Introduction

Since Williams and co-workers reported a highly porous Cu(II) coordination polymer (CP), [Cu2(tma)(H2O)] (tma = benzene-1,3,5-tricarboxylate), with a tripodial tricarboxylate tma as the linker,1 metal–multicarboxylate CP chemistry achieved rather rapid development. A variety of multicarboxylic acid molecules have been designed in the construction of a series of novel metal–multicarboxylate CP materials. As a class of new chemical materials, they not only possess diverse structures,2 but also exhibit potential applications in fields such as adsorption,3 optics,4 magnetism,5 and catalysis.6 For example, 1) owing to the stronger ability to form clusters or 1D chains of carboxylate groups with metal ions, namely, so-called discrete or rod-shaped secondary building units (SBUs), some metal–multicarboxylate CPs possess 3D stable porous structures, which have been confirmed as potential candidates for H2 storage7,8 and CO2 capture.9 Also owing to special porous structures, metal–multicarboxylate CPs are verified to be able to adsorb organic dyes10 and reversibly take up I2 molecules.11 2) Owing to the electron-rich nature of the aromatic multicarboxylate ligand (potential electron donor), the excited-state electron-transfer path of the metal–multicarboxylate CP will be changed, upon encountering highly electron-withdrawing –NO2 groups in nitroaromatics. The excited-state electron would undergo transfer to the –NO2 group, leading to photoluminescence quenching. Thus, ligand-based photoluminescence metal–multicarboxylate CPs can act as sensors to detect traces of nitro explosives.11 Recently, metal–multicarboxylate CPs have been found to have the capability to selectively sense metal ions such as Fe3+ or d8 Cu2+.3 3) Owing to the linkage of the carboxylate groups, strong M–M interactions may be observed in metal–multicarboxylate CPs, which makes these materials exhibit interesting magnetic properties.14

Recently, attention has been paid to a class of semirigid V-shaped multicarboxylic acid molecules. They consist of two aromatic carboxylic acid moieties, connected by a nonmetallic atom, such as carbon (–C(=O)=–, –C(=O)–), O (–O–), or S (–S–, –SO2–) atoms.15 The so-called V shape derives from the tetrahedral configuration of the central nonmetallic atom, and approximately vertical arrangement of two benzene ring planes. The so-called semirigidity means that the tetrahedron of the central atom can be slightly distorted, and two benzene rings can appropriately rotate around the central atom. We have employed semirigid ligands H2L3 and H2L4 (L3 = 4-(4-carboxyphenoxo)phthalate, L4 = 4,4'-oxy((hexafluoroisopropylidene)-dipthalate; see Scheme S1 in the Supporting Information) to self-assemble several 3D transition-metal CPs, namely, [CdL3(bpa)(H2O)]·0.5H2O (bpa = 1,2-bis(4-pyridyl)ethane), [H2bpp][Mn3(L3)(H2O)] (bpp = 1,2-bis(4-piperidyl)pro-
The reactions of Cd(II) salt, H₂L1/H₂L2, and organic N-donor base molecules were performed to create five new L1/L2-based 3D Cd(II) CPs:

- [Cd₂{(L1)(H₂O)}₂·H₂O] (1)
- [Cd₂{(L1)(bpe)(H₂O)}] (2)
- [Cd₂{(L1)(bpa)(H₂O)}] (3)
- [Cd₂{(L1)(bppy)}] (bppy = 1,3-bis(pyridyl)propane; 4), and
- [Cd₂{(L2)(bppy),(H₂O)}]·H₂O (5).

To date, L1/L2-based CPs are still less developed\(^\text{[16]}\). To explore the potential functional properties of the as-synthesized CP materials, the sensing abilities of 2–5 for NB were studied.

