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Fluorescent metal–organic framework for selective sensing of nitroaromatic explosives†

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Highly luminescent micrometre-sized fine particles of a Zn(II) metal–organic framework (MOF) of a new π-electron rich tricarboxylate dispersed in ethanol is demonstrated as a selective sensory material for the detection of nitroaromatic explosives *via* a fluorescence quenching mechanism.

In the past two decades metal–organic frameworks (MOF) have been studied widely as potential materials for gas storage, separation, imaging, drug delivery and heterogeneous catalysis.[1] The tunable size and porosity of these materials can make them useful as chemical sensors. The rapid detection of explosive constituents is important for security screening, homeland security and environmental monitoring.[2] Current detection methods rely on the use of canines[3] or sophisticated instruments.[4] The present instrumental techniques need very expensive instruments and in most of the cases they are not easily accessible. Fluorescence quenching based sensing is a much simpler and very sensitive technique.[5] Due to the presence of electron withdrawing nitro groups, nitroaromatics (TNT, DNT, picric acid *etc.*) are strong oxidants and used as common chemical constituents of commercial explosives. Electron donor conjugated polymers have proven to be excellent candidates for the detection of nitroaromatic explosives. The delocalized π electrons of such systems increase the electrostatic interaction between the polymer and electron deficient compounds.[6] Moreover, the polymeric backbone facilitates efficient exciton migration to enhance sensitivity. Recently, a very few examples of fluorescent MOFs showing explosive vapour sensing have been reported.[7] MOFs are expected to show potential because of their high surface area, which may allow more analyte molecules to come into contact with the MOF surface and may reach high sensitivity. Moreover, MOFs are easy to synthesize. The vapour phase sensing of all nitroaromatics is not always efficient because of very low vapour pressure of the nitroaromatics. However, scaling down of MOFs to a few micrometres to nanoscale dimensions may result in an exciting new class of material known as nanoscale coordination polymers (NCPs).[8] The luminescent behaviour of a MOF is highly dependent on the organic ligand and metal ion. Hence, enhanced performance can be achieved by careful selection of the organic building block and the nature of the metal.

Here, we report the synthesis of a new π-conjugated ligand 5-(4-carboxyphenylethynyl)isophthalic acid (H_3L) and its Zn(II) 3D MOF (**1**). Micrometre-sized particles of this Zn(II)-MOF are strongly fluorescent when dispersed in ethanol and show selective sensing of nitroaromatics (*e.g.* nitrobenzene, DNT, TNT) through a fluorescence quenching mechanism.

The ethynyl group was introduced to make H_3L π-electron rich. Zinc(II) ions were chosen as the metal connector because of their high complexation affinity to carboxylates and non-detrimental nature to fluorescence. In a typical synthesis, H_3L was dissolved in *N*,*N*-dimethylacetamide (DMA) to which $Zn(OAc)_2\cdot 2H_2O$ in ethanol was added dropwise and stirred for 2 h to obtain a very fine powder.‡

X-Ray quality single crystals of the MOF were obtained by solvothermal reaction of $Zn(OAc)_2\cdot 2H_2O$ and H_3L in a DMA/ethanol mixture at 90 °C for 48 h. A single crystal X-ray diffraction study confirmed its composition as $[Zn_4O(L)_2\cdot(H_2O)_3]\cdot 3DMA\cdot 3EtOH\cdot 6H_2O$.

The phase purity of the bulk material was confirmed by powder X-ray diffraction (ESI†). The X-ray single crystal structure of the MOF (**1**) exhibits a three-dimensional porous framework structure with a Zn_4 cluster as a building unit. Each Zn_4 cluster possesses one octahedral, two tetrahedral and a square-pyramidal Zn(II) ion, which are connected to each other through a central four coordinated oxo-bridge (Fig. 1). One-dimensional pores of 14.2 × 13.5 $Å^2$ dimensions were observed along the *b* axis. These pores are filled with coordinated water and guest solvent molecules. The void space accounts for approximately 53.3% of the whole crystal volume (3733.2 $Å^3$ out of the 7004.1 $Å^3$ per unit cell volume) as obtained by PLATON analysis. The sharp diffraction peaks in the powder XRD pattern of the MOF (**1**) (Fig. 2) indicate that these particles are highly crystalline in nature. The SEM image of the MOF (Fig. 2) is also indicative of a highly crystalline nature.

The photoluminescence (PL) spectrum of the micrometre-sized particles of MOF (**1**) dispersed in ethanol exhibits strong fluorescence peaks at 470 nm upon excitation at 350 nm

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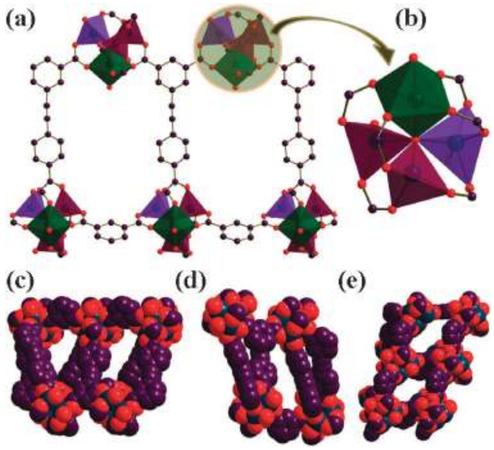

Fig. 1 (a) Structure of the MOF (**1**) showing the binding mode of L^{3-} and coordination environments. (b) Highlighted view of the building Zn_4 cluster where one Zn^{II} is in an octahedral (green), two are in a tetrahedral (purple) and the other one is in a square-pyramidal (violet) coordination environment. Space-filling representations of the 1D channel viewed along (c) the *a* axis, (d) the *b* axis and (e) the *c* axis (colour codes: Zn cyan, O red, C purple).

