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## Syntheses and crystal structures of three coordination polymers based on terphenyl-2,5,2',5'-tetracarboxylic acid

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Solvothermal reactions of terphenyl-2,5,2',5'-tetracarboxylic acid ( $H_4qptc$ ) and  $M^{II}$  ( $M=Co$ ,  $Ni$ ,  $Cu$ ) in the presence of 2,2'-bipyridine (2,2'-bpy) afford three new coordination polymers,  $[M(qptc)_{0.5}(2,2'-bpy)(H_2O)]_n$  ( $M=Co$  (**1**),  $Ni$  (**2**)) and  $[Cu(H_2qptc)(2,2'-bpy)]_n$  (**3**). The structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR, and TGA. Complexes **1** and **2** are isostructural and display a 2-D layer wherein  $qptc^{4-}$  is a twisted H-shaped ligand connecting  $Co^{II}$  centers. Furthermore, 3-D structures in **1** and **2** are formed *via* inter-chain  $\pi \cdots \pi$  interactions between neighboring 2,2'-bpy ligands, with the centroid-centroid distances of 3.619–3.822 Å. In **3**, two deprotonated carboxyl groups of  $H_2qptc^{2-}$  are a Z-shaped ligand linking  $Cu^{II}$  centers to a 1-D zigzag polymeric chain. A 2-D layer structure is built with the help of inter-chain  $\pi \cdots \pi$  interactions between the 2,2'-bpy and  $H_2qptc^{2-}$ .

**Keywords:** Terphenyl-2,5,2',5'-tetracarboxylic acid; 2,2'-Bipyridine; Cobalt(II); Nickel(II); Copper(II)

### 1. Introduction

Synthesis of metal–organic frameworks (MOFs) have attracted research for structural and topological novelty and potential applications in gas storage, microelectronics, ion exchange, chemical separations, nonlinear optics, and heterogeneous catalysis [1, 2]. Structures of such materials depend on metal ion, template, metal–ligand ratio, pH, counteranion, and number of coordination sites provided by ligands [3]. In assembly of MOFs, choice of ligand is very important in construction of MOFs [4, 5]. Metal–organic structural motifs, including honeycomb, brick wall, bilayer, ladder, herringbone, diamondoid, and rectangular grid, have been designed by employing bridging polycarboxylates, 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,

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4-diyl-bis(benzene-3,5-dicarboxylic acid) [6a], 5,5'-(9,10-anthracenediyl)diisophthalic acid [6b], and *p*-terphenyl-3,3'',5,5'''-tetracarboxylic acid [6c]. Aromatic polycarboxylates serve as excellent candidates for building highly connected, self-penetrating, or helical coordination frameworks due to bent backbones and versatile bridging [7, 8]. However, MOFs based on terphenyl-2,5,2',5'-tetracarboxylic acid have not been documented to date.

Aromatic dicarboxylates and a flexible dipyridyl linker 1,3-bis(4-pyridyl)propane (bpp) is a reliable strategy for obtaining new coordination nets [9]. A minor change of carboxylate building block may be applied to realize structural control of the resulting coordination polymers (CPs). These considerations inspired us to explore new coordination frameworks with terphenyl-2,5,2',5'-tetracarboxylic acid ( $H_4qptc$ ). Compared to rigid 1,2,4,5-benzenetetracarboxylic acid,  $H_4qptc$  is more flexible and longer and possesses several interesting features: (i) four carboxyl groups that may be completely or partially deprotonated for structures with higher dimensionalities, (ii) ability to act as hydrogen-bond acceptor and donor, depending upon the degree of deprotonation, (iii) two sets of carboxyl groups separated by a phenyl can form different dihedral angles through rotation of C–C single bonds, and may ligate metal centers in different orientations. These features may lead to cavities, interpenetration, helical structures, and other unique topologies. We began to assemble  $H_4qptc$  and different transition metal ions into polymeric complexes under solvothermal conditions and anticipated that the structural features stored in  $H_4qptc$  will induce new polymeric structures. In this article, we report syntheses and characterizations of three new CPs,  $[M(qptc)_{0.5}(2,2'\text{-bpy})(H_2O)]_n$  ( $M=Co$  (**1**),  $Ni$  (**2**)), and  $[Cu(H_2qptc)(2,2'\text{-bpy})]_n$  (**3**), which exhibit architectures from 1-D zigzag chain to 3-D framework by employing  $H_4qptc$  and 2,2'-bipy ligands.

