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Three Helical chain-based 3D Coordination polymers: Solvent-Induced Syntheses, Tunable Structures and Catalytic property for Strecker reaction

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Three three-dimensional (3D) helical chain-based coordination polymers $[Sc(aip)(OH)\cdot(H_2O)]_n$ (1), $[Sc_2(aip)_3]_n$ (2) and $[Sc_2(nip)_3]_n$ (3) (H₂aip=5-aminoisophthalic acid, H₂nip=5-nitroisophthalic acid) have been synthesized through solvent induction without any chiral auxiliary systematically. We first synthesized CP 1, a 3D network, which contains intertwined left- and right-hand helical chains {-ScO₆-OH-}_n. By changing the polarity of solvents from CH₃CN/H₂O to H₂O, genuine single helix of **2** was constructed, in which adjacent Sc(COO)₆ polyhedra are connected alternately by aip²⁻ ligands to form a 3D framework with intertwined parallel left- hand helical chains {-Sc1(COO)-Sc2(COO)-}_n. Then by changing the substituent of ligand, CP **3** was obtained with right-handed helical chains. As for **3**, the aip²⁻ ligands bridge Sc(III) ions alternately into an infinite right-handed helical chains {-Sc(COO)-}_n, which serve as secondary building units (SBU) to generate a 3D framework. Solid-state circular dichroism spectrum confirms that **3** is optically active. We also studied catalytic properties of **1-3** in the Strecker reaction. Importantly, **1** shows excellent catalytic activity under mild conditions and can be reused for at least four times without significant reduction in catalytic ability.

Introduction

As a foundation of genetic codes in biological systems, helicity has attracted great interest due to its intriguing structures¹⁻⁴. Both left- and right-handed helical chains are ubiquitous in nature⁵. Inspired by sophisticated biological helices, scientists have developed some helical structures to explore the origin of asymmetry in living systems⁶, and their potential applications in advanced materials such as the separation of enantiomers, asymmetric catalysis and nonlinear optical devices⁷⁻⁹. Coordination polymers (CPs), as a flourishing subclass of molecular engineering materials, built from the ordered assembly of organic ligands and metal ions or clusters have offer a unique platform for the construction of helical structure with specific network topologies¹⁰⁻¹⁶. Generally, helical CPs are constructed by coordination interactions, hydrogen bonding interactions, π - π stacking and argentophilic interactions¹⁷⁻¹⁹, of which ligand to metal coordination interaction is the most efficient supramolecular synthon for the constructions of helical CPs²⁰⁻²². Up to date, for the design and constructions of helical CPs, to use enantiopure or racemic ligands as building blocks may be an available process^{23,24}. Besides enantiopure and racemic building blocks, helical chains can also be constructed by achiral building blocks²⁵.

In addition, helical/nonhelical transitions and even inversion of helicity are influenced by all intermolecular interactions and various external factors have the potential to change the sign and degree of helicity²⁶. In 2003, Inoue et al. reported a supramolecular Zn2H·L, in which the higher degree of supramolecular chirality induction was observed in CH₂Cl₂ than in CCl₄²⁷. In 2004, Moore et al. prepared a helicenecontaining foldamer in which the choice of solvent drastically changed the transfer of chiral information²⁸. Although helical CPs have been designed and synthesized, the control of helicity during the constructions still remains difficult.

We have chosen isophthalic acid derivatives 5aminoisophthalic acid (H₂aip), 5-nitroisophthalic acid (H₂nip), and scandium (III) as original materials to generate potential helical structures. Carboxylates are well known to possess versatile coordination modes, strong coordination ability, and high structural stability. More importantly, these ligands potentially generated helical structures in previous reports. As expected, we first synthesized CP 1, a 3D network, which contains intertwined left- and right-hand helical chains {-ScO6-OH-}_n. By changing the polarity of solvents, genuine single helix of 2 was constructed. Then by changing the substituent of ligand, CP 3 was obtained with right-handed helical chains (Fig. 1). In 2 and **3**, adjacent Sc(COO)₆ polyhedra are connected alternately by ligands to form 3D frameworks, which contain intertwined parallel left- hand helical chains {-Sc1(COO)-Sc2(COO)-}n and right-handed helical chains {-Sc(COO)-}_n, respectively. Furthermore, 1 presented high catalytic activity under mild conditions for the Strecker reaction, and can be easily recycled and reused for four successive cycles without significant loss of catalytic activity.

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⁺ Electronic Supplementary Information (ESI) available: CCDC 1585707 for **1**, 1585711 for **2** and 1585712 for **3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.



Experimental section

Materials and methods.

