

## Review: Fluorophores for detecting Nitroaromatic Compounds, Picric Acid



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**ABSTRACT:** Literature surveys of fluorophores for sensing nitroaromatic compounds, during past ten years have been done. Fluorophores have been classified in various categories, based on their structure and their mechanism of sensing is discussed.

**KEYWORDS:** Picric acid, Fluorophores, sensors, Limit of detection,  $K_{sv}$

### 1.1. INTRODUCTION

Environment is the sum total of surrounding of an organism, a combination of external physical conditions that affects and influences the development, growth and survival of an organism. It includes both aquatic and terrestrial plants and animals, along with their habitat. Pollution is an undesirable effect in the environment, which degrades the quality of life in an eco-system. Pollutants are substances, present beyond a limit in the atmosphere, which are responsible for degrading the quality of environment. Volatile organic compounds (VOCs) are responsible for contributing in the formation of ground level ozone<sup>1</sup>. VOCs react with oxides of nitrogen and form ozone. Ground level ozone affects human health and is a major reason of atmospheric pollution. The other such family of pollutants is organic nitro compounds. It is used in dyes, pharmaceuticals, firework industries, and also as a chemical explosive in mining. In recent past these explosives have been frequently used by terrorist organization<sup>2</sup>. Chemical explosives contain huge amount of energy stored in the chemical bonds. After explosion, stable species such as carbon monoxide, carbon dioxide, and nitrogen oxides are formed. Hence most of the explosives are derivatives of organic compounds containing  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NHNO}_2$  groups, which release the above mentioned gases<sup>3</sup>. Their decomposition may take years, days, hours or seconds, depending on their life time<sup>4</sup>. During rapid decomposition, they may deflagrate at a slower speed (speed less than that of sound), while in detonation they decompose at a speed greater than that of sound (leaving shockwave traversing the explosive material).

The nitrated derivatives of the organic and inorganic compounds, once released in the atmosphere pose threat to the normal life of civilians<sup>4</sup>. Picric acid (PA) was extensively used as an explosive in world war II. A large amount of it is released in the environment, and gets lodged in soil and water bodies<sup>5</sup>. Its degradation too is not very fast, and it remains in the water and soil, for a long time. Its harmful effects on human health are many. It causes irritation to eyes, skin, mucous membrane of nose, in addition to causing harm to various organs and body systems (respiratory, digestive and excretory systems)<sup>6</sup>. It is one of the major causes of cancer, dermatitis and sclerosis. Hence, it is declared as one of the major pollutants, by US environment protection agency (EPA). Therefore, the precise, sensitive, selective and accurate detection of these compounds is important. Sensing techniques such as gas chromatography-mass spectrometry (GC-MS), Ion mobility spectroscopy (IMS), Raman spectroscopy and metal detectors are some of the methods, already in use<sup>7,8,9,10</sup>. Amongst these techniques fluorescence spectroscopy is more attractive. In a fluorimeter, the use of photomultiplier tube (PMT) allows the fast and sensitive detection of analyte<sup>10,11,12</sup>. Moreover, the technique is also not very expensive. To use fluorescence technique for the sensing application one requires conjugated organic molecules for which fluorescence emission spectrum changes with the addition of pollutant. The literature survey of the various categories of sensory materials explored in last ten years has also been presented in section 1.4. It was not possible to include all the reported materials in this work, rather we intended to present notable examples from various categories to justify the enthusiasm in this area of research. Sensory materials for detecting explosives

In this section, materials explored for detecting nitro aromatics (NACs) is presented. A number of nitrogen containing fluorophores have been used to sense picric acid (PA). PA has low  $\text{pK}_a$  value ( $\text{pK}_a = 0.42$ ). Owing to its low  $\text{pK}_a$ , it remains in a dissociated form in solution, which can interact with positive centers on the fluorophore<sup>20</sup>. This gives rise to electrostatic interactions with positive charges on the fluorophore. Ultimately it leads to close proximity between positive sites on fluorophore and negative picrate

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anion. For an efficient fluorophore, it should have greater binding affinity for PA or an increased rate of electron/energy transfer from fluorophore to PA. Charge/energy transfer between fluorophore-PA forming a non-fluorescent complex, ultimately leading to quenching of fluorescence.

In general, the mechanism involved in quenching the fluorescence of fluorophore by PA is proposed to be because of the followings possibilities:

1. Proton transfer from PA to electron rich sites on fluorophore.
2. Charge/energy transfer from excited fluorophore having LUMO at higher level to the LUMO of PA which is at lower level<sup>21</sup>. If fluorophore has extended network of conjugation (pyrene, anthracene, derivatives), it may undergo  $\pi$ - $\pi$  interaction, and can also intercalate PA within its layers. A donor-acceptor-donor type system is formed, which exhibits intermolecular charge transfer. Redox potentials of donor and the acceptor can predict the electron transfer. RET/PET are possible in such cases.
3. Electrostatic interaction and hydrogen bonding between differently charged sites on fluorophore and PA<sup>22</sup>.

We have discussed several fluorophores, and their sensing mechanism. In most of the cases, quenching is on account of charge transfer, energy transfer, PET, or proton transfer<sup>22</sup>. Herein we reviewed various types of fluorophores, employed to sense nitro aromatic compounds. Depending upon their structure, we have divided them into several classes and have given a brief review of fluorophores to sense nitro aromatic compounds, explored, in last ten years. The list is as follows:

1. Polymers
2. Supra-molecular system
3. Metal organic framework system
4. Nano materials
5. Small molecule fluorophores

### 1.2.1. Polymers

Polymers are used to detect nitro aromatic compounds. Based on their electronic and structural properties, polymeric fluorophore interact with the analyte, thereby sensing it. Quenching of fluorescence by electron deficient nitroaromatic compounds can be easily monitored by photoluminescence studies. Fluorescent organic polymers and polymetalloles have been discussed underneath.

