Series of Cadmium(II) Coordination Polymers Based on a Versatile Multi-N-Donor Tecton or Mixed Carboxylate Ligands: Synthesis, Structure, and Selectively Sensing Property

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Supporting Information

ABSTRACT: Five Cd(II) metal–organic frameworks (MOFs), \([\text{Cd(HL)}_{2}],\) \([\text{Cd(HL)}_{2}(\text{bipy})],\) \([\text{Cd(HL)}_{2}(\text{H}_{2}\text{O})],\) \([\text{Cd(HL)}_{2}(\text{obda})],\) \([\text{Cd(HL)}_{2}(\text{ohmbda})(\text{DMA})(\text{H}_{2}\text{O})],\) \([\text{Cd(HL)}_{2}(\text{btca})(\text{H}_{2}\text{O})],\) \([\text{Cd(HL)}_{2}(\text{btc})(\text{H}_{2}\text{O})],\) \([\text{Cd(L)}_{2}(\text{bipy})],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{obda})_{2}],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{btca})_{2}],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{btc})_{2}],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{btca})(\text{btc})_{2}],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{btca})(\text{btc})(\text{btc})_{2}],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{btca})(\text{btc})(\text{btc})(\text{btc})_{2}],\) \([\text{Cd}_{3}(\text{HL})_{2}(\text{btca})(\text{btc})(\text{btc})(\text{btc})(\text{btc})_{2}]\) were prepared by reactions of \(\text{Cd(NO}_3)_2\cdot\text{4H}_2\text{O}\) with \(1(1\text{H-imidazol-4-yl})-4(4\text{H-tetrazol-5-yl})\)benzene (\(\text{H}_3\text{L}\)) or mixed carboxylate auxiliary ligands of \(1,2\text{-benzenedicarboxylic acid} \,(\text{H}_2\text{obda}),\) \(5\text{-hydroxy-1,3-benzenetricarboxylic acid} \,(\text{H}_3\text{btc}),\) respectively. Their structures have been characterized by single-crystal X-ray diffraction, elemental analysis, infrared spectroscopy (IR), thermogravimetric analysis, and powder X-ray diffraction. Compounds 1 and 2 are supramolecular isomeric frameworks without consideration of the solvent molecules. Complex 1 exhibits a binodal \((3, 5)-\)connected two-dimensional \((2D)\) layer structure with the point (Schläfli) symbol of \((5^2-6^2)(5^6-6^7),\) while complex 2 shows a \(2D + 2D \rightarrow 3D\) \((3\text{-dimensional})\) framework. Complex 3 is a \((3, 5, 6)-\)connected tetranodal \(3D\) network with the point (Schläfli) symbol of \((4\cdot s^3)(4\cdot s^6-6\cdot s^8)(4\cdot s^6-6\cdot s^8),\) \((4\cdot s^6-6\cdot s^8).\) Compound 4 is a \((3, 5, 8)-\)connected trinodal \(3D\) net with the point (Schläfli) symbol based on a binuclear \([\text{Cd}_2\text{N}_2\text{O}]\) subunit, while 5 is a 2-nodal \((3, 4)-\)connected 2D \(\text{V}_2\text{O}_5\)-type network based on \([\text{Cd}_3\text{N}_2(\text{COO})_2]\) \(\text{SBU}.\) The studies of molecular sensing properties show that the luminescent MOFs can be employed as fluorescent sensors for the detection of \(\text{Fe}^{3+}\) and nitro compounds. Compound 1 and 3 exhibit quenching responses for \(\text{Fe}^{3+}\) in dimethylformamide solution with detection limits of \(2.3 \times 10^{-5}\) and \(8.6 \times 10^{-7}\) M, respectively. Meanwhile, compound 5 can sense 4-nitrophenol with a detection limit as low as \(5.75 \times 10^{-7}\) M.

INTRODUCTION

Metal–organic frameworks (MOFs) have aroused enormous interest in the field of crystal engineering because of their fascinating structures and potential applications such as gas storage and separation,\(^{1-3}\) catalysis,\(^{30}\) luminescence, and sensing.\(^{7-12}\) Structurally, MOFs are infinite structures constructed from organic ligands and metal ions/clusters connected via coordination interactions. Therefore, the functionalities of MOFs are mainly attributable to the nature of the organic ligands and metal centers.\(^{13,14}\) For example, the luminescent MOFs consisting of π-conjugated organic ligands and \(\text{d}^{10}\) metal centers possess excellent luminescence emission properties and have received particular attention as chemical sensors for sensing nitroaromatic compounds and heavy-metal ions because of their high selectivity and sensitivity, quick response, and recoverability.\(^{15-21}\) For example, the Wang group synthesized the complex \([\text{Tb}^3\text{L}_1\text{S}(\text{H}_3\text{O})_5][\text{DMA}-\text{4H}_2\text{O}],\) \([\text{N}-\text{heterocyclic dicarboxylic} \,(2\text{-pyrimidin-5-yl})\] terephthalic acid \((\text{H}_3\text{L})\) ligand], which can sense \(\text{Fe}^{3+}\) as low as \(7.13 \times 10^{-5}\) M.\(^{22}\) Similarly, the crystalline product of \([\text{Cd}(\text{L}_2)0.5(\text{bipy})]\) shows highly selective sensing property for \(\text{Fe}^{3+}\) ions.\(^{23}\) As for the organic ligands, both of the nitrogen-rich ligands and carboxylic acids are most effective building units for the assembly of various MOFs because the multi-N and \(-\text{O}\) coordination atoms are easily apt to link with metal centers.\(^{24-27}\) Particularly, the polyazaheteroaromatic ligands can exhibit flexible coordination modes to build diverse MOFs.\(^{28-33}\) In our previous study, we have deliberately designated multi-N-donor ligands containing \(1\text{H-imidazol-4-yl}\) groups to construct a series of porous frameworks exhibiting favorable gas adsorption properties because of the increasing interaction between the adsorbate and uncoordinated N binding sites as elaborately elucidated by Grand Canonical Monte Carlo simulation calculations.\(^{34-36}\) Besides the polyazaheteroaromatic ligands, carboxylic acid ligands are another kind of building units for constructing MOFs due to...
Table 1. Crystal Data and Structure Refinements for Complexes 1–5