All reagents and solvents were commercially available and used without further purification. Fourier-transform infrared (FT-IR) spectra were recorded using the KBr pellets on a Nicolet Impact 410 spectrometer between 400 and 4000 cm⁻¹. Powder X-ray diffraction (PXRD) data were recorded on an SHIMADAZU XRD-6100 diffractometer equipped with Cu K α radiation (λ = 1.5418 Å). Elemental analyses (C, H and N) were collected on an Elementar Vario EL cube CHNOS Elemental Analyzer. Thermogravimetric analyses (TGA) were conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer in atmospheric environment at a heating rate of 10 °C·min⁻¹. ¹H NMR spectra were measured with a Bruker Avance 400 console at a frequency of 400 MHz. The circular dichroism (CD) spectra were measured on a MOS-450 spectrophotometer (KBr pellets). Ultraviolet-visible (UV-Vis) adsorption spectra were recorded on Rigaku-UV-3100 spectrophotometer. а N_2 adsorption/desorption experiments were performed at 77 K using a Micromeritics ASAP 2010N analyzer.

Synthesis and Characterization of 1-3.

 $[Sc(aip)(OH) \cdot (H_2O)]_n$ (1): A mixture of H_2aip (0.0181 g, 0.1 mmol), $Sc(NO_3)_3 \cdot 6H_2O$ (0.2 mmol·mL⁻¹, 0.5 mL) was added to CH_3CN (5 mL) in a 23 mL Teflon-lined autoclave and then heated under autogenous pressure at 100 °C for two days, then cooled to room temperature under ambient conditions. The brown block crystals were obtained by filtration and washed with distilled water, and dried in air. Yield: 85% for 1 (based on $Sc(NO_3)_3 \cdot 6H_2O$). Elemental analysis (%) for 1: Anal. Calc.: C, 37.07; H, 3.10; N, 5.41; Found: C, 37.35; H, 3.05; N, 5.50. IR (KBr pellet, cm⁻¹): 3441 (s), 1625 (m), 1573 (m), 1546 (s), 1393 (s), 1035 (m), 988 (m), 780 (s), 709 (s), 633 (w), 574 (w), 527 (w).

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C, 45.82; H, 2.55; N, 7.87. IR (KBr pellet, cm⁻¹): 3646 (s), 3476 (s), 3381 (s), 3217 (m), 1535 (s), 1461 (s), 1381 (s), 1317 (w), 1137

 $[Sc_2(nip)_3]_n$ (**3**): A mixture of H₂nip (0.0211 g, 0.1 mmol), Sc(NO₃)₃·6H₂O (0.2 mmol·mL⁻¹, 0.5 mL) was added to CH₃CN (3 mL) in a 23 mL Teflon-lined autoclave and then heated under autogenous pressure at 100 °C for two days, then cooled to room temperature under ambient conditions. The colorless block crystals were obtained by filtration and washed with distilled water, and dried in air. Yield: 72% for **3** (Sc(NO₃)₃·6H₂O). Elemental analysis (%) for **3**: Anal. Calc.: C, 40.17; H, 1.26; N, 5.86; Found: C, 40.25; H, 1.35; N, 5.50. IR (KBr pellet, cm⁻¹): 3089 (s), 2950 (w), 2881 (w), 1682 (m), 1625 (s), 1547 (s), 1461 (s), 1397 (m), 1346 (w), 1087 (m), 914 (m), 722 (s), 583 (w).

$$\label{eq:sc2} \begin{split} & [Sc_2(aip)_3]_n \ \textbf{(2):} \ A \ mixture \ of \ H_2aip \ \textbf{(0.0181 g}_{ie} \textbf{0.4}_{ti} \textbf{mmon}), \\ & Sc(NO_3)\cdot 6H_2O \ \textbf{(0.2 \ mmol \cdot mL^{-1}, \ 0.5 \ mL) \ was added to $H_2O \ \textbf{(2.3 \ mmon)}, \\ & in \ a \ 23 \ mL \ Teflon-lined \ autoclave \ and \ then \ heated \ under \end{split}$$

autogenous pressure at 100 °C for one day, then cooled to room

temperature under ambient conditions. The pink block crystals were obtained by filtration and washed with distilled water, and dried in air. Yield: 80% for **2** (based on Sc(NO₃)·6H₂O). Elemental analysis (%) for **2**: Anal. Calc.: C, 45.93; H, 2.39; N, 6.70; Found:

Single-Crystal X-ray Diffraction.

(w), 997 (s), 893 (m), 783 (s), 629 (w).

The crystallographic data sets for 1 and 3 were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphitemonochromated Mo K α (0.71073 Å) radiation, while **2** was collected on a Bruker SMART APEX-II CCD diffractometer by using graphite-monochromated Mo K α radiation (k = 0.71073 Å) at room temperature. The structures were solved by using direct methods and refined on F² with full-matrix least-squares techniques with the SHELX-97 crystallographic software package²⁹. All nonhydrogen atoms were refined anistropically. All the hydrogen atoms were placed in fixed, calculated positions using a riding model. Solvent molecules were removed by SQUEEZE subroutine in PLATON³⁰. The final molecular formulas of 1-3 were derived from crystallographic data combined with elemental and thermogravimetric analyses data. The crystal data, the data-collection details for 1-3 are summarized in Table S1, selected bond lengths and angles are given in Tables S3-S5. CCDC-1585707, 1585711 and 1585712 contain the supplementary crystallographic data for this paper.

Sample activation.

