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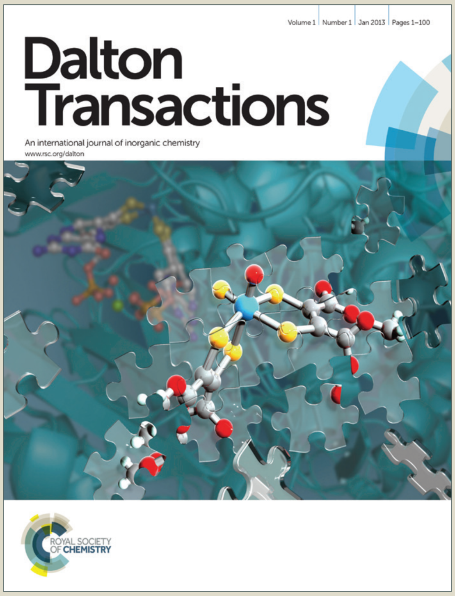

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ARTICLE TYPE

# 4-(4-Carboxyphenoxy)phthalate-based coordination polymers and application in sensing nitrobenzene

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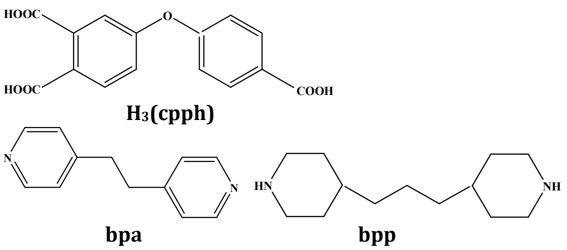
Under the hydro(solvo)thermal conditions, two 4-(4-carboxyphenoxy)phthalate-based three-dimensional (3-D) coordination polymers (CPs) $[Cd_3(cpph)_2(bpa)_2(H_2O)]\cdot 0.5H_2O$ (cpph = 4-(4-carboxyphenoxy)phthalate, bpa = 1,2-bis(4-pyridyl)ethane) **1**, and $[H_2(bpp)][Mn_2(cpph)_2(H_2O)_2]$ (bpp = 1,2-bis(4-piperidyl)propane) **2** were isolated. In both compounds, the cpph molecules extend the metal ions into a 3-D network: a (4,6)-connected net for **1**; a simple 6-connected net with a pcu topology for **2**. The introduced bpa or bpp molecule stabilizes the 3-D metal-cpph architecture in the form of linker or guest molecule. The sensing ability of **1** was investigated, revealing that it can serve as a fluorescence probe to sense ppm-grade nitrobenzene (NB).

## Introduction

Much effort has been taken to the design and synthesis of novel coordination polymers due to their fascinating structures and topologies,[1] and the potential applications in some field as adsorption, optics, magnetism and catalysis.[2] Over the last fifteen years, the polycarboxylic acid molecules have been verified to be the most effective linkers in the construction of novel CPs, in particular the porous CPs, which may be relevant to the strong ability for the carboxyl groups to form the clusters with the metal ions.[3] So far, a variety of polycarboxylic acid molecules as the linear dicarboxylic acids,[4] the trigonal tricarboxylic acids,[5] the tetrahedral or planar tetracarboxylic acids,[6] the hexacarboxylic acids [7] and the octacarboxlic acids [8] have been employed, constructing a series of novel metal-polycarboxylate CPs. It is noteworthy that some of them possess the stable pore structures, and exhibit a potential application in $CO_2$ capture and $H_2$ storage.[9] At recent, the researchers find that some metal-polycarboxylate CPs can also serve as the fluorescence probes to sense some matters such as the dyes,[10] the rare-earth metal ions [11] and the explosives.[12] Moreover, we still address that it is still a great challenge to get a target CP with pre-designed structure and desirable property, since the self-assembling process is rather complicated, and dominated by many factors as the geometry of the metal ions, the nature of the organic ligands and the detailed experimental conditions.[13]

Lately, a class of semi-rigid V-shape polycarboxylic acid molecules have attracted the considerable attention. They are generally composed of two aromatic carboxylic acid moieties linked by a nonmetallic atom (C, O and S). The semi-rigidity means that two benzene rings can appropriately rotate around the centric atom, which maybe leads to the appearance of a new crystalline material with the helix structure. To date, some semi-rigid V-shape symmetric di- and tetracarboxylic acids (spacer: -C=O,[14] $-C(CF_3)_2-$,[15] –O/S- [16] and $-SO_2-$ [17]) have been extensively investigated. The N,N′-donor organic bases were usually introduced to modify the structures and the properties of the as-synthesized metal-polycarboxylate materials. The mixed N,N′-donor organic bases play a crucial role in extending and stabilizing the metal-polycarboxylate CP networks,[16e] and controlling the formation of the porous structures in the form of guest molecules.[18] However, the semi-rigid V-shape asymmetric tricarboxylic acids were seldom developed.[18,19] In this article, the 4-(4-carboxyphenoxy)phthalic acid molecule $H_3(cpph)$ was selected, to react with the transition metal ions in the presence of the N,N′-donor organic bases under the hydro(solvo)thermal conditions. Fortunately, two cpph-based 3-D metal-polycarboxylic CPs $[Cd_3(cpph)_2(bpa)_2(H_2O)]\cdot 0.5H_2O$ (bpa = 1,2-bis(4-pyridyl)ethane) **1** and $[H_2(bpp)][Mn_2(cpph)_2(H_2O)_2]$ (bpp = 1,2-bis(4-piperidyl)propane) **2** were obtained. Their photoluminescence behaviors were studied.



