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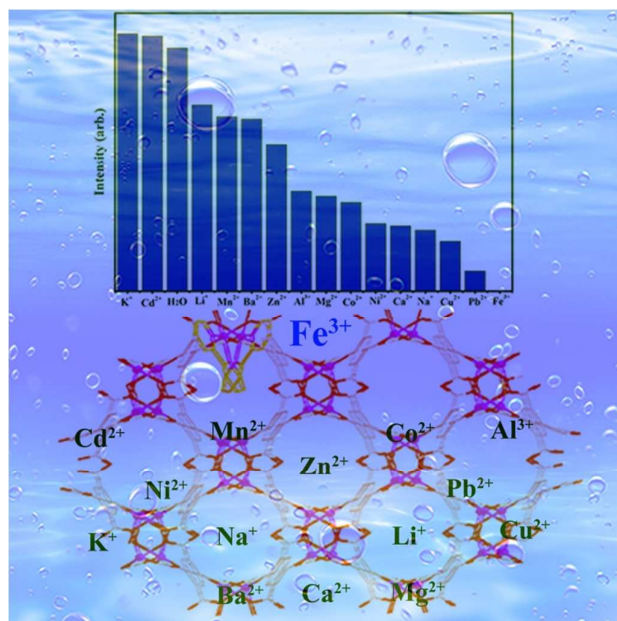
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Graphical Abstract

Three new luminescent Cd(II)-MOFs by regulation of tetracarboxylates and auxiliary co-ligands, displaying high sensitivity for Fe^{3+} in aqueous solution

Yunlong Wu, Guo-Ping Yang*, Xiang Zhou, Jiang Li, Yan Ning, and Yao-Yu Wang*

Three new luminescent Cd(II)-MOFs have been yielded by regulation of the steric effect and tetracarboxylates and auxiliary co-ligands. The solid-state luminescent properties were tested under ultraviolet irradiation at room temperature. Especially for **3**, displaying high sensitivity for Fe^{3+} in aqueous solution with mixed ions.



ARTICLE

Three new luminescent Cd(II)-MOFs by regulation of tetracarboxylates and auxiliary co-ligands, displaying high sensitivity for Fe³⁺ in aqueous solution†

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Three new Cd(II)-MOFs, [Cd(L₁)_{0.5}(bpp)] (**1**), [Cd(L₁)_{0.5}(bipy)] (**2**), and [Cd(L₂)_{0.5}(bipy)] (**3**) [H₄L_n = (1,1':4',1''-terphenyl)-2',*x,x*',5'-tetracarboxylic acid (n = 1, x = 3, and n = 2, x = 4), bpp = 1,3-di(4-pyridyl)propane, and bipy = 2,2'-bipyridine], have been synthesized by Cd(II) ions and isomeric H₄L_n ligands in the presence of auxiliary ligands via solvothermal reaction, which have been fully characterized by elemental analyses, FT-IR spectroscopy, power X-ray diffraction (PXRD), and thermogravimetric analyses (TGA). Complex **1** is a three-dimensional (3D) pillar-layered network built by L₁⁴⁻ and bridging bpp co-ligands, showing a binodal (4,8)-connected **gsp2** topology with symbol of (4⁴.6²)(4¹⁶.6¹²), **2** was successfully yielded by bipy instead of bpp ligand in the assembly of **1**, giving a 2D 4-connected **sql** net, and **3** is a 3D reticular framework with [Cd₂(COO)₄] SBUs based on H₄L₂ ligand, displaying a (4,4)-connected **lvt** (4².8⁴) topology. X-ray diffraction analysis revealed that the structures of MOFs can be mediated by the steric effect of tetracarboxylates and secondary co-ligands. The solid-state luminescent properties of MOFs have been measured carefully by ultraviolet irradiation at room temperature. Especially for **3**, exhibiting a high sensitivity for Fe³⁺ in aqueous solution with mixed metal ions, which make it be a promising crystalline material as luminescent probe to Fe³⁺. Importantly, **3** can keep its original framework and be reused in sensing experiments. The sensing mechanism has also been studied in detail.

