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Nitroaromatic explosives detection by a luminescent Cd(II) based metal organic framework

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ABSTRACT

A Cd(II) based coordination polymer, $[Cd(3-bpd)(N(CN)_2)_2]_n$ (1), where 3-bpd is 1,4-bis(3-pyridyl)-2, 3-diaza-1,3-butadiene, has been synthesized and characterized by standard methods including single crystal X-ray diffraction technique. Singly crystal X-ray diffraction analysis shows that it is a 3-dimensional metallo-organic framework. 1 exhibits strong emission intensity in dispersed acetonitrile at 430 nm when it is excited at 340 nm. Among different explosive and pollutant nitroaromatic compounds (epNACs), trinitrophenol (TNP) is able to quench emission intensity of 1 drastically making 1 as turn-off chemosensor for TNP. Other epNACs, e.g. 2,4,6-trinitrotoluene (TNT), 2,6-dinitro toluene (2,6-DNT), nitrobenzene (NB), 1,3-dinitro benzene (1,3-DNB), 3,4-dinitrotoluene (3,4-DNT) and 4-nitrobenzoic acid (4-NBA) cannot quench the emission intensity of 1 significantly. The quenching constant value of 1 for TNP is determined to be 7.16×10^4 M⁻¹. Limit of detection of the complex towards TNP is 6×10^{-5} M. Resonance energy transfer (RET) is involved in the transfer of energy from the electronically excited donor, 1 to the acceptor, TNP thereby quenching the emission intensity. Some theoretical calculations have been performed to support the electronic transitions and the proposed mechanism.

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1. Introduction

Metal-organic frameworks (MOFs), which are also known as 46 porous coordination polymers (PCPs), are a class of porous materi-47 als. These are built from metal containing nodes and organic/inor-48 ganic linkers [1]. MOFs are in ever increasing interesting research 49 area because of their structural diversities and their potential 50 applications in many fields of scientific research e.g. gas storage 51 and removal [2], catalysis [3], electronic devices [4], sensing [5], 52 magnetism [6] etc. MOFs can be synthesized by the choice of metal 53 center, organic ligand and bridging moiety under suitable reaction 54 conditions. During synthesis of an MOF, one has to be conscious 55 about the reaction conditions. Due to the presence of several reac-56 tants in the reaction medium, control of the reaction is highly 57 important to get desired product which can successfully achieve 58 the required application. Temperature, pressure, solvent, counter 59 60 anion of the metal salt etc. play very crucial role to design different MOFs with various dimensionalities. 61

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On the other hand several nitroaromatic compounds quench the emission intensity of MOFs. This property of MOF can be used to detect explosive and pollutant nitro aromatic (epNAC) compounds. In recent time terrorist activity is a global challenge. Terrorist attack in different part of world occupies to the news headlines almost every week. It is important to develop suitable system that can readily recognize the explosives in order to improve homeland security and restrict terrorist activities. Example of epNACs includes 2,4,6-trinitrotoluene (TNT), 2,6-DNT (2,6-dinitro toluene), NB (nitro benzene), 1,3-DNB (1,3-dinitro benzene), 3,4-DNT (3,4-dinitro toluene), 4-nitrobenzoic acid (4-NBA) and 2,4,6-trinitrophenol (TNP, also known as picric acid) etc. These compounds are often used as explosives or to prepare explosives and some of them are themselves highly explosive.

In recent years several articles have been published related to the sensing of TNT by MOFs but very little attention has been reserved to the detection of 2,4,6-trinitrophenol which is even more powerful than TNT as an explosive [7]. Apart from this, TNP can be used in dyes and fireworks, pharmaceutical industries, 80 staining material, glasses, analytical chemicals [8], etc. When dis-81 charged into the environment it can pollute ground water and soil 82 [9,10] potentially creating several health issues such as anemia,

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84 infertility, respiratory track, carcinogenesis inside human cells and 85 other living organisms [11,12], etc. Hence, detection of picric acid 86 is an important issue considering its role as both explosive and 87 pollutant.