Prior to the catalytic test, the as-prepared **1-3** samples were soaked in CH₃OH for 3 days. Further, the samples were filtrated and dried at 150 °C for 12 h under vacuum to remove the guest molecules, generating the activated **1-3**.

Catalytic experiment.

For the catalytic experiments, activated catalysts, aldimine (0.14 mmol) and trimethylsilyl cyanide (TMSCN) (47 μ L) in CDCl₃ (2.4 mL) were sequentially added to a standard 20 mL vial. The reaction mixtures were stirred at room temperature. The reactions were monitored by ¹H NMR spectroscopy and the conversion yield was determined from the ratio of the integral

of the product signal in relation to the sum of integrals of all signals (aldehyde, aldimine and product).

Results and discussion

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Synthesis.

As is well known, many factors in the synthetic process should be considered, such as reaction temperature, solvents, ligands and concentration of staring materials, in which polarity of mixed solvents and substituent groups of ligands maybe more likely to affect the reaction results. As depicted in Scheme 1, all the CPs were prepared in the presence of isophthalic acid derivatives ligands by solvent induced methods. Distinguishingly, **1** was obtained by the reaction of Scheme 1 The synthetic route to 1-3.

Sc(NO₃)₃·6H₂O, H₂aip, and CH₃CN/H₂O mixed solution. Then, by changing the solvent (replacing CH₃CN/H₂O with H₂O), as the polarity of the solvent increased, the double-helical interactions were eliminated and single helix of **2** was acquired. Furthermore, **3** was also self-assembled into helical chains structure under CH₃CN/H₂O mixed solution system by the H₂nip ligand and Sc(NO₃)₃·6H₂O. In addition, the structural diversities among the three CPs also rely heavily on the substituent groups of ligands. **1** and **2** were obtained by the ligand H₂aip (NH₂) and Sc(NO₃)₃·6H₂O. Based on these, by changing the substituent group of ligand (NO₂ instead of NH₂), CP **3** was obtained successfully.

Crystal structures

Single-crystal X-ray analysis of CP **1** reveals that it crystallizes in the tetragonal space group $l4_1/amd$. The asymmetric unit of 1 contains one central Sc³⁺ ion, a half aip²⁻ ligand, one OH⁻ group and one lattice water molecule. The Sc³⁺ ion is six coordinated environment and exhibits octahedral geometry, in which six O atoms are from four individual aip²⁻ ligands and two O atoms are from two OH⁻ groups. Sc-O bond lengths fall in the region of 2.0554(19)-2.148(3) Å and O-Sc-O bond angles varies from 85.32(18) to 176.9(2)° in **1**, these values are consistent with those of similar Sc-CPs³¹.

In the structure of **1**, all carboxylate groups of H₂aip ligands are completely deprotonated (Scheme S1). The ScO₆ units are linked to each other through OH⁻ groups, which generate intertwined left- and right-hand helical chains $\{-ScO_6-OH_+\}_n$ with a helical pitch of 11.964 Å, as shown in Fig. 2a. These two types of opposite chiral chains are alternately linked by aip²⁻ ligands, resulting in a novel 2D layer along *b* axis (Fig. 2b). These layers are further connected by bridging aip²⁻ ligands to construct a provide the function of the second structure of the second stru

Inspection of the structure of **1** suggests that it is possible to separate the quasi-double-helical chain, forming single helical chains by changing reaction conditions. When the polarity of solvent was increased by introducing H₂O instead of CH₃CN, although the H₂aip ligand was still deprotonated, the 3D structure of **2** with different single helical chains was isolated without chiral additives.



Fig. 2 (a) View of the left- and right-handed helical chains in **1**. (b) 2D layer structure of **1** along *b* axis. (c) 3D open framework of **1** (hydrogen atoms, lattice water molecules are omitted for clarity). Color scheme: carbon, gray; nitrogen, blue; oxygen, red; metal, green. (d) Simple topology of **1**.

2 crystallizes in chiral cubic space group $P2_13$. The asymmetric unit of **2** contains two Sc³⁺ ions, one aip²⁻ ligand. Sc1 ion is surrounded by six carboxylic acid oxygen atoms from six different aip²⁻ ligands, displaying a octahedral coordination geometry Sc1(COO)₆. With a coordination geometry similar to that of Sc1, Sc2 ion is coordinated to six oxygen atoms (Sc2(COO)₆) from six individual aip²⁻ ligands. Sc-O bond lengths fall in the region of 2.047(4)-2.098(4) Å and O-Sc-O bond angles varies from 85.49(15) to 177.95(14)° in **2**, all of which are similar to those reported in the related Sc-CPs³².

In **2**, the aip²⁻ ligand shows the same coordination mode to link four Sc^{3+} ions (Scheme S1). Two adjacent $Sc(COO)_6$ polyhedra in **2** are connected alternately by aip²⁻ ligands to form a 3D framework (Fig 3a). Unlike **1**, the 3D structure of **2** appears

Fig. 3 (a) 3D framework of **2** along *c* axis. (b) 3D $[Sc(COO)_6]$ framework of **2** showing the left-handed helical chains. (c) The left-handed helical chain in **2**. (hydrogen atoms are omitted for clarity). Color scheme: carbon, gray; nitrogen, blue; oxygen, black; metal, red.