**Scheme 1** Structures of organic molecules in **1** and **2**.

## Experimental

### Materials and physical measurement

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum *1* spectrophotometer in 4000-400 cm$^{-1}$ region using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with Cu-$K_\alpha$ radiation ($\lambda$ = 1.5418 Å). Thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 $^{o}$C min$^{-1}$ in air. Fluorescence spectrum was obtained on a LS 55 florescence/phosphorescence spectrophotometer at room temperature.

### Synthesis of the title compounds

**$[Cd_3(cpph)_2(bpa)_2(H_2O)]\cdot 0.5H_2O$ 1.** The colorless block crystals of **1** were obtained from a simple hydrothermal self-assembly of $Cd(CH_3COO)_2{\cdot}2H_2O$ (53 mg, 0.2 mmol), $H_3$(cpph) (30 mg, 0.1 mmol) and bpa (36 mg, 0.2 mmol) in a 10 mL aqueous solution at 120 °C for 3 days. Yield: *ca*. 15 % based on Cd(II). Anal. Calcd $C_{54}H_{41}N_4O_{15.5}Cd_3$ **1**: C 48.72, H 3.10, N 4.21. Found: C 48.56, H 3.16, N 4.23%. IR ($cm^{-1}$): 1610 w, 1601 m, 1549 s, 1399 s, 1303 w, 1258 m, 1240 s, 1018 m, 946 m, 850 w, 830 m, 545 w.

**[$H_2$(bpp)][$Mn_2$(cpph)$_2$($H_2O$)$_2$] 2.** The colorless block crystals of **2** were obtained from a simple hydrothermal self-assembly of $MnCl_2{\cdot}4H_2O$ (20 mg, 0.1 mmol), $H_3$(cpph) (30 mg, 0.1 mmol) and bpp (21 mg, 0.1 mmol) in a 10 mL $CH_3OH$-$H_2O$ solution (1:4) (pH = 7 adjusted by dilute NaOH) at 140 °C for 3 days. Yield: *ca*. 15 % based on Mn(II). Anal. Calcd $C_{43}H_{34}N_2O_{16}Mn_2$ **2**: C 54.67, H 3.63, N 2.98. Found: C 54.07, H 3.53, N 2.89%. IR ($cm^{-1}$): 1595 s, 1572 w, 1542 s, 1396 s, 1384 s, 1231 s, 1155 m, 943 w, 905 m, 790 w, 581 w, 516 w.

## X-ray crystallography

The data were collected with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) on a Rigaku R-AXIS RAPID IP diffractometer for compound **1**, and on a Siemens SMART CCD diffractometer for **2**. With SHELXTL program, the structures of compounds **1** and **2** were solved using direct methods.[20] The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement, and the other hydrogen atoms were treated using a riding model. The H atoms on the water molecules in compounds **1** and **2** were not located, which leads to several B-level alertness as the short Ow···O/Ow contacts in compounds **1** and **2**. Between Ow and O/Ow, there actually exist the hydrogen-bonded interactions. The other B-level alertness in compound **2** derives from the poor crystal quality of compound **2**. Due to this, the piperidyl ring shows a slight distortion. Meanwhile, the alkyl spacer for the bpp molecule is also disordered. So the H atoms on C16, C21 and C22 were not located, either. The structures were then refined on $F^2$ using SHELXL-97.[20] CCDC numbers are 1022512-1022513 for **1** and **2**, respectively. The crystallographic data for the title compounds are summarized in Table 1.

