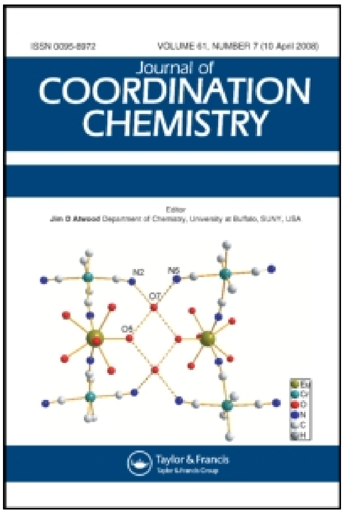

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Homochiral coordination polymers with distorted helices consisting of achiral ligand

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Reactions of achiral ligand N^2,N^6-bis((pyridin-2-yl)methyl)pyridine-2,6-dicarboxamide (L) with $AgAsF_6$ and $AgSbF_6$, respectively, produced $[AgL]_n \cdot nAsF_6$ (**1**) and $[AgL]_n \cdot nSbF_6$ (**2**), where helically chiral 1-D coordination polymers $[AgL]_n^{n+}$ conglomerate through complicated supramolecular interactions to form two 3-D enantiomerically chiral architectures with unusual (10,3) nets, showing spontaneous chiral resolution. Compounds **1** and **2** emit ligand-centered violet-fluorescence with strong intensities and double peaks centered at 329 and 344 nm.

Keywords: Spontaneous resolution; U-shaped bis(amidopyridine) ligand; Homochiral coordination polymer; Chiral (10,3) net; Fluorescence

1. Introduction

Chirality correlated with life, pharmacy, and exploration for innovative multifunctional materials has attracted intense attention [1–4]. Design and syntheses of chiral coordination polymers have become a hot topic in the past decade due to their graceful architectures, advantageous properties, and potential applications in the areas of enantioselective catalysis and separation, nonlinear optics, and multifunctional materials including chiral and polar magnets [5–12]. Chiral coordination polymers can be obtained from self-assembly of metal centers with chiral ligands or achiral ligands in the presence of auxiliary chiral agents as templates [13, 14]. Sometimes, based on an achiral ligand without any chiral sources, artificial homochiral coordination polymers can be unexpectedly engineered by non-covalent, supramolecular interactions (coordination bond, π stacking, hydrogen bonding, and other weak secondary bonding forces), undergoing spontaneous chiral resolution during self-assembly and crystallization [15–17]. Although this phenomenon is relatively rare and the mechanism of spontaneous resolution is more difficult to understand, spontaneous chiral resolution in the design and synthesis of chiral materials is of particular importance [18–21].

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Chirality is the essential characteristic of helices. An effective and simple strategy to introduce chirality into coordination polymers is the self-organization of achiral ligands to metallohelicates, where chiral information is transferred by chiral conformations of the ligands and stored [18, 19]. Spontaneous chiral resolution occurs only as further homochiral recognition of helical compounds takes place in the formation of conglomerates [19–21]. From the reported examples [21–24], the selection for bridging ligands with labile conformations, especially including chiral conformers and substantially strong, selective, and directional bonding sites, is crucial in the construction of homochiral coordination polymers from achiral ligands. Hence, the U-shaped N^2,N^6-bis((pyridin-2-yl)methyl)pyridine-2,6-dicarboxamide (L), a sort of bis(amidopyridine) ligand, which exists in potentially chiral conformations and can self-assemble in a hierarchical fashion through coordination bonds and secondary bonding forces, was selected [25–27]. Herein we report the syntheses, structures, and fluorescence of two 3-D enantiomerically chiral architectures with 3-connected (10,3)-nets made from infinite 1-D helical coordination polymers of Ag(I) and L.

2. Experimental

2.1. *Materials and physical measurements*

Reagents and solvents used were analytical pure grades. Element analyses were performed with a Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on a Bruker VECTOR22 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Electronic absorption spectra were recorded using a double-beam Lambda 35 UV-Vis spectrometer. Fluorescence spectra were determined in solid state at room temperature on a HITRCHI F-4500 fluorophotometer.

