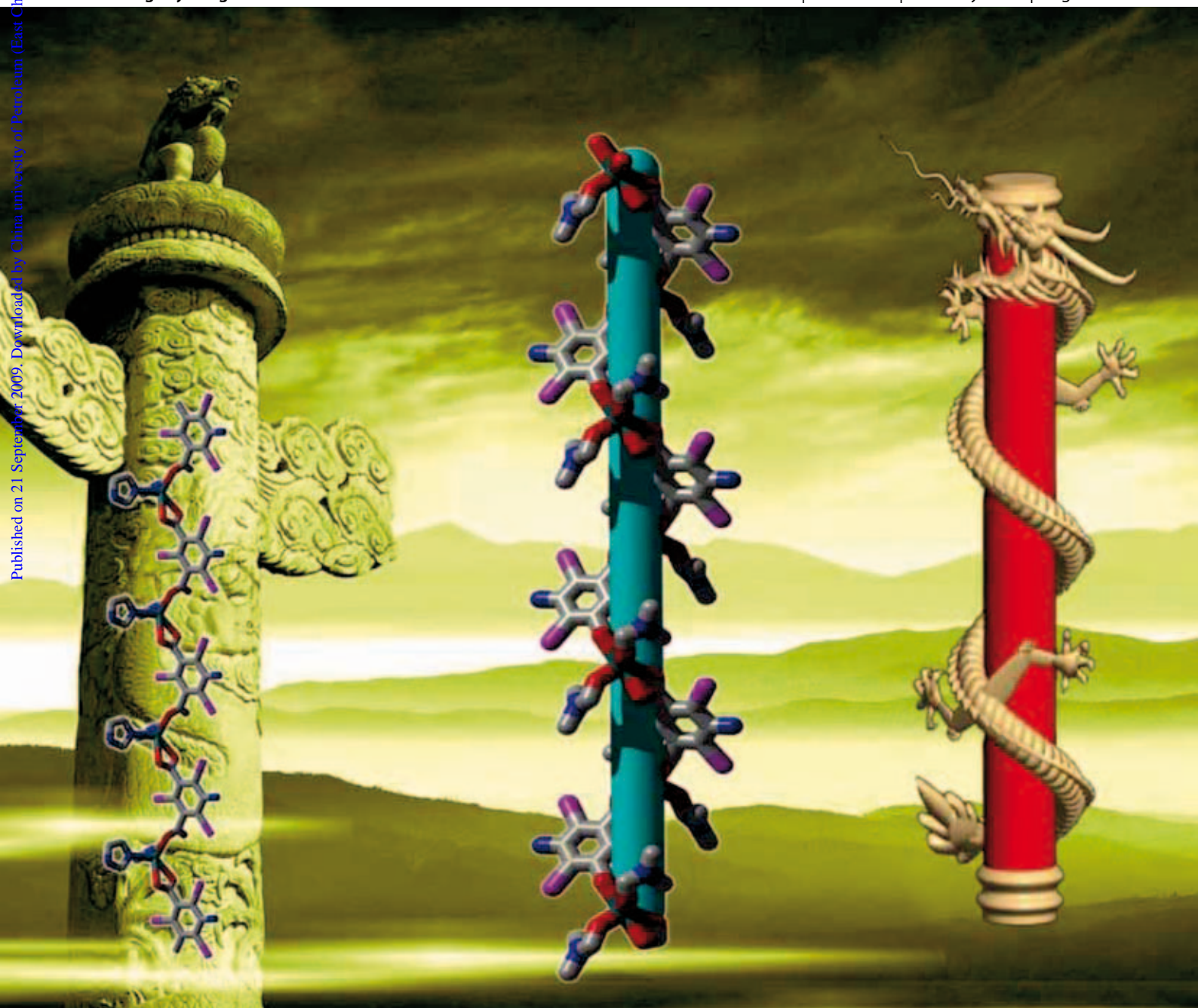


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1D zigzag chain vs. 1D helical chain: the role of the supramolecular interactions on the formation of chiral architecture†

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Two 1D coordination polymers with a 1D zigzag and a helical chain, respectively, have been solvothermally synthesized. The different coordinated small molecules on the cadmium ion have significant influences on the formation of different architectures. Due to the existence of supramolecular interactions between the helices in complex 2, the same chirality is preserved, resulting in a chiral architecture. By introducing a chiral molecule as cosolute, the bulk homochiral crystallization from achiral precursors for 2 can be achieved.

