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Luminescent 3D Interpenetrating Metal-Organic Framework for Highly Selective Sensing of Nitrobenzene

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A three-dimensional (3D), luminescent, 5-fold interpenetrating metal-organic framework (MOF), $[Zn_2(fdc)_2(bpee)_2(H_2O)]_n.2H_2O$ (**1**) exhibiting highly selective sensing of nitrobenzene (NB) via a fluorescence quenching
10 mechanism has been demonstrated.

Metal-organic frameworks (MOFs) have attracted an immense attention during the past two decades due to their fascinating capability to form diverse structural architectures and also for
15 their potential applications in gas storage, separation, heterogeneous catalysis and drug delivery.[1] The high surface areas, tailored pore size and functionality of MOFs makes them suitable candidates as chemical sensors. Rapid detection of explosives and other hazardous chemicals is important for
20 homeland security and environmental safety.[2] The current detection methods of nitrocompounds are limited by the use of sophisticated instruments which are expensive and not easily accessible.[3] Recently, fluorescence quenching based detection of electron-deficient nitroaromatics using luminescent MOFs has
25 attracted considerable interest.[4,5] Compared to other detection methods, fluorescence quenching based detection is highly promising due to its simplicity and high sensitivity.[5] In luminescent MOFs the delocalized π-electrons of the aromatic ligands increases the electrostatic interaction between the
30 framework and the electron deficient nitroaromatics. Further, the photoinduced electron transfer from an excited MOF to the guest molecules results in fluorescence quenching of the MOF.[6] Moreover, the polymeric backbone facilitates efficient exciton migration which enhances the sensitivity of MOFs in the
35 detection.

It has been observed that the shape and connectivity of organic ligands/linkers play an important role in directing the structure, dimensionality and topology of the resulting MOFs. In this regard, use of rigid spacer ligands has often resulted in the
40 formation of interpenetrated/entangled networks which are attracting much attention due to their intriguing artistic and the structure dependent properties.[7] The origin of interpenetration in a MOF has been attributed due to the presence of large void in a single net which promotes further nucleation in the empty space to minimize the systematic energy thorough optimal filling of the void space. However, the factors that influence the resulting
55 degree of interpenetration in MOFs remain unknown. Recently, we have shown the construction of luminescent MOFs with varying degrees of interpenetration using a rigid dicarboxylate ligand and various bipyridine spacers.[8]

Here, we report the synthesis of a new 3D luminescent Zn(II)
60 MOF, $[Zn_2(fdc)_2(bpee)_2(H_2O)]_n.2H_2O$, (**1**) using a rigid aromatic dicarboxylate, 2, 5-furandicarboxylic acid (H_2fdc) ligand and 1,2-bis(4-pyridyl)ethylene (bpee) spacer. The MOF (**1**) shows highly selective sensing of nitrobenzene via fluorescence quenching mechanism. X-ray quality single crystals of **1** were obtained in a
65 solvothermal reaction of $Zn(NO_3)_2.6H_2O$, H_2fdc and bpee in water/isopropanol mixture at 100°C for 48h (ESI). The single crystal X-ray diffraction study confirmed the composition of **1** as $[Zn_2(fdc)_2(bpee)_2(H_2O)]_n.2H_2O$.
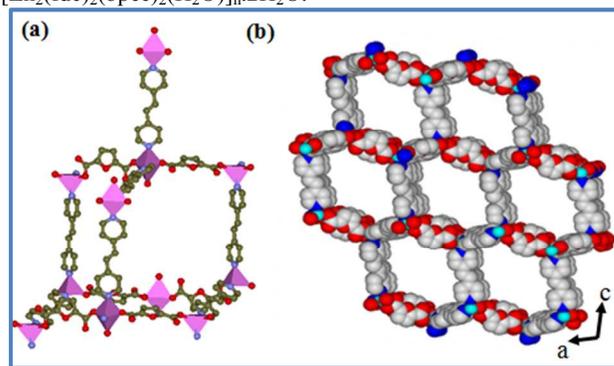
70 **Fig. 1** (a) Perspective view of a single **dia** net and (b) Space-filling model of a 3D single **dia** framework showing the 1D hexagonal channels along the *b*-axis.