1. Introduction

During the last two decades, metal-organic frameworks (MOFs) has been an expanding research spot in the field of coordination chemistry not only because of its fascinating architectures and topologies¹, but also for its potential applications, such as optics, absorption and separation, magnetism, catalysis and sensors². Recently, a large number of MOFs-based fluorescent probes have been yielded for detecting divalent transition metal ions³, however, few studies have been devoted to developing the sensors for triple-charged ions⁴. As is well known, the trivalent metal ions, especially for Fe³⁺, play the vital roles to biological metabolism in cellar systems. Not only for the organisms, is it also a broadly environmental contaminant⁵. Thus, it has been a hot topic for chemists to detect the trivalent metal ions by an accurate way.

There are various methods to monitor these metal ions, such as ion mobility spectroscopy (IMS), inductively coupled plasma (ICP), X-ray dispersion, voltammetry, and atomic absorption spectroscopy etc, some of which are relatively limited for their characteristics. The current studies indicate that the appearance of luminescent MOFs-based sensors can bring some expects for

its unique properties, such as real-time monitor, fast response and high sensitivity etc⁶. Generally, the networks and properties of MOFs could be influenced by various key factors, such as metal ions, ligands, molar ratio of solvents, temperature, pH values and so on⁷. Among them, the selection of ligands is greatly important for the assembly of MOFs with desired motifs and functions⁸. Moreover, it is of equal importance to the metal ions with d¹⁰ configuration for yielding luminescent MOFs.

Motivated by these discussed aspects above and extensions of our previous research works^{2f}, two isomeric tetracarboxylic acids [H₄L_n = (1,1':4',1''-terphenyl)-2',*x,x*',5'-tetracarboxylic acid, n = 1, x = 3, and n = 2, x = 4] and two auxiliary ligands [1,3-di(4-pyridyl)propane (bpp) and 2,2'-bipyridine (bipy)] have been employed as the molecular building blocks (BBMs) with Cd(II) ions to build new luminescent MOFs in this work. Herein, three new MOFs, [Cd(L₁)_{0.5}(bpp)] (**1**), [Cd(L₁)_{0.5}(bipy)] (**2**) and [Cd(L₂)_{0.5}(bipy)] (**3**), have been successfully yielded via solvothermal reaction. X-ray crystallography analysis indicates that the structures of MOFs can be mediated and governed by the steric effect of tetracarboxylates and secondary co-ligands. Moreover, the luminescence of three MOFs have been tested by ultraviolet light irradiation at room temperature, particularly for

3 displaying high sensitivity for Fe³⁺ in aqueous solution with mixed ions because of quenching effect, which thus may be developed as a potential detection material for Fe³⁺. Importantly, 3 can keep its framework and be reused in sensing experiments. And the sensing mechanism has also been discussed in detail.

2. Experimental section

2.1. Materials and measurements

All starting materials and solvents in experiments were purchased commercially and used without further purification. Elemental analyses for C, H and N were carried out on Perkin-Elmer 2400C elemental analyzer. FT-IR spectra were detected on Bruker Equinox 55 spectrometer with KBr pellets in 4000 ~ 400 cm⁻¹. Power X-ray diffraction (PXRD) were conducted by Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K α , λ = 1.5418 Å) with the 2 θ in 5 ~ 50°. The thermogravimetric analyses (TGA) were collected by using NETZSCH STA 449C microanalyzer thermal analyzer at N₂ protection atmosphere with a heating rate of 10 °C min⁻¹. The solid-state luminescent spectra were recorded by the Hitachi F4500 fluorescence spectrophotometer at ambient temperature.

2.2 Synthesis of [Cd(L₁)_{0.5}(bpp)] (1)

A mixture of Cd(NO₃)₂·6H₂O (0.2 mmol, 61.6 mg), H₄L₁ (0.1 mmol, 40.6 mg), bpp (0.05 mmol, 9.9 mg), H₂O (6mL), NMP (4mL) were mixed in 15mL Teflon-lined stainless steel vessel, which heated at 145 °C for 72 h and then cooled to room temperature at the rate of 10 °C h⁻¹, colorless block crystals were obtained. Yield 48% (based on H₄L₁). Elemental analysis of 1, calculated (%): C 56.32, N 5.47, H 3.74; found: C 56.29, N 5.50, H 3.78. FT-IR (cm⁻¹) (Fig. S1, and Table S2, ESI[†]): 3488 (s), 3052 (m), 2939 (m), 2352 (w), 1991 (w), 1577 (s), 1390 (s), 1232 (m), 1089 (w), 1021 (m), 901 (w), 848(s), 765(s), 570(m), 397(w).