MOFs constructed by d^{10} metal ions and aromatic π -conjugated 88 ligands are supposed to be promising candidates to perform as 89 photoactive materials [13-18]. For these reasons, luminescent 90 properties of several MOFs with such constituents have been 91 92 explored. MOFs with Cd, Zn metal ions have been reported as sen-93 sors for nitroaromatic compounds. Mukherjee et al. have devel-94 oped Zn-based MOFs with electron rich aromatic ligands or 95 ligands with fluorophore for sensing of explosives [19,20]. Luminescent Zn-based MOFs with electron rich organic ligand have 96 97 been used for the sensing of TNP [21,22]. A recent report shows 98 the use of Zn-based MOF constructed from π -conjugated thio-99 phene-containing carboxylic acid as ligand for the detection of 100 nitroaromatics [23].

In this connection, we report here the synthesis, characteriza-101 tion and TNP sensing properties of a Cd(II) based MOF, 102 $[Cd(3-bpd)(N(CN)_2)_2]_n$ (1) where 3-bpd is 1,4-bis(3-pyridyl)-2,3-103 104 diaza-1,3-butadiene. 1 was prepared under ambient reaction con-105 ditions and characterized by standard techniques including X-ray 106 single crystal diffraction analysis. 3-bpd was selected because its 07 π -conjugated system is fluorescent, it is an electron rich ligand 108 with good delocalization, and the rotation about the N-N bond of 109 the two pyridyl units can regulate the coordination orientation of 110 the binding atoms. Coordination polymers with bpd ligand also show promising fluorescence properties [24]. This encouraged us 111 to explore the fluorescence properties of 1 towards sensing the 112 113 electron deficient nitroaromatic compounds.

114 2. Experimental

115 2.1. Materials and physical methods

Pyridine-3-carboxaldehyde and hydrazine hydrate were pur-116 117 chased from Aldrich Chemical Co. and were used as received. Cd (NO₃)₂·4H₂O was purchased from Merck, India. 1,4-Bis(3-pyridyl)-118 119 2,3-diaza-1,3-butadiene(3-bpd) was synthesized following the pro-120 cedure reported earlier [24a]. All the other chemicals including 121 solvents were of reagent grade and were used as received without 122 further purification. 2,4,6-Trinitrotoluene (TNT) was prepared by 123 the synthesis procedure reported in the literature [25]. Elemental 124 analyses (carbon, hydrogen and nitrogen) were performed using a 125 Perkin-Elmer 2400C elemental analyzer. FT-IR spectra were 126 obtained on a Perkin Elmer spectrometer (Spectrum Two) with 127 the samples by using the attenuated total reflectance (ATR) tech-128 nique. Powder X-ray diffraction (PXRD) patterns of the samples 129 were recorded on a Bruker D-8 Advance instrument operated at 130 40 kV and 40 mA using Cu K α (λ = 1.5406 Å) radiation. A Perkin-131 Elmer LS-45 fluorometer was used to carry out the fluorescence 132 titration experiments. Vapor sensing experiments were carried 133 out with Perkin-Elmer LS-55 fluorometer.

2.2. Synthesis of $[Cd(3-bpd)(N(CN)_2)_2]_n$ (1) 134

135 An aqueous solution (4.0 mL) of sodium dicyanamide (2.0 mmol, 0.178 g) was added to a methanolic solution (4.0 mL) 136 137 of 1,2-bis-(pyridine-3-ylmethelyne)hydrazine (3-bpd) (1.0 mmol, 138 0.210 g) taken in a beaker and stirred for 30 min to mix well. Cd 139 $(NO_3)_2$ ·4H₂O (1.0 mmol, 0.308 g) was dissolved in 4.0 mL of water 140 in a test tube. Then the previously prepared mixed ligand solution 141 was slowly and carefully layered with the aqueous $Cd(NO_3)_2$ solu-142 tion using 5.0 mL of a 1:1 v/v water/methanol mixture as buffer. 143 The yellow needle-shaped crystals suitable for single crystal

