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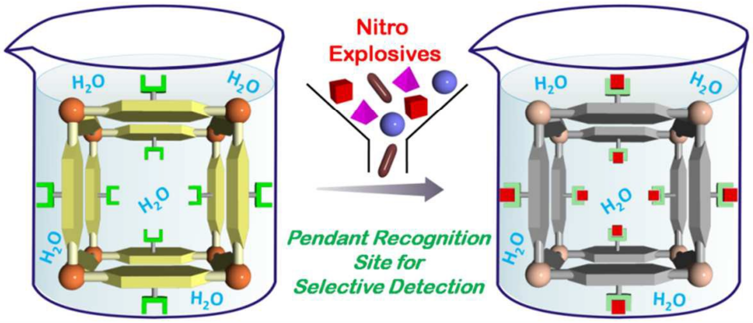
For Graphical Abstract



A metal-organic framework with pendant Lewis basic recognition site is employed to achieve aqueous phase selective nitro explosive TNP detection.

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ARTICLE TYPE

Aqueous phase selective 2,4,6-trinitrophenol detection via fluorescent metal-organic framework with pendant recognition site

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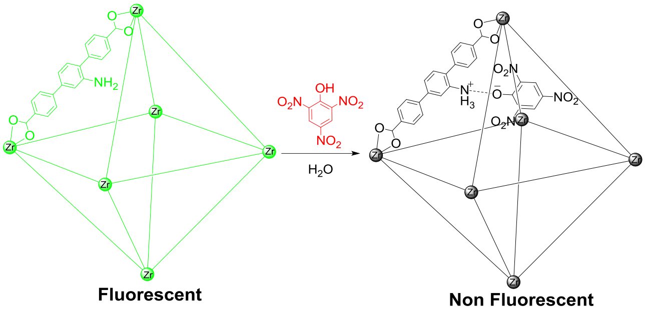
Aqueous phase prompt and selective detection of nitro explosives is highly demanded in regards to homeland security and environmental concerns. Here in we report chemically stable porous metal organic framework UiO-68@NH_2 with pendant recognition site for selective detection of nitro-aromatic explosive TNP in aqueous phase. The pendant Lewis basic amine moieties expected to selectively interact with TNP via electrostatic interaction and act as recognition site for TNP. The MOF can detect presence of TNP in water at concentration as low as 0.4 ppm with response time in few seconds. Additionally, both excitation and emission wavelengths of MOF are in visible region. The high selectivity was observed even in presence of competing nitro analytes in aqueous phase. The quenching constant for TNP was found to be $5.8 \times 10^4\ M^{-1}$ which is 23 times higher than TNT and RDX demonstrating super and selective quenching ability. This unprecedented selectivity is ascribed to electron as well as energy transfer mechanisms and electrostatic interactions between TNP and MOF. The MOF coated paper strip demonstrated fast and selective response for TNP in water beginning a step towards practical application.

Introduction

The selective and sensitive detection of lethal explosives material is decisive for homeland security, anti-terrorist operations and civilian safety.[1] The most commonly used explosive ingredients are nitroaromatics like 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrophenol (TNP), nitro aliphatic compounds like 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), explosive tag like 2,3-dimethyl-2,3-dinitrobutane (DMNB). Among these, TNP has higher explosive power in similar class of explosive compounds.[2] Apart from explosive nature, TNP causes skin/eye irritation, headache, anaemia, liver injury, male infertility.[3] Despite this fact TNP is widely used in fireworks, leather, dyes industries.[4] Because of high water solubility TNP can easily lead to contamination of nearby soil and aquatic system, posing serious health hazards.[2] Furthermore owing to highly electron deficient nature, biodegradation of TNP is very difficult. Curiously, less efforts have been devoted for selective TNP detection, thus the development of efficient sensor material for TNP detection and constant monitoring of soil and aquatic system is highly demanded. However, the selective detection of TNP in presence of competing nitro analytes is very difficult.[5] Fluorescence based chemosensors have attracted great attention for in-field use over current sophisticated detection systems owing to high sensitivity, portability, short response time, low cost and compatibility in both solid and solution state.[6] Numerous luminescent materials have been studied as fluorescence based explosives sensors till date, but their multi-step processing, toxicity and lack of control over molecular organization limits their wide use.[1a]

