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## **Supplementary Information For:**

## A thiadiazole-functionalized Zr(IV)-based metal-organic framework as highly fluorescent probe for the selective detection of picric acid

Mostakim SK and Shyam Biswas\*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039 Assam, India

\* To whom correspondence should be addressed. E-mail: sbiswas@iitg.ernet.in; Tel: 91-3612583309.

## Detailed procedure for the synthesis of compound 1:

In order to achieve the optimum conditions for the synthesis of **1**, high-throughput methods were used. For a particular Zr(IV) salt and the H<sub>2</sub>BTDB ligand in a particular solvent, 6 different additives/modulators (H2O, conc. HCl, benzoic acid, formic acid, acetic acid and trifluoroacetic acid) can be added resulting in 6 different reaction mixtures. Thus, for the preparation of compound 1 at a specific temperature,  $18 (= 3 \times 6)$  different reaction mixtures can be prepared in 3 different solvents (*N*,*N*'-dimethylformamide, *N*,*N*'-diethylformamide and N,N'dimethylacetamide). For three Zr(IV) salts (ZrCl<sub>4</sub>, ZrOCl<sub>2</sub>·8H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O), a total of 54 (=  $3 \times 18$ ) combination of reactants are possible. These reaction mixtures were heated at a particular temperature in a block-heater that can simultaneously heat 24 glass tubes containing the reaction mixtures. The reaction times for all cases were kept constant at 24 h.

The 18 possible combinations of reactants for the synthesis of compound 1 employing  $ZrCl_4$  and  $H_2BTDB$  ligand at 150 °C.

additive	H <sub>2</sub> O	conc. HCl	benzoic acid	formic acid	acetic acid	trifluoro- acetic acid
<i>N,N'</i> -dimethylformamide	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$
<i>N</i> , <i>N</i> ′-diethylformamide	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$
<i>N,N'</i> -dimethylacetamide	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$	$\bigcirc$



**Fig. S1** XRPD patterns of **1'** in different forms: as-synthesized (a); thermally activated (b); after BET analysis (c); treated with water (d); with methanol (e); with acetic acid (f); with 1M HCl (g); after 5 cycles of fluorescence titration experiments with TNP (h).



Fig. S2 Calculated (black) and experimental (red) XRPD patterns of compound 1.



Fig. S3 FT-IR spectra of the as-synthesized (black) and activated (red) samples of compound 1.



Fig. S4  $N_2$  adsorption (filled circles) and desorption (empty circles) isotherms of compound 1' measured at -196 °C.



Fig. S5 TG curves of the as-synthesized (black) and activated (red) samples of compound 1 recorded in an air atmosphere in the temperature range of 25-600 °C with a heating rate of 10 °C min<sup>-1</sup>.



Fig. S6 Fluorescence emission spectra of compound 1' in different organic solvents ( $\lambda_{ex} = 370$  nm).



**Fig. S7** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM 2,4-DNP solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S8** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM PNP solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S9** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM TNT solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S10** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM 2,4-DNT solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S11** Quenching of the fluorescence intensity of compound **1**' by incremental addition of 3 mM 2,6-DNT solution to a 3 mL suspension of compound **1**' in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S12** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM 4-NT solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S13** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM *m*-DNB solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



**Fig. S14** Quenching of the fluorescence intensity of compound **1'** by incremental addition of 3 mM NB solution to a 3 mL suspension of compound **1'** in methanol ( $\lambda_{ex} = 370$  nm and  $\lambda_{max} = 494$  nm).



Fig. S15 Fluorescence quenching profile of 1' upon addition of 2,4-DNT followed by TNP.



Fig. S16 Fluorescence quenching profile of 1' upon addition of 2,6-DNT followed by TNP.



Fig. S17 Fluorescence quenching profile of 1' upon addition of *m*-DNB followed by TNP.



Fig. S18 Fluorescence quenching profile of 1' upon addition of TNT followed by TNP.



Fig. S19 Fluorescence quenching profile of 1' upon addition of NB followed by TNP.



Fig. S20 Fluorescence quenching profile of 1' upon addition of 4-NT followed by TNP.



Fig. S21 Fluorescence quenching profile of 1' upon addition of 2,4-DNP followed by TNP.



