Electronic Supplementary Information

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

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1. Materials and Method

All the chemicals used were obtained from commercial sources and were used without further purification. Elemental analyses of C, H, and N were carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. IR spectra were recorded as KBr pellets on a *Thermo Scientific*Nicolet iS10 *FT-IR* Spectrometer in the region 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) of the compounds was carried out using Metler Toledo Thermogravimetric analyzer in nitrogen atmosphere (flow rate = 50 mL min^{-1}) in the temperature range 30 – 500 °C (heating rate = 3°C min^{-1}). The phase purity of the as-prepared compounds was confirmed by powder XRD data recorded on a PANalytical's X'PERT PRO diffractometer using CuK$_{\alpha}$ radiation (k = 1.542 Å; 40 kV, 20 Ma).

Synthesis of [$Zn_2(fdc)_2(bpee)_2(H_2O).2H_2O$] (1)

Compound **1** was prepared by employing solvothermal condition at 100°C.$Zn(NO_3)_2.6H_2O$ (0.058 g, 0.20 mmol) was dissolved in 4 ml of deionized water to which an aqueous solution (2ml) of H_2fdc (0.031 g, 0.20 mmol) neutralized with NaOH (0.016 g, 0.4 mmol) was added drop wise with constant stirring. To this solution an isopropanolic solution (2 ml) of bpee (0.036g, 0.20 mmol) was added and the contents were stirred for 30min and then taken in a

30 mL glass vial sealed with parafilm and heated at 100 °C for 2 days. After being cooled to room temperature, light yellow rod shaped crystals of **1** were isolated. Yield: 40 % based on Zn(II) ion. Anal. calcd. for $C_{36}H_{26}N_4O_{13}Zn_2$: C, 50.74; H, 2.81; N, 6.47. Found: C, 49.89; H, 2.79; N, 6.02. IR (KBr, cm^{-1}): ν(H_2O), 3444(bw) ; ν(CH-Ar), 3047(w) ; ν(C=N), 1655(s); ν(C=O), 1612(s); ν(C=C),1579-1432(s); ν(C-O), 1347-1254(s); ν(=C-H), 834-781(s).

X-ray Crystallography

X-ray single crystal structural data of compound **1** was collected on a Bruker D8 Venture PHOTON 100 CMOS diffractometer equipped with a INCOATEC micro-focus source and graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The program SAINT was used for integration of diffraction profiles and absorption correction was made with SADABS[1] program. Both the structures were solved by SIR 92[2] and refined by full matrix least square method using SHELXL-97[3] and WinGX system, Ver 1.70.01.[4] All the non hydrogen atoms were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. All the crystallographic and structure refinement data of MOF (**1**) are summarized in Table 1. Selected bond lengths and angles are given in Table 2, respectively.