|   | 1            | 2            | 3            | 4            | 5            |
|---|--------------|--------------|--------------|--------------|--------------|
| empirical formula | C$_2$H$_5$N$_2$Cd | C$_2$H$_5$CdN$_2$O$_2$ | C$_2$H$_5$N$_2$Cd$_3$ | C$_2$H$_5$N$_2$O$_2$Cd$_2$ | C$_2$H$_5$CdN$_2$O$_{14}$|
| formula weight | 534.83 | 570.86 | 1087.86 | 843.34 | 723.13 |
| temperature (K) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) |
| crystal system | monoclinic | orthorhombic | triclinic | monoclinic | triclinic |
| space group | P2$_1$ | Pbam | P2$_1$/a | P2$_1$/a | P2$_1$/a |
| a (Å) | 7.166(5) | 7.4200(4) | 19.0296(10) | 7.5530(3) |
| b (Å) | 13.146(10) | 12.3456(11) | 8.9874(5) | 9.4786(4) |
| c (Å) | 10.4528(8) | 14.0486(8) | 25.2908(14) | 17.6028(8) |
| $\beta$ (deg) | 90.004 | 74.007(10) | 90.7987(10) | 90.8295(10) |
| $\gamma$ (deg) | 90.004 | 90.004 | 90.7987(10) | 90.8295(10) |
| $\nu$ (Å$^3$) | 937.18(12) | 2330.4(3) | 849.56(8) | 3094.7(3) |
| $\nu$ (deg) | 1.004 | 1.059 | 1.185 | 1.026 |
| $\nu$ (cdcm$^{-1}$) | 1.083 | 1.158 | 1.185 | 1.026 |
| $\nu$ (ff) | 0.803 | 0.0228 | 0.0340 | 0.0274 |
| $\nu$ (ff) | 0.0203 | 0.0443 | 0.0173 | 0.0173 |
| Z | 2 | 4 | 1 | 4 |
| $\overline{Z}$ | 2 | 2 | 2 | 2 |
| $\delta$ range (deg) | 2.05–25.50 | 2.50–27.67 | 1.16–25.01 | 1.18–27.68 |
| reflections collected | 892 | 530 | 10578 | 17699 |
| independent reflections | 3160 | 3911 | 5405 | 5366 |
| goodness-of-fit on $F^2$ | 1.004 | 1.043 | 1.063 | 1.026 |
| $R_1$ = [1 > 2σ(I)] | 0.0203 | 0.0228 | 0.0340 | 0.0274 |
| wR$_2$ = [1 > 2σ(I)] | 0.0790 | 0.0793 | 0.1184 | 0.1071 |

$R_1 = \frac{\sum|F_o| - |F_c|/\sum|F_o|, wR_2 = \frac{\sum(w|F_o|^2 - |F_c|^2)/\sum|F_o|^2)^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (ap)^2 + bP]. P = (F_o^2 + 2F_c^2)/3.$

The variable coordination modes for the carboxyl group.\textsuperscript{37–42} Furthermore, the mixed polyazaheteroaromatic ligands and carboxylic acid ligands have favorable compatibility, benefiting to construct diverse MOFs.\textsuperscript{43–45} Using the mixed ligands strategy including polyazaheteroaromatic and carboxylic acids ligands, a series of MOFs with novel structures have been constructed based on 4-imidazolyl ligands and auxiliary carboxylic acid ligands together with varied metal salts.\textsuperscript{46–48} In this paper, we focus our attention on the study of reactions of the π-conjugated 1-(1H-imidazol-4-yl)-4-(4H-tetrazol-5-yl)benzene (H$_2$L) ligand together with varied carboxylate ligands to react with metal Cd(II) salts and obtain a series of Cd(II) complexes. Photoluminescence and molecular sensing properties were investigated.

RESULTS AND DISCUSSION

Crystal Structure of [Cd(HL)$_2$] (1). Complex 1 crystallizes in the monoclinic form with P2$_1$ space group (Table 1) and one Cd(II) atom, two kinds of partially deprotonated HL$^-$ ligands are included in the asymmetric unit. Figure 1A shows the central Cd(II) atom with distorted square-pyramidal coordination geometry is five-coordinated by five N atoms from five individual HL$^-$ ligands. The H$_2$L ligand is deprotonated to give HL$^-$ ligands with variable coordination modes, as shown in Scheme 1 (I and II). Two kinds of deprotonated HL$^-$ anions act as μ$_2$, or μ$_1$ bridge to connect two or three Cd(II) atoms and balance the charges of the framework, respectively. Particularly, a kind of HL$^-$ ligand employs μ$_1$ bridge to link Cd(II) atoms to form a two-dimensional (2D) [Cd(HL)$_2$]$^{2+}$ network in the ab plane, while the other HL$^-$ acts as linear two-connector to link two adjacent Cd(II) atoms up and down the [Cd(HL)$_2$]$^{2+}$ 2D layer, forming the [Cd(HL)$_2$]$^{2+}$ double layer (Figure 1B). Topologically, two kinds of HL$^-$ ligands link two or three Cd(II) atoms, in turn, being treated as 2- and 3-connected nodes, respectively. Cd1 can be regarded as a S-connector because it links five HL$^-$ ligands. Topological analysis calculated by the TOPOS program\textsuperscript{47} suggests that 1 is a binodal (3, 5)-connected 2D net with a point (Schläfli) symbol of (5$^2$6$^3$)-6$^7$ (Figure 1C). Furthermore, the adjacent 2D layers are linked together by N–H···O and C–H···O hydrogen bonds to generate a three-dimensional (3D) structure (Figure 1D and Table S2).

