

Syntheses, structures and photoluminescent properties of cadmium(II), silver(I) and copper(I) complexes with novel long chain tetradentate ligands

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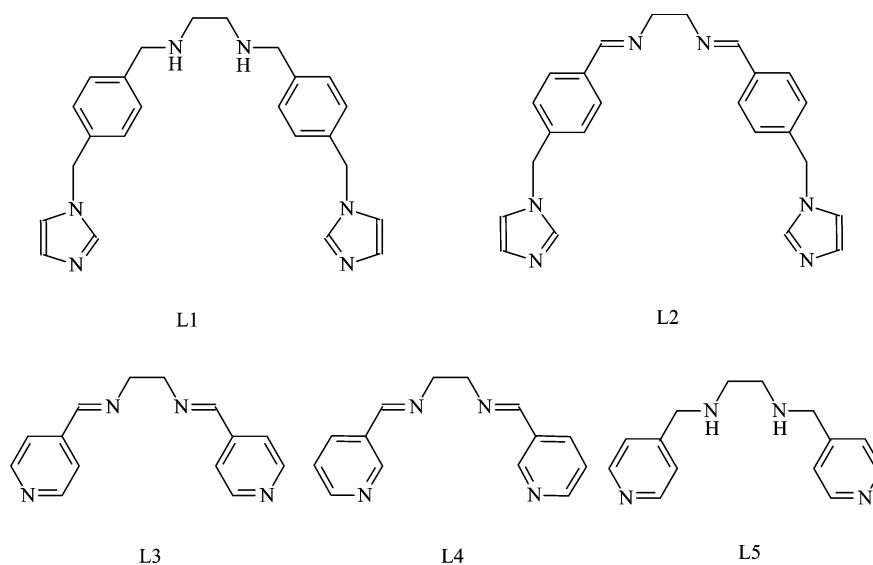
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Two new coordination complexes [Cd(L1)Br₂] (1) and [Ag₃(L1)₂](ClO₄)₃ (2) were obtained by assembly reactions of CdBr₂ and AgClO₄ with long chain tetradentate ligand 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diazahehexane (L1). X-Ray diffraction analyses reveal that complex 1 is composed of neutral 2D grid networks, which are further linked by N–H ⋯ Br and C–H ⋯ Br hydrogen bonds to produce a 3D framework. Complex 2 with four- and two-coordinated silver(I) atoms has a double-stranded wandering chain structure formed by Ag–N coordination, Ag ⋯ Ag and π–π interactions. Complexes [Ag(L2)]NO₃ (3), [Cu(L2)]ClO₄ (4) and [Cu(L2)]BF₄ (5), with a relatively rigid long chain Schiff base ligand 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diaza-1,5-hexadiene (L2), exhibit infinite 1D zigzag chain structures. The results show that the structure of the assemblies is predominated by the nature of organic ligands and the geometric requirements of metal ions. The photoluminescent properties of the synthesized complexes were studied in the solid state at room temperature.

Introduction

In recent years, many efforts have been devoted to the design and synthesis of pre-organized ligands that are able to control the geometric and steric properties of metal ions.^{1–3} Metal-organic frameworks with fascinating topologies, *e.g.* rotaxanes, catenanes, helicates and knots, and interesting one- (1D), two- (2D) and three-dimensional (3D) structures have been achieved by assembly reactions of metal salts with organic ligands, for example macrocycles, tripodal ligands, and short bidentate N-donor rigid ligands.^{4–8} Although it has been reported that long flexible chain-like bidentate ligands have the ability to form unique interwoven extended structural motifs such as polycatenanes, polyrotaxane, double helices and other species,^{9–12} it is not well studied that long chain flexible ligands are used to construct coordination polymers without interpenetration compared with the short rigid ligands like 4,4'-bipyridine. The

crystal engineering of coordination polymeric networks based on multidentate ligands represents a growing area of coordination and supramolecular chemistry. We focused our attentions on the assembly of metal ions with flexible multidentate ligands since they can adopt diverse coordination modes according to the different geometric requirements of the metal ions.¹³ To further expand our work, we designed and synthesized new long chain flexible tetradentate ligands 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diazahehexane (L1) and 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diaza-1,5-hexadiene (L2) (Scheme 1). In these ligands, there are several salient points: (a) unlike rigid groups such as 2,2'-bipyridine or 1,10-phenanthroline, the ethylenediamine unit in L1 and L2 can adopt different conformations, which have been observed in our previous works;¹³ (b) the introduced aromatic rings can offer possible π–π interactions which may stabilize the frameworks; (c) apart from pyridyl group often used as the terminal groups, imidazole is



Scheme 1

also a good choice as a N-donor ligand. All these features provide the networking ability of L1 and L2 ligands.

We describe here the synthesis, structural characterization and luminescent properties of coordination polymers, [Cd(L1)Br₂] (**1**), [Ag₃(L1)₂](ClO₄)₃ (**2**), [Ag(L2)]NO₃ (**3**), [Cu(L2)]ClO₄ (**4**) and [Cu(L2)]BF₄ (**5**) obtained by reactions of L1 with CdBr₂, AgClO₄ and L2 with AgNO₃, [Cu(CH₃CN)₄]ClO₄ and [Cu(CH₃CN)₄]BF₄, respectively.

