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Two luminescent d^{10} metal coordination polymers assembled from a semirigid terpyridyl carboxylate ligand with high selective detecting of Cu²⁺, Cr₂O₇²⁻ and acetone

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Abstract: Using a carboxylic oligopyridine ligand, 4'-(4-carboxyphenyl)-4,2':6',4"-(Hcptpy), and imidazole-4,5-dicarboxylic acid terpyridine (H₃idc). two metal(II)-cptpy compounds formulated as $[Zn_2(cptpy)_4]_n \cdot nH_2O$ (1), $[Zn_2(cptpy)_2(Hidc)(H_2O)_2]_n \cdot nH_2O$ (2) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Compound 1 shows a $2D + 2D \rightarrow 3D$ supramolecular framework structure generated by two-fold interpenetrating 3-connected 2D framework $(2D+2D\rightarrow 2D)$ with the sql topological net and the Schläfli symbol of $\{4^4 \cdot 6^2\}$. Compound 2 displays a 1D ladder chain structure. The luminescent properties of 1 and the ones immersed in various kinds of organic compounds and nitrate@DMF solutions have been investigated. Importantly, 1 shows highly selective and sensitive response to acetone and Cu^{2+} through luminescence quenching effects, making it a promising luminescent sensor for acetone molecule and Cu²⁺. Meaningwhile, compound 2 shows highly selective sensitivity for $Cr_2O_7^{2-}$. 9 way

Graphical Abstract

Two luminescent d^{10} metal coordination polymers assembled from a semirigid terpyridyl carboxylate ligand with high selective detecting of Cu²⁺ ion, Cr₂O₇²⁻ and acetone

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Two Zn(II) coordination polymers based on 4'-(4-carboxyphenyl)-4,2':6',4"-

terpyridine have been obtained. Compound **1** shows high selective detecting for Cu^{2+} ion and acetone molecule. Meaningwhile, compound **2** shows highly selective sensitivity for $Cr_2O_7^{2-}$.



Keywords: Coordination polymer; Carboxylate; Luminescence; Sensor

Accepted

1. Introduction

Currently coordination polymers (CPs) or metal-organic frameworks (MOFs) as a kind of multifunctional materials still have attracted much interest due to their potential applications such as molecular separation [1], catalysis [2], gas storage and

capture [3], drug delivery [4], and sensor devices [5,6]. In particular, as high sensitivity and low cost sensors, researches on MOF-based fluorescence sensors have developed significantly owing to their potential importance in biological and environmental systems [5-7].

Some representative examples for the selective sensing of metal ions such as Cu^{2+} , Cr⁶⁺ have been successfully studied [7-9]. Among those, luminescent MOFs containing free Lewis basic pyridyl sites as the potential receptor units to interact with the target metal ions have also been reported, such as $[Eu(pdc)_{1.5}]$ $(DMF)] \cdot (DMF)_{0.5} (H_2O)_{0.5}$ (pdc=pyridine-3,5-dicarboxylate) [7a], $[H_2N]$ $(Me)_2[Ln_3(L)_2(HCOO)_2(DMF)_2(H_2O)]$ $(H_4L=2,6-di(3',5'-dicarboxylphenyl)pyridine)$ [8]. Generally, selectivity and sensitivity mainly depend on the naked interaction between the host and the guest, and this interaction is highly affected by solvent, hydrogen bonding capability, $\pi \dots \pi$ stacking and electrostatic interaction. Despite recent exciting and compelling developments, the design and construction of MOF-based fluorescence sensors are still a great challenge.

MOFs are constructed from metal ions and bridging organic linkers [10-12]. The successful synthesis of the target MOFs relies heavily on the organic links, so it is extremely important to select an appropriate organic linker to construct MOFs. In this context, 4'-(4-carboxyphenyl)-4,2'.6',4"-terpyridine (Hcptpy, Scheme 1) was selected as our ligand according to the following consideration: (a) Hcptpy, as a semi-rigid bridging ligand, can link metal ions via coordination bond to construct high dimensional and honeycomb porous coordination polymers. (b) It has a large π -conjugated nonlinear structure with N, O donors that can offer additional hydrogen bonding and π - π interactions to consolidate the whole framework structures. (c) Metal ions prefer binding carboxylate O atoms and N atoms of two terminal pyridine groups rather than the N atom of the central pyridine in Hcptpy because of steric effect resulting from two terminal pyridine groups, so this N atom as a functional site is predicted to recognize small Lewis acidic molecules and metal ions. The incoming imidazole-4,5-dicarboxylic acid as auxiliary ligand has abundant coordination modes and is convenient bridging units, which may form much more complicated structures.

Based on above mentioned aspects, we report synthesis and crystal structure of two new compounds $[Zn_2(cptpy)_4]_n \cdot nH_2O$ (1), $[Zn_2(cptpy)_2(Hidc)(H_2O)_2]_n \cdot nH_2O$ (2). Solid-state luminescent properties of 1 were also examined under ultraviolet irradiation at ambient temperature. Compounds 1 and 2 show high selectivity and sensitivity for Cu²⁺ ion, Cr₂O₇²⁻ anion and acetone molecule due to the quenching effect, which may be a potential material for detecting these substances. Meanwhile the mechanisms of the quenching effect and sensing properties of 1 and 2 are discussed.

