Inorganic Chemistry

Linker-Induced Structural Diversity and Photophysical Property of MOFs for Selective and Sensitive Detection of Nitroaromatics

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S Supporting Information

ABSTRACT: The linker [1,1':3',1''-terphenyl]-4,4',4'',6'-tetracarboxylic acid (H₄L) was used to construct two three-dimensional (3D) metal–organic frameworks (MOFs), namely, { $[Cd_2(L)(L_1)(DMF)(H_2O)]$ -(2DMF)(3H₂O)}_n (1) and { $[Cd_4(L)_2(L_2)_3(H_2O)_2](8DMF)(8H_2O)$ }_n (2) (DMF = *N*,*N'*-dimethylformamide) in the presence of colinkers 4,4'-bipyridine (L₁) and 2-amino-4,4'-bipyridine (L₂), respectively, under solvothermal condition. A small change in the colinker leads to significant differences in the overall structure of the MOFs. Topological analysis



reveals that the framework 1 exhibits 6,4-connected forbidden sub-configuration (FSC) topology, while the framework 2 exhibits twofold interpenetrated and (3,4,4)-connected new network topology with Schläfli point symbol $\{4.6^2\}\{4.6^4.8\}\{4^2.6^2.8^2\}$. The crystallographic investigation reveals the framework 2 having single helix structure, which is further coiled through noncovalent interaction, afforded a double-helix structure similar to DNA. These double helices are further connected through the colinker L_2 to form an overall 3D structure. Besides framework 2 exhibits remarkable fluorescence intensity compared to 1. Framework 2 displayed a strong emission at 457 nm when a sample of 2 was dispersed in ethanol and excited at 334 nm. This emission is selectively and completely quenched in the presence of 2,4,6-trinitrophenol (TNP) allowing its detection in the presence of other nitroaromatic compounds. The quenching constant for TNP was found to be 3.89×10^4 M⁻¹, which is 26 times higher than that of TNT demonstrating greater and selective quenching ability. The emission is restored to its original value when the sample after collected by filtration is dispersed in fresh ethanol for 1 d. Interestingly, when solid 2 is exposed to different nitroaromatic compounds, its emission is quenched selectively in the presence of nitrobenzene. In this case, the emission is restored upon heating the sample to 150 °C for 2 h.

INTRODUCTION

The design and synthesis of metal-organic frameworks (MOFs) have attracted enormous interest owing to the capability these frameworks have of forming diverse structural architectures and a wide range of potential applications.¹ The natures of organic linkers/ligands and metal ions play an important role in directing the structure (dimentionality/ topology) and desired properties of the resulting MOFs.² The porous features and capability of host-guest interactions make them as promising candidates like chemical sensors.³ Particularly, detection of explosive compounds or their precursors in a nondestructive manner is of considerable importance in the present-day security environments.⁴ Organic nitrocompounds 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrophenol (TNP), and 2,6dinitrotoluene (2,6-DNT) are explosive in nature and are extensively used in the manufacture of explosive devices. Among them TNP is considered to be a powerful explosive and is used extensively for making explosive devices and landmines.⁵ Additionally, TNP effect on human health and its usage in the chemical industry may lead to fatal environmental consequences. TNP metabolism gives the byproduct picramic acid (2-amino-4,6-dinitrophenol), which shows 10 times more mutagenic activity than TNP.6 Thus, quick and judicious detection of TNP is very imperative. Although literature is