## 2. Experimental

### 2.1. Materials and methods

5-Bromo-2,5-dimethylbenzene (**I**), bis(pinacolato)diborane,  $Pd(dppf)_2Cl_2$ , and  $Pd(PPh_3)_4$  were purchased from Jinan Camolai Trading Company and used without purification. C, N, and H analyses were performed on an EA1110 CHNS-0 CE elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer.

### 2.2. Synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid ( $H_4qptc$ )

**2.2.1. Synthesis of 2-bromoterephthalic acid (II).** Mixture of **I** (1000 mmol, 18.5 g), KOH (110 mmol, 6.0 g), and 600 mL  $H_2O$  was heated to reflux.  $KMnO_4$  (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 residual manganese dioxide was washed with solution of sodium hydroxide. The combined filtrates were acidified with concentrated hydrochloric acid. 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 (Calcd for  $C_8H_5BrO_4$ , 243.9. Anal. Calcd for  $C_8H_5BrO_4$  (%): C, 39.21; H, 2.06. Found: C, 39.08; H, 2.02.

**2.2.2. Synthesis of diethyl 2-bromoyterephthalate (III).** Mixture of **II** (0.1 mol, 24.5 g), 500 mL ethanol, and 10 mL concentrated  $H_2SO_4$  was refluxed for 12 hours, 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 a 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.

**2.2.3. Synthesis of 4,4,5,5-tetramethyl-2-(diethyl 2,5-dicarboxylatephenyl)-1,3-dioxolane (IV).** The synthetic method was modified from that published for 4,4,5,5-tetramethyl-2-(dimethyl 3,5-dicarboxylatephenyl)-1,3-dioxolane [4e]. 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) reacted at 100°C overnight and afterward was extracted with ethyl acetate (200 mL  $\times$  3). The organic layer was decolorized with activated carbon and dried by anhydrous  $Na_2SO_4$ . Crude product was obtained from concentration under vacuum and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 6 v%). Yield: 78%. Anal. Calcd for  $C_{18}H_{25}BO_6$  (%): C, 62.09; H, 7.24. Found: C, 61.89; H, 7.15.

**2.2.4. Synthesis of tetraethyl terphenyl-2,5,2',5'-tetracarboxylate (V).** 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 one week under  $N_2$ . The crude product of **VI** was obtained after 1,4-dioxane was removed under vacuum. Recrystallization from methanol offered pure tetraethyl terphenyl-2,5,2',5'-tetracarboxylate. Anal. Calcd for  $C_{30}H_{30}O_8$  (%): C, 69.49; H, 5.83. Found: C, 69.35; H, 5.71.

**2.2.5. Synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid (**H<sub>4</sub>qptc**, **VI**).** 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 in 92% yield. 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.

## 2.3. Synthesis of 1–3

**2.3.1. Synthesis of 1.** The synthesis is performed in 25 mL Teflon-lined stainless steel vessels. A mixture of **H<sub>4</sub>qptc** (0.15 mmol, 0.020 g), cobalt(II) chloride hexahydrate (0.20 mmol, 0.048 g), 2,2'-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 days, followed by slow cooling (10°C h $^{-1}$ ) to room temperature, giving red block crystals. Yield: 36% (based on Co). Anal. Calcd for  $C_{42}H_{30}Co_2N_4O_{10}$  (%): C, 58.08; H, 3.48; N, 6.45. Found: C, 56.78;

H, 3.72; N, 3.81. IR(KBr pellet,  $\text{cm}^{-1}$ ): 3445(vs), 3069(v), 2934(v), 1708(vs), 1589(vs), 1453(vs), 1231(s), 1098(s), 850(m), 779(m), 523 (w).

**2.3.2. Synthesis of 2.** The synthesis is performed in a 25 mL Teflon-lined stainless steel vessel. A mixture of  $\text{H}_4\text{qptc}$  (0.05 mmol, 0.020 g), nickel(II) sulfate hexahydrate (0.10 mmol, 0.028 g), 2,2'-bpy (0.10 mmol, 0.018 g), NaOH (0.05 mmol, 0.002 g), and 20 mL  $\text{H}_2\text{O}$  was heated to  $150^\circ\text{C}$  for 4 days, followed by slow cooling ( $5^\circ\text{C h}^{-1}$ ) to room temperature, giving green block crystals. Yield: 61% (based on Ni). Anal. Calcd for  $\text{C}_{42}\text{H}_{42}\text{Ni}_2\text{O}_{16}\text{N}_4$  (976.2) (%): C, 51.68; H, 4.34; N, 5.74. Found: C, 50.78; H, 4.32; N, 5.51. IR(KBr pellet,  $\text{cm}^{-1}$ ): 3468(vs), 3071(v), 2921(v), 1697(vs), 1569(vs), 1423(vs), 1228(s), 1109(s), 853(m), 767(m), 527 (w).