**Table 1.** Crystallographic data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Formula | $C_{54}H_{41}N_4O_{15.5}Cd_3$ | $C_{43}H_{34}N_2O_{16}Mn_2$ |
| *M* | 1331.11 | 944.60 |
| *T* (K) | 293(2) | 293(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P*-1 | *P*2$_1$/c |
| *a* (Å) | 10.220(2) | 14.5688(7) |
| *b* (Å) | 12.408(3) | 14.2833(9) |
| *c* (Å) | 21.148(4) | 9.8497(6) |
| | 99.29(3) | |
| $\beta$ (°) | 96.54(3) | 100.280(3) |
| | 97.36(3) | |
| *V* (Å$^3$) | 2599.9(9) | 2016.7(2) |
| *Z* | 2 | 2 |
| $D_c$ (g cm$^{-3}$) | 1.700 | 1.556 |
| $\mu$ (mm$^{-1}$) | 1.291 | 0.706 |
| Reflections collected | 25610 | 11081 |
| Unique reflections | 11741 | 3538 |
| $R_{int}$ | 0.0333 | 0.0389 |
| Gof | 1.090 | 1.056 |
| $R_1$, $I>2\sigma(I)$ | 0.0339 | 0.0504 |
| $wR_2$, all data | 0.0931 | 0.1429 |

## Results and discussion

### Synthetic analysis

Both are obtained under the hydro(solvo)thermal conditions. In an aqueous solution, the reaction of $Cd^{2+}$, $H_3$(cpph) and bpa afforded compound **1**. The reaction of $Cd^{2+}$ and $H_3$(cpph) was also investigated, and the colorless crystals were obtained. Unfortunately, the crystals are unsuitable for X-ray single-crystal diffraction. On the other hand, the high temperature (> 140 °C) is bad for the obtainment of compound **1**. In a mixed $CH_3OH$-$H_2O$ solution, the reaction of $Mn^{2+}$, $H_3$(cpph) and bpp yielded compound **2**. For this reaction, the pH level of the reaction is the most important factor. Only in a narrow pH range of 6.5-7.0, this compound could be obtained. Maybe the pH value of the reactive system has an effect on the existing forms of cpph and bpp in the solution. A series of parallel reactions as changing the metal ion or the N, N′-donor ligand were also performed. Only compounds [$Zn_4(OH)_2$(cpph)$_2$(bpe)$_2$]·bpe (bpe = 1,2-bis(4-pyridyl)ethylene), [$Zn_2$(Hcpph)$_2$(bpe)($H_2O$)]·bpe [18] and [$Zn_6$(cpph)$_4$(bpy)$_2$($H_2O$)$_2$] (bpy = 4,4′-bipyridine) [19d] were obtained, which have been reported by the other groups.

### Structural description

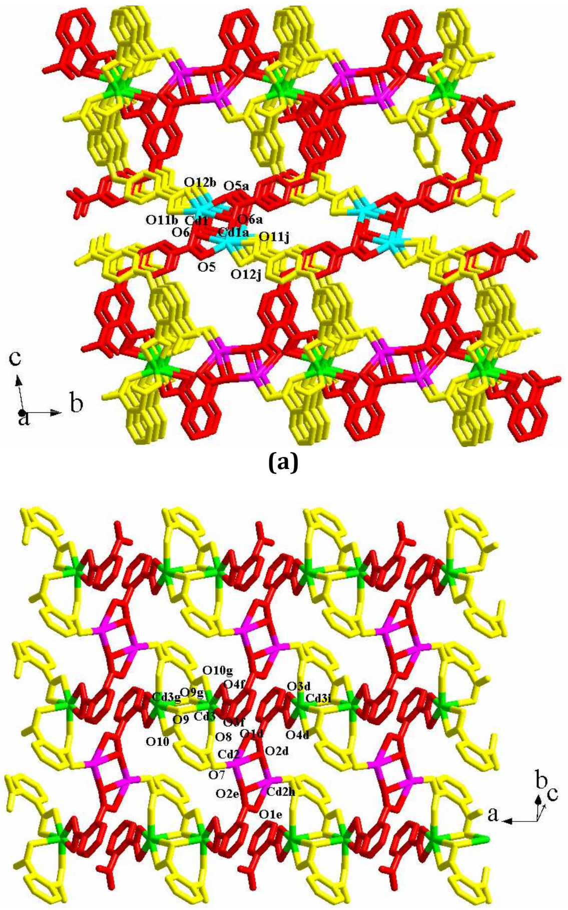
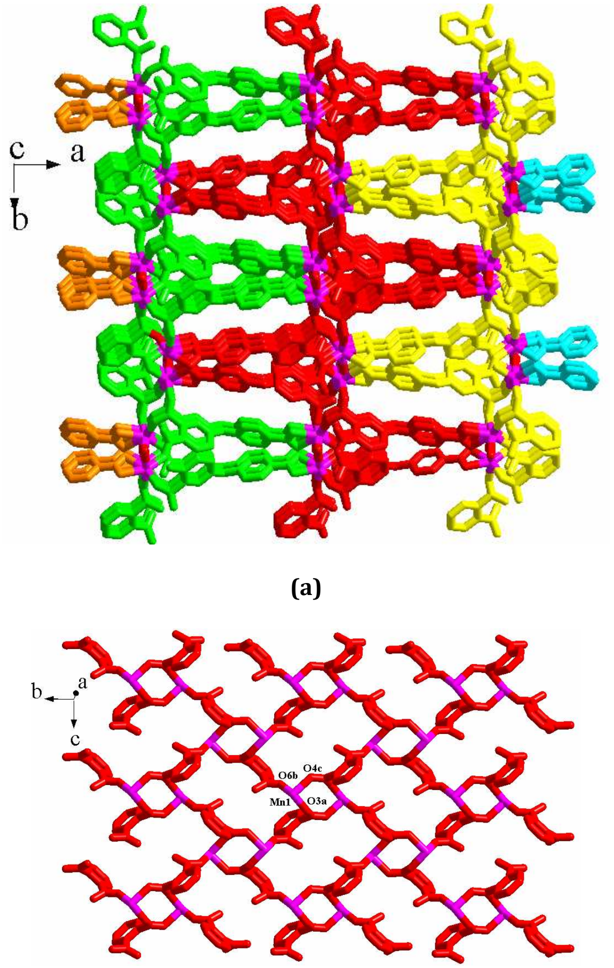


