Supporting Information

Fluorescent metal-organic framework for selective sensing of nitroaromatic explosives

Bappaditya Gole, Arun Kumar Bar and Partha Sarathi Mukherjee*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India. Fax: 91-80-2360-1552; Tel; 91-80-2293-3352

E-mail: psm@ipc.iisc.ernet.in

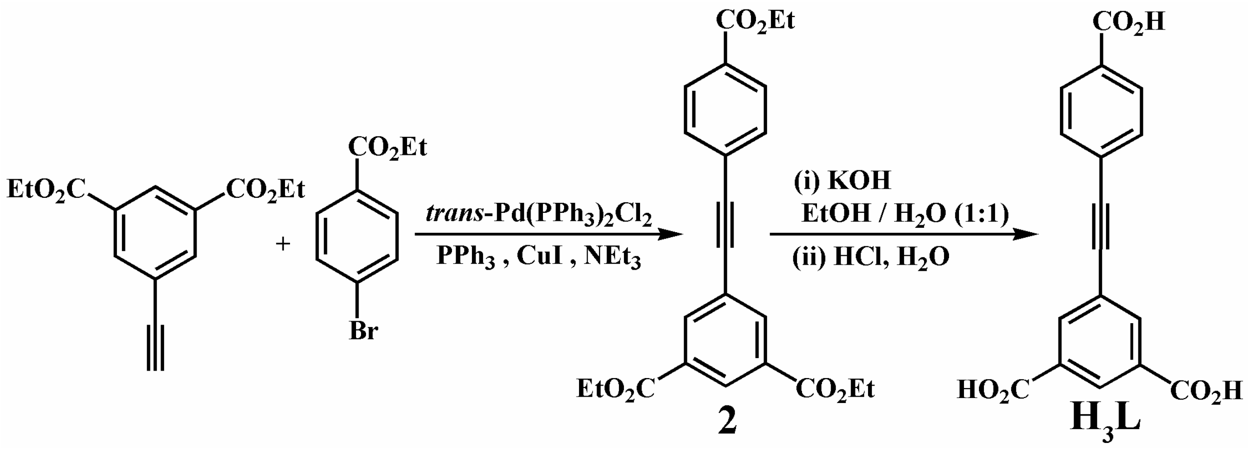
1. Materials and methods:

All the reagents and solvents were obtained from commercial sources and used as received. Diethyl-5-(ethynyl)isophthaloate was prepared according to literature procedure.[1] NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in the ^1H NMR spectra are reported in ppm relative to tetramethylsilane (TMS) as internal standard (0.0 ppm). IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. All the nitro explosives and other aromatic compounds used in this fluorescence experiments were purchased and used as received.

2. Synthesis and general characterizations:

2.1. Diethyl-5-(2-(4-(ethoxycarbonyl)phenyl)ethynyl)benzene-1,3-dioate (2)

To a 50 mL Schlenk flask, diethyl-5-(ethynyl)isophthaloate (492 mg, 2 mmol), ethyl-4-bromobenzoate (687 mg, 3 mmol), *trans* -Pd(PPh_3)$_2$$Cl_2$ (50 mg), PPh_3 (25 mg) and CuI (25 mg) were added. The flask was connected to Schlenk line and evacuated air and refilled with nitrogen. 30 mL of degassed triethylamine was added to the Schlenk flask. The flask was equipped with a water condenser and refluxed under nitrogen for 20 h. The reaction mixture was cooled to room temperature and solvent was removed under vacuum. The residue was dissolved in dichloromethane (DCM) and purified by column chromatography using DCM/Hexane (1:1) mixture to get pale yellow solid in ~76% yield based on diethyl-5-(ethynyl)isophthaloate. IR peaks (ν/cm^{-1}): 3407, 2957, 1725, 1603, 1429, 1368, 1266, 1235, 1151, 1099, 1024, 910, 855, 767, 750, 692, 521. ^{1}H NMR: (400 MHz, $CDCl_3$): *δ* 1.42 (m, 9H), 4.43 (m, 6H), 7.63 (d, 2H), 8.06 (d, 2H), 8.38 (s, 2H) and 8.65 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.434, 165.564, 136.942, 132.101, 131.827, 130.912, 130.820, 130.041, 127.491, 124.146, 90.750, 90.605, 62.139, 61.720 and 14.804.



2.2. 5-(2-(4-carboxyphenyl)ethynyl)benzene-1,3-dioic acid (H_3L)

500 mg (1.27 mmol) of **3** was taken in 50 mL (v/v = 1:1) mixture of EtOH and H_2O. 679.3 mg (12 mmol) of KOH added to that solution and heated to reflux for 15 h. The reddish brown solution was cooled to room temperature and ethanol was removed using rotary evaporator. The aqueous phase upon acidification using dilute hydrochloric acid gave pale brown solid, which was filtered and washed several times with distilled water. Yield: 92%. IR peaks (ν/cm^{-1}): 3334, 2981, 2590, 1682, 1602, 1556, 1447, 1379, 1318, 1300, 1280, 1235, 1225, 1158, 1120, 1104,

1011, 856, 798, 762, 711, 668, 542, 516. ^{1}H NMR (400 MHz, DMSO-d^6): δ (ppm) 7.69 (d, 2H), 7.95 (d, 2H), 8.23 (s, 2H) and 8.41 (s, 1H).