The phase purity of the bulk material was confirmed by powder X-ray diffraction (Fig. S1, ESI). Thermogravimetric
75 analysis revealed that the dehydrated sample of **1** is stable upto 340°C (Fig. S2, ESI). Single crystal X-ray structure determination of **1** reveals a 3D framework constituted by fdc dianion and bpee spacer. The asymmetric unit consists of two crystallographically independent Zn(II) ions, two fdc dianions
80 and two bpee spacers including one coordinated water molecule and two guest water molecules (Fig. S3, ESI). The Zn1 ion is in

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a distorted tetrahedral environment with ZnO_2N_2 chromophore satisfied by two carboxylate oxygen (O1, O2) atoms of two bridging fdc dianions in μ_1-O fashion and two pyridyl nitrogen (N1, N2) atoms of a bpee spacer (ESI). The Zn2 ion is in a trigonal bipyramidal geometry with ZnO_3N_2 chromophore completed by two oxygen (O3 and O4) atoms from two different fdc dianions in μ_1-O fashion and a pyridyl nitrogen (N4) atom of a bpee linker forming the trigonal plane and the
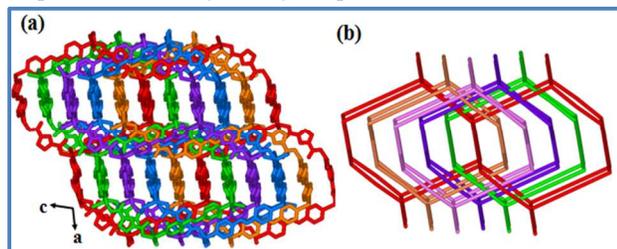
Fig. 2 (a) View of the 5-fold interpenetrated 3D framework of **1** and (b) Topological representation of the 5-fold interpenetrating nets in **1** (five different 3D nets are shown in five different colours).

axial positions are occupied by an oxygen (O1w) atom of water molecule and the pyridyl nitrogen (N3) atom of bpee linker. The Zn-O and Zn-N bond lengths are in the range 1.926(3)-2.303(4) Å and 2.032(2) - 2.221(2) Å (ESI). Both the Zn(II) ions act as 4-connected nodes which are connected with each other in three dimensions by fdc and bpee linkers to generate a 3D diamondoid (**dia**) framework (Fig. 1a and b). Topological analysis by TOPOS[9] revealed the presence of 4-c Zn(II) nodes and the overall structure has **dia** net topology with Schläfli point symbol $\{6^6\}$. As can be seen in Fig. 1b the 3D **dia** framework possesses a large hexagonal channels which are sufficiently large enough to allow further nucleation in the void space to generate a complex 5-fold interpenetrated 3D framework (Fig. 2a). Interpenetration analysis by TOPOS[9] confirmed the presence of 5-fold interpenetration (Fig. 2b) with Schläfli extended point symbol [6(2).6(2).6(2).6(2).6(2).6(2)] and thus reducing the void volume completely.
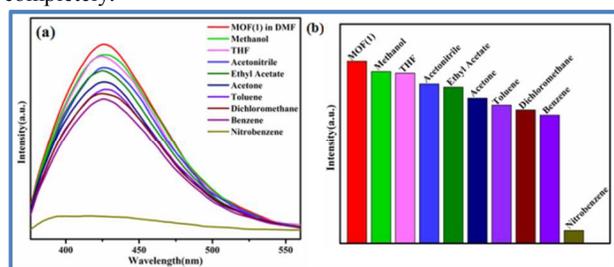
Fig. 3 (a) Emission spectra of **1** dispersed in DMF on addition of different analytes. (b) Reduction in fluorescence intensity (quenching efficiency) observed upon addition of several analytes.

To examine the luminescent properties of MOF (**1**), the photoluminescence spectra of **1** and the free ligand dispersed in dimethylformamide (DMF) were recorded at room temperature. A broad emission band at 425 nm observed for **1** can be attributed to ligand based emission (n-π* and π-π*) since the ligand (fdcH$_2$) shows a peak at 420 nm similar to the peak position of **1** upon excitation at 350 nm (Fig S4, ESI). To investigate the sensing properties of **1**, the emission spectra were recorded with addition of different analytes such as, acetonitrile, chloroform,