Experimental

All commercially available chemicals are of reagent grade and used as received without further purification. 4'-Formylbenzyl-1-imidazole was prepared according to the literature method.¹⁴ Solvents were purified according to standard methods. Elemental analyses for C, H and N were made on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. ¹H NMR spectra were measured on a Bruker DRX500 MHz NMR spectrometer at room temperature. The UV-vis spectral measurements were carried out on a Perkin-Elmer Lambda 35 UV-VIS spectrophotometer. The luminescent spectra for the solid samples were recorded at room temperature on a Hitachi 850 fluorescence spectrophotometer. A SLM 48000 DSCF fluorescence spectrometer was used to perform the lifetime measurements.

Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Preparation of 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diaza-1,5-hexadiene (L2)

A solution of 4'-formylbenzyl-1-imidazole (2.6 g, 13.7 mmol) in 130 ml of CH₃CN was added dropwise to 0.50 ml (7.5 mmol) of ethylenediamine in 140 ml of CH₃CN over 4 h at room temperature with stirring and then, further stirred for 24 h. The mixture was subsequently concentrated *in vacuo* to ca. 30 ml and then allowed to stand at -18 °C overnight. The resulting yellow precipitate was collected by filtration, washed with diethyl ether and dried *in vacuo* to give L2 (2.1 g, 76%). Mp 151–152 °C. ¹H NMR [500 MHz, (CD₃)₂SO]: δ 8.28 (s, 2H, -CH=N-), 7.67 (d, 4H, Ph), 7.58 (s, 2H, imidazole), 7.24 (d, 4H, Ph), 7.03 (s, 2H, imidazole), 6.96 (s, 2H, imidazole), 5.18 (s, 4H, -CH₂Ph-), 3.89 (s, 4H, -CH₂CH₂-). Calc. elem. anal. for C₂₄H₂₄N₆: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.58; H, 6.19; N, 21.15.

Preparation of 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diazaheptane (L1)

2.1 g (5.3 mmol) of ligand L2 was dissolved in 150 ml MeOH. Excess NaBH₄ (1.0 g, 26.5 mmol) was added to the solution with stirring at room temperature. After the addition of the NaBH₄ was completed, the reaction solution was continuously stirred for 12 h and then evaporated to dryness, 20 ml H₂O and 120 ml of CH₂Cl₂ were added to the mixture to extract the product. The organic phase was separated, dried over Na₂SO₄ and evaporated to dryness under reduced pressure. After the addition of diethyl ether, the white precipitate was obtained. The product was recrystallized from MeOH (1.8 g, 88%). Mp 117–119 °C. ¹H NMR (500 MHz, D₂O): δ 7.68 (s, 2H, imidazole), 7.23 (d, 4H, Ph), 7.17 (d, 4H, Ph), 7.04 (s, 2H, imidazole), 6.93 (s, 2H, imidazole), 5.13 (s, 4H, -CH₂Ph-), 3.77 (s, 4H, -CH₂NH-), 2.80 (s, 4H, -CH₂CH₂-). Calc. elem. anal. for C₂₄H₂₈N₆: C, 71.97; H, 7.05; N, 20.98. Found: C, 71.71; H, 7.30; N, 20.99.

Preparation of [Cd(L1)Br₂] (**1**)

The title compound was prepared by layering method. A buffer layer of solution (10 ml) of methanol and water (3 : 1) was carefully layered over an aqueous solution of CdBr₂·4H₂O (34.4 mg, 0.1 mmol). Then a solution of L1 (40.0 mg, 0.1 mmol)

in methanol was layered over the buffer layer. Single crystals appeared after several days. Yield: 47%. Calc. elem. anal. for C₂₄H₃₄N₆Br₂CdO₃: C, 39.66; H, 4.72; N, 11.56. Found: C, 39.47; H, 4.72; N, 11.48.

Preparation of [Ag₃(L1)₂](ClO₄)₃ (**2**)

All procedures for synthesis and measurements of the silver(I) complex were performed in the dark. The compound was prepared by layering method. A buffer layer of solution (10 ml) of CHCl₃ and methanol (3 : 1) was carefully layered over a CHCl₃ solution of L1 (40.0 mg, 0.1 mmol). Then a methanol solution of AgClO₄ (20.8 mg, 0.1 mmol) in methanol was layered over the buffer layer. Single crystals were obtained after several weeks. Yield: 70%. Calc. elem. anal. for C₄₈H₅₆N₁₂Ag₃Cl₃O₁₂: C, 40.52; H, 3.97; N, 11.81. Found: C, 40.71; H, 3.92; N, 11.90.

Preparation of [Ag(L2)](NO₃) (**3**)

The title complex was obtained similarly to complex **1** by using L2 and AgNO₃ instead of L1 and CdBr₂·4H₂O, respectively. Yield: 65%. Calc. elem. anal. for C₂₄H₂₄N₇AgO₃: C, 50.90; H, 4.27; N, 17.31. Found: C, 50.98; H, 4.29; N, 17.35.