3. Synthesis of MOF (1)

$Zn(OOCCH_3)_2 \cdot 2H_2O$ (16.5 mg, 0.075 mmol), H_3L (15.5 mg, 0.05 mmol) were combined in a 8 mL scintillation vial. 2 mL DMA and 1 mL EtOH were then added and the mixture was stirred for 10 min. The reaction vial was then placed in a programmable oven and heated at 90 °C for 48 h followed by slow cooling to room temperature at a cooling rate of 10°C/h. Colorless crystals (10 mg, 60 %) of the product was collected by filtration and washed with DMA (4 × 5 mL). IR peaks (ν/cm^{-1}): 3435, 2990, 1600, 1575, 1538, 1529, 1508, 1423, 1410, 1383, 1365, 1361, 1297, 774, 735, 725, 669, 517. Elemental analysis of the vacuum dried sample: Anal. Calcd (%) for $C_{34}H_{20}O_{16}Zn_4$: C, 43.17; H, 2.13. Found: C, 42.89; H, 1.92.

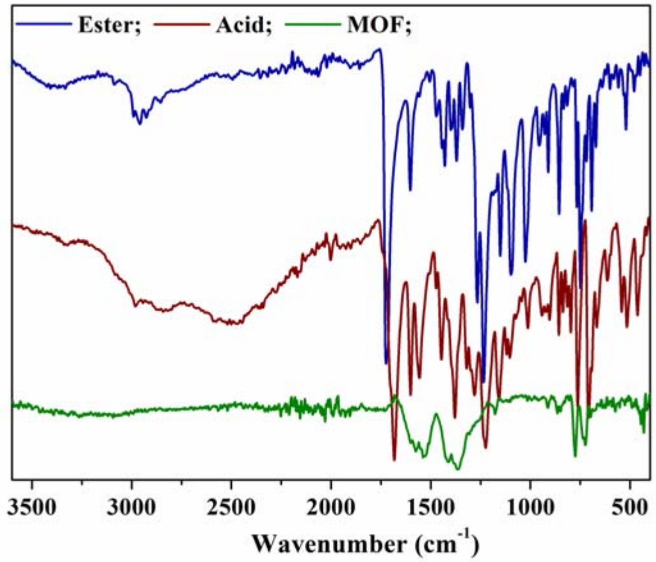


Figure S1: Infra-red spectra of the diethyl-5-(2-(4-(ethoxycarbonyl)phenyl)ethynyl)benzene-1, 3-dioate (blue line), H_3L (maroon) and MOF-**1** (green).

3.1. Activation of MOF (1):

An as-synthesized MOF (**1**) sample (about 200 mg) was soaked in methanol for 24 h, and the extract was discarded. Fresh methanol was subsequently added, and the sample was allowed to stay in methanol for an additional 24 h before methanol was removed. After methanol exchange the sample was treated further in same way with acetone to remove methanol solvates for two times. After decanting the acetone, fresh dichloromethane was added to remove acetone for another two times. Finally, the dichloromethane was decanted and the sample was dried under vacuum under gentle heating condition for 12 h.

4. Powder X-ray diffraction and thermogravimetric analysis:

Powder X-ray diffraction (PXRD) patterns of both the as-made MOF (**1**) and activated MOF (**1′**) samples (Figure S1) were recorded on a *Philips X'pert Pro* using Cu-Kα radiation (λ = 1.5406Å). The spectra were collected between the 2θ of 5° and 40° at a scan speed of 5 deg/min. Graphite monochromator was used and the generator power settings are at 40 kV and 40 mA. As indicated by the sharp peaks after removal of the guest molecules, **1′** was highly crystalline and maintains the framework stability. Thermogravimetric (TG) analysis of **1** was carried out on the *Metler-Toledo* thermal gravimetric analyzer with nitrogen flow (purge rate at 40mL/min, Figure S2). The heating rate was ramped from room temperature to 600 °C at 10°C/min. The weight loss was due to three DMA, three ethanol and 9 water molecule (six non-coordinated, and three coordinated). The framework was stable up to 420°C, before it was collapsed.

