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Luminescent homochiral silver(I) lamellar coordination networks built from helical chains†

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The reactions of 2,2′-dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine) (L) with $AgNO_3$ or $AgClO_4$ at 70 °C gave rise to two novel luminescent homochiral lamellar coordination polymers, AgL_2X ($X = NO_3^-$ for 1 or ClO_4^- for 2), which are built from linking helical chains by Ag(I) atoms as hinges.

Motivated by their diverse intriguing topological architectures and potential applications as functional materials, the synthesis and characterization of extended networks based on metal–ligand coordination or hydrogen bonding have attracted a great deal of interest in the past few years.[1–3] Our recent interest has been focused on the crystal engineering of homochiral coordination networks for potential applications in chirotechnology. Such homochiral coordination networks not only provide entry into technologically useful materials such as NLO materials but also promise to lead to novel heterogeneous asymmetric catalysts and chiral separation media.[4–5] Although homochiral coordination networks can be constructed by several different methods, we have taken the most straightforward and reliable approach by employing chiral bridging ligands as linkers.

We have particularly made significant progress in the synthesis of homochiral solids based on multitopic rigid linkers derived from axially chiral 1,1′-bi-2-naphthol (BINOL) and in the exploration of their applications in enantioselective processes.[6] In order to gain further understanding on the structural features of these homochiral solids, we have initiated research efforts on the synthesis of homochiral solids based on BINOL-derived bipyridines.[7,8] Herein we wish to report the synthesis and characterization of two novel luminescent homochiral 2D polymers, $(Ag\mathbf{L}_2)X$ (L = (*S*)-2,2′-dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine), $X = NO_3^-$ for **1** and ClO_4^- for **2**).

Colorless crystals of compounds **1** and **2** were obtained by heating mixtures of AgX ($X = NO_3$ or ClO_4) and (*S*)-2,2′-dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine) (**L**)[7] in a solution of DMSO and EtOH at 70 °C for two days.‡ Both compounds **1** and **2** are insoluble in water and common organic solvents. Element analysis results and IR spectra have confirmed the formulation of compounds **1** and **2**. Thermogravimetric analysis (TGA) of the polycrystalline samples of **1** and **2** showed no weight losses up to 269 and 274 °C for **1** and **2**, respectively. Compounds **1** and **2** gradually decompose above these temperatures.

A single crystal X-ray diffraction study§ has revealed a lamellar framework structure of **1** that is built from interlinking of helical coordination chains and crystallizes in *C*2 space group. The asymmetric unit contains one half silver cation, one **L** ligand, and one half nitrate anion. Each silver atom is coordinated by four nitrogen atoms from four different **L** ligands to afford a highly distorted tetrahedral coordination environment. The Ag–N distances range from 2.237(2) to 2.410(2) Å, while the N–Ag–N angles are in the 94.4(1)–148.8(1)° range. The dihedral angle between the naphthyl rings in **1** is 94.7 °.

As shown in Fig. 1, each **L** ligand link two silver cations along the *b*-axis to form an interesting right-handed helical chain, which is generated by a 2_1 axis with a pitch of 9.704 Å. The adjacent helical chains are further linked to each other by the Ag(I) ions to form an interesting 2D lamellar framework. Most strikingly, this arrangement of silver atoms and **L** ligands generates a series of interesting tubular channels within the 2D network that are running along the *b*-axis (Fig. 2). The largest dimension of the tubular channel is 18.2 Å. The neighbouring layers interdigitate each other *via* $\pi\cdots\pi$ interactions (the average distance between two aromatic rings is 3.478 Å) to lead to a compact solid with just enough void space to accommodate nitrate anions (Fig. 3 and Fig. 4).

