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PAPER

Three 2D Ag^I-framework isomers with helical structures controlled by the chirality of camphor-10-sulfonic acid†

Peng Guo*

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Three 2D Ag^I-framework isomers were constructed from enantiopure camphor-10-sulfonic acids or racemic camphor-10-sulfonic acids, together with achiral 4-aminobenzoic acids. In complex **1**, (+)-camphor-10-sulfonic acids bridge the single left-handed helices that are made up of Ag ions and 4-aminobenzoic acids, generating a homochiral 2D layer. In such a structure, the interweaving of triple left-handed homohelices was also found. It is worth noting that the helicity of complex **2** could be controlled by the handedness of the camphor-10-sulfonic acid. In complex **2**, there are right-handed helical structures, including single right-handed and triple right-handed helical structures connected by (−)-camphor-10-sulfonic acids. For a comparative study, (±)-camphor-10-sulfonic acids were utilized to synthesize complex **3**, in which equal numbers of right-handed or left-handed double-helical chains are created. All the complexes were characterized by single-crystal X-ray structure determination, powder X-ray diffraction, IR, TGA and element analysis. Circular dichroism spectra of complexes **1** and **2** were been studied to confirm the fact that enantiopure bridging ligands do not racemize.

Introduction

Increasing attention is being paid to the design and synthesis of homochiral solids because of their potential application in asymmetric catalysis,[1] enantioselective separation[2] and non-linear optics.[3] Recently, the flourishing research field of MOFs (metal–organic frameworks) has provided an avenue to construct homochiral crystalline solids by the availability of enantiopure bridging ligands.[4–10] Unfortunately, undesirable achiral crystalline solids are often obtained owing to ligand racemization.[11] Chiral MOFs can also be assembled by achiral ligands and metal ions; however, two phenomena hamper their potential application in enantioselective separation and asymmetric catalysis: one is that the single-crystals are racemic twins (Flack parameter = 0.5) rather than homochiral ones, although they crystallize in chiral space groups; the other is that the bulk materials tend to form conglomerates in which homochiral right-handed and left-handed molecules crystallize in equal proportion.[12,13] In such a system, homochiral bulk materials can be created by chiral catalysis induction, and then be tested by a combination of X-ray single-crystal diffraction and CD (circular dichroism) spectroscopy, which have been extensively investigated by Bu and Morris.[14,15] Therefore, in order to guarantee the homochirality of an individual single-crystal and bulk materials, enantiopure bridging ligands, which are not prone to racemization, can be utilized.[16]

Simultaneously, chirality and absolute helicity are often closely linked with each other in the same structure, although they are two distinct concepts.[17] Metal–organic frameworks also can provide a model to better understand the relationship between chirality and helicity. Camphorsulfonic acids are appropriate candidates because they integrate the merits of a quite inert chiral center with a good acceptor of hydrogen bonding (carbonyl group C═O). The latter merit possesses the potential function to regulate helicity through hydrogen bonding. Sulfonic acid prefers to coordinate with Ag^I ions rather than other transition metals (such as Fe^{2+}, Co^{2+}, Ni^{2+}), especially in the presence of auxiliary N-containing secondary ligands, which has been systematically investigated and elaborately elucidated by several groups.[18–25]

Herein, we report two homochiral silver camphor-10-sulfonic acid frameworks, $[Ag(L2)(L1)]_n$ (**1**) and $[Ag(L3)(L1)]_n$ (**2**) [L1 = 4-aminobenzoic acid, L2 = (+)-camphor-10-sulfonic anion, L3 = (−)-camphor-10-sulfonic anion] (Scheme 1), and one achiral silver camphor-10-sulfonic acid, $[Ag(L4)(L1)]_n$ (**3**), involving the racemic (±)-camphor-10-sulfonic acid ligand. It is worth noting that the orientation of homohelices could be regulated by the handedness of the camphor-10-sulfonic acid. Only right-handed (P) examples are found in complex **2**, unique left-handed (M) examples exist in complex **1**, while there are P and M examples in complex **3**.