**2.3.3. Synthesis of 3.** The synthesis is performed in a 25 mL Teflon-lined stainless steel vessel. A mixture of  $\text{H}_4\text{qptc}$  (0.05 mmol, 0.020 g), copper(II) sulfate pentahydrate (0.20 mmol, 0.049 g), 2,2'-bpy (0.32 mmol, 0.050 g), NaOH (0.3 mmol, 0.012 g), 6 mL  $\text{H}_2\text{O}$ , and 6 mL EtOH was heated to  $120^\circ\text{C}$  for 3 days, followed by slow cooling ( $10^\circ\text{C h}^{-1}$ ) to room temperature, giving blue block crystals. Yield: 36% (based on Cu). Anal. Calcd for  $\text{C}_{42}\text{H}_{30}\text{Cu}_2\text{N}_4\text{O}_{10}$  (840.6) (%): C, 58.08; H, 3.48; N, 6.45. Found: C, 57.78; H, 3.62; N, 6.21. IR(KBr pellet,  $\text{cm}^{-1}$ ): 3436(vs), 3073(v), 2921(v), 1810(vs), 1551(vs), 1417(vs), 1251(s), 1105(s), 852(m), 773(m), 517 (w).

## 2.4. Structure determination

Intensity data collections were carried out on a Siemens SMART diffractometer equipped with a CCD detector using Mo- $\text{K}\alpha$  monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using SADABS based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package [10]. Crystallographic data for **1–3** are given in table 1.

## 3. Results and discussion

### 3.1. Synthesis

The synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid ( $\text{H}_4\text{qptc}$ ) is shown in scheme 1. To obtain pure product and high yield, organic solvents should be dried completely during the syntheses of **III** and **IV**. Synthesis of **V** was performed under  $\text{N}_2$ . The final  $\text{H}_4\text{qptc}$  is white if the obtained crude product was decolorized by refluxing in EtOH with activated carbon. In this study, **1–3** were prepared from the solvothermal reaction of transition metal salts and  $\text{H}_4\text{qptc}$  in the presence of bpy.

### 3.2. Coordination modes of the $\text{H}_2\text{qptc}^{2-}$ and $\text{qptc}^{4-}$ ligands

$\text{H}_2\text{qptc}^{2-}$  and  $\text{qptc}^{4-}$  have different coordination modes for design and synthesis of functional materials. There are two types of different coordination configurations for carboxylates of  $\text{H}_2\text{qptc}^{2-}$  and  $\text{qptc}^{4-}$  ligands (figure 1).

Table 1. Crystallographic data for **1–3**.

|  | 1  | 2  | 3  |
|--|--|--|--|
| Formula  | C <sub>21</sub> H <sub>15</sub> CoN <sub>2</sub> O <sub>8</sub>    | C <sub>21</sub> H <sub>21</sub> N <sub>2</sub> NiO <sub>8</sub>    | C <sub>32</sub> H <sub>20</sub> CuN <sub>2</sub> O <sub>8</sub>    |
| Formula weight   | 482.28   | 488.11   | 624.04   |
| Temperature (K)  | 296(2)   | 293(2)   | 296(2)   |
| Crystal system   | Triclinic  | Triclinic  | Monoclinic   |
| Space group  | <i>P</i> $\bar{1}$   | <i>P</i> $\bar{1}$   | <i>C</i> 2/ <i>c</i>   |
| Unit cell dimensions (Å, °)                                      |  |  |  |
| <i>a</i>   | 10.109(1)  | 10.312(1)  | 10.640(6)  |
| <i>b</i>   | 10.735(0)  | 11.003(1)  | 16.041(8)  |
| <i>c</i>   | 10.928(4)  | 11.297(1)  | 16.498(12)   |
| $\alpha$   | 73.82(5)   | 62.07(2)   | 90.00  |
| $\beta$  | 64.97(1)   | 78.65(3)   | 104.65(1)  |
| $\gamma$   | 83.59(5)   | 70.72(3)   | 90.00  |
| Volume (Å <sup>3</sup> ), <i>Z</i>                               | 1032.03(2), 2  | 1067.6(1), 2   | 2724.3(1), 4   |
| Calculated density (g cm <sup>−3</sup> )                         | 1.398  | 1.518  | 1.521  |
| Absorption coefficient (mm <sup>−1</sup> )                       | 0.865  | 0.960  | 0.860  |
| <i>R</i> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a,b</sup>             | <i>R</i> <sub>1</sub> = 0.0652,<br><i>wR</i> <sub>2</sub> = 0.2261 | <i>R</i> <sub>1</sub> = 0.0562,<br><i>wR</i> <sub>2</sub> = 0.1171 | <i>R</i> <sub>1</sub> = 0.0955,<br><i>wR</i> <sub>2</sub> = 0.1872 |
| <i>R</i> indices (all data) <sup>a,b</sup>                       | <i>R</i> <sub>1</sub> = 0.0721,<br><i>wR</i> <sub>2</sub> = 0.2357 | <i>R</i> <sub>1</sub> = 0.0852,<br><i>wR</i> <sub>2</sub> = 0.1254 | <i>R</i> <sub>1</sub> = 0.1887,<br><i>wR</i> <sub>2</sub> = 0.2255 |
| Goodness-of-fit <sup>c</sup>                                     | 1.000  | 1.001  | 0.992  |
| (Δρ) <sub>max</sub> and (Δρ) <sub>min</sub> (e Å <sup>−3</sup> ) | 2.140 and −0.337   | 0.531 and −0.698   | 1.410 and −0.394   |

