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The Supramolecular Isomerism Based on Argentophilic Interactions: The Construction of Helical Chains with Defined Right-Handed and Left-Handed Helicity

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The reactions of racemic and enantiopure macrocyclic compounds [Ni(α-*rac*-L)](ClO_4)$_2$ (containing equal amounts of *SS* and *RR* enantiomers), [Ni(α-*SS*-L)](ClO_4)$_2$, and [Ni(α-*RR*-L)](ClO_4)$_2$ with K[Ag(CN)$_2$] in acetonitrile/water afford three 1D helical chains of {[Ni(*f*-*rac*-L)][Ag(CN)$_2$]$_2$}$_n$ (**1**), {[Ni(*f*-*SS*-L)]$_2$[Ag(CN)$_2$]$_4$}$_n$ (Δ-**2**), and {[Ni(*f*-*RR*-L)]$_2$[Ag(CN)$_2$]$_4$}$_n$ (Λ-**2**); one dimer of [Ni(*f*-*rac*-L)][Ag(CN)$_2$]$_2$ (**3**); and one trimer of [Ni(*f*-*rac*-L)Ag(CN)$_2$]$_3$·(ClO_4)$_3$ (**4**) (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). Compounds **1**, Δ-**2**, Λ-**2**, and **3**, which are supramolecular isomers, are constructed via argentophilic interactions. In **1**, [Ni(*f*-*RR*-L)][Ag(CN)$_2$]$_2$ enantiomers alternately connect with [Ni(*f*-*SS*-L)][Ag(CN)$_2$]$_2$ enantiomers through intermolecular argentophilic interactions to form a 1D meso-helical chain, and the 1D chains are further connected through the interchain hydrogen bonds to generate a 2D network. When chiral [Ni(α-*SS*-L)](ClO_4)$_2$ and [Ni(α-*RR*-L)](ClO_4)$_2$ were used as building blocks, two supramolecular stereoisomers of Δ-**2** and Λ-**2** were obtained, which show the motif of homochiral right-handed and left-handed helical chains, respectively, and the 1D homochiral helical chains are linked by the interchain hydrogen bonds to form a 3D structure. In **3**, a pair of enantiomers of [Ni(*f*-*RR*-L)][Ag(CN)$_2$]$_2$ and [Ni(*f*-*SS*-L)][Ag(CN)$_2$]$_2$ connect with each other through intermolecular argentophilic interactions to form a dimer. The reaction of [Ni(α-*rac*-L)](ClO_4)$_2$ with K[Ag(CN)$_2$] in acetonitrile gives a trimer of **4**; each trimer is chiral with unsymmetrical *RR*, *RR*, and *SS*, or *RR*, *SS*, and *SS* configurations. The homochiral nature of Δ-**2** and Λ-**2** was confirmed by the results of solid circular dichroism spectra measurements. The solid samples of **1**−**4** show strong fluorescent emissions at room temperature.

Introduction

In the past decade, the designed constructions of metal-organic supramolecular isomers have gained considerable attention in the field of molecular architecture.[1] For given building blocks, different arrangements of these building blocks can lead to the formation of a series of supramolecular isomers. Among the construction approaches, the combination of metal−ligand coordination and secondary noncovalent interactions such as hydrogen-bonding, electrostatic, and π−π interactions between moieties into a supramolecular system is a well-developed method for increasing structure dimensionality.[2−4] Recently, much interest has been focused on the architectures of helical coordination polymers using

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chiral[5] or achiral[6] building blocks, as many important biopolymers such as DNA and peptides possess a helical motif with a single right-handed chirality. In our previous reports,[7,8] a series of 1D helical chains has been constructed via coordination interactions between [Ni(α-*rac*-L)]$^{2+}$ and $[Ni(CN)_4]^{2-}$, or the hydrogen-bond linking of [Ni(*f*-*SS*-L)(*l*-Phe)]$^{+}$ or [Ni(*f*-*RR*-L)(*d*-Phe)]$^{+}$ monomers, while the hydrogen-bond linking of [Ni(*f*-*SS*-L)(*d*-Phe)]$^{+}$ or [Ni(*f*-*RR*-L)(*l*-Phe)]$^{+}$ monomers gave 1D zigzag chains instead of 1D helical chains.[8]

As a continuation of our research on the constructions of chiral helical chains, our interest has been focused on another constructing approach, the ligand-unsupported argentophilic interactions. Although the closed-shell d^{10} configuration of silver(I) tends to cancel any intermetallic bonding in silver(I) complexes, many examples of dimeric or polymeric silver(I) complexes constructed by Ag···Ag interactions have been reported to prove the existence of argentophilicity.[9−11] However, almost all of the argentophilic interactions (Ag(I)···Ag(I) < 3.4 Å) in dimeric or polymeric silver(I) complexes are typically maintained by bridging ligands.[12] Instances for ligand-unsupported Ag···Ag interactions based on structural determinations are scarce.[13,14] 1D helical chains constructed by Ag···Ag argentophilic interactions using macrocyclic compounds as building blocks have not been reported so far. Herein, we report on four supramolecular isomers of {[Ni(*f*-*rac*-L)][Ag(CN)$_2$]$_2$}$_n$ (**1**), {[Ni(*f*-*SS*-L)]$_2$[Ag(CN)$_2$]$_4$}$_n$ (Δ-**2**), {[Ni(*f*-*RR*-L)]$_2$[Ag(CN)$_2$]$_4$}$_n$ (Λ-**2**), and [Ni(*f*-*rac*-L)][Ag(CN)$_2$]$_2$ (**3**), which are constructed via intermolecular argentophilic interactions, and a trimer of [Ni(*f*-*rac*-L)Ag(CN)$_2$]$_3$·(ClO$_4$)$_3$ (**4**). The results exhibit how the different chirality of building blocks, which is related to the helicity of 1D chains, and how the supramolecular isomerism are induced by solvents.