Crystal Structure of [Cd(HL)$_3$(H$_2$O)$_2$] (2). When the reaction solution of 1 was instead of N,N$'$-dimethylacetamide–H$_2$O mixed solution, a new supramolecular isomeric framework of 2 was isolated. Complex 2 crystallizes in the orthorhombic Ibam space group (Table 1). The asymmetric unit of 2 contains a Cd(II) atom with a quarter of occupancy, a half of deprotonated HL$^-$ ligand, and a half of coordinated water molecule. The Cd(II) center is located at an inversion center with an [Cd(N$_2$O$_3$)$_4$] octahedral coordination environment by four nitrogen and two oxygen atoms from four HL$^-$ anions and two terminal water ligands (Figure 1A). Four deprotonated HL$^-$ anions connect four Cd(II) ions to afford a [Cd$_4$(HL)$_4$]$^2+$ square unit (Figure 2B), where the lateral Cd···Cd distances are 14.33 and 14.36 Å. In 2, each HL$^-$ act as a linear connector to link two Cd(II) ions to form a 4$^2$-sq net along the bc plane (Figure 2B). The large rectangular windows lead to mutually inclined interpenetration with another layer with an angle of 63.41° (Figure 2C), forming a 2D + 2D → 3D inclined polycatenation architecture (Figure 2D).

Crystal Structure of [Cd(HL)$_3$(obda)$_2$] (3). When ancillary ligand 1,2-benzenedicarboxylic acid was added to the reaction system of 2, a different complex 3 was isolated. Compound 3 crystallizes in the triclinic space group P1, and the asymmetric unit consists of one and a half of Cd(II) atoms, one partially deprotonated HL$^-$ ligand, and one obda$^-$ ligand. Figure 3A shows that Cd1 has an octahedral coordination by four nitrogen and two oxygen atoms from four HL$^-$ anions and two terminal water ligands (Figure 1B). Topologically, two kinds of HL$^-$ ligands form the basal plane, while two N atoms from two individual HL$^-$ anions occupy the apical positions. The seven-coordinated Cd2 atom is surrounded by two N atoms (N2C, N5) from two different HL$^-$ ligands, five O atoms (O1, O3, O1A, O3B, and O4B) from four carboxylate groups of three.
obda$^{2-}$ ligands (Figure 3A). The Cd–O distances range from 2.292(2) to 2.583(3) Å, Cd–N distances are in the range of 2.225(3)–2.301(3) Å, and the coordination angles around Cd centers vary from 50.55(7) to 180.00(12)° (Table S1). Each obda$^{2-}$ in 3 acts as a $\mu_5$ bridge to link five Cd(II) atoms adopting $\mu_3$-$\eta_1$-$\eta_2$ bridge and $\mu_3$-$\eta_2$-$\eta_2$ bridge coordination modes. When the connections via HL$^-$ are ignored, the Cd(II) atoms are linked through the obda$^{2-}$ ligands to form a 2D [Cd$_5$(obda)$_2$]$^{2+}$ layer (Figure 3B). The just ignored HL$^-$ ligands that link three Cd(II) atoms between adjacent 2D layers to form a pillar-layered 3D structure (Figure 3C). Topologically, each 3-connected HL$^-$ ligand can be treated as a linear 3-connector, while each obda$^{2-}$ ligand links five Cd(II) atoms and can be regarded as a 5-connector. Each Cd1 is a 6-connected node because it links two HL$^-$ ligands and four Cd(II) atoms, while Cd2 is 5-connected node since it links two HL$^-$ and three obda$^{2-}$ ligands. Therefore, the overall structure of 3 is a (3, 5, 6)-connected tetranodal 3D net with stoichiometry (3-c)$_2$(5-c)$_4$(6-c) (Figure 3D) with the point (Schläfl) symbol of (4·8·4·8·4·6·8·5·6·8·6·8).

Crystal Structure of [Cd$_2$(HL)$_2$(ohmbda)(DMA)(H$_2$O)] (4). When the auxiliary ligand of H$_2$obda in 3 was changed to H$_2$ohmbda, a new compound 4 was obtained. There are two unique Cd(II) atoms, two different HL$^-$ ligands, half of the complete deprotonated ohmbda$^{2-}$ ligand, and one $\mu_2$-bridge water molecule in the asymmetric unit. Both Cd(II) atoms

Scheme 1. Flexible Coordination Modes of H$_2$L and Carboxylic Acid Ligands Appearing in Complexes 1–5