[Scheme 1 is here]

2. Experimental section

2.1. Materials and general methods

Hcptpy was prepared according to literature methods with some modifications [13-15], other chemicals were of reagent grade and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 Fourier transform infrared spectrometer in the 400-4000 cm⁻¹ region. Elemental analyses (C, H, N) were performed on an elementar Vario EL III elemental analyzer. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a rate of 10 °C/min in a nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns were carried out by a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K_a, $\lambda = 1.5418$ Å) with the 20 from 5 to 50° under the 0.03° scan step. Photoluminescent spectra of compounds 1 and 2 were measured using a Hitachi F-7200 Fluorescence Spectrometer for the solid powder samples at room temperature. Hitachi U-3310 UV-vis spectrometer was selected to perform diffusion reflectance measurement.

2.2. Synthesis

2.2.1 Synthesis of Mptpy

A mixture of 4-acetylpyridine (3.21 g, 26.7 mmol), p-tolualdehyde (3.208 g, 26.7 mmol) and NaOH (20ml, 2.0 mol/L) was dissolved in ethanol (50 mL) and stirred at 0 °C for 2 h, resulted in the formation of a light yellow solution. Then, added 4-acetylpyridine (3.208 g, 26.7 mmol) and excessive ammonium acetate (10.00 g, 129.7 mmol), stirred at 80 °C for 5 h. After the mixture was cooled to room temperature, the resulting white precipitate was filtered off, recrystallized with methanol, and dried in a vacuum to give 3.56 g (yield 41.3 % based on p-tolualdehyde) Mptpy (confirmed by single-crystal X-ray analysis) as colorless block crystals. Anal. Calcd. (%) for C₂₂H₁₇N₃: C, 81.71; H, 5.30; N, 12.99. Found: C, 81.57; H, 5.34; N, 12.39. IR(KBr, cm⁻¹): 3429(w), 3029(m), 1686(w), 1660(m), 1595(vs), 1548(m), 1514(w), 1406(w), 1340(w), 1225(m), 1043(m), 991(s), 812(vs), 656(m), 513(w). ESI-MS: $[M+H]^+$ calcd. for C₂₂H₁₈N₃: 324.1495; found: 324.1488. ¹H NMR (400) MHz, $(CD_3)_2SO_2$) δ : 8.76 -8.75(m, 4H), 8.45 (s, 2H), 8.33-8.30 (m, 4H), 8.02 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, $(CD_3)_2SO_2$) δ: 154.36, 150.34, 150.10, 145.39, 139.54, 133.86, 129.73, 127.35, 121.20, 118.58, 20.86. (Figs. S1 and S2, supporting information)

Synthesis of Hcptpy.

Method 1: A mixture of Mptpy (2.16 g, 6.7 mmol), KMnO₄ (4.20 g, 26.7 mmol), and H₂O (100 mL) were added to a round bottom flask and stirred at room temperature. In this period, the solution was adjusted to pH=10.0 with the addition of KOH. After stirring for 2h at 100°C, the mixture was filtered and washed with hot water. And then the filtrate was made slightly acidic (pH=5.0) by the addition of HCl (aq., conc.), the precipitate was filtered off and dried in vacuo to give a white powder. Yield: 1.95 g (83%). Anal. Calc. for $C_{22}H_{15}O_2N_3$ (Mr = 353.11) (%): C, 74.78; H, 4.28; N, 11.89. Found (%): C, 74.23; H, 4.92; N, 11.37. IR(KBr, cm⁻¹): 3407(s), 3090(m), 2024(w), 1693(s), 1631(s), 1600(s), 1506(s), 1425(w), 1397(m), 1328(w), 1119(m), 834(m), 778(m), 617(m). ESI-MS: [M-H]⁻ calcd. for $C_{22}H_{14}O_2N_3$: 352.1092; found: 352.1090. ¹H NMR (400 MHz, (CD₃)₂SO₂) δ : 9.02 (m, 4H), 8.85–8.78 (m, 6H), 8.30 (d, J=8.0, 2H), 8.14 (d, J=8.0, 2H). ¹³C NMR (100 MHz, (CD₃)₂SO₂) δ : 166.87,

152.44, 151.38, 149.91, 143.87, 140.01, 132.10, 129.95, 128.05, 123.93, 122.24. (Figs. S1 and S2, supporting information)

[Scheme 2 is here]

Method 2: In a typical preparation, 4-acetylpyridine (1.21 g, 10 mmol) was added to a stirred solution of 4-carboxybenzaldehyde (0.75 g, 5 mmol), KOH (0.8 g, 14 mmol) and NH₃·H₂O (20 mL) in 150 mL ethanol. The reaction mixture was stirred at room temperature whilst open to air for 48 h, after which the solution was made slightly acidic (pH=5) with the addition of HCl (aq., conc.). The resulting light yellow precipitate was filtered off, recrystallized with a mixture of ethanol and methanol, and dried in vacuo to give white powders. Yield: 1.22 g (69%). ESI-MS: [M-H] calcd. for $C_{22}H_{14}N_3O_2$: 352.1092; found: 352.1090. ¹H NMR (400 MHz, (CD₃)₂SO₂) δ : 9.02 (m, 4H), 8.85–8.78 (m, 6H), 8.30 (d, J=8.0, 2H), 8.14 (d, J=8.0, 2H). ¹³C NMR (100 MHz, (CD₃)₂SO₂) δ : 166.87, 152.44, 151.38, 149.91, 143.87, 140.01, 132.10, 129.95, 128.05, 123.93, 122.24. (Figs. S1 and S2, supporting information)

[Scheme 3 is here]