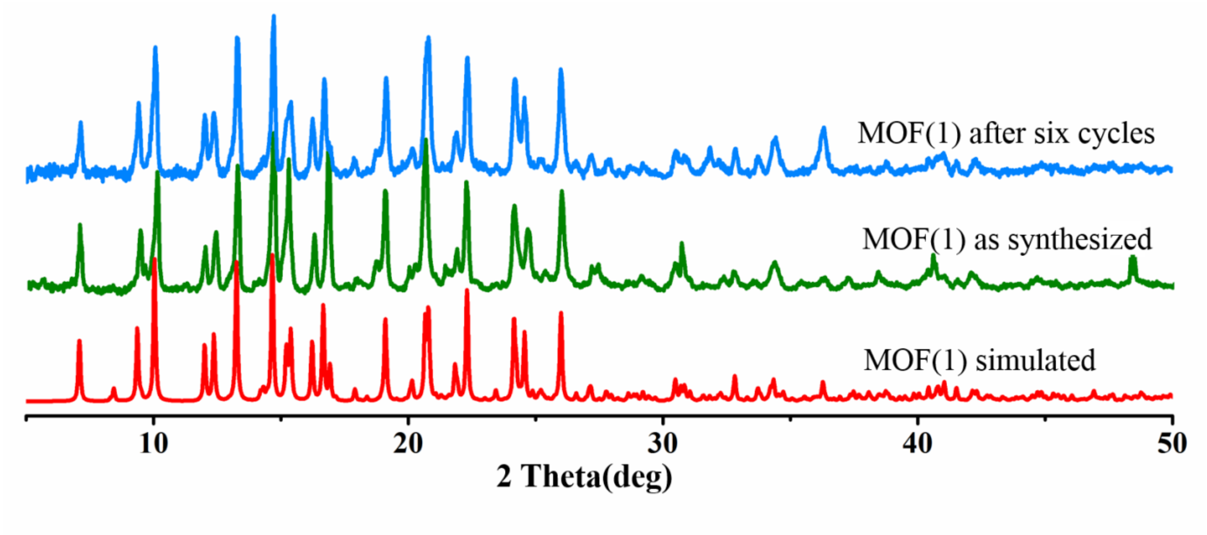

Fig. S1 PXRD patterns of the as-prepared sample of MOF(**1**) (green) with the simulated pattern (red) calculated from the single crystal X-ray data and recycled sample after six cycles of fluorescence quenching experiments.

Thermogravimetric Analysis (TGA)

TGA of MOF(**1**) shows a weight loss of ~ 4.5% around 100 ºC which corresponds to the loss of two guest water molecules (calc. wt% 4.21) and the second weight loss of ~ 2% around the temperature of150 ºC corresponding to loss of the coordinated water molecule (calc. wt% 2.11) (Fig. S2). Interestingly, the dehydrated MOF(**1**) is stable upto ~340ºC. The third major weight loss about 78 % was observed around the temperature range 340-450 ºC corresponding to loss of bpee and fdc linkers (calc. wt% 79.11) (Fig. S2).

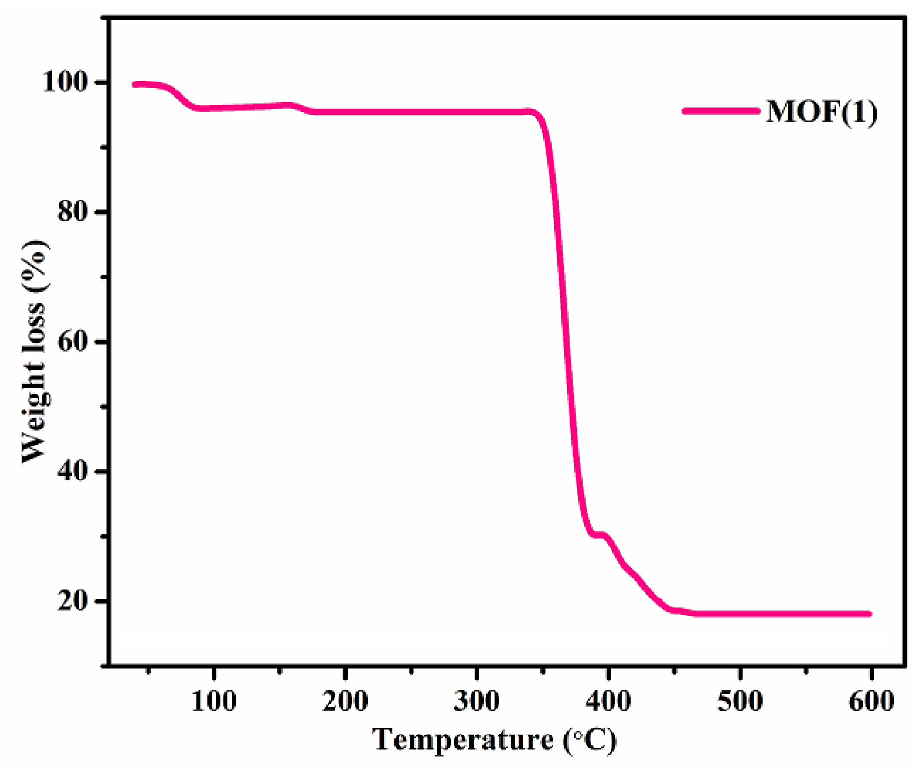

Fig. S2 TGA plot of the as-prepared sample of MOF(**1**)

