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Fluorescent MOFs for selective sensing of toxic cations (TI^{3+}, Hg^{2+}) , highly oxidizing anions $[(CrO_4)^{2-}, (Cr_2O_7)^{2-}, (MnO_4)^{-}]$

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Abstract: The ligand 4,4'-(benzothiadiazole-4,7-diyl) dibenzoic acid was synthesized and employed for the synthesis of two metal organic framework (MOF) compounds, [Mn₄(C₂₀H₁₀N₂O₄S)₂(HCOO)₄(DEF)₂], I and [Pb(C₂₀H₁₀N₂O₄S)(DMF)], II. Single crystal structural studies reveal that compound I has a three dimensional structure and compound II has a two dimensional structure. The luminescent nature of the MOF was gainfully employed as a probe for the detection of highly toxic metal ions such as TI³⁺ and Hg²⁺ ions. The detection limits were found to be in the ppb level. The presence of free S of the ligand appears to help in the detection of these highly toxic metal ions in solution as the metal ions interacts with S, which was revealed employing Raman spectroscopic studies. The compounds were also found to be good candidates for the detection of highly oxidizing anions such as chromate, dichromate and permanganate again in ppb levels of concentration in solution. Magnetic studies on compound I indicate antiferromagnetic behavior. The variable temperature electrical conductivity studies indicate semiconducting nature with comparable behavior to the well known semiconductors such as CdSe. ZnTe. GaP etc.

Introduction

The detection of toxic metals in solution is emerging to be an important area of study. Currently, much effort is being devoted to the rapid detection of many hazardous chemicals that include dangerous explosives and toxic metal ions.^[1-6] It becomes important that the detection of hazardous chemicals needs to be both rapid as well at lower concentrations (trace). A number of different techniques have been employed in this direction and the electrochemical method appears to be the dominate one.^[7-9] The electrochemistry based approaches, however, require considerable care in the preparation of suitable electrodes and the method, in general, are cumbersome and expensive. Fluorescence based methods offer excellent alternate approaches towards the detection of heavy toxic metals such as mercury.^[10-12]

Metal-organic framework (MOF) compounds have been explored extensively for many promising applications such as catalysis, sorption, chemical sensors etc.^[13,14] In this connection, the possibility of incorporating new fluorescent ligands, that can selectively bind heavy metals, as part of the MOF framework can open up many interesting new avenues. Thus, many luminescent MOFs have been developed over the years as potential candidates for chemical sensors.^[15,16] The luminescent MOFs exhibits considerable changes in their luminescent

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intensity when the analyte molecules or ions interact.^[17,18] The selectivity as well as sensitivity depends on the available electron density at the MOFs. Normally, electron rich π -conjugated fluorescent ligands make an excellent candidate for fluorescence based sensing.^[19, 20]

Another approach to detect heavy metal ions such as mercury, cadmium, thallium etc. could be to utilize the affinity of the metal ions to specific functionality in the organic ligand. In this direction, one can attempt to utilize the HSAB theory,^[21] which would form a good basis for the detection of such metal ions. It may be noted that the majority of the toxic heavy metal ions are classified as soft acids. It may be possible to design suitable ligands containing soft bases such as sulfur, nitrogen etc., which would facilitate favorable interactions between the toxic metal ions and the soft bases leading to changes in the fluorescence intensity of the compounds.

Using these strategies, we have developed the ligand, 4,4'-(benzothiadiazole-4,7-diyl) dibenzoic acid (Scheme -1), as possible linker for the preparation of MOFs. Our efforts were successful and we have prepared two new MOF compound, $[Mn_4(C_{20}H_{10}N_2O_4S)_2(HCOO)_4(DEF)_2]$ (I), $[Pb(C_{20}H_{10}N_2O_4S)(DMF)]$ (II) and explored them for possible use as functional sensors for metal ions, anions and adsorbents for harmful dye molecules. In this paper, we present the synthesis, structure, selective detection of toxic metal ions such as thallium (TI^{3+}) and mercury (Hg^{2+}) as well as the detection of chromate, dichromate and permanganate ions from water at room temperature.

