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# **Electronic Supplementary Information**

# Picogram Sensing of Trinitrophenol in Aqueous Medium through a Water Stable Nanoscale Coordination Polymer

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#### **Experimental Section**

**Materials**: All chemicals were of reagent-grade quality obtained from Sigma-Aldrich and used as received without further purification. The FT-IR spectrum was recorded from KBr pellets in the range of 4000-400 cm<sup>-1</sup> on a SHIMADZU FT-IR spectrometer. The TGA was performed on SDT Q600 (Shimadzu) analyser in flowing nitrogen with a heating rate of 10  $^{0}$ C per minute. Powder X-ray diffraction data were collected using an X'pert PRO (PANanalytics) powder diffractometer equipped with Cu K $\alpha$  radiation (1.5405 Å). NMR spectra were recorded on an Avance III-500 (Bruker) NMR spectrometer. : A Tecnai G2 TF20 S Twin transmission electron microscope (TEM) Operating voltage: 200 kV and FEI NOVA NANOSEM 450 scanning electron microscope (SEM) with acceleration voltage 15 kV were used to determine particle size and morphology.

Synthesis of compound 1: 0.5 mmol (0.118 g) of Ca(NO<sub>3</sub>).4H<sub>2</sub>O and 0.5 mmol (0.090 g) of 2amino 1, 4 – benzenedicarboxylic acid were dissolved in 10 mL of N, N'- dimethylformamide (DMF). The mixture was sonicated for 5 min and then transferred to a closed glass vial. It was heated at 100  $^{\circ}$  C for 3 days. After three days of reaction brown color crystals were formed. The crystals were washed with DMF several times to remove the unreacted acid. Then it was vacuum dried for further use. CHN analysis, Calculated C: 45.19, H: 4.14, N: 9.58, Observed C: 44.98, H: 4.08, N: 9.48.

Synthesis of Nano scale 1 (Surfactant assisted synthesis): 0.5 mmol of  $Ca(NO_3).4H_2O$  $Ca(NO_3).4H_2O$  and 0.5 mmol of NH<sub>2</sub>BDC and 5 mL of DMF were mixed at room temperature and placed in oven at 60 °C for 72 h. To the incubated solution, 0.5 mmol of CTAB (Cetyltrimethyl ammonium bromide) were added and heated at 50 °C until the CTAB was completely dissolved. The resulting clear solution was then placed at 105 °C and heated for 1.5 h. 0.5 mmol of triethylamine (TEA) were added under vigorous stirring for 20 min. Products were centrifuged and washed three times with DMF and chloroform. Then product was immersed into chloroform overnight and finally dried under vacuum and characterized using SEM technique and it was found that the formed MOF particles are of size ~ 1.5  $\mu$ m. The other sizes were synthesized by varying either the solvent volume or metal to ligand ratio (Scheme S1 and Table S3). CHN analysis, ~ 1.5  $\mu$ m; C: 44.87, H: 3.98, N: 9.47; ~ 1  $\mu$ m; C: 44.92, H: 4.02, N: 9.52; ~ 500 nm; C: 45.07, H: 4.12, N: 9.38; ~ 200 nm; C: 44.95, H: 4.05, N: 9.48; ~ 80 nm; C: 44.78, H: 3.88, N: 9.42; ~ 50 nm; C: 44.95, H: 4.08, N: 9.49.

**Water Stability:** Water stability of **1** was studied in ultrahigh pure water. Compound **1** was dispersed in water for 24 h. The samples were then vacuum filtered, no significant mass loss was observed. Furthermore, the PXRD pattern of **1** after soaking for 24 h was not changed, suggesting the material is stable in water.

**Single Crystal X-ray Diffraction:** For single crystal XRD measurement, a suitable crystal for the compound was carefully selected under a polarizing microscope and glued to a thin glass fiber. The single crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 150 K. The X-ray generator was operated at 50 kV and 35 mA using MoK $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. Data were collected with  $\omega$  scan width of 0.3°. A total of 606 frames were collected in three different settings of  $\varphi$  (0°, 90°, 180°) keeping the sample to-detector distance fixed at 6.03 cm and the detector position (2 $\theta$ ) fixed at -25°.

