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Homochiral Silver-Based Coordination Polymers Exhibiting Temperature-Dependent Photoluminescence Behavior

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Supporting Information

ABSTRACT: Homochiral coordination polymers based on zigzag or helical polymers are assembled from a semiflexible fluorescent bipyridyl ligand and linear coordinated Ag^I ions; they exhibit unusual temperature-dependent photoluminescence behavior, including multistep changes in energy and intensity upon cooling.

Stimuli-responsive luminescent materials have attracted great attention because of their potential applications in fluorescent sensors and optical recording devices.[1] Controlling and tuning the spatial interactions of organic chromophores in the solid state have been utilized as a strategy for the fabrication of responsive optical materials but remain difficult because of a variety of intermolecular interactions that can affect the packing of molecules in networks.[2] On the other hand, coordination polymers provide an intriguing way to assemble modular building units into designed networks whose structures and functions may be controlled by the geometry and functionality of the molecular components.[3,4] Of particular interest are fluorescent coordination polymers for their potential applications in sensors, light-emitting diodes, and biomedicines.[5,6]

Coordination polymers offer well-defined environments for chromophores in frameworks[5] and could generate unique optical and electronic properties such as tunable UV-to-visible and yellow-to-white emissions by external stimuli.[7] They can exhibit metal-centered luminescence and/or ligand-based luminescence (particularly if the organic linkers are conjugated).[8,9] One possible advantage for the utilization of emission based on ligands is that it could be easily tunable by varying the nature of organic linkers and/or structures of the polymers.[10]

We have shown that C_2-symmetric 1,1′-biphenyl-type ligands are excellent candidates for making helical polymers.[11] To make fluorescent coordination polymers, a conjugated and semiflexible 1,1′-biphenol ligand with ortho positions functionalized by a pyridyl Schiff-base group was selected (Figure 1). We report here utilization of this ligand to build chiral silver(I) coordination polymers displaying strong yellow photoluminescence (PL) and describe their unique temperature-dependent PL behaviors in intensity and energy shift. Combining separated fluorophore in the solid with the d^{10} configuration of Ag^I would minimize the possibility of destructive nonradiation to give highly emissive networks.[5]

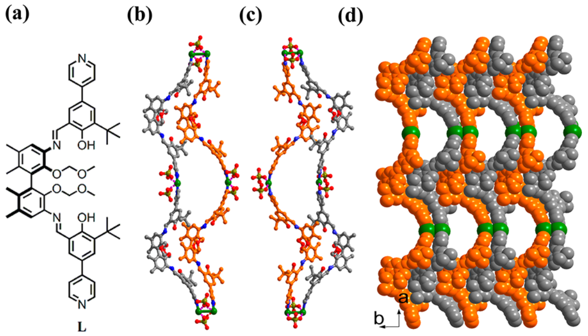

Figure 1. (a) Ligand **L**. (b and c) Pairs of zigzag polymeric chains assembled from alternating Ag^I and **L** in **1** with argentophilic Ag···Ag interactions supported by mono- and bidentate ClO_4^- anions, respectively. (d) 2D structure built of 1D zigzag chains connected by Ag···Ag interactions (ClO_4^- anions omitted for clarity).

Yellow crystals of $[(Ag\mathbf{L})ClO_4]$ (**1**) were afforded by slow evaporation of a solution of $AgClO_4$ and (*R*)-**L** in CH_3CN and isopropyl alcohol, whereas $[(Ag\mathbf{L})BF_4]$ (**2**) and $[(Ag\mathbf{L})NO_3]$ (**3**) were obtained by layering a solution of $AgBF_4$ in CH_3CN and (*R*)-**L** in tetrahydrofuran (THF) and a solution of $AgNO_3$ in CH_3CN and 2-butanol and (*R*)-**L** in CH_2Cl_2, respectively. The complexes were formulated based on thermogravimetric (TGA) and elemental analysis.