2.2. *Synthesis of N^2,N^6-bis((pyridin-2-yl)methyl)pyridine-2,6-dicarboxamide (L)*

A mixture of 2,6-pyridinedicarboxylic acid (10 g, 60 mmol) and thionyl chloride (75 mL) was refluxed for 6 h under anhydrous condition and then excess thionyl chloride was removed by rotary evaporation. The resulting white solid pyridine-2,6-dicarboyl dichloride was dissolved in dry CH_2Cl_2 (50 mL), to which a solution of 2-(aminomethyl)pyridine (13 g, 120 mmol) and triethylamine (24 mL) in dry CH_2Cl_2 (70 mL) was added dropwise with continuous stirring in an ice-bath. After stirring at room temperature for another hour, the mixture was washed with water (5 × 100 mL). The separated organic phase was dried with magnesium sulfate powder and then the solvent was removed by rotary evaporation. Recrystallizing from $CH_3CH_2OH\backslash H_2O$, white crystals of $L \cdot H_2O$ were obtained (Yield: 72%; m.p.: 151.7–152.8°C). Elemental analysis Calcd for $C_{19}H_{19}N_5O_3$ (%): C, 62.46; H, 5.24; N, 19.17. Found (%): C, 62.32; H, 4.89; N, 18.93. Selected IR (KBr, cm^{-1}): 3551(m), 3305(s), 3055(m), 2925(m), 1670(vs), 1593(m), 1542(vs), 1478(m), 1425(m), 1313(m), 1258(m), 1175(m), 1076(m), 1000(s), 864(m), 770(s), 679(m), and 614(w).

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{19}H_{17}AgAsF_6N_5O_2$	$C_{19}H_{17}AgF_6N_5O_2Sb$
Formula weight	644.17	691.00
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Crystal size (mm^3)	0.20 × 0.20 × 0.20	0.51 × 0.20 × 0.16
Temperature (K)	293(2)	293(2)
Unit cell dimensions (Å, °)		
a	11.770(2)	11.748(2)
b	12.731(3)	12.819(3)
c	15.499(3)	15.701(3)
α	90	90
β	90	90
γ	90	90
Volume (Å^3), Z	2322.4(8), 4	2364.5(8), 4
Calculated density (mg m^{-3})	1.842	1.941
Absolute structure parameter	0.053(17)	−0.02(2)
Final R indices [$I > 2\sigma(I)$]	0.0380, 0.1047	0.0248, 0.0611
Goodness of fit on F^2	1.108	1.028
Largest difference peak and hole (e Å^{-3})	0.485 and −0.4816	0.624 and −0.454

2.3. *Synthesis of [AgL]$_n$·nAsF$_6$ (1) and [AgL]$_n$·nSbF$_6$ (2)*

A solution of $AgAsF_6$ (30 mg, 0.1 mmol) in methanol (10 mL) was carefully layered on a solution of L (35 mg, 0.1 mmol) in chloroform (10 mL). Colorless prism single crystals of **1** suitable for X-ray analysis were obtained after 20 days. The yield of **1** is 71% (based on Ag). Elemental analysis Calcd for $C_{19}H_{17}AgAsF_6N_5O_2$ (%): C, 35.43; H, 2.66; N, 10.87. Found (%): C, 35.51; H, 2.56; N, 10.90. Selected IR (KBr, cm^{-1}): 3389(s), 3090(w), 2927(w), 1665(s), 1603(m), 1532(s), 1485(w), 1443(m), 1365(m), 1312(m), 1169(m), 1003(m), 767(m) and 705(vs). Following the same procedure, **2** was obtained only with $AgAsF_6$ being replaced by $AgSbF_6$. The yield of **1** is 67% (based on Ag). Elemental analysis Calcd for $C_{19}H_{17}AgSbF_6N_5O_2$ (%): C, 33.03; H, 2.48; N, 10.14. Found (%): C, 32.94; H, 2.50; N, 10.21. Selected IR (KBr, cm^{-1}): 3395(s), 3054(w), 2927(m), 1666(s), 1604(m), 1534(s), 1482(w), 1442(m), 1366(m), 1313(m), 1172(m), 1003(m), 765(m), and 704(vs).