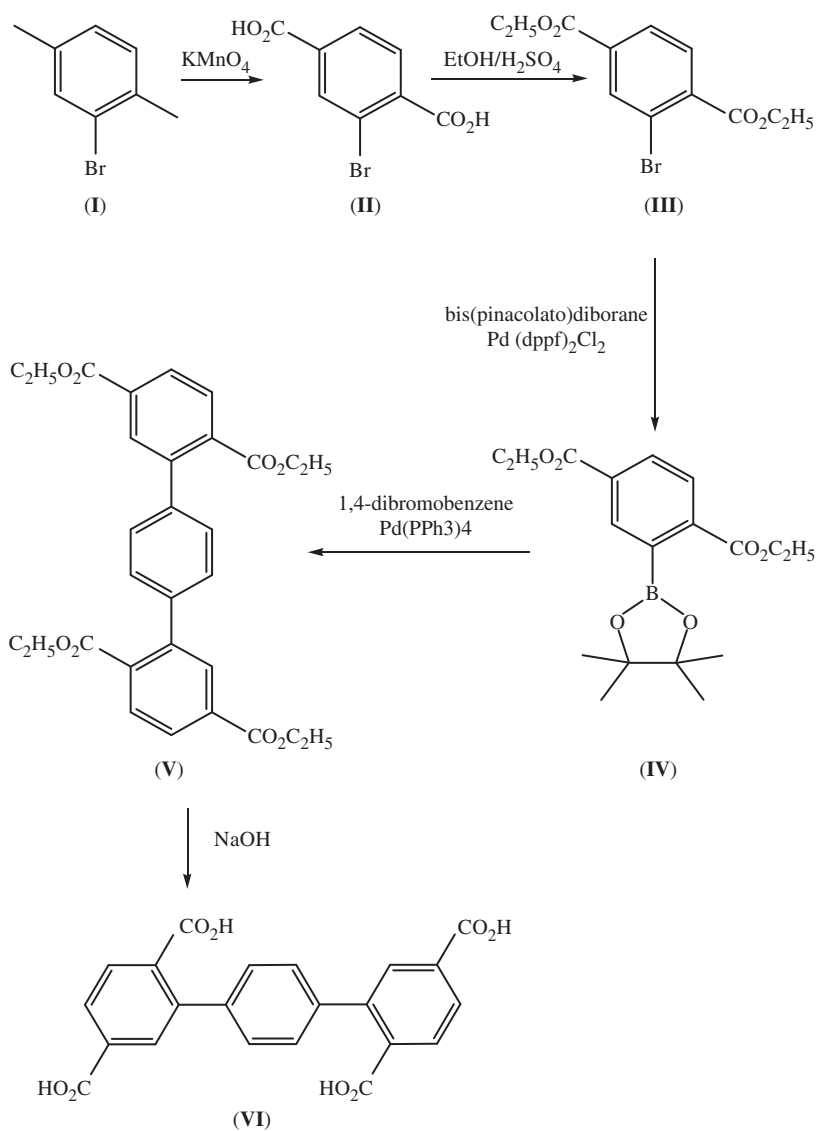
<sup>a</sup>  $R_1 = \Sigma ||F_{\text{obsd}}| - |F_{\text{calcd}}|| / \Sigma |F_{\text{obsd}}|$ . <sup>b</sup>  $wR_2 = \{ \Sigma [w(F_{\text{obsd}}^2 - F_{\text{calcd}}^2)^2] / \Sigma [w(F_{\text{obsd}}^2)^2] \}^{1/2}$ .  $w = 1 / [\sigma^2(F_o^2) + xP + (yP)^2]$ ; with  $P = (F_o^2 + 2F_c^2) / 3$ . <sup>c</sup> Goodness-of-fit on  $F^2 = [\Sigma w(F_{\text{obsd}}^2 - F_{\text{calcd}}^2)^2 / (n - p)]^{1/2}$ , where *n* = number of reflections, *p* = parameter used.