available on the detection of TNT and TNP7 it is still a challenge to selectively detect TNP, as both of them have extremely strong electron affinity.⁸ We show here that TNP is selectively capable of quenching fluorescence. However, nitrobenzene is a highly toxic substance, and its continued exposure even in trace quantities can lead to severe health problems. Therefore, rapid and sensitive detection of these materials is of extreme importance. Nitroaromatic compounds are electron-deficient in nature and can possibly enter the voids of a porous luminescent MOF that provides electron-rich environment for efficient host-guest interactions leading to modulation of emission.⁹ Li and co-workers reported¹⁰ a highly luminescent MOF whose emission is quenched in the presence of traces of nitroaromatic compounds 2,4-DNT and 2,3dimethyl-2,3-dinitrobutane (DMNB). In a recent paper, an amine-functionalized linker was used to construct a porous luminescent MOF that detects TNP in aqueous medium.¹¹ To have porous MOFs with electron-rich interior, a symmetrical π electron-rich tetracarboxylic acid linker (H₄L) was used with colinkers L_1 and L_2 (Scheme 1) for the construction of two MOFs with Cd(II) ion $\{ [Cd_2(L)(L_1)(DMF)(H_2O)](2DMF) \}$ $(3H_2O)_n$ (1) and $\{[Cd_4(L)_2(L_2)_3(H_2O)_2](8DMF)(8H_2O)\}_n$

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Scheme 1. Ligands Used for the Construction of Metal-Organic Frameworks



(2), respectively (DMF = N,N'-dimethylformamide). It is observed that the presence of the amine group in the colinker L_2 has a profound effect on the overall structure of 2 compared to 1 and results in an unknown network structure for 2. Besides, 2 is highly luminescent compare to 1, can selectively and reversibly detect TNP when dispersed in ethanol medium, and can also detect nitrobenzene vapors in the solid state.

EXPERIMENTAL SECTION

Materials and Method. Reagent-grade $Cd(NO_3)_2 \cdot 4H_2O$, 4,4'bipyridine (L_1), trifluoroacetic anhydride, sodium metabisulfite, 4bromotoluene, and trimethyl borate were purchased from Sigma-Aldrich and used as received. All the solvents were procured from S. D. Fine Chemicals, India, and were purified prior to use.

Physical Measurements. All physical measurements were performed as described earlier.¹² The UV–vis spectra were recorded on a Shimadzu 2450 UV–vis spectrophotometer in ethanol at 298 K. Steady-state emission spectra were obtained using a PerkinElmer LS 50B Luminescence spectrometer at 293 K with excitation and emission band-pass of 2.5 nm. In the solid state, the luminescence studies were performed on a Jobin Yvon Horiba Fluorolog-3 spectrofluorimeter at room temperature.

X-ray Structural Studies. Single-crystal X-ray data of the compounds were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Details of the structure solution and refinements are given in the Supporting Information. Lattice parameters of the compounds, data collection, and refinement parameters are summarized in Table S1, and selected bond distances and bond angles are given in Table S4.

Synthesis of Ligands. Synthesis of the tetra-acid linker H_4L (Scheme S1) was reported by us earlier.¹³ The colinker L_2 was synthesized following a literature method.¹⁴

Synthesis of {[$Cd_2(L)(L_1)(DMF)(H_2O)$](2DMF)($3H_2O$)]_n(1). A mixture containing H_4L (20 mg, 0.05 mmol), L_1 (7.68 mg, 0.05 mmol), and Cd(NO₃)₂·4H₂O (30 mg, 0.1 mmol) in DMF (2 mL) and ethanol (1 mL) was heated at 100 °C under autogenous pressure in a Teflon-lined stainless-steel autoclave for 72 h, followed by cooling to room temperature at the rate of 5 °C h⁻¹. Compound 1 was isolated as colorless block-shaped crystals in ~45% yield. Anal. Calcd for C₄₁H₄₇N₅O₁₅Cd₂: C, 45.82; H, 4.41; N, 6.52%. Found: C, 45.40; H, 4.81 N, 6.24. FT-IR (KBr pellets, cm⁻¹): 3446 br, 2937 w, 1659 s, 1359 s, 1096 m, 775 w, 700 w.