Compound **2** is isostructural with compound **1** and the perchlorate anions of **2** occupy the open sites of nitrate anions in **1**. The distances between nitrogen atoms with the distorted tetrahedral coordinated Ag atom are in the 2.270(5)–2.390(5) Å range, while the N–Ag–N angles fall within the 95.4(2)–134.6(3)° range. The dihedral angle between the naphthyl rings in **2** is 89.6 °

Compounds **1** and **2** exhibit interesting photoluminescence in the solid state. Excitation of solid samples at $\lambda = 350$ nm produces luminescence peaks with a maximum at 445 nm for **1** and 442 nm for **2**. These emission peaks are essentially the same as the solution fluorescence signal of free ligand **L** at 438 nm. We thus believe that

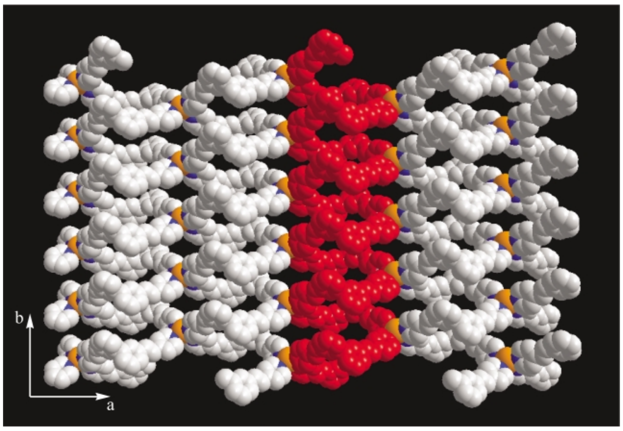

Fig. 1 A view of homochiral lamellar framework of **1** (Ag, yellow; N, blue; C, grey). One of the right-handed helices is highlighted in red. Part of naphthyl rings, methoxy groups, and hydrogen atoms were omitted for clarity.

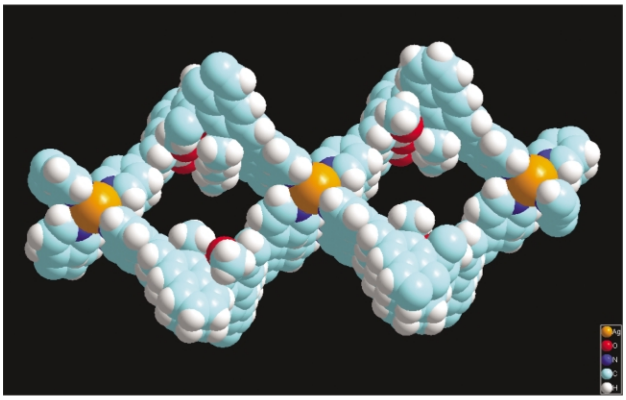

Fig. 2 A view of the tubular channels formed within the lamella down the *b*-axis.

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† Electronic supplementary information (ESI) available: Tables S1–9 and Figures S1–12. See http://www.rsc.org/suppdata/cc/b4/b403609c/

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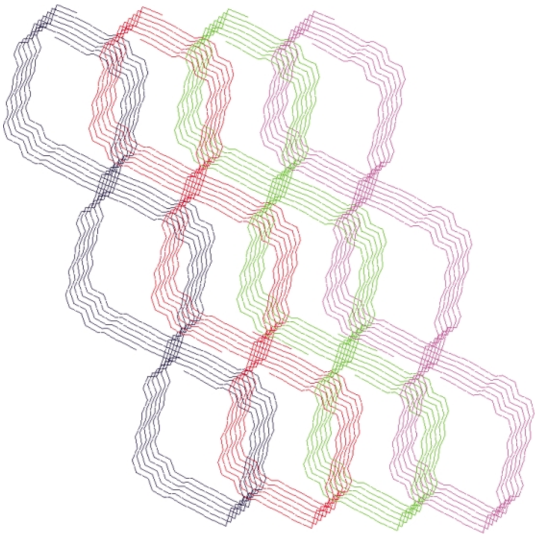

Fig. 3 Scheme representation of the interdigitation of 2D layers in **1** as viewed slightly off the *b*-axis.

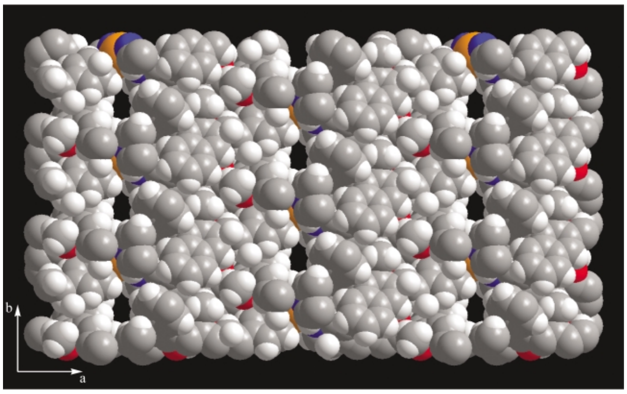

Fig. 4 Space-filling view of **1** down the *c*-axis. The void space is filled by nitrate groups.

