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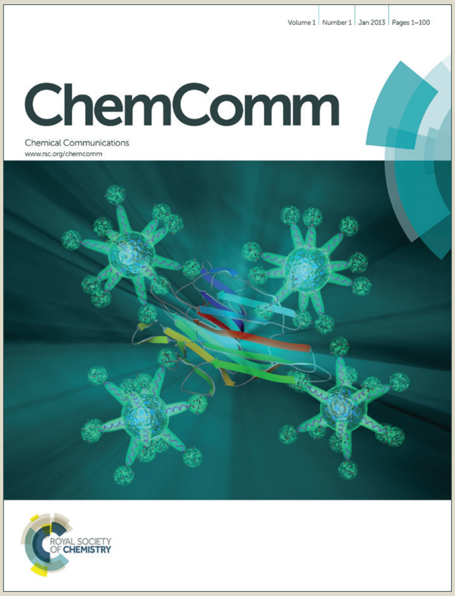

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ARTICLE TYPE

Fluorescent metal-organic framework for highly selective detection of nitro explosive in aqueous phase

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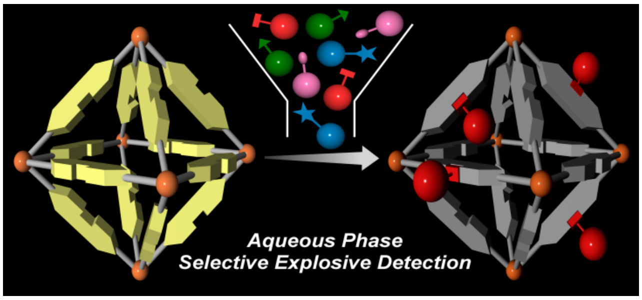
Selective and sensitive nitro explosive detection by a porous luminescent metal-organic framework has been reported. For the first-time MOF based selective explosive detection in presence of other nitro analytes in aqueous media is demonstrated.

Selective and sensitive detection of high explosives and explosive-like substances has become a serious issue concerning national security and environmental protection.[1] The nitro explosives like 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrophenol (TNP), nitrobenzene (NB) are the main constituents of numerous unexploded land mines used during World War II and even in today's landmines.[1c] Amongst these nitro explosives TNP has higher explosive power than TNT and is commonly used in dyes, fireworks, matches, glass, and leather industries.[2] In addition to explosive nature TNP has also been recognized as toxic pollutant. TNP and its mammalian metabolite picramic acid are known for mutagenic activities.[3] The TNP is released into the environment during their commercial production and use, leading to the contamination of soil and aquatic systems. Thus the selective and sensitive detection of TNP present in soil and ground water is very important for tracing buried explosives and environmental monitoring near industries. But the selective and sensitive detection of TNP in presence of other nitro compounds in water is challenge due to their strong electron affinity leading to false response.[4]

Although current explosive detection methods including trained canines and modern analytical techniques are selective and accurate but suffers disadvantages like high operational cost and portability issues during in-field use.[5] Fluorescence based detection method have attracted great attention in recent times by virtue of its high sensitivity, portability, short response time, and applicability in both solid and solution phase.[6] Variety of materials including conjugated organic molecules, nanoparticles and metal complexes have been employed for fluorescence based explosive detection.[7] Despite this fact their wide spread use is limited due to stability, toxicity, multi-step processing and lack of control over molecular organization.[8]



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

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) owing to high surface area, designable architecture and host-guest interactions have been extensively used for gas storage/separation, catalysis, sensing, optoelectronics, clean energy and biomedical applications.[9] Especially, as luminescent sensor MOFs provide several advantages over conventional fluorophores.[10a,b] The designable architecture lets improved host-guest interactions and act as pre-concentrator for target analyte. Also, the immobilization of organic struts in MOFs gives rise to strong emissions due to reduced non-radiative relaxation. The infinite choices of organic linkers and/or metal centers allow fine tuning of electronic properties of MOFs. Furthermore, introduction of secondary functional group endorse preferred binding of chosen analyte giving rise to better selectivity.