Synthesis of { $[Cd_4(L)_2(L_2)_3(H_2O)_2](8DMF)(8H_2O)$ }_n (2). A mixture containing H₄L (20 mg, 0.05 mmol), L₂ (8.5 mg, 0.05 mmol), and Cd(NO₃)₂·4H₂O (30 mg, 0.1 mmol) in DMF (2 mL) and ethanol (1 mL) was heated at 100 °C under autogenous pressure in a Teflon-lined stainless-steel autoclave for 72 h. When cooled to room temperature at the rate of 5 °C h⁻¹ compound 2 was obtained as colorless block-shaped crystals in ~40% yield. Anal. Calcd for C₉₈H₁₁₈N₁₇O₃₄Cd₄: C, 46.57; H, 4.71; N, 9.42%. Found: C, 46.40; H, 4.80 N, 10.05. FT-IR (KBr pellets, cm⁻¹): 3441br, 2937w, 1653 s, 1391w, 1102 m, 706 s.

RESULTS AND DISCUSSION

Under solvothermal conditions, ligand H_4L reacts with $Cd(NO_3)_2$:4 H_2O in the presence of colinker L_1 to form non-

interpenetrated three-dimensional (3D) MOF { $[Cd_2(L)(L_1) (DMF)(H_2O)](2DMF)(3H_2O)\}_n$ (1; L⁴⁻ = L). The bulkphase purity of the sample is confirmed by comparing the experimental powder X-ray diffraction (PXRD) pattern with the simulated one obtained from the single-crystal data (Figure S5, Supporting Information). Single-crystal study reveals the complex crystallizes in the monoclinic space group $P2_1/c$ (Table S1, Supporting Information), and the asymmetric unit contains two crystallographically independent Cd(II) ions, one L^{4-} ligand, one L_1 ligand, one water molecule, and one DMF molecule (Figure S6, Supporting Information). The structure of 1 consists of a dimeric Cd₂ secondary building unit (SBU) composed from one syn-syn bridging carboxylate, one bridging carboxylate, one terminal chelating carboxylate, and one chelating as well as bridging carboxylate from four different L^{4-} units (Figure 1a). The Cd1 further connected by one L_1



Figure 1. Perspective view of (a) coordination environment around Cd2 SBU and (b) linker L_1 connected between the two layers in 1 leads to the formation of 3D structure.

linker gives rise to seventh coordination, while Cd2 apart from L_1 linker additionally connected by one water and DMF molecules afforded a total of six coordination at the metal center (Figure S6, Supporting Information). The Cd–O (2.201(2)–2.495(3)) and Cd–N (2.290(4)–2.322(4)) bond distances are comparable to those reported earlier.¹⁵ The carboxylate groups bind to the metal ions in different fashion, μ_7 ; η^1 : η^1 : η^1 : η^2 : η^2 : η^0 (Figure S7, Supporting Information) in complex 1.

This connectivity initially leads to the formation of twodimensional (2D) layers, and each 2D layer is further connected by the colinker L1 to an overall non-interpenetrated 3D neutral architecture (Figure 1b). Topological analysis¹⁶ shows the SBU $Cd_2(CO_2)_4(L_1)_2$ is connected by four carboxylate groups and two L_1 colinkers. So it is six-connected node, while the ligand is connected to four SBUs and behaves as a four-connected node. Hence, the structure has a 6,4connected net, and the framework contains forbidden subconfiguration (FSC) topology (Figure 2). The cavity of the framework is occupied by disordered solvent molecules, and hence exact solvent composition is evaluated by the combination of TGA and elemental analysis and agreement with PLATON¹⁷ calculated solvent-accessible void volume (1520 Å³, 34.50%).

