103·TNT. These transformations were accompanied by easy-to-visualize color changes. Tweezer 103 displayed both pyrene monomer and excimer emissions, while 104 displayed only monomer-like fluorescence. The differences between 103 and 104 were ascribed to the presence (103)
and absence (104) of intramolecular hydrogen bonds between the amide NH and the pyridyl nitrogen atom. The resulting binding constants for a 1:1 interaction of 103 with TNB and TNT were $7.32 \times 10^4$ and $7.69 \times 10^2$ M$^{-1}$, respectively.

Ding et al.\textsuperscript{99} have demonstrated that choice of the micelle lead to the selective response towards two different NACs which could be assigned different form of encapsulation / non-encapsulation of fluorophore by cationic, anionic and neutral surfactants. In supramolecular assembly 105-SDS, the fluorophore was encapsulated in to the negatively charged micelle of SDS and exhibited selective fluorescence quenching of both monomer structured emission band and more intense excimer emission band with PA. In case of 105-DTAB assembly, the highest response was observed for nitroaromatic explosive PYX. However, due to poor encapsulation in the neutral surfactant TX100 micelles, derivative 105 failed to function as a sensor system. The LOD of PA and PYX were $1 \times 10^{-6}$ M and $1 \times 10^{-7}$ M, respectively.

Lee, Kim and coworkers\textsuperscript{100} designed a calix[4]arene based probe 106 where two pyrene moieties sandwich TNT molecule through intermolecular $\pi-\pi$ interactions between two pyrene units and a TNT molecule held at a distance of 3.2–3.6 Å. As revealed by X-ray, intra- and intermolecular hydrogen-bonds among the amide linkages also contribute to the stability of complex. The solution of 106 in CH$_3$CN gave emission at 375 nm and 470 nm due to monomer and excimer which was quenched by NACs with quenching efficiency order TNB $>$ TNT $>$ 1,3-DNB $>$ NB.

Similarly, calix[4]arene-anthracene conjugate 107, as reported by Tian et al.\textsuperscript{101} showed high binding affinity and selectivity toward PA based on sandwich complex of PA.
between two anthracene moieties of chemosensor 107. The formation of charge transfer complex between PA and anthracene moieties of 107 was quite evident from the appearance of absorption between 400-450 nm. The computational calculations revealed the formation of host-guest complex was driven by $\pi - \pi$ stacking interactions and formed a sandwich structure consistent with the $^1$H NMR. Because of the reciprocity, the signal of protons on the aromatic ring of PA underwent upfield shifting ($H_{PA}$, 0.479 ppm) most significantly while the protons on the anthryl and triazole moieties of 107 were shifted up-field only to a small extent. However, the authors did not report the limit of detection for PA.

Prata et al$^{102}$ reported the synthesis of sensory materials based on $p$-phenylene ethynylene trimer integrating calix[4]arene receptor 108 and its fluorophore analog 109 and their sensitivity and selectivity for the detection of NACs such as NB, 2,4-DNT, TNT and PA in liquid phase and solid-state. The quenching efficiencies for 108 and 109 followed the order PA $\gg$ TNT $>$ DNT $>$ NB, which correlate well with the quenchers electron affinities as evaluated from their LUMOs energies thereby suggesting a photo-induced electron transfer as the dominant mechanism of fluorescence quenching. The quenching efficiencies and response times of the two fluorophores in the solid-state toward NB, 2,4-DNT and TNT vapour were evaluated through steady-state fluorescence quenching experiments with the materials dispersed in polymeric matrices or as neat films. The most significant fluorescence quenching responses were achieved for drop-casted films of 109 upon exposure to nitroaromatics.
Mukherjee et al.\textsuperscript{103} reported two tris-imidazolium salts \textbf{110} and \textbf{111}, which selectively sensed 467 and 354 ppb PA, respectively in both organic and aqueous media. The combination of \textsuperscript{1}H NMR, X-ray and DFT studies revealed that both the sensors adopted cis,cis,cis-conformation with a bowl-shaped structure and formed 1:2 (host-guest) complexes with PA both in the solution phase and solid state. The solid-state packing diagram revealed that picrate moieties formed columnar arrangement intervened between anthracene moieties of the sensor molecules via mainly $\pi-\pi$ stacking interactions.