**Fig. 1** (a) 3-D network constructed from cpph and $Cd^{2+}$, showing interactions between 2-D layers in **1**; (b) 2-D layer network constructed from phthalate moieties, and Cd1 and Cd3 in **1** (a: -*x*+1, -*y*, -*z*+1; b: -*x*+3, -y+1, -*z*+1; d: -*x*+2, -*y*+1, -*z*+2; e: *x*+1, *y*-1, *z*; f: *x*+1, *y*, *z*; g: -*x*+4, -*y*+1, -*z*+2).

**$[Cd_3(cpph)_2(bpa)_2(H_2O)]\cdot 0.5H_2O$ 1.** X-ray single-crystal diffraction analysis revealed that compound **1** is a 3-D $Cd^{2+}$ CP extended by cpph and bpa. It crystallizes in the space group *P*-1, and the asymmetric unit is found to be composed of three types of $Cd^{2+}$ ions (Cd1, Cd2, Cd3), two types of cpph molecules (cpph I, cpph II), two types of bpa molecules (bpa I, bpa II), one coordinate water molecule (Ow1) and a half lattice water molecule (Ow2). As shown in Fig. S1, both Cd1 and Cd3 are involved in a 7-coordinate site, but the detailed environments are different. Cd1 is surrounded by five carboxyl O atoms (O5a, O6a, O6, O11b, O12b) and two bpa N atoms (N2, N3), whereas Cd3 is coordinate with six carboxyl O atoms (O3f, O4f, O8, O9, O9g, O10g) and one water molecule (Ow1). Cd2 is in an octahedral site with four carboxyl O atoms (O1d, O2d, O2e, O7) occupying the equatorial plane, and two bpa N atoms (N1, N4c) occupying the axial positions. The Cd-N bond lengths of 2.266(3)-2.331(3) Å are comparable with each other, but the Cd-O distances span a wide range from 2.242(3) Å to 2.634(3) Å. Two types of cpph molecules exhibit the different coordination modes (see Scheme 2). For cpph I, each carboxyl group chelates to one $Cd^{2+}$ ion. Meanwhile, O2 and O6 further bond respectively to an additional $Cd^{2+}$ ion. So cpph I is involved in a penta-bridged coordination mode. Cpph II adopts a $\mu_4$ coordination mode: two O atoms (O8, O10) from the different carboxyl groups share one $Cd^{2+}$ center; the 4-position carboxyl group further chelates to an addition $Cd^{2+}$ center; the other O atom on 3-position carboxyl group further interacts monodentately with an addition $Cd^{2+}$ center; the 4′-position carboxyl group only chelates to one $Cd^{2+}$ center. Bridged by cpph and bpa, compound **1** shows a 3-D network structure (see Fig. S2). The incorporation of the bpa molecule is mainly to stabilize the 3-D network structure of compound **1**. The cpph molecules actually link the $Cd^{2+}$ centers into this 3-D network (see Fig. 1a). The phthalate moieties for cpph molecules first link two types of $Cd^{2+}$ centers (Cd2, Cd3) into a 2-D layer network. As shown in Fig. 1b, two types dimers (dimer I, dimer II) are found in this 2-D layer. Two cpph I molecules with the 3-position carboxyl groups link two Cd1 centers to form dimer I. In dimer I, two COOCd ring planes and the $Cd_2O_2$ ring plane are co-planar, and the Cd2···Cd2h contacts is 3.931 Å. Two cpph II molecules with the 3-position carboxyl groups link two Cd3 centers to form dimer II. Different from the situation in dimer I, two COOCd ring planes and the $Cd_2O_2$ ring plane show a step shape. The Cd3··Cd3g separation is 4.010 Å. Between dimer I and dimer II, two types of interactions are observed: the 4-position carboxyl group (O3d, O4d) for cpph I chaletes to Cd3 (Cd3i); the 4-position group (O7) for cpph II bonds monodentately to Cd2. Via these Cd-O interactions, the neighboring dimers connect with each other into a 2-D layer network. Each dimer I are surrounded by four dimer II, whereas each dimer II are surrounded by four dimer I. So this 2-D layer can be described as a (4,4) net based on the topological method. Fig. 1a also shows the interactions between the layers. Two 4′-position carboxyl groups for cpph I link two Cd1 centers to form a dimer, which is labeled as dimer III. With the formation of dimer III, the 2-D (4,4) layers are linked together into a 3-D network. The 4′-position carboxyls for cpph II chelate to Cd1 centers, making this 3-D network more stable. Similar to the situation observed in dimer I, two COOCd ring planes and the $Cd_2O_2$ ring plane are co-planar. The Cd1···Cd1a separation is 4.072 Å. Based on the topological methods, the 3-D $Cd^{2+}$-cpph network exhibits a (4,6)-connected topology. In the 3-D $Cd^{2+}$-cpph network, the 1-D channels are observed. But due to the coordination of the bpa molecule to the $Cd^{2+}$ centers, these channels turn small or disappear (see Fig. S2).



