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Metal-organic frameworks based on [1,1':3',1''-terphenyl]-3,3',5,5'-tetracarboxylic acid ligand: syntheses, structures and magnetic properties

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The solvothermal reactions of [1,1':3',1''-terphenyl]-3,3',5,5'-tetracarboxylic acid (H₄TPTA) with transition metal cations afford five novel coordination polymers in the presence of three pyridine ligands (4,4′-bipy = 4,4′-bipyridine, 2,2′-bipy = 2,2′-bipyridine and phen = 1,10-phenanthroline), namely, [M(TPTA)₀.₅(4,4′-bipy)₀.₅(H₂O)ₙ]₀ (M = Co for (1), Ni for (2)), {[Mn₂(TPTA)(2,2′-bipy)H₂O]·1.₅H₂O}₀ (3), [M(H₂TPTA)(phen)]₀ (M = Mn for (4), Co for (5)). Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, powder X-ray diffraction (PXRD), and thermogravimetric (TG) analyses. Polymers 1 and 2 are isomorphous and exhibit 3D 4-fold interpenetrated networks with the point Schläfli symbol of (4,10⁴) (4,10⁵). Polymer 3 shows a 2D layer framework. Polymers 4 and 5 are also isomorphous and each displays a one-dimensional (1D) chain, which further forms a 2D supramolecular architecture via inter-chain π···π interactions. Moreover, variable-temperature magnetic susceptibilities of polymers 3–5 exhibit overall weak antiferromagnetic coupling between the adjacent M(II) ions.

Introduction

The rational design and synthesis of functional coordination polymers has inspired a wide range of research over the past few decades due to their rich structural diversities and important industrial application potentials in the areas of molecular magnetism, gas storage, ion exchange, nonlinear optics, drug delivery and heterogeneous catalysis. The solvothermal method has been widely used to synthesize coordination polymers since it can alleviate the problems of ligand solubility and improve the reactant reactivity during the crystallization process. In this method, the construction of coordination polymers is largely influenced by many factors such as the coordination of metal ions, the structural characteristics of multidentate organic ligands, the metal–ligand ratio, the solvent, and the temperature, etc. Among those mentioned above, the selection of ligands is crucial in the construction of coordination polymers. Up to now, a great number of polybasic carboxylic acids ligands have been employed to assemble coordination polymers due to their rich coordination modes. In addition, carboxylate groups are good hydrogen-bond acceptors as well as donors, depending upon the degree of deprotonation. In the meantime, the pyridine ligands are usually introduced into the reaction system to exchange the frameworks. The reasons can be generalized as follows: firstly, the pyridine rings could provide feasibility for lower dimensional networks to be extended into multi-dimensional ones; secondly, pyridine rings are good candidates in terms of hydrogen-bond formation, and π–π stacking interactions that are significant for affording extended open frameworks via polymerization. Thus, these considerations inspired us to explore new coordination architectures with [1,1':3',1''-terphenyl]-3,3',5,5'-tetracarboxylic acid (H₄TPTA) (Scheme S1) and pyridine ligands including 4,4′-bipyridine (4,4′-bipy), 2,2′-bipyridine (2,2′-bipy) and 1,10-phenanthroline. In this paper, we reported the syntheses and characterizations of five new coordination polymers, [M(TPTA)₀.₅(4,4′-bipy)₀.₅(H₂O)ₙ]₀ (M = Co(1), Ni(2)), {[Mn₂(TPTA)(2,2′-bipy)H₂O]·1.₅H₂O}₀ (3), [M(H₂TPTA)(phen)]₀ (M = Mn(4), Co (5)). And then, we also reported the thermal stability and magnetic property of as-synthesized coordination polymers.

Experimental section

Materials and Synthesis.

All reagents and solvents were commercially available without any further purification, except for ligand H₄TPTA, which was synthesized according to the literature. The IR spectra were...
Chart 1. Different Coordination Modes of H4TPTA in Complexes 1–5.

measured on a Bruker-ALPHA spectrophotometer at the range of 400–4000 cm\(^{-1}\). The elemental analyses (C, H, and N) were performed on a FLASH EA 1112 elemental analyzer. All the PXRD patterns were recorded on a PANalytical X’Pert PRO diffractometer with the use of Cu Kα radiation. Thermogravimetric scanning calorimetry (TG) measurements were performed by heating the sample on a Netzsch STA 409PC differential thermal analyzer with a heating rate of 10 °C min\(^{-1}\) from ambient temperature under an air atmosphere.

