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# Synthesis, structure and properties of interpenetrated twofold 3D pillar-layered coordination polymers based on an N-centered tripodal ligand

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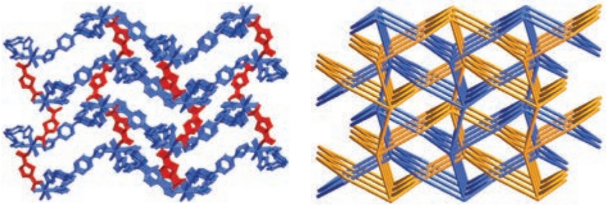
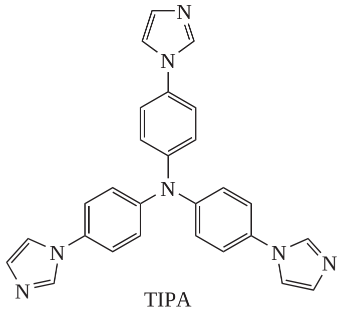
**Two new complexes {[M(TIPA)(tdc)($H_2O$)]·$H_2O$}$_n$ {M = $Co^{II}$, $Mn^{II}$, TIPA = tris[4-(1*H*-imidazol-1-yl)phenyl]amine, $H_2$tdc = = thiophene-2,5-dicarboxylic acid} have been synthesized hydrothermally based on the N-centered tripodal ligand TIPA. These isostructural compounds exhibit twofold interpenetrated 3D pillar-layered structures with ($6^3$)($6^9$·8) gra topology.**



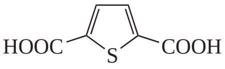
The controllable synthesis of coordination polymers (CPs) is of considerable interest due to their intriguing architectures and adjustable chemical functionalities.[1] However, the rational design and synthesis of CPs with specific structures is still fraught with significant difficulties because many factors, such as the coordination geometry of metal ions, medium, template, metal−ligand ratio, pH value, and counterion, significantly affect the resulting structures.[2] Among these factors, the carefully selected organic ligands play an important role in the rational assemblies of CPs with specified structures.[3]

Our group has long been focusing on the construction of CPs based on the semirigid ligand tris[4-(1*H*-imidazol-1-yl)phenyl]amine (TIPA) owing to its polydentate nature, flexibility and ease of synthesis. Compared with structurally similar ligands, such as triazine-centered and benzene-centered triangular ligands, the bendable and rotatable *N*-phenylimidazole arms of TIPA give it more flexibility, which make it easier to satisfy the requirement of coordination geometries of metal ions in the assembly process.[4] To date, many CPs with intriguing architectures based on the TIPA ligand have been reported.[5–7] As a commonly used strategy, rigid aromatic caboxylate ligands with two or more *exo*-carboxylic groups as ancillary ligands are widely employed to enrich the structural diversities of CPs.[8] For example, two CPs based on isophthalic acid and TIPA, exhibiting diverse structures, were described.[9]

Based on the above considerations, we choose thiophene-2,5-dicarboxylic acid (2,5-$H_2$tdc) as a coligand, which possesses a molecular symmetry similar to isophthalic acid. We believed that new CPs with different structures could be synthesized by the self-assembly of TIPA, 2,5-$H_2$tdc ligands and metal cations. Following this idea, two isostructural CPs {[M(TIPA)(tdc)($H_2O$)]·($H_2O$)}$_n$ [M = $Co^{2+}$ (**1**) or $Mn^{2+}$ (**2**)][†] have been hydrothermally synthesized and structurally characterized. In addition, the solid-state UV-VIS absorption spectra and thermal stabilities of **1** and **2** were investigated in detail.



TIPA



2,5-$H_2$tdc

Single-crystal X-ray crystallographic analyses revealed that both **1** and **2** crystallize in monoclinic crystal system $P2_1/n$.[‡] Since **1** and **2** are isostructural, only the crystal structure of **1** is

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[†] The reagents and solvents were commercially available and used as received. The TIPA ligand was synthesized in accordance with a published procedure.[10]

*General procedure for the preparation of compounds* **1** *and* **2**. A mixture of $MCl_2·6H_2O$ (M = Co or Mn, 0.1 mmol), TIPA (44.4 mg, 0.10 mmol) and thiophene-2,5-dicarboxylic acid (34.4 mg, 0.2 mmol) was dissolved in 15 ml of DMF/$H_2O$ (1:1). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25 ml) under autogenous pressure and heated at 95 °C for three days. Crystals were collected (yields based on the TIPA ligand, ~70% for **1**, ~62% for **2**).