![Diagram](https://example.com/diagram.png)
have the same distorted octahedral coordination geometry with a N₄O₂ coordination sphere (Figure 4A). Different from the complexes 1–3, two different HL⁻ ligands have the same coordination modes, serving as 4-connector to ligate four Cd(II) atoms. The tetrazole fragment from the HL⁻ ligand utilizes the positions of 1, 2, 4-N atoms in μ₂-N₁, N₃, N₄ and link three Cd(II) atoms (type V, Scheme 1), while another imidazole group links one Cd(II) atom. In this sense, one kind of HL⁻ ligands (labeled as N₁, N₂) act as 4-connector to link Cd(II) atoms, forming a 2D network (Figure 4B). Meanwhile, each ohmbda²⁻ ligand acts as a μ₂-bridge to connect adjacent two Cd(II) atoms up and down the 2D layer. In the 2D layer, two Cd(II) atoms together with the two tetrazole fragments from the HL⁻ ligand and a μ₂-bridge water molecule form a binuclear [Cd₂N₄O] subunit with a Cd···Cd distance of 3.88 Å. On the other hand, the other kind of HL⁻ ligands pillar the Cd(II) atoms from the adjacent 2D network to form a 3D structure (Figure 4C). Therefore, the 3D framework of [Cd₂(HL)₂(ohmbda)(H₂O)] is a layered-pillared net, where the layer is a [Cd₂(H₂O)(ohmbda²⁻)(HL⁻)]⁺ sheet and the pillar is HL⁻ ligands (Figure 4D). Topologically, both of the different HL⁻ ligands are neighbored by three binuclear [Cd₂N₄O] subunits, which can be viewed as a 3-connector (Figure S1). Meanwhile, each binuclear [Cd₂N₄O] subunit is an 8-connected node because it ligates six HL⁻ ligands and two [Cd₂N₄O] subunit SBUs (Figure S1). Thus, 4 is a (3, 8)-connected 3D network with the point (Schläfl) symbol of (4·5²)⁴(4·5¹⁰·6⁸·7⁴·8³).

Crystal Structure of [Cd₂(HL)(btc)(H₂O)₂]·3H₂O (5).

When the auxiliary ligand was changed to 1,3,5-benzenetricarboxylic acid, compound 5 was obtained. The asymmetric unit contains two unique Cd(II) atoms, one HL⁻, one btc³⁻ ligand, and two coordinate and three lattice water molecules. Cd1 is six-coordinated by five O atoms from three btc³⁻ ligands, one N atom from one HL⁻ ligand (Figure 5A), and one water molecule, forming a distorted octahedral coordination geometry, while Cd2 is a distorted square-pyramidal coordination geometry with a N₂O₃ donor set. The HL⁻ ligand adopts μ₂-N₁, N₂ of the tetrazole group and the N₁ position of the 4-imidazole group to coordinate with the Cd(II) atom (type VI, Scheme 1). Each btc³⁻ in 5 serves as a μ₂-bridge to link four Cd(II) atoms in μ₁-η¹·η¹-chelating, μ₂-η¹·η¹-bridging.
coordination modes for the three carboxylate groups, respectively. Particularly, two Cd(II) atoms are bridged by two carboxylate groups from two btc$^{3-}$ to form a binuclear [Cd$_2$N$_2$(COO)$_2$] SBU, which are extended by HL$^-$ and btc$^{3-}$ ligands to form a 2D layer structure (Figure 5B). Topologically, the [Cd$_2$N$_2$(COO)$_2$] SBU and each HL$^-$ ligand can be regarded as a 4- or 3-connector in the 2D layer (Figure S2). In this connect, the 2D framework is a (3, 4)-connected V$_2$O$_5$ net of (4$^2$$\cdot$6$^3$)$\cdot$(4$^2$$\cdot$6$^2$$\cdot$8$^4$)$\cdot$(4$^5$$\cdot$6$^5$$\cdot$8$^4$) topology. Between the 2D layers, there exist rich hydrogen bonds (Figure 5D). Particularly, the adjacent 2D layers also have π−π stacking interactions with the centroid−centroid distance of 3.85 Å between aromatic nuclei of L ligands (Figure 5D). Therefore, 5 is a 3D supramolecular polymer built from hydrogen bonds and π−π stacking interactions.

**Synthesis and Coordination Modes of the H$_2$L Ligand.**

The compounds 1−5 were successfully synthesized, and the study further demonstrated that mixed ligands are effective building units to assemble MOFs. Particularly, for ligand H$_2$L, a polydentate nitrogen-containing ligand, the tetrazolyl and 4-imidazolyl groups can be deprotonated to be a polyazaheteroaromatic anion, displaying rich coordination sites and multiform possible conformations. In 1−5, all of the H$_2$L ligands are deprotonated to be HL$^-$ because the tetrazolyl fragment is more easily deprotonated than the other 4-imidazolyl group. Meanwhile, 4-imidazolyl groups of H$_2$L can also utilize differently positioned nitrogen atoms of imidazolyl groups to link with metal atoms (type II, Scheme 1). The diverse coordination modes for the H$_2$L ligand in complexes 1−5 are illustrated in Scheme 1: types I and II in 1, type III in 2; type IV in 3, type V in 4, and type VI in 5. On the other hand, the important families of multidentate O-donor polycarboxylate ancillary ligands of H$_2$obda, H$_2$ohmbda, and H$_2$btc employed in this study are excellent structural constructors because they can control and adjust the structures of coordination polymers in a mixed-ligand system. The carboxylic groups exhibit flexible coordination modes, showing μ$_2$-η$^2$-bridge and μ$_2$-η$^2$-μ$_2$-monodentate in obda$^{2-}$, μ$_2$-η$^1$-η$^1$-chelating and μ$_2$-η$^1$-η$^1$-bridging in btc$^{3-}$. The carboxylic ligands play an...
important role in generating multidimensional networks and interesting topologies as shown in complexes 1–5.