When colinker L_2 is in place of L_1 , the complex 2 is formed. Interestingly, presence of an amine group in the colinker L_2 makes the overall structure of 2 very different compared to 1. The phase purity of the bulk material is confirmed by matching the PXRD pattern of bulk material with that of the simulated pattern (Figure S8, Supporting Information). Single-crystal Xray analysis reveals that 2 crystallizes in the monoclinic space



Figure 2. Topological representation, 6,4-connected net with FSC topology of 1.

group P2/m (Table S1, Supporting Information). The asymmetric unit contains two crystallographically independent Cd(II) ions, one L^{4-} ligand, L_2 ligand (one and half occupancy), and one water molecule (Figure 3a). Both metal



Figure 3. (a) A perspective view of the dimeric unit in 2 and (b) space-filling model of 2 viewed along the b axis.

ions exhibit distorted octahedral coordination geometry (Figure S9, Supporting Information). The Cd1 is ligated by four oxygen atoms of two bridging carboxylates from two L^{4-} ligands and two N atoms from two L_2 colinkers. The Cd2 is connected to five oxygen atoms, four from two carboxylate groups of two L^{4-} ligands and one oxygen atom from water molecule, and six coordination is satisfied by one nitrogen atom from colinker L_2 (Figure S9, Supporting Information). In complex 2 the four carboxylate groups of L^{4-} bonded to the metal in chelating mode μ_4 : η^1 (Figure S10, Supporting Information). All bond distances are comparable to those reported earlier.¹⁵

The combination of such carboxylate binding mode and that of the colinker L_2 with Cd(II) ions leads to the formation of single helical chains extending along the crystallographic *b* axis (Figure 4a). Two such helices wrap each other around the same axis through noncovalent interaction (N₅-H··· π , $d_{N-\pi}$ = 3.733(2) Å and N₄-H··· π , $d_{N-\pi}$ = 3.819(3) Å) and N₅···H-C, d_{N-H} = 3.902(2) Å and N₄···H-C, d_{N-C} = 4.023(3) Å) to form a double helix (Figure 4b and Figure S11 Supporting Information) like in DNA. MOFs having double helical structure are very rarely reported in the literature.¹⁸ The pitch of double helix is 20.48 Å, and the radius is 2.5 Å. The stability of the final helical structure relies on the coordinate bonds that each metal makes with the ligand. Each double helix leading to a twofold interpenetrated 3D architecture (Figure 4c).

Topological simplification shows that the framework is 3,4,4c net forming a new network topology with Schläfli point symbol $\{4.6^2\}\{4.6^4.8\}\{4^2.6^2.8^2\}$ (Figure 5). The solvent molecules in the cavity are disordered, and hence the exact solvent composition is evaluated by the combination of thermogravimetric analysis (TGA), elemental analysis, and agreement with PLATON¹⁷ accessible void volume of 2997 Å³ or 51.32% of the unit cell volume. The channel dimension along the *a* direction is 8.799 × 7.751 Å² and in the *b* direction is 6.010 × 5.975 Å², and these channels are decorated with the amine moiety of the linker.

Luminescence Behavior and Sensing Properties. The MOFs are built by d^{10} metal ions, and different π -conjugated organic ligands are expected to be promising candidates for luminescent materials.³ To examine the luminescence behavior, both the complexes are dispersed in ethanol medium, and their emission spectra are recorded at room temperature (RT; Figure 6). Upon excitation at 270 nm, 1 emits at 374 nm, while 2 emits at 457 nm when excited at 334 nm (Figure S12, Supporting Information). Such a red shift in the emission peak of the complex 2 is due to the strong synergistic effect between the neighboring ligands and metal units.¹⁹ The luminescent intensity of complex 2 is much greater than that of 1 in both solid (Figure S13, Supporting Information) and solution medium (Figure 6; 1 mg of each complex in 20 mL ethanol) under the same experimental conditions. The linker L_2 is found to be more fluorescent compared to that of L₁. Also, a close examination of the structures of 1 and 2 reveal that the colinker L_2 is more strongly bound to the metal compared to the binding of colinker L_1 to the metal (Table S4) hindering deactivation in 2. Thus, 2 is more fluorescent compared to 1.

The luminescent property of **2** was investigated and invariant in different solvents like N,N'-dimethylacetamide (DMA), DMF, methanol (MeOH), ethanol (EtOH), acetonitrile, acetone, dioxane, and tetrahydrofuran. Interestingly, when we used nitrobenzene (NB) as a solvent the, however, the emission quenches (Figure 7a and Figure S14, Supporting Information) and remains unperturbed by the other solvents (Figure 7b). Thus, aforesaid observation clearly manifested complex **2** is potential candidate for the detection of NB. Enthused from such an important outcome we further explore the detection of other nitroaromatic compounds (congener of NB), which are explosive in nature.