### 3.3. Structure descriptions

**3.3.1. [M(qptc)<sub>0.5</sub>(2,2'-bpy)(H<sub>2</sub>O)]<sub>n</sub> (M=Co (**1**), Ni (**2**)).** Single-crystal X-ray diffraction analysis reveals that **1** and **2** are isostructural, crystallizing in the monoclinic system, *P* $\bar{1}$  space group. Only the structure of **1** will be discussed as representative (bond distances and angles are given in table 2). The asymmetric unit of **1** consists of one Co<sup>II</sup>, one 2,2'-bpy, half of a qptc<sup>4−</sup>, and one water molecule. Each Co<sup>II</sup> is a distorted octahedral geometry, coordinated by chelating 2,2'-bpy [Co(1)–N(1)=2.126(5) and Co(1)–N(2)=2.105(4) Å], four oxygen atoms from three qptc<sup>4−</sup> [Co(1)–O(1)=2.134(3), Co(1)–O(3)=2.065(3), Co(1)–O(4)=2.173(3), and Co(1)–O(5)=2.085(4) Å], with distorted octahedral coordination (figure 1a). Axial Co–O distances are a little shorter than equatorial ones (including Co–O and Co–N) due to the Jahn-Teller effect.

The carboxyl groups of qptc<sup>4−</sup> exhibit  $\mu_1-\eta^1 : \eta^0$  and  $\mu_2-\eta^1 : \eta^1$  coordination, acting as a twisted H-shaped ligand (figure 2a) connecting Co<sup>II</sup> centers to generate a 2-D layer (figure 2b). This may be ascribed to dramatic twists between phenyl rings in qptc<sup>4−</sup>. Two side phenyl rings are approximately vertical (dihedral angle 87.7°) and have dihedral angles of 45.5° and 134.5° with the central one. Two sides of the H-shaped building block are perpendicular. Thus, the central metals are interconnected by such building blocks along different directions to give the final framework.

Crystal packing of **1** reveals inter-chain  $\pi \cdots \pi$  interactions exist between neighboring 2,2'-bpy ligands, with centroid–centroid distances of 3.619 and 3.822 Å, respectively. Such contacts link 2-D layers into a 3-D structure (figure 2c).



Scheme 1. The scheme for the synthesis of terphenyl-2,5,2',5'-tetracarboxylic acid ( $H_4qptc$ ).

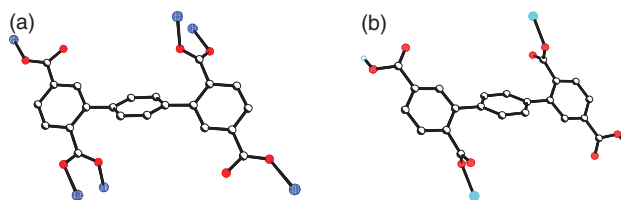


Figure 1. Coordination modes for  $H_2qptc^{2-}$  and  $qptc^{4-}$ : (a) H-shaped for **1** and **2** and (b) Z-shaped for **3**.



Table 2. Selected bond lengths (Å) and angles (°) for 1–3.