Thermal Stabilities and Powder X-ray Diffraction (PXRD) of the Complexes. The thermal stability of the compounds was evaluated by thermogravimetric analyses (Figure S3). For 1, the framework can be stable up to 380 °C, following the collapse. Complex 2 loses a weight loss of 6.19% (calc. 6.31%) with the release of water molecules from 110 to 155 °C and collapses at 295 °C. Weight loss was not found for 3 till it collapsed around 355 °C. Complex 4 exhibited a weight loss of 2.30% (calc. 2.15%) at the temperature ranging from 65 to 105 °C and then displayed a narrow thermogravimetric platform, immediately accompanied with the collapse of the framework, which is consistent with the departure of bridging water molecules. A total weight loss of 12.14% (calc. 12.45%) belongs to the departure of water molecules for 5 in the temperature range of 75–205 °C, until the residue collapses at 365 °C. The pure phases of the synthesized 1–5 complexes were confirmed by PXRD measurements (Figure S4).

Diffuse Reflectance Spectra. The UV-vis spectra for the as-synthesized samples of 1–5 were recorded and applied to calculate the band gap, \( E_g \). The H2L ligand exhibits one strong absorption bands centered at 308 nm, which can be attributable to \( n \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \) transitions. Compounds 1–5 exhibit similar broad bands in the range from 200 to 353 nm in the ultraviolet region, which are dominated by the absorption of H2L ligands. The optical band gaps obtained according to the steep absorption edge are estimated as 3.34, 3.51, 3.13, 3.48, and 3.26 eV for complexes 1–5 (Figure 6), respectively, indicating the existence of optical direct band gap and the characteristic of semiconductivity, which may make them potential wide gap semiconductor materials.\(^{53,54}\)

Photoluminescence Properties. Coordination polymers constructed from closed-shell d\(^{10}\) metal centers and the organic ligand with a delocalized \( \pi \)-system exhibit photoluminescence and have potential applications owing to their ability to adjust the emission of the hybrids.\(^{55,56}\) Therefore, the design and synthesis of compounds containing d\(^{10}\) Cd(II) metal centers have been carried out in this study. Accordingly, luminescence emission spectra of 1–5 were measured, and the results are exhibited in Figure 7. The organic ligand H2L exhibits intense emission at 440 nm upon excitation at 365 nm, which belongs to the \( \pi \rightarrow \pi^* \) electron transition, due to its delocalization (Figure S5). In comparison to those of the conjugated organic ligand, the emission bands resulting from the \( \pi^* \rightarrow n \) transition for the solid-state carboxylate ligands are

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**Figure 4.** (A) Coordination environment of the Cd(II) atoms in 4. Symmetry codes: (A) 3 = x, 1 − y, 1 − z; (B) 0.5 − x, 1.5 − y, 0.5 + z; (C) 1.5 − x, −0.5 + y, 0.5 − z; (D) 1.5 − x, 0.5 + y, 0.5 − z; (E) 0.5 + x, 0.5 − y, 0.5 + z. (B) Two-dimensional [Cd\(_2\)(H\(_2\)O)(ohmaba\(^2\)−)(HL\(^−\))]\(^2\) network of 4. (C) Three-dimensional structure of 4 constructed from 2D networks pillared by HL\(^−\) ligands. (D) Schematic representation of the 3-connected 3D framework of 4 with (4·5\(^3\))(4·2·5·6·8)\(^3\) topology.
usually weak and have no contribution to the fluorescence emission. Emission bands were observed at 428 nm ($\lambda_{ex} = 362$ nm) for 1, 440 nm ($\lambda_{ex} = 365$ nm) for 2, 435 nm ($\lambda_{ex} = 362$ nm) for 3, 386 nm ($\lambda_{ex} = 329$ nm) for 5, and very low fluorescence emission at 424 nm ($\lambda_{ex} = 375$ nm) for 4. The emission bands for complexes 1 and 3−5 are blue-shifted by 12, 5, 16, and 54 nm, respectively, with respect to that of the H$_2$L and can be tentatively assigned to intraligand fluorescence due to their fluorescence similarity. The study of corresponding quantum yield (QY) and decay lifetimes was carried out to further study the luminescence properties of compounds 1−3 and 5 (Figure S6). The QY values of
compounds 1, 2, 3, and 5 are 1.13, 0.74, 1.54, and 0.7%, respectively. In addition, the luminescence lifetimes of compounds 1–3 and 5 are calculated to be 50, 2, 2, and 1 ns, respectively, that arise from a singlet state, much shorter than the ones resulting from a triplet state (>10⁻³ s).\(^6\)\(^2\),\(^3\)

Sensing of Small Organic Molecules. It is known that a considerable amount of fluorescent MOF materials may be sensitive to the presence of guest molecules.\(^6\)\(^2\),\(^3\) As mentioned above, the compounds 1, 3, and 5 exhibit more intense fluorescence intensity in contrast to that of 2 and 4 under the same conditions. Therefore, the luminescent MOFs of 1, 3, and 5 were selected to study their molecular sensing properties. To examine whether 1, 3, and 5 have abilities to detect small solvent molecules, the finely ground samples of complexes 1, 3, and 5 (5 mg) were dispersed in different solvents (10 mL), respectively, namely, dimethylformamide (DMF), DEF, dimethylamine (DMA), methanol (MeOH), toluene, ethanol (EtOH), acetonitrile (CH₃CN), ether (Et₂O), acetone, and nitrobenzene (NB), and then ultrasonically shake for about 30 min. It was found that complexes 1, 3, and 5 are sensitive to the solvent molecules to a some extent as evidenced by the fluorescence intensity (Figures S7–S9). The photoluminescence intensity depends on the identity of the solvent molecules with sequence of DEF > DMA > MeOH > EtOH > DMF > CH₃CN > acetone > Et₂O > toluene > pure NB for 1 (Figure S7), DEF > DMF > DMA > EtOH > toluene > MeOH > CH₃CN > acetone > Et₂O > pure NB for 3 (Figure S8), and DMA > DMF > DEF > MeOH > EtOH > CH₃CN > acetone > toluene > Et₂O > pure NB for 5 (Figure S9). Through a series of fluorescence measurements, it can be found that all of the fluorescent MOF materials dispersed in dipole solvents as DMA, DMF, and DEF show the highest luminescence intensity due to their strong dipole moment.\(^6\)\(^4\),\(^5\) Meanwhile, the polar solvents (MeOH, EtOH) exhibit a relative strong luminescence intensity in contrast to their low fluorescence quenching for the nonpolar solvents (acetone, Et₂O). The above phenomenon can be attributed to the interaction between the dispersible skeleton and solvent molecules having different polarities, such as hydrogen bonding, π−π stacking, and electrostatic interaction.\(^6\)\(^5\),\(^6\)\(^6\)