For **1**: IR (KBr, $\nu$/cm$^{-1}$): 3121 (w), 1587 (s), 1516 (s), 1353 (s), 1307 (m), 1274 (m), 1114 (w), 1062 (m), 966 (w), 837 (m), 769 (m), 731 (w), 649 (w), 543 (w). Found (%): C, 55.58; H, 4.36; N, 13.74. Calc. for $C_{33}H_{29}CoN_7O_5S·H_2O$ (%): C, 55.62; H, 4.38; N, 13.76.

For **2**: IR (KBr, $\nu$/cm$^{-1}$): 3095 (w), 1601 (s), 1558 (s), 1516 (s), 1356 (s), 1302 (m), 1265 (m), 1112 (w), 1057 (m), 966 (w), 934 (w), 824 (s), 769 (m), 732 (w), 653 (w), 566 (w). Found (%): C, 42.15; H, 3.12; N, 10.41. Calc. for $C_{33}H_{29}MnN_7O_5S·H_2O$ (%): C, 42.16; H, 3.11; N, 10.43.

[‡] *Crystallographic data for* **1** *and* **2**.

For **1**: $C_{66}H_{52}Co_2N_{14}O_{11}S_2$, $M_r$ = 1399.22, monoclinic, space group $P2_1/c$, $a$ = 12.9362(3), $b$ = 16.0735(5) and $c$ = 15.2523(5) Å, $\beta$ = 98.136(2)°, $V$ = 3139.49(16) Å$^3$, $Z$ = 2, $d_{calc}$ = 1.480 g cm$^{-3}$, $\mu$(MoKα) = 0.669 mm$^{-1}$,

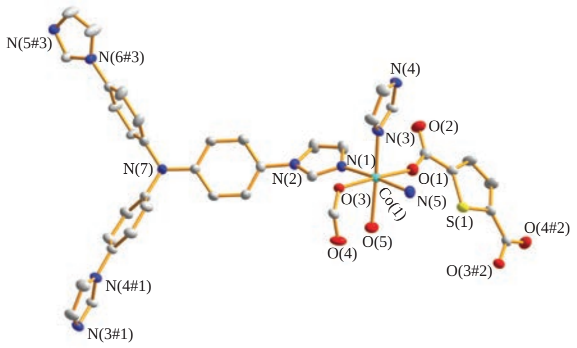

**Figure 1** Coordination environment of the $Co^{II}$ atom in **1** with the thermal ellipsoids drawn at a 30% probability level. Hydrogen atoms are omitted for clarity. The symmetry codes: #1 = $x$, $y$, $-1 + z$; #2 = $-x$, $-1/2 + y$, $3/2 - z$; #3 = $1 + x$, $1/2 - y$, $-1/2 + z$.

discussed in detail. The asymmetric unit of **1** consists of one $Co^{II}$ atom, one $tdc^{2-}$ anion, one TIPA ligand, one coordination water molecule and one free water molecule (Figure 1). The coordination environment of the $Co^{2+}$ ion can be described as a $\{CoN_3O_3\}$ slightly distorted octahedron with axial positions occupied by one O atom from the coordination water molecule and one N donor atom from one TIPA ligand. The equatorial plane consists of two N atoms from two other TIPA ligands and two oxygen atoms from two $tdc^{2-}$ ligands.

The $Co^{2+}$ ions are bridged by the TIPA ligand, giving rise to a 2D undulated layer with $6^3$ grids [Figure 2(*a*)]. These layers are connected in the ABAB fashion by linear $tdc^{2-}$ ligands to form a pillar-layered 3D reticular network [Figure 2(*b*),(*c*)]. A better insight into the nature of this intricate 3D framework can be achieved by a topological approach; the TIPA ligand can be viewed as a three-connected node, and the $Co^{2+}$ atom can be regarded as a five-connected node. Thus, the network of **1** can be simplified to a binodal (3,5)-connected gra topology with a Schläfli symbol of $(6^3)(6^9{\cdot}8)$ [Figure 2(*d*)]. The empty spaces of this 3D network are filled by another identical network leading to a twofold interpenetrated structure [Figure 2(*e*)].