X-ray analysis were obtained after a few days. The crystals were 144 collected and washed with a methanol-water mixture and dried 145 under vacuum. (Yield = 76%.) Anal. Calc. for $C_{16}H_{10}N_{10}Cd$: C, 146 42.22; H, 2.20; N, 30.79. Found: C, 42.28; H, 2.29; N, 30.71%. 147

2.3. Theoretical calculations

All the theoretical calculations were performed with the help of 149 Gaussian 03 program [26]. The optimized geometries and the orbi-150 tal diagram were obtained from B3LYP hybrid function with 6-31G 151 basis set for H, C, N and O atoms. 152

2.4. Detection limit calculation

The detection limit was calculated by using the following empirical equation,

Limit of detection (LOD) =
$$3\sigma/k$$

(where σ : standard deviation and k: slope).

For 1 standard deviation was calculated from fluorescence spectroscopic measurements. The measurement was repeated five times, and then standard deviation (σ) was calculated. Gradual quenching of the emission intensity of the MOFs at 430 nm during fluorometric titration with TNP was plotted against the concentration of epNACs (TNP). The slope (k) was derived from this plot.

2.5. Crystallographic data collection and refinement

A suitable yellow colored block shaped single crystal of complex 167 1 was mounted on the tip of a glass fiber with the help of commer-168 cially available super glue. X-ray single crystal data were collected 169 at room temperature using a Bruker APEX II diffractometer, 170 equipped with a fine-focus, sealed tube X-ray source with graphite 171 monochromated Mo K α radiation (λ = 0.71073 Å). The data were 172 integrated using a SAINT program [27] and the absorption correc-173 tion was made with SADABS [27]. The structure was solved by SHELXT 174 [28] using direct methods and refined by full matrix least-squares 175 on F^2 using SHELXL-2014/7 [29] with anisotropic displacement 176 parameters for all non-hydrogen atoms. All the hydrogen atoms 177 were fixed geometrically and placed in ideal positions. The crystal 178 selected for the X-ray diffraction experiment was refined as a 179 merohedral twin with an almost equal contribution of both com-180 ponents of 0.50(5). Of the possible space groups based on the sys-181 tematic extinctions (C2, Cm, C2/m) the C2 space group was selected 182 due to the non-centrosymmetric intensity statistics, the successful 183 solution and refinement of the structure, and the lack of disorder 184 affecting the dicyanamido anion imposed by the presence of the 185 mirror plane in Cm and C2/m. Data collection and structure refine-186 ment parameters are given in Table 1. 187

3. Results and discussion

3.1. Description of crystal structure of complex 1

An ORTEP diagram of the single asymmetric unit of **1** is shown 190 in Fig. 1. Selected bond lengths and bond angles of it are listed in 191 Table 2. The asymmetric unit consists of Cd^{2+} ion, the organic 192 ligand 3-bpd, and dicyanamide ion in the stoichiometric molar 193 ratio of 0.5:0.5:1. The cadmium atom lies on a twofold axis and dis-194 plays an almost regular octahedral coordination geometry pro-195 vided by the nitrogen atoms of two crystallographically 196 independent 3-bpd ligands and four dicyanamide ions The Cd-N 197 bond distances, trans- and cis-bond angles fall in the ranges 198 2.317(12)-2.376(10) Å, 177.5(6)-180.0(7)°, 85.50(13)-97.0(6)°, 199 respectively. 200