It should be noted that the complexes of 1, 3, and 5 all show complete luminescence intensity quenching for nitrobenzene. Checking the possibility for sensing other nitroaromatic compounds (NACs), including NB, o-nitrophenol (2-NP), m-nitrophenol (3-NP), 4-nitrophenol (4-NP), o-dinitrobenzene (1,2-DNB), m-dinitrobenzene (1,3-DNB), 2,4,6-trinitro-toluene, and Octo (HMX), was inspired by the quenching behavior of NB. The luminescence intensity of different complexes was measured by formulating 1 mmol L⁻¹ DMF solution. The aromatic NACs have great quenching effect on the complexes of 1, 3, and 5 except the aliphatic HMX (Figures 8 and S10 and S11), which can be evaluated by the equation \(\text{QP} = \frac{I_0 - I}{I_0} \times 100\%\) to estimate the quenching percentage (QP), in which \(I_0\) and \(I\) are the fluorescent intensities of the luminescent MOFs dispersed in DMF solution without and with the addition of the analyte, respectively. Particularly, nitrophenol has a strong quenching effect on complex 5 (Figure 8). Particularly, the most effective quenchers is 4-NP with quenching percentage of 99.75%, far more than those of other nitro compounds. The high quenching efficiency of 4-NP has prompted us to further study the sensitivity of luminescence quenching by fluorescence titration. Apparently, the luminescence intensity of 4-NP-incorporated 5 is dependent on the concentration of 4-NP. As shown in Figure 9, nearly 100% of the emission intensity was decreased when 4-NP concentration increased from 0 to 700 μL for 5. The quantified value of the quenching effect of 4-NP was obtained using the Stern–Volmer equation: \(I_0/I = 1 + K_{SV}[M]\),\(^6\)\(^8\) in which \([M]\) is the molar concentration of the analyte and \(I_0\) and \(I\) are the luminescence intensities of 5 dispersed in DMF suspension without and with the addition of 4-NP, respectively. It has a good linear relationship at a low concentration, and the quenching coefficient is \(K_{SV} = 2.69 \times 10^4\) (Figure 9b), almost equal to the value of the reported luminescent MOF [Zn₅(DpImDC)ₓ(DMF)ₓ(H₂O)ₓ]H₂O-

\[\text{Figure 7. Emission spectra of the complexes 1–5.}\]

\[\text{Figure 8. (A) Fluorescence spectra and (B) luminescence quenching percentage of the DMF emulsion of complex 5 in the presence of eight different nitro compounds.}\]
In addition, the detection limit \(3\sigma/K_{SV}\) of 4-NP was deduced to be \(5.75 \times 10^{-7}\) M (Figure S12), which is comparable to that of the reported MOFs for sensing 4-NP \(^{70}\), calculated from the equation \(3\sigma/k\) (\(\sigma\), standard error; \(K_{SV}\), slope). \(^{71}\) Thus, 5 can be considered as a potential candidate for the selective sensing of 4-NP molecules.

Furthermore, the repeatability of 5 for sensing 4-NP was also examined. The samples were reused to sense 4-NP, remarkably, and it was found that the initial fluorescence intensity was almost regained even after five cycles, suggesting a high reversibility of 5 for potential applications (Figure 10).

PXRD patterns of the recovered sample after five cycles of quenching and recovery also are consistent with those of the as-synthesized samples, indicating high stability of the framework (Figure S4).

High sensitivity for sensing 4-NP prompted us to make further investigate the quenching mechanism. Generally, fluorescence quenching mainly depends on the fact that the excited electrons of the fluorescent material are transferred to the electron-deficient analytes, instead of relaxation to the ground state, which may appear as an effective overlap between the UV/vis absorption spectra of analytes and the emission spectra of fluorescent MOFs. As shown in Figure 11, the effective overlap of UV and fluorescence is almost the same, which further verifies that the fluorescence quenching mechanism is an energy transfer mechanism. \(^{72,73}\)

**Sensing of Fe\(^{3+}\) Ion.** Based on the study of the fluorescence sensing effects of organic molecules, the investigation of the ion recognition mechanism based on DMF solutions of different metal ions has attracted our attention to better understand the fluorescence sensing properties of the complexes. Disperse 5 mg of samples 1, 3, and 5 in 10 mL of DMF solution containing the same concentration of \(M(NO_3)_2\) \((1\) mM, \(M = K^+, Al^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Ag^+\)) and then sonicate the mixture for 30 min, respectively. Figure 12 shows that the Fe\(^{3+}\) solution makes the most significant fluorescence quenching effect for the emulsions of 1 and 3 compared to most other ions, while other cations show different changes in fluorescence intensity, as shown in Figure 13; upon Fe\(^{3+}\) addition, the fluorescence intensity of the suspensions of complexes 1 and 3 gradually decreased.