Preparation of [Cu(L2)](ClO₄) (**4**)

All procedures for synthesis of copper(I) complex were carried out under an argon atmosphere. Solid L2 (39.6 mg, 0.1 mmol) was added to a degassed acetonitrile solution (5 ml) of [Cu(CH₃CN)₄]ClO₄ (32.7 mg, 0.1 mmol) to give a yellowish solution. Yellow single crystals suitable for X-ray diffraction were obtained in 56% yield by slow diffusion of diethyl ether into the reaction solution for several days. Calc. elem. anal. for C₂₄H₂₄ClCuN₆O₄: C, 51.52; H, 4.32; N, 15.02. Found: C, 51.51; H, 4.41; N, 15.04.

Preparation of [Cu(L2)](BF₄) (**5**)

The title complex was obtained similarly to complex **4** by using [Cu(CH₃CN)₄]BF₄ instead of [Cu(CH₃CN)₄]ClO₄. Yield: 52%. Calc. elem. anal. for C₂₄H₂₄BCuF₄N₆: C, 52.71; H, 4.42; N, 15.37. Found: C, 52.58; H, 4.60; N, 15.42.

X-Ray crystal structure determinations

The data collections for complexes **1–5** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) at 200 K. The structures were solved by direct method with SIR92,¹⁵ and expanded using Fourier techniques.¹⁶ The absorption correction for all complexes was carried out by multi-scan method. All data were refined anisotropically by the full-matrix least-squares method on F² for non-hydrogen atoms. The hydrogen atoms were generated geometrically. In complex **5**, the tetrafluoroborate anion is disordered. The atoms F2, F3 and F4 are located at two positions with site occupancy factors (s.o.f.) of 0.617(13) and 0.383(13), respectively. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure corporation.¹⁷ Details of the crystal parameters, data collection and refinement for complexes **1–5** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2.

CCDC reference numbers 201027–201031.

See <http://www.rsc.org/suppdata/dt/b3/b300479a/> for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structure of [Cd(L1)Br₂] (**1**)

Reaction of L1 with cadmium(II) bromide gives precipitate immediately which may suggest polymeric species formed. Thus

Table 1 Crystallographic data for complexes **1**, **2**, **3**, **4** and **5**

Complex	1	2	3	4	5
Empirical formula	C ₂₄ H ₂₈ Br ₂ CdN ₆	C ₄₈ H ₅₆ Ag ₃ Cl ₃ N ₁₂ O ₁₂	C ₂₄ H ₂₄ AgN ₇ O ₃	C ₂₄ H ₂₄ ClCuN ₆ O ₄	C ₂₄ H ₂₄ BCuF ₄ N ₆
Formula weight	672.74	1423.01	566.37	559.48	546.84
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄	<i>C</i> ₂ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.504(7)	8.879(7)	15.8499(4)	13.7180(7)	13.70(2)
<i>b</i> /Å	11.790(7)	9.997(12)	9.4345(4)	10.1127(7)	9.979(16)
<i>c</i> /Å	21.347(14)	35.53(3)	16.5889(6)	19.0653(10)	19.23(4)
<i>a</i> /°	90.00	94.69(9)	90.00	90.00	90.00
<i>β</i> /°	97.46(3)	90.38(7)	103.7920(10)	108.971(3)	109.56(15)
<i>γ</i> /°	90.00	115.90(8)	90.00	90.00	90.00
<i>V</i> /Å ³	2621(3)	2824(5)	2409.11(15)	2501.2(3)	2478(8)
<i>Z</i>	4	2	4	4	4
<i>T</i> /K	200	200	200	200	200
<i>μ</i> /mm ^{−1}	3.905	1.241	0.878	1.023	0.936
Unique reflections	5876	12802	2755	5701	5647
Observed reflections	3521	7554	2429	2025	2255
<i>R</i> _{int}	0.0821	0.0578	0.0256	0.0575	0.1550
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0370	0.0525	0.0310	0.0419	0.0558
<i>wR</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0528 ^a	0.1303 ^b	0.0740 ^c	0.0606 ^d	0.0996 ^e

^a $w = 1/[\sigma^2(F_o)^2 + (0.0204P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. ^b $w = 1/[\sigma^2(F_o)^2 + (0.0799P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. ^c $w = 1/[\sigma^2(F_o)^2 + (0.0396P)^2 + 2.5281P]$, where $P = (F_o^2 + 2F_c^2)/3$. ^d $w = 1/[\sigma^2(F_o)^2 + (0.0217P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. ^e $w = 1/[\sigma^2(F_o)^2 + (0.0420P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