2.3 Synthesis of [Cd(L₁)_{0.5}(bipy)] (2)

Similar to that of 1, bpp was instead of bipy in the synthesis procedure, the colorless rod-like crystals of 2 were produced. Yield 52% (based on H₄L₁). Elemental analysis of 2, calculated (%): C 53.69, N 5.96, H 2.79; found: C 53.57, N 6.02, H 2.81. FT-IR (cm⁻¹): 3415 (m), 1580 (s), 1383 (s), 1231 (m), 1151 (w), 1013 (w), 912 (w), 839 (w), 760 (s), 637 (w), 571 (m), 427 (w).

2.4 Synthesis of [Cd(L₂)_{0.5}(bipy)] (3)

Similar to that of 2, except that H₄L₁ was replaced by H₄L₂, the colorless block crystals 3 were formed. Yield of 48% (based on H₄L₂). Elemental analysis of 3, calculated (%): C 53.69, N 5.96, H 2.79; found: C 53.50, N 5.90, H 2.75. FT-IR (cm⁻¹): 3423 (m), 3082 (w), 1645 (s), 1485 (m), 1405 (s), 1325 (s), 1253 (m), 1121 (m), 861 (m), 759 (s), 570 (m), 498 (w), 417 (w).

2.5 Crystal Structure Determinations

Single-crystal X-ray diffraction data of 1–3 were collected on the Bruker SMART APEXII CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) at 296 K. All structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97⁹. The absorption data were corrected by utilizing SADABS routine¹⁰. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were added to their geometrically ideal

positions. The relevant crystallographic data are depicted in Table 1. Selected bonds lengths and angles are listed in Table S1 (ESI[†]). CCDC numbers are 1045867–1045869 for 1–3, respectively.

Table 1 Crystal data and structure refinements for 1–3

Complex	1	2	3
Formula	C ₂₄ H ₁₉ CdN ₂ O ₄	C ₂₁ H ₁₃ CdN ₂ O ₄	C ₂₁ H ₁₃ CdN ₂ O ₄
Mass	511.81	469.73	469.73
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	11.3642(13)	6.2351(18)	15.300(3)
<i>b</i> [Å]	10.8066(12)	20.431(6)	12.482(2)
<i>c</i> [Å]	17.0884(19)	14.646(4)	18.020(3)
α [°]	90	90	90
β [°]	99.153(2)	92.264(5)	90.813(3)
γ [°]	90	90	90
<i>V</i> [Å ³]	2071.9(4)	1864.3(9)	3441.0(10)
<i>Z</i>	4	4	8
<i>D</i> _{calcd} [g·cm ⁻³]	1.641	1.674	1.813
μ [mm ⁻¹]	1.088	1.201	1.302
<i>F</i> [000]	1028	932	1864
θ [°]	1.82–25.00	1.71–25.00	2.11–25.00
Refls collected	10263/3652	9055/3262	8395/3027
GOOF	1.039	1.035	1.003
<i>R</i> ^{int} indices	<i>R</i> ₁ = 0.0351	<i>R</i> ₁ = 0.0289	<i>R</i> ₁ = 0.0373
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> ₂ = 0.0827	<i>wR</i> ₂ = 0.0870	<i>wR</i> ₂ = 0.0758

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

3. Results and discussion

3.1 Structure description of [Cd(L₁)_{0.5}(bpp)] (1)

X-ray crystallography shows that complex 1 crystallizes in monoclinic *P*2₁/*c* space group, revealing a 3D pillared-layer framework. The asymmetric unit consists of one Cd(II) ion, a half of fully deprotonated L₁⁴⁻ and one bpp ligand. Each Cd(II) ion, adopting a distorted octahedral geometry, is coordinated with four oxygen atoms from three deprotonated L₁⁴⁻ ligands and two nitrogen atoms from two bpp ligands, respectively (Fig. 1a). The bond lengths of Cd–O [2.249(3) ~ 2.420(3) Å] and Cd–N [2.289(3) ~ 2.325(3) Å] are consistent with the reported Cd(II)-MOFs with mixed ligands¹¹.