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to contain intertwined left- hand helical chains $\{-Sc1(COO)-Sc2(COO)-\}_n$ running along the screw axis, which are parallel to each other with the same handedness and a screw pitch of 13.99 Å, as shown in Figs. 3b and 3c.

3 crystallizes in the chiral cubic space group $I2_13$. **3** shows structural characteristics very similar to 2. Nevertheless, there are still some differences between the two compounds. Asymmetric unit of 3 consists of one Sc(III) ion and a half nip²⁻ ligand. Sc(III) ion is coordinated by six oxygen atoms, all of which are from six nip²⁻ ligands, overall describing a ScO₆ sixcoordinated environment whose geometry resembles a significantly octahedron. Sc-O bond lengths fall in the region of 2.0564(16)-2.0950(16) Å and O-Sc-O bond angles varies from 87.04(7) to 175.25(7)° in 3, all of which are similar to those reported in the related Sc-CPs³³. As depicted in Fig. 4a, the carboxylate groups bridge Sc(III) ions alternately into an infinite right-handed helical chain $\{-Sc(COO)-\}_n$ with a pitch of 14.3757 Å. The helix is generated around the crystallographic 2₁ screw axis, which is consistent with the compound crystallizing in the 12_13 space group. Each helical chain serves as a secondary building unit (SBU) and is further linked to its four adjacent neighbors with the same handedness along a axis through nip²⁻ linkers, generating a homochiral 3D framework, as shown in Fig. 4c. The chirality in structure $\mathbf{3}$ is a result of the 2_1 axis in the symmetry. Therefore, the chirality in the present compound is derived from the presence of helices.

The asymmetric units of 1 and 2 contain one and two crystallographically independent Sc(III) ions, respectively. For 2, H₂aip ligands link the Sc(III) ions one by one, then forming a 1D single helical chain. Whereas, for 1, the coordination mode of two carboxylic acid groups in H₂aip ligand are mirror symmetrical (Scheme S1). Every carboxyl connects two crystallographically independent Sc(III) ions respectively to form intertwined left- and right-hand helical chains. Then, under the help of aip²⁻ ligands interactions, 1 shows a 3D structure. Perhaps symmetrical coordination patterns contribute to the formation of double-stranded chains for 1. In 2, the asymmetric carboxyl coordination mode maybe the asymmetrical origin of the entire single crystal structure (Scheme S1). If the NO₂ replaces NH₂ in ligands, the coordination mode of carboxyl groups may be changed compared to 1 and 2. In previously report, we have found that the H₂nip (NO₂) ligand could be deprotonated by NaOCH₃ in H_2O/CH_3CH_2OH , and the auxiliary ligand bimb favors the formation of helix chain³⁴. Therefore, using H₂nip instead of H₂aip and changing the solvent into H₂O/CH₃CN compared with 1 and 2, CP 3 consisting of single-helical chains were prepared successfully by spontaneous resolution.

In the absence of any chiral source, to induce chirality into crystal structures from achiral building blocks is a crucial

question in molecular design level. With further study into the structures of **1** and **2**, it can be found that the solvents used in experiments have obvious effects on the formation of products with different helices, left- and right-hand helical chains {-ScO₆-OH-}_n for **1** and left- hand helical chains {-Sc1(COO)-Sc2(COO)-}_n for **2**. When CH₃CN/H₂O is used as solvent, Sc(III) ions are coordinated by aip²⁻, forming left- and right-hand double helices {-ScO₆-OH-}_n. The double helices are further connected by aip²⁻ ligands, resulting in the formation of a 3D meso framework with 1D channels. Upon changing solvent polarity from CH₃CN/H₂O



Fig. 4 (a) The right-handed helical chain in **3**. (b) 3D $[Sc(COO)_6]$ framework of **3** showing the right-handed helical chains. (c) 3D framework of **3** along *a* axis (hydrogen atoms are omitted for clarity). Color scheme: carbon, gray; nitrogen, blue; oxygen, red; metal, green.

to H₂O, although the ligands are still deprotonated, ligand spatial conformations have changed (Scheme S1, a and b). The Sc(III) ions are connected by ligands alternately, only giving rise to one kind of single helix {-Sc1(COO)-Sc2(COO)-}_n for 2. However, 2 is racemic and no optical activity is observed. Nevertheless, it can be seen from the structure of 1 that two carboxylic acid groups of H₂aip ligand are completely symmetrical, which lead to generate extended mesomeric networks. Furthermore, obviously, the twisted spatial conformations of aip^{2-} ligands result in the helicity of the molecular units for 2. Along these lines, further changing the solvent H₂O into CH₃CN/H₂O and using H₂nip (NO₂) instead of H₂aip (NH₂), the chiral **3** with right- handed helical chains {-Sc(COO)- $_{n}$ was constructed, which is similar to **2** in the structure. Therefore, the solvent polarity and spatial conformations of ligands together lead to the structural differences among 1, 2 and 3. Such an accurate strategy to obtain ordered helical coordination polymers, which utilizes the rigid bridging H₂aip and H₂nip ligands by solvent effect, is actually effective.