Experimental Section

The macrocyclic ligand (L) and its nickel(II) complex were prepared according to literature methods[15] and separated as the racemic form *rac*-L. The nickel(II) complexes [Ni(α-*RR*-L)](ClO$_4$)$_2$ and [Ni(α-*SS*-L)](ClO$_4$)$_2$ were prepared according to previously reported methods.[8] All of the other chemicals were commercially available and used without further purification. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000∼400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. Electrospray ionization (ESI) mass spectra were performed on a Thermo Finigan LCQ DECA XP ion trap mass spectrometer in acetonitrile. The solid-state (KBr pellets) circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. The fluorescent spectra study was carried out on powdered samples at room temperature using an Edingburgh FLS 920 spectrometer.

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with care and prepared only in small quantities.*

{[Ni(*f*-*rac*-L)][Ag(CN)$_2$]$_2$}$_n$ (1). A solution of [Ni(α-*rac*-L)](ClO$_4$)$_2$ (54 mg, 0.1 mmol) in acetonitrile (8 mL) was added to a water solution (1 mL) of K[Ag(CN)$_2$] (38 mg, 0.2 mmol). The resulting solution was evaporated slowly at room temperature. After 3 days, purple prismatic crystals of **1**·(H$_2$O)$_n$ were isolated from the solution. Yield: 41 mg, 60%. Anal. calcd for $C_{20}H_{38}Ag_2N_8NiO$: C, 35.27; H, 5.62; N, 16.45. Found: C, 35.43; H, 5.64; N, 16.21%. IR (KBr): 3468, 3273, 3212, 2937, 2162 (ν_{CN}, coordinated), 2143 (ν_{CN}, uncoordinated), 1591, 1449, 1169, 1081, 1042, 964, 816 cm^{-1}. Occasionally, a few crystals of **1**·(H$_2$O·MeCN)$_n$ were found

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Table 1. Crystal Data and Structure Refinements for **1**∼**4**

compound	**1**·$(H_2O)_n$	**1**·$(H_2O·MeCN)_n$	**Δ-2**·$(H_2O)_{2n}$	**Λ-2**·$(H_2O)_{2n}$	**3**·MeCN	**4**·2.5MeCN
formula	$C_{20}H_{38}Ag_2N_8NiO$	$C_{22}H_{41}Ag_2N_9NiO$	$C_{40}H_{76}Ag_4N_{16}Ni_2O_2$	$C_{40}H_{76}Ag_4N_{16}Ni_2O_2$	$C_{22}H_{39}Ag_2N_9Ni$	$C_{59}H_{115.5}Ag_3Cl_3N_{20.5}Ni_3O_{12}$
fw	681.03	722.09	1362.07	1362.07	704.07	1910.31
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*Pca*2/1	$P2_1/n$	$P2_1$	$P2_1$	$P2_1/c$	$P\bar{1}$
cryst size (mm)	0.37 × 0.32 × 0.18	0.40 × 0.33 × 0.31	0.31 × 0.21 × 0.15	0.31 × 0.15 × 0.12	0.42 × 0.40 × 0.37	0.40 × 0.37 × 0.24
a (Å)	12.744(3)	10.708(1)	10.267(6)	10.294(5)	9.578(2)	15.910 (2)
b (Å)	12.330(3)	27.274(1)	13.853(8)	13.873(7)	17.527(4)	16.474 (1)
c (Å)	17.508(4)	10.707(1)	19.38(1)	19.47(1)	17.772(4)	20.024 (2)
α (deg)	90	90	90	90	90	94.159(6)
β (deg)	90	108.296(1)	96.84(1)	96.916(9)	103.326(4)	106.730(7)
γ (deg)	90	90	90	90	90	118.455(8)
V (Å^3)	2751.3(12)	2968.9(4)	2736(3)	2760(2)	2903(1)	4279.7(7)
Z/D_{calcd} (g cm^{-3})/μ (mm^{-1})	4/1.644/2.113	4/1.615/1.964	2/1.653/2.124	2/1.639/2.106	4/1.611/2.004	2/1.482/1.475
max/min. transmission	0.7023/0.5086	0.5811/0.5072	0.7411/0.5588	0.7861/0.5613	0.5243/0.4866	0.7185/0.5899
reflns collected	13160	11534	13743	9527	15739	29475
unique reflns (R_{int})	5677(0.0592)	5661(0.0679)	9249(0.0625)	7734(0.0661)	6307 (0.0379)	15979 (0.0382)
GOF	1.059	0.906	1.031	1.000	1.035	0.955
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0453, 0.0922	0.0380, 0.0824	0.0600, 0.1044	0.0602, 0.0879	0.0312, 0.0611	0.0588, 0.1433
R_1,[a] wR_2[b] (all data)	0.0838, 0.1175	0.0590, 0.0862	0.1577, 0.1379	0.1375,0.1076	0.0549, 0.0678	0.0932, 0.1555

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

coexisting with **1**·$(H_2O)_n$, in which the crystal parameters of **1**·$(H_2O·MeCN)_n$ were different from those of **1**·$(H_2O)_n$ (see Table 1).

{[Ni(*f*-*SS*-L)]$_2$[Ag(CN)$_2$]$_4$}$_n$ (Δ-2) and {[Ni(*f*-*RR*-L)]$_2$[Ag(CN)$_2$]$_4$}$_n$ (Λ-2). The use of [Ni(α-*SS*-L)]$(ClO_4)_2$ and [Ni(α-*RR*-L)]$(ClO_4)_2$ in a procedure analogous to that detailed for the preparations of **1** afforded 36 mg (53%) and 31 mg (45%) of purple prismatic crystals of **Δ-2**·$(H_2O)_{2n}$ and **Λ-2**·$(H_2O)_{2n}$, respectively. Anal. calcd for $C_{40}H_{76}Ag_4N_{16}Ni_2O_2$ (**Δ-2**·$(H_2O)_{2n}$): C, 35.27; H, 5.62; N, 16.45. Found: C, 35.41; H, 5.78; N, 16.58%. IR (KBr): 3460, 3271, 3213, 2966, 2159 (ν_{CN}, coordinated), 2141 (ν_{CN}, uncoordinated), 1628, 1449, 1169, 1080, 1041, 962, 815 cm^{-1}. Anal. calcd for $C_{40}H_{76}Ag_4N_{16}Ni_2O_2$ (**Λ-2**·$(H_2O)_{2n}$): C, 35.27; H, 5.62; N, 16.45. Found: C, 35.38; H, 5.58; N, 16.35%. IR (KBr): 3419, 3271, 3215, 2966, 2159 (ν_{CN}, coordinated), 2140 (ν_{CN}, uncoordinated), 1627, 1447, 1168, 1081, 1044, 962, 815 cm^{-1}.