Results and Discussion

Structure of [Mn4(C20H10N2O4S)2(HCOO)4(DEF)2], (I) . The compound crystallizes in $P2_1/c$ space group and the asymmetric unit consists of four crytallographically independent Mn²⁺ ions (Mn1, Mn2, Mn3 Mn4), two N, N'- diethyl formamide molecules, four formate and two 4,4'-(benzothiadiazole-4,7-diyl) dibenzoate ions. Each ligand is bonded to four Mn2+ ions (Mn1, Mn2, Mn3, Mn4) (Figure S1a in the Supporting Information). All the manganese centers are octahedrally coordinated with oxygens from the carboxylate, formate and N, N'- diethyl formamide (Figure S1b in the Supporting Information). The formate ion in I resulted by the hydrolysis of N, N'- diethyl formamide employed as the solvent during the synthetic conditions. Similar hydrolysis of N, N'- dimethyl formamide molecules forming formic acid have been reported earlier.^[22] The Mn-O bond lengths are in the range of 2.075(3) - 2.306(3) Å, (Average = 2.188 Å) and O-Mn-O bond angles are in the range 71.90(10)° and 175.56(11)° Table S1 in the Supporting Information). The manganese atoms, Mn1 and Mn2 are bridged by the formate ions forming -Mn-O-Mndimers (Figure S2a in the Supporting Information), which are connected together forming a right handed helical one dimensional manganese formate chain (Figure 1a). The right handed helical one dimensional manganese formate chains are bridged by another formate, which connected to a left - handed helical -- Mn-O-Mn- formate chains forming a -- Mn-O-Mn- two dimensional layer (Figure 1b). Identical two dimensional -Mn-

O–Mn– layers are also formed involving Mn3 and Mn4 atoms (Figure S2b, S2c, S2d and S2e in the Supporting Information). The two –Mn–O–Mn– layers (Mn1-Mn2 and Mn3-Mn4) are connected together by the 4,4'-(benzothiadiazole-4,7-diyl) dibenzoate giving rise to the three dimensional structure (Figure 1c). The overall arrangement of the structure gives rise to C-H… π interactions (Figure S3, Table S2 in the Supporting Information).

 $\label{eq:Scheme 1. The reaction scheme employed in the synthesis of 4,4'- (benzothiadiazole-4,7-diyl) dibenzoic acid ligand.$



Structure of [Pb(C20H10N2O4S)(DMF)], (II). The compound crystallizes in $P2_1/n$ space group and the asymmetric unit consists of one crytallographically independent Pb²⁺ ion, one N, N'dimethyl formamide molecule and one 4.4'-(benzothiadiazole-4,7-diyl) dibenzoate ion. The Pb center is coordinated with eight oxygen atoms from the carboxylate and DMF forming a bicapped distorted octahedral geometry (Figure S4 in the Supporting Information). The Pb-O bond lengths are in the range of 2.471(3)-2.912(4) Å, (Average = 2.682 Å). Of the eight Pb-O bonds, we observed three bonds are much longer in the range of 2.863(3)-2.912(4) Å. The longer bonds may be considered as secondary interactions and similar bond distances have been observed earlier.^[23, 24] A detailed bond valence sum calculations^[25] (Table S3 in the Supporting Information) for the Pb-O bonds gave a value of 1.564 when only five shorter Pb-O bonds were considered. On considering the longer Pb-O bonds, we obtained a valence sum of 1.925, which suggested that the Pb is indeed 8-coordinated. The ligand, 4.4'-(benzothiadiazole-4.7-divl) dibenzoic acid bonds with the five metal centers through the carboxylate oxygen (Figure S4 in the Supporting Information). The lead centers are connected by the carboxylate oxygens forming a 4-membered ring, which resembles the secondary building unit, SBU-4, proposed to understand the metal phosphate structure.^[26] The SBU-4 units are connected through their edges forming a one-dimensional -Pb-O-Pb- chain (Figure 2a). Similar SUB-4 units connecting to form a onedimensional chains have been observed in an iron arsenate structure.^[27] The one-dimensional -Pb-O-Pb- chains are connected through the ligand, 4,4'-(benzothiadiazole-4,7-diyl) dibenzoic acid forming a two-dimensional layer structure (Figure 2b). The two-dimensional layers are arranged in a AAA.....

fashion. The bound DMF molecules hang from the metal centers in the inter-lamellar region (Figure 2c). The presence of free N and S atoms and in close proximity (N···S distance = 3.216 Å) suggests some non-covalent N···S interactions between the layers.





Figure 1. (a) The -Mn-O-Mn- connectivity through the formate units forming the right handed one dimensional helical manganese formate chain, (b) The connectivity between the right handed helical -Mn-O-Mn- chain and the left handed helical -Mn-O-Mn- chains forming the two dimensional layer, (c) The three dimensional structure of compound I.

