

基于三联苯-2,5,2',5'-四羧酸的两个配位聚合物 (Ni(II), Zn(II))的合成、结构和性质

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摘要: 采用水热法合成了两个新颖的配合物 $[\text{Ni}(\text{H}_2\text{qptc})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})_n$ (**1**) 和 $[\text{Zn}_2(\text{H}_2\text{O})_2(\text{qptc})(4,4'\text{-bpy})]_n$ (**2**) (H_4qptc : 三联苯-2,5,2',5'-四羧酸, 4,4'-bpy: 4,4'-联吡啶), 并对其进行了元素分析、热重、红外光谱和、磁性和 X-射线单晶衍射测定。化合物 **1** 和 **2** 都是三维结构, 分别显示 $(6^5.8)\text{-cds}$ 、 $(4^2.6)_2(4^3.6^2.8)(4^5.6^4.8)_2$ 拓扑结构。

关键词: 三联苯-2,5,2',5'-四羧酸; 4,4'-联吡啶; 镍(II)配合物; 锌(II)配合物

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Syntheses, Crystal Structures and Properties of Two Mixed-Ligand Coordination Polymers (Ni(II), Zn(II)) Based on Terphenyl-2,5,2',5'-tetracarboxylic Acid Ligand

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Abstract: Solvothermal reactions of aromatic terphenyl-2,5,2',5'-tetracarboxylic acid (H_4qptc) ligand and transitional metal cations of M^{II} ($\text{M}=\text{Ni}, \text{Zn}$) in the presence of 4,4'-bipyridine (4,4'-bpy) afford two new coordination polymers (CPs), namely, $[\text{Ni}(\text{H}_2\text{qptc})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})_n$ (**1**) and $[\text{Zn}_2(\text{H}_2\text{O})_2(\text{qptc})(4,4'\text{-bpy})]_n$ (**2**). Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, TGA, and magnetism. In **1**, the $\text{H}_2\text{qptc}^{2-}$ acts as a Z-shaped ligand linking the Ni^{II} centers to a 1D zigzag polymeric $[\text{Ni}(\text{H}_2\text{qptc})]_n$ chain, based on which a unique 3D 4-connected framework with distorted $(6^5.8)\text{-cds}$ topology is formed. For **2**, the qptc^{4-} acts as a H-shaped ligand linking the Zn^{II} centers together to form a 2D polymeric $[\text{Zn}(\text{qptc})]_n$ layer, which is further connected by 4,4'-bpy, thus generating a 3D (3,4)-connected network with the Schläfli symbol of $(4^2.6)_2(4^3.6^2.8)(4^5.6^4.8)_2$. CCDC: 864143, **1**, 864144, **2**.

Key words: terphenyl-2,5,2',5'-tricarboxylic acid; 4,4'-bipyridine; nickel(II) complex; zinc(II) complex

The design and synthesis of metal-organic frameworks (MOFs) have attracted upsurging research interest not only because of their appealing structural

and topological novelty but also owing to their tremendous potential applications in gas storage, microelectronics, ion exchange, chemical separations,

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nonlinear optics and heterogeneous catalysis^[1-2]. Generally, the diverse structures of such materials are always dependent on many factors, such as metal ion, template, metal-ligand ratio, pH value, counteranion, and number of coordination sites provided by organic ligands^[3]. In the assembly process of MOFs, the rational design and reasonable use of the characteristic ligand are very important in the construction of the desired MOFs^[4-5]. To date, a series of metal-organic structural motifs, including honeycomb, brick wall, bilayer, ladder, herringbone, diamondoid, and rectangular grid, have been deliberately designed by employing bridging polycarboxylate ligands, such as 2',5'-dimethyl-1,1':4',1''-terphenyl-3,3'',5,5''-tetracarboxylic acid^[6a], 2',5'-difluoro-1,1':4',1''-terphenyl-3,3'',5,5''-tetracarboxylic acid^[6a], 2',3',5',6'-tetrafluoro-1,1':4',1''-terphenyl-3,3'',5,5''-tetracarboxylic acid^[6a], naphthalene-1,4-diyl-bis(benzene-3,5-dicarboxylic acid)^[6a], 5,5'-(9,10-anthracenediyl)diisophthalic acid^[6b], *p*-terphenyl-3,3'',5,5'''-tetracarboxylic acid^[6c]. The aromatic polycarboxylate ligands can serve as excellent candidates for building highly connected, self-penetrating, or helical coordination frameworks due to their bent backbones and versatile bridging fashions^[7]. However, to the best of our knowledge, MOFs based on terphenyl-2,5,2',5'-tetracarboxylic acid have never been documented to date.