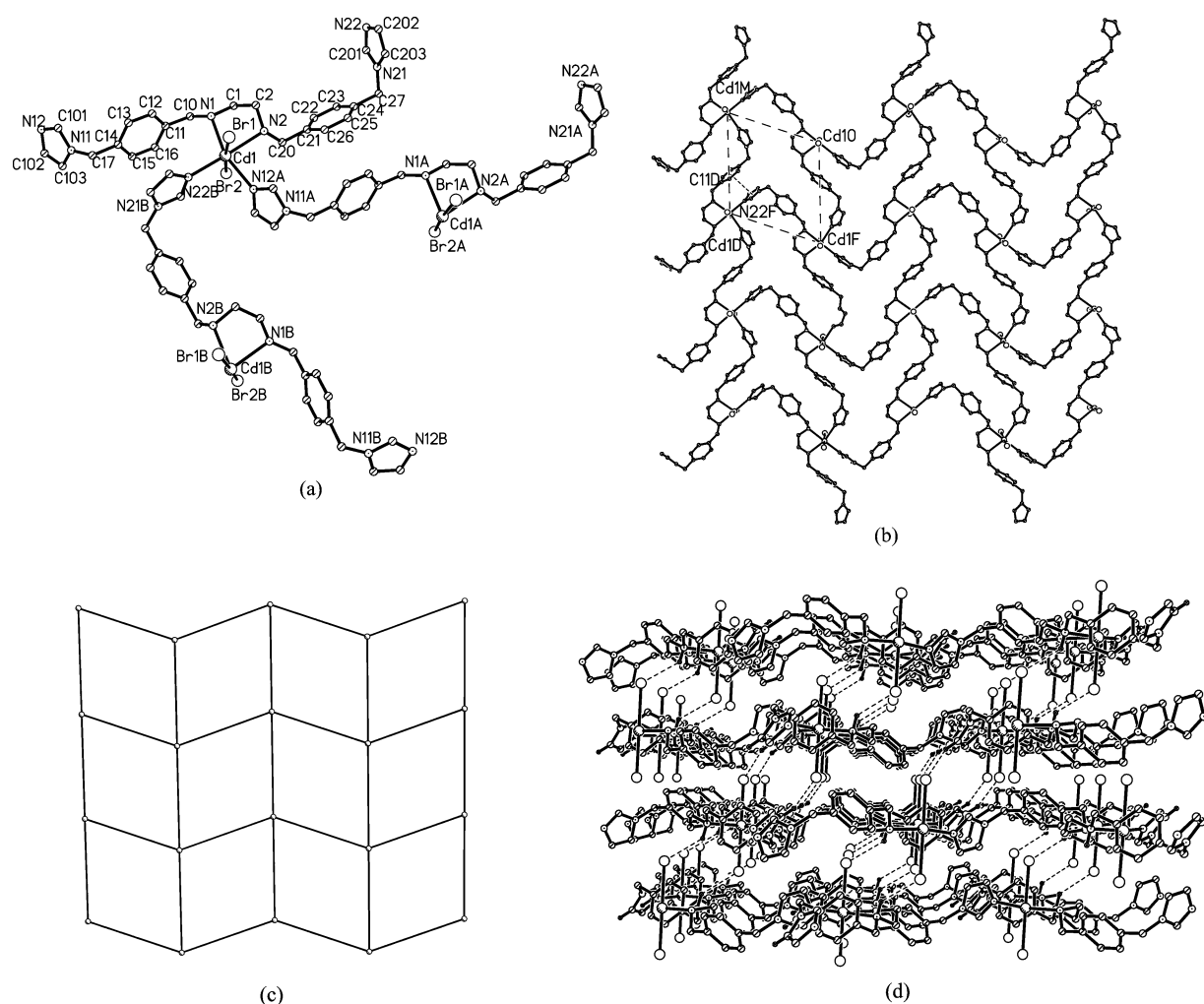


Fig. 1 (a) The coordination environment around the cadmium(II) atom in [Cd(L1)Br₂] (**1**); hydrogen atoms were omitted for clarity. (b) The 2D grid network structure of **1**; a π - π stacking interaction is indicated by a dotted line. (c) The 2D sheet consists of rhombohedral grids and only the cadmium(II) atoms are presented. (d) The 3D structure of **1** linked by hydrogen bonds between the adjacent sheets.

the complex was prepared by layering method. The polymeric structure of **1** was confirmed by X-ray single crystal structure determination. The coordination environment around the Cd(II) atom is exhibited in Fig. 1a along with the atom numbering scheme. Each Cd(II) atom is six-coordinated with a distorted octahedral geometry by two bromide atoms at axial

positions [Cd(1)–Br(1), 2.8167(19) Å; Cd(1)–Br(2), 2.7500(19) Å; Br(1)–Cd(1)–Br(2), 175.083(16)°, Table 2] and four nitrogen atoms at the equatorial plane [Cd(1)–N, 2.291(3) ~ 2.430(3) Å], two of which are from one ethylenediamine unit of one L1 ligand and two from imidazole N atoms of other two L1 ligands. Thus each Cd(II) atom links three L1 ligands and in

Table 2 Selected bond distances (Å) and angles (°) for **1**, **2**, **3**, **4** and **5**^a