Optical studies. Solid state UV-Vis spectroscopic studies indicated that the ligand exhibits absorption bands at ~ 215 nm, ~ 251 nm, ~ 289 nm, which can be assigned to the π - π^* transitions. The absorption band at ~ 435 nm could be due to the n- π^* transition. Both the compounds (I and II) also exhibited similar absorption bands at ~ 214 nm, ~ 255 nm, ~ 315 nm, which could be due to the π - π^* transition and the absorption

band at ~ 430 nm may be due to the n- π^* transitions (Figure S5 in the Supporting Information). Solid state luminescence for both the compounds (I and II) as well as the ligand were excited employing a wavelength of 420nm. In all the cases, we observed a single emission peak centered around ~500nm for the compounds (I) and (II). This band may be due to the π^* - π transition of the ligand (Figure S6 in the Supporting Information). Similar bands have been observed and reported in the literature.^[28]



Figure 2. (a) View of the one-dimensional -Pb-O-Pb- chain in II, the SUB-4 unit is highlighted (see text) (b) The connectivity between the -Pb-O-Pb-chains through the carboxylate forming the two-dimensional layer structure, (c) The arrangement of layers of II, [Pb($C_{20}H_{10}N_2O_4S$)(DMF)].

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) were carried out in oxygen atmosphere (flow rate = 40 mL/min) in the temperature range 30-800 °C (heating rate = 10 °C/min). For compound I we observed a three-step weight loss. The first step weight loss in the temperature range (245-350°C) was 29% (Figure S8 in the Supporting Information), which corresponds to the loss of two DEF molecules and four formate ions (calculated weight loss 28.3%). The second more sharper loss in the temperature range 350-375°C is followed by a broader tail that extends upto 550°C. The total observed weight loss in this temperature range was ~ 59.4%, which corresponds to the loss of two ligands (calculated weight loss 55.5%). The final calcined product was found to be Mn₂O₃ (JCPDS No: 89-2809) (Figure S29a in the Supporting Information). For compound II a small initial weight loss was observed around 200°C followed by a sharp weight loss at 410°C. The total observed weight loss was found to be ~ 65 %, which corresponds to the loss of DMF and the carboxylate unit (cal. 68.8 %). The final calcined product was found to be a mixture of Pb₃O₄ (JCPDS No: 89-1947) and PbS (JCPDS No: 77-0244) (Figure S29b in the Supporting Information).

Magnetic Studies. Compound I contains Mn and we carried out the study of the magnetic behavior in the temperature range 300-2K (Figure 3a). The magnetic susceptibility increases slowly from 300K up to 10K and then exhibits a sharp increase (Figure S10 in the Supporting Information). The room temperature $\chi_m T$ value (1000 Oe) was found to be 17.34 emu mol⁻¹ K, which is close to the expected spin only $\chi_m T$ values for four Mn²⁺ ions (17.48 emu mol⁻¹ K). The high temperature magnetic data was fitted to a Curie-Weiss behavior in the temperature range 50-300 K, which gave a θ_p value of -36.41 K (inset Figure 3a). The negative value for the θ_p suggests that the magnetic centers are anti-ferromagnetically coupled. The magmetic behavior was initially modeled using the Fischer's expression for the dimer interactions (Figure 3b).

$\chi_{HT} = A \exp(-\Delta/k_BT)/k_BT$

The fitting was latter modified incorporating the term, τ , which accounts for the anti-ferromagnetic interactions at lower temperature.

$\chi_{HT} = A \exp(-\Delta/k_BT)/(k_BT)^{T}$

A value for τ = 0.859, gave a good agreement with the experimental data (Figure 3b). This exponent, T, provides an idea regarding the optimum length scale of the exchange process in the system in the temperature range 300-10K. Below 10 K, the susceptibility value increases sharply, indicating possible ferromagnetic interactions in the low temperature region. The magnetic behavior may be explained from a structural perspective. As mentioned earlier, manganese centers are bridged through the oxygen atoms (O11, O12, O14) with -Mn-O-Mn anlges in the range 98.94(11)°-115.21(12)°, which would support the antiferromagnetic interactions.^[29] Below 10K, the interactions between Mn-centers involving the formate bridges would be more dominant compared to the carboxylate bridged interactions giving rise to the possible ferromagnetic exchanges (Figure S11 in the Supporting Information). A low temperature and low magnetic field M-H study at 2K exhibited a

small hysteresis loop (Figure S12a in the Supporting Information), suggestive of ferromagnetic exchanges. At higher applied fields, the M-H loop (Figure S12b in the Supporting Information) was not observed suggesting that the Mn-centers could exhibit frustration. Similar magnetic behaviour has been observed in Mn-containing MOF compounds.^[30]



Figure 3. (a) The thermal variation of $\chi_m T$ for compound I. Inset shows the $1/\chi_m$ vs. T plot (b) Temperature variation of the magnetic susceptibility (solid black line) with the high temperature data fitted to the Fisher's formula (blue line; $\tau = 1.0$, red line; $\tau = 0.859$) (see text).