(a)

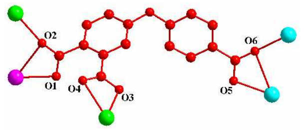
(b)

**Fig. 2** (a) Cpph-extended 3-D $Mn^{2+}$ network for **2**; (b) 2-D layer constructed from phthalate moieties and $Mn^{2+}$ in **2** (a: *x*+1, *y*, *z*; b: *x*+1, -*y*+1/2, *z*+1/2; c: -*x*, -*y*, -*z*).

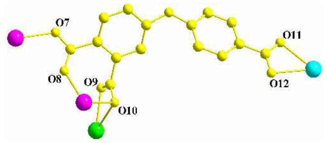
**$[H_2(bpp)][Mn_2(cpph)_2(H_2O)_2]$ 2.** Compound **2** is a cpph-propagated 3-D $Mn^{2+}$ CP with $H_2(bpp)^{2+}$ as the templating agent. It crystallizes in the space group $P2_1/c$, and the asymmetric unit is found to be composed of one $Mn^{2+}$ ion (Mn1), one cpph molecule, a half bpp molecule and one coordinate water molecule (Ow1). Different from the situation in compound **1**, bpp acts as the guest molecule in compound **2**. Bpp should be diprotonated in order to balance the systemic charge. Templated by $H_2(bpp)^{2+}$, the cpph molecules link the $Mn^{2+}$ ions to form a 3-D network (see Fig. 2a). It is not difficult to find that there exist some similarities between the 3-D networks of compounds **1** and **2**: (i) the phthalate moieties of the cpph molecules link the $Mn^{2+}$ centers into a 2-D layer (see Fig. 2b); (ii) this 2-D layer possesses a (4,4) topological structure; (iii) from the 2-D layer to the 3-D network, the 4′-position carboxylate group for cpph molecule plays a key role. However, in the 2-D layer network of compound **2**, only a kind of dimer is observed. The 4-position carboxylate groups double bridge two Mn1 centers to form this dimer. The eight-membered $Mn_2(COO)_2$ dimer adopts a chair-mode configuration, and the Mn···Mn contact is 5.054 Å. Via the interaction between Mn1 and O6b, each dimer connects with neighboring four dimers. The adjacent 2-D layers array in an interdigition way. Via the chelation of the 4′-position carboxyl group to Mn1 center, the neighboring 2-D layers interlock into a 3-D network of compound **2**. Based on the topological point of view, compound **2** has a simple 6-connected pcu topology. In compound **2**, the crystallographically unique Mn 1 center is in an octahedral site. O1, O2, O3a and O6b are located at the equatorial plane, whereas Ow1 and O4c lie at the axial positions (see Fig. S3). The cpph molecule adopt a new $\mu_4$ coordination mode: the 4′-position carboxylate group chelates to one Mn(II) center; the 3-position carboxylate group bidentately bridges two Mn(II) centers; one O atom (O6) on the 4-position carboxylate group interacts monodentately to one Mn(II) center (see Scheme 2). As shown in Fig. S4, the $H_2(bpp)^{2+}$ molecules occupy the space of the channels. The bpp N atom (N1) forms a hydrogen bond to the other O atom (O5d; d: $x+1$, $-y+1/2$, $z+1/2$) on the 4-position carboxylate group. The N1···O5d distance of 2.841 Å is comparable with those observed in the reported compounds.[21]