#### 1.2.1.1. Organic polymers

**Poly(p-phenylenevinylenes)** (OP1)<sup>23</sup> like polyacetylene are luminescent conjugated polymers, which absorb nitroaromatics and its emission get quenched. Chart 1 show the molecular structure of all organic polymers (Ops) discussed in this manuscript. Bulky phenyl substituents of (OP2)<sup>21</sup> and (OP3)<sup>24</sup> hinder  $\pi$ - $\pi$  stacking and self-quenching. Dialkoxy-substituted aromatic ring of (OP6)<sup>21</sup> is more electron rich than diphenyl-substituted aromatic ring of (OP4)<sup>25</sup>, thus permitting stronger columbic interactions with the nitro aromatics. Backbone of (OP2)<sup>26</sup> is almost planar, while that of (OP3) is twisted. Greater degree of planarity of (OP2) makes it a better sensor. Non planarity of (OP4)<sup>26</sup> makes it poor sensor. Thicker films are less sensitive. In (OP5)<sup>21</sup> addition of surfactants to poly (p-phenylenevinylenes (PPV) was also explored. Addition of cationic surfactant to PPV increased interaction between organic analyte and the polymer, thereby amplifying efficiency of quenching<sup>27</sup>. In (OP6) the pendant phenyl group with branched alkoxy substituents encapsulated the polymer backbone. This led to porous structure, which facilitated the penetration of analyte. This improved the sensitivity of the fluorophore<sup>15, 28</sup>.

#### **Poly(p-phenyleneethynylenes) (PPE)**

Thin film of (OP7)<sup>23</sup> PPE, showed quenching with nitro aromatics. The polymer contains two bulky pentyptcene moieties on either side of the polymer backbone. Pentyptcene groups rendered porosity and prevented inter-chain  $\pi$  stacking and self-quenching.<sup>24</sup> This rendered stability to the polymer film.

#### **Polymeric porphyrins**

Porphyrins (OP8)<sup>25</sup> with substitutions are excellent polymer sensors. Polymer contains cavities that are specific for specific target analyte. The polymer is highly porous, with shape selective cavity for analyte. Properties such as stability, porosity, rigidity, and hydrophobicity can be altered by varying porphyrin, functional groups, cross linking reagents and reaction conditions.

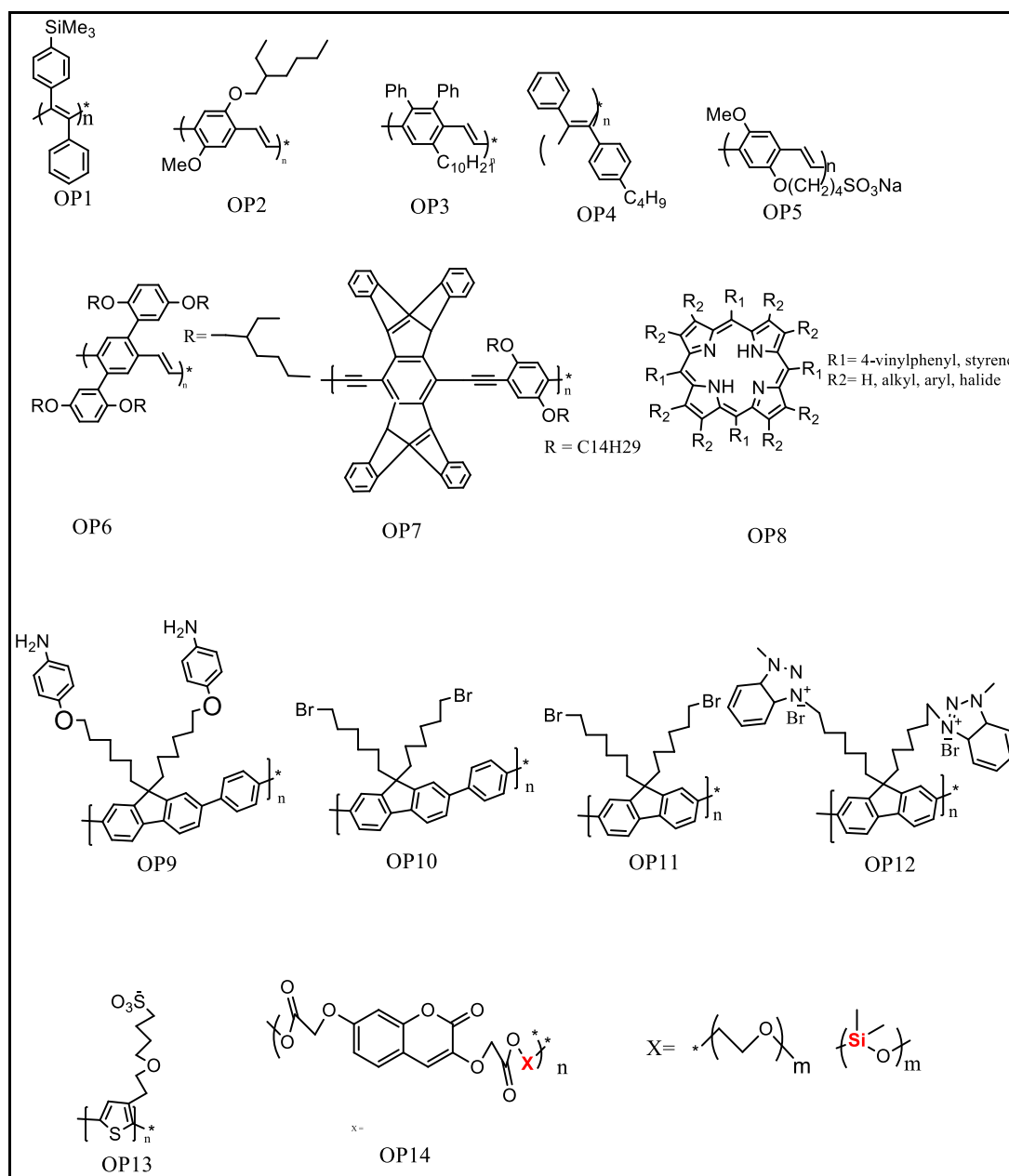


Chart 1: Structure of fluorophores of organic polymers

**Polyfluorene backbone** (OP9, OP10, OP11, OP12)<sup>21,29</sup> gives overlap between absorption spectra of PA with emission as well as excitation spectra of the polymer. Polyfluorene derivatives with Cationic side chains involve resonance energy transfer (RET), photo-induced electron transfer (PET) etc for sensing PA (Chart 1).