In 1, the four carboxylate groups of L₁⁴⁻ ligand adopt two coordination models with Cd(II) ions: the chelating bidentate ($\eta^2\mu_1\chi^2$) and bridging bidentate ($\eta^2\mu_2\chi^2$) fashions (Scheme 1a). Thus, each Cd(II) ion is connected by four oxygen atoms from three independent L₁⁴⁻ ligands and each L₁⁴⁻ take coordination with six Cd(II) ions to build an unlimited 2D [Cd₂L₁] layer (Fig. 1b). Moreover, these adjacent 2D layers are further supported by the flexible bridging bpp ligands as the pillars to produce a 3D pillar-layered framework (Fig. 1c, and S2, ESI[†]). The bpp ligand can often generate four steric conformations with respect to the free rotations of three methylene groups, such as TT, GG, TG, and GG' fashions (T = trans and G = gauche)¹². Herein, the

bpp ligands exhibit TG fashion with a shorter N-to-N distance of 9.255 Å to link the adjacent Cd(II) ions, and there thus are no residual solvent accessible voids in the 3D network of **1**. Topologically, when the dimeric $[\text{Cd}_2(\text{COO})_4]$ motifs as the secondary build units (SBUs) are simplified as eight-connected nodes, and L_1^{4-} ligands are considered as four-connected nodes (Fig. S3, ESI[†]), the framework of **1** is therefore designated as an unprecedented binodal (4,8)-connected **gsp2** topological net with symbol of $(4^4.6^2)(4^{16}.6^{12})$, as shown in Fig. 1d.

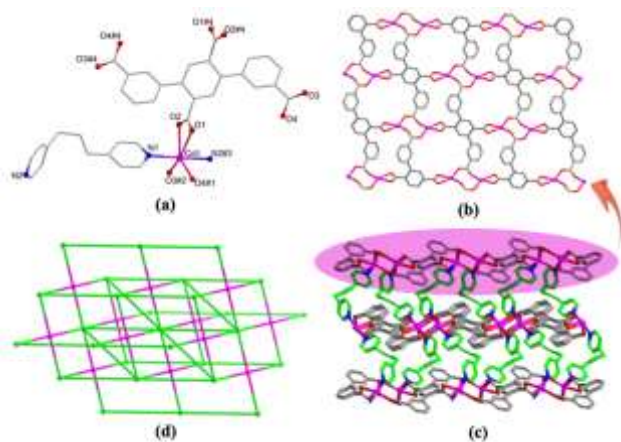
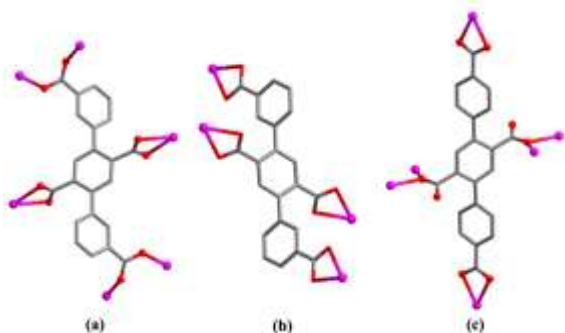


Fig. 1 (a) Coordination environment of Cd(II) in **1**. Symmetry codes: #1: $-x+1, -y+1, -z+2$; #2: $-1+x, y, z$; #3: $x+1, -y+0.5, z+1/2$; #4: $-x+1, -y, -z+2$. (b) 2D layer structure. (c) 3D framework of **1** viewed along a axis, the hydrogen atoms have been omitted for clarity. (d) Schematic view of the (4,8)-connected topology of **1** (The green balls is dimeric Cd(II) SBUs and pink balls represent L_1^{4-} ligands).



Scheme 1 The coordination modes of L_1^{4-} and L_2^{4-} with Cd(II) ions.