[Cd(L1)Br ₂] (1)			
Cd(1)–N(1)	2.400(3)	Cd(1)–N(2)	2.430(3)
Cd(1)–N(22) ⁱ	2.291(3)	Cd(1)–N(12) ⁱⁱ	2.371(3)
Cd(1)–Br(1)	2.8167(19)	Cd(1)–Br(2)	2.7500(19)
N(22) ⁱ –Cd(1)–N(12) ⁱⁱ	95.41(11)	N(22) ⁱ –Cd(1)–N(2)	173.14(10)
N(22) ⁱ –Cd(1)–N(1)	104.41(11)	N(12) ⁱⁱ –Cd(1)–N(2)	84.72(11)
N(12) ⁱⁱ –Cd(1)–N(1)	160.04(10)	N(1)–Cd(1)–N(2)	75.90(10)
N(22) ⁱ –Cd(1)–Br(2)	92.81(8)	N(12) ⁱⁱ –Cd(1)–Br(2)	89.68(8)
N(1)–Cd(1)–Br(2)	86.99(7)	N(2)–Cd(1)–Br(2)	94.05(8)
N(22) ⁱ –Cd(1)–Br(1)	90.60(8)	N(12) ⁱⁱ –Cd(1)–Br(1)	86.47(8)
N(1)–Cd(1)–Br(1)	95.59(7)	N(2)–Cd(1)–Br(1)	82.56(8)
Br(1)–Cd(1)–Br(2)	175.083(16)		
[Ag ₃ (L1) ₂](ClO ₄) ₃ (2)			
Ag(1)–N(1)	2.461(5)	Ag(1)–N(2)	2.317(5)
Ag(1)–N(3)	2.332(4)	Ag(1)–N(4)	2.423(6)
Ag(2)–N(102)	2.100(5)	Ag(2)–N(402)	2.103(5)
Ag(3)–N(202)	2.113(5)	Ag(3)–N(302)	2.119(5)
Ag(2)–Ag(2) ⁱⁱⁱ	3.081(3)	Ag(3)–Ag(3) ^{iv}	3.054(4)
N(2)–Ag(1)–N(3)	139.24(15)	N(2)–Ag(1)–N(4)	123.34(16)
N(3)–Ag(1)–N(4)	77.85(17)	N(2)–Ag(1)–N(1)	75.70(16)
N(3)–Ag(1)–N(1)	133.40(15)	N(4)–Ag(1)–N(1)	110.70(17)
N(102)–Ag(2)–N(402)	169.8(2)	N(102)–Ag(2)–Ag(2) ⁱⁱⁱ	99.40(15)
N(402)–Ag(2)–Ag(2) ⁱⁱⁱ	90.07(15)	N(202)–Ag(3)–N(302)	168.68(18)
N(202)–Ag(3)–Ag(3) ^{iv}	113.62(16)	N(302)–Ag(3)–Ag(3) ^{iv}	77.37(16)
[Ag(L2)](NO ₃) (3)			
Ag(1)–N(12)	2.295(2)	Ag(1)–N(1)	2.352(2)
N(12)–Ag(1)–N(12) ^v	88.54(12)	N(12)–Ag(1)–N(1)	120.87(8)
N(12) ^v –Ag(1)–N(1)	127.90(8)	N(1)–Ag(1)–N(1) ^v	76.16(11)
[Cu(L2)](ClO ₄) (4)			
Cu(1)–N(1)	1.984(3)	Cu(1)–N(12) ⁱⁱⁱ	2.001(3)
Cu(1)–N(22) ^{vi}	2.014(3)	Cu(1)–N(2)	2.335(3)
N(1)–Cu(1)–N(12) ⁱⁱⁱ	133.18(12)	N(1)–Cu(1)–N(22) ^{vi}	112.70(11)
N(12) ⁱⁱⁱ –Cu(1)–N(22) ^{vi}	105.79(11)	N(1)–Cu(1)–N(2)	82.30(11)
N(12) ⁱⁱⁱ –Cu(1)–N(2)	107.16(11)	N(22) ^{vi} –Cu(1)–N(2)	112.11(12)
[Cu(L2)](BF ₄) (5)			
Cu(1)–N(1)	1.986(4)	Cu(1)–N(12)	1.996(4)
Cu(1)–N(22)	2.000(5)	Cu(1)–N(2)	2.318(5)
N(1)–Cu(1)–N(12)	132.85(17)	N(1)–Cu(1)–N(22)	112.55(17)
N(12)–Cu(1)–N(22)	105.67(18)	N(1)–Cu(1)–N(2)	82.16(18)
N(12)–Cu(1)–N(2)	107.7(2)	N(22)–Cu(1)–N(2)	112.75(18)

^a Symmetry codes: (i) $x, -y + 1.5, z + 0.5$; (ii) $x, y + 1, z$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x + 1, -y, -z - 1$; (v) $-x, y, -z + 0.5$; (vi) $-x + 2, -y, -z + 1$.

turn each L1 ligand connects three Cd(II) atoms to meet the geometric requirement of the Cd(II) atom. Such a coordination mode gives complex **1** a neutral two-dimensional (2D) rhombohedral grid network with (4,4) topology (Fig. 1b), in which the cadmium(II) atoms are in the same plane. A simplified 2D network where only the Cd(II) atoms are presented is shown in Fig. 1c. In each Cd₄ rhombus, the Cd ⋯ Cd edge distances are 11.29 Å for Cd(1M) ⋯ Cd(1O) and 11.79 Å for Cd(1M) ⋯ Cd(1D) (Fig. 1b), respectively. The internal angles of the rhombus are 70.9 and 109.1°, respectively. In addition, there are π – π interactions between the imidazole ring containing N(22F) and benzene ring containing C(11D) within each Cd₄ rhombus (Fig. 1b). The distance between the two ring centroids is 3.51 Å and the dihedral angle is 3.3°. Such π –stacking interactions between the imidazole ring and benzene ring have

been reported in the biological system.¹⁸ For example, it has been reported that the distance between the phenyl group of the inhibitor Phe residue and the imidazole group of chymotrypsin His57 is 3.75 Å indicating the presence of π – π stacking interactions.^{18a}

The 2D layers of complex **1** are packed in an –ABAB– sequence and the Cd(II) atoms in one layer sit above or below the grids of the adjacent layers (Fig. 1d). Consequently there are no open channels in complex **1**. Furthermore, the 2D layers are linked by hydrogen bonds to generate a 3D structure. Two bromide atoms, binding to one cadmium(II) atom, form a N–H ⋯ Br(1) hydrogen bond with one of the ethylenediamine N–H from one adjacent layer and a C–H ⋯ Br(2) one with an imidazole C–H from another neighboring layer. The hydrogen bonding data are summarized in Table 3.