[Ni(*f*-*rac*-L)][Ag(CN)$_2$]$_2$ (3). A solution of [Ni(α-*rac*-L)]$(ClO_4)_2$ (54 mg, 0.1 mmol) in acetonitrile (25 mL) was added to a water solution (1 mL) of K[Ag(CN)$_2$] (38 mg, 0.2 mmol). The resulting solution was evaporated slowly at room temperature. After about 2 weeks, purple block-shaped crystals of **3**·MeCN were obtained at the bottom of the solution. Yield: 36 mg, 53%. Anal. calcd for $C_{22}H_{39}Ag_2N_9Ni$ (**3**·MeCN): C, 37.53; H, 5.58; N, 17.91. Found: C, 37.55; H, 5.57; N, 18.15%. IR (KBr): 3468, 3273, 3212, 2949, 2162 (ν_{CN}, coordinated), 2143 (ν_{CN}, uncoordinated), 1591, 1484, 1449, 1169, 1081, 1042, 964, 816 cm^{-1}.

[Ni(*f*-*rac*-L)Ag(CN)$_2$]$_3$·$(ClO_4)_3$ (4). A solution of [Ni(α-*rac*-L)]$(ClO_4)_2$ (54 mg, 0.1 mmol) in acetonitrile (5 mL) was added to a stirring suspended solution of K[Ag(CN)$_2$] (38 mg, 0.2 mmol) in acetonitrile (10 mL). The resulting purple solution was filtered and evaporated slowly at room temperature. After 2 days, purple-red prismatic crystals of **4**·2.5MeCN were obtained at the bottom of the solution. Yield: 46 mg, 53%. Anal. calcd for $C_{59}H_{115.5}Ag_3Cl_3N_{20.5}Ni_3O_{12}$ (**4**·2.5MeCN): C, 37.10; H, 6.09; N, 15.03. Found: C, 36.84; H, 5.90; N, 14.92%. IR (KBr): 3459, 3257, 2971, 2169 (ν_{CN}, coordinated), 1640, 1483, 1459, 1170, 1095, 959, 817, 623 cm^{-1}.

X-Ray Structure Determination. Single-crystal X-ray diffraction data for **1**−**4** were collected on a Bruker Smart 1000 CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). The empirical absorption corrections were applied using the SADABS program.[16] The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All of the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of the water molecules in **1** and **2** were located in the difference Fourier maps and refined isotropically. In the asymmetric unit of **4**·2.5MeCN, one and a half MeCN molecules and two ClO_4^- anions are disordered. For the disordered MeCN molecules, the carbon−carbon and nitrogen−carbon distances were fixed according to those of one disordered MeCN molecule, and the disordered carbon and nitrogen atoms were refined isotropically. The occupancies were converged to the ratios of 80:20 and 35:15 for one and a half disordered MeCN molecules, respectively. For the disordered ClO_4^- anions, the Cl−O distances and temperature factors were also restrained. The two disordered ClO_4^- anions were modeled with 50:20:20:10 occupancy of the four orientations (Cl(1), Cl(1′), Cl(1A), and Cl(1B)) and 32:68 occupancy of the two orientations (Cl(2) and Cl(2′)). All calculations were performed using the SHELXTL system of computer programs.[17] The crystallographic data for **1**−**4** are summarized in Table 1. The Ag···Ag distances of **1**−**3** are listed in Table 2, and the other selected bond lengths and angles of **1**−**4** are listed in the Supporting Information (Table S1).

Results and Discussion

Preparation Chemistry. The reactions of [Ni(α-*rac*-L)]$(ClO_4)_2$, [Ni(α-*SS*-L)]$(ClO_4)_2$, and [Ni(α-*RR*-L)]$(ClO_4)_2$ with K[Ag(CN)$_2$] in a molar ratio of 1:2 in acetonitrile/water (8:1) mixture afford three novel 1D helical chains of **1**, **Δ-2**, and **Λ-2**, respectively. The reactions of [Ni(α-*rac*-L)]$(ClO_4)_2$ with K[Ag(CN)$_2$] in the same molar ratio in acetonitrile/water (25:1) and pure acetonitrile generate two polymeric

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Table 2. The Ag···Ag Distances (Å) in **1**−**3**[a]

1·$(H_2O)_n$	Ag(1)−Ag(2)#1	3.0481(12)	Ag(2)−Ag(1)#2	3.0481(12)		
1·$(H_2O\cdot MeCN)_n$	Ag(1)−Ag(2)#1	2.9956(7)	Ag(2)−Ag(1)#2	2.9956(7)		
Δ-**2**·$(H_2O)_{2n}$	Ag(1)−Ag(3)#1	3.066(2)	Ag(3)−Ag(1)#2	3.066(2)	Ag(2)−Ag(4)	3.353(3)
Λ-**2**·$(H_2O)_{2n}$	Ag(1)−Ag(3)#1	3.073(2)	Ag(3)−Ag(1)#2	3.073(2)	Ag(2)−Ag(4)	3.327(2)
3·2.5MeCN	Ag(1)−Ag(2)#1	3.2479(6)	Ag(2)−Ag(1)#1	3.2479(6)		

[a] Symmetry transformations used to generate equivalent atoms. For **1**·$(H_2O)_n$: (#1) $x - 1/2, -y + 2, z$; (#2) $x + 1/2, -y + 2, z$. For **1**·$(H_2O\cdot MeCN)_n$: (#1) $x - 1/2, -y + 1/2, z - 1/2$; (#2) $x + 1/2, -y + 1/2, z + 1/2$. For Δ-**2**: (#1) $-x + 2, y - 1/2, -z + 1$; (#2) $-x + 2, y + 1/2, -z + 1$. For Λ-**2**: (#1) $-x + 2, y + 1/2, -z$; (#2) $-x + 2, y - 1/2, -z$. For **3**: (#1) $-x + 2, -y + 1, -z + 2$.