3.2. Structure description of $[\text{Cd}(\text{L}_1)_{0.5}(\text{bipy})]$ (**2**)

Complex **2** crystallizes in monoclinic system with $P2_1/c$ space group, displaying a 2D layered network built on the bridging L_1^{4-} and chelating bipy co-ligands. The asymmetric building unit contains one Cd(II) ion, a half of L_1^{4-} and one bipy ligand. As depicted in Fig. 2a, Cd(II) ion shows a distorted octahedral coordination geometry defined by the four oxygen atoms from two L_1^{4-} ligands and two nitrogen atoms from one bipy ligand. The distances of Cd–N and Cd–O are in the range of 2.291(2) ~ 2.397(2) Å and 2.300(3) ~ 2.330(3) Å, respectively.

Different from that of **1**, the four carboxylate groups of L_1^{4-} ligands all adopt the bidentate coordination ($\eta^2\mu_1\chi^2$) fashion to bind four centre Cd(II) ions (Scheme 1b). Each Cd(II) ion is coordinated with two carboxylates from two L_1^{4-} ligands to

produce 2D grid-like layer (Fig. S4, ESI[†]), and the coordinated bipy tectons are just occupied in these grids of the 2D layer. Obviously, the L_1^{4-} ligands can be considered as four-connected nodes, thus, the network of **2** forms a uninodal 4-connected **sql** net with symbol of $(4^4.6^2)$ (Fig. 2c). Finally, the strong π - π stacking interactions between the adjacent bipy ligands (the distance of centroids is 3.634 Å, Fig. 2b) can sustain the neighbouring 2D layers to further accumulate into a 3D supramolecular structure (Fig. 2d).

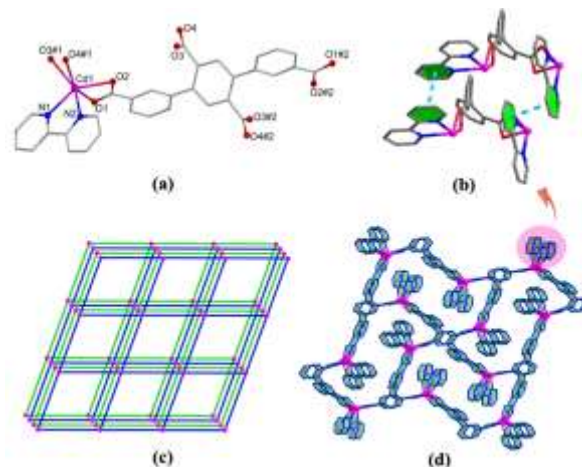


Fig. 2 (a) Coordination environment of Cd(II) ion in **2**. Symmetry codes: #1: $x, -y+0.5, z+0.5$; #2: $-x, -y+1, -z$. (b) The π - π stacking interactions of the 2D adjacent layers. (c) Topological net of 2D layers. (d) View of the 3D supramolecular network.

3.3. Structure description of $[\text{Cd}(\text{L}_2)_{0.5}(\text{bipy})]$ (**3**)

X-ray structural determination reveals that **3** crystallizes in monoclinic crystal system with $C2/c$ space group, resulting in a 3D dense framework built by the deprotonated L_2^{4-} and bipy ligands. The fundamental asymmetric building unit includes one Cd(II) ion, a half of L_2^{4-} and one bipy ligand. The coordination environment of Cd(II) ion can be described as a distorted octahedral geometry with four oxygen atoms from three L_2^{4-} tectons and two nitrogen atoms from one bipy ligand (Fig. 3a). The bond lengths of Cd–O and Cd–N lie in the normal range of 2.280(3) ~ 2.454(3) Å and 2.292(3) ~ 2.339(4) Å, respectively.

In **3**, the four carboxylates of L_2^{4-} ligand take coordination with six centre Cd(II) ions, adopting the bidentate ($\eta^2\mu_1\chi^2$) and bridging monodentate ($\eta^1\mu_2\chi^2$) models (Scheme 1c), and a 3D dense framework is thereby formed by the connection of Cd(II) ions and L_2^{4-} ligands. Similarly to that of **1**, there are also no residual solvent accessible voids in the network of **3**, the reason of which is that the 1D channels are filled with the coordinated bipy ligands and carboxylate groups (Fig. 3c). Notably, when the dimeric $[\text{Cd}_2(\text{COO})_4]$ SBU motifs and L_2^{4-} ligands are considered as four-connected nodes (Fig. 3b, and S5, ESI[†]), the whole framework of **3** can be simplified as a binodal (4,4)-connected **lvt** topology with point symbol of $(4^2.8^4)$ (Fig. 3d).