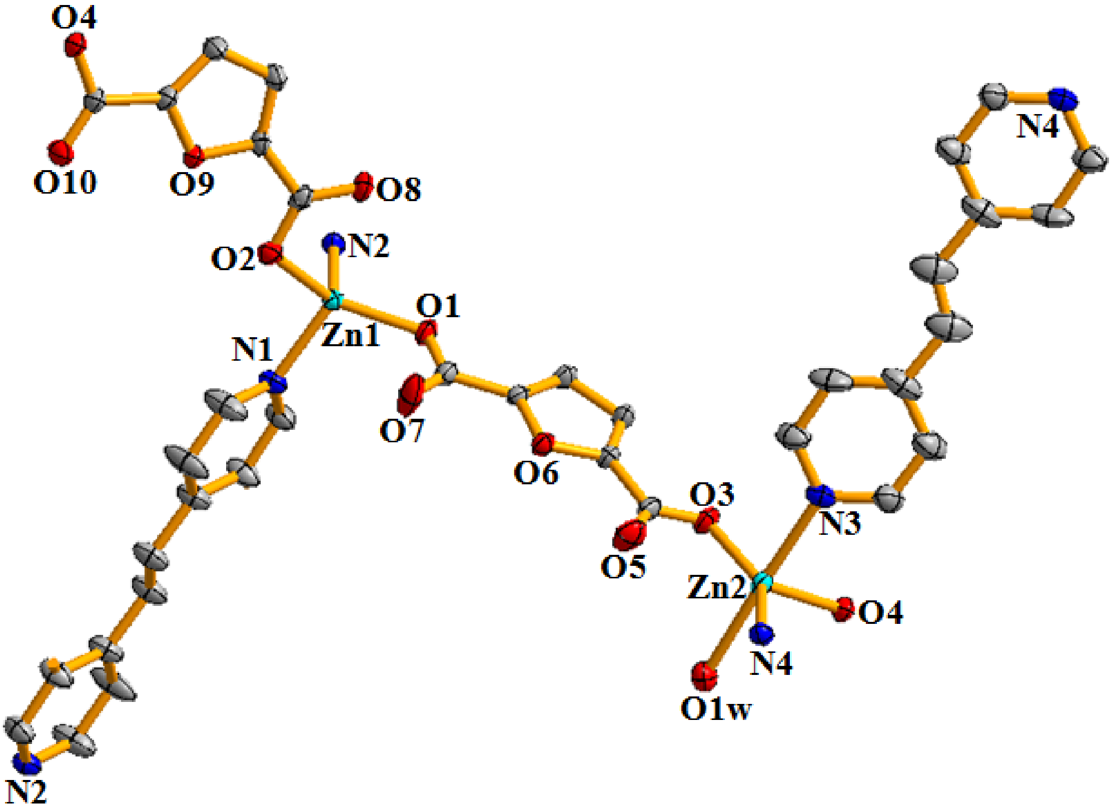

Fig. S3 Thermal ellipsoid probability plot of the basic unit of MOF (**1**) showing the coordination environment around Zn(II) ions; the H atoms are omitted for clarity.