|                                |           |                                |           |                                |            |  |            |
|--------------------------------|-----------|--------------------------------|-----------|--------------------------------|------------|--|------------|
| Complex 1                      |           |                                |           |                                |            |  |            |
| Co(1)–O(3)                     | 2.065(3)  | Co(1)–O(5)                     | 2.085(4)  | Co(1)–N(2)                     | 2.105(4)   | Co(1)–N(1)                                   | 2.126(5)   |
| Co(1)–O(1)                     | 2.134(3)  | Co(1)–O(4)                     | 2.173(3)  |                                |            |  |            |
| O(3)–Co(1)–O(5)                | 95.16(16) | O(3)–Co(1)–N(2)                | 94.36(15) | O(5)–Co(1)–N(2)                | 169.85(16) | O(3)–Co(1)–N(1)                              | 171.00(17) |
| O(5)–Co(1)–N(1)                | 93.55(19) | N(2)–Co(1)–N(1)                | 77.10(19) | O(3)–Co(1)–O(1)                | 88.18(14)  | O(5)–Co(1)–O(1)                              | 90.53(15)  |
| N(2)–Co(1)–O(1)                | 93.27(15) | N(1)–Co(1)–O(1)                | 89.45(16) | O(3)–Co(1)–O(4)                | 92.52(13)  | O(5)–Co(1)–O(4)                              | 86.19(14)  |
| N(2)–Co(1)–O(4)                | 89.90(15) | N(1)–Co(1)–O(4)                | 90.34(15) | O(1)–Co(1)–O(4)                | 176.69(13) |  |            |
| Complex 2                      |           |                                |           |                                |            |  |            |
| Ni(1)–O(2)                     | 2.043(5)  | Ni(1)–O(6)                     | 2.055(6)  | Ni(1)–O(4) <sup>#i</sup>       | 2.086(5)   | Ni(1)–O(5)                                   | 2.087(6)   |
| N(1)–Ni(1)                     | 2.049(6)  | N(2)–Ni(1)                     | 2.058(6)  |                                |            |  |            |
| O(2)–Ni(1)–N(1)                | 90.4(2)   | O(2)–Ni(1)–N(2)                | 94.9(2)   | N(1)–Ni(1)–N(2)                | 79.1(2)    | O(2)–Ni(1)–O(6)                              | 90.6(2)    |
| N(1)–Ni(1)–O(6)                | 172.5(2)  | N(2)–Ni(1)–O(6)                | 93.3(2)   | O(2)–Ni(1)–O(4) <sup>#i</sup>  | 175.5(2)   | N(1)–Ni(1)–O(4) <sup>#i</sup>                | 90.8(2)    |
| N(2)–Ni(1)–O(4) <sup>#i</sup>  | 89.6(2)   | O(6)–Ni(1)–O(4) <sup>#i</sup>  | 88.8(2)   | O(2)–Ni(1)–O(5)                | 84.6(2)    | N(1)–Ni(1)–O(5)                              | 92.6(2)    |
| N(2)–Ni(1)–O(5)                | 171.7(2)  | O(6)–Ni(1)–O(5)                | 94.9(2)   | O(4) <sup>#i</sup> –Ni(1)–O(5) | 91.0(2)    |  |            |
| Complex 3                      |           |                                |           |                                |            |  |            |
| Cu(1)–O(1) <sup>#i</sup>       | 1.941(5)  | Cu(1)–O(1)                     | 1.941(5)  | Cu(1)–N(1)                     | 1.975(6)   | Cu(1)–N(1) <sup>#i</sup>                     | 1.975(6)   |
| O(1) <sup>#i</sup> –Cu(1)–O(1) | 93.5(3)   | O(1) <sup>#i</sup> –Cu(1)–N(1) | 172.6(2)  | O(1)–Cu(1)–N(1)                | 92.9(2)    | O(1) <sup>#i</sup> –Cu(1)–N(1) <sup>#i</sup> | 92.9(2)    |
| O(1)–Cu(1)–N(1) <sup>#i</sup>  | 172.6(2)  | N(1)–Cu(1)–N(1) <sup>#i</sup>  | 81.0(4)   |                                |            |  |            |

Symmetry codes: i: x, y, z–1 for 2; #i: –x+1, y, –z+1/2 for 3.