Fluorescence titrations were performed with different nitroaromatic compounds such as TNP, TNT, 2,6-DNT, 2,4-DNT, 2,4-dinitrochlorobenzene (DNCB), and NB (Figures S15-S19, Supporting Information). Addition of the same amount of analytes (400 μ L) results different extent fluorescence quenching takes place. The quenching efficiency was calculated by using the equation $(I_0 - I)/I_0 \times 100\%$, where I_0 and I are the luminescence intensities of 2 before and after the addition of the analyte, respectively. It was observed that all the analytes quench the fluorescence to some extent except TNP, which shows highly sensitive as well as significant quenching of the fluorescence (94.28%; Figure 8). The quenching efficiency by all the analytes is in the following order: TNP ≫ TNT > 2,6-DNT > NB > 2,4-DNT > DNCB (Figure 9a). To understand such a high sensitivity of complex 2 toward TNP a quenching mechanism was thoroughly investigated. To comprehend the sensing ability of 2 for TNP, the emission spectra were recorded by a gradual addition



Figure 4. A perspective view of (a) single helical chain in 2, (b) double helical chain (c) colinker L_2 connected double helices to the interpenetrated 3D framework, and (d) its space-filling model.



Figure 5. A representation of the new 3,4,4-c net of 2.



Figure 6. Emission spectra of 1 and 2 dispersed in ethanol medium (left) and (right) complex 1 and 2 were subjected to the UV light under the same experimental condition.

of TNP. As shown in Figure 8 the fluorescence intensity of **2** is deliberately decreased with increasing amount of TNP. The

quenching performances were calculated and estimated to be 42.82% for 100 μ L, 76.11% for 200 μ L, 83.99% for 300 μ L, and 94.28% for 400 μ L.

Such diversity in quenching efficiency can be clearly interpreted by using the Stern–Volmer (SV) equation (I_0/I) $= K_{SV}[A] + 1$, where I_0 represents the initial intensity of the of 2 in absence of analyte, I is the fluorescence intensity in the presence of analyte with molar concentration [A], and K_{SV} is the quenching constant (M^{-1}).²⁰ The SV plot for TNP deviates from linearity at low concentration and bending upward upon incremental addition of TNP (Figure 9b), while other analytes give linear variation with concentration in their corresponding SV plot (Figure S20, Supporting Information). This nonlinear nature in the SV plot supports dynamic quenching processes or energy transfer between TNP and the host.²¹ Additionally, the electronic features of the analytes will help us to rationalize the reason behind this sensing ability. Generally, the conduction band (CB) of MOFs lies above the lowest unoccupied molecular orbital (LUMO) of these electron deficient analytes.22

Upon excitation photoinduced electron transfer takes place from the CB band of 2 to LUMO of the analyte leading to the quenching effect.²³ The highest occupied molecular orbital (HOMO)–LUMO energies of the given analytes were calculated by density functional theory by using the B3LYP/ 6-31G* method with Gaussian 09,²⁴ and the obtained results support the maximum quenching for TNP as observed²² (Figure 10b). Such an electron-transfer phenomena is not the sole mechanism behind the reason for high degree of fluorescence quenching efficiency. It has been well-established that when the absorption band of the analytes overlaps with the emission band of the fluorophore (here complex 2) then resonance energy can occur adequately. The extent of resonance energy transfer depends on the spectral overlap between analytes absorption band and emission band of 2. The

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Figure 7. (a) The emission spectra of 2 in the presence of different solvent and (b) fluorescence intensity ratio histograms of 2 dispersed in different solvents (red) and subsequent addition of nitrobenzene (black).