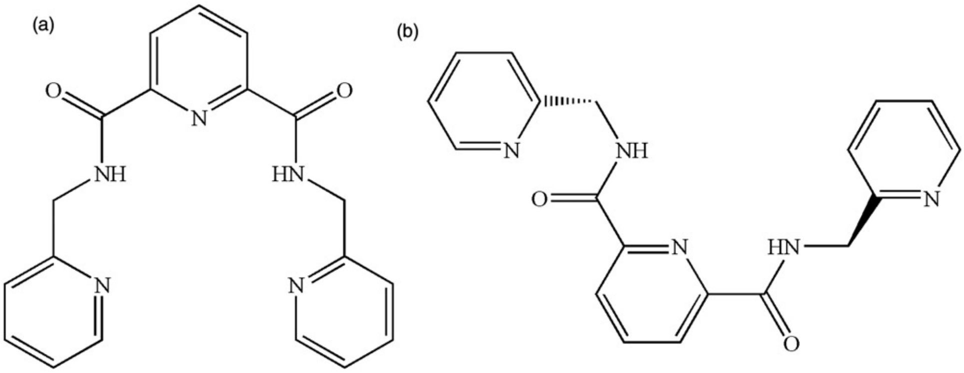
2.4. *X-ray structure determination*

Crystal data for **1** and **2** were collected on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Absorption corrections were performed using SADABS. Structures were solved with direct methods and refined with full-matrix least-squares on F^2 using the SHELXTL program package [28]. All of the non-hydrogen atoms were refined anisotropically. All hydrogens were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. Crystal data are summarized in detail in table 1. Selected bond lengths and angles are listed in table 2.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Ag1–N1	2.181(4)	Ag1–N5A	2.180(4)
Ag1 ··· O1A	2.618(3)	N1–Ag1–N5A	172.23(17)
2			
Ag1–N1	2.172(3)	Ag1–N5A	2.179(3)
Ag1 ··· O1A	2.625(3)	N1–Ag1–N5A	171.93(12)

Symmetry codes: A = $x+1/2$, $-y+3/2$, $-z+1$ for **1**; A = $x+1/2$, $-y+3/2$, $-z+2$ for **2**.



Scheme 1. Schematic representations of free ligand L (a), and chiral helical conformer (b) in **1** and **2**.

3. Results and discussion

Ligand N^2,N^6-bis((pyridin-2-yl)methyl)pyridine-2,6-dicarboxamide was readily prepared through the reaction of pyridine-2,6-dicarboyl dichloride with 2-(aminomethyl)pyridine in a 1 : 2 ratio and characterized by IR, elemental analysis, and melting point [29]. Free L shown in scheme 1 possesses C_{2v} symmetry, but can adopt many conformational isomers due to flexibility. Occasionally, the hindrance of free rotation of (pyridin-2-yl)methyl groups along $C_{(methylene)}$–$N_{(amido)}$ bonds can result in symmetry breaking to form a chiral helical conformer (scheme 1). Layering methanol solutions of $AgAsF_6$ or $AgSbF_6$ on the chloroform solution of L gave colorless prism crystals of $[AgL]_n \cdot nAsF_6$ (**1**) or $[AgL]_n \cdot nSbF_6$ (**2**). Compounds **1** and **2** were determined by IR, element analysis, UV-Vis, and fluorescence measurements as well as single-crystal X-ray diffraction analysis.

3.1. *Crystal structures of 1 and 2*

Complexes **1** and **2** have allomerism, and the structure of **1** is described in detail. Complex **1** crystallizes in an orthorhombic $P2_12_12_1$ chiral space group. The structure of **1** is depicted in figures 1–3. The basic structure built from ligands L and silver(I) is a polymer $[AgL]_n^{n+}$ with essentially linear two-coordinated silver(I) centers (figure 1). In the structure, the (pyridin-2-yl)methyl arms of each L are twisted relative to the center plane of pyridine-2,6-dicarboyl, defining the chiral helical conformation B (scheme 1). All ligands L in a given polymer chain have the same chiral conformation

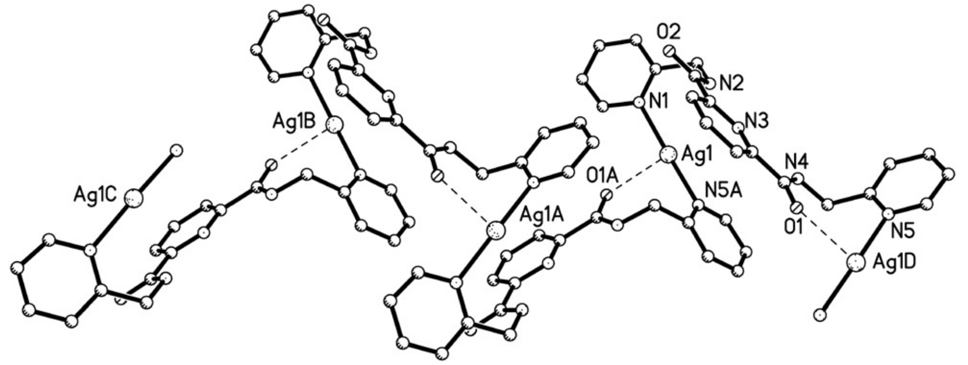


Figure 1. View of a section of the distorted helical polymer chain of (*P*)-$[AgL]_n^{n+}$ in **1**, showing intrachain secondary Ag···O1 bonds.