Electrical property. There has been considerable interest in the study of organic semiconductors based on benzothiadiazole due to their applications in the area of organic field effect transistors (OFETs).^[31,32] Since the present compounds posses some of these aspects, we desired to explore the DC electrical conductivity of those compounds in the range 200-300K. For this study, the single crystals were powdered and pressed into pellets of 0.4 cm in diameter (thicknesses of 0.034–0.045 cm) and silver paint was coated on both sides. The conductivity values at 300K were found to be in the range of 10⁻¹⁰ S/m for the

Mn-compound and 10⁻⁸ S/m for Pb-compound. The conductivity values for both the compounds increases exponentially with decreasing temperature (Figure S13 in the Supporting Information). The conductivity data was fitted to an Arrhenius plot, which gave values of the activation energy (Ea) as 0.27 eV for I and 0.24 eV for II. The activation energies indicate that the compounds could be semi-conducting and the conductivity could be due to the thermally generated carriers with variable-range hopping. The optical band gap of the compounds were also obtained from the diffuse reflectance data using the Kubelka-Munk (KM) method [33] [which is given by the following equation: $F(R) = [(1-R)^2]/2R$, where R is the reflectance, F(R) is the KM function]. From the Tauc Plot ($[F(R) \times hu]^{1/2}$ vs hu), the band gap values were found to be 2.41 eV for I, 2.42 eV for II and 2.47 eV for the ligand (Figure S14 in the Supporting Information). As can be noted, the band gap values for the present compounds is comparable with some of the well-known semiconductor materials, such as CdSe, CdTe, ZnTe, GaP, etc.[34-36]

Metal ion sensing. The present compounds possess free S and N functionality, which may be exploited. Both S and N can be considered as soft bases, according to the HSAB theory [21] and may facilitate binding of heavier and toxic chemicals. To this end, we have attempted metal sensing studies using both the compounds by simple fluorimetric analysis. In a typical study, 1 mM solution of the respective metal ions (Mg2+, Mn2+, Fe2+ Co2+, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺, Hg²⁺, Tl⁺, Tl³⁺, Pb²⁺) and 3mg of the compound I and II dispersed in 15 mL of water was taken. For the fluorescence measurements 2.5mL of the MOF solution was taken and an excitation wavelength of 420nm was employed. The metal ion detection studies were carried out by the incremental addition of the metal ions solution to the MOF dispersed solution. The variations in the fluorescence intensity was monitored and measured as a function of the quantity of addition of the metal ion solution. We observed a gradual decrease in the fluorescence intensity on addition of TI3+ and Hg²⁺ solutions (Figure 4). The fluorescence intensity, however, did not change significantly in case of other common metal ions (Figure 5). The effect of fluorescence quenching was analyzed by the Stern-Volmer equation, $I_0/I = 1+K_{SV}[M]$, where I_0 and I are the emission intensities in the absence and presence of the metal ions, respectively, [M] is the concentration of the metal ions, Ksv is the Stern-Volmer constant. The value of Ksv was determined from the slope of I_0/I vs. [M] plot (Figure S15 in the Supporting Information). The Ksv values were found to be 195270 M⁻¹ and 21000 M⁻¹ for TI³⁺ and Hg²⁺ for I and 21900 M⁻¹ and 3300 $M^{\text{-1}}$ for TI^{3+} and Hg^{2+} for II. The larger Ksv value suggests better sensitivity of the present compounds towards the detection of TI3+ and Hg2+ ions in solution. The possible recycling of these compounds for the detection of TI³⁺ and Hg²⁺ ions was attempted and the quenching efficiency of the fluorescence intensity was followed employing the relationship, $[(I_0 - I)/I_0] \times 100$ (%), where I₀ is the initial emission intensity and I is the intensity after the addition of the metal solution. The quenching efficiency for the repetitive measurements appears to be similar to the fresh sample for the detection of TI³⁺ ions,

whereas the quenching efficiency reduces for the detection of Hg²⁺ (Figure S16 in the Supporting Information). The detection limits for both the ions were estimated and we find that the detection limit was 146 ppb for Tl³⁺, 432 ppb for Hg²⁺ (I) whereas it was 629 ppb for Tl³⁺, 1.82 ppm for Hg²⁺ (II)(Table S5 and Figure S17 in the Supporting Information). The detection limits observed for the Hg²⁺ ions in solution is comparable to those reported before.^[37, 38] The limits of detection for the Tl³⁺ ions are high and the sensitivity remaining more or less constant on repetitive use of the MOF suggests that the present compounds, especially I, could be an excellent sensor for Tl³⁺ ions.