Table 3 Hydrogen bond data for the complexes **1**, **2**, **3**, **4** and **5**

Compound	D–H ... A ^a	D ... A/Å	∠D–H ... A/°
1	N(1)–H(1) ... Br(1) ⁱ	3.445(4)	138
	C(103)–H(25) ... Br(2) ⁱⁱ	3.639(5)	159
2	N(2)–H(2) ... O(24)	3.125(7)	145
	N(3)–H(3) ... O(12)	3.279(7)	149
	N(4)–H(4) ... O(23) ⁱⁱⁱ	3.080(10)	142
	C(13)–H(16) ... O(31) ^{iv}	3.442(10)	158
	C(27)–H(27) ... O(14)	3.400(9)	142
	C(32)–H(31) ... O(13)	3.299(9)	153
	C(37)–H(36) ... O(11) ^v	3.445(10)	164
	C(40)–H(37) ... O(24) ^{iv}	3.457(10)	158
	C(101)–H(45) ... O(33)	3.265(14)	132
	C(103)–H(47) ... O(31) ^{iv}	3.332(13)	149
	C(301)–H(51) ... O(14) ^v	3.229(10)	144
	C(402)–H(55) ... O(34) ^{vi}	3.430(12)	153
3	C(10)–H(3) ... O(3)	3.354(7)	141
	C(13)–H(5) ... O(3) ^{vii}	3.413(6)	156
	C(17)–H(8) ... O(1) ^{vii}	3.477(13)	161
	C(17)–H(8) ... O(2) ^{viii}	3.199(10)	149
	C(101)–H(10) ... O(3) ^{ix}	3.361(8)	148
	C(101)–H(10) ... O(2) ^x	3.067(10)	137
	C(103)–H(12) ... O(2) ^{xi}	3.330(9)	137
	C(103)–H(12) ... O(1) ^{xii}	3.160(10)	130
4	C(10)–H(5) ... O(4) ^{xiii}	3.418(4)	164
	C(101)–H(12) ... O(4)	3.337(5)	150
	C(27)–H(21) ... O(3) ^{xiv}	3.405(6)	148
5	C(10)–H(5) ... F(2) ^{xv}	3.358(10)	166
	C(17)–H(10) ... F(3) ^{xvi}	3.486(12)	164
	C(20)–H(12) ... F(4) ^{xvii}	3.304(11)	137
	C(27)–H(18) ... F(4)	3.399(12)	158
	C(101)–H(19) ... F(2) ^{xvi}	3.350(11)	148
	C(203)–H(24) ... F(1) ^{xviii}	142	3.350(9)

^a Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, -0.5+y, 1.5-z$; (iii) $1+x, 1+y, z$; (iv) $x, 1+y, z$; (v) $-1+x, -1+y, z$; (vi) $1-x, -y, 1-z$; (vii) $x, -1+y, z$; (viii) $0.5-x, 0.5-y, 1-z$; (ix) $-x, 1-y, 1-z$; (x) $-0.5+x, -0.5+y, z$; (xi) $-x, -1+y, 0.5-z$; (xii) $-0.5+x, 0.5-y, -0.5+z$; (xiii) $x, 1+y, z$; (xiv) $2-x, -y, 1-z$; (xv) $x, -1+y, z$; (xvi) $2-x, 1-y, -z$; (xvii) $x, 0.5-y, 0.5+z$; (xviii) $1-x, -0.5+y, -0.5-z$.

Crystal structure of [Ag₃(L1)₂](ClO₄)₃ (**2**)

In contrast to the usual six-coordinated Cd(II) atom, the Ag(I) atom can adopt different coordination numbers from two to five according to its surrounding environments. When the ligand L1 reacted with Ag(I) salt, for example AgClO₄, instead of CdBr₂, a new coordination polymer **2** was obtained and its structure was determined by X-ray crystallography. The coordination mode in complex **2** was found to be remarkably different from that in complex **1**. As depicted in Fig. 2, the silver(I) atoms in **2** have two different coordination environments. The Ag(1) with a distorted tetrahedral geometry is coordinated by four ethylenediamine N atoms from two L1 ligands resulting a double-stranded helicate, similar to the previous reported silver(I) complexes with di-Schiff base ligands 1,2-bis(4'-pyridylmethyleneamino)ethane (L3) and 1,2-bis(3'-pyridylmethyleneamino)ethane (L4).¹⁹ The four-coordinated Ag(1) has N–Ag(1)–N bond angles ranging from 75.70(16) to 139.24(15)° and an average Ag(1)–N bond length of 2.383(8) Å as listed in Table 2. Similar Ag–N bond lengths have been reported for silver(I) complex with the same AgN₄ binding site, for example [Ag(L5)]NO₃ [L5 = 1,6-bis(4'-pyridyl)-2,5-diaza-hexane] has an average Ag–N bond length of 2.360(3) Å.¹³ In addition to the four-coordinated silver(I) atoms, the N(102)–Ag(2)–N(40D) angle of 169.8(2)° and N(20F)–Ag(3)–N(302) angle of 168.68(18)° indicate that the Ag(2) and Ag(3) atoms have near linear coordination geometry as shown in Fig. 2b. The double-stranded helicates are linked through the coordination of these two-coordinated Ag(I) atoms with the terminal imidazole groups of L1 ligands to generate an infinite 1D wandering chain structure (Fig. 2b). In the reported complex with the L3 ligand, [Ag₃(L3)₂](NO₃)₃·H₂O, the helicates are linked by