State Key Laboratory of Rare Earth Resource Utilizations, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China. E-mail: pguo@ciac.jl.cn; Tel: +86 0431-85262941

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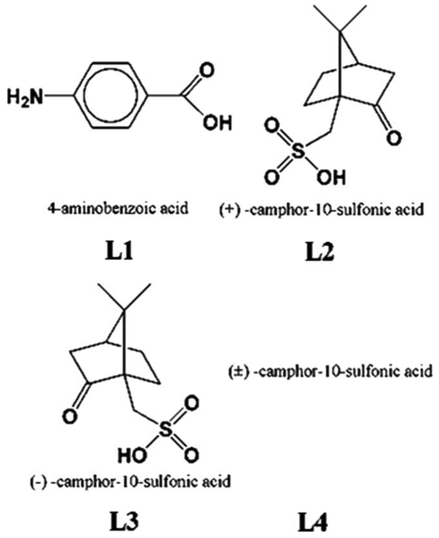

Scheme 1 The structures of the ligands in this work.

Experimental section

Materials

All the reagents and solvents employed were commercially available and used as received without further purification. All other reagents of analytical grade were purchased and used without further purification.

Physical measurements

IR spectra were obtained from KBr pellets on a Perkin-Elmer 580B IR spectrometer in the 400–4000 cm^{-1} region (SI). Elemental analyses (C, H and N) were performed using a VarioEL analyzer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TG-7 analyzer heated from 40 to 800 °C under nitrogen. Powder X-ray diffraction data were collected on a Bruker D8-AVANCE diffractometer equipped with Cu-Kα (λ = 1.5418 Å) radiation at a scan speed of 6° min^{-1}. Experimental patterns were in good agreement with the corresponding simulated ones, indicating the phase purity of the as-synthesized products.

Synthesis

Synthesis of complex 1. An aqueous solution (10 mL) of (+)-camphor-10-sulfonic acids (0.095 g, 0.5 mmol) was added to solid Ag_2CO_3 (0.069 g, 0.25 mmol) and stirred for several minutes until no further CO_2 was given off. 10 mL of ethanol containing 4-aminobenzoic acid (0.070 g, 0.5 mmol) was added to the aqueous solution. Colorless crystals of complex **1** were obtained by evaporation of the solution for 5 d at room temperature (52% yield). Anal. calc. for the complex **1** (M_r = 476.30): C, 42.87; H, 4.66; N, 2.94. Found: C, 43.10; H, 4.78; N, 3.01%.

Synthesis of complexes 2 and 3. These complexes were obtained by the same method with (–)-camphor-10-sulfonic acids and racemic camphor-10-sulfonic acids instead of (+)-camphor-10-sulfonic acids, respectively. Anal. calc. for the complex **2** (M_r = 476.30): C, 42.87; H, 4.66; N, 2.94. Found: C, 42.91; H, 4.72; N, 3.12%. Anal. calc. for the complex **3** (M_r = 476.30): C, 42.87; H, 4.66; N, 2.94. Found: C, 42.75; H, 4.56; N, 2.82%.

X-Ray Crystallography

The X-ray intensity data of compounds **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) operating at 2.0 kW (50 kV, 40 mA). The structures were solved by the direct method of SHELXS-97[26] and refined with full-matrix least-squares techniques using the SHELXL-97 program[27] within WINGX.[28] The hydrogen atoms attached to carbons and nitrogens were generated geometrically, while those attached to oxygens were located from difference Fourier maps and refined with isotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and details of the structure determination for complexes **1–3** are listed in Table 1. Selected bond lengths and angles are given in Table 2, and the hydrogen bonds for complexes **1–3** are described in Table 3.

Results and discussion

Description of the structure

Structure descriptions of complexes 1 and 2. Complex **1** crystallizes in chiral space group $P2_12_12_1$, and there is one crystallographically independent Ag^I ion, one L2 ligand and one L1 ligand. The Ag^I ion shows a distorted five coordinate square pyramidal configuration (ζ = 0.044)[29] with O2 and N1 atoms from the L1 ligand, and O3 and O5 atoms from the L2 ligand in a square configuration, and O3 from another L2 ligand in an apical position (Fig. 1). It is of particular interest to note that the left-handed 2_1 helices along the a axis are constructed from Ag^I ions and L1 ligands (Fig. 2). The bond angle of Ag1–N1–C1 (112.53(15)°) and the torsion angle of C1–N1–Ag1–O2 (28.54°) are mainly responsible for the construction of the left-handed 2_1 helix, with a pitch of about 6.252 Å, which is reinforced through O3 and O5 atoms from the L2 ligand. The unique μ_2-O3 atom from L2 makes a great contribution to form a 2D homochiral layer by the connection of adjacent homohelices along the b axis (Fig. 3(a)).