and adopt head-to-tail link with silver(I) through the coordination of nitrogen in the (pyridin-2-yl)methyl arms with Ag···Ag separation of 8.279 Å. Consequently, the chirality of the special helical conformer B is amplified and transmitted along the infinite 1-D distorted right-handed (*P*) helix along the *a*-axis, with the helical pitch given by one full rotation of the 2-fold screw axis being 11.770 Å (figure 1).

These homochiral polymers conglomerate through supramolecular interactions to give a chiral crystal with a 3-D network, displaying spontaneous chiral resolution on crystallization. Notably, the formation of secondary bonds between Ag(I) and oxygen of carboxyl groups may play a significant role in the construction process. In the helically chiral polymer shown in figure 1, secondary Ag···O1 bonds [Ag···O1 = 2.618(3) Å] obviously stabilize the chiral helical conformation of L. As represented in figure 2(a), every helically chiral polymer chain of (*P*)-$[AgL]_n^{n+}$ is connected with four adjacent homochiral helices by secondary Ag···O2 bonds [Ag···O2 = 2.637(3) Å], and hence the chiral 3-D supramolecular network is formed. In the structure, the secondary Ag···O bonds, with bond lengths slightly longer than the reported values of normal Ag–O bonds [26] are rather strong as coordination bonds in the topological building. Thus, both L and Ag(I) nodes can be simplified as three connectors, and every L in a μ-*k*N,O : N′:O″ coordination mode links with tetrahedral Ag(I) nodes to fabricate an unusual chiral (10,3) net (figure 2b). In the chiral assemblies of **1** and **2** contribution from AsF_6^- and SbF_6^- should be mentioned. Figure 3 displays complicated N–H···F and C–H···F hydrogen-bonding interactions as well as weaker secondary Ag···F bonds in **1**. Those supramolecular interactions not only drive the formation of chiral helical conformer B, but also aid in the recognition of helically homochiral polymers $[AgL]_n^{n+}$ to give a chiral crystal with a 3-D net. The crystallographic Flack parameters of 0.053(17) and −0.02(2) for **1** and **2**, respectively, indicate that spontaneous resolution was almost absolute [30]. Although every single crystal is homochiral, the complexes are racemic mixtures of enantiopure crystals.

3.2. *IR and UV-Vis spectral properties*

In the IR spectrum of L, a moderate peak at 3305 cm^{-1} is assigned to the vibration of N–H of the imide of L, while the very strong absorption at 1670 cm^{-1} is for the