2.2.2 Synthesis of [Zn₂(cptpy)₄]_n·nH₂O (1)

Method 1: Compound **1** was prepared by hydrothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0136 g, 0.1 mmol) and Hcptpy (0.0277 g, 0.1 mmol) in distilled water (8 mL) and N,N-dimethylacetamide (DMA) (2 mL) and using 0.5 mol·L⁻¹ NaOH aqueous solution to adjust the pH to 6.0 that was placed in a Teflon-lined stainless steel vessel (25 mL), heated to $180^{\circ}C$ for 72h and then cooled to room temperature at a rate of 5°C/h. The yellow block crystalline product was obtained, washed with distilled water (5 mL), and dried in air to give 0.0484 g, yield 62.2% based on Zn. Elemental anal. calcd for: $C_{88}H_{56}N_{12}Zn_2O_9$ (%): C 67.92, H 3.63, N 10.80; found: C 67.75, H 3.65, N 10.39. IR(KBr, cm⁻¹): 3414(s), 3132(s), 1597(s), 1548(s), 1399(vs), 1221(w), 1138(w), 1066(w), 1021(w), 831(w), 781(m), 700(m),

632(m), 489(w).

Method 2: Compound **1** was synthesized in a similar procedure as Method **1**, by using ZnCl_2 (0.0166 g, 0.1 mmol) in place of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The yellow block crystalline product was obtained, washed with distilled water (5 mL), and dried in air to give 0.0383 g, yield 49.2% based on Zn. Elemental anal. calcd for: $C_{88}\text{H}_{56}\text{N}_{12}\text{Zn}_2\text{O}_9$ (%):C 67.92, H 3.63, N 10.80; found: C 67.75, H 3.65, N 10.39. IR(KBr, cm⁻¹): 3414(s), 3132(s), 1597(s), 1548(s), 1399(vs), 1221(w), 1138(w), 1066(w), 1021(w), 831(w), 781(m), 700(m), 632(m), 489(w).

2.2.3. Synthesis of $[Zn_2(cptpy)_2(Hidc)(H_2O)_2]_n \cdot nH_2O$ (2)

Method 1: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0291 g, 0.1 mmol), Hcptpy (0.0277 g, 0.05 mmol), and H₃idc (0.0126 g, 0.1 mmol) in distilled water (10 mL) that adjusted the pH value to 4.5 with 0.5 mol⁻¹ NaOH aqueous solution was placed in a Teflon-lined tainless steel vessel (25 mL), heated to 180°C for 72 h and then cooled to room temperature at a rate of 5°C/h. The yellow sheet crystalline products of **2** were obtained, washed with distilled water (5 mL), and dried in air to give 0.0321 g (yield 61.8% based on Zn). Anal. Calc. for C₄₉H₃₁N₈Zn₂O₁₁ (%): C, 56.67; H, 3.00; N, 10.79. Found: C, 56.52; H, 3.08; N, 10.32%. IR(KBr, cm⁻¹): 3133(s), 1596(m), 1548(m), 1401(vs), 1251(w), 1132(w), 870(w), 829(m), 784(m), 707(m), 634(w), 517(w).

Method 2: Compound **2** was synthesized in a similar procedure as Method **1**, by using distilled water (8 mL) and N, N-dimethylacetamide (DMA) (2 mL) in place of distilled water (10 mL). The yellow sheet crystalline product was obtained, washed with distilled water (5 mL), and dried in air to give 0.0281 g, yield 54.1% based on Zn. Anal. calcd for: $C_{49}H_{31}N_8Zn_2O_{11}$ (%):C, 56.67; H, 3.00; N, 10.79. Found: C, 56.52; H, 3.08; N, 10.32%. IR(KBr, cm⁻¹): 3133(s), 1596(m), 1548(m), 1401(vs), 1251(w), 1132(w), 870(w), 829(m), 784(m), 707(m), 634(w), 517(w).

2.2.4. Crystal structure determinations

Suitable single crystals of compounds 1-2 were tested on a Bruker SMART APEXII CCD diffractometer equipped with graphite-monochromated Mo-K_{α}

radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods and refined by a full-matrix, least-squares refinement on F^2 with SHELXL-97 and SHELXS-97 [16]. The hydrogen atoms were calculated and assigned their ideal positions with isotropic displacement factors and included in the final refinement by use of geometric restraints. The relevant crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table S1 (ESI[†]). CCDC numbers are 1478584-1478586 for **Mptpy** and compounds **1-2**, respectively.

2.3. Quantum-chemical calculation

The optimized geometry and natural bond orbital (NBO) charge distributions of the free ligand Hcptpy were given by the GAUSSIAN 03 suite of programs [17]. And all calculations were carried out at the B3LYP/6-31G(d, p) level of theory.

3. Results and discussion

3.1. Synthesis

The optimized geometry and natural bond orbital (NBO) charge distributions of Hcptpy have been calculated by the B3LYP/6-311G(d, p) level [17]. The calculated results reveal that Hcptpy has one characteristics: The negative NBO charges mainly distribute on the oxygen and nitrogen atoms. The NBO charges are -0.598 and -0.716 for two carboxylate oxygen atoms, -0.455, -0.455 and -0.455 for three pyridyl nitrogen atoms in the free ligand Hcptpy (Scheme 1). These values show that the N and O atoms may have strong coordination abilities under appropriate reaction conditions, which are confirmed by our present experimental results. In **1** and **2**, the carboxyl group from Hcptpy is deprotonated to form the (cptpy)⁻ unit. These findings further confirm our views about the coordination ability of Hcptpy.