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| Formula | C ₁₆ H ₁₀ CdN ₁₀ | | |
|---|---|--|--|
| Formula weight | 454.74 | | |
| Crystal system | monoclinic | | |
| Space group | C2 | | |
| a (Å) | 15.594(2) | | |
| b (Å) | 7.0695(9) | | |
| <i>c</i> (Å) | 9.5798(12) | | |
| α (°) | 90 | | |
| β (°) | 125.4951(14) | | |
| γ(°) | 90 | | |
| V (Å ³) | 859.86(19) | | |
| Ζ | 2 | | |
| $D_{\text{calc}} (\text{g cm}^{-3})$ | 1.756 | | |
| $\mu (\mathrm{mm}^{-1})$ | 1.295 | | |
| F(000) | 448 | | |
| Т (К) | 294(2) | | |
| θ (°) | 2.61-27.50 | | |
| Reflections collected | 5615 | | |
| Unique reflections | 1980 | | |
| Reflections $(I > 2\sigma(I))$ | 1980 | | |
| R _{int} | 0.02 | | |
| Goodness-of-fit (GOF) on (F^2) | 1.167 | | |
| $R_1 (I > 2\sigma(I))^{\rm a}$ | 0.0195 | | |
| wR_2^a | 0.0517 | | |
| Δho maximum/minimum/e Å $^{-3}$ | -0.30, 0.83 | | |

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$.

201 The 3-bpd ligand is nearly planar (the dihedral angle between the pyridine rings is $2.2(7)^{\circ}$) and acts as a bridge between the adja-202 cent metal centers through the pyridine N atoms. The dicyanamide 203 ions adopt a μ 1, 5 bridging mode resulting in the formation of 204 205 tetranuclear twenty-four-membered metallacycles connected into polymeric undulated layers parallel to the *ab* plane, which are fur-206 207 ther linked by the bridging role of the 3-bpd ligands into a three-208 dimensional network (Fig. 2).

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3.2. Powder X-ray diffraction study

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To check the purity of bulk material, powder X-ray diffraction 210 211 212

(PXRD) analysis has been performed on bulk material of complex 1. It has been observed that the peak position obtained from PXRD pattern of bulk matches well with the simulated PXRD pattern obtained from single crystal X-ray diffraction data (Fig. s1).

3.3. Nitroaromatic explosives detections

The photoluminescence studies of complex 1 have been performed with the MOF dispersed in acetonitrile at room temperature. 1 displays an emission peak at 430 nm when it is excited at 340 nm with high intensity. As Cd²⁺ possesses d¹⁰ electronic configuration, it is very difficult to be either oxidized or reduced [30,31]. Thus, its emission peak could not be interpreted as an MLCT (metal-to-ligand charge transfer) or an LMCT (ligand-tometal transfer) [32]. This peak may be assigned to an intraligand $(\pi^* \rightarrow n \text{ or } \pi^* \rightarrow \pi)$ emission [33,34]. In addition to this, complexation of the ligand with the metal center may increase the rigidity of the system reducing thereby nonradiative decay [35-37].

As this MOF has shown high emission intensity, this property may be explored in some practical applications. Thus, we have next tried to explore its potential as sensor for the detection of different nitroaromatic compounds. The sensing property of MOF with 2,6-DNT (2,6-dinitro toluene), NB (nitro benzene), 4-NBA (4-nitro benzoic acid), 1,3-DNB (1,3-dinitro benzene), 3,4-DNT (3,4-dinitro toluene), TNT (2,4,6-tri nitro toluene) and TNP with 10⁻⁴ M concentration has been investigated. To check the detection ability of the MOF, nitroaromatic compounds in deionized water have been gradually added with gradual increasing concentration (1 mg/10 mL) to MOF dispersed in acetonitrile and the emission intensity at 430 nm has been monitored. The emission intensity of the 1 is quenched to great extent in the presence of TNP whereas



Fig. 1. The asymmetric unit of 1 with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i) 1 – x, y, 1 – z; (ii) 1 + x, y, 1 + z; (iii) 1/2 + x, -1/2 + y, z; (iv) 1/2 - x, 1/2 + y, -z; (v) -x, y, -z; (vi) -1/2 + x, 1/2 + y, z.