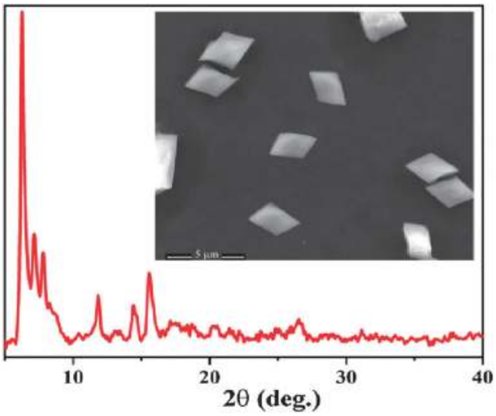

Fig. 2 Powder XRD spectrum of MOF (**1**) as obtained after stirring $Zn(OAc)_2 \cdot 2H_2O$ and H_3L in DMA/ethanol mixture for 2 h. Inset: SEM image.

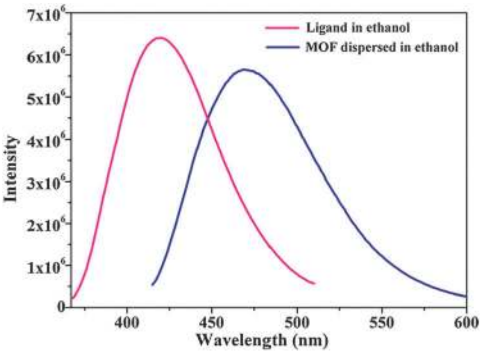

Fig. 3 Emission spectra of H_3L (pink line) dissolved in ethanol (excited at 305 nm) and of micrometre-sized particles of MOF (**1**) (blue line) dispersed in ethanol (excited at 350 nm).

(Fig. 3). The fluorescence of the MOF is completely different from that of the ligand, which gives a strong fluorescence peak at 420 nm upon excitation at 305 nm. This observed red-shift is likely due to the strong electronic coupling between the neighbouring ligands through Zn(II) ions.

Most interestingly, different electron deficient aromatics have different effects on the fluorescence intensity of the dispersed solution of MOF (**1**) in ethanol. The fluorescence intensity of the dispersed MOF (**1**) in ethanol was almost unchanged upon addition of analytes such as chlorobenzene (CB), bromobenzene (BB), xylene, *p*-cresol, benzoic acid (BA), 4-methoxybenzoic acid (4-MeO-BA) and non-aromatic nitro compounds. But significant quenching of fluorescence intensity was observed upon addition of nitroaromatics such as nitrobenzene, nitrotoluene, nitrophenol, DNT, TNT. Such observations demonstrate the potential of MOF (**1**) for selective sensing of nitroaromatics. Benzoquinone has considerable quenching efficiency due to its high reduction potential. Fig. 4 shows the reduction in fluorescence intensity of MOF (**1**) upon addition of different volumes of a 1 mM solution of TNT. The bright blue fluorescence of the dispersed solution of micrometre-sized MOF particles under UV-light totally disappeared upon addition of TNT solution (inset of Fig. 4). The quenching efficiencies (%) of different electron deficient aromatics are plotted in Fig. 5.

Encapsulation of nitroaromatics into the pores of the MOF is ruled out due to the lack of porosity within this MOF. Due to the dispersible nature of the micrometre-sized fine particles of MOF (**1**), close contact with the analyte molecules is expected and the fluorescence quenching observed can be attributed to the photoinduced electron transfer from the excited MOF to the electron deficient analytes adsorbed on the surface of the MOF particles. The reason for the considerably high efficiency in fluorescence quenching of nitroaromatics compared to other aromatics/nitroalkanes is presumably due to their more electron deficient nature. The detectable response of the MOF dispersed in ethanol towards the TNT solution is found to be at parts per billion (ppb) concentrations (ESI†) and such a level of sensitivity falls below the permissible level of TNT in drinking water established by the US EPA.[9] The micrometre-sized MOF could be regenerated and reused for a significant number of cycles by centrifuging

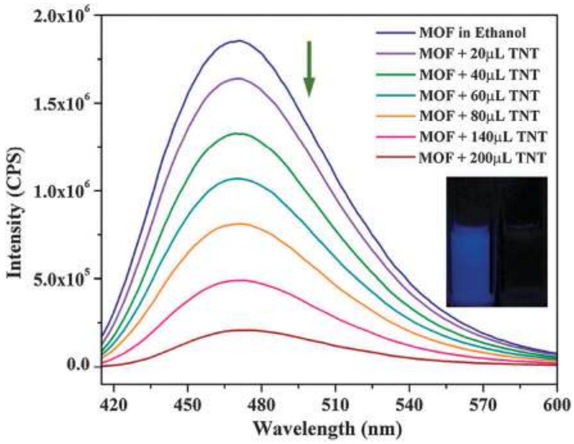

Fig. 4 Fluorescence titration of the dispersed MOF (**1**) in ethanol by gradual addition of 1 mM solution of TNT in ethanol. (Inset: visual colour change of **1** before and after titrating with TNT under UV-light).