Recent study on coordination assemblies using aromatic dicarboxylate derivatives and a flexible dipyridyl linker 1,3-bis(4-pyridyl)propane (bpp) states a reliable strategy for obtaining new topological prototypes of coordination nets^[8]. Also, a minor change of the carboxylate building blocks may be applied to realize good structural control of the resulting coordination polymers. Thus, these considerations inspired us to explore new coordination frameworks with designed terphenyl-2,5,2',5'-tetracarboxylic acid (H_4qptc) ligand. Compared to rigid 1,2,4,5-benzenetetracarboxylic acid, H_4qptc is a more flexible and longer ligand, which possesses several interesting characters: (i) It has four carboxyl groups that may be completely or partially deprotonated, inducing rich coordination modes and allowing interesting structures

with higher dimensionalities, (ii) It can act as hydrogen-bond acceptor as well as donor, depending upon the degree of deprotonation, (iii) two sets of carboxyl groups separated by one phenyl ring can form different dihedral angles through the rotation of C-C single bonds, thus it may ligate metal centers in different orientations. These characters may lead to cavities, interpenetration, helical structures, and other novel motifs with unique topologies. Taking account of these, recently we began to assemble H_4qptc and different transitional metal ions into polymeric complexes under solvothermal conditions and anticipated the rich structural features stored in H_4qptc will induce novel polymeric structures. In this paper, we reported the syntheses and characterizations of two new coordination polymers, $\{[Ni(H_2qptc)(4,4'-bpy)(H_2O)_2] \cdot 2(H_2O)}\}_n$ (**1**) and $[Zn_2(H_2O)_2(qptc)(4,4'-bpy)]_n$ (**2**).

1 Experimental

1.1 Materials and methods

5-bromo-2,5-dimethylbenzene (**I**), bis(pinacolato)diborane, Pd(dppf)₂Cl₂, Pd(PPh₃)₄, and 1,2-bis(diphenylphosphino)ethane were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification. Elemental analyses of C, N, and H were performed on an EA1110 CHNS-0 CE elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer.

1.2 Synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid (H_4qptc)

1.2.1 Synthesis of 2-bromoterephthalic acid (**II**)

The mixture of **I** (1 000 mmol, 18.5 g), KOH (110 mmol, 6.0 g), and 600 mL H₂O was heated to reflux. KMnO₄ (440 mmol, 70.0 g) was added in portions to the refluxing solution. Refluxing was continued until **I** was completely oxidized. After cooling to room temperature, the mixture was filtered and the residual manganese dioxide was washed with the solution of hydroxide sodium. The combined filtrates were acidified with concentrated hydrochloric acid. The white solid precipitate was filtered off, washed several times with water, and dried to afford **II** (82%). EI-MS: *m/z* [M-H] 242.9 (C₈H₅BrO₄, 243.9).

Anal.(%) calcd. for $C_8H_5BrO_4$: C, 39.21; H, 2.06. Found: C, 39.08; H, 2.02.

1.2.2 Synthesis of diethyl 2-bromoyterephthalate (III)

The mixture of **II** (100 mmol, 24.5 g), 500 mL ethanol, and 10 mL concentrated H_2SO_4 was refluxed for 12 h, and then poured into 500 mL H_2O . The solution was extracted with ethyl acetate (200 mL \times 3), dried with anhydrous magnesium sulfate, and then concentrated on rotary evaporator to give a white powder (92%). Anal.(%) calcd. for $C_{12}H_{13}BrO_4$: C, 47.86; H, 4.35. Found: C, 47.79; H, 4.32.