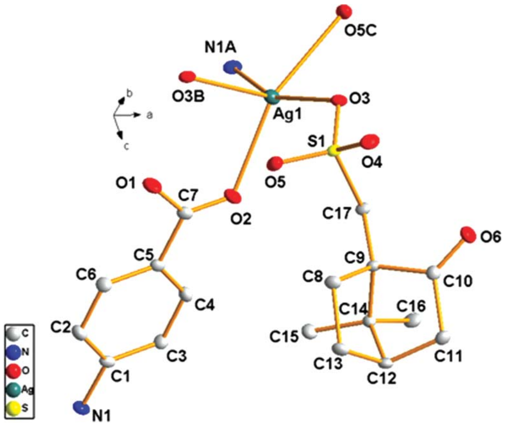

Fig. 1 A view of the local coordination of the Ag^I atom in complex **1**. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity [symmetry codes: (A) $x + \frac{1}{2}, -y - \frac{1}{2}, -z$; (B) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (C) $x + \frac{1}{2}, y - \frac{1}{2}, -z$].

Another interesting feature of complex **1** is the interweaving of triple left-handed homohelices, in which each single left-handed

Table 1 Crystal data and structure refinements for complexes **1–3**†

	Complex **1**	Complex **2**	Complex**3**
Empirical formula	$C_{17}H_{22}NO_6SAg$	$C_{17}H_{22}NO_6SAg$	$C_{17}H_{22}NO_6SAg$
F_w	476.30	476.30	476.30
Crystal size/mm	0.16 × 0.15 × 0.13	0.18 × 0.15 × 0.14	0.20 × 0.16 × 0.14
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
a/Å	6.2517(2)	6.2347(4)	15.1059(7)
b/Å	11.4326(4)	11.4209(7)	6.1847(3)
c/Å	24.1372(9)	24.0805(15)	18.7605(9)
α (°)	90	90	90
β (°)	90	90	97.099(1)
γ (°)	90	90	90
V/Å^3	1725.16(10)	1714.67(19)	1739.27(14)
Z	4	4	4
F(000)	967.9	967.9	967.9
θ range (°)	1.7–26.0	2.0–26.1	1.9–26.1
No. of parameters	238	238	238
No. of total reflections	9652	9634	9821
No. of unique reflections	3398	3412	3452
No. of observed $[I \geq 2\sigma(I)]$	3284	3088	2744
Flack parameter	0.06(2)	−0.01(3)	
R_{int}	0.0226	0.0413	0.0274
R_1 $[I > 2\sigma(I)]$	0.0205	0.0299	0.0280
wR_2 (all data)	0.0514	0.0565	0.0741
Largest residuals/e Å^{-3}	0.249/−0.362	0.434/−0.498	0.569/−0.547

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1–3**

Complex 1[a]			
O(2)–Ag(1)	2.4732(18)	O(3)–Ag(1)	2.3240(17)
O(5)–S(1)	1.4452(19)	Ag(1)–N(1)#2	2.3123(19)
O(3)–Ag(1)–O(2)	105.40(7)	C(1)–N(1)–Ag(1)#1	112.50(14)
N(1)#2–Ag(1)–O(2)	94.06(7)	N(1)#2–Ag(1)–O(3)	157.04(7)
Complex 2[b]			
N(1)–Ag(1)	2.309(3)	O(2)–Ag(1)#1	2.464(3)
O(3)–Ag(1)	2.320(2)	Ag(1)–O(2)#2	2.464(3)
C(7)–O(2)–Ag(1)#1	127.5(2)	N(1)–Ag(1)–O(3)	157.00(10)
N(1)–Ag(1)–O(2)#2	94.00(9)	O(3)–Ag(1)–O(2)#2	105.39(9)
Complex 3[c]			
N(1)–Ag(1)	2.282(2)	O(1)–Ag(1)#1	2.485(2)
O(3)–Ag(1)	2.305(2)	Ag(1)–O(1)#1	2.485(2)
N(1)–Ag(01)–O(3)	154.26(8)	N(1)–Ag(01)–O(1)#1	97.24(8)
O(3)–Ag(01)–O(1)#1	103.74(7)	C(7)–O(1)–Ag(01)#1	126.24(19)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x - \frac{1}{2}, -y - \frac{1}{2}, -z$; #2 $x + \frac{1}{2}, -y - \frac{1}{2}, -z$. [b] Symmetry transformations used to generate equivalent atoms: #1 $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; #2 $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$. [c] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z + 1$.