**The synthesis of [Co(TPTA)\(_{0.5}\)(4,4′-bpy)\(_{0.5}\)(H\(_2\)O)\(_2\)]\(_n\) (1).** A mixture of H\(_4\)TPTA (0.020 g, 0.05 mmol), 4,4′-bpy (0.0156 g, 0.1 mmol), Co(NO\(_3\))\(_2\)·6H\(_2\)O (0.0291 g, 0.1 mmol), 4 mL CH\(_3\)CN and 4 mL H\(_2\)O was sealed in a Teflon-lined stainless steel vessel and heated to 160 °C for 3 days, which was followed by slow cooling (a descent rate of 5 °C h\(^{-1}\)) to room temperature. The red block crystals of 1 were obtained. Yield of 71% (based on Co). Anal. (%) calcd for C\(_{16}H_{13}NO\(_6\)Co (374.21): C, 51.35; H, 3.50; N, 3.74. Found: C, 51.18; H, 3.41; N, 3.49. IR (KBr pellet, cm\(^{-1}\)): 3613 m, 3373 s, 3127 s, 1616 v, 1545 v, 1426 v, 1404 s, 1254 m, 1219 w, 820 w, 717 w, 636 m, 586 w.

**The synthesis of [Ni(TPTA)\(_{0.5}\)(4,4′-bpy)\(_{0.5}\)(H\(_2\)O)\(_2\)]\(_n\) (2).** A mixture of H\(_4\)TPTA (0.020 g, 0.05 mmol), 4,4′-bpy (0.0156 g, 0.1 mmol), Ni(NO\(_3\))\(_2\)·6H\(_2\)O (0.0290 g, 0.1 mmol), 4 mL CH\(_3\)CN and 4 mL H\(_2\)O was sealed in a Teflon-lined stainless steel vessel and heated to 160 °C for 3 days, which was followed by slow cooling (a descent rate of 5 °C h\(^{-1}\)) to room temperature. The green block crystals of 2 were obtained. Yield of 63% (based on Ni). Anal. (%) calcd for C\(_{16}H_{13}NO\(_6\)Ni (373.97): C, 51.35; H, 3.50; N, 3.76. Found: C, 51.18; H, 3.41; N, 3.49. IR (KBr pellet, cm\(^{-1}\)): 3613 m, 3373 s, 3127 s, 1616 v, 1545 v, 1426 v, 1404 s, 1254 m, 1219 w, 820 w, 717 w, 636 m, 586 w.

**The synthesis of {[Mn\(_2\)(TPTA)(2,2′-bpy)(H\(_2\)O)]\(_{1.5}\)H\(_2\)O}\(_n\) (3).** A mixture of H\(_4\)TPTA (0.020 g, 0.05 mmol), 2,2′-bpy (0.0156 g, 0.1 mmol), MnCl\(_2\)·4H\(_2\)O (0.0100 g, 0.05 mmol), 4 mL CH\(_3\)CN and 4 mL H\(_2\)O was sealed in a Teflon-lined stainless steel vessel and heated to 160 °C for 3 days, which was followed by slow cooling (a descent rate of 5 °C h\(^{-1}\)) to room temperature. The yellow block crystals of 3 were obtained. Yield of 54% (based on Mn). Anal. (%) calcd for C\(_{32}H_{22}N\(_2\)O\(_{10}\)Mn\(_2\) (704.40): C, 54.56; H, 3.14; N, 3.97. Found: C, 54.58; H, 2.99; N, 4.06. IR (KBr pellet, cm\(^{-1}\)): 3426 s, 3132 w, 1619 v, 1548 v, 1396 v, 1304 v, 770 m, 639 m, 552 m.
The synthesis of [Mn(H_2TPTA)(phen)]_n (4). A mixture of H_2TPTA (0.020 g, 0.05 mmol), phen (0.0198 g, 0.1 mmol), MnCl_2·4H_2O (0.0100 g, 0.05 mmol), 5 mL CH_3CN and 5 mL H_2O was sealed in a in a Teflon-lined stainless steel vessel and heated to 130 °C for 3 days, which was followed by slow cooling (a descent rate of 5 °C h\(^{-1}\)) to room temperature. Yellow block crystals of 4 were obtained. Yield of 51% (based on Mn). Anal. (%) calcd for C_{34}H_{32}N_6O_3Mn (639.47): C, 63.86; H, 3.15; N, 4.38. Found: C, 63.53; H, 3.08; N, 4.21. IR (KBr pellet, cm\(^{-1}\)): 3128w, 1723v, 1612v, 1540v, 1396v, 1145v, 1102v, 775m, 725m, 630w.