(*R*)-**1** reveals a chiral 2D lamellar network assembled from interlinked 1D polymeric chains by argentophilic interaction. (*R*)-**1** crystallizes in the monoclinic space group C2, and the asymmetric unit contains two Ag ions, two ClO_4^-, two **L**, one CH_3CN, and two H_2O guest molecules. Four independent Ag atoms in half-occupancy each coordinates to two **L** ligands in a trans fashion via two pyridyl groups, with N−Ag−N angles in the range of 152.6(3)−177(4)° (Figure 1). The dihedral angles of twisted phenyl rings along the pivotal 1,1′ bond of **L** are 69.8(2) and 70.6(2)°. Adjacent Ag ions are thus linked by **L** ligands, forming two independent zigzag chains running along the *a* axis. The chains exhibit turning angles (defined by three neighboring Ag centers) of 163.6(1) and 163.8(2)° and repeated periods of 51.6398(14) Å (equal to the *a*-axis length). Strong interchain Ag···Ag interactions [3.167(2) and 3.195(2) Å] supported by mono- or bidentate ClO_4^- anions through weak Ag−O contacts [2.436(11) or 2.522(11) and 2.748(11) Å] direct the pack of 1D chains in parallel into a 2D structure in the *ab* plane, which could further stack on top of each other to generate a 3D structure along the *c* axis.

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(*R*)-**2** is also a 2D chiral framework built from intertwined polymeric chains. It crystallizes in the monoclinic space group *C*2, and the asymmetric unit contains two Ag ions, two BF_4^-, two **L**, three THF, and one H_2O. Two independent Ag ions each coordinates to two different **L** in a trans fashion via two pyridyl groups, with N−Ag−N angles ranging from of 172(3) to 173.3(17)°. The dihedral angles of the phenyl rings of **L** are 79.2(7) and 69.9(6)°. Adjacent metal ions are thus linked by the biphenyl backbones of the ligand to give an infinite zigzag chain along the [101] direction, with a turning angle of 168.6(4)° and a repeated period of 55.8806(1) Å. These 1D strands (Figure 2a) are interlinked by ligand-unsupported short argentophilic interactions with a Ag···Ag separation of 3.0976(13) Å (significantly shorter than the van der Waals contact distance of 3.44 Å) to form 2D lamellar frameworks, which stack on top of each other along the *a* axis in a staggered fashion to generate a 3D supramolecular structure.

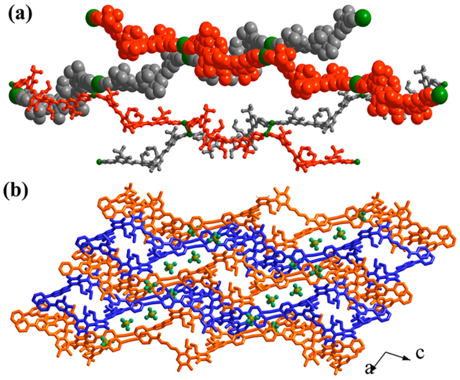

Figure 2. (a) Zigzag polymeric chains assembled from alternating Ag^I ions and **L** linked by unsupported Ag···Ag interactions in **2**. (b) 1D polymeric chains connected by Ag···Ag interactions, generating a 2D lamellar structure with voids occupied by BF_4^- anions.