metal rings, a dimer of **3** and a trimer of **4**. Interestingly, **1** could be converted to **3** in DMF/acetonitrile (1:25), and **3** could be converted to **1** in acetonitrile/water (8:1), and these conversions are easy to distinguish by the shape of crystals of **1** and **3** (see Figure 1). The results of ESI-MS measurements (see Figure S1, Supporting Information) indicate that the conversions between **1** and **3** are in equilibrium in solution. At a higher ratio of MeCN/H_2O (25:1), isomer **3** was isolated from the solution due to its low solubility in this solution. At a lower ratio of MeCN/H_2O (8:1), the solubility of **3** was increased, thus isomer **3** formed but did not crystallize out from the solution, and it was converted to the less soluble isomer **1**. This indicates that the supramolecular isomerism and the formations of isomers **1** and **3** are rather dependent on their solubility. A similar case has also been found in our previous studies,[7b,c] in which the isomer of molecular square $\{[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]\}_2$ prefers to isolate from a higher ratio of MeCN/H_2O (≥ 1) solution, while the isomer of 1D helical chain $\{[Ni(f\text{-}rac\text{-}L)][Ni(CN)_4]\}_n$ was isolated from a lower ratio of MeCN/H_2O (<0.5) solution. Likewise, when the crystals of **4** were not isolated from the mother liquor, and left there in an open vessel, all of the crystals of **4** were transformed to **3** due to the introduction of atmospheric moisture into the solution.

The IR spectra show two absorption bands at about 2160(2) and 2141(2) cm^{-1} in **1**·$(H_2O)_n$, Δ-**2**, Λ-**2**, and **3**, indicating the coexistence of coordinated (to Ni^{2+}) and uncoordinated cyano groups. Compound **4** only shows one absorption band at 2169 cm^{-1}, indicating that all of the CN groups are coordinated to Ni(II).

Crystal Structures of 1 and 3. It is interesting to note that **1** crystallizes from the same solution containing different solvents,**1**·$(H_2O)_n$ and **1**·$(H_2O\cdot MeCN)_n$, Both **1**·$(H_2O)_n$ and **1**·$(H_2O\cdot MeCN)_n$ possess the same structures of $\{[Ni(f\text{-}rac\text{-}L)][Ag(CN)_2]_2\}_n$ (**1**), in which the asymmetric unit contains one monomer of $[Ni(f\text{-}RR\text{-}L)][Ag(CN)_2]_2$ (Figure 2a) or $[Ni(f\text{-}SS\text{-}L)][Ag(CN)_2]_2$ (Figure 2b), and Ni(II) displays a distorted octahedral geometry by coordinating with four nitrogen atoms of the macrocyclic ligand L in a folded conformation, and two nitrogen atoms of two $[Ag(CN)_2]^-$ in cis positions. In **1**, $[Ni(f\text{-}RR\text{-}L)][Ag(CN)_2]_2$ enantiomers alternately connect with $[Ni(f\text{-}SS\text{-}L)][Ag(CN)_2]_2$ enantiomers through intermolecular argentophilic interactions to form a 1D achiral meso-helical chain[6g] (Figure 1b), with Ag···Ag distances of 3.048(1) Å in **1**·$(H_2O)_n$ (Figure 1b) and 2.996(1) Å in **1**·$(H_2O\cdot MeCN)_n$. In **1**·$(H_2O)_n$ and **1**·$(H_2O\cdot MeCN)_n$, the water molecules locate between the meso-helical chains, and the adjacent chains are connected through the interchain hydrogen bonds between water molecules and the terminal nitrogen atoms of the cyano groups and the secondary amines of L, generating a 2D network (Figure S2 and Table S1, Supporting Information). It is interesting to note that **1**·$(H_2O)_n$ crystallizes in a noncentrosymmetric space group $Pca2/_1$, in which all of the 1D chains are packed parallel via interchain hydrogen bonds (Figure 1c). Complex **1**·$(H_2O\cdot MeCN)_n$ crystallizes in a centrosymmetric space group, $P2_1/n$, in which the 1D chains are arranged antiparallel