1.2.3 Synthesis of 4,4,5,5-tetramethyl-2-(diethyl 2,5-dicarboxylatephenyl)-1,3 -dioxolane (IV)

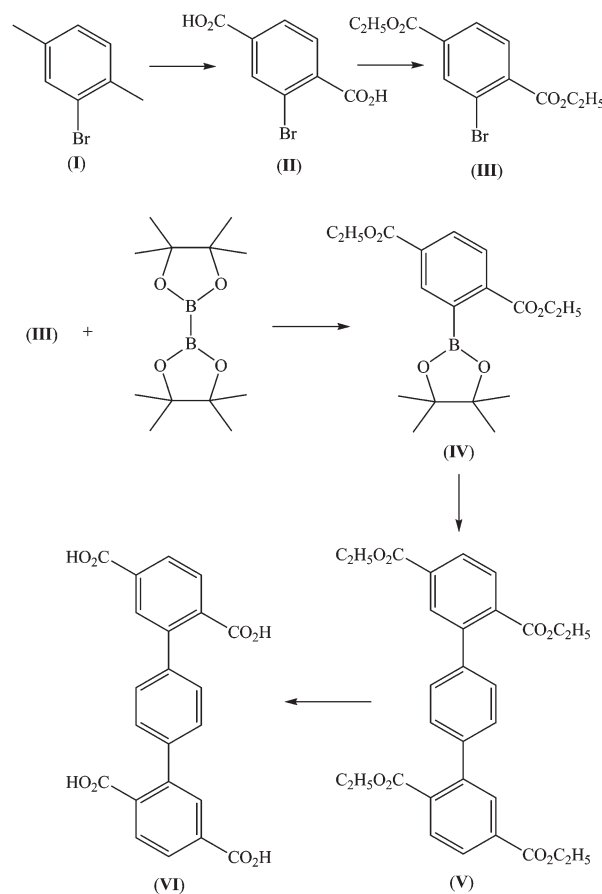
The synthetic method was modified from the published 4,4,5,5-tetramethyl-2-(dimethyl 3,5-dicarboxylatephenyl)-1,3-dioxolan^[4e]. The mixture of **III** (100 mmol, 30.0 g), bis(pinacolato)diborane (11.8 mmol, 3.0 g), potassium acetate (0.29 mmol, 28.0 g), $Pd(dppf)_2Cl_2$ (7.0 mmol, 5.0 g), and dried 1,4-dioxane (500 mL) at 100 °C overnight and afterward extracted with ethyl acetate (200 mL \times 3). The organic layer was decolorized with activated carbon, and dried by anhydrous Na_2SO_4 . The crude product was obtained from concentration under a vacuum and purified by column chromatography (silica gel, ethylacetate/petroleum ether, 6vol%). Yield 78%. Anal. (%) calcd. for $C_{18}H_{25}BO_6$: C, 62.09; H, 7.24. Found: C, 61.89; H, 7.15.

1.2.4 Synthesis of tetraethyl terphenyl-2,5,2',5'-tetracarboxylate (V)

The mixture of **IV** (100 mmol, 34.82 g), 1,4-dibromobenzene (50 mmol, 11.7 g), and K_3PO_4 (200 mmol, 42.4 g) were mixed in 1,4-dioxane (500 mL), and the mixture was deaerated using N_2 for 10 min. $Pd(PPh_3)_4$ (4 mmol, 5.0 g) was added to the stirred reaction mixture and the mixture was heated to reflux for ca. one week under N_2 atmosphere. The crude product of **VI** was obtained after 1,4-dioxane was removed under a vacuum. Recrystallization from methanol offered the pure tetraethyl terphenyl-2,5,2',5'-tricarboxylate. Anal. (%) calcd. for $C_{30}H_{30}O_8$: C, 69.49; H, 5.83. Found: C, 69.35; H, 5.71.

1.2.5 Synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid (H_4qptc , VI)

The mixture of **V** (50 mmol, 25.9 g) and 10 g NaOH in 500 mL H_2O was refluxed for 2 h, and then cooled to room temperature. The solution was neutralized with concentrated HCl. White powder was obtained with the yield of 92%. EI-MS: m/z [M-H], 405.1 (calcd for $C_{22}H_{14}O_8$, 406.1). Anal.(%) calcd. for $C_{22}H_{14}O_8$: C, 65.03; H, 3.47. Found: C, 64.93; H, 3.39.



Scheme 1 Scheme for the synthesis of terphenyl-2,5,2',5'-tricarboxylic acid (H_4qptc)

1.3 Synthesis of complexes 1 and 2

Synthesis of complex 1: The synthesis is performed in 25 mL Teflon-lined stainless steel vessels. A mixture of H_4qptc (0.15 mmol, 0.050 g), manganese(II) sulfate monohydrate (0.20 mmol, 0.048 g), 4,4'-bpy (0.32 mmol, 0.050 g), NaOH (0.3 mmol, 0.012 g), 6mL H_2O , and 6mL EtOH was heated to 120 °C for 3 d, followed by slow cooling (a descent rate of 10 °C \cdot h⁻¹) to room temperature, giving block crystals. Yield of 52% (based on Mn). Anal. (%) calcd. for $C_{32}H_{28}N_2NiO_{12}$: C, 55.60; H, 4.08; N, 4.05. Found: C, 55.56; H, 3.98; P, 4.03.