Therefore, the helicity induction based on solvent polarity is very significant for the study of chiral transformation. The polarity of solvent dramatically affects dispersion forces between CPs and solvent molecules to afford some perturbation to intramolecular interactions³⁵.

Characterization

Powder X-ray diffraction (PXRD) patterns for the bulk samples were measured at room temperature and the diffraction peaks perfectly match well with the simulated patterns, confirming the phase purity of the obtained crystal samples (Figs. S1, S4 and S6). The intensity differences may be due to the preferred orientation of the crystalline samples. Thermogravimetric analyses (TGA) experiments were performed on pure single crystal samples of **1**, **2** and **3** under air atmosphere with a

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heating rate of 10 °C·min⁻¹ in the range of 25-800 °C. 1 displays a continuous weight loss (13.8 wt.%) in the temperature range of 25-220 °C, which corresponds to the loss of the coordinated OH⁻ groups, lattice water molecules in the framework (calc. 13.5 wt.%). The sharp weight loss above 400 °C corresponds to the decomposition of the framework (Fig. S11). The TGA plots indicate that 2 and 3 display continuous weight loss (75.5 wt.% and 80.9 wt.%) in the temperature range of 330-550 °C and 420-520 °C, respectively, which correspond to the loss of the ligands in the frameworks (calc. 78.0 wt.% and 80.8 wt.%). (Figs. S12 and S13). The IR spectra of CPs 1-3 show the characteristic bands of the carboxylic groups in the usual region. The peaks observed at 1546, 1535, 1547 cm⁻¹ for 1-3 are assigned to the stretching bands of $v_{as}(COO^{-})$, respectively, while the peaks observed at 1393, 1381, 1397 cm⁻¹ can be assigned to the stretching bands of $v_s(COO^-)$ (Figs. S8-S10). In addition, the bands at 3420 and 3390 cm⁻¹ correspond to the symmetric and asymmetric stretching of the primary amine^{36,37} in 1 and 2, respectively.

The circular dichroism spectra (CD) analysis

combination of single-crystal The X-rav structure determinations and circular dichroism spectra (CD) is the most common way of gaining as much evidence as possible for the homochirality or enantioenrichment of the bulk material. In order to confirm the homochirality of 2 and 3, the solid-state CD spectra were measured on crystals with a KBr pellet. The CD spectrum of **3** exhibits strong positive Cotton effects, indicating that the crystals of 3 are optically active (Fig. S15). However, the CD spectrum of **2** reveals the presence of racemic mixture in **2**.

N₂ adsorption properties

The permanent porosity of activated 1-3 were confirmed by N₂ adsorption measurements. As shown in Fig. S20, N₂-uptake (77 K) measurements gave typical I-type isotherms with an adsorption of 35.5 cm³·g⁻¹ for **1**. However, almost no sorptions of N₂ at 77 K were detected, particularly at low pressure, implying non-porous structures of 2 and 3. The surface areas of Brunauer-Emmett-Teller (BET) from the N₂ adsorption isotherms was 92.4 m²·g⁻¹ for 1, and the surface areas of Langmuir calculated was 123.4 m²·g⁻¹.

Catalytic activity

Strecker reactions are one of the most classical ways for the syntheses of aminonitriles, which are significant organic intermediates in the synthesis α -amino acids, β -amino acids, other nitrogen-containing heterocycles etc.³⁸⁻⁴⁰. Meanwhile, Strecker reactions are well known as Lewis acid or base catalyzed C-C bond formation. In the past decades, plenty of homogeneous catalysts, such as metal salts, metal oxides, metal-salen complexes, have been extensively utilized for Strecker reactions⁴¹⁻⁴⁵. Moreover, some CPs with catalytic sites have been validated to be high catalytic activity for Strecker reactions⁴⁶⁻⁴⁸. $[In_xGa_{1-x}(O_2C_2H_4)_{0.5}(hfipbb)],$ prepared bv Gandara et al., showed how the activity of a heterogeneous catalyst can be controlled in one-pot Strecker reaction⁴⁹.

Copper(I)/copper (II)-salen CP reported by Li et al. could be used as an efficient heterogeneous multifunctional catalyst for three component Strecker reactions with 99% conversion rate⁵⁰.

To evaluate the effectiveness of 1-3 as catalysts, compare the ability of each of the catalytic sites in Strecker reactions of benzylidene-phenyl-amine, catalytic studies were divided into two categories. About activated catalyst 1, 1D channels with dimensions of approximately 7.5×7.5 Å² decorated with pendent -NH₂ groups, acts as lewis acid and base cooperative catalyst in Strecker reaction. However, for activated catalysts 2 and 3, Sc(III) ions as lewis acid catalytic centers during the reaction. At first, Strecker reaction of benzylidene-phenylamine, TMSCN, and different catalysts at ambient temperature was performed, and the results are listed in Table 1. Since 1-3 are insoluble and stable in most organic solvents (Figs. S2, S5 and S7), meanwhile, a great deal of literatures prove that chloroform performed well as a reaction medium for Strecker reaction^{51,52}. We used chloroform as reaction medium.