We have also attempted to investigate the selectivity of the present compounds towards both TI^{3+} and Hg^{2+} ions in the presence of other metal ions in solution. This would facilate

identification of these toxic metal ions more precisely. To this end, we have employed a number of metal ions in solution such as Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺, Pb²⁺, Tl⁺ along with Tl³⁺ and Hg²⁺ ions (Figure 6). From the plot, it is clear that the compound I and II is not only sensitive but also selective to Tl³⁺ and Hg²⁺. From the Ksv values it is clear that the Mncompound exhibits better detection sensitivity compared to the Pb-compound. In both the compounds, the Tl³⁺ ions are detected more readily compared to the Hg²⁺ ions. The relative acidities of Tl³⁺ vs. Hg²⁺ ions in solution (both are soft acids according to the HSAB principle)^[39] and their interaction with the free S atom present in the ligand would have played an active role in the detection of these ions. We believe that the detection of these ions proceeds via the soft-acid soft-base idea of Pearson.^[21]





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To confirm and validate this idea, we sought to employ Raman spectroscopy studies. For the 2,1,3-benzothiadiazole molecule, the Raman scattering peak of the N-S bond appears in the region of 840-860 cm⁻¹ on excitation using 514 nm wavelength.^[40] We have employed the same excitation in the Raman spectroscopy analysis of I and II as well as TI³⁺ and Hg²⁺ adsorbed compounds (for this study the compounds I and II

were allowed to be in contact with 10 mM Tl(NO₃)₃ and HgCl₂ solution overnight and the solution was decanted and dried under vacuum). The N-S scattering peak in the Raman spectra appears at 840 cm⁻¹ for I and for the Tl³⁺ and Hg²⁺ adsorbed I give peaks at 826 cm⁻¹ and 824 cm⁻¹, respectively. For compound II the N-S scattering peak appears at 844 cm⁻¹ and the Tl³⁺ and Hg²⁺ adsorbed II exhibit peaks, at 829 cm⁻¹ and 835



Figure 5. The comparison of the fluorescence quenching intensity among the metal ion solutions investigated in the present study: (a) Mn-compound (I), (b) Pb-compound (II).



cm⁻¹ respectively (Figure 7). This clearly indicates that the N-S bond of the ligand is affected during the adsorption of TI³⁺ and Hg²⁺ ions. It is likely that there are interactions between the sulfur of the N-S bond and TI³⁺ / Hg²⁺, which would be responsible for this. This study indicates the presence of free N and S functionality in the ligand aid in the detection of TI³⁺ and Hg²⁺ ions in the solution. Further the stability of the MOF compounds were examined by PXRD (Figure S18 in the Supporting Information).

As part of this study, we desired to explore whether the present compounds can also be employed to detect TI⁺ ions in solution. To this end, we carried out an experiment similar to the study employed for the detection of TI³⁺ and Hg²⁺ ions. The studies indicated a small sensitivity for TI⁺ ions with compound I, whereas compound II exhibited even poorer sensitivity (Figure S19 in the Supporting Information). This suggests that the present compounds are selective towards the detection of TI³⁺ and Hg²⁺ ions in solution by fluorescence spectroscopic technique.



Figure 7. Figure shows the Raman spectra for the MOF compounds along with TI^{3+} / Hg^{2+} ions loaded MOF compounds: (a) Mn-compound (b) Pb-compound. Please note the shift in the Raman peak (see text).

Anion sensing. Once the toxic metal ion sensing based on the interactions between S and the metal ions was established, we wanted to explore whether the present compounds are also useful for the sensing of anions as well. Anion sensing studies using MOFs have been reported earlier.[41] Of the many common anions, we were particularly interested to learn whether the present compounds would be useful for sensing highly oxidizing anions such as chromate $(CrO_4)^{2-}$, dichromate $(Cr_2O_7)^{2-}$ and permanganate (MnO₄)⁻. It is known that the permanganate ions act as pesticide [42] and other related uses. Overexpose to Mn4+ ion can affect the central nervous system (neurotoxicity) through accumulation of the metal ion in brain tissue leading to Parkinson disease.[43] Hexavalent chromium has been well established as a genotoxic carcinogen. Human exposes to Cr6+ ions are at increased risk of developing lung cancer, asthma or damage to nasal epithelia and skin.^[44] Their concentrations in the environment needs to be monitored and controlled. Thus, the upper limit for the presence of Cr⁶⁺ and Mn⁷⁺ ions in solution needs to 50 ppb and 100 ppb, respectively.^[45] In this connection, it may also be noted that the chromate anions are routinely employed by leather industries for tanning and related purpose.^[46] Their presence in the effluents needs to be checked for the prevention of complete environmental damage.