The data were reduced using SAINTPLUS<sup>[1]</sup> and an empirical absorption correction was applied using the SADABS program.<sup>[2]</sup> The crystal structure was determined by direct methods using SHELXS97 and refined using SHELXL97 present in the SHELXTL V6.14<sup>[3]</sup> package. All hydrogen atoms were placed in calculated positions during the final step of the refinement process. For the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined using the riding mode. The last cycles of the refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against F<sup>2</sup> was carried out using the WINGX <sup>[4]</sup> package of programs. The crystallographic parameter for compound **1** is provided in table S1. CCDC 1027772 contains the crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc. cam.ac.uk/data request/cif

- SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL, Bruker AXSInc., Madison, WI, 2004.
- [2] G. M. Sheldrick, Siemens Area Correction Absorption Correction Program, University of Göttingen, Göttingen, Germany, **1994**.
- [3] G. M. Sheldrick, SHELXL-97 Program for Crystal Structure Solutionand Refinement, University of Göttingen, Göttingen, Germany, **1997**.
- [4] J. L. J. Farrugia, App. Crystallography 1999, 32, 837

**Steady-State Spectroscopic Studies:** The absorption were collected at room temperature on a UV-3800 SHIMADZU UV-vis-NIR spectrometer and the emission spectra was recorded using a Horiba JobinYvon- Fluorolog 3 spectrofluorimeter. All the steady-state emission studies were carried out by exciting the sample at 330 nm. The spectral range was kept to 200 - 600 nm with the slit width being kept to one. All the solution phase absorption studies were done in a quartz cuvette having a path length of 1 cm. The fluorescent spectra of the sample in water were collected before and after addition of nitro aromatics.

The quenching studies: 5 mg of the sample was dispersed in 10 mL water. 200  $\mu$ L from this stock solution was diluted to 3 mL. This dispersed solution was used for the analysis. 2.2 mM solution of TNP was prepared in water for the quenching experiments. Other nitro aromatics were dissolved in acetonitrile: water (v:v ratio; 2:8) solution (2.2 mM).

**Quantum Yield Measurement:** The relative quantum yield was calculated for the compound by using 0.1 M quinine sulfate ( $\phi_r = 0.546$ ) as the reference. The optical density of both the reference and the compound were made close to 0.1 by keeping the slit width equal to one. The emission spectra were also noted for both at the same slit width by exciting at 310 nm. Now the quantum yield of the compound can be measured relative to the reference by using the following equation

$$\phi_{\rm s} = \phi_{\rm r} \left( {\rm OD}_{\rm r} / {\rm OD}_{\rm s} \right) \left( {\rm I}_{\rm s} / {\rm I}_{\rm r} \right) \left( {\rm n}_{\rm s}^2 / {\rm n}_{\rm r}^2 \right)$$

where  $\phi_s$  and  $\phi_r$  are quantum yields of sample and reference respectively, OD is the optical density, I is the area under the curve for the emission spectra, and n is the refractive index of the medium.

Time-Resolved Emission Studies: The emission lifetimes were estimated using a picosecond time-correlated single photon counting system (TCSPC, model Horiba JobinYvon-IBH). The samples were excited at 330 nm using a pulsed diode laser and the repetition rate was fixed at 500 kHz. The lifetime measurement for the compound before and after addition of the analyte was done at longer time scale keeping time to amplitude convertor (TAC) in the range of 200 ns (0.224 ns per channel). The luminescence lifetime values were evaluated using DAS 6.3 fluorescence decay analysis software. The decay curve was fitted using a di exponential fit with goodness of fit based on reduced  $\chi^2$  (1 ± 0.2) statistics.