The synthesis of [Co(H_2TPTA)(phen)]_n (5). A mixture of H_2TPTA (0.020 g, 0.05 mmol), phen (0.0198 g, 0.1 mmol), Co(NO_3)_2·6H_2O (0.0291 g, 0.1 mmol), 5 mL CH_3CN and 5 mL H_2O was sealed in a in a Teflon-lined stainless steel vessel and heated to 130 °C for 3 days, which was followed by slow cooling (a descent rate of 5 °C h\(^{-1}\)) to room temperature. Red block crystals of 5 were obtained. Anal. (%) calcd for C_{34}H_{32}N_6O_4Co (643.46): C, 63.46; H, 3.13; N, 4.35. Found: C, 63.27; H, 3.13; N, 4.36. IR (KBr pellet, cm\(^{-1}\)): 3126w, 1722v, 1613v, 1542v, 1396v, 1150v, 1110v, 773m, 725m, 633w.

Crystal Data Collection and Refinement. Single X-ray diffraction measurements for polymers 1–5 were carried out on a Rigaku Saturn 724 CCD at 298 K, using graphite-monochromated Mo Kα radiation (\(\lambda = 0.71073\) Å). The structures were solved by direct methods and refined with anisotropically, whereas hydrogen atoms were located and refined geometrically. The position of water molecules could not be resolved from Fourier maps in the crystal of 3. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities. The final chemical formula of 3 was calculated from SQUEEZE results combined with the TGA and elemental analysis data. The crystal parameters, data collection, and refinement results for all compounds are summarized in Table S1. Selected bond lengths and angles are listed in Table S2 (in the Supporting Information).

Crystallographic data for 1–5 have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1009774–1009778.

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibilities of 3–5 were carried out on a SQUID MPMS XL-7 instrument with phase-pure crystalline samples under the applied field of 1000 Oe in the temperature region of 2–300 K. The diamagnetic corrections were conducted utilizing Pascal’s constants.

Results and Discussion

Description of Crystal Structures

[Co(TPTA)_n(H_2TPTA)_2(4,4′-bpy)]_n (1) and [Ni(TPTA)_n(H_2TPTA)_2(4,4′-bpy)]_n (2). The single crystal X-ray structural analysis reveals that polymers 1 and 2 crystallize in the monoclinic space group C2/c, and they are isostructures. Therefore, polymer 1 is employed as a representative structure to be described in detail.

The asymmetric unit of polymer 1 contains a divalent Co atom on the crystallographic 2-fold rotation axis, one-half of fully deprotonated TPTA, and one-half of a 4,4′-bpy. The unique Co ion maintains a distorted octahedral coordination environment and is coordinated by three carboxylate oxygen atoms from two TPTA\(^{2-}\), two oxygen atoms from two water and one nitrogen atom from the 4,4′-bpy. The Co–O bond distances are in the range of 2.023–2.232 Å, and the Co–N bond distance is 2.082 Å. In polymer 1, all the carboxyl groups of H_2TPTA ligands are deprotonated, showing two different coordination modes: \(\mu_1\eta_1\eta_1\)-chelating coordination mode and \(\mu_1\eta_1\eta_2\)-coordination mode, respectively (Mode I of Chart 1). The TPTA\(^{2-}\) connect with four Co\(^{2+}\) ions forming an infinite chain that is arranged parallel to the c crystal direction (Fig. 1a). These chains are in turn linked by 4,4′-bpy, producing a 3D framework (Figure 1b). The substantial apertures (~11.2 Å × ~11.2 Å) within a single neutral network permit the interpenetration of three other identical nets, resulting in an overall 4-fold interpenetrated network in 1 (Figure 1c). From a topology view, the network of 1 can be rationalized...
of \((4^2 \cdot 10^4)\) \((4 \cdot 10^5)\) by denoting the Co(II) atoms to four-connected nodes and TPTA\(^2\) to four-connected nodes, respectively.\(^{15b-15d}\) PLATON\(^{16}\) analysis indicates that the effective free volume of 1 is 6.9%.