To use the current compounds as possible sensor for chromate, dichromate and permanganate anions, we took 1 mM solution of these ions. In a typical experiment, 3 mg of the MOF compounds was dispersed in 15 mL of water. 2.5 mL MOF solution was taken in a in a cuvette and the anion solutions was added in an incremental fashion. Similar to the metal ion detection, the intensity of the luminescence at 500 nm (λ_{ex} = 420 nm) was monitored (Figure 8). The fluorescence intensity appeared to be affected only in the case of the addition of chromate, dichromate and permanganate anions (Figure 8) and we did not observed any significant changes in the fluorescent intensity in the case of other common anions such as Cl⁻, Br⁻, NO₃⁻, OAc⁻, SCN⁻, CO₃²⁻, PO₄³⁻, SO₄²⁻, ClO₄⁻ (Figure 9).

The sensitivity of detection of the three ions was detected employing the Stern-Volmer equation, which was similar to what was employed during the detection of the metal ions (Figure S20 in the Supporting Information). From the Ksv values, we determined the sensitivity of detection similar to the detection of TI^{3+} and $Hg^{2+}.$ The present compounds exhibited a good detection of 69 ppb, 71 ppb, 303 ppb (for I) and 398 ppb, 153 ppb and 441 ppb (for II) for the $(MnO_4)^-$, $(Cr_2O_7)^{2-}$ and $(CrO_4)^{2-}$ ions, respectively (Figure S21 and Table S6 in the Supporting Information). Thus, the compounds are not only selective but also sensitive for the detection of these ions in solution. The quenching efficiency was calculated employing $[(I_0 - I)/I_0] \times 100$ (%) equation, where I_0 is the initial emission intensity and I is the intensity after the addition of the anion solutions. The quenching efficiency after 3rd cycle of measurement were 95.47 % (for MnO₄⁻), 96.75 % (for Cr₂O₇²⁻), 55.93 % (for CrO₄²⁻) (Mncompound) and 73.79 % (for MnO₄-), 93.51 % (for Cr₂O₇²⁻), 46.89 % (for CrO42-) (Pb-compound) (Figure S22 in the Supporting Information). We also wanted to explore the detection of these ions in the presence of the common ions listed above. Our studies clearly indicated that the present



Figure 8. Luminescence titrations plots between the MOF compounds: For Mn-compound (a) CrO4²⁻, (b) Cr₂O7²⁻, (c) MnO4⁻; For Pb-compound (d) CrO4²⁻, (e) Cr₂O₇²⁻, (f) MnO₄⁻



Figure 9. Comparison of the fluorescence quenching intensity among the different anion solutions (a) Mn-compound (I), (b) Pb-compound (II).

compounds exhibited good selectivity for the detection of these highly oxidizing ions only and we did not observe any significant interference from other ions (Figure S23 in the Supporting Information). In addition, we also examined the possible recyclability of these compounds for the detection of these ions in solution. Thus, the present compounds can be employed for the detection of these ions for upto three times (Figure S23 in the Supporting Information). A PXRD study of these compounds after this study did not reveal any significant changes in the PXRD patterns, which suggests that the compounds are stable (Figure S24 in the Supporting Information).



Figure 10. UV-vis spectra of the MOF compounds dispersed in water and the chromate, dichromate and permanganate ion solutions.

We sought to investigate the possible reason for the selectivity/sensitivity of the present compounds towards the chromate, dichromate and permanganate ions compared to the other common anions examined as part of the study. From our luminescence studies, we observed that the present compounds exhibited a strong emission (π^* - π transition) at 500 nm (λ_{ex} = 420 nm) (Figure S6 in the Supporting Information). This emission falls in the blue-green region of the visible spectrum. The anions, $(CrO_4)^{2-}$, $(Cr_2O_7)^{2-}$ and $(MnO_4)^{-}$ are intensely colored due to the LMCT effect. The absorbance spectra exhibits maxima at 370 nm and 268 nm for the chromate, 354 nm and 260 nm for dichromate and 546 nm, 350 nm, 308 nm and 230 nm for the permanganate ions in solution.[47] The transition would generally, correspond to the transition from the filled oxygen π_p orbitals to the empty manganese 3d orbitals. There could be four ligand to metal transitions possible in a tetrahedral coordination. Thus, in the present case, the observed transitions correspond to t1-e (370nm), t1-t2* (268nm) for chromate, t₁-e (354nm), t₁-t₂* (260 nm) for dichromate, t₁-e (546 nm), t1-t2* (350 nm), t2-e (308 nm), t2-t2 * (230 nm) for the permanganate ions (Figure S25 in the Supporting Information). It is likely that there could be significant overlap between the π^* - π emission band of the compounds with the absorption band of these anions. This favorable interaction would be responsible for the selectivity as well as the sensitivity towards these ions (Figure 10).