**Poly (3-alkylthiophene)** (OP13): Encapsulated Poly (3-alkylthiophene) (OP13) in poly (*N*-iso-propylacrylamide) (PNIPAM) microgels is a fluorescent probe for sensing aqueous picric acid. Encapsulation of the poly (thiophene) in the PNIPAM micro gels breaks  $\pi$ - $\pi$  interactions between polymer chains that would normally lead to aggregation quenching of fluorescence. The sensing capacity of the micro gels could be recovered after quenching by heating the aqueous suspensions. Structural collapse of the micro gels forces out the quencher molecules and restores the initial fluorescence signal of the polymer<sup>30</sup>.

**Coumarin-based copolymer** (polyethylene oxide or poly dimethylsiloxane units in the backbone),(OP14)<sup>24</sup> display excellent sensing for PA. These gel like polymers exhibit result in polymer thin film. They can sense PA with high sensitivity.

### 1.2.1.2. Inorganic polymers

**Poly silanes** They have Si-Si backbone. The electronic properties are on account of  $\sigma$ - conjugation along the Si-Si chain. It gives high mobility of hole, high NLO susceptibility and high emission in the spectral region. Poly(3,3,3-trifluoropropylmethylsilane),(IP1)<sup>31</sup> is a rigid polymer having F atom in the adjacent pendant group. Helical, and rod shaped poly silanes have been obtained. The sensitivity of

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the polymer is due to electron withdrawing  $\text{CF}_3$  groups, which stabilize the HOMO and LUMO. Owing to electron withdrawing nature of  $\text{CF}_3$ , a positive center develops at Si, thereby increasing its ability to bind with nitro group of the analyte.<sup>1</sup>

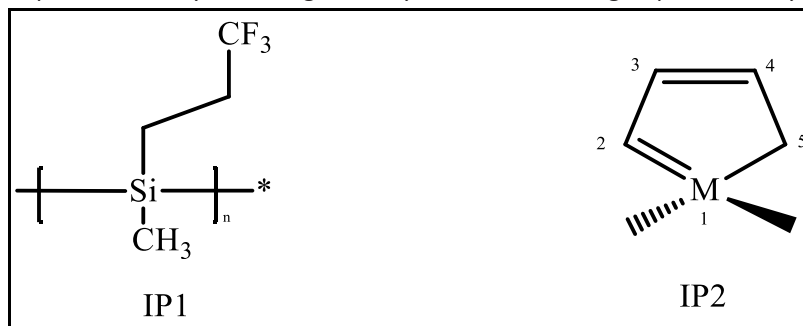


Chart 2: Structure of fluorophores of inorganic polymers

### Metallole-silane copolymer

Metalloles are analogues of cyclopentadiene having elements of group 14 (Si, Ge, Sn, Pb) substituted at  $\text{sp}^3$  carbon. There is reduction in HOMO-LUMO band gap which makes metalloles highly luminescent, and electron transporting materials (Chart 2). Tuning of HOMO-LUMO can be done by using appropriate functional group (IP2)<sup>32</sup>.

An example of poly (1,1-metallole) is poly (tetraphenyl) silole, having Si-Si backbone surrounded by organic and bulky phenyl substituents on silacyclopentadiene ring. The polymer provides pathway for electron transfer. The hydrophobic exterior separates the metallole chain and prevents self-quenching.

### 1.2.2. Supra molecular fluorophores

Chart 3 show the molecular structure of supra molecular fluorophores (SMF). SMF 1, SMF 2, and SMF 4 are highly fluorescent compounds. Their fluorescence gets quenched by PA. The formation of ground state complex and electrostatic interactions between fluorophore and PA are proposed to be the reasons for the formation of charge transfer complex (CTC)<sup>33</sup>.

Systems consisting of macro cycles, dendrimers,<sup>34</sup> supra molecular polymers, metal organic frameworks, have been utilized in detection of explosives. In (SMF 3), protonation of pyridine nitrogen, along with charge transfer was the reason for quenching.<sup>35</sup>