Bianchi, Dalcanale coworkers\textsuperscript{104} exploited host–guest interactions of the quinoxaline based cavitand \textbf{112} for the selective sampling of nitroaromatic explosives and explosive taggants at trace levels in air and soil samples using both dynamic head space and SPME. With GC responses, \textbf{112} showed 3-20 times higher extraction efficiency than those achieved using the other adsorbents, thus proving that the synergistic presence of $\pi-\pi$, CH–$\pi$, and H-bonding interactions is able to strengthen the retention of nitro compounds. The LOD values were 0.004 ppb for NB and highest 0.60 ppb for TNT in the air samples. LOD values for soil samples varied from 12 ng / kg 2,4-DNT to 38 ng/kg for NB.
Baumgartner et al.\textsuperscript{105} synthesized dithienophosphole 113 cyclodextrin hybrid sensor for detection of nitroaromatic-based explosives in water. Chemosensor 113 exhibited emission maxima at ~470 nm which was gradually quenched with increasing concentration of PA through an energy and/or electron transfer from 113 to the PA acceptor, triggered by the inclusion of the PA inside the CD cavity. The binding constant (log $K_{sv} = 4.80 \pm 0.02$) was obtained from a nonlinear least-squares fit for 1:1 binding. The detection limit for PA was in nanomolar range.

Anslyn et al.\textsuperscript{106} prepared inclusion complex 114 by the inclusion of 9,10-bis(phenylethynyl)anthracene in γ-cyclodextrin (CD) in water-THF (19:1) and used it for fluorescence sensing of nitroaromatic compounds. The quenching interactions as measured by $K_{sv}$ were enhanced by the CD-complexed fluorophore by 1.6 times for TNT and 1.3 times for Tetryl than in the absence of γ-CD, possibly due to better fit in the γ-CD cavity.
Tetraphenylethylene based Schiff-base macrocycle 115, reported by Zheng et al\textsuperscript{107}, aggregated into nanospheres in 90:10 water/THF and emitted strong yellow fluorescence due to AIE effect. By virtue of its AIE effect, the macrocycle showed a sensitive and selective response to PA and 2,4-DNP among a number of NACs. Moreover, macrocycle 115 exhibited a superamplified quenching effect with PA and 2,4-DNP and on applying an exponential quenching equation ($I/I_0 = Ae^{-k[Q]} + B$), the quenching constants of 115 with PA and 2,4-DNP were calculated as $3.0 \times 10^4$ M\(^{-1}\) and $8.0 \times 10^4$ M\(^{-1}\), respectively. PA and 2,4-DNP formed complexes in the ground state by interaction with the four Schiff-base groups of macrocycle 115, and then photoinduced electron transfer (PET) within the complex resulted in fluorescence quenching. Open-chain TPE Schiff-base 116 exhibited less efficient fluorescence quenching with PA, 2,4-DNP, and 4-NP. Moreover, the changes in the fluorescence intensity ratio ($I_0/I$) of 116 with the concentrations of PA, 2,4-DNP, and 4-NP were all linear, indicating that the quenching was dynamic and that complexation between 116 and the nitrophenolic molecule in the ground state occurred less readily.

Moore et al\textsuperscript{108} reported the selective detection of TNT vapour using the nano-porous fibers fabricated by self-assembly of carbazole-based macrocyclic molecules allowing slow Oswald ripening in a binary solvent system. The authors based on X-ray studies proposed that the molecules of 117a-b adopted a cofacial orientation with a tilting angle of 23° relative to the long axis of the resulting column resulting in long-range order of the porous tubular nanostructure which was consistent with the red-shifted absorption and emission maxima as measured over the nanofibers, in comparison to that of individual molecules dissolved in solutions. The nano-porosity allowed time-dependent diffusion of TNT molecules inside the material, resulting in further fluorescence quenching of the material even after removal from the TNT vapour source. In case of
the presence of longer chain length resulted in increased sensitivity towards 2,4-DNT and TNT. On 60 s exposure, the quenching efficiency of TNT (83%) was comparable to that of 2,4-DNT (90%) and the quenching was reversed on exposure to saturated vapour of hydrazine.