dichloromethane, ethyl acetate, ether, methanol and nitrobenzene (NB). As shown in Fig. 3, the fluorescence intensity of **1** was almost unchanged upon addition of most of the analytes but in case of NB, significant quenching of fluorescence intensity of **1** was observed.
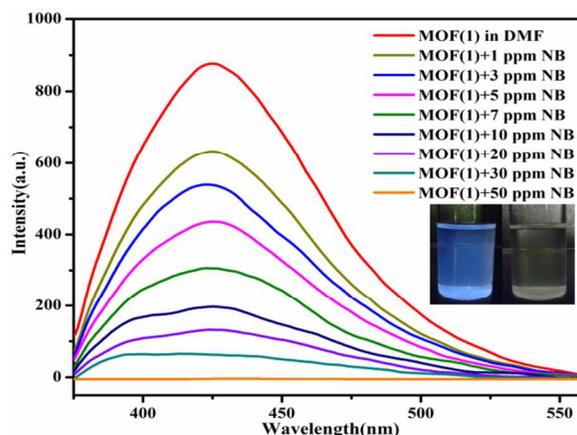
Fig. 4 Fluorescence titration of the dispersed MOF (**1**) in DMF with addition of increasing concentration of NB (Inset: visual colour change of **1** before and after addition of NB under UV-light.

Further, to examine the sensitivity of fluorescence quenching by NB, the fluorescence spectra were recorded with addition of increasing concentration of NB. As can be seen from Fig. 4, the fluorescence intensity of **1** reduces gradually as the concentration of NB increases and at 50ppm of NB the fluorescence intensity of **1** was almost completely quenched. The quenching efficiency, defined by $(I_0-I)/I_0$ X 100%, where I_0 and I are the luminescence intensities of **1** before and after the addition of NB, respectively was estimated to be 26 % for 1ppm of NB, 51% for 5ppm of NB, and 98% for 45 ppm of NB. Furthermore, the quenching efficiency of NB was not affected with the addition of other analytes (Fig. S5, ESI). These observations clearly demonstrate the potential of MOF (**1**) as highly selective sensor for NB. It is noteworthy that even very low concentration of NB (1ppm) is good enough to show significant quenching (26%) of the fluorescence intensity of **1**. Such a high sensitivity of nitrobenzene detection using an interpenetrating MOF has not been reported so far.[10] Furthermore, the detection ability of MOF can be restored and it can be recycled for significant number of cycles by centrifuging the dispersed solution after use and
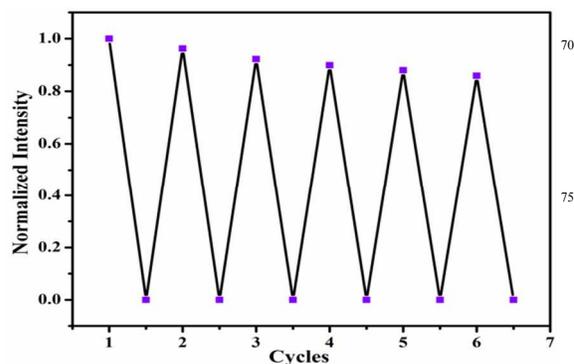
Fig.5 The quenching and recyclability test of **1**, the upper dots represent the initial luminescent intensity and the lower dots represent the intensity upon addition of 50 ppm of DMF solution of nitrobenzene.
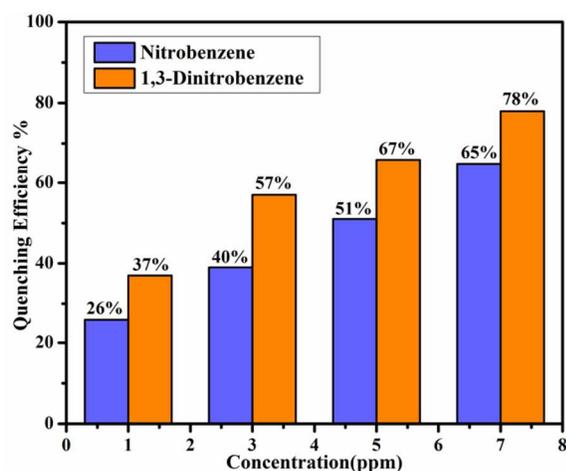
Fig.6 Fluorescence intensity of **1** plotted as quenching efficiency upon addition of different concentrations of NB and DNB.