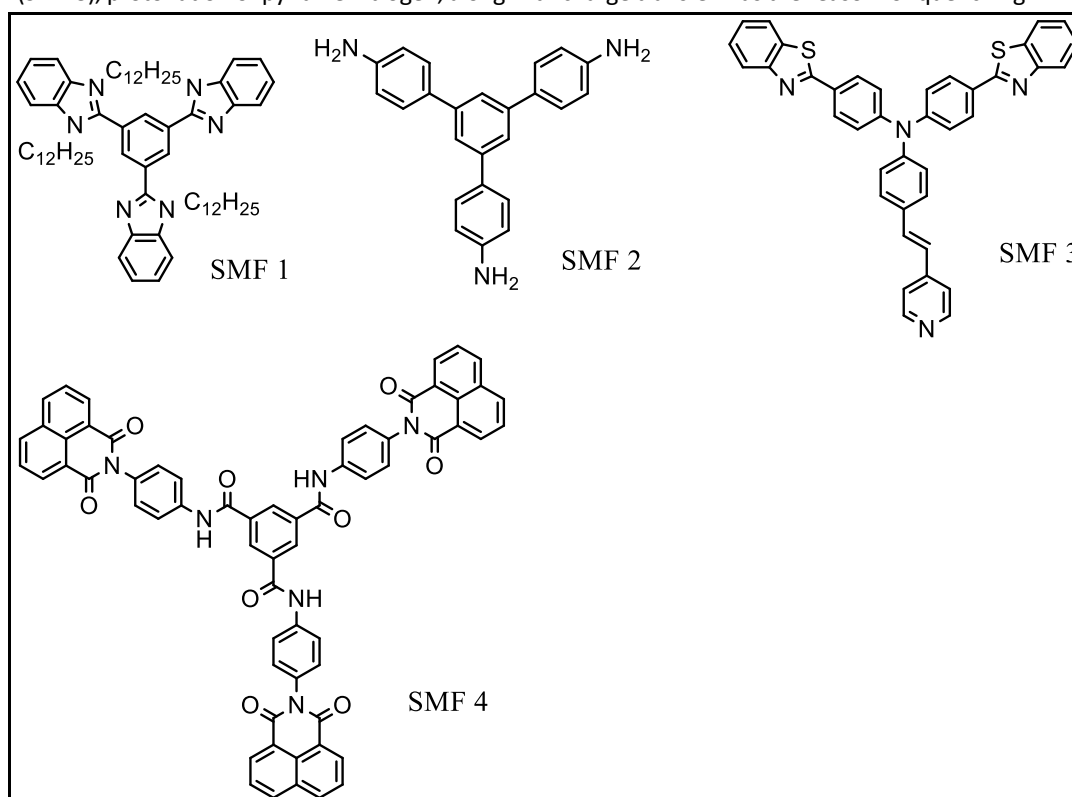


Chart 3: Structure of supra molecular fluorophores

### 1.2.2.2. Dendrimers

Dendrimers are branched polymeric macromolecule, consisting of a core and attached dendrons in the form of branches. Dendrons separate the inner core from the surrounding environment. The groups on the surface of dendrons interact with the surrounding environment. Fluorophore can serve as core. If the surrounding dendrons are also fluorescent, the fluorescence

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intensity of dendrite will depend on the number of branching. Most of the dendrimers are spherical in shape. Porous films of such materials can serve as effective solid sensors for detecting NACs. Carbazole and florene based dendrimers showed effective sensing for NACs. The quenching affinities of dendrimer were found to increase with increase in branching of dendrons. Strong intermolecular interactions between carbazole dendrimers (D1, D2, and D3)<sup>35</sup> and fluorene dendrimer (D10)<sup>35</sup> and nitro aromatic compounds were responsible for fluorescence quenching of their dendrimers.

Dendrimers can combine with polymers and small molecules. D4 and D5 (chart 4) can detect nitro aromatic compounds<sup>36</sup>. Their emission is quenched by the nitro aromatic compounds due to strong donor-acceptor binding. Electron deficient PA assists in proton transfer from acidic -OH to -NH<sub>2</sub> group of D4 and D5. Thus D4 and D5 are protonated and complex is formed by electrostatic interaction between them and PA, and fluorescence is quenched<sup>37</sup>.

The above compounds D6<sup>34</sup> and D7<sup>34</sup>(chart 4) form aggregates, which showed enhanced fluorescence. PA being strong acid undergoes dissociation readily. The protons released from PA, results in protonation of -NH<sub>2</sub> groups of the aggregates. Electrostatic interaction between aggregates of protonated fluorophore and picrate anion result in fluorescence quenching<sup>37</sup>. (D8)<sup>35</sup> and bifluorene based dendrimers (D9)<sup>35</sup> are excellent fluorophores, and they form thin film, display reversible quenching interactions with nitrated analytes (chart 4). Mechanism of quenching of dendrimers is collisional quenching, in contrast to static binding interaction in case of polymer sensors.

(D10)<sup>35</sup> proved as an excellent sensor for NACs, the compounds exhibited AIEE. The aggregates were excellent fluorophores, whose fluorescence was quenched by NACs. The mechanism of quenching is attributed to charge transfer because of lower energy level of LUMO of nitro aromatic compound. Higher energy level of LUMO of fluorophore allows electron jump to the LUMO of analyte.