Table 3 Hydrogen bonds for complexes **1–3**

D–H···A	d(D–H/Å	d(H···A/Å	d(D···A/Å	<(DHA) (°)
Complex 1[a]				
N(1)–H(1A)···O(4)#3	0.92	2.34	3.109(3)	141.1
N(1)–H(1A)···O(6)#3	0.92	2.58	3.025(3)	110.4
O(1)–H(18)···O(3)#4	0.77(3)	1.98(3)	2.720(3)	163(3)
Complex 2[b]				
N(1)–H(1B)···O(4)#3	0.92	2.33	3.101(5)	141.1
N(1)–H(1B)···O(6)#3	0.92	2.58	3.025(4)	110.2
O(1)–H(1)···O(3)#4	0.80(4)	1.94(4)	2.716(3)	163(4)
Complex 3[c]				
N(1)–H(1A)···O(4)#2	0.92	2.29	3.150(3)	154.6
N(1)–H(1B)···O(6)#3	0.92	2.23	3.008(3)	142.5
O(2)–H(18)···O(3)#4	0.80(4)	1.91(4)	2.696(3)	170(3)

[a] Symmetry transformations used to generate equivalent atoms: #3 $x - 1, y - 1, z$; #4 $x - \frac{1}{2}, -y + \frac{1}{2}, -z$. [b] Symmetry transformations used to generate equivalent atoms: #3 $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; #4 $x, y + 1, z$. [c] Symmetry transformations used to generate equivalent atoms: #2 $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; #3 $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; #4 $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

helix around the crystallographic 2_1 axis has a repeat unit of two Ag^I ions, two L1 ligands, and O3, O5 and S1 atoms from L2 with a pitch of about 18.755 Å (Fig. 3(b)). Metal–ligand coordination interactions (O3–Ag1 2.3240(17) Å), allowing the left-handed helicity of the originally formed chains to be transferred uniformly, also could lead to the formation of a homochiral 2D sheet.

When (−)-camphor-10-sulfonic acid is used in place of (+)-camphor-10-sulfonic acid, complex **2**, with helices that are opposite to those in complex **1**, is obtained. This demonstrates that the absolute helicity in complexes **1** and **2** can be controlled by the absolute chirality of camphor-10-sulfonic acid. As a result, there are a single right-handed helix and triple right-handed homohelices in complex **2**, resembling structure of complex **1** (Fig. 4 and Fig. 5). Complexes **1** and **2** obtained here are good illustrations of the construction of helix-integrated rigid ligands with metal ions, which differ from the traditional strategy of helices built from flexible ligands.[30,31]

Structure description of complex 3. For a comparative study $[Ag(L4)(L1)]_n$ (**3**) was synthesized using L4 ligands. Albeit **1**, **2** and **3** (with the same formula) are isomeric, **3** crystallizes in a centrosymmetric crystal structure ($P2_1/n$) based on racemic (±)-camphor-10-sulfonic acid ligands, rather than a chiral space group. The coordination geometry for the five-coordinate Ag^I ion is close to a distorted square pyramidal configuration ($\zeta = 0.077$),[26] with a long Ag1–O5 (2.746 Å) bond that is slightly longer than the normal Ag–O range but is similar to other reported values.[19,20] It is of great interest to note that the Ag^I ion and the L4 ligand generate a closed circle, rather than a M or P helix as in complexes **1** and **2**, respectively. The closed circle is linked by μ_2-O3 atoms alternately

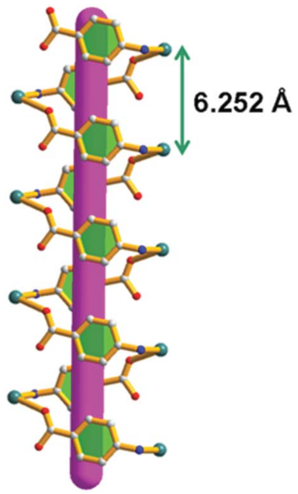

Fig. 2 A single left-handed helix along the a axis.