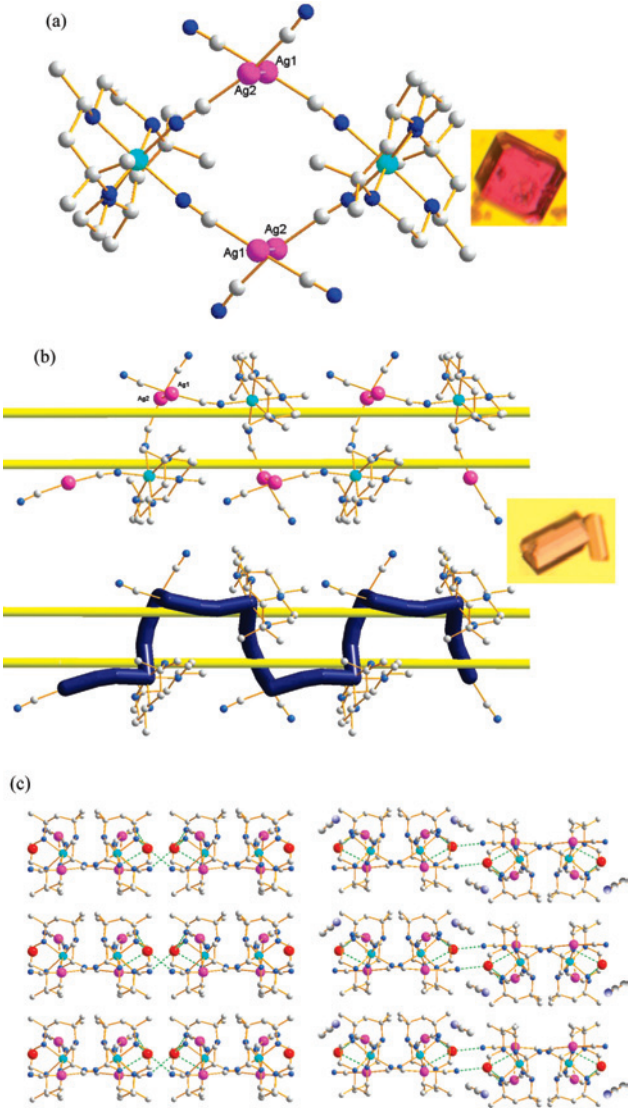

Figure 1. Two supramolecular isomers of (a) a dimer of **3** containing a pair of enantiomers of $[Ni(f\text{-}RR\text{-}L)][Ag(CN)_2]_2$ and $[Ni(f\text{-}SS\text{-}L)][Ag(CN)_2]_2$ (left) and a photograph of a single crystal of **3** (right) and (b) a 1D meso-helical chain in **1** constructed via argentophilic interactions (left; the yellow lines are a guide) and a photograph of a single crystal of **1**·$(H_2O)_n$ (right). (c) The two different packing arrangements in **1**·$(H_2O)_n$ (left) and **1**·$(H_2O\cdot MeCN)_n$ (red balls represent H_2O; H atoms are omitted for clarity).

as a result of the acetonitrile molecules filling in the void between the helical chains (Figure 1c).

The asymmetric unit in **3** also contains a monomer of [Ni(*f*-*RR*-L)][Ag(CN)$_2$]$_2$ (Figure 2a) or [Ni(*f*-*SS*-L)][Ag(CN)$_2$]$_2$ (Figure 2b), and a pair of enantiomers of [Ni(*f*-*RR*-L)][Ag(CN)$_2$]$_2$ and [Ni(*f*-*SS*-L)][Ag(CN)$_2$]$_2$ are connected with each other through argentophilic interactions to form a dimer, with a Ag···Ag distance of 3.248(1) Å (Figure 1a). The assembly of a pair of enantiomers with opposite chirality results in the crystallization of **3** in a centrosymmetrical space group, $P2_1/c$. Compounds **1** and **3** are supermolecular isomers. The conversion process from the discrete closed structure of **3** to the helical structure of **1** can be described as ring-opening polymerization or ring-opening isomerism.[1d,20,21]

Crystal Structures of Δ-2, Λ-2, and 4. The reactions of [Ag(CN)$_2$]$^-$ with enantiomers [Ni(α-*SS*-L)](ClO$_4$)$_2$ and [Ni(α-*RR*-L)](ClO$_4$)$_2$gave two supramolecular stereoisomers of Δ-**2** and Λ-**2**, respectively. Complexes Δ-**2** and Λ-**2** can also be regarded as supramolecular isomers with **1** and **3**, as they possess the same compositions and different structures. In contrast to **1**·(H$_2$O)$_n$, both Δ-**2** and Λ-**2** crystallize in a chiral space group, $P2_1$, with the absolute configuration parameters of 0.01(4) and 0.02(4), respectively. Complexes Δ-**2** and Λ-**2** both possess 1D homochiral helical chain structures with defined right-handed and left-handed helicity for Δ-**2** and Λ-**2**, respectively. In Δ-**2**, two {[Ni(*f*-*SS*-L)][Ag(CN)$_2$]}$^+$ cations are bridged by a μ_2-[Ag(CN)$_2$]$^-$ to form a {[Ni(*f*-*SS*-L)]$_2$[Ag(CN)$_2$]$_3$}$^+$ cation (Figure 3a), each Ni(II) is coordinated to four nitrogen atoms of L in a folded conformation, and two nitrogen atoms of two [Ag(CN)$_2$]$^-$ anions in cis positions. The {[Ni(*f*-*SS*-L)]$_2$[Ag(CN)$_2$]$_3$}$^+$ cations are connected through intermolecular argentophilic interactions between Ag(1) in one cation and Ag(3) in an adjacent cation to form a 1D right-handed helical chain (Figure 3b), with a Ag···Ag distance of 3.066(2) Å. Each uncoordinated [Ag(CN)$_2$]$^-$ interacts with one {[Ni(*f*-*SS*-L)]$_2$[Ag(CN)$_2$]$_3$}$^+$ through intermolecular argentophilic interactions between Ag(2) in the cation and Ag(4) in the anion, with a Ag···Ag distance of 3.353(3) Å. A 1D left-handed homochiral helical chain is generated by the connections of corresponding {[Ni(*f*-*RR*-L)]$_2$[Ag(CN)$_2$]$_3$}$^+$ in Λ-**2** through the same intermolecular argentophilic interactions, with a Ag···Ag distance of 3.073(2) Å. This demonstrates that the helicity of a 1D chain is dependent on the chirality of its building blocks; under the same preparation conditions, the reactions of racemic [Ni(α-*rac*-L)]$^{2+}$ and enantiopure [Ni(α-*SS*-L)]$^{2+}$ and [Ni(α-*RR*-L)]$^{2+}$ with [Ag(CN)$_2$]$^-$ generate a meso- and a homochiral right-handed and left-handed helical chain, respectively.