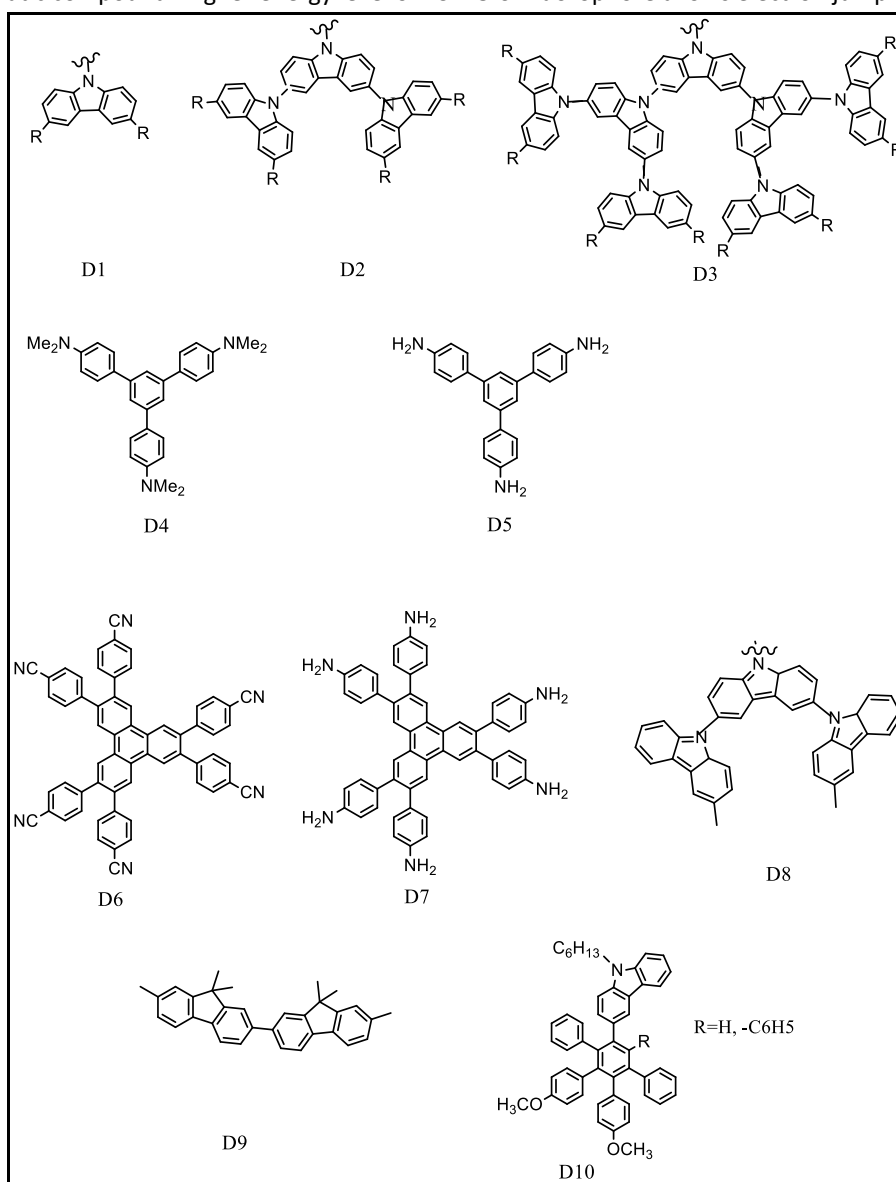


Chart 4: Structure of dendrimer fluorophores

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### 1.2.2.3. The Curcumins

The curcumin based probe C1 and C2 have curcumin linked with L-cysteine and L-tryptophan respectively<sup>36</sup>. Presence of basic amine groups help it to binds with PA. Electrostatic interaction of protonated fluorophores (C1 and C2) with PA anion causes strong aggregation and association, responsible for fluorescence enhancement. Curcumin cysteine (C1) and curcumin tryptophan(C2) exhibit turn on fluorescence sensing with PA. Fluorescence of C1 and C2 gets enhanced on binding with PA. Curcumin shows strong absorbance at 380 nm due to  $\pi$ - $\pi^*$  transition, exhibiting yellow colour. When curcumin binds with amino acids cysteine and tryptophan, a red shift is observed in the absorption spectra. This is attributed to binding of amino acid with curcumin, leading to extended conjugation. These compounds C1 and C2 exhibit emission at around 535 and 540 nm respectively. On binding with PA an enhancement in fluorescence intensity is observed<sup>38</sup>.

Sensing of PA by C3 and C4 is attributed to electrostatic interaction between the probes and PA<sup>37</sup>. Basic amine group of C3 and C4 interacts with phenolic group of PA. Fluorophores C3 and C4 interact with PA and are quenched. PA transfers its proton to the basic amine group and forms hydrogen bond interactions. Charge transfer complex between C3/C4 and PA occurs, (Chart 5) which leads to decrease in energy of thus formed complex. Internal charge transfer (ICT) is the reason of fluorescence quenching<sup>39</sup>.

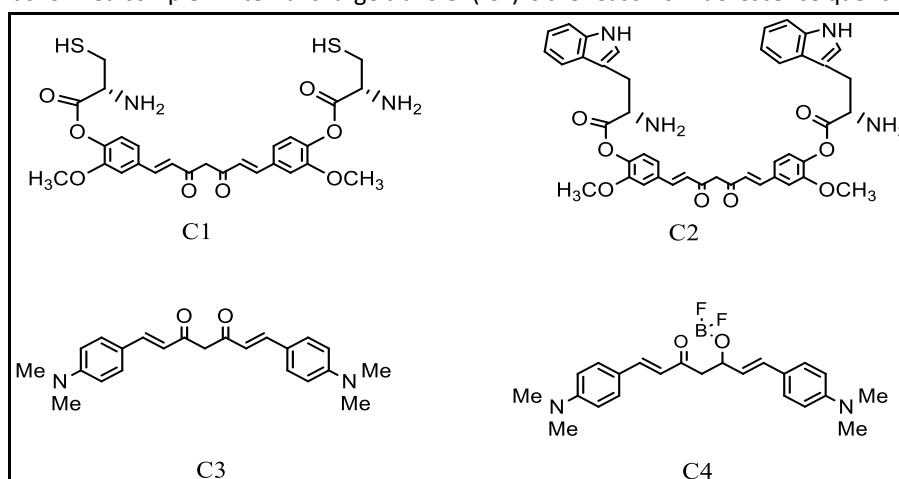


Chart 5: Structure of curcumin fluorophores

### 1.2.2.4. Hexaphenylbenzene Derivatives

These molecules exhibit aggregation induced emission enhancement (AIEE)<sup>38</sup>. The hexaphenylbenzene (HPB) unit in probes (H1, H2 and H3) lend rotation through phenyl spacers. These molecules form supra molecular assemblies. Due to difference in HOMO levels between fluorophore and NACs, they render energy transfer. The aggregates of HPB derivatives form porous spherical aggregates. The donor methoxy group contributes significantly towards enhancing the sensitivity of the fluorophore aggregates (Chart 6). Derivative H1 has hydrophobic methoxy groups at the periphery of the aggregates<sup>40</sup>.