3.4. Regulation of the steric effect of tetracarboxylates and secondary co-ligands on 1–3

The previous works have been proven that the final framework of CPs can often be fine-tuned by various key factors, such as

choice of centre metal ions, organic ligands, molar ratio of the reactants, reaction temperature, and pH value et al¹³. Herein, two isomeric tetracarboxylic acids (H_4L_1 , and H_4L_2) and two auxiliary ligands (bpp, and bipy) have been chosen with Cd(II) ions to build luminescent MOFs for the investigations of the roles of the steric effect of tetracarboxylates and secondary co-ligands (Scheme 2). Compared with the structures of **1–3**, it is found that complexes **1** and **3** possess the higher dimensional frameworks (3D) with the dimeric $[Cd_2(COO)_4]$ SBU motifs, while **2** has the lower dimensional network (2D). The major reason is that when the flexible bridging bpp ligand is used in the assembly of **1**, it can support the adjacent 2D $[Cd_2L_1]$ layers to form the 3D network. While the chelating bipy ligand has a negative effect on the assembly of **2**, which can hinder the L_1^{4-} ligands to link more centre Cd(II) ions, thus only resulting in a 2D layered net. For **3**, although the bipy ligand is still used in the assembly, the further distance between the two carboxylates of L_2^{4-} ligands can guarantee the 3D architecture to be produced successfully. Besides, the roles of the secondary ligands can also meditate and influence the coordination modes of L_n^{4-} ligands in **1–3**. The L_n^{4-} ligands took coordination with six Cd(II) ions in **1** and **3**, forming different dimeric $[Cd_2(COO)_4]$ SBU motifs and scarcely unprecedented topologies, whereas L_1^{4-} ligand is only linked with four centre Cd(II) cations in **2**. Therefore, it could be concluded that the regulation of the steric effect of the tetracarboxylates and secondary co-ligands can fine-tune and govern the skeletons and topologies of desired MOFs from above discussions.

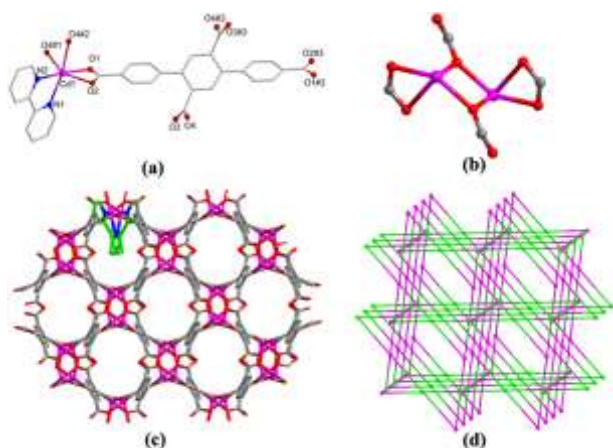
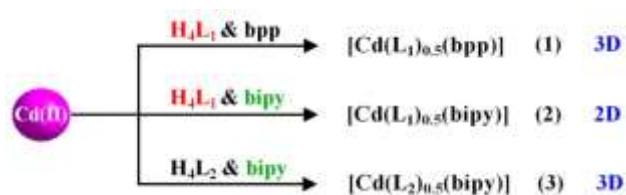


Fig. 3 (a) Coordination environment of Cd(II) ion in **3**. Symmetry codes: #1: $x, -y, z-0.5$; #2: $-x+1.5, y+0.5, -z+1.5$; #3: $-x+1, -y, -z+2$. (b) The $[Cd_2(COO)_4]$ SBU unit in **3**. (c) 3D framework of **3**, and the bipy ligands are only highlighted in the left grid. (d) View of the topology net for **3** (The green balls represent $[Cd_2(COO)_4]$ SBUs and pink balls represent L_1^{4-} ligands).