Fig. S22 Fluorescence quenching profile of 1' upon addition of PNP followed by TNP.



**Fig. S23** Stern-Volmer plot for the fluorescence quenching of 1' upon addition of TNP. Inset: non-linearity of the plot at higher concentrations of TNP.



Fig. S24 Change in the fluorescence intensity of 1' in methanol suspension as a function of TNP concentration.



Fig. S25 HOMO and LUMO energies for the selected nitroaromatic explosive compounds.

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S1.	MOF	$K_{ m sv}$	Detection Limit	Medium Used	Ref.		
No.		$(\times 10^4 \mathrm{M}^{-1})$					
1	$[Zr_6O_4(OH)_4(BTDB)_6]\cdot 8H_2O\cdot$	2.49	$1.63 \times 10^{-6}$	Methanol	This		
	6DMF				work		
2	$[Cd_5Cl_6(L)(HL)_2]\cdot 7H_2O$	4.05	$1.87 \times 10^{-7} \mathrm{M}$	Ethanol	1		
3	$[Cd_{3}(TPT)_{2}(DMF)_{2}] \cdot (H_{2}O)_{0.5}$	6.56		Ethanol	2		
4	$Zr_6O_4(OH)_4(L)_6(UiO-67@N)$	2.9		Water	3		
5	Cd(NDC) <sub>0.5</sub> (PCA)	3.5		Acetonitrile	4		
6	$[Zn_2(NDC)_2(bpy)].G_x$	0.422		Ethanol	5		
7	Bio-MOF-1	4.6	2.9 ppb	Water	6		
8	[Tb(1,3,5-BTC)]	3.41	$8.1  imes 10^{-8} \mathrm{M}$	Ethanol	7		
9	$Zn_2(PAM)_2(1,3-PDA)_2$		$1.27 \times 10^{-8} \mathrm{M}$	DMSO	8		
10	[Eu <sub>2</sub> (MFDA) <sub>2</sub> (HCOO) <sub>2</sub>		$4.5 \times 10^{-7} \mathrm{M}$	DMF	9		
	$(H_2O)_6] \cdot (H_2O)_n$						

**Table S1.** A comparison of the Stern-Volmer constant ( $K_{sv}$ ), detection limit and medium used for the detection of TNP by luminescent MOFs reported till date.

Volume of TNP	<b>B</b> <sub>1</sub>	<b>B</b> <sub>2</sub>	a1	a <sub>2</sub>	$\tau_1$ (ns)	$\tau_2$ (ns)	<\alpha>* (ns)
added (µL)							
0	0.080	0.041	0.79	0.21	1.238	9.039	2.949
45	0.093	0.061	0.81	0.19	1.057	6.888	2.165
90	0.104	0.067	0.82	0.18	0.974	6.868	2.034
135	0.066	0.066	0.88	0.12	0.967	6.864	1.674
180	0.054	0.067	0.90	0.10	0.979	6.799	1.561
225	0.096	0.072	0.85	0.15	0.900	6.743	1.776

**Table S2.** Average excited state lifetime ( $\langle \tau \rangle$ ) values of compound **1'** before and after addition of different volumes of 3 mM TNP solution ( $\lambda_{ex} = 370$  nm,  $\lambda_{em} = 494$  nm)

\*< $\tau$ > =  $a_1\tau_1 + a_2\tau_2$ 

**Table S3.** HOMO and LUMO energy levels of selected analytes calculated by density functional theory (DFT) at B3LYP/6-31G\* accuracy level using Gaussian 09 package of programs<sup>10</sup>.

Analytes	HOMO (eV)	LUMO (eV)	Band Gap (eV)
TNP	-8.2374	-3.898	4.3394
DNP	-7.6644	-2.8202	4.8442
PNP	-6.9207	-2.2213	4.6994
TNT	-8.4793	-3.479	5.0003
4-NT	-7.3626	-2.3171	5.0455
2,4-DNT	-8.1131	-2.9769	5.1362
2,6-DNT	-7.8913	-2.8501	5.0412
1,3-DNB	-8.4129	-3.135	5.2779
NB	-7.5917	-2.4294	5.1623

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