## Structural discussion

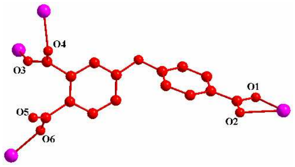
Both compounds exhibit the 3-D network structures. The introduced N,N′-donor organic bases do not play a role in the formation of the 3-D networks. The cpph molecules propagate the metal ions into the 3-D networks. The phthalate moieties for cpph molecules first extend the metal ions into a 2-D layer network. Then the 4′-position carboxylate groups for cpph molecules propagate the 2-D layers into a 3-D network structure. In both compounds, the metal ions and the carboxylate groups form three types of clusters, namely the so-called secondary building units (SBUs), which contributes to the formation of the stable 3-D networks. In both compounds, the mixed N,N′-donor organic bases exist in the different forms. In compound **1**, in a coordination mode the bpa molecules alter the coordination environments of the $Cd^{2+}$ ions, fabricating a new 3-D CP material of **1**. In compound **2**, the bpp molecule exists in a diprotonated form. By the size, form and the charge, the bpp molecule influences the formation of the 3-D $Mn^{2+}$-cpph CP network. In order to ensure the carboxyl groups to deprotonate into the carboxylates, the reactions were generally carried out in a neutral or basic condition. In some reported metal-polycarboxylate CPs, the introduced N,N′-donor organic bases were found to act as the guest molecules, but it exists in a non-protonated way.[18] In compound **2**, all of the carboxyl groups deprotonated, and bpp exists in a diprotonated form, which indicate that why compound **2** was only obtained in a narrow pH range. Besides acting as the templating agent, another important role for bpp is to stabilize the $Mn^{2+}$-cpph CP framework. The rigid polycarboxylate molecules can link the metal ions into a 3-D CP with a larger pore. The pores are occupied by the solvent molecules DMF and/or $H_2O$, stabilizing the porous metal-polycarboxylate architecture.[3-9] In compound **2**, bpp should play a similar role to that of DMF and/or $H_2O$. In compound **1**, the cpph molecules link the $Cd^{2+}$ ions into a 3-D network. Note that the larger cavities are observed, which suggests that this 3-D $Cd^{2+}$-cpph architecture is unstable. So another unnegligible role for bpa is to stabilize the 3-D $Cd^{2+}$-cpph framework via the coordination to the $Cd^{2+}$ centers, although the larger pores in compound **1** turn small or disappear. In both compounds, three types of coordination modes for cpph molecule are found. Almost all of the carboxyl O atoms are involved in the coordination to the metal centers. Only O5 in compound **2** shows an exception, since this O atom forms the intermolecular hydrogen bond to the piperidyl N atom. In both compounds, the cpph molecules exhibit the semi-rigid character. The dihedral angles of two benzene ring planes of cpph molecules are 65.7 ° for cpph I in **1**, 57.7 ° for cpph II in **1**, and 75.4 ° for cpph in **2**, respectively.



**cpph I in 1**



**cpph II in 1**



**cpph in 2**

**Scheme 2** Coordination modes of cpph in **1** and **2**.

## Characterization

Fig. 3 presents the experimental and simulated powder XRD patterns of **1** and **2.** The experimental powder XRD pattern for each compound is in accord with the simulated one generated on the basis of structural data, confirming that the as-synthesized product is pure phase. The TG behaviors of compounds **1** and **2** were investigated. Fig. 4 gives the temperature *vs.* weight-loss curves. The TG curve of compound **1** shows a minor weight loss of *ca.* 2.5% from the room temperature to *ca.* 200 °C, corresponding to the release of the coordinate and lattice water molecules (Calcd: 2.0%). In the temperature range of 280-330 °C, compound **1** underwent the second step of weight loss, which should be ascribed to the removal of all of the carboxylate molecules (Calcd: 19.8%; Found: *ca.* 20.0%). Note that this should not be assigned to the decomposition of the bpa molecule (Calcd: 27.6%). In the end, the remaining organic molecules lost, and $Cd^{2+}$ combined synchronously with $O_2$. So the final residue was CdO (Calcd: 28.8%; Found: *ca.* 29.5%). Compound **2** also underwent the three steps of weight loss. The first step of *ca.* 5.0% weight loss corresponds to the departure of the coordinate water molecule (Calcd: 3.8%). *Ca.* 22.0% weight loss for the second step should be attributed to loss of the bpp molecule (Calcd: 22.0), which suggests that the bpp molecule departed prior to the cpph molecule in compound **2**. The residue was confirmed to be MnO (Calcd: 15.0%; Found: *ca.* 14.0%). Based on the TG curves, we can find that the host framework of compound **1** possesses the better thermal stability, and can be thermal stable up to *ca.* 280 °C. While the thermal stability of the $Mn^{2+}$-cpph framework for compound **2** is even better than that of compound **2**, and the temperature for the onset of decomposition is *ca.* 400 °C. Fig. S5 presents the IR spectra of compounds **1**, **2**, bpp and $H_3$(cpph). In the IR spectrum of bpp, the shape peak at 3230 $cm^{-1}$ corresponds to stretching vibration of N-H single bond. When bpp exists in a non-protonated or monoprotonated form, this peak still appears, and only slight red/blue-shift is observed. However, once bpp is diprotonated, this sharp peak will disappear.[22] No sharp peak around 3230 $cm^{-1}$ was found in the IR spectrum of compound **2**, indicating that bpp exists in a diprotonated form in compound **2**.