The average lifetime was analyzed using the following equation

$$\tau_{(avg)} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3}$$

where  $\tau$  is the lifetime and  $\alpha$  is the pre-exponential factor with subscripts 1, 2, and 3 representing various species.

Adsorption studies: To examine the surface area of 1 we have carried out adsorption studies with  $N_2$  at 77 K. Gas adsorption measurements were performed by using a BelSorpmax (BEL Japan) automatic volumetric adsorption instrument. All the gases used were ultra-pure research grade (99.99 %). Before every measurement samples were pretreated for 12 h at 423 K under 10<sup>-2</sup> kPa continuous vacuum using BelPrepvac II and purged with  $N_2$  on cooling.

Contact mode visual detection of TNP: The TLC test strips were made by coating the compound 1 dispersed in water followed by the removal of solvent under vacuum at room temperature. The aqueous samples of TNP of desired concentration was also prepared. The explosive solutions (10  $\mu$ L each) were spotted onto the test strips using a micropipette. After spotting to a particular area the strips are dried again under vacuum. The dark spots were identified when the strips were illuminated by UV light (~ 330 nm).

Metal ion Sensing studies: 5 mg of the sample was dispersed in 10 mL water. 200  $\mu$ L from this stock solution was diluted to 3 mL. This dispersed solution was used for the analysis. All the metal ions were dissolved in water separately making the concentration of 1mM. Then 100  $\mu$ L of each metal ion solution was added to the compound and noted down the change in fluorescence intensity for ach case.

### <sup>1</sup>H-NMR-studies

The <sup>1</sup>H-NMR studies were done in  $D_2O$ .

TNP: <sup>1</sup>HNMR (500MHz, D<sub>2</sub>O) δ8.87 (s, 1H)

Compound 1: <sup>1</sup>HNMR (500MHz,  $D_2O$ )  $\delta$  7.83(s, 1H), 7.67(d, 1H), 7.20 (s, 1H), 7.12 (d, 1H)

2.92(s, 3H), 2.76(s, 3H)

## **IR** studies

 $v_s$ (N-H) (sym and asym) 3475 cm<sup>-1</sup> and 3345cm<sup>-1</sup>,  $v_s$ (C-H) 2932cm<sup>-1</sup>,  $v_s$  (C =O)1654cm<sup>-1</sup>,  $\delta_s$ (N-

H)1577cm<sup>-1</sup>,  $\delta_{S}$ (C-H)1394cm<sup>-1</sup>, and  $v_{S}$  (C – N)1248cm<sup>-1</sup>



Scheme S1: Schematic representation of synthesis of compound **1** in nanoscale.

Empirical formula	$C_{5.50}H_2Ca_{0.50}NO_{2.50}$
Formula weight	142.12
Crystal system	Orthorhombic
Space group	<i>Pnma</i> (No. 62)
Crystal size (mm)	$0.120 \times 0.100 \times 0.080$
a (Å)	7.001 (5)
b (Å)	18.025 (5)
c (Å)	10.004 (5)
Volume (Å <sup>3</sup> )	1262.4 (12)
Ζ	8
Calculated density (g/cm <sup>3</sup> )	1.496
Absorption coefficient (mm <sup>-1</sup> )	0.514
θ range ()	2.260 to 28.254
Reflections collected	6175
Unique	1609
Parameters	110
Goodness-of-fit	1.171
Final R indices [I>2sigma(I)]	$R_1 = 0.0526, wR_2 = 0.1390$
R indices (all data)	$R_1 = 0.0675, wR_2 = 0.1581$
Largest diff. peak and hole (e. Å <sup>-3</sup> )	0.548 and -0.432

Table S1. Crystallographic data parameters for structure of compound 1<sup>a</sup>.

<sup>[a]</sup> $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ ; wR<sub>2</sub> = {[ $w(F_0^2 - F_c^2)^2$ ]/ [ $w(F_0^2)^2$ ]}<sup>1/2</sup>;  $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$ ;  $P = [\max(F_0^2, 0) + 2(F_c)^2]/3$ , where a = 0.0911 and b = 0.6097, respectively.