The construction of fascinating metal–organic frameworks (MOFs) such as chiral architectures, nanotubes, and multi-dimensional open frameworks have attracted much attention due to their interesting structural topologies and potential applications in catalysis, separation and gas storage, *etc.*^{1–3} Many works have focused on low-dimensional MOFs, such as 1D helical chains,⁴ 1D ladders,⁵ 1D metal-organic tubes,^{6,7} 1D zigzag chains,⁸ 1D double or triple-stranded chains⁹ with their omnifarious conformations, among which 1D homochiral MOFs have prompted great enthusiasm particularly for their industrial applications, such as enantioselective catalysis, separation, *etc.*^{10,11} On the basis of current research, three main strategies can be achieved to construct chiral MOFs: (i) the use of a chiral organic ligand to bind metal ions;¹² (ii) introducing small chiral molecules to coordinate the central metal ions, which is an effective strategy to construct a chiral framework;¹³ (iii) the use of achiral organic ligands.¹⁴ Recently, there have been some reported approaches to constructing homochiral MOFs from achiral ligands, such as seeding,¹⁵ unexpected spontaneous resolution¹⁶ and chiral catalysis.¹⁷ To date, the construction of homochiral MOFs based on achiral ligands is still a big challenge.

Our work focuses on the design and synthesis of functional MOFs with interesting structural topologies and special properties based on multitopic organic ligands. We select 5-amino-2,4,6-

triiodoisophthalic acid (H₂atiip) as the assembly ligand, considering its following characteristics: (a) it is a bent ligand with the two carboxylate groups located at appropriate angles (approximately 120°), which may allow it to connect metal ions to generate 1D helical chains; (b) the three large iodine atoms can preclude interpenetration; (c) the amino groups of the ligand can act as hydrogen-bond donors (Scheme 1). In our previous studies, we used this ligand with zinc ions in the presence of a second different organic ligand to construct 1D metal organic nanotubes and 2D layers containing 1D helical chains.¹⁸ In this communication, we report the syntheses, crystal structures, and luminescent properties of two 1D coordination polymers, [Cd(atiip)(Im)₂] (**1**) and [Cd(atiip)(dmf)] (**2**) (Im = imidazole), with 1D zigzag and helical chains, respectively. The role of the organic ligand and the coordinated small molecules, as well as the supramolecular interactions between chains, in the formation of the achiral coordination polymer of **1** and the chiral architecture of **2** has also been discussed.

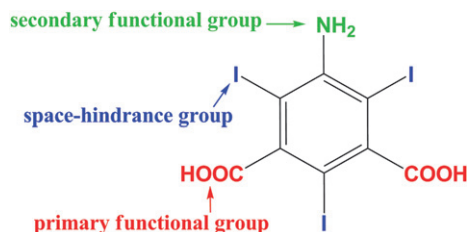
The solvothermal reaction‡ of H₂atiip and Cd(NO₃)₂·4H₂O in dimethylformamide (dmf)/ethanol/H₂O (5:2:1) with and without the imidazole ligand resulted in the formation of a large amount of block crystals of **1** and **2**, respectively, which were structurally characterized by single crystal X-ray diffraction.§ The formulae of [Cd(atiip)(Im)₂] (**1**) and [Cd_{1/2}(atiip)_{1/2}(dmf)]·dmf (**2**) were further confirmed by elemental analysis and TGA.

Single-crystal X-ray diffraction measurements reveal that complexes **1** and **2** crystallize in the achiral monoclinic *P*2₁/*c* space group and the chiral tetragonal *P*4₃2₁2 space group, respectively. The asymmetric units consist of one cadmium ion, one atiip ligand and, for **1**, two imidazole molecules, or, for **2**, half of a cadmium atom on a twofold axis, half of an atiip ligand on another twofold axis and one dmf molecule in a general position, respectively. The central cadmium ion in **1** is four-coordinated by two oxygen atoms from two different atiip ligands and two nitrogen atoms from the coordinated Im molecules. The O1 atom is weakly coordinated to the central cadmium ion with a Cd–O distance of 2.481 Å, as shown in Fig. 1. Each cadmium ion in complex **1** is coordinated by two atiip ligands, which are related by a simple *a*-axis translation. However, in

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† Electronic supplementary information (ESI) available: Experimental details; crystal and structure refinement data for **1** and **2**; A summary of the 10 structure determinations of complex **2**; the structure of (*R*)-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)acetamide; TGA curves and photoluminescence spectra for **1** and **2**. CCDC reference numbers 737145 and 737146. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917264p



Scheme 1 The selected H₂atiip ligand.