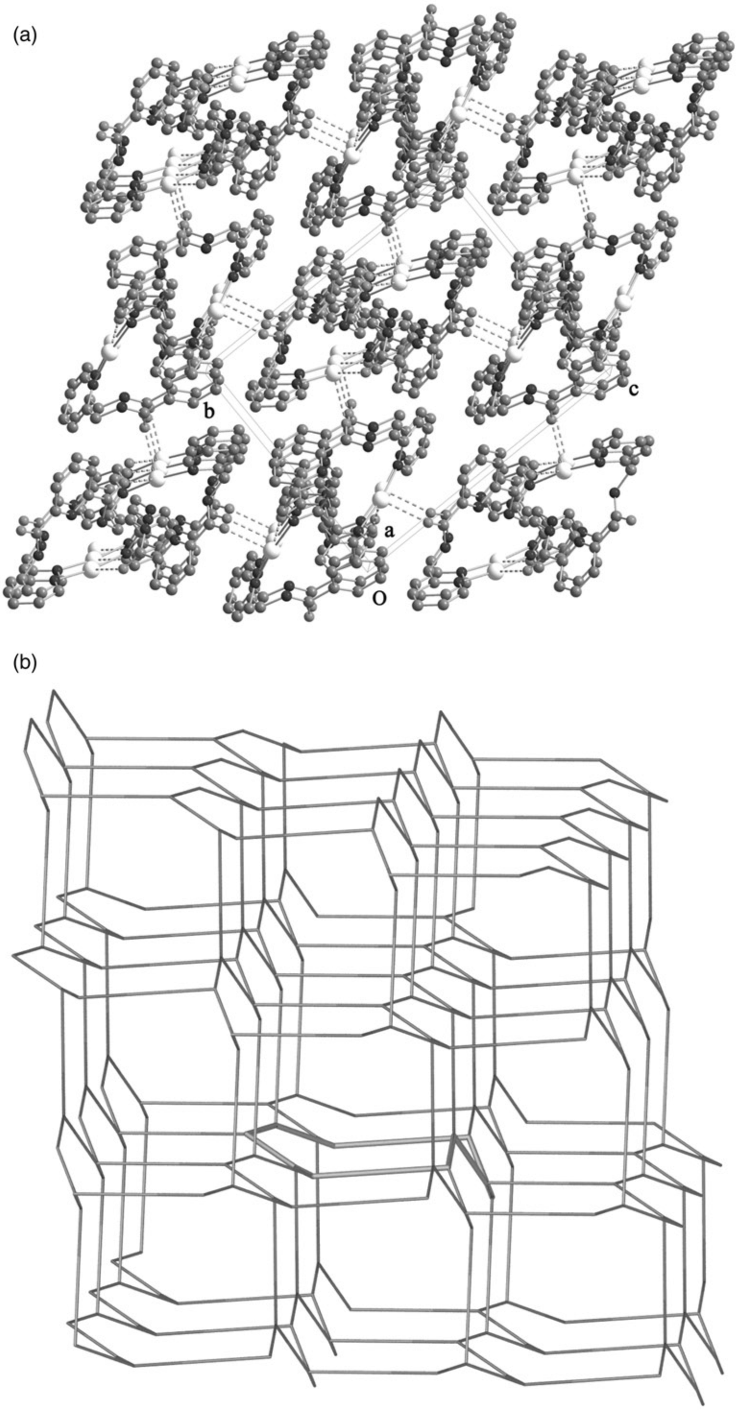


Figure 2. (a) View of every helically chiral polymer chain of (P)-$[\mathrm{AgL}]_n^{n+}$ being connected with four adjacent homochiral helices by secondary Ag···O2 bonds to form a chiral 3-D supramolecular network, and (b) schematic illustrating the 3-D three-connected (10,3) topological network in **1**.

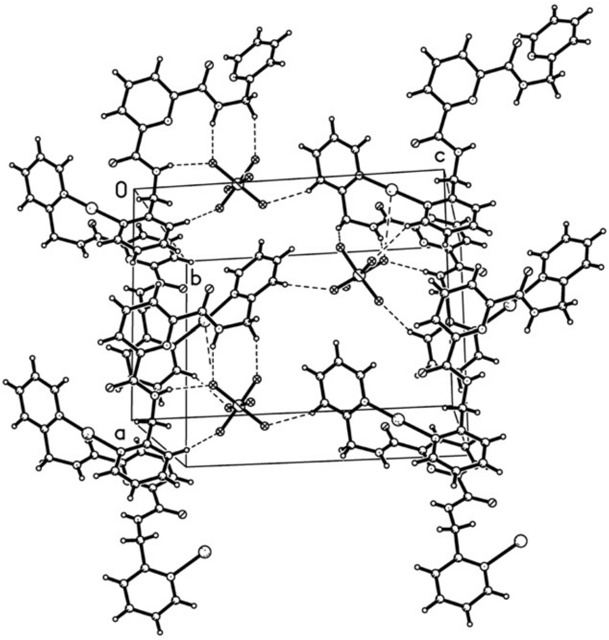


Figure 3. View of complicated N–H···F and C–H···F hydrogen-bonding interactions as well as weak secondary Ag···F bonds in the homochiral assemblies of **1**, with N–H···F and C–H···F hydrogen-bonding lengths ranging 3.00(7)–3.08(5) and 3.10(0)–3.45(6) Å, respectively, and secondary Ag···F bond length being 3.595 Å.

carbonyl of L. The corresponding absorptions for N–H and carbonyl of L are at 3389 and 1665 cm^{-1} for **1** and 3395 and 1666 cm^{-1} for **2**. Strong peaks at 705 and 704 cm^{-1} are assigned to the absorptions of free AsF_6^- and SbF_6^-, respectively.