Metal-organic frameworks (MOFs), have emerged as promising material for gas storage/separation, chemical sensing, heterogeneous catalysis, biomedicine, magnetism, clean energy technology and optoelectronics in recent time.[7] Especially, as fluorescence based chemical sensor, MOF offer great promise by virtue of its crystalline nature, permanent porosity, designable/modifiable pores, systematically tuneable band gaps and electronic structures.[8] The fluorescence sensing performance of MOF is determined by interactions between target analyte and MOF backbone. The porosity allows host-guest interaction between analyte and MOF matrix while the designable pore size/shape renders molecular sieving effect. The pendant recognition sites allow selective interaction with adsorbate via open metal sites, hydrogen bonding, Mulliken-type interactions, Lewis acidic/basic sites, etc. and thus can selectively accumulate the targeted analyte in MOF matrix giving rise to improved sensing performance, also called pre-concentration effect.[8b] Additionally, immobilization of organic ligands in rigid MOF framework leads to stronger emissions. Most importantly the limitless combinations of organic ligands and metal centres allow tuning of valance and/or conduction band and in turn the band gap, crucial for sensing applications. Owing to above advantages, variety of MOFs have been designed and studied for detection of cations, anions, small molecules, explosives and biomolecules.[9]

Despite recent advances, the reports of fluorescent MOF for selective and sensitive TNP detection in presence of other nitro analytes are rare and that exhibit unprecedented selectivity in aqueous system are rarer still.[9,10] The UiO (University of Oslo) series porous MOFs are composed of less absorbed Zr(IV) metal centres and are chemically stable, making them most suitable



Scheme 1 Fluorescent MOF **1** based sensor for highly selective nitro explosive detection in aqueous phase.

candidates for sensing.[11] Recently, we have reported a Zirconium based chemically stable porous fluorescent MOF for aqueous phase selective TNP detection.[10b] We deployed Lewis basic pyridyl functionality in 3D (three dimensional) MOF matrix to achieve highly selective TNP detection in aqueous phase. We reasoned that, similarly Lewis basic amine functionality can also be promising recognition site for selective TNP detection owing to its possible ionic and hydrogen bonding interactions with TNP.[12] Thus on similar line, we chose Zr(IV) based chemically stable porous MOF $Zr_6O_4(OH)_4(\mathbf{L})_6$ (**1**, UiO-68@NH_2, **L** = 2'-amino-[1,1':4',1"-terphenyl]-4,4"-dicarboxylate) with pendant amine functionality for aqueous phase selective TNP sensing (Scheme 1).[13] The porous MOF has large pores of 11 and 22 Å, which are expected to allow easy diffusion and concentration of analytes and facile host-guest interactions. The guest accessible Lewis basic amine functionalities will act as recognition sites for TNP via ionic and hydrogen bonding interactions. Also excitation and emission wavelengths of MOF **1**, are in visible region making it an ideal material to study TNP sensing performance.

Experimental Section

Caution:

TNT, RDX and TNP are highly explosive and should be handled carefully and in small amounts. The explosives should be handled as dilute solutions and with safety measures to avoid explosion.

Materials:

TNT and RDX were provided by HEMRL Pune (India). TNP, 2,4-DNT, 2,6-DNT, DMNB were purchased from Aldrich, while 1,3-DNB (1,3-dinitrobenzene), NB (nitrobenzene) purchased from local company. All the chemicals were used as received. Dry solvents were used during complete analysis and were obtained locally.

