



# Structural diversity and magnetic properties of six metal–organic coordination polymers based on semi-rigid V-shape tetracarboxylic acid ligand



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## ABSTRACT

Six Mn metal-organic frameworks have been synthesized under solvothermal conditions with V-shaped terphenyl tetracarboxylate ligands (H<sub>4</sub>ttac). Their structures were characterized by elemental analysis, infrared spectra, PXRD, thermogravimetric analysis, and single-crystal X-ray diffraction analysis. Crystal structures reveal that the coordination number of H<sub>4</sub>ttac ligand varies from 6 to 10, and each ligand links 4–8 Mn(II) ions. Coordination modes vary from  $\eta^6_{\mu_4}$  to  $\eta^{10}_{\mu_8}$ . The existence of DMF solvent can increase coordination number of the ligand. The first coordination saturated phthalate is presented. The variable-temperature magnetic studies indicate that complexes exhibit dominant antiferromagnetic behaviors. Structural parameters and coordination modes were summarized. The porosity of these complexes is less than 15%, indicating that the V-shape ligand is not a good choice to construct porous coordination polymers.

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## 1. Introduction

The rational design and assembly of coordination polymers (CPs) and metal-organic frameworks (MOFs) are rapidly progressing due to their intriguing structural variety and interesting functional properties, such as luminescence, magnetism, ferroelectric, chirality, catalysis, and porous absorption [1–7]. Over the past decade, much effort has been invested in the purposeful design and controllable synthesis of these functional complexes [8–14]. However, it is still a great challenge to construct target coordination polymers with desired structures and functional properties because many factors affect the final results, such as metal ion, organic ligand, reagent ratio, solvent, pH value, temperature, and so on [15–17]. Amongst many strategies for constructing coordination polymers, the self-assembly of polycarboxylate anions and N-heterocyclic neutral ligands with metal ions under hydro(solvo)thermal conditions has become one of the most effective approaches

[18–21].

Organic aromatic multicarboxylates have been widely used to build fascinating structures due to their versatile coordination fashions and higher thermal stability. Rigid polycarboxylates, such as phthalic acid, trimesic acid and pyromellitic acid, are highly symmetric exo-polydentate ligands, used widely to produce vast coordination polymers [22–24]. We choose semi-rigid (1,1',2',1''-terphenyl)-4,4',4'',5'-tetracarboxylic acid (H<sub>4</sub>ttac) as the building block to construct new coordination polymers [25–27]. It is a V-shape ligand and may be completely or partially deprotonated. This property holds true in various coordination modes and higher dimensionality structures. Furthermore, it can act as the hydrogen bond acceptor/donor, depending upon the degree of deprotonation. On the other hand, the V-shaped ligand containing three sets of carboxyl groups separated by the phenyl group can form different dihedral angles through the rotation of C–C single bonds, thus it may ligate metal centers in different orientations [25–27]. These characteristics may lead to various motifs with unique topologies [28–30]. Compared to rigid trimesic and flexible carboxylate ligands, multicarboxylate ligands like the one in this paper are of special interest because of their varied configurations. Different from the exo-bidentate/tridentate ligands, the V-shape

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tetradentate ligands are quite new and less-explored [27]. To explore the structures, porosity and properties of coordination polymers of V-shaped ligand, six new Mn(II) coordination polymers based on this V-shape tetracarboxylate and N-donor ligands (Scheme 1), namely  $[\text{Mn}_3(\eta_6\text{-Httac})_2 \cdot (\text{H}_2\text{O})_8]_n \cdot 2n\text{H}_2\text{O}$  (**1**),  $[\text{Mn}_4(\eta_{10}\text{-ttac}) \cdot (\eta_9\text{-ttac}) \cdot (\text{DMF})_2 \cdot (\text{H}_2\text{O})_5]_n \cdot n\text{H}_2\text{O} \cdot n\text{DMF}$  (**2**),  $[\text{Mn}_2(\eta_7\text{-ttac}) (4,4'\text{-bipy})_{0.5} \cdot (\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$  (**3**),  $[\text{Mn}_2(\eta_7\text{-ttac}) (\text{bpe})_{0.5} \cdot (\text{H}_2\text{O})_4]_n \cdot 2n\text{H}_2\text{O}$  (**4**),  $[\text{Mn}_2(\eta_9\text{-ttac}) (4\text{-azpy}) \cdot (\text{H}_2\text{O})_2]_n \cdot 3n\text{H}_2\text{O}$  (**5**),  $[\text{Mn}_4(\eta_{10}\text{-ttac}) \cdot (\eta_9\text{-ttac}) (\text{bpp}) \cdot \text{DMF} \cdot (\text{H}_2\text{O})_4]_n \cdot 5n\text{H}_2\text{O}$  (**6**) (where 4,4'-bipy is 4,4'-bipyridine, bpe is 1,2-bis(4-pyridyl)ethylene, 4-azpy is 1,2-bis(4-pyridyl)diazene, bpp is 1,3-di(pyrid-4-yl)propane) were synthesized successfully. As expected, they have various coordination fashions (Scheme 2) with high thermal stability. Unfortunately, the porosity of these coordination polymers is quite low.