Table S2.	Selected	bond	lengths	in com	pound <b>1</b> .
					P =

Moiety	Bond lengths (Å)
Ca(1)-O(1)	2.327(2)
Ca(1)-O(1)#1	2.327(2)
Ca(1)-O(2)#1	2.445(2)
Ca(1)-O(2)	2.445(2)
Ca(1)-O(3)	2.509(3)
Ca(1)-O(3)#2	2.546(3)
Ca(1)-O(1)#3	2.548(2)
Ca(1)-O(1)#4	2.548(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z #2 x+1/2,y,-z+1/2 #3 x-1/2,-y+3/2,-z+1/2

#4 x-1/2,y,-z+1/2

Size	Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	NH <sub>2</sub> -BDC	DMF (mL)	CTAB	TEA
	(mmol)	(mmol)		(mmol)	(mmol)
$\sim 1.5 \ \mu m$	0.5	0.5	5	0.5	0.5
~ 1 µm	0.5	0.5	10	0.5	0.5
$\sim 500 \text{ nm}$	0.5	0.5	30	0.5	0.5
$\sim 200 \text{ nm}$	0.33	0.99	10	0.99	0.99
$\sim 80 \text{ nm}$	0.33	1.65	10	1.65	1.65
~ 50 nm	0.33	1.65	30	1.65	1.65

Table S3. Synthetic conditions for different size of micro/nano scale MOF.

Table S4. A comparative chart of the limit of detection of different Metal- organic Frameworks for TNP

	System	Detection limit	Journal
1	MOF	1.69 ppb (10 <sup>-9</sup> M)	Present manuscript
2	MOF	10 <sup>-4</sup> M	Angew. Chem. Int. Ed. 2013, 52, 2881
3	MOF	10 <sup>-7</sup> M	Dalton Trans. 2013, 42, 12403
4	MOF	ppm level	Chem. Eur. J. <b>2014</b> , 20, 3589
5	MOF	10 <sup>-6</sup> M	Chem. Commun. <b>2014</b> , 50, 8915
6	MOF	10 <sup>-7</sup> M	<i>Chem. Asian J.</i> <b>2013</b> , <i>8</i> , 1321
7	MOF	23 ppb	Eur. J. Inorg. Chem. 2015, 1390
8	MOF	1 ppm	Dalton Trans. 2015, 44, 7822
9	MOF	1.76 X 10 <sup>-8</sup> M	Chem. Eur. J. 2015, 21, 2029
10	MOF	10 <sup>-4</sup> M	<i>RSC Adv.</i> <b>2015</b> , <i>5</i> , 93
11	MOF	10 <sup>-5</sup> M	<i>RSC Adv.</i> <b>2015</b> , <i>5</i> , 28092
12	MOF	4.98 X 10 <sup>-6</sup> M	Adv. Funct. Mater. 2014, 24, 4034
13	MOF	10 <sup>-6</sup> M	Dalton Trans. 2015, 44, 230

	Compound	Compound + TNP
X <sup>2</sup> value	0.954	1.13
T <sub>1</sub>	8.14	7.78
α1	0.02	0.04
T <sub>2</sub>	15.72	15.26
α2	0.98	0.96
Average lifetime, τ (ns)	15.64	15.10

Table S5: The  $\chi^2$  values and average lifetime calculated for compound 1 before and after addition of TNP.

TNP added		Shift in	δ values	
	TNP		MOF	
	δ 8.87	δ 7.83	δ 7.67	δ 7.20
1 drop	-0.015	+0.01	+0.01	+0.02
2 drops	-0.03	+0.01	+0.025	+0.035
3 drops	-0.035	+0.015	+0.03	+0.05
4 drops	-0.04	+0.02	+0.04	+0.06

Table S6: The continuous shift in chemical shift values of aromatic protons in TNP as well as compound 1 upon increasing addition of TNP (  $x \ 10^{-3} \text{ M}$ ).