**Results and Discussion**

**Synthetic analysis**

Compounds 1–5 were prepared under hydrothermal conditions. The reactions of Cd(II) salt, H₂L1/H₂L2, and organic base molecules in a molar ratio of 1:1:1 or 1:1:0.5 were investigated to afford Cd(II) CPs 1–5. Based on the synthetic procedures for 1–5, the following points need to be stressed: 1) When preparing 1, the organic base molecule did not appear in the final framework of 1. The direct reaction of Cd(II) with H₂L1 was also performed, but only a solid product unsuitable for single-crystal XRD was obtained. This solid product has the same IR spectrum as that of 1. 2) The 2:1:1/2:1:0.5 reactions were also performed, but only powder samples were obtained. 3) Compounds 1, 2, 4, and 5 were obtained at 120 °C, whereas compound 3 was obtained at 140 °C. When this reaction was performed at 120 °C, only a clear solution was obtained. 4) The growth of single crystals for all compounds was strictly controlled by the pH level of the reactive system: pH 6 for 1, pH 5 for 2, pH 5 for 3, pH 5 for 4, and pH 8 for 5.

**Structural description of 1**

Single-crystal XRD analysis revealed that compound 1 was a 3D Cd(II) CP with a unique ligand of L1. The asymmetric unit of 1 was composed of two types of Cd(II) ions (Cd1, Cd2), one L1 molecule, and five coordinated water molecules (Ow1, Ow2, Ow3, Ow4, Ow5). Compound 1 exhibits the same host framework structure as that of the reported compound [Cd₂{(L1)(H₂O)}]\(^\text{[16]}\), so we only give a brief description for the formation of its 3D network: 1) L1 molecules with 3'- and 4'-position carboxylate groups link Cd1 centers into a slightly helical chain (see Figure 1c). 2) Neighboring helical chains array in an interdigitated form. Through the Cd2 centers as the connectors, the adjacent helical chains interlock into a 2D layer network (see Figure 1b). 3) Through the interaction between Cd2 and O7b, compound 1 self-assembles into a 3D network, in which two types of channels (A and B) are found (see Figure 1a). Notably, in the asymmetric unit of 1, there is one lattice water molecule, as ascertained by elemental and thermogravimetric (TG) analyses. The lattice water molecule should occupy the space of channel B. Figure S1 in the Supporting Information shows the coordination environments of Cd1 and Cd2. Figure 2 plots the coordination mode of L1.
Structural description of 2

Compound 2 is a 3D Cd\textsuperscript{II} CP with a mixture of ligands L1 and bpe. The asymmetric unit of 2 is composed of two types of Cd\textsuperscript{II} ions (Cd1, Cd2), one L1 molecule, one bpe molecule, and one coordinated water molecule (Ow1). As shown in Figure S2 in the Supporting Information, Cd1 is in an octahedral site, surrounded by five carboxylate oxygen atoms (O2, O2c, O3c, O6a, O7b), and one water molecule (Ow1), whereas Cd2 is in a rectangular pyramidal site, coordinated by four carboxylate oxygen atoms (O1, O4c, O5d, O8b) and one bpe nitrogen atom (N1). L1 adopts an \(\eta^1\cdot\eta^1\cdot\eta^1\cdot\eta^1\cdot\eta^1\cdot\eta^1\cdot\mu_6\) coordination mode (see Figure 2). The bpe molecule has no contribution to the formation of the 3D network of 2. It only completes the coordination sphere of Cd2. The L1 molecules link two types of Cd\textsuperscript{II} ions into a 3D network of compound 2 (see Figure 3a). Two phthalato moieties link four Cd\textsuperscript{II} ions into a tetranuclear cluster (see Figure 3c), in which a type of carboxylate-bridged SBU Cd\textsubscript{4}(COO)\textsubscript{4} is observed (see Figure 3d). Two carboxylate groups bridge two Cd\textsuperscript{2+} ions (Cd1, Cd2) in a dinuclear unit. Then through interactions between Cd1 and O2 (Cd1–O2 = 2.374(3) Å), two such dinuclear units aggregate into this tetranuclear SBU. Synchronously, a rhomboid Cd\textsubscript{2}O\textsubscript{2} dimer forms with a short Cd–Cd separation of 4.029 Å. Through interactions between the 1-position carboxylate groups and the Cd\textsuperscript{2+} ions from the neighboring SBU (O6–Cd1a = 2.213(4) Å, O5–Cd2e = 2.303(3) Å), the L1 molecules doubly bridge the tetranuclear SBUs to form a 1D infinite chain that extends along the c-axial direction (see Figure 3b). With the 3-position carboxylate group as the donor (O7–Cd1f–O = 2.228(3) Å; O8–Cd2f = 2.253(3) Å), each 1D chain has a chance to interact with four neighboring 1D chains to form a 3D network of 2. Based on the topological viewpoint, compound 2 possesses a simple pcu topology.