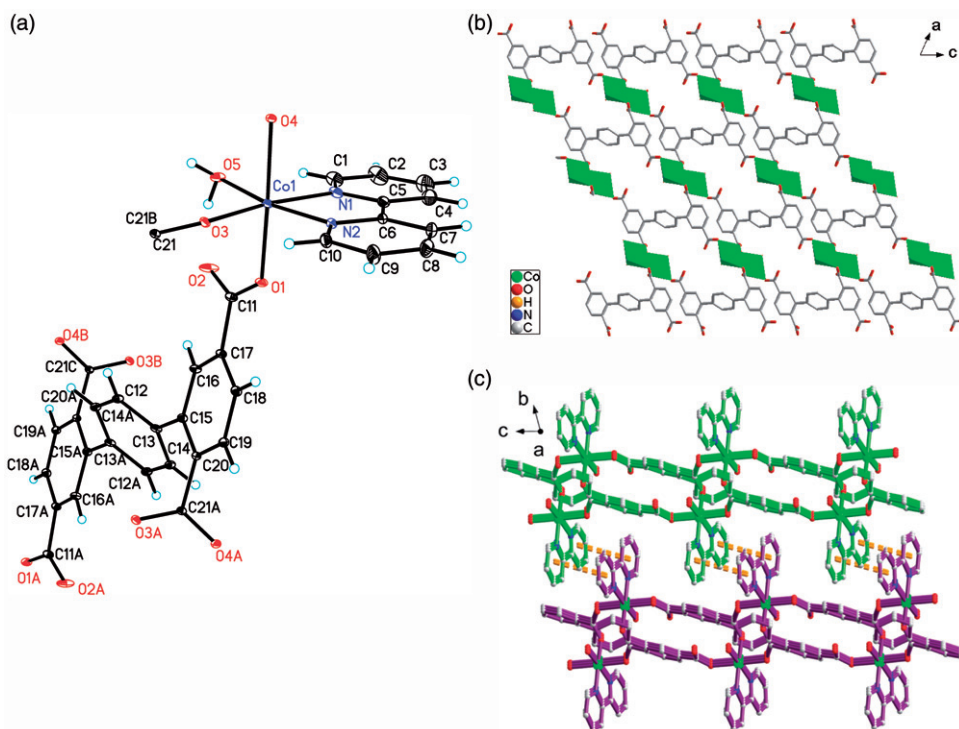


Figure 2. (a) Coordination environment of  $\text{Co}^{\text{II}}$  in **1** with the thermal ellipsoids at 30% probability (Symmetry codes: (A):  $-x, -y+1, -z+1$ , (B)  $-x+1, -y+1, -z-1, -z+1$ , (C)  $-x+1, -y+1, -z$ ), (b) view of the 2-D layer of **1**, and (c) perspective view of the 3-D supramolecular structure of **1** via inter-chain  $\pi \cdots \pi$  interactions.

**3.3.2.  $[\text{Cu}(\text{H}_2\text{qptc})(2,2'\text{-bpy})]_n$  (**3**).** Single-crystal X-ray diffraction analysis reveals that **3** crystallizes in the monoclinic system,  $C2/c$  space group. The asymmetric unit of **3** consists of half of a  $\text{Cu}^{\text{II}}$ , half of a 2,2'-bpy and half of a partly deprotonated  $\text{H}_2\text{qptc}^{2-}$ . Each  $\text{Cu}^{\text{II}}$  locates in a distorted square plane, coordinated by a chelating 2,2'-bpy [ $\text{Cu1-N1}=1.975(6) \text{ \AA}$ ] and two oxygen atoms from two  $\text{H}_2\text{qptc}^{2-}$  [ $\text{Cu1-O1}=1.941(5) \text{ \AA}$ ] (figure 3a).

Different from **1** and **2**, the  $\text{H}_4\text{qptc}$  ligand in **3** is only partly deprotonated under the solvothermal condition. The two deprotonated carboxylates of  $\text{H}_2\text{qptc}^{2-}$  show  $\mu_1\text{-}\eta^1:\eta^0$  coordination and  $\text{H}_2\text{qptc}^{2-}$  is a Z-shaped ligand (figure 3b) linking  $\text{Cu}^{\text{II}}$  centers to a 1-D zigzag polymeric  $[\text{Cu}(\text{H}_2\text{qptc})]_n$  chain along the crystallographic  $[101]$  direction with adjacent  $\text{Cu} \cdots \text{Cu}$  separation of  $10.940 \text{ \AA}$ . Terminal 2,2'-bpy ligands decorate the chain alternately in an outward fashion along the two sides (figure 3b). Crystal packing of **3** reveals that inter-chain  $\pi \cdots \pi$  interactions exist between 2,2'-bpy and  $\text{H}_2\text{qptc}^{2-}$ , with centroid-centroid distances of  $3.766 \text{ \AA}$ . Such contacts link 1-D zigzag chains into a 2-D layer structure (figure 3c).