(*R*)-**3** crystallizes in the chiral hexagonal space group $P6_522$, and the asymmetric unit contains one Ag ion, one NO_3^-, one **L**, and three H_2O guest molecules. It is a framework assembled from interlocking nanotubes, which are built from triple helices. The Ag atom coordinates to two different **L** in a trans fashion with a N−Ag−N angle of 173.3(5)° (Figure 3). Each Ag ion is also involved in weak Ag−O contacts [2.716(1) Å] with a chelate nitrate anion. Neighboring Ag ions are bridged by **L** ligands to form an infinite right-handed helical chain along the *c* axis, generating around a 6_1 axis with a pitch of 148.452(4) Å. The dihedral angle of the phenyl rings of **L** is 78.0(5)°. The bulky phenyl moieties point away from the helical axis, giving rise to a hollow cylinder. Five helices associate in parallel to form a hexagonal nanotube with a channel of ~3.5 × 3.5 nm, and each helix further intertwines with six adjacent helices from another four nanotubes to give a quintuple intertwined helix, thus giving a 3D chiral framework with significant eclipsing of the nanotube corners. In the known nanotubular coordination polymers, there are only a very few exceptional cases in which nanotubes are formed as a result of the parallel alignment of multiple helices, including a chiral tetragonal nanotube formed from quintuple helices and a chiral hexagonal nanotube from octuple helices.[12] The assembly of a nanotube from 6-fold helices has not been reported yet. A comparison of the structures of these interlocking multiple helices indicates that the extralong helical pitch is a key factor in the formation of this striking motif resembling the single-wall carbon nanotube.

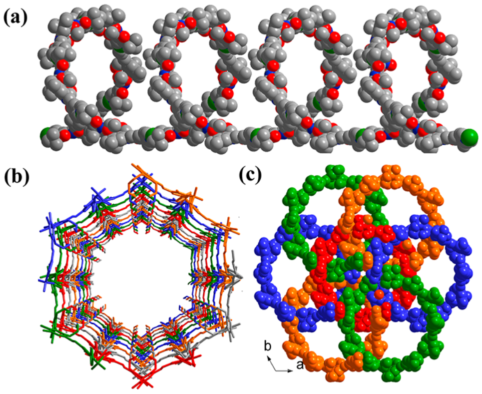

Figure 3. (a) One right-handed 6_1 helical chain in **3** formed by alternating Ag^I ions and **L** with a helical pitch of 148.452(4) Å (5 times the *c*-axis length). (b) Five helices associated in parallel to form a chiral nanotube. (c) Interlocking of each nanotube with six other nanotubes, giving a 3D framework.

Although the basic skeleton of complexes **1**−**3** is a cationic polymeric strand, the anions and crystallization conditions utilized have a significant effect on control of the molecular architectures via supramolecular interactions. In **2**, the BF_4^- anion acts only as free counterion and does not bind to Ag^+ ions at all, while the ClO_4^- anion in **1** is weakly attached to two Ag^+ ions in a mono- or bidentate bridging fashion and NO_3^- in **3** is weakly attached to one Ag^I ion in a chelate fashion. The metal-directed assembly process is accompanied by adaptive variations of the skeleton conformations of the ligand and the geometries of coordinated Ag ions. In addition, complexes **1**−**3** were crystallized in different solvents, and the solvents may also influence the final structures.

The labile binding of anions and the accessibility of the internal cavity of the polymeric frameworks can be confirmed by selective anion-exchange reactions. A qualitative anion-exchange experiment, monitored by IR, shows that ClO_4^- anions in **1** can be reversibly exchanged by BF_4^- or NO_3^- and BF_4^- anions in **2** can be reversibly exchanged by ClO_4^- or NO_3^-. After anion exchange, the frameworks of **1** and **2** remain intact, as indicated by their PXRD patterns (Figure S15 in the Supporting Information, SI). In contrast, in **3**, NO_3^- anions that strongly interact with Ag^+ ions could not be exchanged by BF_4^- or ClO_4^-. Selective anion exchange in complexes **1**−**3** indicates that these solid-state exchange reactions may be concentrated, induced, and controlled by the polymeric structure.[13]

The phase purity of the samples **1**−**3** was verified by a comparison of their observed and calculated PXRD patterns. *PLATON* calculations indicate that **1**−**3** respectively contain 24.5, 34.8, and 27.9% void spaces that are accessible to anions and solvent molecules. A TGA study indicates that the frameworks of **1**−**3** are stable up to 250−300 °C. Circular dichroism spectra of **1**−**3** in the solid state, which are produced from *R* and *S* enantiomers of **L**, are mirror images of each other, suggesting their enantiomeric nature.