It is well-known that the purposeful design and controllable synthesis of functional MOFs are influenced by many factors. The effect of the N, O-donor auxiliary ligands has also attracted increasing interest in recent years because the auxiliary ligands used in the assembly processes may play an important role in directing the construction of MOFs. Obviously, compared with compound **1**, the

auxiliary ligand (H₃idc) has a significant influence on the structure formation of **2**. Interestingly, In the two preparation methods of **1**, when using ZnCl_2 (0.0166 g, 0.1 mmol) in place of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ under similar condition, the crystals of **1** are also obtained. The results indicate that anions has no influnce on crystal structure of **1**.

3.2. Structure description of crystalline polymer [Zn₂(cptpy)₄]_n·nH₂O (1)

X-ray single crystal structural analysis reveals compound 1 shows a two-fold interpenetrating 2D framework. The asymmetric unit of 1 contains two crystallographically independent Zn(II) (Zn1 and Zn2) ions, four (cptpy)⁻ anions and one lattice water molecule. As shown in Fig. 1a, Zn1 center is four-coordinated to two oxygen atoms (O1, O3A) from different (cptpy)⁻ anions and two nitrogen atoms (N1A, N4) from two different (cptpy)⁻ anions, respectively. The coordination geometry of Zn1 center can be described as a distorted tetrahedron, the O1, O3A, N1A atoms comprise the basal plane and N4 occupies vertex position. The coordination geometry of Zn2 center can be described as a distorted trigonal bipyramid geometry (Fig. 1a), the O5, O8B and N7A atoms comprise the equatorial plane, and the N10, O7B atoms occupy the axial positions [N10-Zn2-O7B=149.8(2)°], the Zn–N distances fall in the range of 2.065(6) Å to 2.086(6) Å, and the Zn–O bond lengths vary from 1.917(7) to 2.210(6) Å, which is similar to previously reported values [18a]. In compound 1, the three pyridyl rings of (cptpy)⁻ ligand are non-planar, each outer pyridyl group is twisted with respect to the central one, the dihedral angles between the central and outer pyridyl rings are 20.28° (N1 pyridyl ring), 34.96° (N2 pyridyl ring), 1.90° (N4 pyridyl ring), 23.42° (N6 pyridyl ring), 9.36° (N7 pyridyl ring), 21.43° (N9 pyridyl ring), 10.40° (N10 pyridyl ring) and 34.58° (N12 pyridyl ring), respectively. The rotation of the N1, N4, N7 and N10 pyridyl ring with the central pyridyl ring is larger than that of N2, N6, N9 and N12 pyridyl ring, the reason for this phenomenon is the repulsion force arising from the central pyridyl- β -hydrogen atoms and the formation of intermolecular bridging hydrogen bonds to stabilize the complexes [18b, c].

Notably, the Zn1 ions are connected by two pyridyl nitrogen atoms and two carboxylate oxygen atoms of the different (cptpy)⁻ ligands with a μ_2 - η^1 : η^1 bridging

mode to form a 2D layers, and the Zn2 ions are connected by two pyridyl nitrogens atom and three carboxylate oxygen atoms of the different (cptpy)⁻ ligands with a μ_2 - η^1 : η^1 and μ_2 - η^1 : η^2 bridging mode to form a similar 2D layer. The through-space apertures within a single layer motif measure 15.102×15.117 Å (Fig. 1b). The large rectangular windows within the layers allow interpenetration of parallel sets of layers with each other. Therefore, each individual 2D layer is parallel-interpenetration with another generating a $2D+2D\rightarrow 2D$ interpenetration bi-layer structure (Fig. 1c). From the topological perspective, if each Zn(II) ion acts as 4-connected node and (cptpy)⁻ anion is also severed as 4-connected node, the architecture of **1** is simplified to a (4, 4)-connected 2D sql topological network with the Schläfli symbol of $\{4^4 \cdot 6^2\}$. The π ... π stacking interaction between the pyridyl rings and phenyl rings in adjacent layers sustains the system of interpenetrated bi-layers (Fig. S4). Interestingly, the uncoordinated pyridyl rings of (cptpy) anion ligands serve as side arms hanging on the opposite side of the layer. As a result, the bi-layer networks generate a 2D + 2D \rightarrow 2D tetra-layer structure (Fig. S5) through $\pi \dots \pi$ stacking interaction between pyridyl rings (centroid-to-centroid distances of 3.738 Å and 3.882 Å), and then the tetra-layer structures are further superimposed by π ... π stacking interaction between pyridyl rings and phenyl rings (centroid-to-centroid distances of 3.631 Å to 3.866 Å) to form a $2D + 2D \rightarrow 3D$ interdigitation architecture (Fig. S6). To the best of our knowledge, example of $2D+2D\rightarrow 2D$ parallel interpenetration, $2D+2D\rightarrow 2D$ interdigitation and $2D+2D\rightarrow 3D$ interdigitation based on both $2D+2D\rightarrow 2D$ parallel interpenetration and $2D+2D\rightarrow 2D$ interdigitation have been reported [18-21].

Comparing with the reported Cd(II) compound [18a], the ionic radius of Cd(II) is longer than that of Zn(II), which means the Cd(II) center can adopt a higher coordination number and different coordination geometry, while leading to a similar polymeric framework. The result indicates that metal ions have no remarkable influence on the formation of target coordination polymeric frameworks.