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Table 2

| Coloria hand langths () |) and colooted bond anote | (0) of complex 1 |
|--------------------------|----------------------------|-------------------|
| Selected Dona lengths (A |) and selected bond angles | (*) of complex I. |

| Cd1–N1 | 2.327(2) |
|--|--|
| Cd1–N3 | 2.376(10) |
| Cd1–N5 ^{iv} | 2.317(12) |
| N5 ^{iv} -Cd1-N5 ^{vi} N5 ^{iv} -Cd1-N1 ^v N5 ^{iv} -Cd1-N1 N5 ^{iv} -Cd1-N1 N1 ^v -Cd1-N1 N5 ^{iv} -Cd1-N3 N5 ^{vi} -Cd1-N3 N1 ^v -Cd1-N3 N1 ^v -Cd1-N3 N1 ^v -Cd1-N3 N5 ^{iv} -Cd1-N3 ^v N5 ^{iv} -Cd1-N3 ^v N5 ^{vi} -Cd1-N3 ^v N5 ^{vi} -Cd1-N3 ^v N5 ^{vi} -Cd1-N3 ^v N1 ^v -Cd1-N3 ^v N1 ^v -Cd1-N3 ^v N3-Cd1-N3 ^v | $\begin{array}{c} 2.317(12)\\ 97.0(6)\\ 89.5(4)\\ 90.6(4)\\ 90.5(4)\\ 89.5(4)\\ 180.0(7)\\ 85.50(13)\\ 177.5(6)\\ 90.0(4)\\ 90.0(4)\\ 177.5(6)\\ 85.50(13)\\ 90.0(4)\\ 90.0(4)\\ 90.0(4)\\ 90.0(4)\\ 92.1(6)\end{array}$ |
| C5–N1–Cd1 | 120.01(18) |
| C1–N1–Cd1 | 122.2(2) |
| C7–N3–Cd1 | 121.1(6) |
| C8–N5 ^{vi} –Cd1 | 152.0(10) |

Symmetry codes: (iv) 1/2 - x, 1/2 + y, -z; (v) -x, y, -z; (vi) -1/2 + x, 1/2 + y, z.

the intensity remains almost unperturbed with other epNACs. In
this connection, it could be mentioned that water didn't show
any influence on the initial fluorescence intensity of MOFs dispersed in MeCN (Fig. s5). Other than TNP epNACs like 4-NBA,
2,6-DNT, NB, 1,3-DNB, 3,4-DNT and TNT do not show any appreciable influence in MOFs emission (Fig. 3).

As quenching of emission intensity of **1** occurs in the presence of TNP, we have performed a titration experiment (Fig. 4). It is evident from the figure that the emission intensity of the MOF is quenched severely by its presence. To perform the titration, an aqueous solution of TNP (10^{-4} M) was gradually added to **1** dispersed in acetonitrile (1 mg/10 mL). ~95.0% of emission intensity of **1** is quenched in the presence of 240 µL of TNP.

The sensing ability of **1** towards TNP in solution encourages us to explore the emission quenching experiment in the presence of TNP vapor. The emission spectra of **1** have been recorded on a quartz glass slide before and after its exposure to equilibrated vapor of TNP over a period of specific time interval (0, 2, 5, 10, 15 min, Fig. 5). After 2 min of its exposure to TNP vapor, appreciable quenching in emission intensity of the MOF has been noticed.



Fig. 3. Fluorescence response of 1 towards epNACs [upon addition of 0–300 μ L of epNAC solution (conc. 10^{-4} M)].



Fig. 4. Quenching in emission intensity of 1 upon gradual addition (0–240 $\mu L)$ of TNP solution (10 $^{-4}$ M).



Fig. 2. Crystal packing of 1 showing the formation of a polymeric three-dimensional network. Hydrogen atoms are omitted for clarity.

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Fig. 5. Emission spectra of 1 upon exposure to TNP vapor after certain time interval.