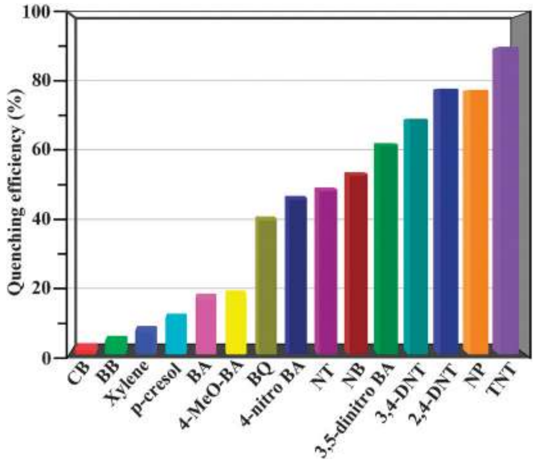

Fig. 5 Reduction in fluorescence intensity (plotted as quenching efficiency) observed upon the addition of several quenchers. CB = chlorobenzene, BB = bromobenzene, BA = benzoic acid, 4-MeO-BA = 4-methoxybenzoic acid, BQ = benzoquinone, NT = nitrotoluene, NB = nitrobenzene, DNT = dinitrotoluene, NP = nitrophenol and TNT = 2,4,6-trinitrotoluene.

the dispersed solution after use and washing several times with ethanol. It is noteworthy that almost regaining the initial fluorescence intensity over repeated cycles implies a high photostability of the material for its long time infield explosive detection application (Fig. 6).

In conclusion, a luminescent Zn(II) MOF (**1**) has been synthesized using a new π-electron rich tricarboxylic acid incorporating ethynyl functionality. The dispersed solution of the micrometre-sized particles of **1** in ethanol exhibits strong fluorescence emission and its initial fluorescence intensity was quenched efficiently upon addition of small amounts of nitroaromatic explosives. The choice of the highly conjugated π-electron rich organic ligand makes this material fluorescent and an efficient sensory material for explosive sensing. Our study revealed that **1** is quite selective towards explosive nitroaromatics such as DNT and TNT over other electron deficient aromatics. Excited state electron transfer from the electron rich fluorophore to electron deficient nitroaromatics is a probable mechanism of such quenching. Bulky macroscopic MOFs need to be processed in several steps like activation and incorporation of the sensed species before realizing as a sensor material. The dispersible nature of the MOF (**1**) particles of a few micrometre dimension makes this material an attractive candidate for straightforward use. This methodology of designing π-electron rich fluorescent MOFs for selective and efficient sensing of electron deficient oxidising explosives may enable the future development of much improved sensors for infield explosives sensing.

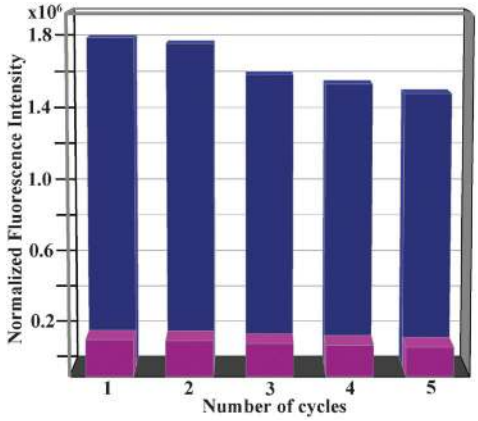

Fig. 6 Reproducibility of the quenching ability of **1** dispersed in ethanol to TNT solution. The material was recovered by centrifuging after each experiment and washed several times with ethanol. The blue bars represent the initial fluorescence intensity and the purple bars represent the intensity upon addition of 200 μL (1 mM) of a solution of TNT.

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Notes and references

‡ In a typical synthesis procedure H_3L (15 mg) was dissolved in DMA (2 mL) to which 1.5 equivalents of $Zn(OAc)_2 \cdot 2H_2O$ dissolved in ethanol (1 mL) was added dropwise. Upon addition of $Zn(OAc)_2 \cdot 2H_2O$ the solution turned turbid, which indicated the formation of fine particles of MOF (**1**). The mixture was kept under gentle stirring for a further 2 h at room temperature. The mixture was centrifuged to isolate the micrometre-sized fine powder of MOF (**1**). Single crystals of **1** were grown upon solvothermal treatment at 90 °C followed by slow cooling.

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