\([\text{Mn}_n\text{TPTA}(2,2'\text{bipy})(\text{H}_2\text{O})][1.5\text{H}_2\text{O}]_n\) (3). Polymer 3 crystallizes in the space group crystallizes in space group P-1, showing a 2D polymeric layer. The structure of 3 contains two crystallographical unique Mn(II) ions, as depicted in Fig. 2a. The Mn1 with slightly distorted octahedral coordination geometry is six-coordinated by five carboxylate oxygen atoms from four individual TPTA\(^{2-}\), and one oxygen atom from the coordinated water, while the Mn2 atom adopts six-coordinated distorted octahedral geometry formed by four carboxylate oxygen atoms from three individual TPTA\(^{2-}\) and two nitrogen atoms from one 2,2'-bipy. The Mn–N bond lengths fall in the range of 2.232–2.397 Å, and the Mn–O bond lengths are in the range of 2.09–2.363 Å. The Mn1···Mn2 distance in the binuclear unit is 3.275 Å, and the Mn–O bond lengths are in the range of 2.108–2.363 Å.

In polymer 4, only two carboxyl groups of the H\(_2\)TPTA are completely deprotonated (Mode III of Chart 1). The H\(_2\)TPTA acts as a µ-bridge linking two Mn(II) centers via one \(\mu_1\eta^2:\eta^2\)-chelating coordination mode carboxylate group and one \(\mu_2\eta^2:\eta^2\)-bridging mode carboxylate group into a one-dimensional (1D) double chain along the c axis. The polymer displays centrosymmetric 8- and 16-membered rings with metal-metal separations of 3.843 and 7.390 Å, respectively (Figure 3b). The terminal phen decorate the chain alternately in an outward fashion along two sides (Fig. 3b). Additional investigation of this structure indicates that interchain π···π interactions exist between these phen, with the centroid–centroid distances of 3.699 Å. Such contacts link 1D chain into a 2D layer structure (Fig. 3c).

**X-ray Power Diffraction (PXRD) Analyses and Thermogravimetric (TGA) Analyses.**

Powder X-ray diffraction has been used to confirm that the crystal structures are truly representative of the bulk samples in the solid state. For 1–5, the measured PXRD patterns closely match the simulated one based on the single-crystal X-ray data, indicative of pure products (Fig. S2).

TGA was carried out to examine the thermal stability of 1–5 in the temperature range of 30–800 °C. As shown in Fig. 4, the TG curve of 1 shows the first weight loss of 9.64% ranging from 140 to 200 °C, which can be ascribed to the removal of two coordinated water molecules (calc. 9.62%). With temperature increasing, it began to decompose at 360 °C. Polymer 2 lost the weight of 9.2% ranging from 180 to 260 °C, which can be attributed to the removal of coordinated water molecules (calc. 9.6%). The departure of the organic components occurred at 380 °C, giving final metal oxides. The TG curve of 3 shows the mass loss of 6.09% from 112 to 358 °C, which may be due to the release of one coordinated water molecule and one a half lattice water molecules (calc. 6.30%). Polymer 4 began to decompose when the temperature was raised up to 340 °C, while 5 began to decompose at 440 °C.

**Magnetic Property.**

The magnetic properties of 3–5 were investigated over the temperature range 2–300K. The \(\chi_mT\) value of polymer 3 at 300 K is 8.15 cm\(^3\) K mol\(^{-1}\), which is lower than the expected value (8.75 cm\(^3\) K mol\(^{-1}\)) of two uncoupled spins of Mn(II) ions \((S = 5/2)\) based on \(g = 2.0\). With the temperature decreases, the value of \(\chi_mT\) decreases continuously to 0.47 cm\(^3\) K mol\(^{-1}\) at 2 K (Fig 5a). The plot of \(\chi_m\) versus \(T\) for 3 is consistent with the Curie-Weiss
law in the temperature range of 20–300 K, with C = 8.54 cm$^3$ K mol$^{-1}$ and $\theta = -13.67$K.