Physical Measurements:

^1H NMR was recorded in 400 MHz Jeol ECS-400 Instrument. Thermogravimetric analyses were recorded on Perkin-Elmer STA 6000 TGA analyser under N_2 atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction patterns (PXRD) were measured on Bruker D8 Advanced X-Ray diffractometer using Cu K_α radiation (λ= 1.5406 Å) with a tube voltage of 40 kV and current of 40 mA in 5 to 40° 2θ range. The FT-IR spectra were recorded using NICOLET 6700 FT-IR spectrophotometer with KBr pellet in 400-4000 cm^{-1} range. Fluorescence measurements were done using Horiba FluoroMax 4 with stirring attachment. The UV-Vis measurements were performed using Chemito SPECTRASCAN UV-2600.

Synthesis of UiO-68@NH_2(1):

The ligand 2'-amino-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid (**LH₂**) was synthesized using procedure previously reported (Fig. S1†).[13a] For synthesis of **1**, $ZrCl_4$ (24 mg), **LH₂** (56 mg) were dissolved in N,N-dimethylformamide (DMF, 3 mL) in a Teflon lined Parr stainless steel vessel (17 mL). The vessel was sealed and placed in oven and heated at 120 °C for 16 h. After cooling to room temperature, the crystalline product was isolated by filtration the solid was washed with DMF.

Activation of UiO-68@NH_2 (1'):

The occluded solvent and starting material in MOF was then exchanged with MeOH by dipping it in MeOH for 3 days. Over 3 days the MeOH was replaced with fresh MeOH every 24 h. The guest free porous MOF (**1'**) was obtained by heating the MeOH exchanged MOF at 130 °C under vacuum for 24h which was then used for fluorescence measurements.

Photophysical study:

In typical experiment, 1 mg of **1'** was weighed and added to cuvette containing 2 mL of water and stirred. Upon excitation at 395 nm, fluorescence response of **1'** (0.5 mg/mL) dispersed in water was measured *in-situ* in 410-780 nm range and corresponding fluorescence intensity was monitored at 500 nm. For fluorescence titration, emission was recorded upon incremental addition of freshly prepared analyte solutions (1 mM or saturated). To maintain homogeneity solution was stirred at constant rate during experiment.

Result and Discussion

Synthesis

The MOF **1** was synthesized by reaction between $ZrCl_4$ and **LH₂** in DMF at 120 °C solvothermally.[13] Overlapping PXRD patterns of as-synthesized sample and simulated pattern confirmed the successful formation of **1** (Fig. S2†). The MOF composed of hexameric Zr node $Zr_6O_4(OH)_4(CO_2)_{12}$ connected by ligand **L** forming 3D porous structure. The decrease in $\nu(COO)_{as}$ frequency from 1685 cm^{-1} to 1608 cm^{-1} in FT-IR spectra of **LH₂** and MOF **1** respectively, also supported the bond formation (Fig. S3†). Thermogravimetric analysis (TGA) of as-synthesized MOF **1**, showed ~60 weight loss below 300 °C, ascribed to loss of DMF and starting material present in free volume of MOF matrix (Fig. S4†). The DMF and starting material was removed by solvent exchange method reported previously to get guest free or activated form **1'**. The thermogravimetric analysis of activated MOF **1'**, did not show any weight loss below 300 °C confirming the successful guest removal (Fig. S4†). The activated MOF remains stable even after guest removal as confirmed by PXRD analysis (Fig. S2†). The larger pore window has size of 22 Å while the smaller pore has size of 11 Å, which enables concentration of nitro analytes in MOF matrix (Table S1†). The pores are decorated with the guest accessible amine moieties which can act as recognition site for TNP giving rise to efficient quenching response.