Synthesis of complex **2**: The synthesis is performed in 25 mL Teflon-lined stainless steel vessels. A mixture of H_4qptc (0.15 mmol, 0.050 g), zinc acetate dihydrate (0.30 mmol, 0.066 g), 4,4'-bpy (0.32 mmol, 0.050 g), NaOH (0.3 mmol, 0.012 g), 6 mL H_2O and 6 mL EtOH was heated to 120 °C for 3 d, followed by slow cooling (a descent rate of 10 °C \cdot h $^{-1}$) to room temperature, giving block crystals. Yield of 45% (based on Zn). Anal.(%) calcd. For $\text{C}_{32}\text{H}_{22}\text{N}_2\text{O}_{10}\text{Zn}_2$: C 52.99, H 3.86, N 3.86. Found: C, 52.83; H, 3.78; N, 3.82.

1.4 Structure determination

Intensity data collection was carried out on a

Siemens SMART diffractometer equipped with a CCD detector using Mo $K\alpha$ monochromatized radiation ($\lambda = 0.071\ 073\ \text{nm}$) at 293(2) K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX package^[9]. Crystallographic data for compounds **1** and **2** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC: 864143, **1**, 864144, **2**.

Table 1 Crystallographic data and details of diffraction experiments for complexes of **1** and **2**

| | 1 | 2 |
|---|---|--|
| Formula | $\text{C}_{32}\text{H}_{28}\text{N}_2\text{NiO}_{12}$ | $\text{C}_{32}\text{H}_{22}\text{N}_2\text{O}_{10}\text{Zn}_2$ |
| Formula weight | 691.27 | 725.26 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $C2/c$ | $P\bar{1}$ |
| a / nm | 1.688 6(8) | 1.004 62(19) |
| b / nm | 1.239 2(8) | 1.046 6(2) |
| c / nm | 1.427 4(7) | 1.453 0(3) |
| $\alpha / (^\circ)$ | 90.00 | 86.279(4) |
| $\beta / (^\circ)$ | 91.696(7) | 81.283(4) |
| $\gamma / (^\circ)$ | 90.00 | 70.878(4) |
| V / nm^3 | 2.985(3) | 1.426 6(5) |
| Z | 4 | 2 |
| $\rho / (\text{g} \cdot \text{cm}^{-3})$ | 1.538 | 1.688 |
| μ / mm^{-1} | 0.721 | 1.748 |
| T / K | 298(2) | 298(2) |
| R_{int} | 0.051 7 | 0.022 7 |
| R ($I > 2\sigma(I)$) | $R_1=0.087\ 4$, $wR_2=0.137\ 6$ | $R_1=0.051\ 6$, $wR_2=0.161\ 2$ |
| R (all data) | $R_1=0.101\ 7$, $wR_2=0.157\ 7$ | $R_1=0.062\ 4$, $wR_2=0.166\ 2$ |
| Goof | 1.004 | 1.003 |
| $(\Delta\rho)_{\text{max}} / (\text{e} \cdot \text{nm}^{-3})$ | 440 | 399 |
| $(\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$ | -508 | -385 |

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for **1** and **2**

| Complex 1 | | | | | |
|------------------|------------|-------------|------------|------------|------------|
| Ni1-N1 | 0.203 8(4) | Ni1-O1 | 0.203 6(3) | Ni1-O5 | 0.210 8(4) |
| O1A-Ni1-O1 | 180.00(5) | O1A-Ni1-N1 | 87.83(12) | O1-Ni1-N1 | 92.17(12) |
| O1A-Ni1-N1A | 92.17(12) | O1-Ni1-N1A | 87.83(12) | N1-Ni1-N1A | 180.0(2) |
| O1A-Ni1-O5 | 88.92(14) | O1-Ni1-O5 | 91.08(14) | N1-Ni1-O5 | 89.97(16) |
| N1A-Ni1-O5 | 90.03(16) | O1A-Ni1-O5A | 91.08(14) | O1-Ni1-O5A | 88.92(14) |
| N1-Ni1-O5A | 90.03(16) | N1A-Ni1-O5A | 89.97(16) | O5-Ni1-O5A | 180.0 |

Continued Table 2

| Complex 2 | | | | | |
|------------------|------------|------------|------------|-------------|------------|
| Zn1-N1 | 0.208 1(5) | Zn1-O2 | 0.198 4(4) | Zn1-O9 | 0.203 8(6) |
| Zn1-O7B | 0.197 8(4) | Zn2-O2A | 0.206 4(4) | Zn2-O4 | 0.196 0(4) |
| Zn2-O5 | 0.197 8(4) | Zn2-O10 | 0.200 1(5) | | |
| O7A-Zn1-O2 | 120.36(17) | O7A-Zn1-O9 | 108.7(2) | O2-Zn1-O9 | 110.7(2) |
| O7A-Zn1-N1 | 110.28(19) | O2-Zn1-N1 | 95.12(18) | O9-Zn1-N1 | 111.0(2) |
| O4-Zn2-O5 | 114.32(17) | O4-Zn2-O10 | 115.71(19) | O5-Zn2-O10 | 107.50(18) |
| O4-Zn2-N2B | 119.79(19) | O5-Zn2-N2B | 95.30(17) | O10-Zn2-N2B | 101.62(19) |

Symmetry code: **1**: (A) $-x+1/2, -y+1/2, -z$; **2**: (A) $x+1, y-2, z$; (B) $x+1, y-2, z$.