Conclusions

The synthesis, structure, and characterization of two new luminescent MOFs based on 4,4'-(benzothiadiazole-4,7-diyl) dibenzoic acid ligand [Mn₄(C₂₀H₁₀N₂O₄S)₂(HCOO)₄(DEF)₂] (I), [Pb(C₂₀H₁₀N₂O₄S)(DMF)] (II) has been accomplished. The luminescences of these MOFs were exploited as a probe for the detection of highly toxic metal ions like thallium, mercury in ppb level. The present compounds exhibit a good degree of selectivity towards Tl³⁺ and Hg²⁺ ions, especially in the presence of many other similar ions. The free S of the ligand would have acted as a soft base and help in the detection of these soft acid

metal ions, which was also confirmed by Raman spectral studies. In addition, highly oxidizing anions such as chromate, dichromate and permanganate were also detected in ppb level employing fluorimetry. The compounds retain their sensitivity and selectivity for the detection of both the cations and anions at least three cycles. Magnetic studies on the Mn-compound suggest antiferromagnetic behavior. The temperature dependent electrical conductivity studies indicate a semiconducting nature, comparable to some well known compounds such as CdSe, ZnTe, GaP etc.

 Table 1. Crystal data and structure refinement parameters for I and II.

Structural	I	II
parameter		
Empirical formula	[Mn ₄ (C ₂₀ H ₁₀ N ₂ O ₄ S) ₂ (HCO O) ₄ (DEF) ₂]	$[Pb(C_{20}H_{10}N_2O_4S)(DMF)] \\$
Formula weight	1350.86	654.66
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/n
a (Å)	38.150(5)	13.848(9)
b (Å)	8.960(5)	4.377(3)
c (Å)	16.245(5)	35.016(2)
α (°)	90	90
β (°)	96.465(5)	93.821(2)
γ (°)	90	90
V (Å ³)	5518(4)	2117.5(2)
Z	4	4
T/K	120	120
ρ (calc/gcm ⁻³)	1.626	2.053
µ (mm ⁻¹)	1.051	8.109
λ(Mo Kα/Å)	0.71073	0.71073
θ range (°)	2.51 - 25.00	2.95- 25.00
R indexes [I > 2σ (I)]	R1 = 0.0577 wR2 = 0.1148	R1 = 0.0232 wR2 = 0.0445
R indexes (all data)	R1 = 0.0897 wR2 = 0.1320	R1 = 0.0341 wR2 =0.0469

^a $R_1 = \Sigma ||F_0| - |F_0||/\Sigma |F_0|; wR_2 = {\Sigma |w(F_0^2 - F_0^2)]/\Sigma [w(F_0^2)^2]}^{1/2}. w = 1/[\rho^2(F_0)^2 + (aP)^2 + bP]. P = [max (F_0 O) + 2(F_0)^2]/3, where a = 0.0355 and b = 8.2024 for I and a = 0.0201 and b = 2.8968 for II.$

Experimental Section

Materials. The chemicals, 4-(methoxycarbonyl) benzeneboronic acid, Tetrakis(triphenylphosphine) palladium(0), TI(NO₃)₃.3H₂O were purchased from Sigma–Aldrich. 1,2-phenylenediamine, thionyl chlorid, bromine, THF, CHCl₃, CH₂Cl₂, N,N-dimethylformamide, N,N'diethylformamide, 1,4-dioxane, potassium carbonate, potassium hydroxide, hydrochloric acid, PbCl₂, $MnCl_2.4H_2O$, HgCl₂ were acquired from SDfine (India). All the chemicals were used without further purification.