Structural description of 3

Compound 3 is a 3D Cd\textsuperscript{II} CP with a mixture of ligands of L1 and bpa. The asymmetric unit of 3 is composed of two types of Cd\textsuperscript{II} ions (Cd1, Cd2), one L1 molecule, one bpa molecule, and one coordinated water molecule (Ow1). Generally, by using bpa to displace bpe, the compound will show a different network.\textsuperscript{16, 17} However, because bpe and bpa only employ one nitrogen atom to serve as the donor atom, the L1 molecules link the Cd\textsuperscript{2+} ions to form the same networks in compounds 2 and 3. The structure of compound 3 is not described again herein.

Structural description of 4

Compound 4 is a 3D Cd\textsuperscript{2+} CP with a mixture of ligands of L1 and bpp. The asymmetric unit of 4 is composed of two types of Cd\textsuperscript{2+} ions, one L1 molecule, one bpp molecule. As shown in Figure S3 in the Supporting Information, Cd1 is five-coordinate with four carboxylate oxygen atoms (O1, O6a, O7b,
O8b) and one bpp nitrogen atom (N1), whereas Cd2 is six-coordinate with five carboxylate oxygen atoms (O3, O4, O5e, O6f, O8e) and one bpp nitrogen atom (N2). L1 adopts an $h_1h_0h_1h_1h_0m_4$ coordination mode (see Figure 2). With the aid of bpp, the L1 molecules link the Cd$^{2+}$ ions to form a 3D network different from that of compounds 2 and 3 (see Figure 4a). As shown in Figure 4c, the phthalate moieties link two types of Cd$^{2+}$ ions into a 1D endless chain, in which a carboxylate-bridged rod-shaped SBU is found (see Figure 4d). The 4'-position carboxylate group with O8 as a bridge link the first two Cd$^{2+}$ ions (Cd1c, Cd2h) together. Then, the 3'-position carboxylate groups extend these dinitrile units into this rod-shaped SBU to produce synchronously a rhombic Cd$_2$O$_2$ ring. The Cd$_2$O$_2$ ring is not planar, but slightly folded around the O–O line (dihedral angle: 19.3°). The short Cd–Cd contact distance is 3.697 Å. Through the 1-position carboxylate group acting as a donor to the Cd$^{2+}$ center (Cd1-O1 = 2.224 Å), the adjacent 1D chains mentioned above are interlocked into a 2D layer network (see Figure 4b). According to the topological method, this layer exhibits a simple (4,4) net. As shown in Figure 4a, the 3-position carboxylate group plays a key role in linking the layers into a 3D network of 4, by chelating to the Cd2 center from the adjacent layer (Cd2–O3 = 2.294 Å, Cd2–O4 = 2.325 Å). Clearly, compound 4 also has a simple pcu topology. In compound 4, the bpp molecule is mainly there to stabilize the 3D metal–multicarboxylate network.

### Structural description of 5

Compound 5 is a 3D Cd$^{2+}$ CP with a mixture of ligands of L2 and bpp. The asymmetric unit of 5 is composed of two types of Cd$^{2+}$ ions (Cd1, Cd2), one L2 molecule, two types of bpp molecules (bpp I, bpp II), two types of coordinated water molecules (Ow1, Ow2), and one lattice water molecule (Ow3). L2 adopts an $h_1h_0h_1h_1h_0m_4$ coordination mode (see Figure 2). Seven-coordinate Cd1 is surrounded by five carboxylate oxygen atoms (O1, O2, O5a, O6a), two bpp nitrogen atoms (N1, N3), and one water molecule (Ow1), whereas Cd2, with rectangular pyramidal geometry, is completed by two carboxylate oxygen atoms (O4, O7b), two bpp nitrogen atoms (N2c, N4d), and one water molecule (Ow2; see Figure S4 in the Supporting Information). In compound 5, the L2 molecules link two types of Cd$^{2+}$ centers into a 2D layer network. As shown in Figure 5b, no carboxylate-bridged

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**Figure 4.** a) The 3D network, b) 2D layer, c) 1D chain, and d) SBU in 4: h) $x+1/2, y-1/2, z; i) x, -y, z+1/2; j) x+1/2, -y-1/2, z+1/2; k) x, y-1, z.