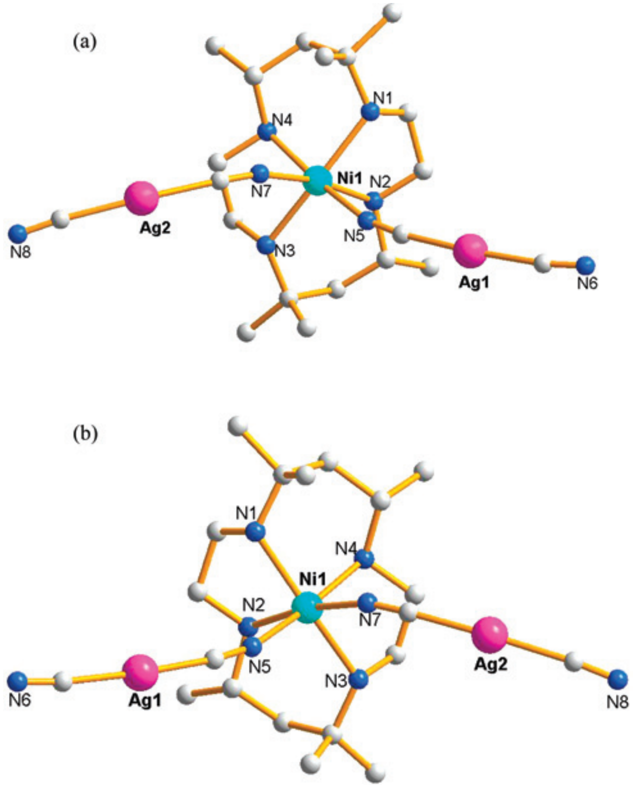

Figure 2. The enantiomers of (a) [Ni(*f*-*RR*-L)][Ag(CN)$_2$]$_2$ and (b) [Ni(*f*-*SS*-L)][Ag(CN)$_2$]$_2$ in **1**·(H$_2$O)$_n$ and **3** (H atoms are omitted for clarity).

Similar to **1**·(H$_2$O)$_n$ and **1**·(H$_2$O·MeCN)$_n$, the water molecules in Δ-**2**·(H$_2$O)$_{2n}$ and Λ-**2**·(H$_2$O)$_{2n}$ also locate between the adjacent helical chains, and O(2W) connects the adjacent 1D helical chains through the interchain hydrogen bonds between water molecules and the terminal nitrogen atoms of the cyano groups and the secondary amine of L, generating a 2D sheet. The 2D sheets are further connected through the interlayer hydrogen bonds between O(1W) and two terminal nitrogen atoms of uncoordinated [Ag(CN)$_2$]$^-$ anions to form a 3D network (Figure S3 and Table S1, Supporting Information).

It has been found that using racemic or achiral building blocks often leads to the formation of either a meso compound containing an equal amount of right-handed and left-handed helices[7b,19] or a racemic conglomerate of homochiral crystals as a result of a spontaneous resolution process.[20] The structure of the 1D meso-helical chain of **1**·(H$_2$O)$_n$ can fall into the first situation, with pairs of enantiomers coexisting within a chain. To obtain homochiral helical chains with defined right-handed or left-handed helicity, it is necessary to use chiral building

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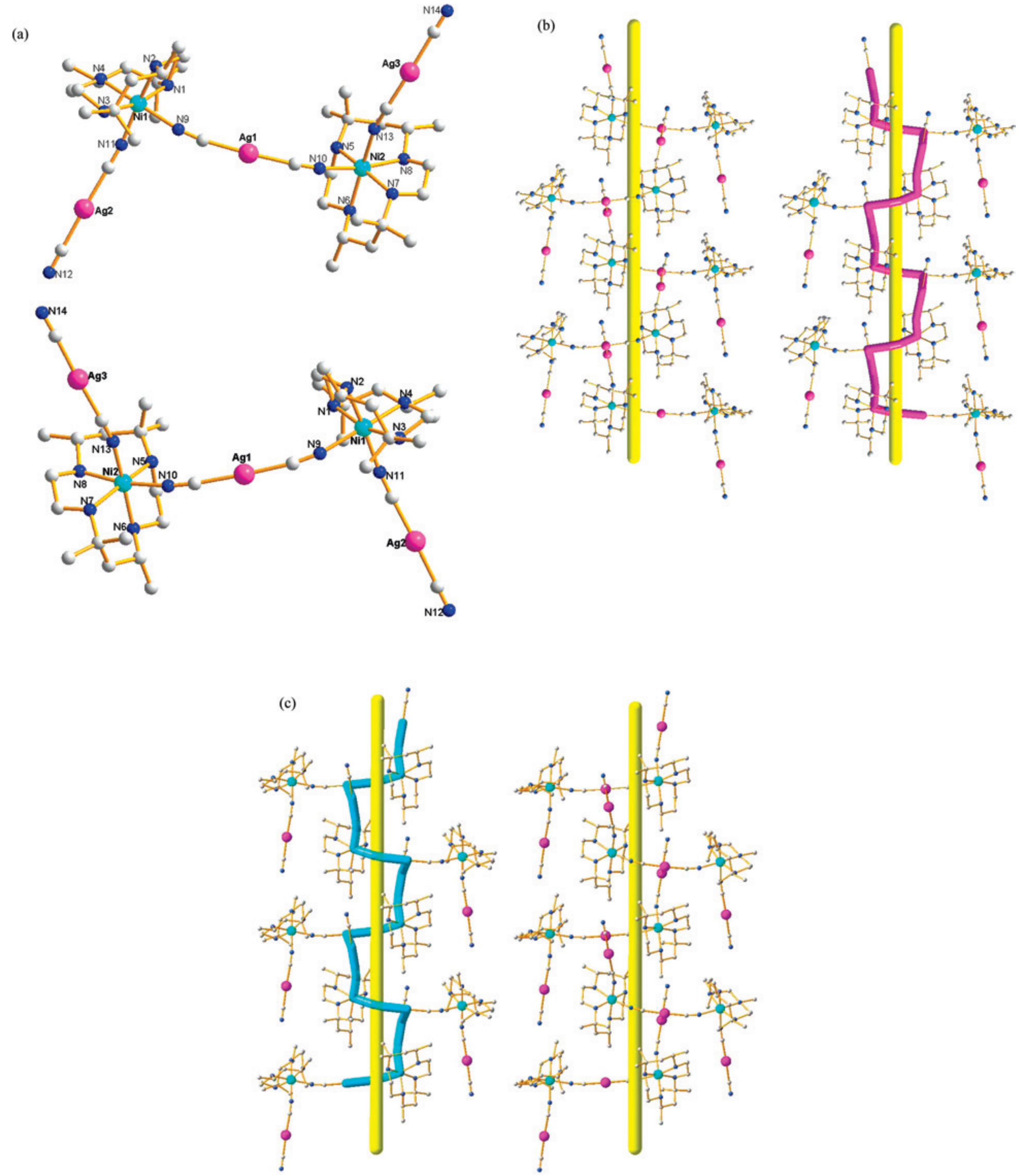