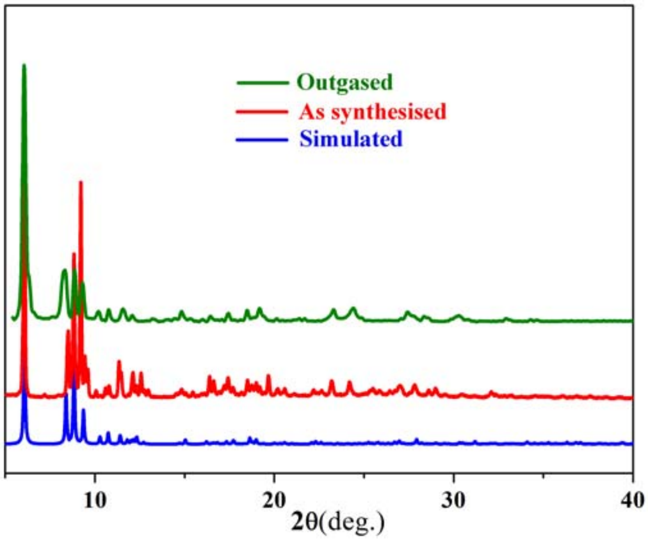


Figure S2. PXRD patterns of the as-made sample of $[Zn_4O(L)_2{\cdot}(H_2O)_3]{\cdot}3DMA{\cdot}3EtOH{\cdot}6H_2O$ (**1**) (red) with the simulated pattern (blue) calculated from the single crystal X-ray data and outgassed sample of MOF (green).

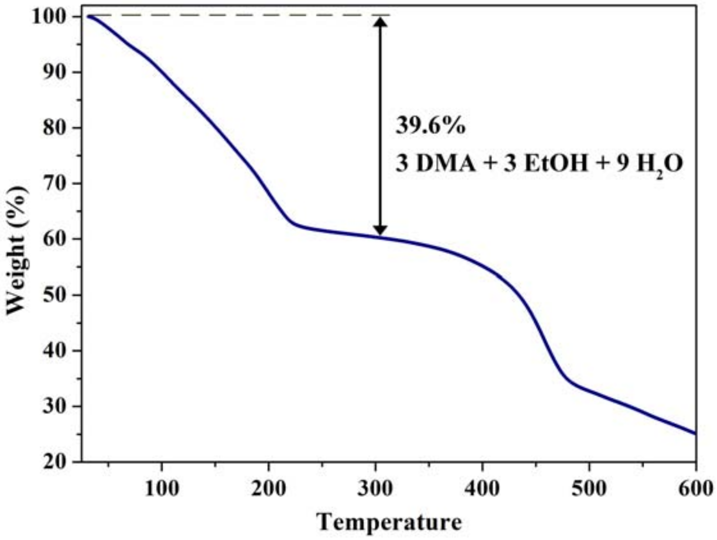


Figure S3. Thermogravimetric (TG) profile of $[Zn_4O(L)_2{\cdot}(H_2O)_3]{\cdot}3DMA{\cdot}3EtOH{\cdot}6H_2O$ (**1**) under nitrogen atmosphere. The weight loss upto 220°C was calculated to be due to the loss of three DMA, three ethanol and nine water molecules.

5. Single crystal X-ray diffraction analysis:

A crystal of MOF-**1** was coated with paratone oil, and the diffraction data were collected at 90 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (0.71073 A°) at 293 K. The structures were solved by direct methods using the SHELX-97 program incorporated into WinGX. Empirical absorption corrections were applied with SADABS. All nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms attached to the oxygen atoms of noncoordinating water molecules for the complexes **2** and **3** were located from differential Fourier maps. Structures were drawn using either ORTEP-3 or PLUTON. The crystallographic refinement parameters are given in Table 1.

Table S1. Crystal data and structure refinement parameters for **1**.

Compound	$[Zn_4O(L)_2\cdot(H_2O)_3]\cdot 3DMA\cdot 3EtOH\cdot 6H_2O$ (**1**)
Formula	$C_{52}H_{77}N_3O_{28}Zn_4$
M	1453.69
Crystal system	Orthorhombic
Space group	P n a 21
a/Å	21.312(3)
b/Å	11.295(15)
c/Å	29.097(4)
α/°	90

β/°	90
γ/°	90
V/Å^3	7004.1(2)
Z	4
Temperature (K)	90(2)
μ (Mo-Kα)mm^{-1}	1.430
D, g/cm^3	1.361
F(000)	2944.0
Reflections collected	7028
R1^a [I > 2σ(*I*)]	0.0215
wR2^b [I > 2σ(*I*)]	0.0723
Goodness-of-fit	1.122

^{a}R1= $\Sigma | F_o - F_c | / \Sigma | F_o |$; ^{b}wR2= $\Sigma[w(F_o^2 - F_c^2)^2] / w(F_o^2)^2]^{1/2}$