**Figure 5.** a) The 3D network, b) 2D layer, c) tetranuclear unit, and d,e) Cd$^{2+}$–bpp chain in 5.
cluster or chain is found within the layer. The layer exhibits a simple (4,4) net, and a tetranuclear unit acts as the planar four-connected node (see Figure 5c). The L2 molecule has donor carboxylate groups in 2-, and 3-positions to link two Cd\(^{2+}\) ions into a dinuclear unit with a Cd–Cd distance of 5.812 Å. Then, L2 molecules with donor carboxylate groups in the 1-, and 3-positions doubly bridge these two units to form the tetranuclear unit. Two types of bpp molecules play different roles in both of these two units to form a 3D network of 5 (see Figure 5a). Thus, compound 5 also has a simple puck topology. Two types of bpp molecules link theCd\(^{2+}\) centers to form a 1D chain (see Figure 5e). An alternate linkage of four bpp molecules and four Cd\(^{2+}\) ions produces a larger cyclic ring. The neighboring cyclic rings interlock to form this 1D chain and stabilize the 3D network of 5. In compound 5, the Cd–O and Cd–N ranges are 2.242(3)–2.479(3) and 2.324(4)–2.358(4) Å, respectively.

**Structural discussion**

Compounds 1–5 possess 3D network structures. For the L1 molecule, it can link the Cd\(^{2+}\) ions to form a 3D network, as observed in compound 1 and the reported Cd\(^{2+}\)–L1 compound.\(^{[18b]}\) As found in 2–4, the L1 molecules can still link metal ions into a 3D network, although an N,N'-donor organic base molecule, such as bpy, bpe, or bpp, is introduced. However, once 4,4'-bipyridine (bpy) is incorporated, a different situation appears, and only a 1D Cd\(^{2+}\)–L1 chain forms, as observed in the reported compound (Cd\(_2\)(L1)((bpy))\(_2\)(H\(_2\)O))\(_2\)H\(_2\)O.\(^{[18b]}\) This phenomenon might be related to the length and rigidity/flexibility of the introduced base molecule. As exemplified by compounds 2/3 and 4, the introduced N-donor ligand affects the 3D network structure constructed from Cd\(^{2+}\) and L1. Because it directly alters coordination of the Cd\(^{2+}\) center, the coordination mode of the L1 molecule as well as the linkage between Cd\(^{2+}\) and L1 is indirectly changed. Hence, a different 3D network is obtained. In compounds 2 and 3, the Cd\(^{2+}\) ions and L1 molecules aggregate into the same network structures; this is due to the monodentate coordinate of the organic base molecule to the Cd\(^{2+}\) center. For the L2 molecule, as observed in compound 5, it only can link the Cd\(^{2+}\) center to form an oligomer (2D layer in 5). This is unrelated to the introduction of the organic base molecule because compound [Cd\(_2\)([L2](H\(_2\)O))\(_2\)]xH\(_2\)O also exhibits a 2D layer network. Regrettably, the crystal data of this compound does not pass the cif-checking examination. This could be related to the position of the substituted carboxylate group, especially the positions of two o-positioned carboxylate groups. In the metal CP networks, the incorporated organic base molecules generally play three roles. As mentioned above, by coordinating to the metal center, the linkage between the metal center and multicarboxylate molecule is changed and produces a new network. Once the formed pore for the 3D metal–multicarboxylate network is smaller, and such a 3D network is stable, the organic base molecule will only complete the coordination of the metal center. Once the formed pore is large, the organic base molecule mainly stabilizes the 3D metal–multicarboxylate network. Moreover, in compounds 1–5, two types of multicarboxylate molecules show a semirigid nature. The dihedral angles of two benzene ring planes span a rather wide range from 90.4 (in 1) to 88.3° (in 5). The C-O\(_{amidic}\)–C angles in 1–5 deviate severely from the normal value of 109.5° (121.3° in 1, 116.9(4)° in 2, 116.2(6)° in 4, 117.3(3)° in 5).