3.5. PXRD and the thermogravimetric analyses

The purities of the as-synthesized bulk samples of three MOFs were examined by the powder X-ray diffraction (PXRD) experiments at room temperature (Fig. S6, ESI†). The PXRD patterns of the obtained crystalline samples are well consistent with the simulated from the single crystal data, indicating high phase purity of samples to support the further experiments. And the thermal stabilities of three MOFs were also tested by the thermogravimetric analysis (TGA) under N_2 atmosphere (Fig. S7, ESI†). Due to the absence of guest molecules in three MOFs, it can be seen that they have the same thermal stabilities

from the TGA curves, and thus, they have the relatively higher stabilities, and their structures will be destroyed beyond their stable temperatures.



Scheme 2 The synthetic processes of MOFs **1–3**.

3.6. Luminescent properties

The MOFs including d^{10} ions have been becoming the potential fluorescent materials and widely used in the optical field¹⁴. Therefore, the solid state luminescent properties of three MOFs and H_4L_n ligands have been studied at room temperature (Fig. 4a). The maximum emission peaks were observed at 383, 369, 388, and 414 nm for **1–3** and H_4L_n ligands, respectively. The maximum emissions of **1–3** are obvious blue shift compared with those of H_4L_n ligands, which may arise from ligand-to-metal charge transformations (LMCT). Moreover, complex **3** shows an enhanced luminescent intensity compared with those of **1** and **2**, which can be explained by the differences of the structures. In **1** and **2**, the flexible bridging bpp ligands and π - π stacking interactions can enhance the structural flexibilities to result in reducing the luminescent intensities¹⁵, whereas the rigid and stable framework of **3** can decrease the loss of energy and thereby keep the strengthened luminescent intensity. More importantly, because of the visible emission of **3** under the ultraviolet light, its sensing properties have been further studied to probe the different metal ions in aqueous solution.

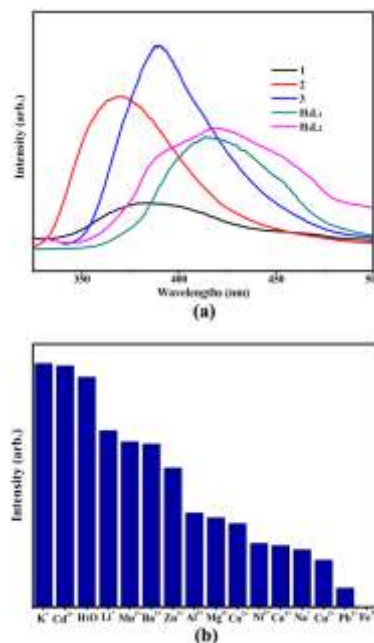


Fig. 4 (a) Luminescent emission spectra of three MOFs and H_4L_n ligands ($\lambda_{ex} = 310$ nm for **1** and **2**, 320 nm for **3**, and 280 nm for H_4L_n ligands). (b) The relative luminescent intensities of $M^{n+}@3$ in aqueous solutions.

3.7. Chemosensor for Fe³⁺ ion

The as-synthesized products of **3** were grinded and scattered in distilled water with 0.01 mol L⁻¹ M(NO₃)_n (M = K⁺, Cd²⁺, H₂O, Li⁺, Mn²⁺, Ba²⁺, Zn²⁺, Al³⁺, Mg²⁺, Co²⁺, Ni²⁺, Ca²⁺, Na⁺, Cu²⁺, Pb²⁺ and Fe³⁺) for 24h to form the Mⁿ⁺@**3** for sensing experiments. The luminescent intensities have no effect on the addition of K⁺ and Cd²⁺ ions in solutions compared with blank sample (Fig. 4b, and S9, ESI[†]), while other metal ions show the different quenching effect by depending on the nature of metal ions, and the visual change of Mⁿ⁺@**3** was also recorded in the aqueous solution (Fig. S10, ESI[†]). Especially for Fe³⁺ ion, there exists a significant quenching behavior to the luminescence of the system. Also, the selective sensing properties were further studied to different mixed ions in the aqueous solution. It is found that the luminescence of **3** is slightly weakened by the mixed ions in the absence of Fe³⁺ (Fig. 5a); however, the luminescence will be completely quenched by the addition of Fe³⁺ in the above system immediately.