The search in the RCSR of (3,5)-connected topology gives 64 three-periodic nets and 4 two-periodic nets.[12] The TTD collection of the TOPOS project (topospro.com) contains almost 30 examples of CPs with the gra topology.[13] We noticed that nearly all reported CPs with the gra topology were constructed from 2D metal-carboxylate layers and linear N-containing ligands as pillars, while compound **1** adopts a reverse process to form a pillar-layered structure, which was constructed by Co–TIPA $6^3$ layer and bicarboxylate organic linker $tdc^{2-}$ as a pillar.

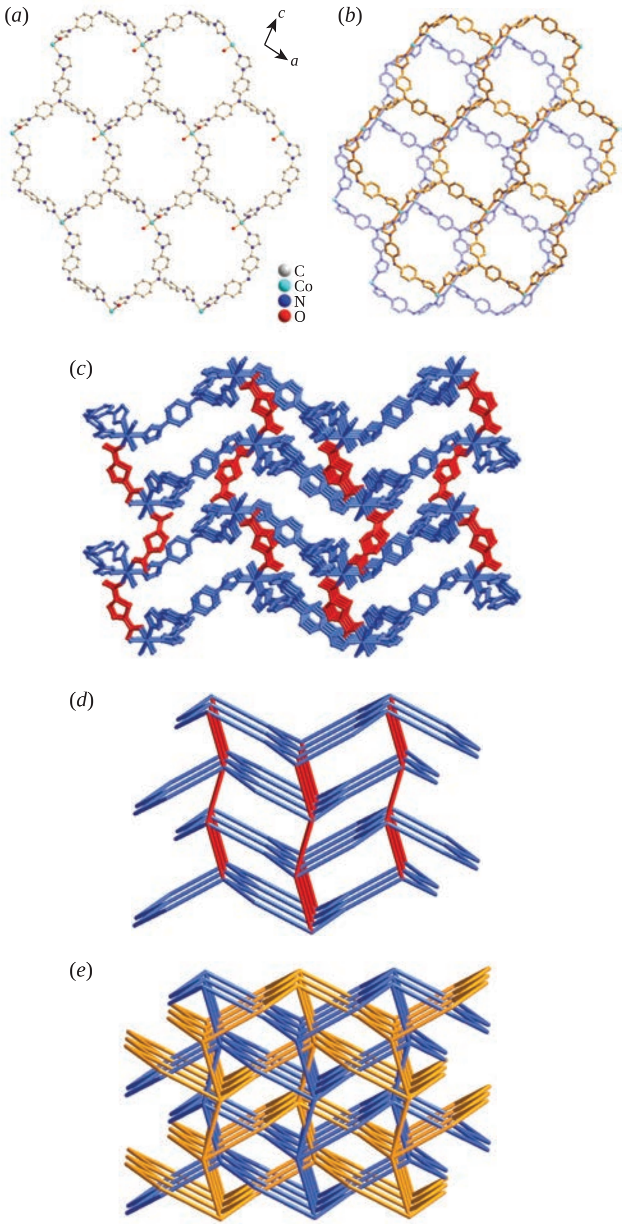

**Figure 2** (*a*) Schematic representation of the undulated $6^3$ layer of **1**. (*b*) The packing mode of parallel 2D layers in **1**. (*c*) The pillared-layer architecture of **1**. (*d*) View of the (3,5)-connected gra topology of **1**. (*e*) The twofold interpenetrated 3D network of **1**.

The PXRD patterns of compounds **1** and **2** were obtained at room temperature (Figure 3). The patterns for the as-synthesized samples are consistent with the simulated patterns from the single crystal structure analysis, confirming their pure solid-state phases.

Thermogravimetric analysis (TGA) was carried out to investigate the thermal stability of complexes **1** and **2** in an atmosphere of $N_2$ in a temperature range of 25–800 °C with a heating rate of 10 K $min^{-1}$ (Figure 4). For **1**, it displays a weight loss of 5% at 100–195 °C, which is ascribed to the departure of one coordinated water molecule and one free water molecule. Remarkably, compound **1** keeps high stability up to 310 °C. Further heating led to the rapid framework collapse with a weight loss of 24.7%, which is close to the calculated value (24.16% based on the TIPA). The TGA curves of compounds **1** and **2** have almost the same falling tendency, which means that they are isomorphic from sides.

The solid-state UV absorption spectra of compounds **1** and **2**, TIPA and 2,5-$H_2$tdc were recorded at room temperature (Figure 5). TIPA and compounds **1** and **2** showed broad intense absorption peaks at 250–360 nm, which can be ascribed to the $\pi$–$\pi$* transitions of ligands. A peak at 530 nm [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$] was observed

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$T = 296(2)$ K, 14834 reflections measured, 6156 independent reflections ($R_{int} = 0.048$), final $R_1$ [$I > 2\sigma(I)$] = 0.0469, $wR(F^2) = 0.1238$, GOF = 1.07.