**Characterization**

Figure S6 in the Supporting Information plots the experimental and simulated powder XRD patterns of compounds 1–5. The experimental powder XRD pattern for each compound is in accordance with the simulated one generated on the basis of structural data, which confirms that the as-synthesized product is of a pure phase. To characterize the thermal stability of the as-synthesized CPs, the thermal behavior was studied. As shown in Figure S7 in the Supporting Information, compound 1 underwent two weight-loss steps. About 16.5% weight loss for the first step before 250 °C corresponds to the removal of the six water molecules (calcld: 16.0%). This means that there is one lattice water molecule in a symmetric unit of 1. This conclusion is in agreement with that of elemental analysis results for 1. In the second step, the sublimation of the organic ligands occurs. The final remaining product was proved to be CdO (calcld: 38.0%; found: ≈ 38.5%). Compounds 2, 3, and 5 show similar weight-loss processes. All underwent two steps of weight loss. The initial minor weight loss (calcld: 2.4%; found: ≈ 2.2%; for 2; calcld: 2.39%; found: ≈ 2.5%; for 3; calcld: 5.31%; found: ≈ 5% for 5) is ascribed to the removal of water molecules in the compounds. The framework collapsed at approximately 380 °C for 2, approximately 370 °C for 3, and approximately 300 °C for 5. The second step of weight loss was assigned to decomposition of the organic ligands, and the final residues for all compounds were CdO (calcld: 34.2%; found: ≈ 34% for 2; calcld: 34.1%; found: ≈ 34% for 3; calcld: 25.2%; found: ≈ 26% for 5). No weight loss is observed before 370 °C, which indicates that there are no coordinated and/or lattice water molecules in 4. An abrupt decomposition weight loss of approximately 70% took place, leaving CdO as the final residue (calcld: 33.6%; found: ≈ 32%). Figure S8 in the Supporting Information illustrates the IR spectra of compounds 1–5.

**Photoluminescence sensing investigation**

For the reported L1/L2-based CPs, the Cu\(^{2+}\) compound [Cu\(_2\)(L1)\(_2\)(OH)\(_2\)(H\(_2\)O)]\(_2\)H\(_2\)O and the Ni\(^{2+}\) compound [Ni\(_2\)(L2)\(_2\)(db)\(_2\)(H\(_2\)O)]\(_4\)H\(_2\)O (db = 1,4-di(1H-imidazole-1-yl)-benzene) show interesting ferromagnetic properties, whereas the solid-state Cd\(^{2+}/\)Zn\(^{2+}\) compounds possess photoluminescence properties.\(^{[18]}\) As expected, compounds 1–5 in the solid state also possess photoluminescence properties. Upon excitation (λ = 330 nm for 1, λ = 335 nm for 2, λ = 330 nm for 3, λ = 340 nm for 4, and λ = 350 nm for 5), all emit high-energy violet
or blue light with maxima at \( \lambda = 430 \text{ nm} \) for 1, \( \lambda = 370 \text{ nm} \) for 2, \( \lambda = 370 \text{ nm} \) for 3, \( \lambda = 440 \text{ nm} \) for 4, and \( \lambda = 420 \text{ nm} \) for 5. The emission for all should be assigned to the L1/L2-centered electronic excitation (\( \pi^* \rightarrow \pi^* \)) because the L1/L2 molecule exhibits a similar emission than that of the corresponding complex \( \lambda_{\text{ex}} = 370 \text{ nm}, \lambda_{\text{em}} = 415 \text{ nm} \) for L1; \( \lambda_{\text{ex}} = 390 \text{ nm}, \lambda_{\text{em}} = 455 \text{ nm} \) for L2; see Figure S9 in the Supporting Information).