The electronic absorption spectra of L and **1** and **2** were recorded in methanol at 1.0×10^{-5} mol L^{-1} in the 190–600 nm region. They all display multiple strong absorptions in UV-Vis areas (figure 4). Three intense bands with maxima at 211, 225, and 261 nm arise from free L, assigned to intraligand contribution of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ [31]. Complexes **1** and **2** have absorption spectra very similar to those of free L; the absorption intensities of **2** are stronger and the peak of 211 nm is covered.

3.3. *Photoluminescence*

Silver(I) complexes built from heterocycle-containing ligands usually display photoluminescent activity originating from silver(I)-perturbed intraligand transitions, and ligand-to-metal (LMCT) or metal-to-ligand charge-transfer transitions (MLCT) [32–35]. The photoluminescence spectra of **1**, **2**, and free L in the solid-state at room temperature are depicted in figure 5. As excited at 322 nm, **1**, **2**, and L emit almost the same violet-fluorescence with strong intensities and double peaks centered at 329 and 344 nm. The lower energy emission bands of 344 nm for **1**, **2**, and L are slightly stronger than the higher energy emission bands of 329 nm. The luminescence of **1** and **2**

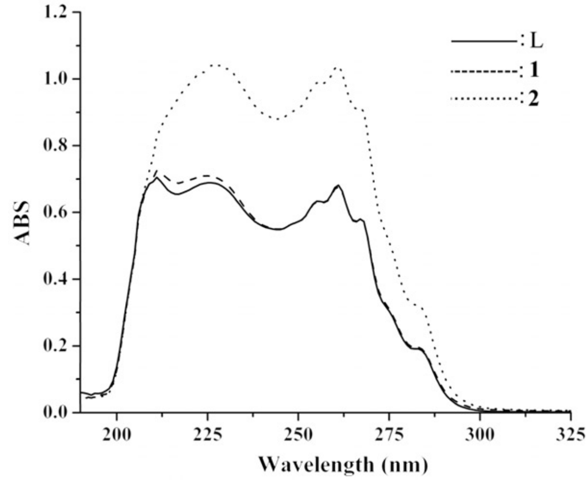


Figure 4. The electronic absorption spectra of ligand L and complexes **1** and **2** were recorded in methanol at $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ in the 190–600 nm region at room temperature (*ca* 24°C).

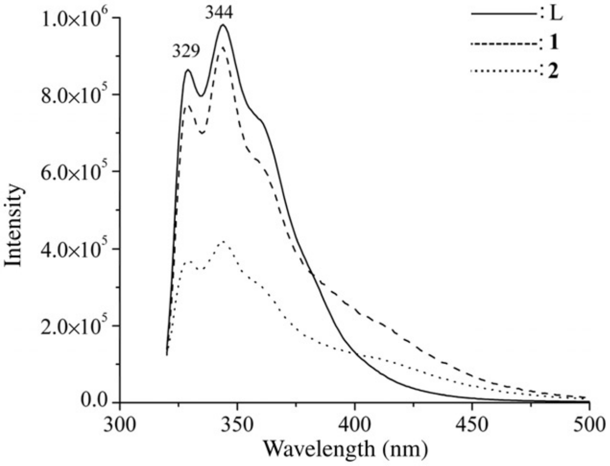


Figure 5. Solid state photoluminescence spectra of **1**, **2** and free ligand L at room temperature.

completely belong to that of L, only with intensities weakened, and the emission bands of **1** and **2** are due to an intraligand emission state.

4. Conclusions

Through spontaneous chiral resolution, $[\mathrm{AgL}]_n \cdot n\mathrm{AsF_6}$ (**1**) and $[\mathrm{AgL}]_n \cdot n\mathrm{SbF_6}$ (**2**), where helically chiral 1-D coordination polymers $[\mathrm{AgL}]_n^{n+}$ consisting of achiral ligands L, conglomerate to form two enantiomerically 3-D chiral architectures with unusual (10,3) nets, have been synthesized. Both free ligand L and **1** and **2** display the same multiple strong absorptions with maxima at 211, 225, and 261 nm in UV-Vis, which may be assigned to intraligand contribution of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Compounds **1** and **2** emit ligand-centered violet-fluorescence with strong intensities and double peaks centered at 329 and 344 nm.

Supplementary material

Crystallographic information of **1** and **2** has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 753378 and 753379. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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