the same two-coordinated silver(I) atom, however, to form a 2D network.¹⁹ Such a difference between the topologies of complex **2** and [Ag₃(L3)₂](NO₃)₃·H₂O is considered to be attributed to the difference of the length and the flexible degree of the ligands L1 and L3. It is noteworthy that, in addition to the Ag–N coordination interactions, there are Ag ... Ag interactions since the distances of Ag(2)–Ag(2A) and Ag(3)–Ag(3B) (atom numbering shown in Fig. 2b) are 3.081(3) and 3.054(4) Å, respectively, close to the 3.089(1) Å observed in the complex [Ag(bpp)](CF₃SO₃) [bpp = 1,3-bis(4-pyridyl)propane],²⁰ and shorter than the 3.179(1) Å observed in the reported complex [Ag₃(py-hep)₂](ClO₄)₃·0.5CH₃CN [py-hep = 1,7-bis(4'-pyridyl)-2,6-diazaheptane].²¹ Furthermore, each pair of two imidazole rings binding to Ag(2) and Ag(2A) atoms, are nearly parallel with a dihedral angle of 7.6° and separated by a centroid–centroid distance of 3.62 Å, indicating the presence of π–π stacking interactions.²² However, such π–π stacking interactions between two imidazole rings binding to the Ag(3) and Ag(3B) atoms are much weaker since the corresponding dihedral angle and distance are 24.4° and 3.92 Å, respectively. In complex **2**, the ClO₄[−] anions are located in the vacancy of the 1D chains and held there by nine C–H ... O and three N–H ... O hydrogen bonds between the ClO₄[−] anions and cationic chains (Fig. 2c and Table 3).

Crystal structures of [Ag(L2)](NO₃) (**3**), [Cu(L2)](ClO₄) (**4**) and [Cu(L2)](BF₄) (**5**)

To further investigate the effect of the nature of organic ligands on the assembly, we prepared a long chain Schiff base ligand L2 by reducing the flexibility of the ligand L1 and reactions of L2 with Ag(I) and Cu(I) salts were carried out.

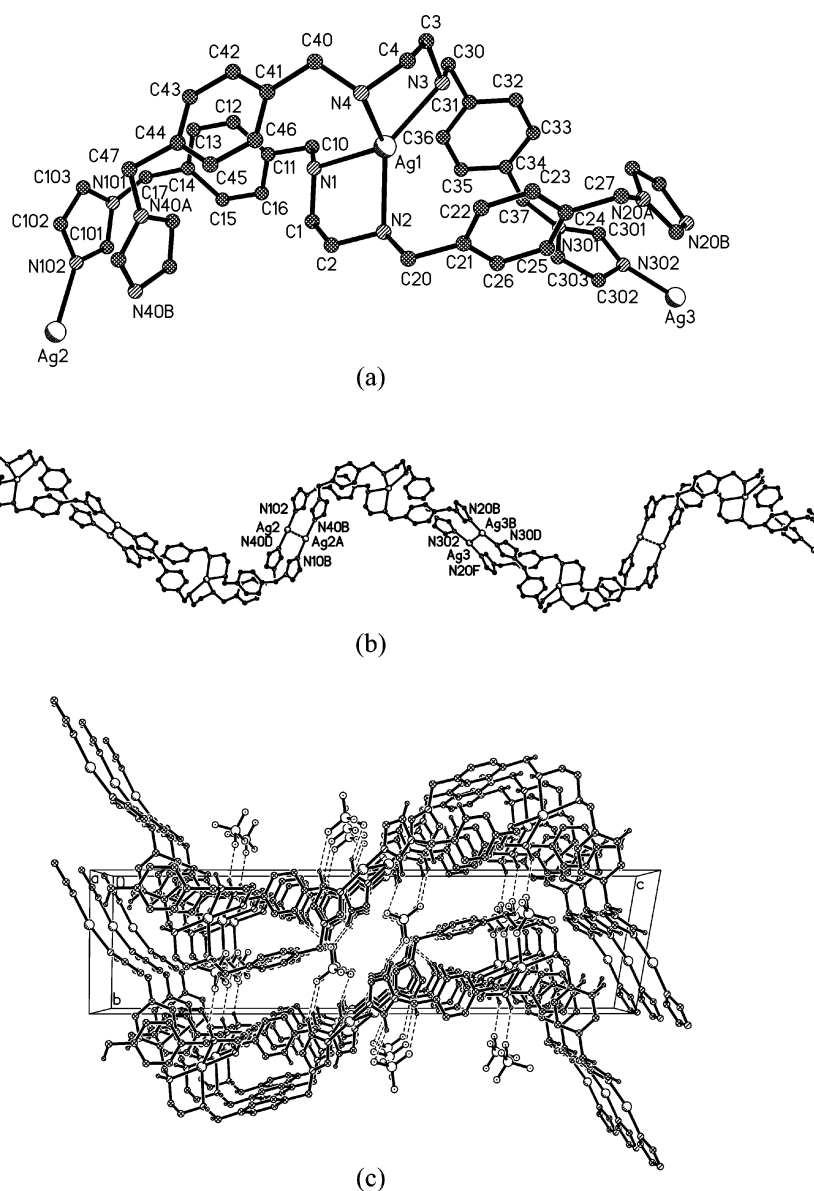
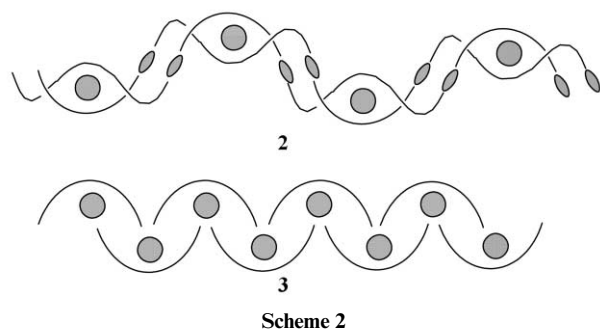