For in-field selective detection of nitro explosives present in soil and ground water, probe working in aqueous media is highly desirable. Although MOF has been employed for the liquid phase explosive detection to the best of our knowledge there is no report of MOF based probe which can selectively detect the nitro explosive in aqueous medium.[10] Recently, we reported fluorescent MOF $[Cd(NDC)_{0.5}(PCA)]\cdot G_x$ which exhibits highly selective response towards TNP even in presence of competing nitro analytes owing to free basic site.[11] But similar to most of the MOFs its poor water stability limits its application to organic solvents. The smaller pore size than the analytes prevents the pre-concentration of

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

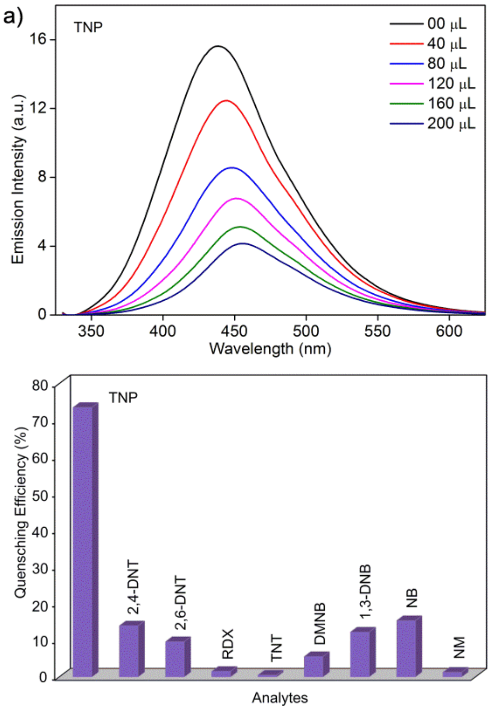

Fig.1 a) Change in the fluorescence intensity of **1'** in water upon incremental addition of aqueous TNP solution 1 mM. (λ_{ex}= 320, [**1'**] = 0.5 mg/mL). b) Efficiency of fluorescence quenching obtained for different analytes.

analytes in coordination space of MOF. More over the toxic nature of Cd(II) hinders its wide spread use for environmental applications. In our efforts to develop fluorescent MOFs working in aqueous media for selective detection of for nitro explosive, we got attracted to the 2-phenylpyridine-5,4'-dicarboxylic acid (LH_2) and Zr(IV) based MOF $Zr_6O_4(OH)_4(L)_6$ (**1**, UiO-67@N).[12] The MOF is composed of non-toxic Zr(IV) metal centre and remains highly stable in water. We envisioned that larger size of pore windows (11.5 Å and 23 Å) than analytes can permit easy diffusion of analytes inside the MOF keeping electron rich MOF and electron deficient nitro analytes in close proximity (Scheme 1). Also the free basic sites (pyridyl) may allow selective interaction between TNP and MOF giving rise to efficient response.

The guest free MOF (**1'**) when dispersed in water exhibited strong fluorescence upon excitation at 320 nm (Fig. S7). To trace the explosive sensing ability of **1'**, change in fluorescence intensity of **1'** dispersed in water towards different nitro aromatic compounds like TNP, TNT, 2,4-DNT, 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (DNB), NB, 1,3,5-trinitro-1,3,5-triazacyclohexane (nitro-amine RDX) and nitro-aliphatic compounds such as 2,3-dimethyl-2,3-dinitrobutane (DMNB), nitromethane (NM), in aqueous solutions were studied (Fig. 1 and S8-S15). Fig. 1 shows the change in the fluorescence spectra of **1'** with increasing amounts of TNP in water. As expected the incremental addition of TNP to **1'** resulted in fast and high fluorescence quenching (73%). The fluorescence quenching can be clearly determined at as low as 2.6 µM concentration. On the other hand, all the other nitro analytes showed petite effect on fluorescence intensity of **1'** (Fig. 1b). This clearly demonstrates the high selectivity of **1'** towards TNP over other nitro analytes. The Stern-Volmer (SV) plots in water used to calculate the quenching constant and analyse the quenching efficiency of the analytes (Fig. 2). Using SV equation $(I_0/I) = K_{SV}\ [A] + 1$ where, I_0 and I are the fluorescence intensities before and after addition of respective analyte, $[A]$ is molar concentration of analyte and K_{SV} is quenching constant (M^{-1}). At low TNP concentrations linear increase in SV plot was observed which upon further increase in concentration diverged from linearity bending upwards while other nitro analytes showed linear increase in SV plot. This non-linear nature of SV plot of TNP suggests self-absorption or combination of a static and dynamic quenching or energy transfer process between TNP and MOF.[11] The fitting of SV plot for TNP gave quenching constant to be $2.9 \times 10^4\ M^{-1}$ which is amongst highest value known for MOFs. Notably, the quenching constant for TNP was found to be comparable to organic polymers and is much higher than TNT, RDX or other nitro analytes demonstrating super-quenching ability of TNP towards **1'**.[13]

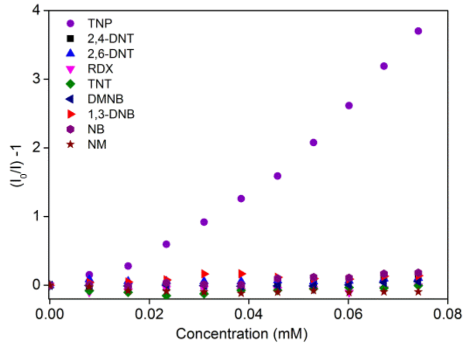

Fig. 2 Stern-Volmer (SV) plots for various nitro analytes in water. ([**1'**] = 0.5 mg/mL)