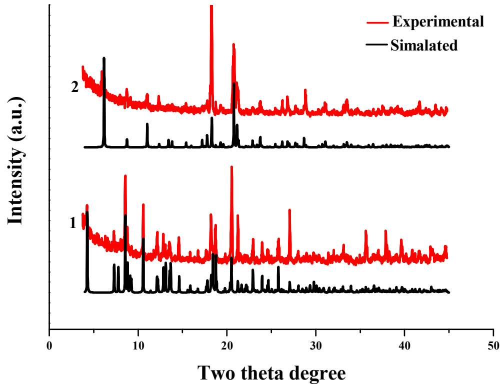


**Fig. 3** Powder XRD patterns for **1** and **2**.

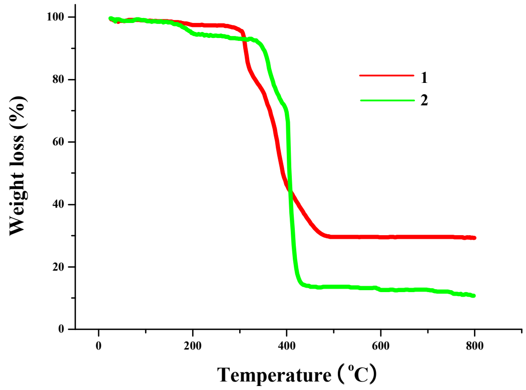


**Fig. 4** TG curves of **1** and **2**.

## Photoluminescence sensing property

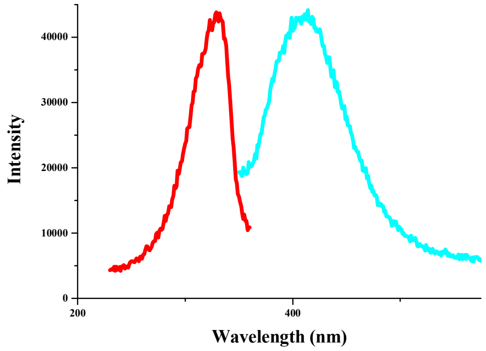


**Fig. 5** Photoluminescence excitation (red) and emission spectra (blue) of **1** in solid state.

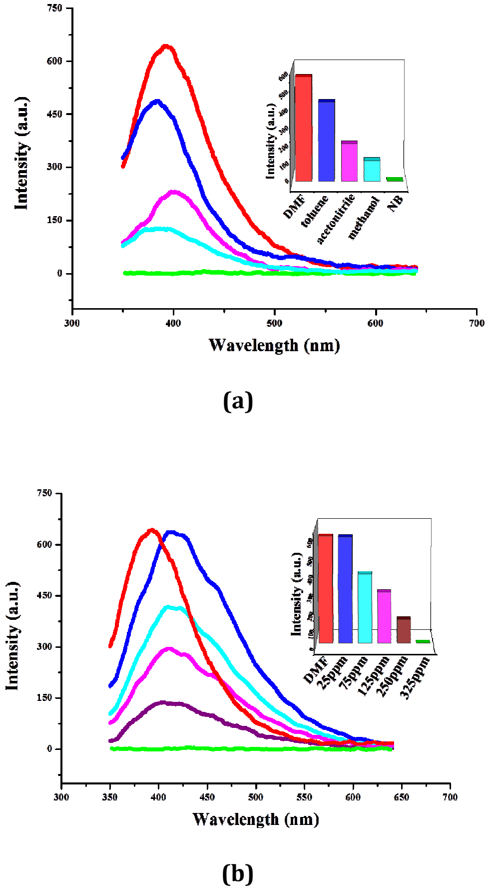


**Fig. 6** (a) Emission spectra of **1** dispersed in different solvents ($\lambda_{ex}$ = 330 nm); (b) Emission spectra of **1** dispersed in DMF with addition of different concentrations of NB ($\lambda_{ex}$ = 330 nm).