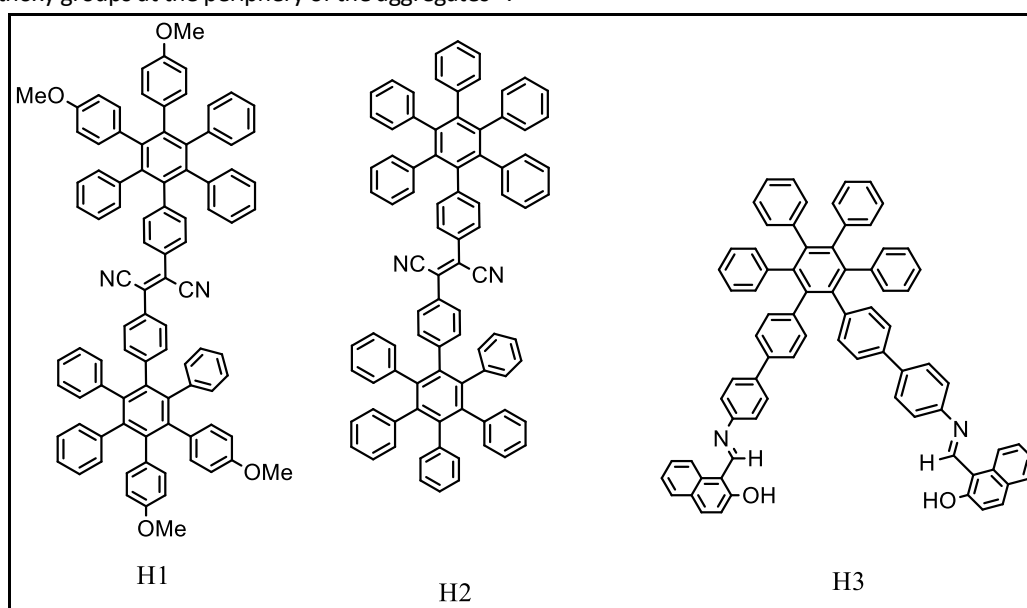


Chart 6: Structure of hexaphenylbenzene fluorophores

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### 1.2.2.5 Pentacene based derivatives

Pentacene scaffold is rigid and planar molecule. P1 has single pyridine attached. Increasing the number of pyridine rotors (P2 and P3) on the pentacene core, leads to an increase in fluorescence intensity<sup>41</sup>. Derivative P4<sup>41</sup> and P5<sup>41</sup> are donor-acceptor-donor type system, exhibiting intermolecular charge transfer, when reacted with PA. The presence of alkyl chain on P5, in the aggregated state is responsible for enhancement in the emission efficiency. In P5 the presence of alkyl chain provides more porosity to the aggregates of fluorophore (Chart 7). Its efficiency is greater as PA gets lodged in the porous fluorophore<sup>41</sup>.

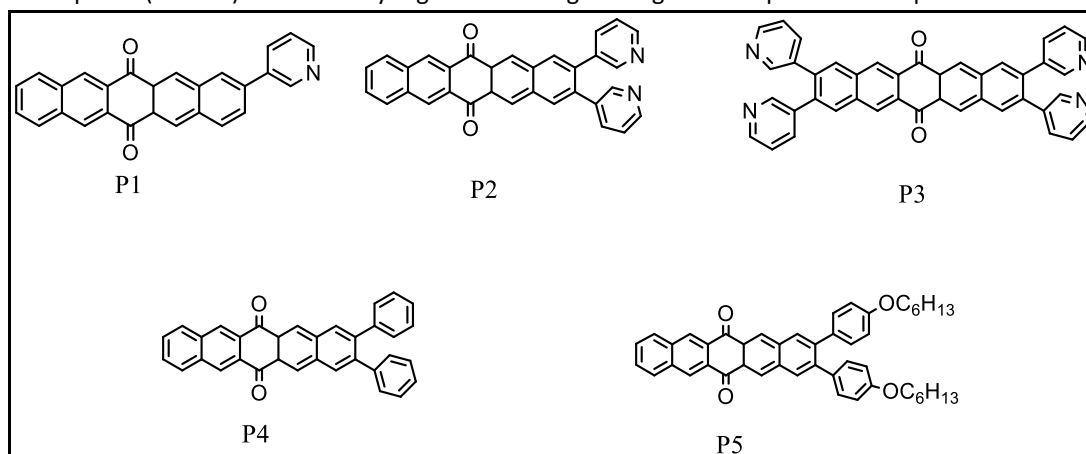


Chart 7: Structure of pentacene based fluorophores

### 1.2.3. Metal Organic Framework

MOFs contain of metal ions or clusters coordinated to organic ligands. This give rise to one, two or three dimensional coordination polymers. Often, they are porous. MOFs are inherited with properties such as porosity, rigidity and hold applications in catalysis, adsorption, sensing, drug delivery etc. with transition metals as nodes, luminescent MOFs can be developed which can recognize electron deficient molecules such as NACs<sup>42,43,29</sup>. Endowed with secondary functional groups have better binding site for the analyte. Small size of MOFs is favored for attaining better surface area and porosity, thereby increasing the diffusion of analyte into the MOFs<sup>42,43,29</sup>. Cd(II) /Zn(II) luminescent MOFs with electron donors have been proved as excellent sensors for detecting NACs.

Zn-MOF with 9,10-bis(4-carboxyphenyl)anthracene ligands (MOF 1) exhibited quenching with PA. (MOF 1) bearing a mixture of 4,4'-biphenyldicarboxylate and 1,2-dipyridylethene ligands<sup>44</sup> has the ability to detect nitro aromatics (Figure 1.7)

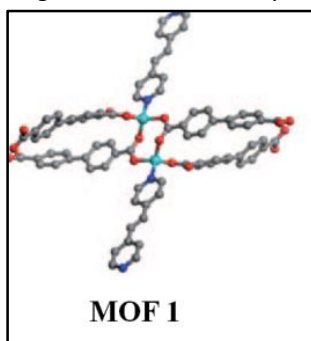


Figure 1.7: Structure of MOF of Tb<sup>3+</sup>

Mechanism of quenching in (MOF 1) (Figure 1.7) was on account of (PET) from MOF to nitro aromatic. Resonance coupling between neighboring anthryl groups enhance exciton migration and facilitate charge transfer, thereby quenching the fluorescence of (MOF 2)<sup>44</sup> is zeolite like porous MOF, luminescent in solid state. The highly efficient  $\pi$  system acts as binding site for nitroaromatics. Large optical band gap provides reduced excited state, and is the driving force for electron transfer to quencher.

MOF 2 (Figure 1.8) was designed using organic ligand- terphenyl-3,3',5,5'-tetracarboxylic acid and terbium nitrate. The asymmetric unit of MOF2 contained two Tb<sup>3+</sup> ions, two ptpc<sup>4-</sup> ligands, one coordinated DMF, one coordinated water molecule, two dimethylammonium ions, one lattice DMF molecule and six lattice water molecules. This 3D framework contained (1D) channels along a and b axis, which facilitated the diffusion of PA. The host-guest interaction were mainly electrostatic in nature. The MOF sensor had good recyclability for PA<sup>45</sup>.