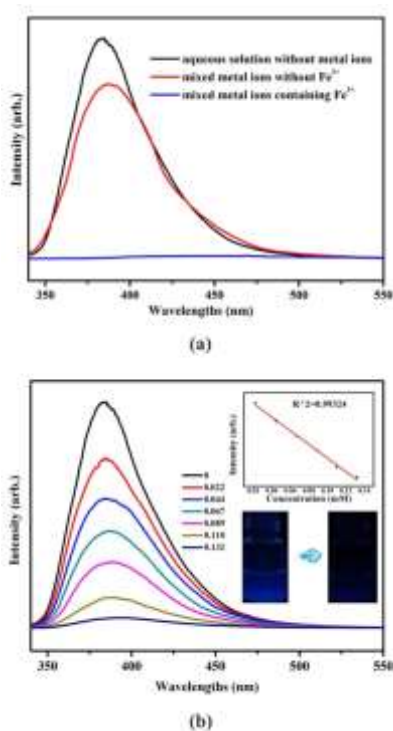


Fig. 5 (a) The emission spectra of **3** with different mixed metal ions. (b) Emission spectra of Fe³⁺@**3** aqueous suspension with the concentration of Fe³⁺ in 10⁻⁵ ~ 10⁻⁴ M; the inset shows that the relationship of the luminescent intensities and concentration of Fe³⁺, and the colour change of the solution.

The relationship between the concentration of Fe³⁺ ions and the luminescent intensities of **3** has also been studied by changing the amount of Fe³⁺ ions in aqueous solution in the range of 10⁻⁵ ~ 10⁻⁴ M (Fig. 5b). The titration experiments show that the luminescence of **3** is gradually decreased by increasing the concentration of Fe³⁺, showing the diffusion controlled quenching process¹⁶, and the concentration is to 10⁻⁴ M, then the luminescence will be almost quenched. Moreover, the relationship is closely consistent with the equation: $I_0/I = -8.6 [\text{Fe}^{3+}] + 1.2$ ($R^2 = 0.993$), where I_0 and I are the luminescent intensity of the blank sample and Fe³⁺@**3**, respectively. The mechanism of quenching effect caused by Fe³⁺ can be explained

as the electron transformation from the donor (organic ligands) to the acceptor (metal ions). In **3**, there exist the uncoordinated oxygen atoms of carboxylates of L₂⁴⁻ ligands, acting as the electrons donors, when Fe³⁺ ions are incorporated with **3** (Fe³⁺@**3**), the lone-pair electrons will be given from oxygen atoms to Fe³⁺ ions to form an electron-deficient region¹⁷. Upon the ultraviolet light excitation, the electrons will be transferred from the donor to the acceptor, resulting in the luminescent quenching. Clearly, the crystalline products of **3** should be a highly selective sensing probe for Fe³⁺ based on the above discussions. In addition, the ICP experiments have also been performed to check the release of Cd(II) ions from **3** after each cyclic sensing experiments. The four cyclic concentration of Cd(II) ions is 0.18 (1.6*10⁻⁶), 0.20 (1.8*10⁻⁶), 0.17 (1.5*10⁻⁶), 0.22 (2.0*10⁻⁶) μg/mL (mol/L), respectively, which is close to that of the blank sample (0.15 μg/mL) and much lower than that of tested metal ions (0.01 mol/L). Therefore, it can be concluded that there is no release of Cd(II) ions from products of **3** in the sensing experiments, and **3** can stably keep its framework and be reused as probes (Fig. S11, ESI[†]).

Conclusions

In summary, three new luminescent Cd(II)-MOFs have been synthesized successfully by using isomeric tetracarboxylates and auxiliary co-ligands via solvothermal condition. The X-ray diffraction results indicate the steric effect of tetracarboxylates and secondary co-ligands have the positive influence on the structural diversities of the desired MOFs. The solid-state luminescent properties of three MOFs were tested carefully by the ultraviolet irradiation at ambient temperature. The results of luminescent sensing experiments show that the crystalline product of **3** is a highly selective sensing material for Fe³⁺ ions in the aqueous solution with mixed metal ions, and more importantly, which can be recycled friendly after the series of sensing experiments. The further research works in this filed are undergoing in the way.

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Notes and references

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† Electronic Supplementary Information (ESI) available: FT-IR, TGA, and PXRD patterns, and the additional figures of MOFs. For the ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/b000000x/

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