Encouraged form these results, the selectivity of **1'** towards TNP in presence of other nitro analytes in water was investigated. Initially fluorescence spectrum of **1'** dispersed in water was recorded. To this aqueous TNT solution (40 µL in two equal portions) was added so that high affinity basic sites will be accessible to TNT. Negligible fluorescence quenching was observed upon TNT addition. To this equal amount of aqueous TNP (40 µL) was added which resulted in significant quenching (Fig. 3). The trend also repeated in next addition

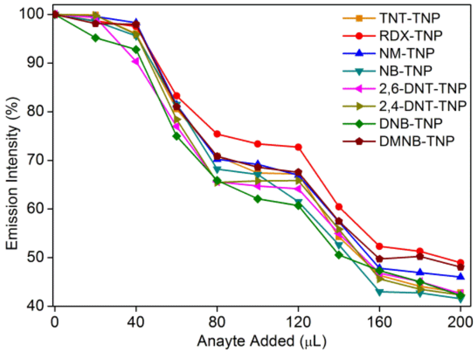

Fig. 3 Decrease in fluorescent intensities upon addition of various nitro analytes (1mM) followed by TNP (1mM) in aqueous medium.

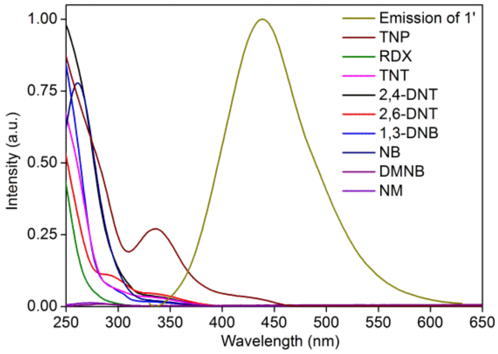

Fig. 4 Spectral overlap between normalized absorbance spectra of nitro analytes and normalized emission spectra of **1'** in water.

cycles and the quenching ability of TNP remains unaffected. Similar results were observed when other nitro analytes were used instead of TNT. This ascertains the exceptional selectivity of **1'** towards TNP even in presence of competing nitro analytes in water. We also checked the interference from mineral acids HCl on the fluorescence of **1'**. The addition of HCl showed negligible effect on fluorescence intensity of **1'** (Fig. S16). The high selectivity and sensitivity of **1'** towards TNP in water makes **1'** reliable and efficient in field sensor for TNP working in aqueous medium.

Usually, the conduction band (CB) of electron rich MOF lies higher than the LUMO energies of nitro analytes and upon excitation the excited electron from CB transfers to the LUMO orbitals of nitro analytes, thus quenching the fluorescence intensity.[14] The efficient fluorescence quenching observed for TNP is well in accordance with the low LUMO energy of TNP compared to other nitro analytes (Fig. S18). But the correlation of quenching efficiency and corresponding LUMO energies of the nitro analytes suggests that the electron transfer is not the only mechanism of fluorescence quenching.

As mentioned previously the non-linear trend of SV plot for TNP gives hint for presence of resonance energy transfer mechanism of fluorescence quenching. More the spectral overlap between absorbance spectrum of analyte and emission spectrum of MOF, more is the probability of energy transfer and hence the fluorescence quenching. Fig. 4 shows the greater spectral overlap between TNP and **1'** while all the other nitro analytes showed negligible spectral overlap with emission spectrum of **1'**. Also due to confinement of analytes in MOF pore keeps the MOF analytes in close proximity improving the energy transfer process. Thus it is clear that TNP can efficiently quench the fluorescence of **1'** via both electron and long range energy transfer process as against other nitro analytes which quench fluorescence only by electron transfer process. In addition, increasing quenching efficiency with increasing acidity of the phenolic analytes and red shift in emission maxima upon addition of TNP suggested the presence of electrostatic interaction between TNP and MOF which is absent in other nitro analytes (Fig. 1a, S19-S21). Thus due to presence of electron transfer and energy transfer process in addition to electrostatic interaction, TNP shows highly selective and sensitive fluorescence quenching response over other nitro analytes in water.

In conclusion, a fluorescent porous MOF demonstrates highly selective and sensitive detection of TNP in aqueous medium even in presence of competing nitro analytes. Presence of both electron and energy transfer process in addition to electrostatic interaction MOF with TNP is assigned to the unprecedentedly selective fluorescence quenching. Present work for the first-time demonstrates the potential of fluorescent MOF for real-time aqueous phase explosive detection for environmental application.

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