Figure 8. Emission spectra of **2** dispersed in ethanol upon incremental addition of TNP solution (1 mM) in ethanol.

Figure 10a depicts a substantial spectral overlap between the absorption spectrum of TNP and the emission spectrum of 2, and almost negligible overlap happens in all other analytes. These observations clearly support the highest quenching efficiency by TNP compare to the other nitroanalytes. The quenching constant (K_{SV}) value for TNP was calculated and found to be 3.89×10^4 M⁻¹, which indicates strong interaction between TNP and framework 2. It is worth mentioning that this quenching constant value is higher than the many reported

MOFs.⁹ The compound **2** can sense the TNP at very low concentration with a detection limit 1.98 ppm (Figure S21, Supporting Information).

Inspiring of these worthy denouement, next we verified the selectivity of TNP in the presence of other nitro compounds. The selectivity of TNP in the presence of other nitroaromatic compounds was also probed. In a typical experiment, the fluorescence spectrum of **2** was monitored upon addition of each analyte ($400 \ \mu$ L) separately and allowed to stand for 5 h at RT. The spectra showed insignificant changes. Upon addition of TNP ($400 \ \mu$ L) the fluorescence shows considerable quenching in 30 min at RT (Figure 11).

The visual recognition of TNP is also probed due to its relevance in terms of security threats, environmental pollution, and so on. With the addition of 2-3 drops of ethanolic solution of TNP (1×10^{-3} M) to a dispersion of 2 in ethanol monitored under UV light, the bright fluorescence completely vanished within 3 min by naked eye detection (Figure 12). The detection ability of 2 can be revived at least to three cycles by centrifuging the dispersed solution after use and washing it several times with ethanol (Figure S22, Supporting Information). The PXRD pattern after three cycles exactly matches with the initial sample proving its structural integrity (Figure S23, Supporting Information). In a different experiment, when solid 2 is exposed to different nitroaromatic compounds listed above at RT, only NB is able to quench the emission intensity



Figure 9. (a) Quenching efficiency of 2 for different nitroaromatics in ethanol and (b) SV plot of 2 upon incremental addition of TNP solution (1 mM) in ethanol.



Figure 10. (a) Spectral overlap between the absorption band of the analytes and the emission band of 2 and (b) HOMO and LUMO energies of electron-deficient nitroaromatics.



Figure 11. Emission intensity of 2 after the addition of an analytes separately followed by addition of same amount of TNP. In each set, (a, black) = initial intensity of 2, (b, red) = intensity of 2 after addition of an analyte, (c, blue) = after addition of TNP.



Figure 12. Response of 2 to various analytes in ethanol monitored under UV light (left to right) 2 and 2 in the presence of TNT, NB, DNCB, 2,6-DNT, 2,4-DNT, and TNP.

of 2 due to its higher vapor pressure (Figure S24 and Table S2, Supporting Information). Like in case of solution, this solidstate phenomenon is also reversible (Figure S24, Supporting Information).

CONCLUSIONS

In summary, the introduction of amine functional moiety in the linker tailored the structure and the photophysical property of MOF. Importantly the framework 2 showed a double helical

structure similar to DNA and forms a new network topology. The luminescent intensity of 2 is high and is found to be useful in the selective and sensitive detection of TNP. The favorable energy transfer between the electron-deficient TNP and electron-rich 2 efficiently quenches its emission intensity. The construction of different MOFs helps the idea of crystal engineering through the design of linkers to tune their properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02645.

Details of syntheses, including illustrated schemes for synthetic routes to H_4L and L_2 ; table for selected bonds and distances for complexes 1 and 2; complete data for IR, TGA analysis, and PXRD; NMR, UV–vis, and luminescence spectra; perspective drawings including the asymmetric unit in complex 1, the coordination environment around metal centers Cd1 and Cd2, and the carboxylate binding mode of ligand H_4L in complex 2, among others. (PDF)

X-ray crystallographic data in CIF format. (CIF)

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Notes

The authors declare no competing financial interest.

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