the luminescence signals of **1** and **2** originate from ligand-centered n $\rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ process, which is different from previously reported $4d\sigma^* \rightarrow 5p\sigma$ transitions for group 11 metal complexes.[9] It is also interesting to note that we have not observed any exiplex emission from **1** and **2** in the solid state in spite of their strong π–π stacking interactions. Solid-state circular dichroism (CD) spectra indicate that **1** and **2** exhibit similar CD signals as **L**, suggesting their potential utility as chiroptical materials.

In summary, we have synthesized and characterized two luminescent homochiral 2D coordination networks based on an axially chiral bipyridine. Interdigitation of neighboring layers has led to the elimination of potential porosity. Further studies are directed toward the design of highly porous homochiral solids for applications in enantioselective processes.

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Notes and references

‡ *Synthesis of* $(AgL_2)NO_3$, **1**. A mixture of $AgNO_3$ (34.0 mg, 0.2 mmol), (*S*)-**L** (52.1 mg, 0.1 mmol), DMSO (2 mL) and EtOH (2 mL) in a capped vial was heated at 70 °C for 2 days. Colorless crystals of **1** were filtered, washed with EtOH, Et_2O and dried at room temperature. Yield: 50.5 mg (83.4% based on **L**). Anal. Calcd. For **1** (%): C, 71.4, H, 4.66, N, 5.78; Found: C, 68.0, H, 4.46, N, 5.57 (low in C, H, and N due to contamination of trace amount of Ag_2O). IR (KBr pellet, ν/cm^{-1}): 1601(s), 1548(w), 1493(m), 1456(m), 1415(m), 1351(s), 1234(m), 1220(m), 1149(m), 1101(m), 1064(w), 1035(m), 1008(m), 971(w), 905(w), 873(m), 811(w), 749(m), 743(m).

Synthesis of $(AgL_2)ClO_4$, **2**. Compound **2** was synthesized similarly to **1** except that $AgClO_4$ was used in place of $AgNO_3$. Yield: 75.0% based on **L**. Anal. Calcd. For **2** (%): C, 69.3, H, 4.52, N, 4.49; Found: C, 67.3, H, 4.47, N, 4.36 (low in C, H, and N due to contamination of trace amount of Ag_2O). IR (KBr pellet, ν/cm^{-1}): 1600(s), 1548(m), 1493(m), 1457(m), 1420(m), 1357(m), 1235(s), 1150(m), 1103(s), 1034(w), 1007(m), 977(m), 901(w), 871(m), 813(m), 751(m), 744(m).

§ *Crystal structure determinations*. Data collections for colorless crystals of **1** and **2** were performed on a Siemens SMART CCD using graphite-monochromatic Mo–Kα radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected by SADABS program.[10] The structures were solved by direct methods, and refined by full-matrix least-squares methods with the SHELXTL-97[11] program package. Crystallographic data for **1**: space group *C*2, a = 33.74(12), b = 9.704(3), c = 8.672(2) Å, β = 95.92(4), U = 2824(2) Å^3, Z = 2, ρ_{calcd} = 1.424 g cm^{-3}, μ(MoKα) = 0.421 mm^{-1}. Least-squares refinements based on 4670 reflections with $I > 2s(I)$ and 385 parameters led to convergence, with a final $R1$ = 0.0262, $wR2$ = 0.0596, Flack parameter = 0.02(1) and GOF = 1.043. Crystallographic data for **2**: space group *C*2, a = 34.631(1), b = 10.218(1), c = 8.380(1) Å, β = 91.78(1), U = 2964.0(1) Å^3, Z = 2, ρ_{calcd} = 1.399 g cm^{-3}, μ(MoKα) = 0.448 mm^{-1}. Least-squares refinements based on 3620 reflections with $I > 2s(I)$ and 389 parameters led to convergence, with a final $R1$ = 0.0466, $wR2$ = 0.1068, Flack parameter = 0.07(4) and GOF = 1.031.

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