### 3.4. TGA analysis

TGA measurements have been carried out on a Perkin-Elmer Diamond TG/DTA instrument with a flow of dry air and a heating rate of  $5^\circ\text{C min}^{-1}$  from room

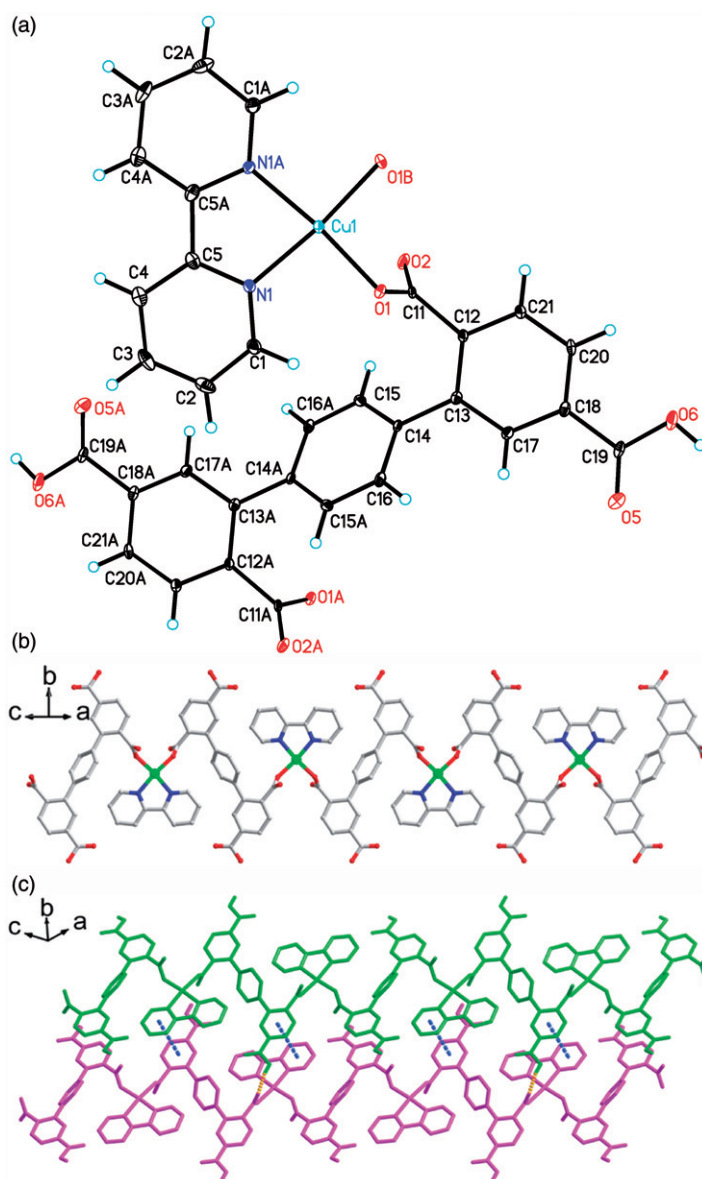


Figure 3. (a) Coordination environment of Cu<sup>II</sup> in **3** with the thermal ellipsoids at 30% probability (Symmetry codes: (A):  $-x+1, y, -z+1/2$ , (B)  $-x+1/2, -y+1/2, -z$ ), (b) view of the 1-D zigzag chain of **3**, and (c) perspective view of the 2-D supramolecular layer of **3** via inter-chain  $\pi \cdots \pi$  interactions.

temperature to 1000°C (Supplementary material). For **1**, weight loss takes place from 85°C to 437°C with residual weight of 15.10% (Calcd for CoO: 15.5%). For **2**, weight loss takes place from 65°C to 440°C. The residual weight of the sample is 15.3% (Calcd for NiO: 15.1%). For **3**, weight loss takes place from 291°C. The residual weight of the sample is 17.8% (Calcd for CuO: 16.9%).

#### 4. Conclusion

We have developed a strategy for synthesizing CPs by employing terphenyl-2,5,2',5'-tetracarboxylic acid (H<sub>4</sub>qptc). Three new CPs, [M(qptc)<sub>0.5</sub>(2,2'-bpy)(H<sub>2</sub>O)]<sub>n</sub> (M=Co (**1**), Ni (**2**)), and [Cu(H<sub>2</sub>qptc)(2,2'-bpy)]<sub>n</sub> (**3**), based on H<sub>4</sub>qptc and 2,2'-bpy have been obtained under solvothermal conditions. Structural comparisons among **1–3** indicate that the backbone of the H<sub>4</sub>qptc ligand plays an important role in governing the structures of these metal–organic coordination architectures. Further systematic studies for the design and synthesis of such crystalline materials with H<sub>4</sub>qptc and other N-donor building blocks are underway in our laboratory.

#### Supplementary material

Further details on the crystal structure investigations can be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: +44-(0)1223-762-910, Fax: +44-(0)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; or <http://www.ccdc.cam.ac.uk/deposit>], on quoting the depository number CCDC-855668 for **1**, 855670 for **2**, and 855669 for **3**.

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