Table 1 Comparison of the performance of different catalysts in the Strecker reaction ^a .					
		N		HN	
	+ TMSCN $\frac{Cat.}{CDCl_{1}r.t.}$ CN				
_					
	conversion yield(%) ^b				
_	time(h)	CP 1	CP 2	CP 3	none
	6.5	58	23	24	trace
	12	91	36	67	trace
_	24	99	82	88	trace

^a Reaction conditions unless specified otherwise: aldimine (0.14 mmol), TMSCN (47 µL), catalyst (0.02 mmol for 1, 0.01 mmol for 2 and 3), CDCl₃ (2.4 mL) at room temperature. ^b Yield calculated by ¹H NMR with aldimines.

The results demonstrated that higher yields were obtained at room temperature. It is necessary to mention that in the absence of a catalyst, the reaction rate is slow, and even after extending the reaction time, the reaction yields still remain low. In contrast with 2 and 3, 1 features the large open channels (about 7.5 ×5.7 Å) and has accessibly functional NH₂ groups imparting basic character to the material. The subsequent experimental results show the catalytic activity of 1 is obviously better than the catalyst 2 and 3 (Table 1). Moreover, we performed the FT-IR experiments of catalysts before and after catalytic reactions (Figs. S8-S10). The FT-IR spectra of 1-3 after catalytic reaction displayed a small peak at 2234 cm⁻¹, which resulted from the CN⁻ vibration characteristics, implying the presence of cyano-group in the catalysts⁵³.

To further examine the general application of the catalyst 1, the scope of the reaction was extended to the synthesis of various aldimines under the above mentioned conditions (Table 2). The results show that the catalytic activity decreases with an increase in the size of aldimines (Table 2, entries 5, 6). The reduced catalytic activity can be attributed to the steric effects, which result in restricted diffusion of the bigger substrates into the pore, and the observed catalytic activity could be mostly

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due to surface catalysis by Sc(III) ions exposed to the surface of the CPs.



^a Reaction conditions unless specified otherwise: aldimine (0.14 mmol), TMSCN (47 $\mu L),$ catalyst (0.02 mmol), CDCl_3 (2.4 mL) at room temperature. $^{\rm b}$ Yield calculated by ¹H NMR with aldimines. ^c The same reaction conditions without catalyst **1**.

Besides the fact that small-scale substrates have better efficiencies than the bulk-sized samples for the Strecker reaction, the results show that the presence of the electrondonating group on the aldimines leads to greater desirability for the reaction. 4-Substituted aldimines with an electron-donating group (-OCH₃) gave higher conversions than those with electron-withdrawing group (-CF₃) (Table 2, entries 2-4). As an electronic-donating group, -OCH₃ group can result in the carbon atom of aldimine being polarized and attacked by TMSCN affording the corresponding α -amino nitriles. Thus, the high efficiency observed for aldimines suggest the utility of 1 as a promising heterogeneous catalyst for Strecker reaction.

Compared to the binary reaction, three-component Strecker reactions can omit the separation and purification of intermediate products, and improve atom economy⁵⁴. The

synthesis of α -aminonitriles was also investigated, by threecomponent Strecker reactions of a variety of alder wdes and amines with TMSCN using activated 1 under identical reaction conditions.

The results of the reaction are summarized in Table S2. To our delight, benzaldehyde showed good conversion rate (99%) which further inspired us to check the more reluctant substrate, different aldehydes and amines, for the reaction. The results of the catalytic activity of 1 reveal that both aldehydes of electronwithdrawing as well as amines of electron-donating groups give good vields.

PXRD pattern was further applied to verify the framework robustness of the recovered 1 sample. As depicted in Fig. S3, similar diffraction peaks can be observed before and after the reaction, indicating the integrity of the framework structure. It is noticed that the catalyst 1 can be simply filtrated from the reaction system and could be reused at least four times with only a slight decrease in the reactivity (Fig. S16).

Conclusions

In summary, we successfully designed and prepared three 3D Sc-CPs with different helical chains from isophthalic acid derivatives by solvent induced methods. 1 displays a 3D network with ScO₆ units connected by OH⁻ groups, exhibiting left- and right- handed double helical chains. Interestingly, by changing the polarity of solvents, the 3D structures can be successfully induced from 1 with double helical chains to 2 with single helix. In 2, adjacent Sc(COO)₆ polyhedra are connected alternately by aip²⁻ ligands to form a 3D framework, which contains intertwined parallel left- hand helical chains {-Sc1(COO)-Sc2(COO)- $\frac{1}{n}$. Then by changing the substituent group of ligand (NO₂ replaces NH₂) and solvents, the right- handed single helical structure of 3 was constructed. As for 3, the nip²⁻ ligands bridge Sc(III) ions alternately into infinite right-handed helical chains $\{-Sc(COO)-\}_n$. Each helical chain serves as a secondary building unit (SBU) connected by ligands to generate a 3D framework. Furthermore, 1 exhibits good catalytic activity for the Strecker reactions. Solvent-induced switching of helicity may open up a promising approach to rationally design and control helical structures.