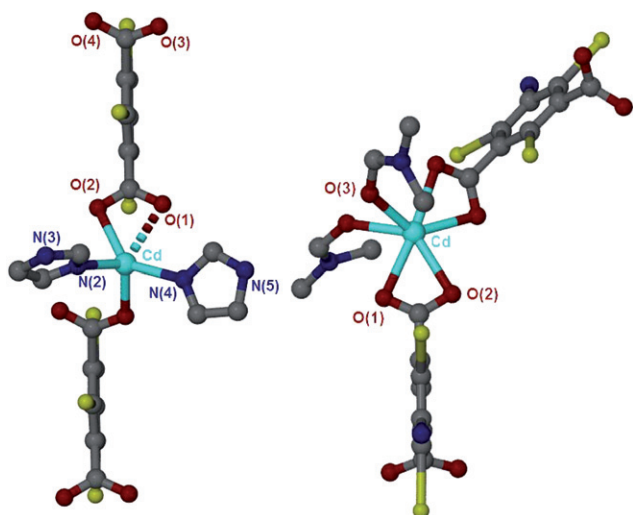


Fig. 1 The coordination environment of central Cd ions in **1** (left) and **2** (right), showing that the two benzene rings of the atiiip ligands are in a plane and a twist arrangement for **1** and **2**, respectively.

complex **2**, the central cadmium ion is six-coordinated by four oxygen atoms from two atiiip ligands and two from two coordinated dmf molecules. Every cadmium ion is coordinated by two atiiip ligands, with a dihedral angle of 52.3° between the two benzene rings. The different coordination environments of cadmium ions in **1** and **2** may derive from the different coordinated small molecules. In **1**, two coordination sites of cadmium are occupied by two Im molecules and the steric hindrance between the Im molecules and the atiiip ligands makes the two carboxylate groups of atiiip adopt a monodentate coordination mode to link one cadmium ion. However, in **2**, the steric hindrance between the two coordinated dmf molecules and the atiiip ligands is much weaker than that in complex **1**, which makes the two carboxylate groups of atiiip adopt a bidentate chelating mode to chelate one cadmium ion, as shown in Fig. 1.

The planar arrangement of the atiiip ligands in complex **1** results in an achiral zigzag array of the Cd-atiiip coordination polymer with a nearest Cd–Cd distance in the chain of 9.701 \AA (Fig. 2a). All the

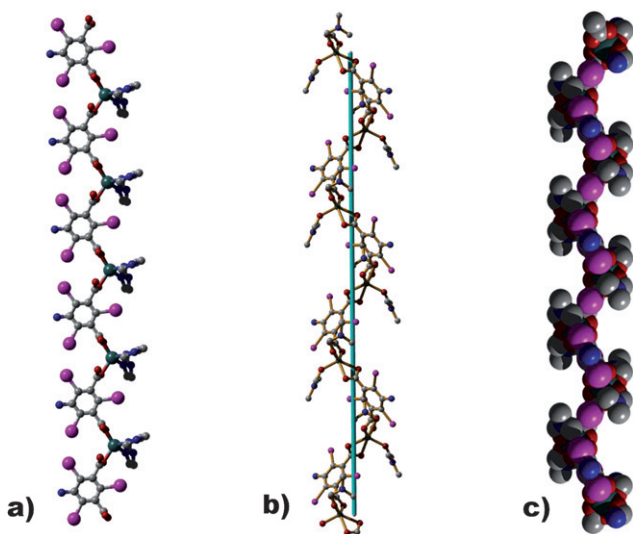


Fig. 2 The 1D zigzag chain of **1** (a) and helix of **2** (b and c).