washing several times with methanol (Fig. 5). Remarkably, the initial fluorescence intensity was almost regained even after six cycles suggesting a high photostability and reversibility of **1** for detection applications. Meanwhile, powder XRD analysis of isolated samples of MOF(**1**) after immersing in different analytes for 48 hrs confirmed retaining of the original framework structure (Fig.7).
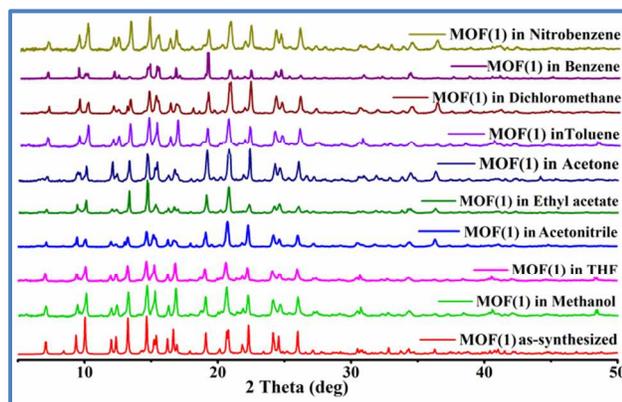
Fig.7 Powder X-ray diffraction pattern of MOF(**1**) obtained after immersing in different analytes for 48 hrs.

Since the void space of the 3D diamondoid framework of **1** is blocked due to 5-fold interpenetration, the encapsulation of NB into the pores of the MOF is ruled out. Therefore, the mechanism of fluorescence sensing can be attributed due to photoinduced electron transfer from an excited MOF to the electron deficient NB adsorbed on the surface of the MOF through interspecies contacts.[11] Similar fluorescence quenching phenomena for nitroaromatics with fluorescent MOFs has been observed before.[12] Furthermore, to test the effect of electron withdrawing (nitro) groups on the aromatic ring, the fluorescence measurements were repeated with addition of 1,3-dinitrobenzene (DNB). It is interesting to note that the quenching efficiency of DNB on the fluorescence intensity of MOF (**1**) was much higher than that of NB (Fig. 6). This observation clearly supports the fact that the fluorescence quenching efficiency of nitroaromatics

increases with the number of nitro-substituents on the aromatic ring through donor-acceptor electron transfer process.[4f,12] The electron withdrawing nitro-substituent stabilizes the lowest unoccupied molecular orbital (LUMO) of the aromatic analyte through conjugation which facilitates facile transfer of excited electrons of **1** to the LUMO of nitrobenzene resulting in efficient quenching of fluorescent intensity of **1**.

In conclusion a 3D luminescent, 5-fold interpenetrating Zn(II) MOF (**1**) has been synthesized using a rigid dicarboxylate (fdc) and bpee spacer. The dispersed solution of **1** in DMF exhibits strong fluorescence emission which could be quenched by trace amounts (1ppm) of nitrobenzene. The high selectivity and sensitivity of fluorescence quenching by nitrobenzene and dinitrobenzene suggest the potential application of **1** as an efficient fluorescence sensor for nitroaromatics. This high sensitivity of fluorescence quenching observed here can be attributed to high rigidity of the framework which facilitates efficient transfer of excited state electron from the π-electron rich ligand to nitrobenzenes through inter species contacts which quenches the fluorescence emission of **1**. .

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Graphical abstract
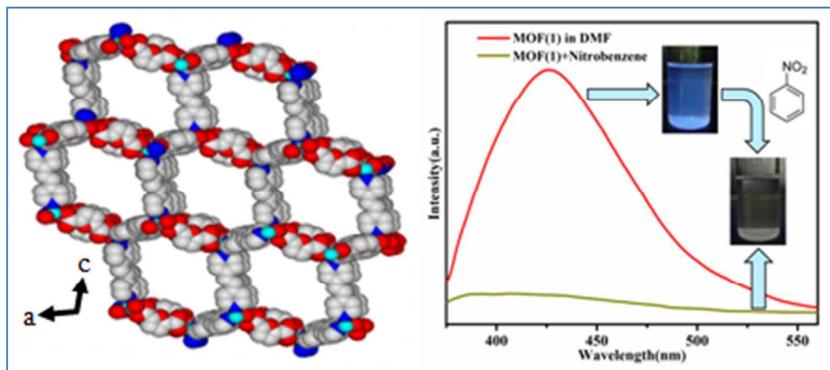
A three-dimensional (3D), luminescent, 5-fold interpenetrating metal-organic framework (MOF), [Zn$_2$(fdc)$_2$(bpee)$_2$(H$_2$O).2H$_2$O] (**1**) exhibiting highly selective sensing of nitrobenzene (NB) via a fluorescence quenching mechanism has been demonstrated.