Taking their high fluorescence quenching effect on Fe\(^{3+}\) ions into account, the Stern–Volmer equation was also employed to investigate the sensitivity to Fe\(^{3+}\) ions for the complexes of 1 and 3. The linear Stern–Volmer curves for complexes 1 and 3 in Fe\(^{3+}\) solution fit the exponential equation well and also give

![Figure 9](image1.png)  
(a) Fluorescence intensity curve of complex 5 at different concentrations of 4-NP. (b) Stern–Volmer plot of 5 for 4-NP at a low concentration.

![Figure 10](image2.png)  
Quenching and recyclability test of 5; the upper dots represent the initial luminescence intensity, and the lower dots represent the intensity upon addition of 1 mM DMF solution of 4-NP.

![Figure 11](image3.png)  
Spectral overlap between the UV/vis absorption spectra of 4-NP analytes and the emission spectrum of 5.
values for low concentrations of $K_{SV}$ ($K_{SV1} = 1.22 \times 10^4, K_{SV3} = 1.60 \times 10^4$), equivalent to the complexes $[\text{Cd} \,(L_1)(\text{oba})] \cdot \text{DMF}$ and $[\text{Zn}_2(L_1)_2(\text{HBPT})_2] \cdot \text{H}_2\text{O}$ ($L_1 = 1,3$-di($1\text{H}$-imidazol-4-yl)benzene, $\text{H}_2\text{oba} = 4,4'$-oxybis-(benzoic acid), $\text{H}_3\text{BPT} = \text{biphenyl-3,4',5-tricarboxylic acid}$) with $2.69 \times 10^4$ and $3.38 \times 10^4$ M$^{-1}$, respectively (Figure 13).$^{74}$ According to the slope and standard error of the fitting lines, the detection limits are calculated to be $2.3 \times 10^{-6}$ M for 1 and $8.6 \times 10^{-7}$ M for 3 based on the equation $3\sigma/k$ (Figures S13 and S14), indicating higher sensitivity than those of the reported MOFs.$^{75-77}$ In addition, to test the influence of recognition in the case of other ion interferences, in the presence of other ions, Fe$^{3+}$ is added to measure the fluorescence intensity before comparison with other ions. As shown in Figure 14, 1 and 3 have high selectivity for the detection of Fe$^{3+}$ ion because no intensity change was observed in the case of other metal ions. Moreover, the multiple cycles of the Fe$^{3+}$ sensing experiments were performed and the obtained results showed that the material

Figure 12. Emission intensities of complexes 1 (a) and 3 (b) in DMF and different metal ion DMF solutions.

Figure 13. Fluorescence intensity curves of complexes 1 (a) and 3 (b) in different concentrations of Fe$^{3+}$ in DMF and linear curves showing fluorescence quenching at low concentrations.

Figure 14. Bar graph of anti-interference performance of Fe$^{3+}$ in different metal ion solutions of complexes 1 (a) and 3 (b).
could greatly regain its intensity after being washed with DMF several times (Figures S15 and S16). The result also reveals that 1 and 3 can be employed as fluorescent sensors for detecting Fe\(^{3+}\) with high sensitivity and recyclability.

Thus, compounds 1 and 3 can be regarded as potential candidates for selective sensing of the Fe\(^{3+}\) ion. Such fluorescence quenching attributes to maximum spectral overlap between the UV–vis wide absorption spectrum at around 300 nm of the Fe\(^{3+}\) ion solution and the excitation spectra of 1 and 3 (Figure S17). The wide absorption of Fe\(^{3+}\) may hinder the absorption of 1 and 3 upon excitation and lead to the decrease or quenching of the fluorescence.\(^{70}\)

**CONCLUSIONS**

Five Cd(II) coordination polymers with diverse structures were obtained by hydrothermal methods based on multi-N-donor ligands with a delocalized π-system or mixed carboxylates. The results further demonstrate that the multi-N-donor H\(_2\)L ligand can exhibit diverse coordination modes, while carboxylate ligands possess supercompatibility to build coordination frameworks as auxiliary ligands. The MOFs constructed from closed-shell d\(^{10}\) Cd(II) centers and the H\(_2\)L organic ligand with a delocalized π-system have favorable photoluminescence properties, which could serve as fluorescent sensors for the detection of Fe\(^{3+}\) and nitro compounds with high sensitivity, selectivity, and recyclability. The luminescent materials exhibit the clear “turn-off” quenching responses for Fe\(^{3+}\) in DMF solution with high selectivity and sensitivity of 2.3 × 10\(^{-6}\) M for 1 and 8.6 × 10\(^{-7}\) M for 3. Meanwhile, compound 5 can sense the 4-nitrophenol with a detection limit as low as 5.75 × 10\(^{-7}\) M. In this context, this study provides an easy and facile route to design and yield new luminescent MOFs as promising luminescent sensors.

**EXPERIMENTAL SECTION**

The ligand \(\text{H}_2\text{L}\) was prepared according to the literature.\(^{80}\) Infrared spectra (IR) used KBr pellets and was carried out on a Bruker Vector22 FT-IR spectrophotometer. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10 °C min\(^{-1}\) on a simultaneous SDT 2960 thermal analyzer. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu \(K\alpha\) (\(\lambda = 1.5418\) Å) radiation. Photoluminescence spectra were tested on a HORIBA FluoroMax-4 fluorescence spectrophotometer with a xenon arc lamp as the light source. The decay lifetimes were measured with an FLS920P fluorescence spectrometer.