[Fig. 1 is here]

3.3. Structure description of [Zn₂(cptpy)₂(Hidc)(H₂O)₂]_n·nH₂O (2)

Compound **2** crystallizes in the monoclinic system with P2₁/n space group and exhibits a 1D ladder chain structure. The asymmetric unit of **2** contains one Zn ion, one (cptpy)⁻ anion and half a (Hidc)²⁻ anion. As shown in Fig. 2a, Zn1 center is six-coordinated with four oxygen atoms (O1A, O2A, O3, O5) from one (cptpy)⁻ anion, one (Hidc)⁻ anion and water molecule and two nitrogen atoms (N1, N4) from one (cptpy)⁻ anion and one (Hidc)⁻ anion, respectively. The coordination geometry of Zn1 center can be described as a distorted ZnN₂O₄ octahedron, the O2A, O3, O5, N1 atoms comprise the equatorial plane, and the O1A and N4 atoms occupy the axial positions (N4-Zn1-O1A=159.0(2)°). In **2**, the Zn-N bond lengths are 2.046(6) Å and 2.075(6) Å, and the Zn-O distances are in the range of 2.068(7) Å to 2.312(7) Å, which are slightly longer than the corresponding values of **1**. The three pyridyl rings of the (cptpy)⁻ anion ligand are non-planar, each terminal pyridine group is twisted with respect to the central one, and the dihedral angles between the central and terminal pyridyl rings are 4.60° (N1 pyridyl ring) and 18.19° (N3 pyridyl ring), respectively.

As shown in Fig. 2b, the (Hidc)²⁻ anion adopts μ_4 - η^2 : η^2 bridging mode to link two Zn(II) centers to form a binuclear Zn unit with the Zn...Zn distance of 6.280 Å. Furthermore, these binuclear units are linked by (cptpy)⁻ anion (μ_2 - η^2 : η^1) to form a 1D chain structure. The chains are connected through hydrogen bonding interactions between the coordination water molecule and uncoordinated oxygen atoms from carboxylate of (Hidc)²⁻ anion (O5-H...O4ⁱ, 2.702 Å, symmetric code i, (x, 1+y, z)) to form a 2D supramolecular structure (Figs. 2c and S7). The 2D structure is further piled up through π ... π interactions between pyridyl rings and phenyl rings (centroid-to-centroid distances of 3.984 Å and 4.071 Å) to form a 3D supramolecular structure (Fig. 2d).

[Fig. 2 is here]

3.4. PXRD and thermogravimetric analyses

The powder X-ray diffraction (PXRD) experiments for the two MOFs were carried out carefully to check phase purity at room temperature. The patterns show that the main peaks of the synthesized CPs are closely consistent with those of the simulations from the single-crystal X-ray diffraction data, which imply high quality of the obtained products (Figs. S8 and S9, Supporting information). Moreover, the thermal stabilities of compounds **1** and **2** were also detected via thermogravimetric analysis (TGA) (Fig. S10, Supporting information). For **1**, the weight loss of 1.56% below 150 °C (calculated: 1.16%) corresponds to the loss of one lattice water molecule. After about 440 °C, the whole framework structure begins to collapse with continuous weight loss until heating to 1000 °C. The TGA curve of **2** reveals that the weight loss of 5.64% below 180 °C (calculated: 5.20%) corresponds to the loss of one lattice and two coordination water molecules. After about 395 °C, the whole framework structure begins to collapse with continuous weight loss until heating to 200 °C. TGA results reveal the compounds possess good thermal stability.

3.5. Optical band gaps

The UV-Vis absorption spectra of the ligands (Hcptpy, H₃idc) and complexes **1** and **2** were conducted in the crystalline sample at room temperature (Fig. S11). The Hcptpy ligand exhibits strong absorption bands from 200 nm to 340 nm with two peaks at 262 and 311 nm. Meanwhile, The H₃idc ligand displays absorption bands with maxima at 226 nm, which can be ascribed to π - π * transitions of the ligands. Furthermore, the higher energy absorption bands in the Hcptpy ligand is higher than that of H₃idc in the energy level, indicating that it might be more influenced when coordinated with the transition metal ion. With this regard, it's notable that the lowest energy absorption bands of complexes **1** ($\lambda_{max} = 334$ nm, 29940 cm⁻¹) and **2** ($\lambda_{max} = 331$ nm, 30211 cm⁻¹) are red-shifted when compared with the corresponding Hcptpy ligand (λ max = 311 nm, 30487 cm⁻¹), which may be attributed to the decreased energy gap of the intraligand (IL) transition when coordinated to the metal center ion [22].

The optical band gap (Eg) have been reported to be one of the principal factors to affect the photocatalysis degradation process of the organic dye in previous literature

[23, 24]. Inspired by this, we obtain the band gaps (E_g) of compounds 1 and 2 through transforming the diffuse reflectance data into a Kubelka-Munk function [25-27]. As depicted in Fig. S12, the Eg values evaluated from the steep absorption edge for 1 and 2 are 2.42 eV and 1.92 eV, respectively, indicating that compounds 1 and 2 are potential wide gap semiconductive materials [28, 29].

3.6. Luminescence measurements and discussions

The luminescence of compounds 1 and 2 and Hcptpy ligand was evaluated in the solid state at room temperature, and their emission spectra are given in Fig. S13. Hcptpy ligand exhibits a strong emission at 415 nm upon excitation at 300 nm, which maybe assigned to the π^* - π transitions. Compounds 1 and 2 exhibit broad emission banks at 405 nm and 378 nm, respectively, at the same excitation condition, which mean blue-shifts of ca. 10 nm and ca. 37 nm relative to the free Hcptpy ligand. The slight blue-shift maybe mainly originated from the coordination interactions between the metal atom and the ligand [30]. Interestingly, compound 2 exhibts stronger luminescence, which maybe result from stronger hydrogen-bonding interactions between 1D chains. As **1** keeps one protonated carboxylic group in every (Hidc)²⁻ anion ligand, whether the carboxyl group will affect luminescence properties has aroused our great interest. To explore the luminescent responses of 1 under protonation and deprotonation conditions, the luminescence emission spectra of 5 mg 1 in 5 mL H₂O were recorded with gradual addition of NaOH (0.03 M). As shown in Figs. 3a and 3b, with the increase of NaOH, the maximum emission wavelength slight moved from 377 to 373 nm gradually. Obviously, the emission intensity also decreased gradually. The phenomenon should be related to the free carboxylic groups and their deprotonation process. Structure analysis shows that there exist significant hydrogen bonds between the adjacent 1D chains. The addition of bases into the system will gradually react with the carboxylic groups in 2, leading to the breaking of hydrogen bonds, accompanied by increasing instability and reduced conjugation in 2, resulting in luminescence decay. The instability and reduced conjugation of the system should be responsible for the blue shifts of the maximum emission wavelength