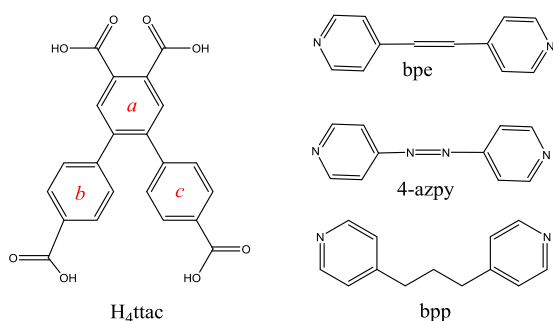
## 2. Experimental section

### 2.1. Materials and methods

All chemical materials were purchased commercially and used directly without further purification. C, H, and N analyses were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer using KBr pellets in 400–4000  $\text{cm}^{-1}$  range. Powder X-ray diffractions were measured at a scanning rate of  $5^\circ \text{min}^{-1}$  on a Rigaku DLMAX-2550 diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Thermogravimetric analyses were completed on Netzsch STA 449C thermal analyzer at a heating rate of  $10^\circ \text{C min}^{-1}$  in air. Variable-temperature magnetic susceptibilities in the temperature range of 2–300 K and field dependence of magnetization at 2 K were performed on an MPMS-XL Quantum Design SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

### 2.2. Syntheses of $[\text{Mn}_3(\eta_6\text{-Httac})_2 \cdot (\text{H}_2\text{O})_8]_n \cdot 2n\text{H}_2\text{O}$ (**1**)

A mixture of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.1 mmol, 0.025 g),  $\text{H}_4\text{ttac}$  (0.05 mmol, 0.020 g),  $\text{H}_2\text{O}$  (8 mL) was sealed in a 25-mL Teflon-lined reactor. The reactor was heated at  $100^\circ \text{C}$  for 72 h, and then cooled to room temperature at a rate of  $5^\circ \text{C h}^{-1}$ . Colorless block crystals of **1** were obtained in 58% yield based on  $\text{H}_4\text{ttac}$ , washed with water, and air-dried. Anal. Calcd for  $\text{C}_{44}\text{H}_{42}\text{Mn}_3\text{O}_{26}$ : C, 45.89; H, 3.68; Found: C, 45.59; H, 3.49. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3365 m, 1638w, 1567w, 1520s, 1409s, 1292s, 1188s, 1091w, 918s, 865s, 777s, 715 m, 675 m, 428s.



**Scheme 1.** Structures of  $\text{H}_4\text{ttac}$  and ancillary N-donor secondary ligands. Benzene rings are labeled in a, b and c.

### 2.3. Syntheses of $[\text{Mn}_4(\eta_{10}\text{-ttac}) \cdot (\eta_9\text{-ttac}) \cdot (\text{DMF})_2 \cdot (\text{H}_2\text{O})_5]_n \cdot n\text{H}_2\text{O} \cdot n\text{DMF}$ (**2**)

A mixture of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.1 mmol, 0.025 g),  $\text{H}_4\text{ttac}$  (0.05 mmol, 0.020 g), DMF (2 mL) and  $\text{H}_2\text{O}$  (6 mL) was sealed in a 25-mL Teflon-lined reactor. The reactor was heated at  $85^\circ \text{C}$  for 72 h, and then cooled to room temperature at a rate of  $5^\circ \text{C h}^{-1}$ . Colorless block crystals of **2** were obtained in 40% yield based on  $\text{H}_4\text{ttac}$ , washed with water, and air-dried. Anal. Calcd for  $\text{C}_{53}\text{H}_{53}\text{Mn}_4\text{N}_3\text{O}_{25}$ : C, 47.09; H, 3.95; N, 3.11. Found: C, 46.91; H, 3.59; N, 2.87. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3315w, 2935w, 1665s, 1646w, 1587m, 1538m, 1400s, 1182s, 1108s, 1014 m, 923 m, 858m, 789s, 731 m, 671 m.