To estimate the sensing ability, the photoluminescence behavior of the suspension states of 2–5 dispersed in different organic solvents were investigated (see Figure 6). Before the measurements were performed, a series of emulsions were prepared as follows: a finely ground powder sample (5 mg) was immersed in an organic solvent (5.00 mL), treated by ultrasonication for 30 min, and then aged for 72 h. The organic solvents used were \( N,N' \)-dimethylformamide (DMF), CHCl\(_3\), THF, CH\(_2\)Cl\(_2\), dimethyl sulfoxide (DMSO), toluene, ethanol, acetonitrile, n-butanol, isopropanol, and NB. As shown in Figure S8 in the Supporting Information, for each compound, dispersed in all organic solvents, they still emit light, although the emission intensities show larger differences; however, in NB, a special situation is observed. Suspensions of 2–5 do not emit light. That is, the emissions of 2–5 are completely quenched by NB, which implies that 2–5 can serve as fluorescence probes to detect NB, based on a photoluminescence quenching mechanism. To explore the quenching efficiency, the photoluminescence behavior of suspensions of 2–5 (5 mg) with gradually increasing concentrations of NB were measured. The dispersible solvents selected (5.00 mL) were THF for 2, THF for 3, DMF for 4, and DMF for 5. As shown in Figure S10 in the Supporting Information, for each compound, the emission intensities of the suspensions gradually decrease with the addition of different concentrations of NB. For compounds 2 and 3, the emissions of the suspensions are thoroughly quenched, if the addition of NB is 300 ppm. For compounds 4 and 5, the corresponding NB concentrations are 400 and 250 ppm, respectively. These results suggest that 2–5 possess the ability to sense the ppm level of NB. Figure S11 in the Supporting Information plots the quenching efficiency (\( I_o/I_0/C_0 \)) versus NB concentration curves for 2–5 (Stern–Volmer plot), showing a linear relationship within the concentration range of 25–200 ppm. The \( K_{sv} \) values are \( 9.27 \times 10^{-2} \text{ ppm}^{-1} \) for 2, \( 3.86 \times 10^{-2} \text{ ppm}^{-1} \) for 3, \( 3.24 \times 10^{-2} \text{ ppm}^{-1} \) for 4, and \( 3.93 \times 10^{-2} \text{ ppm}^{-1} \) for 5.