Upon excitation at 470 nm, the solid-state samples of **1**−**3** all display intensive yellow PL at room temperature (Figure S7 in the SI). Their emission maxima are at 560, 553, and 552 nm, respectively, and are red-shifted by 30 nm from that (525 nm, green luminescence) of **L**. The yellow emissions have nanosecond-order decay lifetimes ~4.89, 4.89, and 4.89 ns for **1**−**3**, respectively. The longer luminescence lifetime with respect to **L**

(0.50 ns) reveals less competitive nonradiative decay of the silver complexes. The yellow emission of the complexes is much brighter (readily visible to the naked eye) than that of **L**, indicating the internal heavy-metal effects via d^{10} metal coordination, which have been utilized to adjust the PL emission in molecular complexes.[14]

The PL energies and intensities of **1**−**3** are temperature-dependent. Figure 4 shows a blue-shift emission with the stepwise decrease of room temperature in **1**, and the peak located at 560 nm at 298 K gradually shifts to shorter wavelengths and reaches 547 nm at 77 K. However, no peak shift was observed when heating **1** between 298 and 343 K (Figure S8 in the SI). A similar thermal behavior was obtained for **2**, **3**, and **L**. Upon cooling, the luminescence bands of complexes generally shift to lower energies,[15] and the blue shift of the PL bands upon cooling is scarce,[16] especially for coordination polymers.[17]

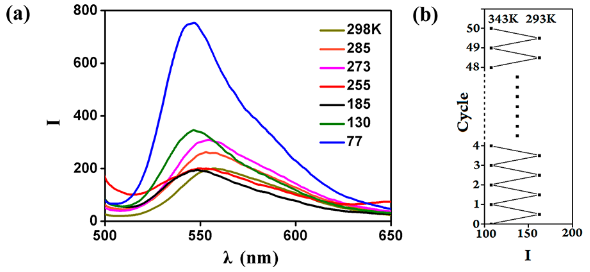

Figure 4. (a) PL spectra of **1** in the solid state at different temperatures. (b) PL changes of **1** in the heating−cooling process between 293 and 343 K.

While the temperature is progressively lowered between 343 and 273 K, the band intensity of **1** increases. A sudden decrease of the intensity is seen between 273 and 255 K, and then a big increase of the intensity is observed upon continuous cooling to lower temperatures (Figure 4a). **2**, **3**, and **L** exhibit similar behavior (Figure S8 in the SI). Generally, the PL intensity of a complex increases monotonously with decreasing temperature, as a result of inhibition of the nonradiative depopulation of the emitting state at cryogenic temperature.[14] The multistep change observed here is unusual[18] and suggests that different mechanisms are present in these silver species that cause the PL spectra to be quite different.

Note that the PL of **1**−**3** responding to temperature change is very fast and reversible. After the heating−cooling process was repeated between 293 and 343 K for 50 cycles, all three silver complexes and **L** still had intensive and clear PL properties (Figures 4b and S9 in the SI). These results demonstrate their high thermostability and reversibility, underlying their potentials as optical sensors for temperature measurements.[19] The thermal behavior of PL presented here is quite complicated, so it is difficult to give a conclusive interpretation owing to a variety of factors contributing to such processes.[20] The behavior may be due to the molecular arrangement at low temperature. The lattice contraction at lower temperatures may strengthen intermolecular forces, which can affect the metal ion's coordination geometry and the ligand's symmetry in the solid state, thereby leading to changes in the emission bands.[19] This explanation was supported by the fact that cell parameters of **1**−**3** contract 3.6−5.2% upon cooling from 298 to 77 K.

In summary, we reported three homochiral coordination polymers assembled from zigzag or helical polymers that are constructed from a conjugated and semiflexible bipyridyl ligand and linear coordinated Ag ions. We have demonstrated that the polymers not only have intensive yellow PL but also have temperature-dependent behavior of PL in energy and intensity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectral data, and crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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