[8]. PXRD after NaOH titration (Fig. S9) was measured and the patterns showed that the basic framework of **2** was kept and added new peak. Then the sample was titrated with HNO₃ (1:60) straight after NaOH titration to see whether the process is reversible. However, along with the increase of HNO₃, the emission intensity decreased sharply (Figs. 3a and 3c), the suspension gradually turned clear. As a result, HNO₃ titration proved nonreversible, and the reason may be the instability of **2** in base condition where the structure may have been broken down, which has been confirmed by powder X-ray diffraction (PXRD) patterns after NaOH titration.

The most interesting feature is that its luminescence spectrum in **1** is largely dependent on the solvent molecules, particularly in the case of acetone, which exhibit the most significant quenching effects (Fig. 4). PXRD pattern performed after solvent immersion (Fig. S14a) proves the structure is well preserved. Such solvent-dependent luminescence properties are of interest for the sensing of acetone solvent molecules. When the acetone solvent content was gradually added and increased to **1**-DMF standard emulsion, the fluorescence intensity of the **1** emulsion gradually decreased with the addition of acetone solvent (Fig. 5a). The fluorescence decrease was nearly proportional to the acetone concentration. The decreasing trend of the fluorescence intensity of **1** at 405 nm versus the volume ratio of acetone could be well fitted with a first-order exponential decay (Fig. 5b), indicating that fluorescence quenching of **1** by acetone is diffusion-controlled [31].

[Fig. 3 is here]

[Fig. 4 is here]

[Fig. 5 is here]

3.7. Detection of Metal Ions-Photoinduced Electron Transfer.

Acci

The most significant structural feature of 1 is the presence of free Lewis basic pyridyl and carboxyl sites on the framework structure, highlighting the potential for

sensing functions and recognizing metal ions. Therefore, in order to research the luminescent responses of **1** to different metal ions, the products of **1** were ground into powder and suspended in DMF solution containing the same concentration of different nitrate $(Na(NO_3)_2, K(NO_3)_2, Ca(NO_3)_2, Mn(NO_3)_2, Pb(NO_3)_2, Zn(NO_3)_2, Cd(NO_3)_2, Co(NO_3)_2, Ni(NO_3)_2, Cu(NO_3)_2)$ for 48h, and then their luminescent spectra are recorded. Interestingly, the Cu²⁺ ion shows a significant quenching effect on the luminescence intensity of **1**; in contrast, luminescence intensity for **1** in other metal ions system are little enhance or decreased to a degree, indicating highly selective sensing of **1** for Cu²⁺ ions (Fig. 6a).

To gain more insight into the quenching effect resulted from Cu^{2+} , titration experiments were carried out via changing the concentration of Cu^{2+} cations in solution. The titration experiments indicated that the luminescent intensities at 415 nm were gradually weakened by increasing the amount of Cu^{2+} ions (Fig. 6b), and the intensity was reduced to 50% at a concentration about 0.42 mM for $Cu(NO_3)_2$. Importantly, the luminescence intensity of the suspension follows the first-order exponential decay formula I=779.66×exp(- $C_V/0.50$)+116.92 (insert of Fig. 6b), by which Cu^{2+} could be detected quantitatively (I=luminescence intensity of 1- $Cu(NO_3)_2$ @DMF suspensions, $C_V=Cu^{2+}$ volume concentration, $R^2=0.99$), displaying the diffusion-controlled quenching process for the Cu^{2+} ions [32, 33]. The excellent result indicate that the crystalline products of **1** can be used as the excellent luminescent sensor to detect Cu^{2+} ions as highly selective luminescent crystalline materials (Fig. 6c),

In order to further evaluate the selectivity of complex 1 toward the Cu^{2+} ion, we studied the quenching effect of Cu^{2+} ion and all the other mixed transition metal ions $(Na^+, K^+, Ca^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+})$ on the luminescent intensity of 1. As illustrated in Fig. 7a, Cu^{2+} ion exhibited much more significant quenching effect on 1 than the mixed ions. Furthermore, when Cu^{2+} ion was incorporated in the mixed ions, the luminescence intensity of 1 is nearly complete quenching, which demonstrated the high selectivity of 1 toward the Cu^{2+} ion. To further examine the sensing sensitivity for Cu^{2+} ion, 1 was immersed in DMF solutions with gradually

decreased Cu^{2+} concentration in the range of 10^{-1} - 10^{-5} mol/L. Noteworthy, the luminescence intensity of $Cu^{2+}@1$ is heavily relied on the concentration of Cu^{2+} ion. As shown in Fig. 7b, the luminescence intensity of 1 is almost completely quenched at a Cu^{2+} concentration of 10^{-2} M. It is remarkable that complex 1 features such highly sensitive sensing for Cu^{2+} ions in DMF solution.