Because the structure of polymer 3 consists of Mn(II) dimer subunits, the magnetic data were analyzed through the expression for a dinuclear Mn(II) system derived from the isotropic spin Hamiltonian $H = -2JS_S$ with the interaction between adjacent dinuclear units considered:

$$\chi = \frac{\chi_{\text{dimer}}}{1 - (2zJ'/Ng^2\beta^2)\chi_{\text{dimer}}}$$

The best fitting parameters are $J = -1.13$ cm$^{-1}$, $zJ' = -0.09$ cm$^{-1}$, $g = 1.97$, and $R = 2.17 \times 10^{-5}$. These results support operation of a weak intradimer antiferromagnetic interaction and very weak inter-dimer interaction in 3.

The $\chi_mT$ value of 4 at 300 K is 9.41 cm$^3$ K mol$^{-1}$, which is close to the expected value (8.75 cm$^3$ K mol$^{-1}$) of two uncorrelated spins of Mn(II) ions ($S = 5/2$, $g = 2.0$). As T decreases, the value of $\chi_mT$ decreases continuously to 4.05 cm$^3$ K mol$^{-1}$ at 2 K (Fig. 5b). The plot of $\chi_m^{-1}$ versus $T$ for 4 is consistent with the Curie–Weiss law in the temperature range of 2–300 K, with $C = 9.39$ cm$^3$ K mol$^{-1}$ and $\theta = -2.17$ K.

Although the structure is one-dimensional chain, it can be considered as a dinuclear entity in which two Mn(II) ions are linked by two distorted syn-syn carboxylate bridges. So the magnetic behaviour of 4 is also simulated with the same equation like 3, and the best fitting parameters are $J = -0.15$ cm$^{-1}$, $zJ' = -0.02$ cm$^{-1}$, $g = 2.06$, and $R = 1.46 \times 10^{-5}$. These negative $J$ and $\theta$ values indicated weak intra-dimer antiferromagnetic interactions between Mn(II) ions and the inter-dimer interaction is very weak in 4.

The magnetic interactions in the polymers 3 and 4 are weak antiferromagnetic coupling interactions. The magnetic exchange pathway in 3 is the exchange between dimeric Mn(II) ions to the carboxyl bridge (Mn-OCO-Mn) and $\beta_2$-O$_2$carboxyl bridge with the superexchange angle Mn-O$_2$carboxyl-Mn of 94.55(14), 92.77(14), respectively, while the magnetic exchange pathway in 4 only is the exchange between dimeric Mn(II) ions to the carboxyl bridge (Mn-OCO-Mn). According to some articles recorded, the magnetic interaction of 3 is stronger than 4, and the $|J|$ value of 3 is larger than 4, which has been confirmed above.
stand for the activation energies corresponding to the spin-orbit coupling and the antiferromagnetic exchange interaction, respectively.

The best fit of the experimental data gives that \( A + B = 5.41 \text{ cm}^{-1} \) and \( K \text{ mol}^{-1} \), \( E_2/k = 20.93K \), \( E_2/k = -0.92K \) and \( R = 3.88 \times 10^{-5} \) respectively. According to the Ising chain approximation \( \chi_m T \propto \exp(+/2K T) \), the exchange interaction \( J \) is \(-1.28 \text{ cm}^{-1}\), and the antiferromagnetic exchange interaction is very weak.

### Conclusions

In summary, five new coordination polymers based on \( [1,1',3',1'\text{-Terphenyl}]-3,3',5,5'\text{-tetracarboxylic acid} \) (H\(_2\)TPTA) and three pyridine ligands (4,4′2bipy, 2,2′2bipy and phen) have been synthesized. The structural diversities indicate that the pyridine ligands have influence in modulating the formation of the structures of these crystalline materials. Variable-temperature magnetic susceptibility measurements exhibit antiferromagnetic interactions between M(II) ions for polymers 3, 4 and 5.

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### References


Metal-organic frameworks based on [1,1\':3',1"-terphenyl]-3,3",5,5"
-tetracarboxylic acid ligand: syntheses, structures and magnetic properties

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Five coordination polymers containing transition metals (Mn, Co, Ni) and organic ligand [1,1\':3',1"-terphenyl]-3,3",5,5"-tetracarboxylic acid (H₄TPTA) were synthesized and characterized. Moreover, the magnetism of the complexes 3–5 was also discussed.