### 2.4. Syntheses of $[\text{Mn}_2(\eta_7\text{-ttac}) (4,4'\text{-bipy})_{0.5} \cdot (\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ (**3**)

A mixture of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.1 mmol, 0.025 g),  $\text{H}_4\text{ttac}$  (0.05 mmol, 0.020 g), 4,4'-bipy (0.05 mmol, 0.0078 g),  $\text{H}_2\text{O}$  (8 mL) was sealed into 25-mL Teflon-lined reactor. The reactor was heated at  $120^\circ \text{C}$  for 72 h, and then cooled to room temperature at a rate of  $10^\circ \text{C h}^{-1}$ . Colorless block crystals of **3** were obtained with 80% yield based on  $\text{H}_4\text{ttac}$ , washed with water, and air-dried. Anal. Calcd for  $\text{C}_{27}\text{H}_{22}\text{Mn}_2\text{NO}_{12}$ : C, 48.96; H, 3.35; N, 2.11. Found: C, 48.75; H, 3.58; N, 2.01. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3307 m, 2306w, 1940w, 1533s, 1400s, 1348m, 1016 m, 918m, 868m, 788s, 728s, 625s.

### 2.5. Syntheses of $[\text{Mn}_2(\eta_7\text{-ttac}) (\text{bpe})_{0.5} \cdot (\text{H}_2\text{O})_4]_n \cdot 2n\text{H}_2\text{O}$ (**4**)

Complex **4** was prepared in a similar procedure as that of **3** by using bpe in place of 4,4'-bipy. Pale yellow needle crystals of **4** were obtained in 55% yield based on  $\text{H}_4\text{ttac}$ , washed with water, and air-dried. Anal. Calcd for  $\text{C}_{28}\text{H}_{27}\text{Mn}_2\text{NO}_{14}$ : C, 47.27; H, 3.83; N, 1.97. Found: C, 47.37; H, 3.81; N, 2.15. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3399w, 2926w, 1665s, 1592s, 1534s, 1396s, 1172 m, 1102 m, 866 m, 792s, 720s, 671s.

### 2.6. Syntheses of $[\text{Mn}_2(\eta_9\text{-ttac}) (4\text{-azpy}) \cdot (\text{H}_2\text{O})_2]_n \cdot 3n\text{H}_2\text{O}$ (**5**)

Complex **5** was synthesized in a similar procedure as that in synthesis of **3** except 4-azpy instead of 4, 4'-bipy. The solvent contains 2 mL DMF and 6 mL  $\text{H}_2\text{O}$ . Golden brown yellow block crystals of **5** were obtained in 82% yield based on  $\text{H}_4\text{ttac}$ . Anal. Calcd for  $\text{C}_{32}\text{H}_{28}\text{Mn}_2\text{N}_4\text{O}_{13}$ : C, 48.87; H, 3.59; N, 7.12. Found: C, 48.79; H, 3.59; N, 7.02. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3304w, 1589s, 1533s, 1399s, 1008w, 847s, 787m, 721 m, 570w.

### 2.7. Syntheses of $[\text{Mn}_4(\eta_{10}\text{-ttac}) \cdot (\eta_9\text{-ttac}) (\text{bpp}) \cdot \text{DMF} \cdot (\text{H}_2\text{O})_4]_n \cdot 5n\text{H}_2\text{O}$ (**6**)

This compound was synthesized in similar way as that in synthesis of **5** except bpp instead of 4-azpy, reaction temperature at  $100^\circ \text{C}$ , and cool rate of  $5^\circ \text{C h}^{-1}$ . Colorless block crystals of **6** were obtained in 68% yield based on  $\text{H}_4\text{ttac}$ . Anal. Calcd for  $\text{C}_{60}\text{H}_{59}\text{Mn}_4\text{N}_3\text{O}_{26}$ : C, 49.42; H, 4.08; N, 2.88. Found: C, 49.48; H, 4.10; N, 3.00. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3487w, 3368w, 2934w, 1661s, 1606s, 1531 m, 1390s, 1018w, 864 m, 789s, 725 m, 670 m, 511 m.

### 2.8. X-ray crystallography

The single crystal X-ray diffraction data of **1–6** were collected on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296(2) K. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and absorption correction were applied. The structures were solved by direct methods and refined

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