Synthesis. The ligand 4,4'-(benzothiadiazole-4,7-diyl) dibenzoic acid was synthesized employing the reported procedure Scheme -1 (in the Supporting Information).^[48, 49]

Synthesis of [$Mn_4(C_{20}H_{10}N_2O_4S)_2(HCOO)_4(DEF)_2$]. A mixture of MnCl₂.4H₂O (79 mg, 0.398 mmol), 4,4⁻(benzothiadiazole-4,7-diyl) dibenzoic acid (50 mg, 0.133 mmol) and N,N'-diethylformamide (7 mL) were taken in a 14 mL Teflon-lined autoclave and heated at 150°C for 3 days. The resulting product contained yellow colored plate like crystals, which were filtered, washed with N, N-diethylformamide and methanol and dried in vacuum. Yield: 79.6 mg (44.3 %). Elemental analysis (%) for [Mn₄(C₂₀H₁₀N₂O₄S)₂(HCOO)₄(DEF)₂] found (calculated): C 47.60 (48.01), H 3.35 (3.43), N 6.34 (6.22), S 4.68 (4.75).

Synthesis of Structure of [Pb($C_{20}H_{10}N_2O_4S$)(DMF)]. A mixture of PbCl₂ (74 mg, 0.266 mmol), 4,4'-(benzothiadiazole-4,7-diyl) dibenzoic acid (50 mg, 0.133 mmol), N, N-dimethylformamide (7 mL) and HClO₄ (20 µL) were taken in a 14 mL Teflon-lined autoclave and heated at 150°C for 3 days. The resulting product contained yellow colored needle like crystals, which were filtered, washed with N, N'-dimethylformamide and methanol and dried in vacuum. Yield: 34.26 mg (39.35 %). Elemental analysis (%) for [Pb($C_{20}H_{10}N_2O_4S$)(DMF)] found (calculated): C 41.89 (42.19), H 2.28 (2.62), N 6.12 (6.42), S 4.71 (4.89).

Initial Characterizations: The ligand was characterized employing ¹H-NMR spectroscopy, UV-Vis spectroscopy and infrared spectroscopy. ¹H-NMR data were collected using Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm using TMS as the internal reference (Figure S34-S36 in the Supporting Information). UV-Vis spectra were recorded at room temperature using Perkin Elmer Lambda 35 spectrophotometer (Figure S5 in the Supporting Information). Solid state photoluminescence studies were carried out at room temperature using Perkin Elmer LS 55 luminescence spectrophotometer (Figure S6 in the Supporting Information). IR spectra were recorded as KBr pellets using a FTIR spectrometer (Perkin Elmer, model no: L125000P) (Figure S7, Table S4 in the Supporting Information). Powder X-ray diffraction (XRD) patterns were recorded in the 20 range 5–50° using Cu K α radiation (Philips X'pert) (Figure S9 in the Supporting Information). The observed PXRD patterns were found to be consistent with the PXRD patterns simulated from the single crystal structure study, indicating the purity of the phase. Elemental analyses (carbon, hydrogen, and nitrogen) were performed in a Thermo Finnigan EA Flash 1112 Series. Thermogravimetric analysis (TGA) (Metler-Toledo) were carried out in oxygen atmosphere (flow rate = 40 mL/min) in the temperature range 30-800°C (heating rate = 10°C / min) (Figure S8 in the Supporting Information). Magnetic studies were carried out in the temperature range of 2-300 K using a SQUID magnetometer (Quantum Design, USA).

Single–Crystal Structure Determination. Suitable single crystals were carefully selected under a polarizing microscope and mounted to a thin fiber loop with the help of paratone oil. Single crystal data were collected at 120 K on an Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector. The X–ray generator was operated at 50 kV and 0.8 mA using Mo K_a (λ = 0.71073 Å) radiation. The cell refinement and data reduction were accomplished using CrysAlis RED.^[50] The structure was solved by direct methods and refined using SHELX-2016/6 present in the WinGX suit of programs (version 1.63.04a).^[51] The hydrogen positions were fixed in a geometrically ideal position and refined employing a riding model. The final refinements included the atomic positions for all the atoms, anisotropic thermal parameters for all the non–hydrogen atoms,

and isotropic thermal parameters for all the hydrogen atoms. The details of the structure solution and final refinement parameters are given in Table 1. The CCDC numbers for the compounds 1539918 (I) and 1539919 (II). These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Luminescent MOF • highly toxic metal ions • highly oxidizing anions • sensing • dye adsorption/desorption

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FULL PAPER

New luminescent MOFs were shown to exhibit considerable selectivity towards toxic metal ions (TI^{3+} , Hg^{2+}), anions such as chromate, dichromate and permanganate ions. Figure shows the fluorescence quenching response towards TI^{3+} and (Cr_2O_7)²⁻ ions in solution.



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Fluorescent MOFs for selective sensing of toxic cations (TI^{3+} , Hg^{2+}), highly oxidizing anions [(CrO_4)²⁻, (Cr_2O_7)²⁻, (MnO_4)⁻]

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