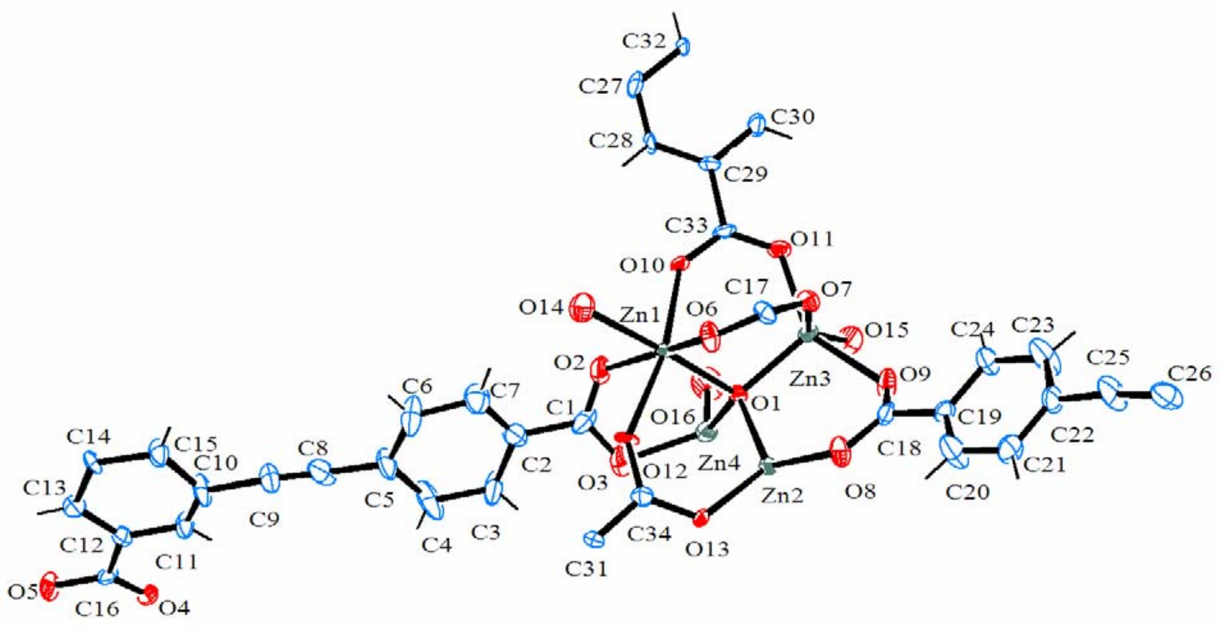


Figure S4: ORTEP of the asymmetric unit of MOF-**1** using 30% probability.

6. Gas sorption and pore size characterization

N_2 (77 K) adsorption study of the dehydrated sample of **1** was carried out using Micromeritics ASAP 2020 surface area analyser. The sample chamber was maintained at *T* ± 0.03 K and 150 mg of adsorbent sample was placed, which had been degased at 473 K under a high vacuum (10-1 Pa) for 18 h prior to measurement of the isotherms. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state. All operations were computer controlled and automatic.

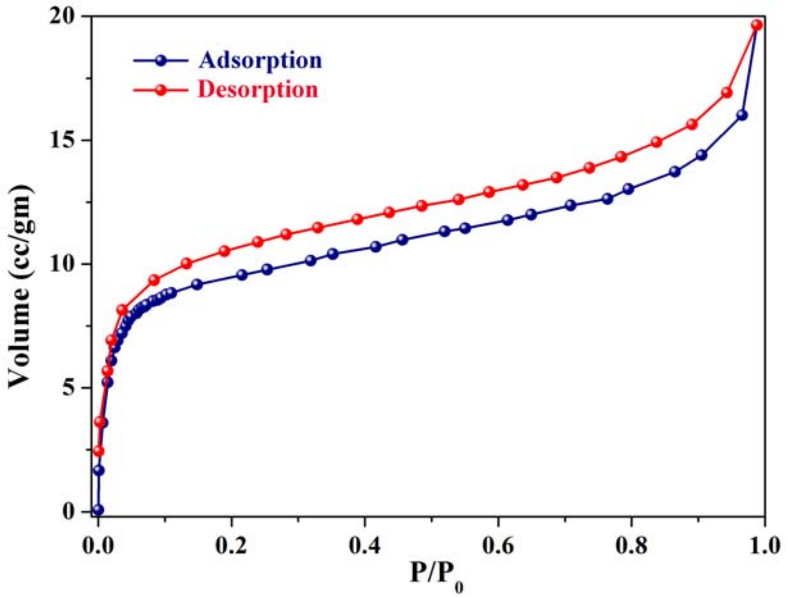


Figure S5: Nitrogen adsorption (blue) and desorption (red) isotherms of **1′** at 77 K.

Topological characterization

Topological analysis using TOPOS software[2] identifies the three-dimensions net as tcg. The organic linker was taken as connector (purple line) and Zn_4 cluster as a node (red ball).