2 Results and discussion

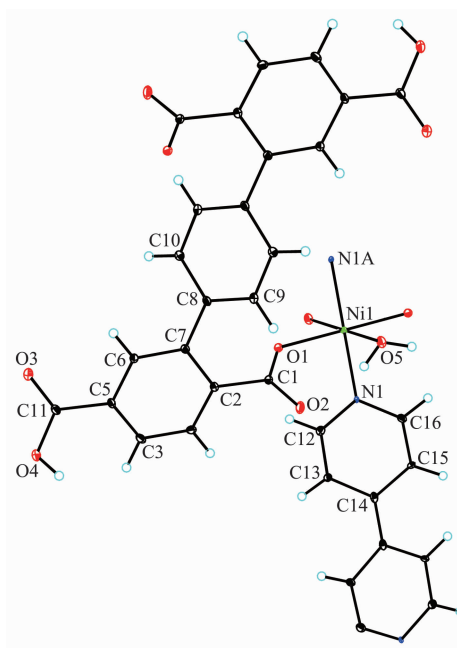
2.1 Synthesis

The synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid (H_4qptc) is shown in Scheme 1. In order to obtain the pure product and the high yield, the used organic solvents should be dried completely during the synthesis of compounds **III** and **IV**. The synthesis of **V** was performed under the He atmosphere. The final product of H_4qptc is white if the obtained crude product of **V** was decolored by refluxing in EtOH with activated carbon. In the present study, complexes **1** and **2** were prepared from the solvothermal reaction of the related first transitional metal salts and the ligand of H_4qptc in the presence of phen. The reactions without phen as a secondary ligand were performed at a different temperature, giving only some unknown precipitates. However, when the auxiliary phen ligand was introduced, satisfactory single crystals of five complexes were obtained.

2.2 Structure description of $[\text{Ni}(\text{H}_2\text{qptc})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})_n$ (**1**)

The single-crystal X-ray diffraction analysis reveals that complex **1** crystallize in the monoclinic system, with the space group: $C2/c$. The asymmetric unit of **1** consists of half of a Ni^{II} atom, half of a 4,4'-bpy, half of a partly deprotonated $\text{H}_2\text{qptc}^{2-}$, one coordinated water molecules, and one lattice water molecules. Each Ni^{II} center locates in a distorted octahedral geometry, coordinated by two oxygen atoms from two qptc^{4-} ligands ($\text{Ni}(1)\text{-O}(1)$ 0.203 4(3) nm), two 4,4'-bpy bridging ligands ($\text{Ni}(1)\text{-N}(1)$ 0.2039(4) nm), and

two coordinated water molecules ($\text{Ni}(1)\text{-O}(5)$ 0.210 9(4) nm), showing a distorted octahedral coordination geometry (Fig.1). The axial $\text{Ni}\text{-O}_{\text{water}}$ distances are a little shorter than the ones (including $\text{Ni}\text{-O}$ and $\text{Ni}\text{-N}$) in the square due to the John-Teller effect.



Symmetry codes: (A) $-x, -y+1, -z+1$

Fig.1 Coordination environment of Ni^{II} atom in **1** with the thermal ellipsoids at 30% probability level

The two deprotonated carboxyl groups of $\text{H}_2\text{qptc}^{2-}$ show $\mu_1\text{-}\eta^1\text{:}\eta^0$ coordination mode, and the $\text{H}_2\text{qptc}^{2-}$ acts as a Z-shaped ligand (Scheme 2a) linking the Ni^{II} centers to a 1D zigzag polymeric $[\text{Ni}(\text{H}_2\text{qptc})_n]$ chain along the crystallographic $[101]$ direction with the adjacent $\text{Ni} \cdots \text{Ni}$ separation of 1.047 2 nm (Fig.2a). Each four $[\text{Ni}(\text{H}_2\text{qptc})_n]$ chains are further linked through the bridging 4,4'-bpy ligands along two