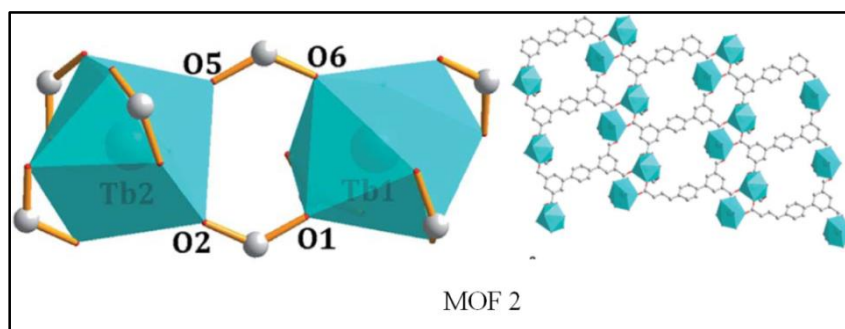


Figure 1.8: Structure of MOF of Tb<sup>3+</sup>

7-amino-4-methyl coumarin was used to construct (MOF 3) and (MOF 4) (Figure 1.9) contain amino-4-methyl coumarin- detected PA to 0-100 μM range (Fig 1.9). The absorption spectra of PA overlapped with the emission spectra of MOFs, leading to RET and quenching of fluorescence<sup>46</sup>.

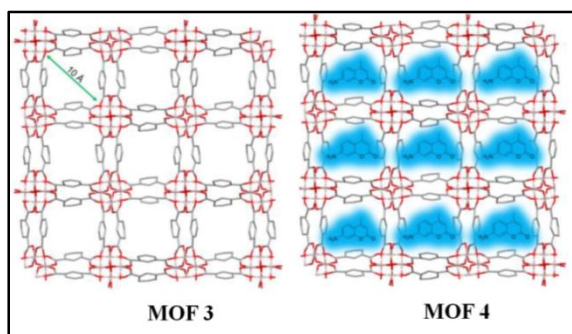


Figure 1.9: Structure of MOF of coumarin

Cd-MOF (MOF 5) (Figure 1.10) has asymmetric units consisting of one and a half independent Cd(II) ions, one fully deprotonated organic ligand and one dimethylammonium ion. Fluorescence resonance energy transfer (FRET) between MOF 5 and PA was responsible for fluorescence quenching<sup>47</sup>.

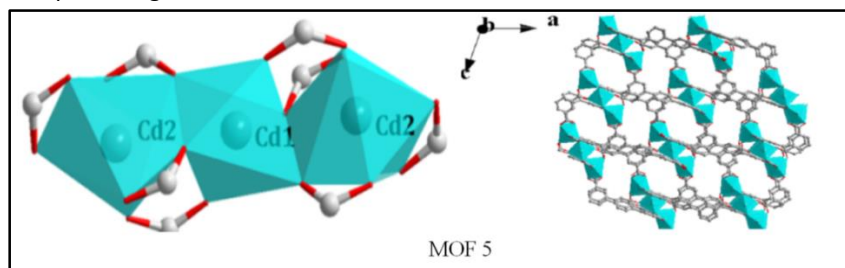


Figure 1.10: Structure of MOF of cadmium

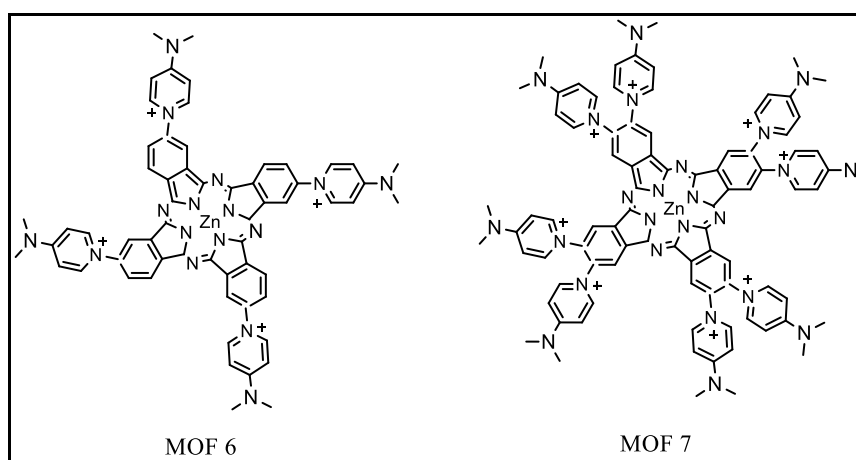


Chart 8: Structure of MOF of zinc

MOF 6 and MOF 7 (Chart 8) are zinc phthalocyanine derivatives, having 4 and 8 pyridinium units. They exhibited aggregation induced emission enhancement (AIEE). The π rich conjugated system exhibited emission in red region. Electron deficient NACs



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undergo  $\pi$ - $\pi^*$  interaction and hydrogen bonding interaction, thereby quenching the fluorescence. MOF 7 is a better sensor of PA<sup>48</sup>.

### 1.2.4. Nanomaterials

Nanomaterials have been recently used for detecting explosives<sup>49</sup>. Nanomaterial in the form of quantum dots, quantum clusters, metal organic frameworks, carbon dots having fluorescent properties have been synthesized<sup>50</sup>. Because of their Nano size, they provide a large surface to volume ratio, and hence large surface area for detection of explosives<sup>5</sup>. Due to Nano sized structure, increased sensitivity could be easily achieved<sup>51,52</sup>.

High surface to volume ratio of nanoparticles make them good choice to interact with analyte. Nanofibres can be coated with fluorophore. These in turn can interact with the explosive, and thus behave as sensors for them. Fluorophore can be coated on the surface of SiO<sub>2</sub> and on glass surface by spin coating. And such surfaces can be used as probe to sense the explosive<sup>1</sup>.

Graphene quantum dots (GQDs) are small fragments of graphene<sup>53,54</sup>. Graphene is a semiconductor with zero band gap and dimension in the range below 20nm. Nitrogen doped GQDs exhibit excellent fluorescence. The fluorescence was quenched by NACs. Spectral overlap of absorption spectra of NACs and emission spectra of GQDs was responsible for FRET mechanism, leading to quenching.