For **2**: $C_{66}H_{52}Mn_2N_{14}O_{11}S_2$, $M_r$ = 1391.24, monoclinic, space group $P2_1/c$, $a$ = 12.9106(5), $b$ = 16.1943(6) and $c$ = 15.5128(7) Å, $\beta$ = 98.765(4)°, $V$ = 3205.5(2) Å$^3$, $Z$ = 2, $d_{calc}$ = 1.441 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 0.532 mm$^{-1}$, $T$ = 296(2) K, 12890 reflections measured, 6296 independent reflections ($R_{int} = 0.035$), final $R_1$ [$I > 2\sigma(I)$] = 0.0435, $wR(F^2) = 0.1125$, GOF = 1.03. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromatic MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL (version 6.14) using full-matrix least-squares procedures based on $F^2$ values.[11]

CCDC 1439989 and 1439990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

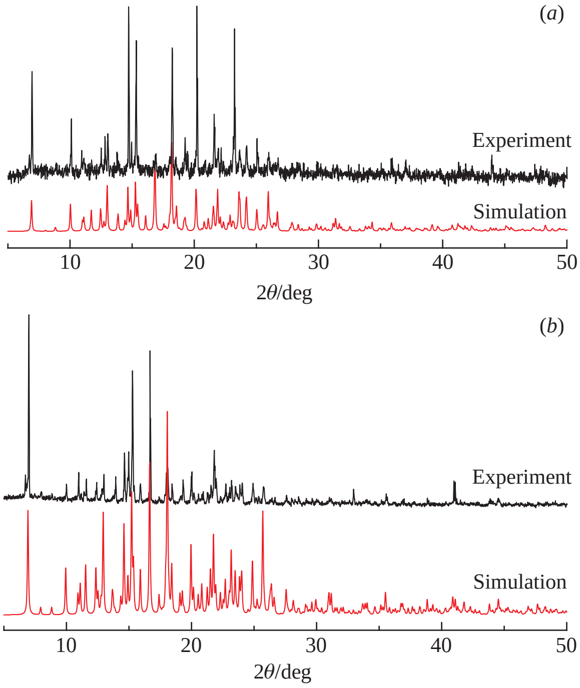

**Figure 3** Experimental and simulated PXRD patterns for (*a*) **1** and (*b*) **2**.

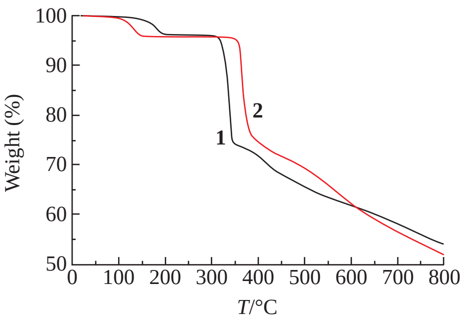

**Figure 4** TGA curves of compounds **1** and **2**.

for compound **1**, which is typical of octahedrally coordinated $Co^{II}$ compounds.[14,15]

In summary, we have synthesized two isostructural pillar-layered CPs based on TIPA and 2,5-$H_2$tdc ligands under hydrothermal conditions. Both compounds reveal a twofold interpenetrated 3D structure with the gra topology. Note that the formation of their pillar-layered structures is different from that in previously reported examples. The successful preparation of the complexes has once again proved that the synthetic strategy adopted in this work is effective. More research around rational design and synthesis of CPs based on the TIPA ligand with suitable caboxylate ligands is on going in our group.

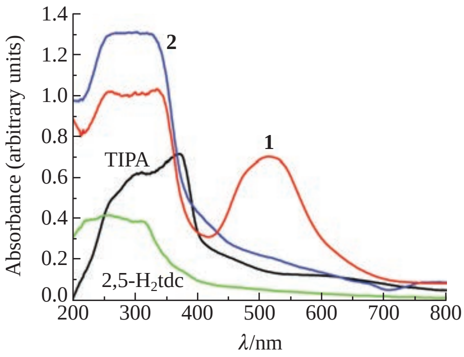

**Figure 5** UV-VIS absorption spectra of TIPA, 2,5-$H_2$tdc and compounds **1** and **2**.

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