260 3.4. Insight into the TNP sensing mechanism

261 There may be different possible explanations behind the fluo-262 rescence quenching of 1 in the presence of TNP. Among them photoinduced electron transfer (PET) and resonance energy transfer 263 264 (RET) are extremely well known. Generally, in PET easy transfer 265 of electron in the excited state takes place, which ultimately results 266 in fluorescence quenching. On the other hand, RET involves the transfer of energy from an electronically excited donor chro-267 mophore to the acceptor. In large MOFs such as **1**, one can treat 268 the valence and conduction band similarly as molecular orbitals 269 (MOs) [38]. Usually it has been found that the LUMOs of epNACs 270 271 lie lower in energy in comparison to the conduction bands of MOFs, which influence the transfer of electron density from the electron-272 rich MOFs to the electron-deficient epNACs and as a result, 273 quenching in the emission intensity of MOFs may be observed. 274 275 The HOMO and LUMO energies along with their orbital diagrams 276 of these epNACs have been obtained from density functional the-277 ory (DFT) calculations. The HOMO-LUMO energy level diagram for some selected epNACs is represented in Fig. 5 and the values 278 of their respective energies (in eV) are tabulated (Table 3). The 279 280 DFT calculations have been carried out using the Gaussian 03 program [26] and geometry optimizations have been performed with 281 B3LYP hybrid function with 6-31G basis set for H, C, N and O 282 283 atoms.

As shown in Fig. 6, it can be clearly seen that among the several epNACs used so far, the LUMO energy of TNP is the lowest and its HOMO-LUMO energy gap is also minimum. Alternatively it can be said that the LUMO of TNP lies in a favorable energy state to the conduction band of **1** which may favor maximum electron transfer, resulting in quenching of emission intensity of the MOF. One can determine whether the quenching in emission intensity relies on

electron transfer by adding an electron-rich aromatic compound (e.g. toluene) to recover the lost emission. If the fluorescence quenching, mainly, involves the electron transfer process, then addition of electron-rich analytes can recover the lost emission [39], as this can facilitate the transfer of the excited electron from the high-energy LUMO of the analyte to the conduction band of MOF. This electron transfer can enhance the radiative band gap emission and finally yield a recovery in fluorescence. Accordingly, when toluene is added into the system containing TNP and the MOF (i.e. emission-quenched solution), there is no recovery in emission. This fact establishes that the photo induced electron transfer process is not the operating mechanism in the present work.

The Stern–Volmer (SV) plot for **1** (Fig. 7) strongly implies the existence of resonance energy transfer (RET) mechanism between TNP and **1** in the present case $[(I_o/I) = K_{sv}(A) + 1$; where $I_o =$ initial fluorescence intensity of **1** and I = fluorescence intensity in the presence of epNACs for **1**, {*A*} = molar concentration of the nitroaromatic compounds and $K_{sv} =$ quenching constant (M^{-1})]. The non linear feature in the S–V plot of **1** indicates that the quenching process is based on self-adsorption or an energy transfer pathway. The modified SV equation can be used in this regard. The equation, log $(I_o/I - 1) = \log K_{sv} + n \log[Q]$, can be used for the determination of the quenching constant value, where *n* is the number of association



Fig. 6. HOMO-LUMO energy level diagram of some epNACs (violet: LUMO energy level and magenta: HOMO energy level). (Color online).

HOMO-LUMO energy levels of different explosives obtained from theoretical calculations.

| epNACs | LUMO energy (eV) | HOMO energy (eV) | HOMO-LUMO energy gap (eV) |
|---------|------------------|------------------|---------------------------|
| NB | -2.9089 | -7.7484 | 4.8395 |
| 2,6-DNT | -3.4684 | -8.3465 | 4.8781 |
| 3,4-DNT | -3.4782 | -7.9795 | 4.5013 |
| 4-NBA | -3.5818 | -8.1245 | 4.5427 |
| 1,3-DNB | -3.6379 | -8.6121 | 4.9742 |
| TNT | -4.0295 | -8.7427 | 4.7132 |
| TNP | -4.5225 | -8.5892 | 4.0667 |

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Fig. 7. Stern–Volmer (SV) plot of 1 with epNACs.