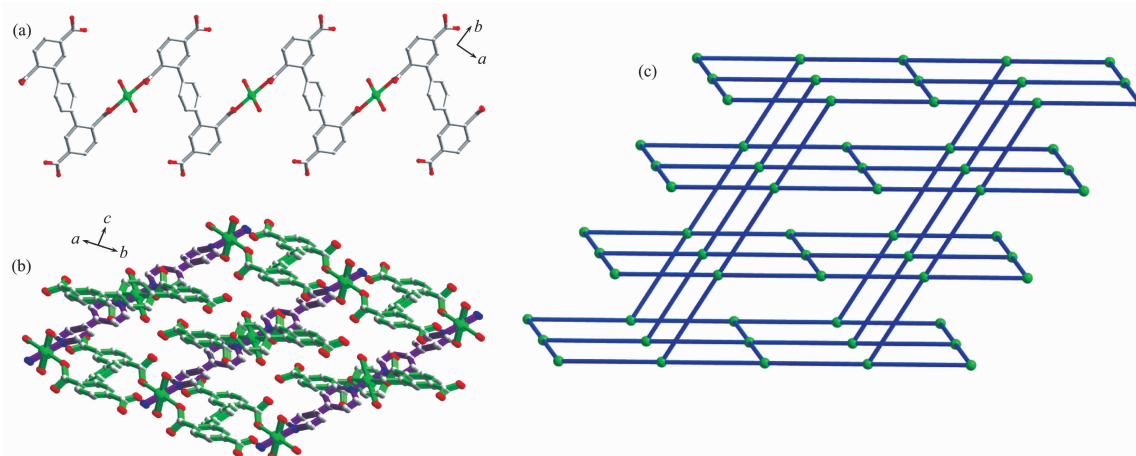
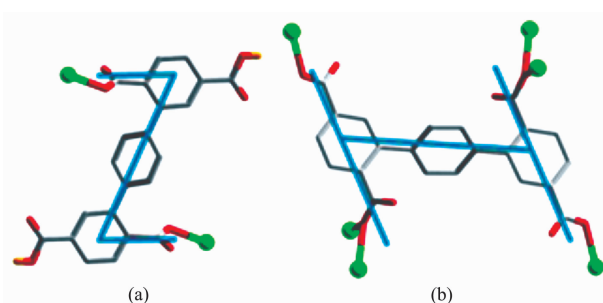


Fig.2 (a) View of the 2D layer of **1**; (b) View of the 2D layer of **1** containing right-handed helices; (c) A perspective view of the 3D supramolecular structure of **1** with (6^{5.8})-cds topology



Scheme 2 Coordination modes of qptc ligand: (a) Z-shaped for **1**, (b) H-shaped for **2**

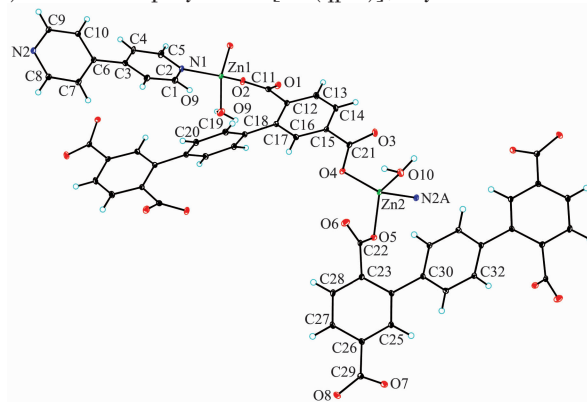
perpendicular directions, [001] and [010], thus resulting in a unique 3D 4-connected framework (Fig.2b). The Ni \cdots Ni distance due to 4,4'-bpy ligand is 1.121 6(2) nm. The neighboring 4,4'-bpy ligands orientate nearly perpendicularly to one another with the side C-H bonds directed to the pyridyl plane of the adjacent bpy ligand. The H-to-plane distances in the region are 0.295~0.318 nm, indicating weak C-H $\cdots\pi$ interactions^[10]. Different from the coplanar 4,4'-bpy molecule, the bpy ligand is twisted with the dihedral angle of 9.2(2) $^\circ$ between two pyridyl components. It is worth noting that the present net has the same short vertex symbol as CdSO₄, the simplest planar 4-connected net or distorted (6^{5.8})-cds topology (Fig.2c).