### 1.2.5. Small Molecule Fluorophore

These have proved as good sensor for NACs. They differ from polymeric system in their quenching mechanism<sup>55-60</sup>. The advantages of using small molecules are:

Easy synthesis

- Their isolation and purification by chromatographic techniques.
- Their high quantum yield.
- The easy structure and characterization.

Their reproducibility is certain<sup>56-65</sup>, as compared to that of polymeric systems.

Small molecule (SM1)<sup>57</sup> emits weakly in THF, but addition of water increases its fluorescence intensity. But addition of picric acid quenches the fluorescence. SM1 also behaves as acid-base indicator owing to its ratio metric fluorescence emission.

(SM2) exhibited emission, which was quenched by picric acid. The pyridine nitrogen accepts proton from picric acid (Chart 9). The overlap of emission of SM2 with absorption spectra of PA resulted in FRET mechanism of quenching<sup>58</sup>.

Pyrene probe SM3, displayed transition. Pyridine nitrogen forms hydrogen bond with -OH of picric acid and quenched the fluorescence of pyrene fluorophore<sup>59</sup>.

SM4 has pyrene moiety. It exhibits host-guest complex formation with multiple hydrogen bond interactions with PA<sup>9</sup>.

The bright green fluorescence of SM5 is quenched, due to protonation of pyridine nitrogen, followed by PET from excited fluorophore to ground state of PA<sup>60</sup>.

SM6 showed quenching of fluorescence with PA, but with higher concentration of PA a weak emission band appeared. The appearance of new emission band could be attributed to increased ICT upon protonation of pyridine nitrogen<sup>71</sup>.

SM7 also exhibited fluorescence quenching with PA, but, with increasing concentration of PA, the emission spectra of SM6 showed slight red shift. This led to conclusion that SM6 caused fluorescence quenching by combined ICT and FRET mechanisms<sup>61</sup>.

SM8 formed 1:1 complex with PA SM9-SM11 showed blue emission. They formed ground state charge transfer complex with PA. Protonation of imidazole nitrogen increased efficiency of PET and caused fluorescence quenching. Probe SM9 having -OH, exhibited additional hydrogen bonding with PA, hence, showed efficient quenching with PA, compared to SM10 and SM11<sup>62</sup>.

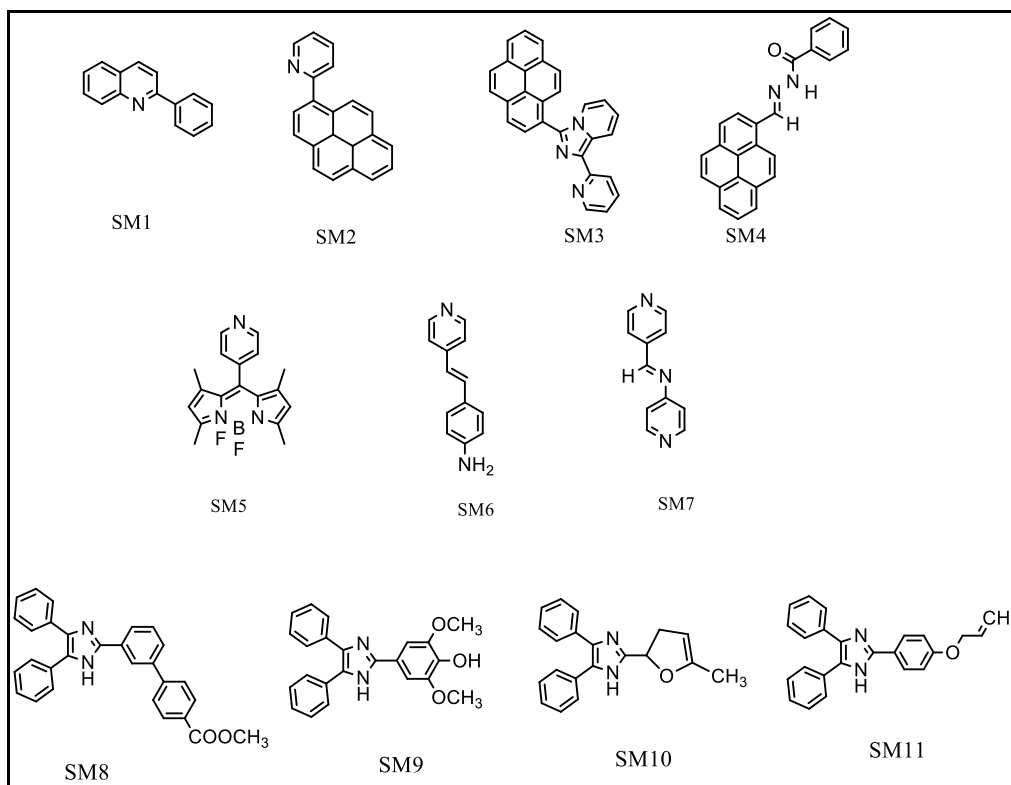


Chart 9: Structure of small molecule fluorophores

Naphthalene diimide (NDMI)(SM13)<sup>73</sup>, based cation derivative also exhibits excellent electrical, optical and visual changes. Response to PA is on account of anion-exchange induced  $\pi$ - $\pi$  interaction, leading to ground state (GS) charge transfer mechanism.  $\pi$ - $\pi$  stacking interaction leads to complex formation between PA and NDMI derivatives. HOMO/LUMO energy levels decide probability of ground state charge transfer complex formation (Chart 10).

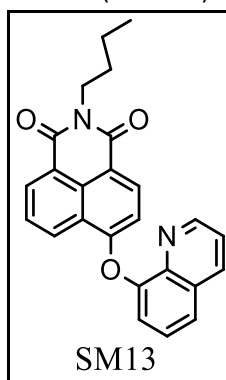


Chart 10: Structure of small molecule fluorophores (Naphthalene diimide)

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