Analyte	$\lambda_{max}$ (Red shift) (nm)	(1-F/F <sub>0</sub> ) %
NP	6	23
DNP	24	36
ТЛР	32	48

Table S7: The comparison of percentage of quenching for different nitro phenols.



Fig. S1. (a) The Ca ion coordination in compound 1 and (b) acid connectivity in compound 1.



Figure S2: The characteristics IR peaks for compound 1 (a) of size > 20  $\mu$ m (b) of size ~ 200 nm.



Figure S3: Thermogravimetirc analysis plot for compound 1 (a) of size > 20  $\mu$ m (b) of size ~ 200 nm.



Figure S4: The absorption and emission spectra of compound **1** and the absorbance spectra for TNP.



Figure S5: The emission spectra for compound **1** after addition of different nitro analytes (a) DNB (b) DNT (c) TNT (d) NB (e) NT.



Fig. S6: The simulated and experimental powder X-ray diffraction of different micro and nanoscale of compound **1**.



Figure S7: The DLS plot of compound 1 in DMF of size (A) ~ 500 nm (B) ~ 200 nm (C) ~ 1  $\mu$ m (D) ~ 1.5  $\mu$ m.



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**(I)** 



(III)



(IV)



1 µm

(VI)

**(V)** 



(VII)



(VIII)



Figure S8: SEM images of 1 of different sizes (I) ~ 1.5  $\mu$ m (II) ~ 1  $\mu$ m (III) ~ 500 nm (IV) ~ 200 nm (V) ~ 80 nm (VI), (VII), and TEM images of (VIII) ~ 80 nm, and (IX) ~ 50 nm.



(A) (B)

Figure S9: Adsorption isotherm of  $N_2$  for (A) micron sized sample and (B) the nano scale sample (~ 200 nm). The BET surface area was calculated for both samples and the values are 6.7 m<sup>2</sup>g<sup>-1</sup> and 370 m<sup>2</sup>g<sup>-1</sup> respectively.



Figure S10: The emission spectra for different micro and nano scale MOF 1 after addition of TNP (a) ~ 1.5  $\mu$ m (b) ~ 1  $\mu$ m (c) ~ 500 nm (d) ~ 200 nm (e) ~ 80 nm and (f) ~ 50 nm.



Figure S11: The detection limit of the compound **1** (A) micron scale (B) nanoscale for TNP sensing.



Figure S12: (a) Absorption spectra (b) the relative change in fluorescence intensity of **1** by incremental addition of TNP (c) the effect of temperature on rate of quenching and (d) life time measurement of compound **1** before and after addition of TNP. Note: In Fig. S12a the hump at 415 nm may be due to ground-state complex formation.



Figure S13: The excitation spectra for compound 1 before and after addition of TNP. (a) 300 - 420 nm and (b) zoomed one (400-420 nm)



Figure S14: The change in fluorescence intensity of **1** by the addition of TNP (2.2 mM) in DMF solvent.





Figure S15: (i) The shielding and

deshielding effect of aromatic protons in NMR spectra of TNP and 1 respectively when they are mixed, (ii) the continuous shift in the chemical shift value in NMR spectra of 1 by the increasing addition of TNP: (a) expanded and (b) normal spectra, (iii) the complete NMR spectrum for the compound 1 and that after addition of TNP.



Figure S16: pH effect on the emission spectra of **1**.



Figure S17. The PXRD of compound 1 before and after treatment with TNP.



Figure S18. The reusability of compound **1** sensor for TNP.



Figure S19. The  $N_2$  adsorption isotherm for compound 1 (of microscale) before and after treatment with TNP.



Figure S20. The efficiency of quenching of fluorescence of compound by the addition of various metal ions (of concentration  $4 \times 10^{-5}$  M)







Figure S21. The change in fluorescence intensity of compound **1** by the addition of  $Cu^{2+}$  ions before and after addition of ethylenediamine (*en*) ((a) and (b)) and the detection of TNP in presence of masking agent (c) to (e).