Figure 3. (a) The structures of $\{[\mathrm{Ni}(f\text{-}SS\text{-L})]_2[\mathrm{Ag(CN)}_2]_3\}^+$ in Δ-**2** (top) and $\{[\mathrm{Ni}(f\text{-}RR\text{-L})]_2[\mathrm{Ag(CN)}_2]_3\}^+$ in Λ-**2** (bottom). (b) Side view of 1D right-handed helical chain in Δ-**2**, and (c) side view of 1D left-handed helical chain in Λ-**2** (yellow lines are a guide; H atoms, water molecules, and uncoordinated $[\mathrm{Ag(CN)}_2]^-$ anions are omitted for clarity).

blocks as starting materials, and the reaction of $[\mathrm{Ni}(f\text{-}SS\text{-L})]^{2+}$ with $[\mathrm{Ag(CN)}_2]^-$ gives 1D homochiral helical chains with right-handed helicity, while the reaction of $[\mathrm{Ni}(f\text{-}RR\text{-L})]^{2+}$ with $[\mathrm{Ag(CN)}_2]^-$ leads to the formation of 1D homochiral helical chains with left-handed helicity, indicating that the helicity of 1D chains can be controlled by the chirality of the building blocks.

In **4**, three μ_2-$[\mathrm{Ag(CN)}_2]^-$ anions alternately bridge three $[\mathrm{NiL}]^{2+}$ cations to generate a trimer (Figure 4), in which each Ni(II) displays a distorted octahedral geometry by coordinating with four nitrogen atoms of L and two nitrogen atoms of two μ_2-$[\mathrm{Ag(CN)}_2]^-$ anions in the cis position. The three macrocycles within a trimer adopt unsymmetrical configurations of *RR*/*RR*/*SS* or *RR*/*SS*/*SS*; thus, each trimer is chiral, while compound **4**, which crystallizes in space group $P\bar{1}$, is achiral. There are no obvious argentophilic interactions in **4**, as the closest intramolecular and intermolecular Ag···Ag distances are 5.764(6) and 8.117(20) Å, respectively.

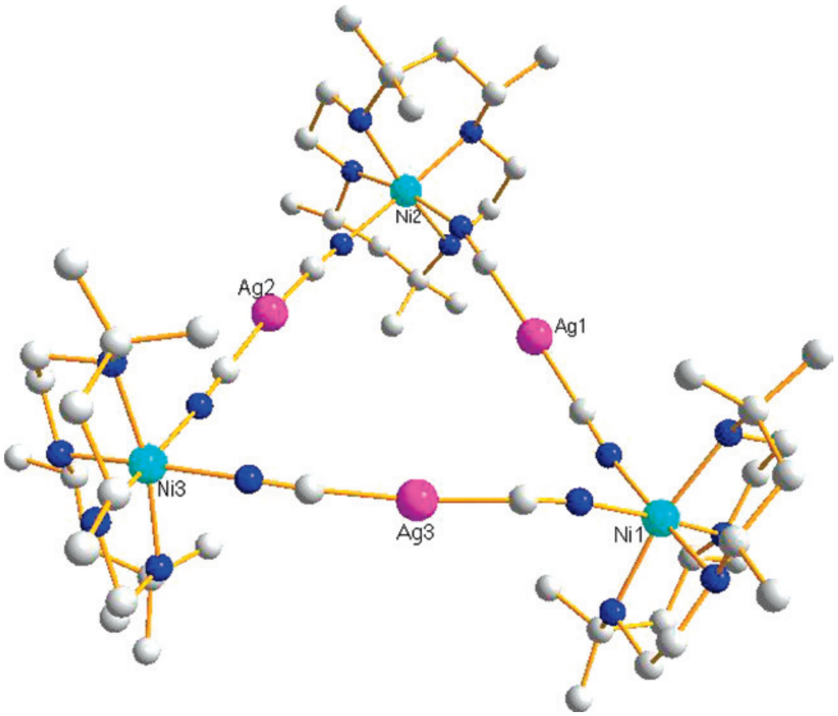

Figure 4. An unsymmetrical trimer in **4** containing two *SS*-L's and one *RR*-L.

The Argentophilic Interactions. From the structures of **1**−**3**, it can be found that the argentophilic interactions play an important role during the formations of these supramolecular isomers and stereoisomers. The alternate connections of [Ag(CN)$_2$]$^-$ with [Ni(α-*rac*-L)]$^{2+}$ and [Ni(α-*SS*-L)]$^{2+}$/[Ni(α-*RR*-L)]$^{2+}$ through the intermolecular argentophilic interactions afford 1D meso-helical chains in **1**, and 1D *right/left*-handed homochiral helical chains in Δ-**2** and Λ-**2**, respectively. Owing to the weak argentophilic interactions, the supramolecular isomerism of **1** and **3** is easily affected by the ratios of MeCN/H$_2$O, and isomers **1** and **3** were generated from the 8:1 and 25:1 ratios of MeCN/H$_2$O, respectively.

CD Spectra. The results of solid-state CD measurements of Δ-**2** and Λ-**2** confirm the chiral nature of two stereoisomers. As shown in Figure 5, the bulk crystals of Δ-**2** in the solid state show two negative Cotton effects at 365 and 550 nm, respectively, while the bulk crystals of Λ-**2** in the solid state show opposite Cotton effects at the same wavelengths. This result confirms the enantiomerism of Δ-**2** and Λ-**2**. It has been reported that the solid CD spectra of [Ni(α-*SS*-L)](ClO$_4$)$_2$ and [Ni(α-*RR*-L)](ClO$_4$)$_2$ show the opposite Cotton effects at 265, 440, 503, and 636 nm.[8] The obvious difference between the helical chains of Δ-**2** and Λ-**2** and the building blocks of [Ni(α-*SS*-L)](ClO$_4$)$_2$ and [Ni(α-*RR*-L)](ClO$_4$)$_2$ reveals that the displayed Cotton effects of Δ-**2** and Λ-**2** not only are contributed by the chiral macrocyclic ligand L but also originate from the helicity of 1D helical chains.