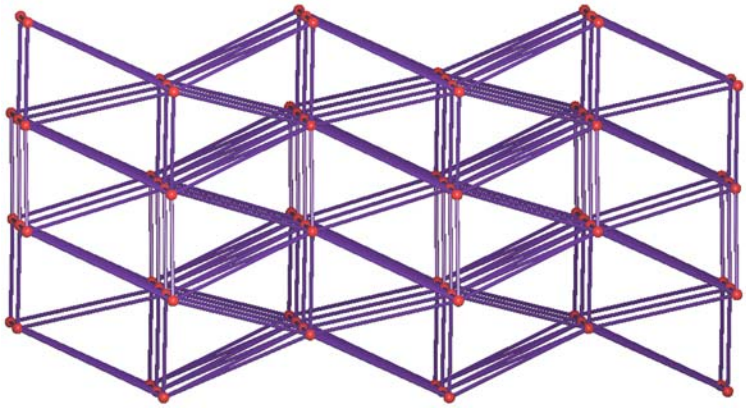


Figure S6: Topological presentation of the 3-D MOF net derived from MOF **1** by reducing the organic linkers as bold lines (purple line) and Zn_4 cluster as node (red ball).

7. Fluorescence quenching titrations in dispersed medium

The fluorescence of micrometer-sized particles of MOF-**1** was measured by dispersing 5 mg of it in 2 mL of ethanol and subsequently placed in a quartz cell of 1 cm width. All titrations were carried out by gradually adding quenchers (1.0×10^{-3} M) solution in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated at least three times to get concordant value. For all measurement, disperse solution of MOF were excited at λ_{ex} = 350 nm and their corresponding emission wavelength was monitored from λ_{em} = 415 nm to 600 nm. Relative fluorescence intensities were measured for disperse solution of MOF in ethanol and the various analytes were used as quenchers in methanol. There was no change in shape of the emission spectra by gradual addition of quenchers, only quenching of the initial fluorescence emission intensity was observed upon titration with electron deficient nitroaromatic quenchers. Nitroaromatics and other aromatics like chlorobenzene, bromobenzene, xylene, *p*-cresol were used as quenchers to check the selectivity of MOF-**1**. 400 μL of (1×10^{-4} M) solution of each quencher was added to the dispersed solution of the MOF-**1** (5 mg in 2 mL) in ethanol. The fluorescence efficiency was calculated by $[(I_0\text{-}I)/I_0]\times100$ %, where I_o is the initial fluorescence intensity.

The recyclability of the MOF towards TNT sensing has been checked. The fluorescence of the micrometer-sized particles of MOF was recorded by dispersing in ethanol. TNT was added to this dispersion and fluorescence was measured. The material was recovered by centrifuge after each quenching experiment and washed several times by ethanol. That material was dried and used for several other cycles.

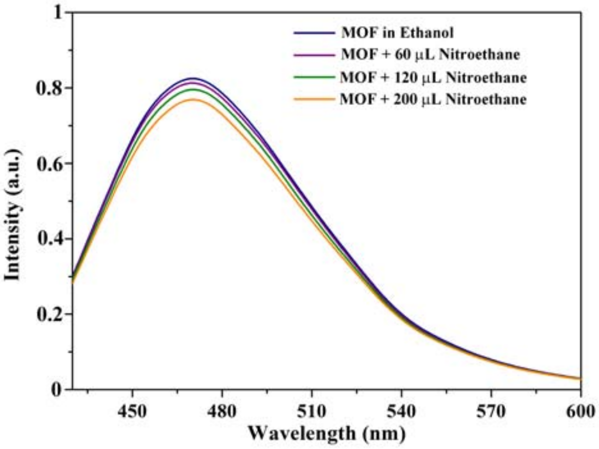


Figure S7: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of nitroethane in ethanol. Excited at 350 nm and fluorescence emission was monitored from 430 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

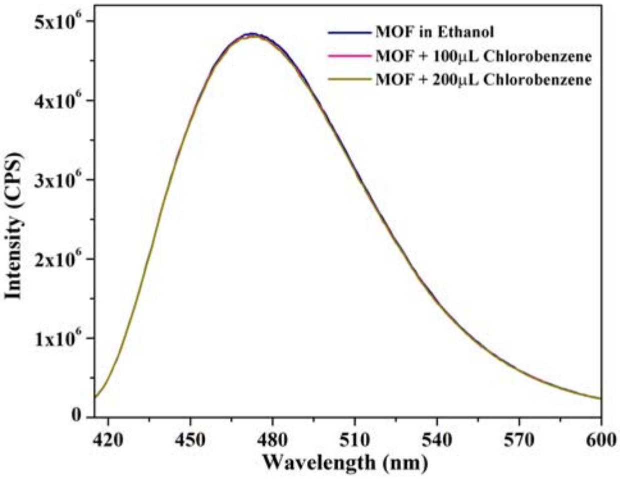


Figure S8: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of chlorobenzene in ethanol. Excited at 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