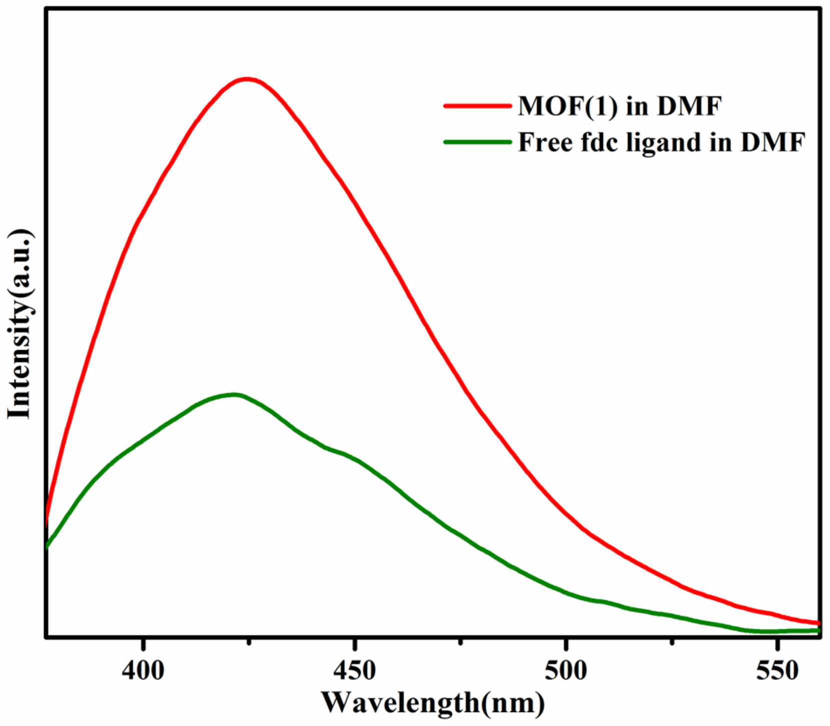

Fig.S4 Luminescence emission of MOF (**1**) and free ligand (fdcH_2) dispersed in DMF upon excitation at 350 nm.