2.3 Structure description [Zn₂(H₂O)₂(qptc)(4,4'-bpy)]_n (**2**)

The single-crystal X-ray diffraction analysis reveals that complex **2** also shows a 3D framework. There are two crystallographically independent Zn^{II} atoms, one 4,4'-bpy, two half qptc⁴⁻, and two coor-

ordinated water molecules in the asymmetric unit of **2**. Both Zn1 and Zn2 have the similar distorted octahedral coordination environment, formed by one N atoms from one 4,4'-bpy ligand (Zn(1)-N(1) 0.208 1(5) and Zn(2)-N(2A) 0.206 4(4) nm, Symmetry code: (A) $x-1, y+1, z+1$), two O atoms from two qptc⁴⁻ ligands (Zn(1)-O(2) 0.198 4(4) nm, Zn(2)-O(4) 0.196 0(4) nm, and Zn(2)-O(5) 0.197 8(4) nm), and one coordinated water molecule (Zn(1)-O(9) 0.203 8(6) nm and Zn(2)-O(10) 0.200 1(5) nm) (Fig.3).

Different from **1**, the H₄qptc ligand in **2** is completely deprotonated under the solvothermal condition. The carboxyl groups of qptc⁴⁻ exhibit μ_1 - η^1 : η^0 coordination mode and the qptc⁴⁻ acts as a H-shaped ligand (Scheme 2b) linking the Zn^{II} centers together to form a 2D polymeric [Zn(qptc)]_n layer (Fig. 4). Each 2D polymeric [Zn(qptc)]_n layers are further



Symmetry codes: (A) $-1+x, 1+y, 1+z$; (B) $-x, -y+1, -z+1$

Fig.3 Coordination environment of Zn^{II} atom in **2** with the thermal ellipsoids at 30% probability level

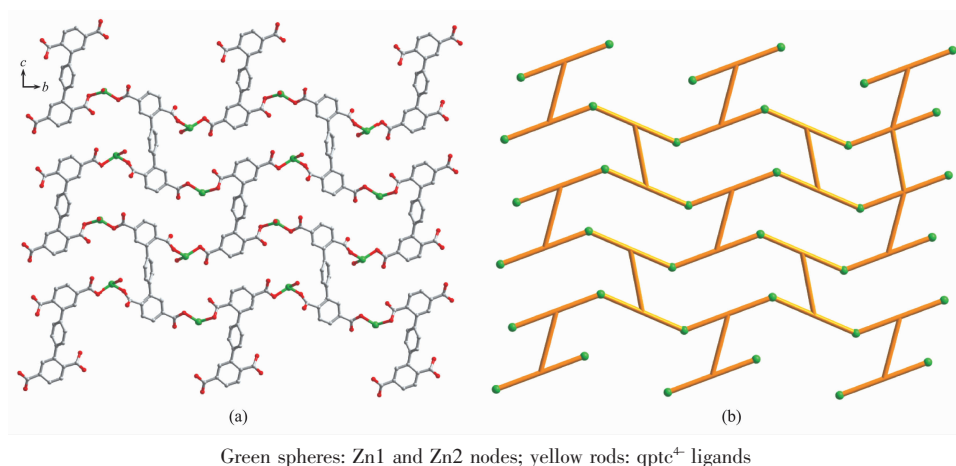


Fig.4 (a) View of 2D polymeric $[\text{Zn}(\text{qptc})]_n$ layer **2**; (b) Schematic view of the the 4-connected node for qptc^{4-} in **2**

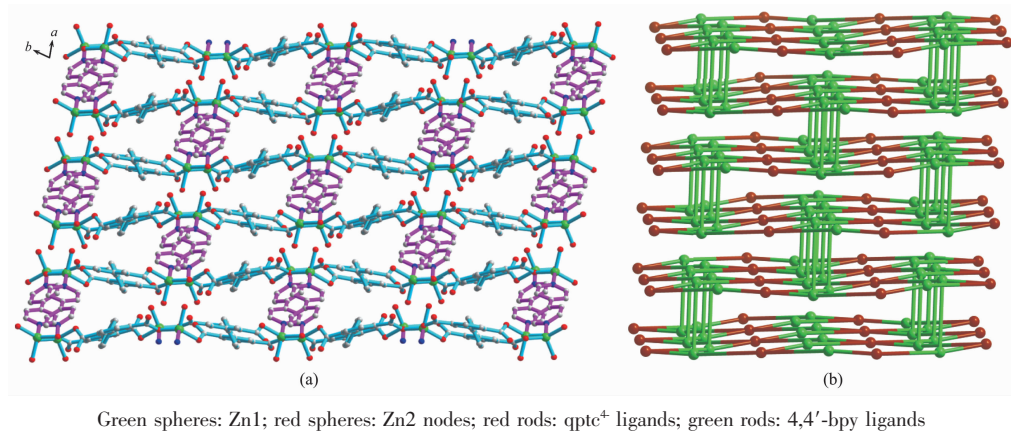


Fig.5 (a) View of the 3D network of **2**; (b) Schematic view of the $(3,4,5)$ -connected $(4^2.6)_2(4^3.6^2.8)(4^5.6^4.8)_2$ topology of **2**