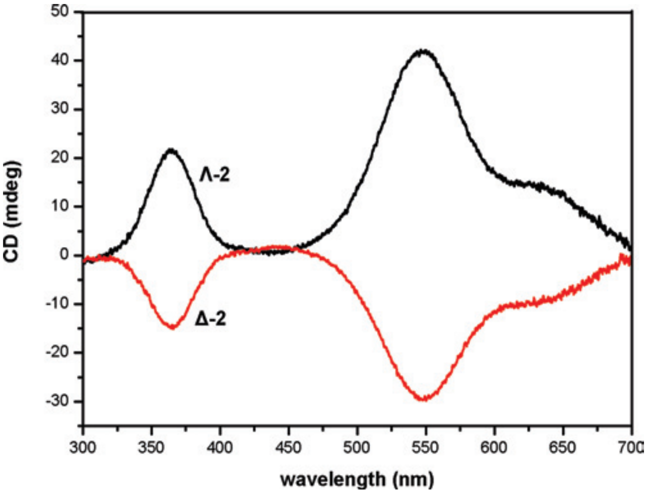

Figure 5. The solid CD spectra of Δ-**2** and Λ-**2**.

Photoluminescent Properties of 1−4. Figure 6 shows the photoluminescent emission spectra of **1**−**4** in the solid state at room temperature. Upon excitation at 310 nm, **1**·(H$_2$O)$_n$, **3**, and **4** exhibit a single broad emission band at 404, 410, and 418 nm, respectively. Photoexcitation of Δ-**2** and Λ-**2** with 324 nm UV light gives strong and broad emissions centered at 423 and 421 nm, respectively. The similar emission shapes and close emission bands of Δ-**2** and Λ-**2** can be ascribed to the similar structures of two stereoisomers. In order to understand the nature of these emission bands, the photoluminescent properties of the starting materials of [Ni(α-*rac*-L)](ClO$_4$)$_2$ and K[Ag(CN)$_2$] were measured. The results indicate that both [Ni(α-*rac*-L)](ClO$_4$)$_2$ and K[Ag(CN)$_2$] do not emit any luminescence in the range of 280−400 nm. Thus, the observed luminescence of **1**−**4** can be assigned to a ligand-to-metal charge transfer. The slight difference in the emission spectra of the compounds is attributed to the different structures among **1**·(H$_2$O)$_n$, **3**, **4**, and Δ-**2**/Λ-**2**, and different intensities of Ag$\cdots$Ag interactions among **1**·(H$_2$O)$_n$, **3**, and Δ-**2**/Λ-**2** (3.048(2) Å in **1**·(H$_2$O)$_n$, 3.248(1) Å in **3**, 3.066(2) Å in Δ-**2**, and 3.073 2) Å in Λ-**2**).

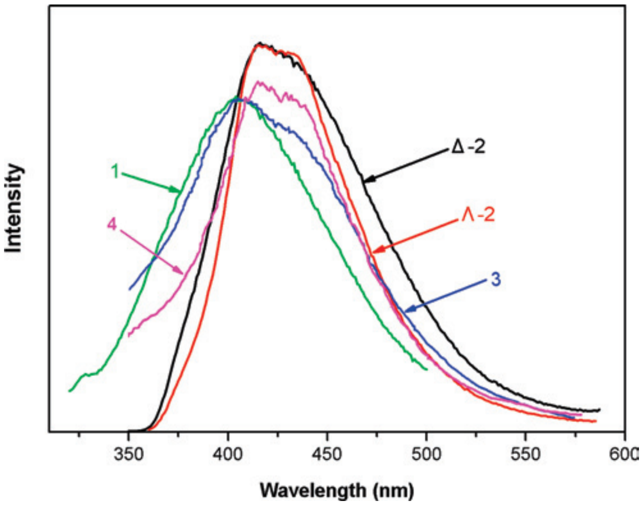

Figure 6. The solid-state luminescent emission spectra of **1**−**4** (**1** is **1**·$(H_2O)_n$).

Conclusions

In summary, as we expected, argentophilic interaction is an effective approach for the construction of 1D helical chains. In addition, [Ni(α-*rac*-L)]$(ClO_4)_2$, which contains two potential coordination sites in the cis position, is beneficial for the construction of a 1D helical chain. Therefore, when [Ni(α-*rac*-L)]$(ClO_4)_2$, [Ni(α-*SS*-L)]$(ClO_4)_2$, [Ni(α-*RR*-L)]$(ClO_4)_2$, and K[Ag$(CN)_2$] are used as building blocks, four supramolecular isomers with three 1D helical chains of **1**, **Δ-2**, and **Λ-2** and one dimer of **3** were obtained. All four supramolecular isomers of **1**, **Δ-2**, **Λ-2**, and **3** are constructed via intermolecular argentophilic interactions, with Ag···Ag distances ranging from 2.996(1) to 3.248(1) Å. The helicity of 1D helical chains is dependent on the chirality of the building blocks, and 1D meso-helical chains of **1** and 1D homochiral right-handed and left-handed helical chains of **Δ-2** and **Λ-2** were constructed when [Ni(α-*rac*-L)]$^{2+}$, [Ni(α-*SS*-L)]$^{2+}$, and [Ni(α-*RR*-L)]$^{2+}$ were used as building blocks, respectively. The presence of water molecules in **1**, **Δ-2**, and **Λ-2** increases the dimensionality of the structures into 2D networks in **1** and 3D networks in **Δ-2** and **Λ-2**. In addition, the ratios of acetonitrile/water dramatically affect the supramolecular isomerism.

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Supporting Information Available: X-ray crystallographic files in CIF format; selected bond lengths and angles of **1**−**4**; ESI-MS spectra of **1**·$(H_2O)_n$ and **3**; hydrogen bonding interactions in **1**·$(H_2O)_n$, **1**·$(H_2O\cdot MeCN)_n$, **Δ-2**·$(H_2O)_{2n}$, and Λ-**2**·$(H_2O)_{2n}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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