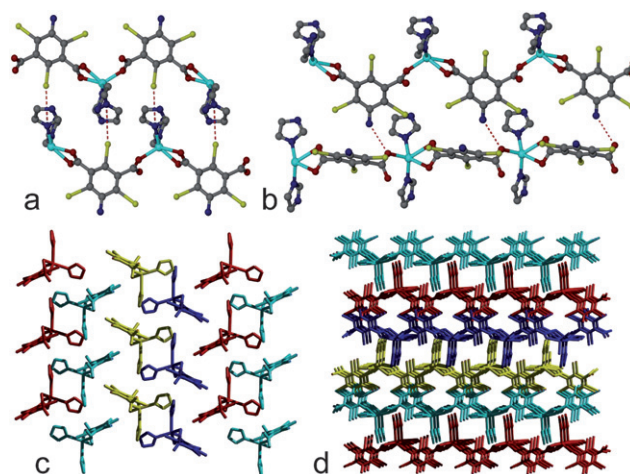


Fig. 3 The supramolecular interactions that exist in **1**: I \cdots N interactions (a) and hydrogen bonding interactions (b), and the 3D supramolecular architecture of **1**: (c) viewed along the *a* axis; (d) viewed along the *c* axis.

atiiip ligands, which are nonplanar with an average dihedral angle between the carboxylate groups and the central benzene ring of 94.5° , are located in the same side of the zigzag chain. In complex **2**, the chirality arises from the twist of the two benzene rings of the atiiip ligands. This results in the formation of a helical array of the Cd-atiiip coordination polymer with a nearest Cd–Cd distance in the chain of 9.353 \AA (Fig. 2b and 2c), which is slightly shorter than that in **1**. The helices are generated around the crystallographic 2_1 screw axes with a distance between coils of 16.566 \AA . The atiiip ligand in **2** is also nonplanar with a dihedral angle between the carboxylate groups and the benzene ring of 89° .

The 1D coordination polymers of **1** and **2** are further stabilized *via* interchain supramolecular interactions. In **1**, there exist weak I \cdots N interactions (3.806 \AA)¹⁹ between the iodine atoms and nitrogen atom of the Im molecules, and hydrogen bonding interactions (2.980 \AA) between the coordinated carboxyl oxygen atoms and nitrogen atoms of the atiiip ligand (Fig. 3a,b), which further connect with **1** to form a 3D supramolecular architecture (Fig. 3c,d). In **2**, the helix is further stabilized *via* interchain weak I \cdots O contacts between the iodine and the two coordinated oxygen atoms of the dmf molecules, and the hydrogen bonding interactions between the carboxyl oxygen atoms and the nitrogen atoms of the atiiip ligands (Fig. 4a and 4b). Each helical chain connects four adjacent helices through such supramolecular interactions, which make the neighbouring helices possess the same chirality (Fig. 4c and 4d). Thus, complex **2** possesses a chiral supramolecular architecture due to the existence of supramolecular interactions between helical chains,²⁰ through which the same chirality is preserved.

It has been reported that the bulk homochiral crystallization from achiral precursors can be achieved through chiral catalysis.¹⁷ In our work, the chiral molecule, (+)-N-(1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (see the ESI[†]), was used as a cosolute. The crystal data for nine randomly and consecutively selected crystals were recollected and the crystal structures were refined to give the $P4_32_12$ space group with Flack parameters near 0 (ESI[†]), which indicate that the chiral $P4_32_12$ is preferred to the $P4_12_12$ in the bulk sample.

TGA measurements revealed that compound **1** can be stable up to 320°C . For complex **1**, the first weight loss of 14.02% from 50 to

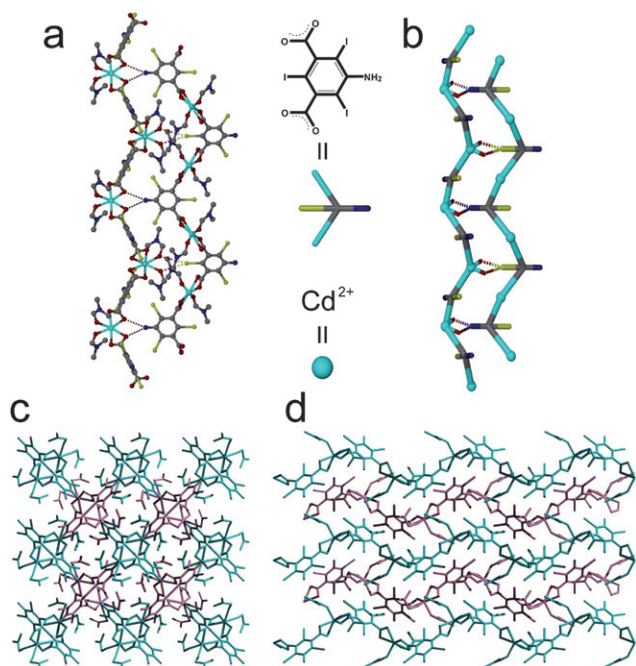


Fig. 4 (a) and (b) The I...O contacts and the hydrogen bonding interactions that exist in **2**, and the 3D chiral supramolecular architecture of **2**: (c) viewed along the *c* axis; (d) viewed along the *a* axis.