**Preparation of [Cd(HL)]\(_2\) (1).** A mixture of H\(_2\)L (21.2 mg, 0.1 mmol), \(\text{Cd(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O}\) (23.6 mg, 0.1 mmol), and \(\text{H}_2\text{O}\) (8 mL) was prepared and adjusted to pH 7 with 0.5 mol L\(^{-1}\) H\(_2\text{SO}_4\) solution. The mixture was added to a steel container and heated at 160 °C for 3 days. Colorless block crystals of 1 were obtained with a yield of 72%. Anal. calcd for \(\text{C}_{20}\text{H}_{14}\text{N}_{12}\text{Cd}\) (%): C, 44.92; H, 2.64; N, 31.43. Found: C, 45.31; H, 2.45; N, 31.26. IR (KBr pellet, cm\(^{-1}\)): 3745–2970 (m, br), 1642 (s), 1488 (w), 1446 (m), 1412 (m), 1346 (w), 1292 (w), 1137 (s), 1104 (m), 1089 (m), 1069 (m), 1007 (w), 949 (m), 843 (s), 767 (s), 716 (m), 647 (m), 617 (s), 555 (m).

**Preparation of [Cd(HL)]\(_2\)(\(\text{H}_2\text{O}\))\(_2\) (2).** Complex 2 was obtained by a hydrothermal procedure as that for the preparation of 1 but the solvothermal conditions using DMA–H\(_2\)O (1:10, v/v, 10 mL) as a mixture solvent. Complex 2 was obtained in 65% yield. Anal. calcd for \(\text{C}_{20}\text{H}_{16}\text{N}_{12}\text{O}_2\text{Cd}\) (%): C, 42.08; H, 3.18; N, 29.44%. Found: C, 41.25; H, 3.32; N, 29.53%. IR (KBr pellet, cm\(^{-1}\)): 3716–2875 (s, br), 1623 (s), 1450 (s), 1417 (w), 1365 (m), 1130 (m), 1073 (w), 1011 (w), 947 (m), 837 (m), 760 (m), 644 (m), 522 (w).

**Preparation of [Cd\(_3\)(HL)\(_2\)(obda)]\(_3\) (3).** Reaction of \(\text{H}_2\text{obda}\) (18.2 mg, 0.1 mmol) was used instead of \(\text{H}_2\text{obda}\). Colorless block crystals of 3 were obtained in 65% yield. Anal. calcd for \(\text{C}_{36}\text{H}_{22}\text{N}_{12}\text{O}_8\text{Cd}_3\) (%): C, 41.31; H, 2.92; N, 19.57. Found: C, 40.78; H, 2.61; N, 19.89. IR (KBr pellet, cm\(^{-1}\)): 3689–2908 (s, br), 1614 (s), 1584 (vs), 1459 (s), 1412 (w), 1361 (s), 1282 (w), 1136 (s), 1053 (s), 970 (m), 835 (m), 776 (m), 709 (w), 695 (s), 543 (w), 486 (w). C\(_{36}\)H\(_{22}\)N\(_{12}\)O\(_8\)Cd\(_3\).

**Preparation of [Cd\(_2\)(HL)\(_2\)ohmbda][\(\text{DMA}\)\(_2\)][\(\text{H}_2\text{O}\)] (4).** Complex 4 was synthesized as 3, except that \(\text{H}_2\text{ohmbda}\) (21.0 mg, 0.1 mmol) was used instead of \(\text{H}_2\text{obda}\). Colorless block crystals of 4 were collected in 62% yield after being washed by water and ethanol several times. Anal. calcd for \(\text{C}_{40}\text{H}_{24}\text{N}_{12}\text{O}_8\text{Cd}_2\) (%): C, 31.56; H, 1.39; N, 11.62. Found: C, 31.32; H, 1.52; N, 11.48. IR (KBr pellet, cm\(^{-1}\)): 3666–2920 (s, br), 1613 (s), 1553 (s), 1441 (s), 1373 (s), 1138 (w), 1108 (w), 954 (w), 847 (m), 758 (m), 737 (s), 645 (w), 542 (w), 494 (w). C\(_{40}\)H\(_{24}\)N\(_{12}\)O\(_8\)Cd\(_2\).

**X-ray Crystallography.** X-ray crystallography of compounds 1–5 was carried out on a Bruker Smart Apex CCD area detector diffractometer using graphite-monochromated Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) at 23(2) °C. The diffraction data was integrated by the SAINT program.\(^{81}\) Semiempirical absorption corrections were applied using the SADABS program.\(^{82}\) The structures were solved by direct methods and all nonhydrogen atoms were refined anisotropically on \(F^2\) by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.\(^{83}\) The hydrogen atoms were generated geometrically, but the hydrogen atoms of the water molecules in 5 could not be found. There exist one free DMA molecule in the asymmetric unit, which is squeezed by PLATON. Table 1 shows the details of the crystal parameters, data collection, and refinements for the complexes 1–5, and Table S1 exhibits the selected bond lengths and angles.

**ASSOCIATED CONTENT**

\(\text{S Supporting Information}\)

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01108.

Selected bond lengths and angles (Table S1), hydrogen bonding data (Table S2), structure illustrations for complexes 4 and 5 (Figures S1 and S2), TGA (Figure S3), PXRD data (Figure S4), photoluminescence spectra...
of H$_2$L (Figure S5), decay curves and QY (Figure S6), emission spectra in different solvents for complexes 1, 3, and 5 (Figures S7–S9), emission spectra in nitrobenzene derivatives for complexes 1 and 3 (Figures S10 and S11), fitting curve of the luminescence intensity of 1, 3, and 5 (Figures S12–S14), recyclability test (Figures S15 and S16), and UV–vis spectra of Fe$^{3+}$ and emission spectrum (Figure S17) (PDF)

Crystallographic data of CCDC 1907337–1907341 (CIF)

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**Notes**

The authors declare no competing financial interest.

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