points between $\mathbf{1}$ and epNACs, I_o is initial fluorescence intensity and 315 *I* is fluorescence intensity of **1** in the presence of epNACs, [Q] is the 316 molar concentration of epNACs and K_{sv} is the quenching constant 317 318 (M^{-1}) . Mathematically, the intercept of the log $(I_0/I - 1)$ versus log 319 [Q] plot gives the K_{sv} . The calculated K_{sv} value is found to be $7.16 \times 10^4 \, \text{M}^{-1}$. The quenching constant value is larger with some 320 321 recently published values e.g. $[Cd_3(TPT)_2(DMF)_2] \cdot (H_2O)_{0.5}$ 322 $(6.56 \times 10^4 \text{ M}^{-1})$ [40]; $[Cd_5(TCA)_4(H_2O)_2]$ $(6.56 \times 10^4 \text{ M}^{-1})$ [41]; 323 $\{ [Cd_4(L)_2(L_2)_3(H_2O)_2] (8DMF) (8H_2O) \}_n$ $(3.89 \times 10^4 \,\mathrm{M}^{-1})$ [42]: $[Cd_4(\mu_3-0)(TTHA)(H_20)_2] \cdot 3H20$ (3.83 × 10⁴ M⁻¹) [43]; { $[Eu_2(-$ 324 TDC)₃(CH₃OH)₂]·CH₃OH} $(1.6 \times 10^4 \text{ M}^{-1})$ [44]; [Zn₈(ad)₄(BPDC)₆-325 $O(2Me_2NH_2)G$ (G = DMF and water) (4.6 × 10⁴ M⁻¹) [45]. The 326 limit of detection for **1** has been found to be 6×10^{-5} M. 327

The resonance energy can be transferred easily from the excited fluorophore to the electron deficient TNP if there is suitable overlapping between the absorption band of TNP with the emission band of the fluorophore **1**. The RET process, mainly, depend on the extent of overlap of the absorption spectrum of TNP with the emission spectrum of the MOF. It is evident from Fig. 8 that among



Fig. 8. Overlap of epNACs absorption spectra with fluorescence spectra of of MOF.

the investigated epNACs the maximum overlap has been observed334between the emission spectrum of 1 and the absorption spectrum335of TNP. For other epNACs the extent of overlap is considerably less.336Therefore, it may be concluded that resonance energy transfer is337responsible for the speedy and selective emission quenching of 1338with high sensitivity towards TNP.339

Nitrophenols are acidic in nature. We examine whether these 340 compounds including trinitrophenol are able to coordinate with 341 the metal center under the experimental conditions when 3-bpd 342 or thiocyanato moieties may vacate coordination site for the nitro-343 phenol. It has been found that phenolic oxygen atoms are unable to 344 bind with the cadmium atom as revealed by the IR spectral studies. 345 FT-IR spectrum was recorded with the recovered compound 1 after 346 its treatment with TNP. Comparison of FT-IR spectra of 1 and 1 347 after recovery shows that they are exactly identical (Fig. s2). This 348 indicates that nitrophenols are unable to replace the existing 349 ligands around the metal center. When we repeat the experiment 350 with 4-NBA instead of TNP, results remain same i.e. 4-NBA is also 351 unable to coordinate with Cd center. Moreover, oxygen atom is 352 hard compared to nitrogen or sulfur and Cd(II) is a soft center. 353 Thus, it is expected the coordination of Cd and N or S will be stron-354 ger compared to Cd and O. 355

3.5. Selectivity of sensing TNP in the presence of other epNACs

It is evident from the previous studies that **1** has high selectivity 357 towards TNP compared to other epNACs. Therefore, it could be 358 interesting to explore the selectivity of 1 towards TNP in the pres-359 ence of other epNACs. The selectivity has been tested by the fol-360 lowing steps: (i) first of all, the emission intensity of 1 in a 361 highly dispersed state in MeCN has been found out; this value is 362 about 490 a.u. (ii) An aqueous solution of 2,6-DNT (10^{-1} M) is then 363 added to the highly dispersed solution of 1 in MeCN, and the cor-364 responding emission is measured. Addition of 2,6-DNT shows a 365 negligible change in the emission intensity of 1. A similar trend 366 has been observed also for the other epNACs (3,4-DNT, 1,3-DNB, 367 4-NBA, NB, TNT). In conclusion it can be said that all the epNACs 368 except TNP do not have any noticeable effect on the emission 369 intensity of **1**. (iii) The selectivity has been finally verified by 370 addition of an aqueous solution of TNP to solutions of epNACs 371

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Fig. 9. Selectivity of 1 for TNP in the presence of other epNACs.