Ema, sakai and co-workers\textsuperscript{109} a molecular probe 118 having two porphyrin rings in a parallel but chiral manner at a distance suitable for the intercalation of aromatics via double $\pi-\pi$ stacking interactions. The greater affinity of 118 for electron-deficient aromatic guests, suggested that the electrostatic contribution is a predominant factor in complexation between the electron-rich ($\pi$-basic) porphyrin and the electron-deficient ($\pi$-acidic) aromatic compounds. A dark-red solution of 118 in CHCl$_3$ turned into a colloidal suspension upon addition of TNB, and the light illuminated from the front side was scattered. Red fluorescence of 118 was selectively quenched in the presence of TNB.

Mukherjee et al\textsuperscript{110} synthesized cage 119 by employing a one-pot Schiff base condensation of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene with 4,4’-diformyltriphenylamine followed by sodium borohydride reduction of the imine bonds.
The addition of 2 equiv. of PA quenched the FI of the solution of cage 119 in dichloromethane by 96% with LOD of PA 6.4 ppb. Other nitroaromatics exhibited negligible effects on the fluorescence intensity of cage 119. The non-linear curve fitting of titration data of cage 119 with PA gave $K_{SV} = 2.2 \times 10^5 \text{M}^{-1}$. Based on the formation of charge transfer complex between cage 119 with PA (420 nm absorption band) and down field shift of NCH$_2$ protons in the presence of PA, the authors proposed the formation of ground state charge transfer complex (ion pair complex) by transfer of OH proton of PA to amine nitrogen of 119. Mukherjee et al. synthesized cage compounds 120 by N-alkylation of 120 using copper(I)-catalysed multicomponent reaction of secondary amine, formaldehyde and terminal alkyne, known as $A^3$-coupling. Similar to derivative 119, the cage 120 was selective towards nitrophenols with most efficient quenching with PA. The comparisons of sensitivity amongst 119 and 120 are not available.

VI  NACs induced aggregation and fluorescence enhancement

Menon et al. have demonstrated that curcumin NPs (~52 nm) undergo aggregation in the presence of trace amount of TNT to give large aggregates with size ~ 271 nm. These aggregates formed through donor-acceptor interactions exhibited upto 800 fold fluorescent enhancements with limit of detection of 1 nM TNT. The detection of TNT could be performed in the pH range 4.0–10.0 though best results were obtained under basic conditions. On addition of TNT (1- 500 nM) to the solution of curcumin NPs, ground state charge transfer complex with absorption between 400 – 600 nm appeared which on excitation at 371 nm gave emission centered at 650 nm. NACs viz. RDX, HMX, PETN and PA did not interfere even at 0.1 mM concentration.
Sarma et al\textsuperscript{112} have reported curcumine-cysteine (122) and curcumine-tryptophan (123) conjugates which exhibit fluorescence enhancement on interaction with picric acid. These probes are primarily non-fluorescent in nature due to intramolecular quenching and achieved about 26.5-fold fluorescence enhancement at 70 nM PA concentration without any shift in spectral energies. These probes were efficient only at acidic pH = 4 and the electrostatic interactions between the ammonium group of amino acids and picrate ion played the determinative role in fluorescence turn on by aggregation induced emission (AIE). The initial and final average particle size was ~823 and ~1368 nm, as determined by DLS experiments. The limit of detection for 122a and 122b were 13.51 and 13.54 nM of PA, respectively. Though the probes detected PA in very narrow range of concentration of PA (15-70 nm) but were highly effective as significant amount of change in fluorescence intensity could be observed between 10 to 20 nM of PA. The presence of 0.1 M NaNO\textsubscript{3} hindered the electrostatic interactions and fluorescence enhancement with PA became very weak compared to that without salt addition.

Therefore, small organic molecules based on their structural design and mode of interaction with the NACs can be classified into various categories. However, their organization in the confined materials like organic and inorganic polymers or their interaction on the surface of the aggregate, or in the cavity can be classified into many categories. Amongst these, the small organic molecules which can be crystallized or spin coated into well defined and porous morphology exhibit better sensitivity towards NACs detection. In the present research programme, the tripodal molecules with an ability to act as single discrete molecules with a defined cavity have been synthesized and evaluated for their interactions towards NACs. The results of these findings have been discussed in chapters 2-5.
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