Additionally, multiple cycles of Cu²⁺ sensing experiments have been conducted and the material could greatly regain its intensity after filtration and washing by DMF (Fig. 8). PXRD pattern performed after Cu(NO₃)₂ immersion (Fig. S14b) proves the structure is well preserved. UV-Vis absorption spectra for Cu(NO₃)₂ solutions has been recorded. The absorption spectrum of Cu²⁺ solution has no obvious overlap with the emission spectrum of 1 (Fig. S15). Therefore, the quenching should origin from the electron transfer from 1 to Cu^{2+} , instead of the resonance energy transfer [34]. Moreover, the quenching effect of Cu^{2+} on the luminescence intensity of 1 has been further examined by fluorescence lifetime studies of 1 and $1@Cu^{2+}$. The fluorescence lifetime of τ_1 =2.76 ns and τ_2 =8.64 ns in the **1** is significantly reduced to τ_1 =1.80 ns and $\tau_2=3.45$ ns in the presence of Cu²⁺ (see the Supporting Information, Fig. S16), which maybe result from an interaction between Cu^{2+} ions and compound 1. XPS (X-ray photoelectron spectroscopy) experiment on 1-Cu(NO₃)₂@DMF sample (Figs. 9a and S17) founds that the peak at 933.9 eV especially, which accordance with the standard value of $Cu \cdots O$ (933.9 eV), suggesting the existence of interaction between Cu^{2+} and the terminal carboxyl groups [35]. To explore the possible mechanism for such luminescence quenching by metal cations, N1s and O1s X-ray photoelectron spectroscopy (XPS) studies were carried out on Cu^{2+} -incorporated 1 (Figs. 9b and 9c). The N 1s peak from nitrogen atoms at 398.2 eV and O1s peaks from oxygen atoms at 531.0 eV and in 1 are respective shifted to 399.2 eV (N 1s) and 513.5 eV (O1s) induced by the addition of Cu^{2+} in **1**, indicating the probable weak binding of pyridyl nitrogen atoms and carboxylate oxygen atoms to Cu^{2+} in Cu^{2+} -incorporated 1. Such binding of the pyridyl nitrogen atoms and carboxylate oxygen atoms to Cu²⁺ maybe cause the electrons of Hcptpy ligands to transfer from 1 to Cu^{2+} ions as electron acceptors, thus resulting in quenching of the luminescence. In addition, the well

recovered intensities after multiple cycles of Cu^{2+} sensing experiments may provide proof that Cu^{2+} ions are mainly absorbed on the surface.

[Fig. 6 is here]

[Fig. 7 is here]

[Fig. 8 is here]

[Fig. 9 is here]

Finally, aqueous solutions containing sodium salts of Cl⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, $CO_3^{2^-}$, $PO_4^{3^-}$, and $Cr_2O_7^{2^-}$ at the same concentration (1.0 × 10⁻³ M) were also prepared, and their effects on the fluorescence intensity of 2 were explored. The most interesting feature is that the PL intensities of the different suspensions are strongly dependent on the various anions. The analytes, such as halide ions, ClO_4 , NO_3 , and $CO_3^{2^-}$, have negligible effects on the PL intensity, whereas other anions, in particular $Cr_2O_7^{2-}$, significantly decrease the luminescence intensity (Fig. 10). The unusually selective quenching of $Cr_2O_7^{2-}$ prompted us to apply 2 in the detection of trace Cr^{6+} in water. To further evaluate the sensitivity of 2 to Cr^{6+} , we carried out measurements in the presence of varying concentrations of $Cr_2O_7^{2-}$. This result indicates that the fluorescence intensity of 2 is remarkably suppressed with increasing amounts of $Cr_2O_7^{2-}$ (Fig. 11). The quenching of 2 in the presence of $Cr_2O_7^{2-}$ is most likely due to a decrease in energy transfer between the π and π^* orbitals of (Hidc)²⁻ because of electron-transfer transitions of $Cr_2O_7^{2-}$ [36]. The highly selective and sensitive detection of Cr^{6+} in aqueous solutions by compound 2 is remarkable; therefore, it may be considered as a MOF sensor for the quantitative detection of $Cr_2O_7^{2-}$ with the highest sensitivity.

[Fig. 10 is here]

[Fig. 11 is here]

4. Conclusion

In summary, two new Zn(II)-MOFs were solvothermally synthesized in solvent systems. It was found that the Hcptpy ligands displayed three different coordination modes in the obtained MOFs and thus gave rise to the various MOF structural diversities. The luminescent properties of two products were studied via ultraviolet light at room temperature, especially for 1, which showed highly selective sensitivity for Cu²⁺ ions and acetone. The 1-MOF can potentially be used to detect these poisonous substances. We also discussed the mechanisms for the quenching effect and sensing properties of 1. Importantly, complex 2 shows highly selective sensitivity for $Cr_2O_7^{2-}$. The fluorescence quenching caused by Cu^{2+} can be ascribed to a binding interaction between the uncoordinated pyridine motif of (cptpy)⁻ and Cu²⁺ in the Cu²⁺-incorporated compounds, whereas the fluorescence depression caused by Cr⁶⁺ may be associated with electron-transfer transitions of $Cr_2O_7^{2-}$. This work provides an easy and facile route to design and yield the new luminescent MOFs as promising functional materials. Further research into the sensing materials is underway in our group. Meanwhile, the optical absorption spectra show that the title compounds may be a potential wide gap semiconductor material.