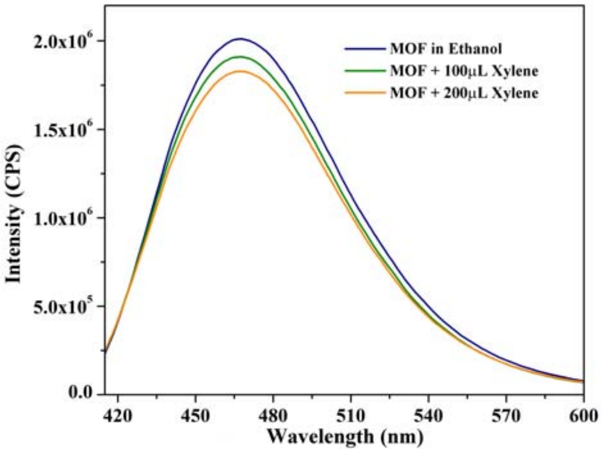


Figure S9: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of xylene in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 3 nm.

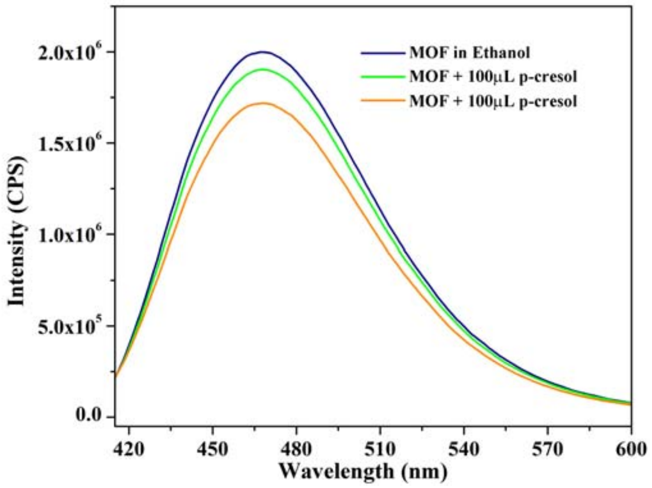


Figure S10: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of p-cresol in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 3 nm.

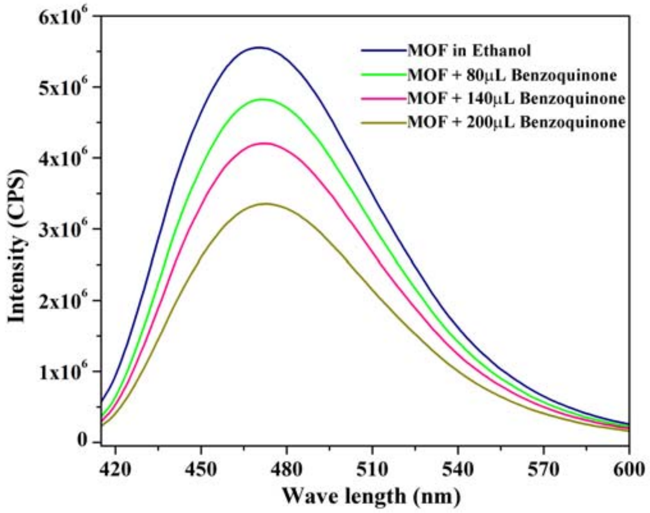


Figure S11: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of benzoquinone in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

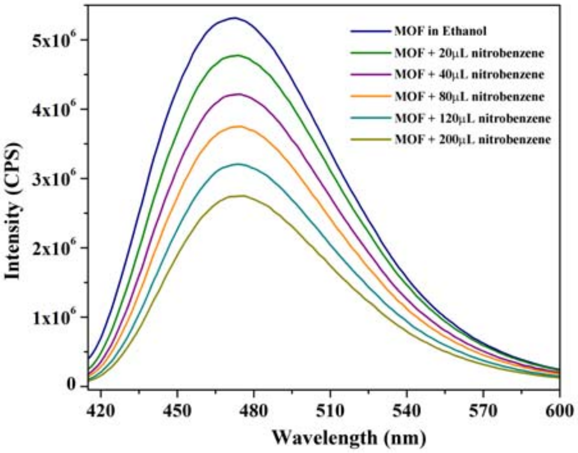


Figure S12: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of nitrobenzene in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

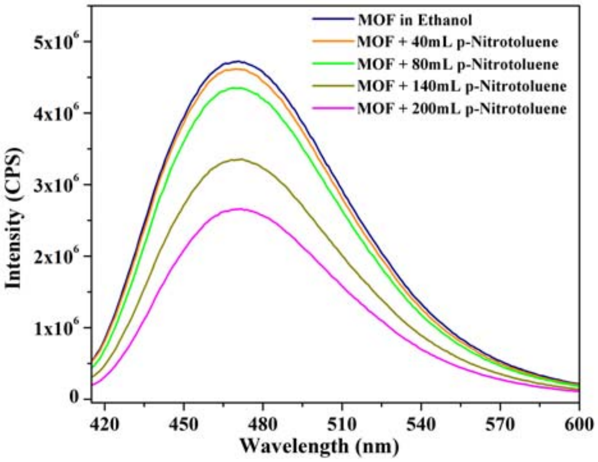


Figure S13: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of p-nitrotoluene in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