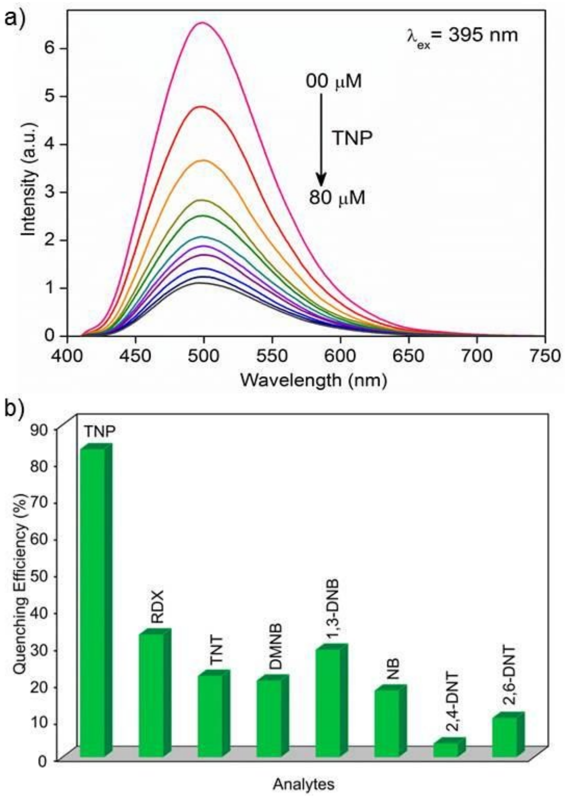


Fig. 1 a) Decrease in fluorescence intensity of **1'** dispersed in water upon incremental addition of aqueous TNP solution. b) Comparison of fluorescence quenching efficiency of different nitro analytes towards **1'** in water.

Photophysical Studies

The photoluminescence spectra of **1'** in water exhibit strong emission peak at 500 nm upon excitation at 395 nm at room temperature (Fig. 1a and S5†). To explore the potential application of **1'** to detect TNP in aqueous medium, fluorescence-quenching titration was performed by gradual addition of aqueous TNP solution. As anticipated the incremental addition of TNP resulted in fast and efficient fluorescence quenching of 86 % (Fig. 1). The **1'** can recognize TNP at as low as 0.4 ppm concentration, which is comparable to/or better than previous MOF reports.[10a] We also checked the quenching ability of other competing nitro analytes like TNT, RDX, 2,4-DNT, 2,6-DNT, DNB, NB, DMNB in water (Fig. 1b and S6-S12†). Compared to TNP, the competing nitro analytes showed small effect on emission intensity of **1'** (Fig. 1b). This clearly demonstrates the high selectivity of **1'** towards TNP compared to potentially interfering nitro analytes. To further quantify the quenching efficiency, Stern-Volmer (SV) plots of relative luminescent intensities (I_0/I) of all the nitro analytes were compared where, I_0 and I are the intensities in absence and in presence of respective nitro analytes (Fig. 2). All the nitro analytes except TNP showed linear SV plots. Interestingly, at low concentration TNP showed linear SV plot, which upon further increase in TNP concentration preceded in slightly non-linear fashion. This non-linear SV plot suggests presence of consolidation of both dynamic as well as static quenching and/or presence of energy transfer phenomenon between **1'** and TNP.[14] Using SV plot the quenching constant for TNP was calculated to be 5.8×10^4 M^{-1}. The observed quenching constant for TNP is equivalent to organic polymer based probes and is ~23 times higher than its aromatic (TNT) and aliphatic (RDX) tri-nitro analogues respectively, demonstrating the superior detection performance.[15]

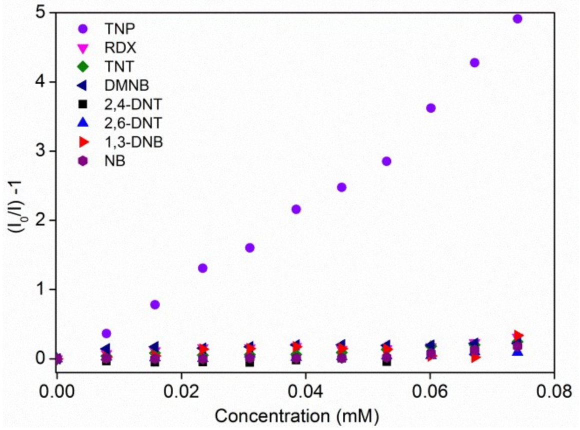


Fig. 2 Stern-Volmer plots for nitro analytes added to **1'** in water.