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Table 1. Crystallographic data and structural refinement parameters for Mptpy and $1-2^a$

Compound	Mptpy	1	2
Empirical formula	$C_{22}H_{17}N_3$	$C_{88}H_{56}N_{12}Zn_2O_9$	$C_{49}H_{31}N_8Zn_2O_{11}$
Formula weight	323.39	1556.23	1038.56

ACCEPTED MANUSCRIPT					
Crystal system	Triclinic	Triclinic	Monoclinic		
Space group	P-1	P-1	C2/c		
A /Å	8.5524(16)	15.102(6)	35.07(2)		
B/Å	9.5677(18)	15.117(6)	7.469(5)		
C/Å	11.444(2)	17.397(7)	21.491(14)		
$\alpha/^{\circ}$	89.151(2)	86.631(5)	90		
$eta/^{\circ}$	69.103(2)	69.642(4)	120.585(11)		
$\gamma/^{\circ}$	73.378(2)	79.346(5)	90		
$V/\text{\AA}^3$	834.3(3)	3659(3)	4847(5)		
Ζ	2	4	4		
$\rho_{\rm calc} ({\rm g} \cdot {\rm cm}^{-3})$	1.287	1.412	1.423		
F (000)	340	1600	2116		
Reflections collected	4209	26012	11431		
$S ext{ on } F^2$	1.068	1.040	1.052		
R _{int}	0.0190	0.0493	0.1311		
$R_1, w R_2^a [I > 2\sigma(I)]$	0.0472, 0.1268	0.0847, 0.2263	0.0883, 0.1991		
R_1 , wR_2^a (all data)	0.0655, 0.1437	0.1221, 0.2490	0.1701, 0.2443		

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}$

Figure captions:

- Scheme 1. The optimized geometry and NBO charge distributions of the free ligand Hcptpy (the blue ball represents N atom, the red ball represents O atom and the gray ball represents C atom).
- Scheme 2. Synthetic route I to the Hcptpy ligand
- Scheme 3. Synthetic route II to the Hcptpy ligand

- Fig. 1. (a) The coordination environments of Zn1 and Zn2 ions in 1 with 30% thermal ellipsoids (all hydrogen atoms and solvent molecules are omitted for clarity). (b) 2D layer structures based on the Zn1 and Hcptpy in 1 (blue ball:N atom, green ball:oxygen atom in Zn1 layer. All ball atoms represent Lewis base sites). (c) Perspective view of the parallel penetration of the layers constructed by the Zn1 and Zn2 motifs in 1.
- Fig. 2. (a) The coordination environment of Zn1 ions in 2 with 30% thermal ellipsoids (all hydrogen atoms and solvent molecules are omitted for clarity). (b) 1D ladder chain in 2. (c) 2D supramolecular layer in 2. (d) 3D supramolecular structure based on π..π stacking interaction in 2.
- Fig. 3. (a) Emission spectra of 1 in H₂O on (b) NaOH titration and (c) HNO₃ titration.
- Fig. 4. (a) The photoluminescence spectra and (b) the luminescence intensities of 1 introduced into various pure solvent emulsions when excited at 300 nm.
- Fig. 5. (a) The photoluminescence spectra of 1@DMF emulsion in the presence of various content acetone solvent (excited at 300 nm). (b) The fluorescence intensity of 1@DMF emulsion as a function of acetone content.
- Fig. 6. (a) Comparison of the relative luminescence intensities of various 1- $M(NO_3)_x$ @DMF suspensions. (b) Luminescence spectra of 1 in DMF in the presence of different amounts of Cu²⁺ (excited at 300 nm) (inset: the plot of intensity versus Cu²⁺ concentration). (c) Visual change upon the addition of various M(NO₃)_x.
- Fig. 7. (a) Luminescence intensity at 405 nm of 1-Zn dispersed in DMF and 1-Zn dispersed in DMF with Cu²⁺ (10⁻² M), mixed ions (Na²⁺, K²⁺, Ca²⁺, Mn²⁺, Pb²⁺, Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺, 10⁻² M), mixed ions+Cu²⁺ (10⁻² M). (b) Luminescence spectra of 1 in DMF solutions with Cu(NO₃)₂ at different concentrations.
- Fig. 8. Multiple cycles for the quenching by $Cu(NO_3)_2$ and the recovery after filtration and ultrasonic washing by DMF for a few times. The red bars show the pristine intensity and regenerated ones after washing; while the

green bars show the intensities after addition of Cu(NO₃)₂@DMF solutions.

- Fig.9. (a) X-ray photoelectron spectroscopy for complex 1 and Cu²⁺ incorporated complex 1; (b) N 1s XPS for complex 1 and Cu²⁺ incorporated complex 1. (c) O 1s XPS for complex 1 and Cu²⁺ incorporated complex 1.
- Fig. 10. (a) The photoluminescence spectra and (b) the luminescence intensities of1 introduced into various pure solvent emulsions when excited at 300 nm.
- Fig. 11. (a) The photoluminescence spectra of $2@H_2O$ emulsion in the presence of various content $Cr_2O_7^{2-}$. (b) The fluorescence intensity of $2@H_2O$ Accepted manuscript emulsion as a function of $Cr_2O_7^{2-}$.

Scheme 1.









Fig. 1.

(a)





(b)



(c)



Fig. 2.

(a)





(b)



(c)

(d)









Fig. 6.

(a)













Highlights

- 1. Two luminescent d¹⁰ metal coordination polymers was constructed.
- 2. Compound 1 shows highly selective and sensitive response to acetone and Cu^{2+} .
- 3. Compound 2 shows highly selective sensitivity for $Cr_2O_7^{2-}$.

Accepted