linked through the bridging 4,4'-bpy ligands, thus resulting in a unique 3D 4-connected framework (Fig. 5a). The $\text{Zn} \cdots \text{Zn}$ distance due to 4,4'-bpy ligand is 1.121 1(2) nm. Similar with compound **1**, the neighboring 4,4'-bpy ligands orientate nearly perpendicularly to one another with the side C-H bonds directed to the pyridyl plane of the adjacent bpy ligand. The H-to-plane distances in the region are 0.296~0.317 nm, indicating weak $\text{C-H} \cdots \pi$ interactions^[10]. Different from the coplanar 4,4'-bpy molecule, the bpy ligand is twisted with the dihedral angle of 9.3(2)° between two pyridyl components. Considering the coordination modes of qptc^{4-} , which is linked four times to the metal center (two Zn1 and two Zn2 atoms), it can be viewed as a four-connected node (6.6.8.8.10₂.10₂). Zn1 and Zn2 atoms can be viewed as three-connected nodes (6.6.8₂), respectively. Thus, the ligands and metals are combined to generate a 3D (3,4)-connected

network (Fig.5b) with the Schläfli symbol of $(4^2.6)_2(4^3.6^2.8)(4^5.6^4.8)_2$.

2.4 Magnetic studies

The temperature dependence of the magnetic susceptibility of a powdered sample was measured on complex **1**, by a Quantum Design SQUID magnetometer

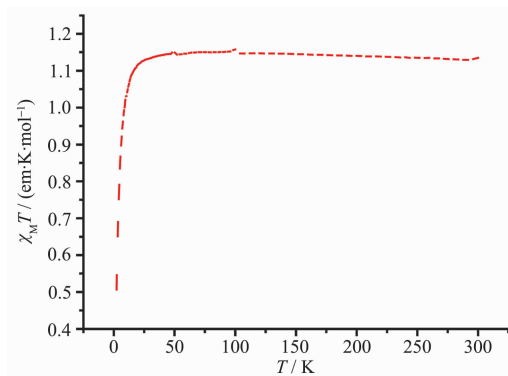


Fig.6 Plot of the effective magnetic moment as a function of temperature for complex **1** in a constant magnetic field of 1 000 Oe

on the MPMS-7 system and their magnetic behavior is shown in Fig.6. The overall magnetic behavior of complex **1** corresponds to the paramagnetic property. As can be found from Fig.6, the magnetic moment value obtained for the experiment is $1.13\mu_B$, consistent with the magnetic moment of the single Mn^{2+} cation ($1.00\mu_B$).

2.5 TGA analysis

To reveal the thermal stabilities of compounds **1** and **2**, TGA measurement has been carried out on a Perkin-Elmer Diamond TG/DTA instrument with a flow of dry air and a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature to $1\text{ }000\text{ }^{\circ}\text{C}$, shown in Fig.6. For **1**, TGA curve indicates that the weight loss below $85\text{ }^{\circ}\text{C}$ is 5.22%, which is attributed to the elimination of lattice water molecules (Calcd. 5.22 %). With the temperature increasing to $183\text{ }^{\circ}\text{C}$, the coordinated water molecules were lost (Found. 5.92; Calcd. 5.22%). The ligands of H_2qptc^{2-} and 4,4'-bpy are decomposed when the temperature reached $480\text{ }^{\circ}\text{C}$. For **2**, the coordinated water molecules were lost (Found. 6.26; Calcd. 4.97%) below $229\text{ }^{\circ}\text{C}$. The ligands of $qptc^{4-}$ and 4,4'-bpy are decomposed when the temperature reached $538\text{ }^{\circ}\text{C}$.

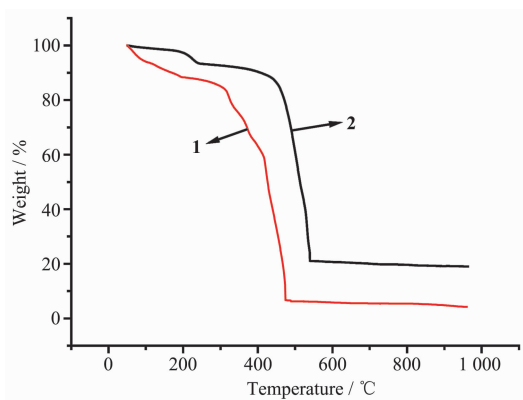


Fig.7 TG curve for compound **1** and **2**

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