(2,6-DNT, NB, 4-NBA, 1,3-DNB, 3,4-DNT, and TNT) containing 1.372Addition of TNP results in appreciable quenching in the emission373intensity (from 490 a.u. to ca. 25 a.u.). These results show the selective sensitivity of 1 for TNP even in the presence of several other374epNACs (Fig. 9).376

3.6. Recyclability and recovery experiments

Fig. 10 shows that the fluorescence intensity remains almost same after four cycles of TNP sensing compared to the MOF's initial state. This result suggests that the material have high stability and recyclability for TNP detection. The recyclability of MOF is comparable with recent reports of MOFs in related area [40,46].

Complex 1 is insoluble in common solvents including water. It 383 is recovered by simple filtration. There is no detectable amount 384 of Cd in the solution after recovery of the complex. If 1 were disso-385 ciated in aqueous medium, then free 3-bpd should have been 386 found the medium. It has distinct fluorescence peak and spectrum. 387 But we did not get any other peak. Dissociation of the MOF in water 388 would also produce Cd²⁺ ion. Interaction of Cd²⁺ with sulfide ion in 389 slightly acidic or basic medium produces precipitation of CdS 390 which is yellow in color [47]. Addition of sufficient amount of 391



Fig. 11. Quenching in emission intensity of 1 upon gradual addition of TNP solution in river water.

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392 sodium sulfide to the filtrate after recovery of the complex does 393 not produce any precipitation confirming no dissociation of **1** in 394 water.

395 3.7. Detection of TNP in river water

396 Apart from being a highly explosive material, TNP is also a toxic 397 pollutant. When it enters into mammalian metabolic system it is 398 converted to mutagenic picramic acid. Municipality water is generally supplied from river, lake, sea, ocean after its purification. 399 Water from river Ganga is used in Kolkata, India. Contamination 400 of TNP in this river water is possible due to the presence of the 401 industrial wastes. This kind of contamination may create severe 402 403 health hazard. Therefore, selective detection of TNP is necessary 404 not only in deionized water but also in water obtained from natural resources. For this purpose different river water specimens have 405 406 been collected from Ganga at Diamond Harbour (60 km downstream from Kolkata, specimen 1) and Barrackpore (30 km 407 408 upstream from Kolkata, specimen 2). To ensure the effectiveness 409 of the MOF, different sets of TNP solution (1 mM) have been pre-410 pared separately with the water (specimen 1 and specimen 2) 411 and its influence on the MOF dispersed acetonitrile solution has been monitored. A highly appreciable quenching of emission inten-412 sity has been observed in each case (Fig. 11). It should be men-413 414 tioned here that water sample without TNP (black line) showed 415 no influence on emission spectrum of 1. Thus, it can be said that 416 irrespective of the source of water, the emission intensity of 1 is 417 always guenched in the presence of TNP. Therefore, 1 can be trea-418 ted as a universal sensor for TNP.

4. Conclusion 419

In this article, synthesis and characterization of a new Cd-based 420 421 MOF $[Cd(3-bpd)(N(CN)_2)_2]_n$ have been possible and the fluorescence quenching of this MOF in the presence of TNP extensively 422 423 studied. It has been found that the TNP sensing capability of the MOF is highly selective even in the presence of other nitroaromatic 424 425 compounds. Apart from studying its sensitivity towards TNP in 426 deionized water, it has been observed that its sensitivity remains intact in river water. This eventually established this Cd-based 427 MOF as a universal sensor for TNP-like organic explosives and 428 mutagenic pollutants. 429

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Appendix A. Supplementary data 437

CCDC 1501522 contains the supplementary crystallographic 438 439 data for **1**. These data can be obtained free of charge via http:// 440 www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge 441 Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, 442 UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in 443 444 the online version, at http://dx.doi.org/10.1016/j.poly.2016.11.039.

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