The sensing ability of some metal–multicarboxylate CPs for NB has also been investigated by using a similar method.\(^{[19]}\)
The sensing ability of compounds 2–5 is clearly stronger than those of the reported CPs [(CH$_3$)$_2$NH$_2$][Zn(HL)$_5$](H$_2$O)$_4$·4H$_2$O (H$_2$L$_5$ = 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octacarboxymethoxyalkyl[4]arene; 300 ppm,$^{[20]}$ [(CH$_3$)$_2$NH$_2$][Cd$_2$(HL)$_6$] (L$^6$ = 5,5'-S',5'-S'-5,5'-S'-1,2,3,4,5-6-phenylhexamethoxyl)hexaisophthalate; 1000 ppm)$^{[21]}$ [(Zn$_2$(L)$_7$)(bpy)$_3$H$_2$O]·3H$_2$O·2DMF (H$_2$L$_7$ = bis(3,5-dicarboxyphenyl)terephthalamide; 2000 ppm)$^{[22]}$ and [Zn(tib)(HLB)$(_{10}$)H$_2$O]·2H$_2$O (L$_8$ = biphenyl-3,3',4,4'-tetracarboxylate, tib = 1,3,5-tris(1-imidazolyl)benzene; 1000 ppm)$^{[23]}$. The reported metal–multicarboxylate CPs [Cd$_2$(L$_3$)$_3$](bpa)$_4$(H$_2$O)$_2$·0.5H$_2$O (L$_3$ = 4-(4-carboxyphenoxyl)phthalate; 325 ppm)$^{[14]}$ [(CH$_3$)$_2$NH$_2$][Cd$_2$(L)$_9$(dmf)(HCOO)]·1.5H$_2$O (L$_9$ = 2,4,6-tris[(3-carboxyphenoxy)methyl]mesitylene; 300 ppm)$^{[24]}$ [Zn$_2$(L)$_{10}$](bib)$·$3.6DMF·4H$_2$O (L$_{10}$ = 4-[3-(4-carboxyphenoxyl)-2-[(4-carboxyphenoxy)methyl]-2-methylpropoxy]benzoate, bib = 1,4-bis(1-imidazolyl)benzene; 250 nm), and [Zn$_2$(L)$_{10}$](bib)$·$(500 ppm)$^{[25]}$ possess similar sensing abilities to those of compounds 2–5. The aromatic multicarboxylate molecule is an electron-rich aromatic ligand (potential electron donor), whereas the NB molecule possesses an electron-deficient nature (potential electron acceptor). The good dispersible nature of the as-synthesized CP particles in organic solvent allows the introduced NB molecule to access easily these particles and be closely adsorbed on the surface of these particles. Owing to the close contact, the excited-state electron-transfer path of the compound is changed. The excited-state electron would undergo transfer to the highly electron-withdrawing –NO$_2$ group in the NB molecule, instead of returning to the ground-state energy level, and thus, quenching is observed.$^{[19]}$ Therefore, the following two factors may play a key role in determining the sensing ability of the CP material on NB. 1) The good dispersible nature of the solid particles in the organic solvent. The size of the solid particle and the solvent character will influence the dispersible nature of the solid particles. 2) The larger π-conjugated structure of the organic base molecule have been confirmed to play a key role in the single-crystal growth of compounds 1–5. Single crystal XRD analysis revealed that L$_1$ could link Cd$^{2+}$ into a 3D network. In the presence of bpe, bpa, or bpp, L$_1$ could still link Cd$^{2+}$ into a 3D network. The porous size determined the role of the introduced organic base molecule. Additionally, L$_2$ molecules only linked Cd$^{2+}$ into an oligomer. The mixed organic base molecule served as a pillar linker to extend the oligomers into a 3D network. Photoluminescence analysis revealed that 2–5 could all act as fluorescence sensors to detect NB at ppm concentrations (250–400 ppm) based on a photoluminescence quenching mechanism.

**Experimental Section**

**General**

All chemicals were of reagent-grade quality, obtained from commercial sources without further purification. Elemental analysis (C, H, and N) was performed on a PerkinElmer 2400LS II elemental analyzer. IR spectra were recorded on a PerkinElmer Spectrum 1 spectrophotometer in the $\nu$ = 4000–400 cm$^{-1}$ region by using a powdered sample on a KBr plate. Powder XRD data were collected on a Rigaku/max-2500 diffractometer with CuKa radiation ($\lambda$ = 1.5418 Å). TG behavior was investigated on a PerkinElmer TGA-7 instrument with a heating rate of 10°C min$^{-1}$ in air. Fluorescence spectra were obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

**Syntheses of coordination polymers**

Colorless block crystals of 1 were obtained from a simple hydrothermal self-assembly of Cd(CH$_3$COO)$_2$·2H$_2$O (13.5 mg, 0.05 mmol), H$_2$L$_1$ (18 mg, 0.05 mmol), and 1,2,4-triazole (3.5 mg, 0.05 mmol) in an aqueous solution (10 mL; pH 6 adjusted with H$_2$O(ox); ox = oxalate) at 120°C for 3 days. Yield: ≈ 15% based on Cd$^2+$; IR: $\nu$ = 1610 (w), 1552 (s), 1427 (w), 1384 (s), 1254 (m), 1149 (m), 1005 (m), 990 (w), 903 (w), 870 (m), 831 (m), 778 cm$^{-1}$ (m); elemental analysis calc (%) for Cd$_{20}$H$_{28}$O$_{22}$N$_2$: C 48.24, H 2.69, N 3.73; found: C 48.21, H 2.81, N 3.73.