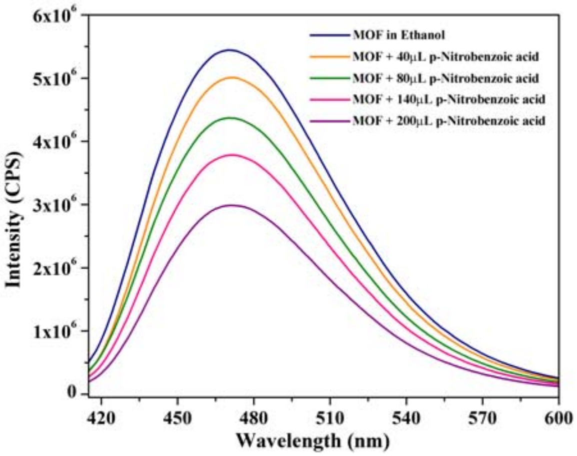


Figure S14: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of p-nitrobenzoic acid in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

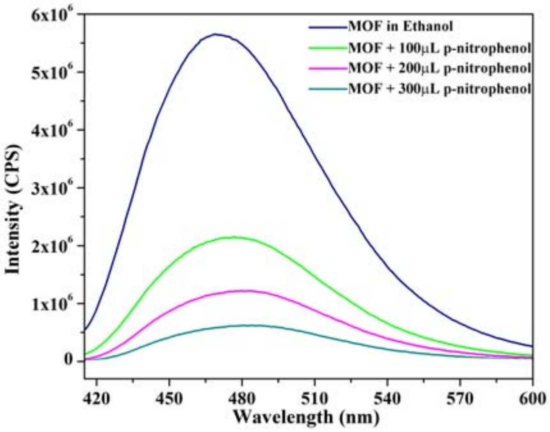


Figure S15: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of p-nitrophenol in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

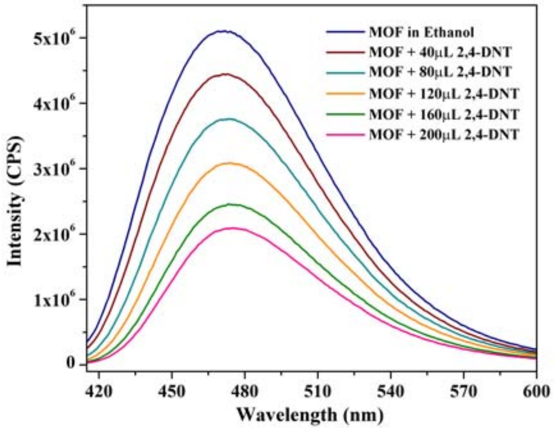


Figure S16: Fluorescence titration of MOF-**1** dispersed in ethanol with the addition of different volume of 0.001M solution of 2,4-DNT in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

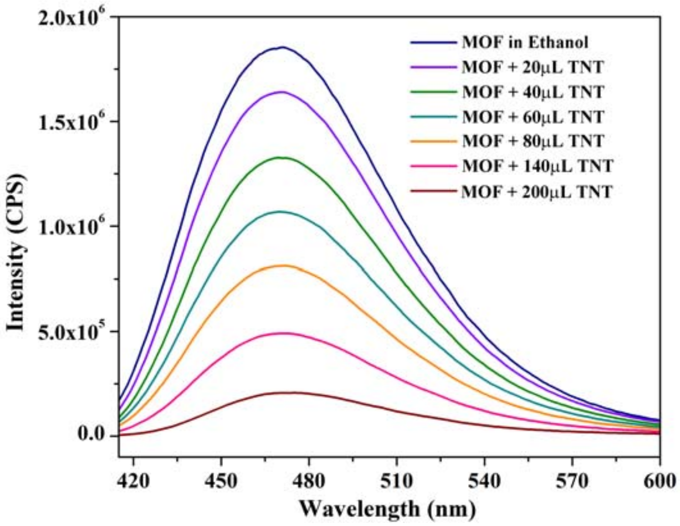


Figure S17: Fluorescence titration of MOF-1 dispersed in ethanol with the addition of different volume of 0.001M solution of TNT in ethanol. Excitation wavelength was 350 nm and fluorescence emission was monitored from 415 nm to 600 nm. The slit width for both excitation and emission was 3 nm.

Sensitivity:

Sensitivity of the nanoscale MOF-**1** towards TNT sensing has been checked. In the typical experiment 2.5 mg of nanoscale MOF dispersed in ethanol. The fluorescence of this dispersed medium was recorded before and after addition of 10 ppb TNT solution in methanol and almost 18.4 % quenching was noticed. This observation indicates that it can sense the TNT solution up to 10 ppb level.