Conflicts of interest

There are no conflicts to declare.

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References

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- 1 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005-2062.
- 2 V. Berl, I. Huc, R. G. Khoury, M. J. Krische and J. M. Lehn, *Nature*, 2000, **407**, 720-723.
- 3 C. Piguet, M. Borkovec, J. Hamacek and K. Zeckert, *Coord. Chem. Rev.*, 2005, **249**, 705-726.
- 4 X. -H. Bu, M. -L. Tong, H. -C. Chang, S. Kitagawa and S. R. Batten, *Angew. Chem., Int. Ed.*, 2004, **43**, 192-195.
- 5 R. M. Hazen and D. S. Sholl, *Nat. Mater.*, 2003, **2**, 367-374.
- 6 X. -D. Zheng and T. -B. Lu, *CrystEngComm*, 2010, **12**, 324-336.
- 7 Y. Okamoto, *Adv. Polym. Sci.*, 2013, **261**, 391-414.
- 8 S. Wang, J. -X. Chen, X. -Y. Feng, G. Shi, J. Zhang and X. -H. Wan, *Macromolecules*, 2017, **50**, 4610-4615.
- 9 E. Botek, F. Castet and B. Champagne, *Chem. Eur. J.*, 2006, **12**, 8687-8695.
- 10 J. -H. Qin, Y. -Y. Jia, H. -J. Li, B. Zhao, D. -Q. Wu, S. -Q. Zang,; H. -W. Hou and Y. -T. Fan, *Inorg. Chem.*, 2014, 53, 685-687.
- 11 C. -C. Zou, Q. -Q. Li, F. -J. Cheng, H. -J. Wang, J. -G. Duan and W. -Q. Jin, *CrystEngComm*, 2017, **19**, 2718-2722.
- 12 H. -J. Lun, S. -S. Cui, H. -J. Li, Q. Ping, H. -H. Song, Y. -M. Li, Y. Ru, Y. -L. Bai and S. -C. Xiang, *CrystEngComm*, 2015, **17**, 7029-7033.
- 13 B. -L. Hou, D. Tian, J. Liu, L. -Z. Dong, S. -L. Li, D. -S. Li and Y. -Q. Lan, *Inorg. Chem.*, 2016, **55**, 10580-10586.
- H. -T. Ye, C. -Y. Ren, G. -F. Hou, Y. -H. Yu, X. Xu, J. -S. Gao,
 P. -F. Yan and S. -W. Ng, *Cryst. Growth Des.*, 2014, 14, 3309-3318.
- 15 Q. -G. Zhai, X. -H. Bu, X. Zhao, D. -S. Li, and P. -Y. Feng, Acc. Chem. Res., 2017, 50, 407-417.
- 16 X. -M. Lin, J. -L. Niu, P. -X. Wen, Y. Pang, L. Hu and Y. -P. Cai, Cryst. Growth Des., 2016, 16, 4705-4710.
- 17 X. -D. Zheng and T. -B. Lu, *CrystEngComm*, 2010, **12**, 324-336.
- 18 T. Zhang, H. -Q. Huang, X. -Y. Cheng, D. Guo, H. -X. Mei, R. -B. Huang and L. -S. Zheng, *CrystEngComm*, 2016, **18**, 670-673.
- 19 Y, -Q. Sun, J. -C. Zhong, L. Ding and Y. -P. Chen, *Dalton Trans.*, 2015, 44, 11852-11859.
- 20 E. V. Anokhina and A. J. Jacobson, J. Am. Chem. Soc., 2004, **126**, 3044-3045.
- 21 G. -X. Guan, X. Liu, Q. Yue and E. -Q. Gao, Cryst. Growth Des., 2018, 18, 1364-372.
- 22 J. Heo, Y. -M. Jeon and C. A. Mirkin, J. Am. Chem. Soc., 2007, **129**, 7712-7713.
- 23 H.-Y. An, Z. -B. Han, T. -Q. Xu, C. -G. Meng and E. -B. Wang, Inorg. Chem. Commun., 2008, **11**, 914-917.
- 24 X. Ouyang, Z. -X. Chen, X. -F. Liu, Y. -T. Yang, M. -L. Deng, L. -H. Weng, Y. -M. Zhou and Y. Jia, *Inorg. Chem. Commun.*, 2008, **11**, 948-950.
- 25 L. Jiang, T. -B. Lu and X. -L. Feng, *Inorg. Chem.*, 2005, 44, 7056-7062.
- 26 V. V. Borovkov, G. A. Hembury, Y. Inoue, Acc. Chem. Res., 2004, 37, 449-459.
- 27 V. V. Borovkov, G. A. Hembury, N. Yamamoto and I. Yoshihisa, J. Phys. Chem. A, 2003, **107**, 8677-8686.
- 28 M. T. Stone, J. M. Fox and J. S. Moore, *Org. Lett.*, 2004, 6, 3317-3320.
- 29 G. M. Sheldrick, SHELX 97, Program for Crystal Structure Solution and Refinement; Göttingen University: Göttingen, 1977.
- 30 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7-13.
- 31 Y. Cui, W. -K. Gu, Y. -R. Wang, B. Zhao, Y. -M. Yao and Q. Shen, *Catal. Sci. Technol.*, 2015, **5**, 3302-3312.