The solid-state photoluminescence behaviors of compounds **1** and **2** at the room temperature were investigated. As shown in Fig. 5, compound **1** possesses the photoluminescence property, exhibiting a strong blue-light emission with the maximum at 412 nm when excited at 330 nm. The blue-light emission for compound **1** should be attributed to the cpph-centered electronic excitation, because the $H_3$(cpph) molecule exhibits a similar blue-light emission (*ca.* 420 nm) upon excitation.[19d] Compound **2** does not emit light, which may be relevant to the heavy-atom effect [23] and the excited state intermolecular proton transfer (EXIPT) associated with the N-H···O hydrogen bond.[24]

To investigate the sensing ability of compound **1**, the suspension-state photoluminescence properties of compound **1** dispersed in the different organic solvents were investigated. The solvents selected have N,N-dimethylformamide (DMF), acetonitrile, methanol, toluene and nitrobenzene (NB). Before the photoluminescence properties were measured, the stable emulsions were prepared: a finely ground powder sample of compound **1** (5 mg) was immersed in the different organic solvents (5.00 mL), treated by ultrasonication for *ca.* 30 min, and then aged for 3 days. Fig. 6a illustrates the emission spectra of compound **1** dispersed in different solvents ($\lambda_{ex}$ =

330 nm). We found that the locations of the maximum emissions for all of the samples have hardly changes, and only the minor blue-shifts (< 30 nm) are observed, compared with that of compound **1** in the solid state. This may be due to the solvent effect,[25] and an increasing conjugation upon metal coordination.[12e] However, the intensities of the maximum emissions for all of the emulsions are largely dependent on the solvent molecules. DMF was proved to be the strongest enhancer, while NB was the most effective quencher. Nearly 100% photoluminescence quenching was observed. These results suggest that compound **1** has a selective response to NB. In order to further explore the sensing property of compound **1**, we conducted a systematic investigation of the quenching effect for the NB molecule. A group of emulsions of compound **1** immersed in DMF with gradually increased NB concentrations were prepared to monitor the emissive response. As shown in Fig. 6b, with the addition of 125 ppm NB (molar ratio: 1.35:1 for NB:compound **1**), the emission intensity of compound **1** decreased by *ca*. 50%. While with the addition of 325 ppm NB (molar ratio: 3.51:1 for NB:compound **1**), the emission intensity was quenched by nearly 100%. These data indicate that compound **1** can serve as a fluorescence sensor to detect the ppm-grade NB. Considering the structural feature of compound **1**, due to the introduction of the bpe molecule, the porosity formed by $Cd^{2+}$ and cpph became smaller or even disappeared. The absence of the effective porosity excludes the possibility of the encapsulation of the analytes during the sensing process. Therefore, the sensing mechanism might be quite different from those of guest-induced quenching, in which the analyte molecules are included in the pores and interact with the host framework resulting in the photoluminescence response. However, the dispersible nature of compound **1** in the analyte solutions enabled the adsorption of analyte molecules on the surface of particles and facilitates possible electron transfer. Thus, upon excitation, the electron transfer from the electron-donating framework of compound **1** with rich conjugate $\pi$-electron to the highly electron-withdrawing nitro group in NB molecule adsorbed on the surface of particles, resulting in the detectable photoluminescence quenching. Although the specific quenching mechanism is still not clear, two factors may play an important role: the dispersible nature of the sample in different solvents; the electron withdrawing nature of $-NO_2$ group in NB.[12]

## Conclusion

In summary, we selected a semi-rigid V-shape asymmetric tricarboxylic acid molecule, namely $H_3$(cpph), to self-assemble two new $Cd^{2+}$ and $Mn^{2+}$ CPs under the hydro(solvo)thermal conditions. Synthetically, the reactive temperature, the pH level of the mixed reactive precursors and the introduced N,N′-donor organic bases play a key role in controlling the crystal growth. Structurally, in both compounds, the cpph molecules act as the connectors, propagating the $Cd^{2+}$ or $Mn^{2+}$ ions into a 3-D network. In the formation of both 3-D networks, five factors play a crucial role: (i) the carboxylate groups and the metal ions aggregate to form three types of dinuclear clusters, namely so-called SBUs; (ii) the phthalate moieties for cpph link the metal ions into a 2-D layer network; (iii) the 4′-position carboxylate groups further propagate the layers into a 3-D network; (iv) the introduced N,N′-donor organic bases stabilize the 3-D metal-cpph networks in the form of linker or guest molecule; (v) based on the semi-rigid character of the cpph molecule, the dihedral angles of two benzene ring planes for cpph exhibits a wide range. The photoluminescence analysis revealed that compound **1** can act as the fluorescence sensor to detect the ppm-grade NB via a fluorescence quenching mechanism.

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## Notes and references

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