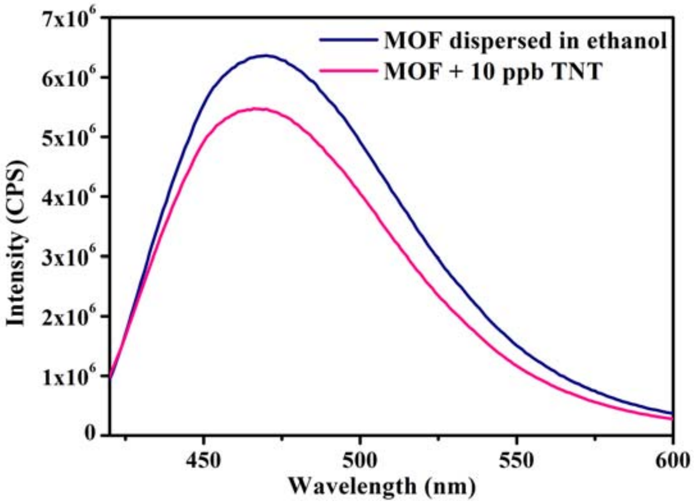


Figure S18. Reduction in the emission intensity of the MOF (2 mg in 2 mL ethanol) recorded upon addition of TNT (10 ppb in methanol) at room temperature, excited at 350 nm and fluorescence emission was monitored from 420 nm to 600 nm. The slit width for both excitation and emission was 5 nm.

8. Preparation of thin layers and solid state fluorescence study:

For making the thin layers of the sample on quartz slide, black tape was applied to the middle of the cleaned and air dried quartz slide. After few minutes the tape was peeled off from the slide, so that the glue from the tape is stuck on the glass slide. The ground powder of the degassed sample of MOF (**1**) was then sprinkled evenly onto the glued surface of the slide. The loosely bounded samples were removed by gentle shaking and putting the face of the slide down. Very thin continuous layer of sample was formed on the glass surface by this process. This glass was then used for the fluorescence study of the sample.

3 mL of nitrobenzene was placed in small (25 mL) covered glass vessel for three days to ensure that the equilibrated vapour pressure was reached. The original fluorescence spectra of the thin layers were collected before putting the glass slide into the beakers containing nitrobenzene. After specified exposure time, the slide was taken out and without any further delay mounted to the sample holder of the fluorescence spectrophotometer and the emission spectrum was recorded. Vapour sensing of 2,4-dinitrobenzene was performed exactly same way as mentioned above.

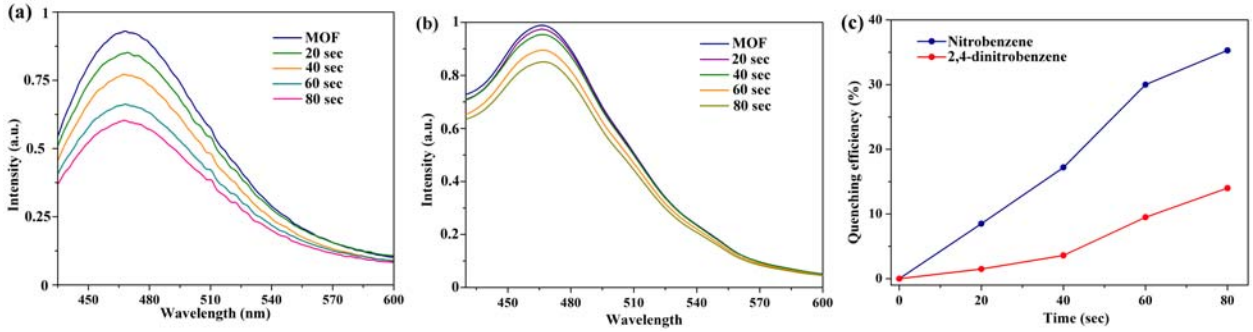


Figure S19: Fluorescence titration of the thin layer of MOF by exposing to (a) nitrobenzene and (b) 2,4-dinitrobenzene vapour with specified time. Excitation wavelength was 350 nm and fluorescence emission was monitored from 430 nm to 600 nm. The slit width for both excitation and emission was 5 nm. (c) Plot of fluorescence quenching efficiency (%) of nitrobenzene and 2,4-dinitrobenzene with respect to time.

References:

1) I. Aujard, J. –P. Baltaze, J. –B. Baudin, E. Cogne, F. Ferrage, L. Jullien, E. Perez, V. Prevost, L. M. Qian and O. Ruel, *J. Am. Chem. Soc.*, 2001, **123**, 8177.

2) V. A. Blatov, *IUCr CompComm. Newsletter,* 2006, 7, 4; see also http://www.topos.ssu.samara.ru.