- 32 A. J. Graham, A. M. Banu, T. Düren, A. Greenaway, S. C. McKellar, J. P. S. Mowat, K. Ward, A. Morgatt, and Strate Online Moggach, J. Am. Chem. Soc., 2014, 136, 8606-8613.
- 33 J. Cepeda, S. P. Yanez, G. Beobide, O. Castillo, E. Goikolea, F. Aguesse, L. Garrido, A. Luque and P. A. Wright, *Chem. Mater.*, 2016, **28**, 2519-2528.
- 34 X. -J. Li, Z. -J. Yu, X. -X. Li and X. -F. Guo, *Chem. Eur. J.*, 2015, **21**, 16593-16600.
- 35 S. Yagi, T. Morinaga, T. Nomura, T. Takagishi, T. Mizutani, S. Kitagawa and H. Ogoshi, *J. Org. Chem.*, 2001, 66, 3848-3853.
- 36 T. Lescouet, E. Kockrick, G. Bergeret, M. P. Titus and D. Farrusseng, *Dalton Trans.*, 2011, **40**, 11359-11361.
- 37 T. Lescouet, E. Kockrick, G. Bergeret, M. P. Titus, S. Aguado and D. Farrusseng, J. Mater. Chem., 2012, 22, 10287-10293.
- 38 A. Heydari, P. Fatemi and A. A. Alizadeh, *Tetrahedron Lett.*, 1998, **39**, 3049-3050.
- 39 Y. M. Shafran, V. A. Bakulev and V. S. Mokrushin, *Russ. Chem. Rev.*, 1989, **58**, 148-162.
- 40 A. Mishra, A. Ali, S. Upreti, M. S. Whittingham, R. Gupta, Inorg. Chem., 2009, 48, 5234-5243.
- 41 M. S. Sigman and E. N. Jacobsen, J. Am. Chem. Soc., 1998, **120**, 5315-5316.
- 42 N. S. Josephsohn, K. W. Kuntz, M. L. Snapper and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2001, **123**, 11594-11599.
- 43 V. Banphavichit, W. Mansawat, W. Bhanthumnavin and T. Vilaivan, *Tetrahedron*, 2004, **60**, 10559-10568.
- 44 C. A. Krueger, K. W. Kuntz, C. D. Dzierba, W. G. Wirschun, J. D. Gleason, M. L. Snapper and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 4284-4285.
- 45 H. Ishitani, S. Komiyama, Y. Hasegawa and S. Kobayashi, J. Am. Chem. Soc., 2000, **122**, 762-766.
- 46 A. P. Singh, A. Ali and R. Gupta, *Dalton Trans.*, 2010, **39**, 8135-8138.
- 47 S. -Y. Wang, J. -N. Xu, J. -F. Zheng, X. -D. Chen, L. Shan, L. -J. Gao, L. Wang, M. Yu and Y. Fan, *Inorg. Chim. Acta*, 2015, **437**, 81-86.
- 48 J. Xia, J. -F. Zheng, J. -N. Xu, L. Wang, L. Yang, Z. -D. Su and Y. Fan, *Inorg. Chim. Acta*, 2014, **411**, 35-39.
- 49 L. M. A. Díaz, F. Gándara, M. Iglesias, N. Snejko, E. G. Puebla and M. Á. Monge, *J. Am. Chem. Soc.*, **2015**, 137, 6132-6135.
- 50 Y.-L. Hou, R. W.-Y. Sun, X.-P. Zhou, J.-H. Wang and D. Li, *Chem. Commun.*, 2014, **50**, 2295-2297.
- 51 A. Sadhukhan, D. Sahu, B. Ganguly, N. H. Khan, R. I. Kureshy, S. H. R. Abdi, E. Suresh and H. C. Bajaj, *Chem. Eur. J.*, 2013, **19**, 14224-14232.
- 52 A. Nasreen, *Tetrahedron Lett.*, 2013, **54**, 3797-3800.
- L. Hu, G. -X. Hao, H. -D. Luo, C. -X. Ke, G. Shi, J. Lin, X. M. Lin, U. Y. Qazi and Y. -P. Cai, *Cryst. Growth Des.*, 2018, 18, 2883-2889.
- 54 M. J. Climent, A. Corma and S. Iborra, *RSC Adv.*, 2012, 2, 16-58.

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Graphical abstract

Three three-dimensional (3D) helical chain-based coordination polymers have been synthesized through solvent induction without any chiral auxiliary systematically. We first synthesized CP **1**, which contains intertwined left- and right-hand helical chains $\{-ScO_6-OH_{-}\}_n$. By changing the polarity of solvents from CH₃CN/H₂O to H₂O, genuine single helix of **2** was constructed. Then by changing the substituent of ligand, CP **3** was obtained with right-handed helical chains.



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