Colorless block crystals of 2 were obtained from a simple hydrothermal self-assembly of Cd(CH$_3$COO)$_2$·2H$_2$O (27 mg, 0.1 mmol), H$_2$L$_1$ (35 mg, 0.1 mmol), and bpe (9.1 mg, 0.05 mmol) in an aqueous solution (10 mL; pH 5 at 120°C for 3 days. Yield: ≈ 20% based on Cd$^2+$; IR: $\nu$ = 1614 (s), 1573 (s), 1396 (s), 1206 (w), 1152 (w), 977 (m), 832 (m), 780 (m), 712 (m), 656 (m), 550 cm$^{-1}$ (s); elemental analysis calc (%) for Cd$_{20}$H$_{28}$O$_{22}$C$_2$: C 44.76, H 2.42, N 3.73; found: C 44.39, H 2.52, N 3.86.

Colorless block crystals of 3 were obtained from a simple hydrothermal self-assembly of Cd(CH$_3$COO)$_2$·2H$_2$O (27 mg, 0.1 mmol), H$_2$L$_1$ (35 mg, 0.1 mmol), and bpa (18.4 mg, 0.1 mmol) in an aqueous solution (10 mL; pH 5 adjusted with H$_2$O(ox)) at 140°C for 3 days. Yield: ≈ 25% based on Cd$^2+$; IR: $\nu$ = 1614 (s), 1573 (s), 1396 (s), 1306 (w), 1222 (m), 1152 (w), 977 (m), 832 (m), 780 (m), 712 (m), 656 (m), 550 cm$^{-1}$ (s); elemental analysis calc (%) for Cd$_{20}$H$_{28}$O$_{22}$C$_2$: C 44.64, H 2.68, N 3.72; found: C 44.51, H 2.81, N 3.81.

Colorless block crystals of 4 were obtained from a simple hydrothermal self-assembly of Cd(CH$_3$COO)$_2$·2H$_2$O (27 mg, 0.1 mmol), H$_2$L$_2$ (35 mg, 0.1 mmol), and bpa (9.9 mg, 0.05 mmol) in an aqueous solution (10 mL; pH 5 adjusted with H$_2$O(ox)) at 120°C for 3 days. Yield: ≈ 20% based on Cd$^2+$; IR: $\nu$ = 1723 (m), 1615 (m), 1575 (s), 1547 (s), 1429 (w), 1373 (s), 1266 (m), 986 (m), 821 (m), 740 (m), 656 (w), 516 cm$^{-1}$ (w); elemental analysis calc (%) for Cd$_{20}$H$_{28}$O$_{22}$C$_2$: C 45.51, H 2.63, N 3.66; found: C 46.08, H 2.98, N 3.81.

Colorless block crystals of 5 were obtained from a single hydrothermal self-assembly of Cd(CH$_3$COO)$_2$·2H$_2$O (27 mg, 0.1 mmol), H$_2$L$_2$ (35 mg, 0.1 mmol), and bpa (19.8 mg, 0.1 mmol) in an aqueous solution (10 mL; pH 8 adjusted with NaOH) at 120°C for 3 days. Yield: ≈ 25% based on Cd$^2+$; IR: $\nu$ = 1614 (s), 1566 (s), 1501 (w), 1427 (w), 1385 (s), 1246 (m), 1065 (w), 1015 (m), 776 (m), 738 (m), 612 (w), 571 cm$^{-1}$ (w); elemental analysis calc (%) for Cd$_{20}$H$_{28}$O$_{22}$C$_2$: C 49.57, H 3.96, N 5.51; found: C 49.63, H 3.99, N 5.30.

X-ray crystallography

Data were collected with MoKα radiation (λ = 0.71073 Å) on a Rigaku R-AXIS RAPID IP diffractometer for C2 and 4, and on a Siemens SMART CCD diffractometer for 1, 3, and 5. With the SHELXTL program, the structures of all compounds were solved by using direct methods. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement, and the other hydrogen atoms were treated by using a riding model. Hydrogen atoms on water molecules in compounds 1–5 were not located. The hydrogen atoms on C23 in 4 were not located. The lattice water molecule in 1 was not located. The structures were then refined on F2 by using the SHELXTL-97 program.[26]

CCDC 1063776 (1), 1063777 (2), 1063778 (3), 1063779 (4), and 1063780 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The crystallographic data for compounds 1–5 are summarized in Table 1.

Table 1. Crystal data for 1–5.

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Keywords: coordination modes · luminescence · photochemistry · polymers · sensors