Investigation of Possible Quenching Mechanism

To gain more insight in to the superior sensing ability of **1'**, we sought to examine the electronic properties of both MOF and nitro analytes. The fluorescence quenching by electron transfer from conduction band (CB) of MOF to LUMO orbitals of electron deficient nitro analyte is well established quenching mechanism.[16] Lower the LUMO energy higher is the electron accepting ability of nitro analyte and thus the efficiency of fluorescence quenching. The effective fluorescence quenching by TNP is in good agreement with its lowest LUMO energy compared to other nitro analytes, as calculated by density functional theory at the B3LYP/6-31G* level (Fig. S13†). However, the fluorescence quenching performance of other nitro analytes does not follow the LUMO energy trend indicating simultaneous presence of other quenching mechanism in addition to electron transfer. The resonance energy transfer is another effective fluorescence quenching mechanism. The non-linear SV plot advocates the presence of long range resonance energy transfer. The effectiveness of energy transfer heavily depends on extent of spectral overlap between emission of fluorophore and absorption spectrum of analyte. The absorption spectrum of TNP shows higher extent of overlap with MOF emission as against

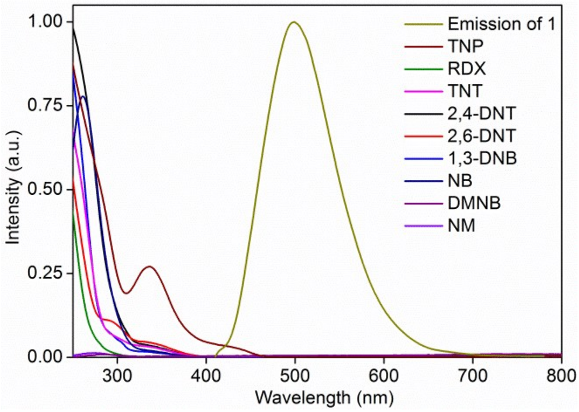


Fig. 3 Extent of spectral overlap between absorption spectra of nitro analytes and emission spectrum of **1'** in water.

other competing nitro analytes (Fig. 3). This observation is in good agreement with observed higher quenching efficiency obtained for TNP compared to other nitro analytes. Thus it is apparent that in case of TNP both electron and energy transfer mechanism are operational while for other nitro analytes only electron transfer mechanism operates.

TNP is known to interact with Lewis basic sites owing to acidic phenolic proton. To probe the role of pendant Lewis basic free amine present in **1**, towards the observed selectivity, fluorescence quenching titrations were performed with 2,4-DNP (2,4-dinitrophenol) and NP (4-nitrophenol). The fluorescence quenching performance of phenolic analytes is in accordance with acidity of phenolic protons TNP>2,4-DNP>NP. This indicates the presence of electrostatic interaction between TNP and pendant amine functionality, similar to pyridyl functionalized MOF reported earlier (Fig. S14-16†).[12] This supports the observed selectivity for TNP. The highly acidic TNP selectively and strongly interacts with pendant Lewis basic amine group via ionic and hydrogen bonding interactions leading to amplified quenching response. While in case of other nitro analytes such interactions are absent and so result in low quenching effect. Thus the Lewis basic amine functionality act as recognition site for TNP and combination of electron transfer, energy transfer quenching mechanism gives rise to unprecedented selectivity for TNP in aqueous phase. The solution pH has petite effect on MOF fluorescence in range 4.5 to 7, which is the range observed for TNP, 2,4-DNP, NP added solutions.