320 °C corresponds to the loss of two coordinated imidazole molecules (calcd: 16.9%). After 320 °C, **1** starts to decompose. Compound **2** can be stable up to 305 °C. For complex **2**, the first weight loss of 35.03% from 260 to 305 °C corresponds to the loss of one coordinated dmf molecule and one uncoordinated dmf molecule (calcd: 35.77%). After 305 °C, **2** starts to decompose.

The solid state fluorescence spectra of **1** and **2** have been measured (Figure S8†). At room temperature, **1** shows moderate photoluminescence, with an emission maximum at 360 nm upon excitation at 280 nm in the solid state (as powder samples). However, compound **2** exhibits stronger luminescence between 420 nm and 605 nm (excitation at 240 nm). Both emissions can be assigned to a ligand-to-metal charge transfer (LMCT),²¹ or a metal-to-ligand charge transfer (MLCT).²²

In conclusion, two 1D coordination polymers, a 1D zigzag chain (**1**) and a 1D helix (**2**), have been solvothermally synthesized. The supramolecular interactions, such as hydrogen bonds and I...N contacts, play important roles in the formation of the chiral architecture of complex **2**. Further studies will focus on the synthesis of other complexes with this ligand.

Acknowledgements

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Notes and references

† *Synthesis* of compound **1**: H₂atiip (0.01 g, 0.02 mmol), imidazole (0.01 g, 0.15 mmol) and Cd(NO₃)₂·4H₂O (0.01 g, 0.04 mmol) were dissolved in a 6 mL mixture of dimethylformamide (dmf), ethanol and H₂O (v/v = 5:2:1), to which one drop of pyridine was added. The clear solution was sealed in

a glass tube and heated at 90 ° for two days to give a large amount of colorless block crystals of **1**. Elemental analysis calcd (%) for **1**: C 20.93, H 1.0, N 8.72; found: C 21.35, H 1.23, N 8.11%. *Synthesis* of compound **2**: H₂atiip (0.02 g, 0.04 mmol) and Cd(NO₃)₂·4H₂O (0.02 g, 0.08 mmol) were dissolved in a 16 mL mixture of dmf, ethanol and H₂O (v/v = 5:2:1), to which one drop of pyridine was added. The clear solution was allowed to evaporate at 90 ° for two days to give colorless block crystals of **2**. Elemental analysis calcd (%) for **2**: C 20.62, H 1.98, N 5.15; found: C 21.08, H 1.79, N 5.11%.

§ Crystal data for **1**: C₁₄H₈CdI₃N₅O₄, *M* = 803.35, monoclinic, space group *P*2₁/*c*, *a* = 9.701(2), *b* = 24.227(5), *c* = 9.861(2) Å, β = 111.821(4)°, *U* = 2151.6(8) Å³, *Z* = 4, *D*_c = 2.486 Mg m⁻³, μ(Mo Kα) = 5.348 mm⁻¹, *T* = 273 K, 12343 reflections collected. Refinement of 4889 reflections (244 parameters) with *I* > 1.5σ(*I*) converged at a final *R*1 = 0.1077, *w**R*2 = 0.2923, *gof* = 1.064. Crystal data for **2**: C₁₄H₁₂CdI₃N₅O₅, *M* = 795.37, tetragonal, space group *P*4₃2₁2, *a* = 11.3689(3), *c* = 16.5658(11) Å, *U* = 2141.16(16) Å³, *Z* = 4, *D*_c = 2.467 Mg m⁻³, μ(Mo Kα) = 5.373 mm⁻¹, *T* = 298 K, 14 185 reflections collected. Refinement of 2194 reflections (125 parameters) with *I* > 1.5σ(*I*) converged at a final *R*1 = 0.0383, *w**R*2 = 0.0986, *gof* = 1.053.

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