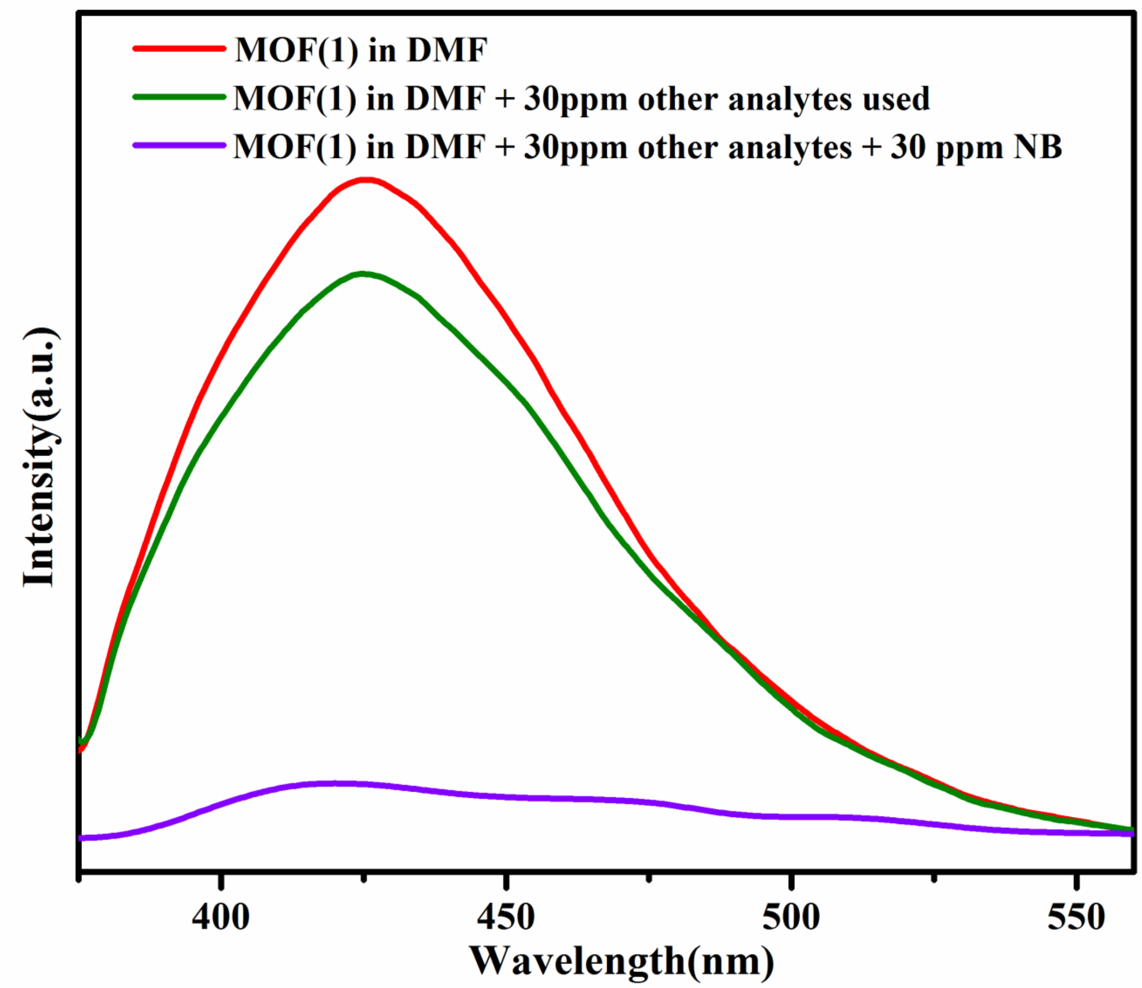

Fig.S5 Luminescence emission of as-prepared MOF (**1**) dispersed in DMF and with addition of 30 ppm of different analytes (acetonitrile, chloroform, dichloromethane, ethyl acetate, ether, methanol) and with the addition of analytes plus NB.

Table S1. Crystal data and structure refinement parameters of MOF (**1**)

Parameters	**MOF (1)**
Chemical formula	$C_{36}H_{26}N_4O_{13}Zn_2$
Formula mass	853.9
Cryst. system	Triclinic
Space group	$P\bar{1}$
a /Å	12.0348(4)
b /Å	12.8584(4)
c /Å	13.6481(4)
α (°)	89.712(2)
β (°)	66.644(1)
γ(°)	75.338(1)
V(Å^3)	1864.99(10)
Z	2
D_c (g cm^{-3})	1.520
μ(mm^{-1})	1.357
F(000)	868
T(K)	293
λ(Mo K_α)(Å)	0.71073
Θ_{min}(°)	2.2
Θ_{max}(°)	28.2
Total data	72634
Unique data	9269
R_{int}	0.084
Data[I>2σ(I)]	5976
$^aR_1$	0.0547
$^bwR_2$	0.1511
S	1.04

$^aR_1 = \sum \| F_0 | - | F_c \| / \sum | F_o |$, $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(Fo^2)^2]^{1/2}$

Table S2. Selected bond lengths and angles for MOF (**1**)

Zn1-O1	1.926(3)	O2-Zn01-N1	98.82(13)
Zn1-O1	1.926(3)	O2-Zn01-N2	106.59(14)
Zn1-N1	2.037(4)	N1-Zn01-N2	103.05(15)
Zn1-N2	2.046(4)	O1W-Zn02-O3	90.99(14)
Zn2-O1w	2.303(4)	O1W-Zn02-O4	89.46(10)
Zn2-O3	1.942(4)	O1W-Zn02-N3	177.91(12)
Zn2-O4	1.965(3)	O1W-Zn02-N4	87.13(14)
Zn2-N3	2.221(4)	O3-Zn02-O4	109.03(14)
Zn2-N4	2.032(4)	O3-Zn02-N3	90.33(15)
O1W-H1w	0.91(8)	O3-Zn02-N4	140.64(12)
O1W-H2w	0.82(6)	O4-Zn02-N3	88.58(12)
O1-Zn01-O2	138.57(14)	O4-Zn02-N4	110.27(14)
O1-Zn01-N1	106.61(13)	N3-Zn02-N4	92.87(15)
O1-Zn01-N2	98.95(13)		

References:

1. *SMART* (V 5.628), *SAINT* (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
2. G. M.Sheldrick, *Siemens Area Detector Absorption Correction Program*, University of Göttingen, Göttingen, Germany, 1994.
3. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.*, 1993, **26**, 343.
4. G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Solution and Refinement;* University of Göttingen, Göttingen, Germany, 1997.