In real scenario, the selective detection of TNP in presence of other competing nitro analytes in aqueous system is highly desirable. To assess the selectivity of **1'** towards TNP in presence of competing nitro analytes we designed a competitive fluorescence quenching assay. Initially, the fluorescence spectrum of **1'** dispersed in water was recorded. To above solution aqueous TNT solution was added in two equal portions (total 40 μL) to allow effective access to pendant free Lewis basic amine sites and the fluorescence response was recorded. No significant fluorescence quenching was observed upon addition of aqueous TNT solution (Fig. 4). However when same quantity of aqueous TNP solution (40 μL in two equal portions) was added to above solution significant fluorescence quenching was observed. The trend repeated even in next TNT and TNP addition cycles. Similar phenomenon was observed in competitive assay for other nitro analytes demonstrating unprecedented selectivity of 1' for TNP in presence of competing nitro analytes (Fig 4).

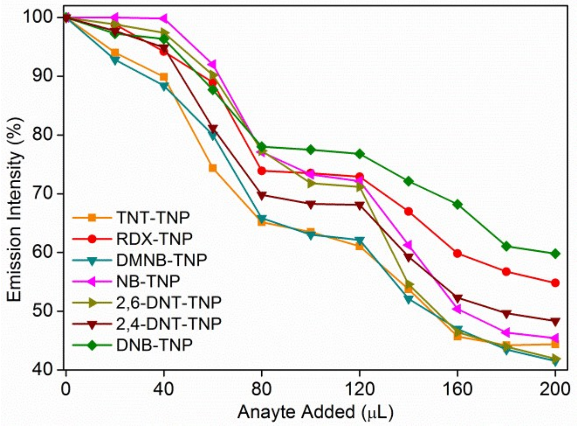


Fig. 4 Competitive fluorescence quenching efficiency of TNP upon addition of other competing nitro analytes followed by TNP to **1'**.

MOF based Paper Strip

For in-field aqueous phase explosive detection, the paper strip method comes handy. We prepared MOF **1'** coated black paper strips for in-field aqueous phase TNP detection. The pristine strip under UV illumination showed good fluorescence. The individual strips were then partially dipped in aqueous nitro analytes solutions (Fig. 5a). The part of strip dipped in TNP solution showed significant fluorescence quenching when visualized under UV light (Fig. 5b strip A) while the unexposed part of same strip still showed good fluorescence. All the other strips dipped in competing nitro analytes showed negligible fluorescence quenching response (Fig. 5b strip B-H). Thus the MOF **1'** coated paper strip provides an efficient way to trace the presence of TNP in aqueous system and demonstrates the potential of **1'** towards real-time in-field sensing application.

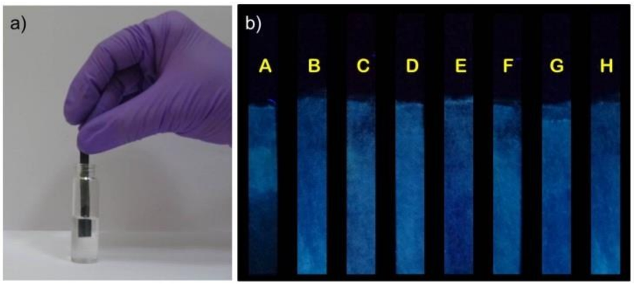


Fig. 5 a) MOF **1** coated paper strip for aqueous phase explosive detection. b) Response of MOF coated paper strips towards various nitro analytes under UV light (A = TNP, B = TNT, C = RDX, D= 2,4-DNT, E = DNB, F = 2,6-DNT, G = NB, H = DMNB).

Conclusions

In conclusion, we have reported a chemically stable porous fluorescent MOF with Lewis basic free amine functionality as pendant recognition sites for selective and sensitive detection of TNP in aqueous phase. Both the excitation and emission wavelengths of MOF are in visible region. The MOF can detect TNP at as low as 0.4 ppm concentration in seconds and the quenching constant for TNP was found to be 5.8×10^4 M^{-1} which is 23 times higher than TNT and RDX. Importantly the high selectivity is observed even in presence of competing nitro analytes. The combination of electron and energy transfer mechanism along with selective recognition sites is credited to high selectivity of **1'** towards TNP. The MOF based paper strip provides an effective and efficient way to in-field aqueous phase TNP detection for security and environmental monitoring applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: For details of MOF synthesis, PXRD patterns and photo physical studies. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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