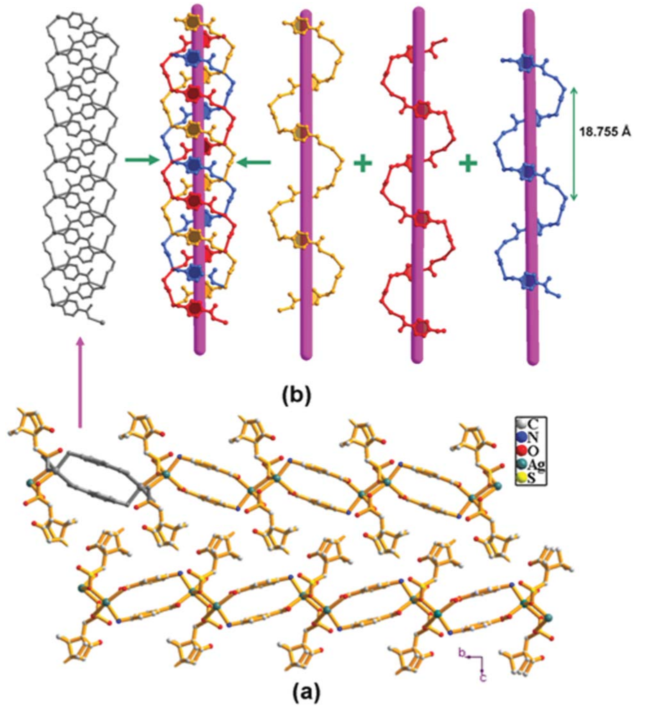

Fig. 3 (a) The 2D homochiral layer of complex **1**. (b) Interweaving of triple left-handed homohelices along the a axis.

of L2 and L3 to generate an achiral 2D layer (Fig. 6(a)). O3, O5 and S1 atoms, and the closed circle based on the Ag$^{\text{I}}$ ion and the L4 ligand, are incorporated to form equal numbers of double-helical chains, which are either left-handed double-stranded or right-handed double-stranded helices (Fig. 6(b), Fig. 7).

Influence of the chirality of the camphor-10-sulfonic acid

Although helicity and homochirality are intimately associated with living processes, their origin remains unclear.[17] The regulation of the revolving orientation of homohelices by the handedness of camphor-10-sulfonic acid may be attributed to the synergism of such hydrogen bonds as $\mathrm{N_{amino\ group}–H\cdots O_{carbonyl\ oxygen}}$ and $\mathrm{O_{carboxyl\ oxygen}–H\cdots O_{sulfonic\ acid}}$. $\mathrm{O_{carbonyl\ oxygen}}$ and $\mathrm{O_{sulfonic\ acid}}$ atoms are close to the chiral center of camphor-10-sulfonic acids, reflecting the chiral signal and transferring it into the Ag-L1 system. $\mathrm{N_{amino\ group}–H\cdots O_{carbonyl\ oxygen}}$ and $\mathrm{O_{carboxyl}–H\cdots O_{sulfonic\ acid}}$ hydrogen bonds may play dual roles in regulating the orientation of

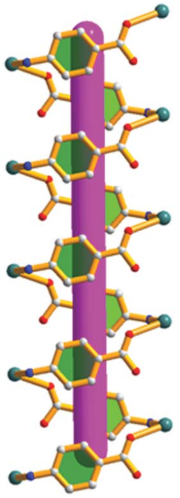

Fig. 4 The single right-handed helix along the a axis.

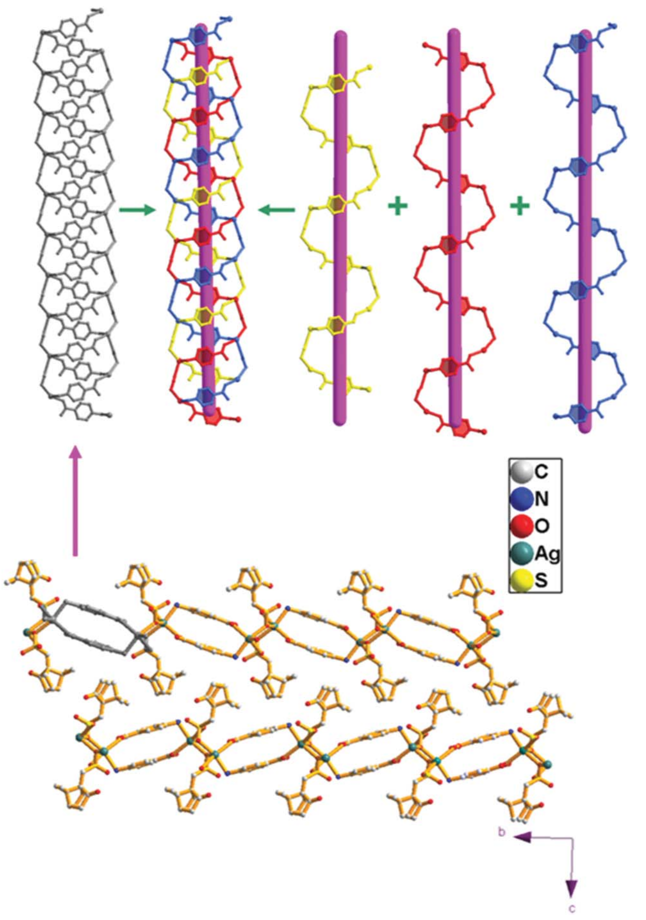

Fig. 5 (a) The 2D homochiral layer of complex **2**. (b) Interweaving of triple right-handed homohelices along the a axis.

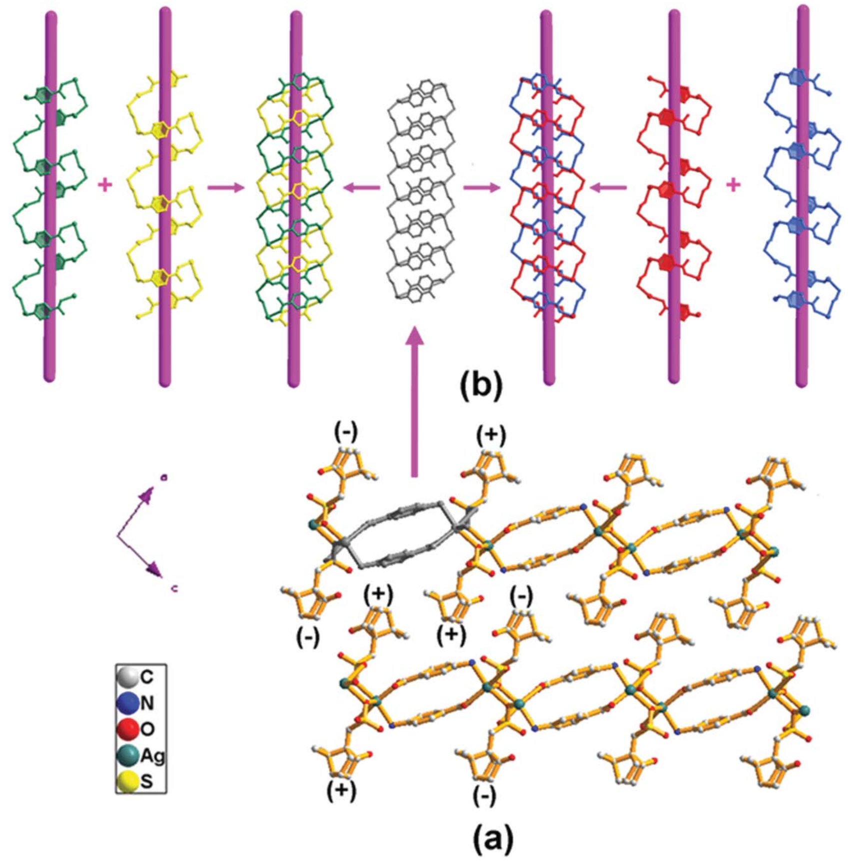

Fig. 6 (a) The 2D achiral layer of complex **3**. (b) Left-handed or right-handed double-stranded helices are found in complex **3**.

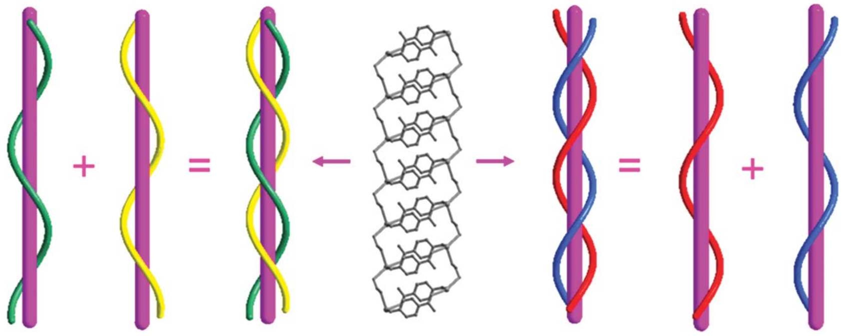

Fig. 7 A schematic diagram of left-handed double-stranded and right-handed double-stranded helices in complex **3**.

homohelices and strengthening them in this model. In complex **3**, L1 ligands and Ag ions form circles, which are maintained by $\mathrm{O_{carboxyl}{-}H\cdots O_{sulfonic\ acid}}$ and $\mathrm{N_{amino\ group}{-}H\cdots O_{carbonyl\ oxygen}}$ hydrogen bonds. However, the driving force from the hydrogen bonds is exactly the opposite for the circle because the chirality of the camphor-10-sulfonic acids coordinating with the circles are opposite (Fig. 8(a)). In complex **2**, (+)-camphor-10-sulfonic acid is used to break circles, leading to the formation of a single left-handed helix, which is also reinforced by $\mathrm{O_{carboxyl}{-}H\cdots O_{sulfonic\ acid}}$ and $\mathrm{N_{amino\ group}{-}H\cdots O_{carbonyl\ oxygen}}$ hydrogen bonds (Fig. 8(b)). This single left-handed helix is the backbone of the interweaving of triple left-handed homohelices. The single right-handed helix is created by the same driving force in complex **2**, where (−)-camphor-10-sulfonic acid is utilized (Fig. 8(c)).

Complexes **1** and **2** were also tested by CD (Fig. 9), which is widely used in the construction of chiral porous solids by the availability of achiral building blocks.[14] However, in this paper, it is used to detect whether the homochiral ligands happen to racemize or not. The CD spectra of complexes **1** and **2** in DMF (dimethylformamide) were investigated, revealing that, in the wavelength range λ = 270–450 nm, complex **1** shows a positive Cotton effect at λ = 298 nm, while complex **2** shows a negative one at the same wavelength. The results of CD show the fact that homochiral camphorsulfonic acids do not racemize and that the

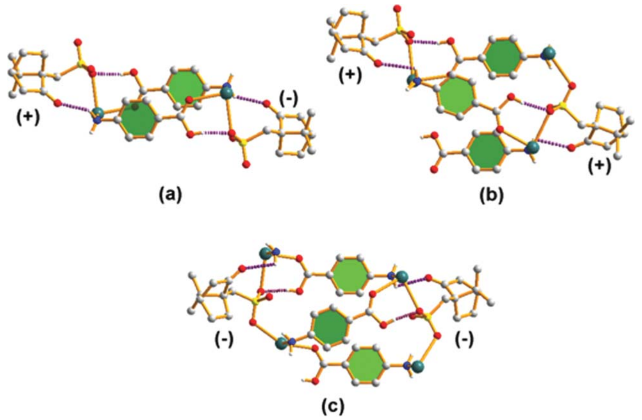

Fig. 8 (a) Hydrogen bonds in complex **3**. (b) Hydrogen bonds in complex **1**. (c) Hydrogen bonds in complex **2**.

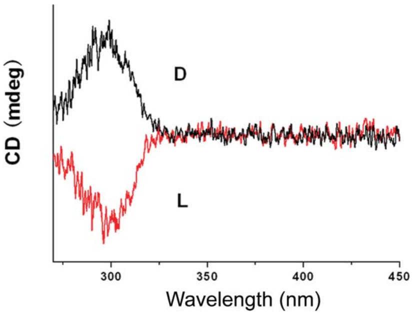

Fig. 9 The CD spectra of complexes **1** and **2** in DMF.

handedness of bulk materials can be controlled by the chirality of enantiopure bridging ligands.

Conclusion

In summary, complexes **1** and **2** were constructed from the assembly of left-handed and right-handed homohelices, respectively. The revolving orientation of the homohelices can be regulated by the handedness of camphor-10-sulfonic acid. For a comparative study and to better understand how the helicity is controlled, the racemic (±)-camphor-10-sulfonic acid ligand was utilized to generate left-handed or right-handed helices. This is a good model to mimic living systems and understand the relationship between chirality and helicity.

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