Fig. 2 (a) A perspective view of double-stranded helicate motif in the structure of $[\text{Ag}_2(\text{L}1)_2](\text{ClO}_4)_3$ (**2**). (b) The 1D infinite wandering chain with $\text{Ag} \cdots \text{Ag}$ interactions. (c) The packing diagram of **2** with hydrogen bonds indicated by dashed lines.

When the ligand L2 reacts with silver(I) nitrate, a novel coordination complex $[\text{Ag}(\text{L}2)](\text{NO}_3)$ (**3**) was obtained. The crystallographic analysis reveals that complex **3** is composed of an infinite 1D cationic chain, which is different from that of complex **2** (Scheme 2). The coordination environment of silver(I) atom is shown in Fig. 3a with the atom numbering scheme. Each silver(I) atom is coordinated by two nitrogen atoms of an ethylenediamine unit from one L2 ligand and two imidazole nitrogen atoms from other two L2 ligands. Thus the coordination geometry of the $\text{Ag}(\text{I})$ atom is distorted tetrahedral with the average $\text{Ag}(\text{I})\text{--N}$ bond length 2.323(1) Å and

$\text{N--Ag}(\text{I})\text{--N}$ bond angles ranging from 76.14(8) to 128.1(2)°. Therefore, complex **3** shows an infinite 1D zigzag chain structure (Fig. 3b). The coordination mode of silver(I) atoms in **3** is same as the one in the previous reported complex $[\text{Ag}(\text{L}5)]\text{NO}_3$,¹³ that exhibited an infinite 1D hinged chain structure. The L5 has a “Z” shape in this hinged chain due to the flexibility of L5 while the shape of L2 in **3** is “U”. The formation 1D zigzag chain of **3** is attributed to the long chain structure of L2. The NO_3^- anions occupy the voids among the chains through eight $\text{C--H} \cdots \text{O}$ hydrogen bonds as shown in Fig. 3c and Table 3.

To investigate the influence of metal ion and anion on the structures of assembly product, reactions of L2 with copper(I) salts with different anions were carried out, and complexes **4** and **5** were obtained, since the copper(I) is usually four-coordinated with tetrahedral geometry. The results of crystallographic analyses indicate that the complexes **4** and **5** crystallize in the same monoclinic space group $P2_1/c$ as listed in Table 1. It is clear that the two compounds are isomorphous and isostructural, which implies that the anions have no obvious influence on the structure of these complexes. In the reported complexes with the flexible ligand L5, it has been demonstrated that the anions play an important role in determining the structure of complexes.¹³ In both complexes **4** and **5**, each copper(I) atom is coordinated by two nitrogen atoms from



Scheme 2



a diimine unit of one L2 ligand and two imidazole nitrogen atoms from other two L2 ligands (Fig. 4). This coordination mode in **4** and **5** is very similar to that of complex **3**. However, there is difference between the structures of complexes **3** and **4** (as well as **5**). The two benzene ring planes of one L2 ligand in complex **3** are almost parallel each other since the dihedral angle between them is 3.6° and the $\text{Ag}(1\text{A}) \cdots \text{Ag}(1\text{B})$ (Fig. 3a) non-bonded distance is 16.59 \AA , while the corresponding dihedral angle and $\text{Cu}(1\text{A}) \cdots \text{Cu}(1\text{B})$ distance are 98.0° and 13.72 \AA in complex **4**, and 98.3° and 13.70 \AA in complex **5**, respectively. This means that the complexes **4** and **5** are compressed zigzag chains compared with that of complex **3**. Therefore, the metal ions with the same coordination geometry react with relatively rigid ligand L2 to form complexes with same topology but subtle difference in their structures as observed in complexes **3** and **4** (as well as **5**). The anions of **4** are located in the voids of the chains and held there by $\text{C-H} \cdots \text{O}$ hydrogen bonds as shown in Fig. 4c and Table 3.

The photoluminescent properties of the synthesized complexes were studied in the solid state at room temperature. 2D grid network complex **1** exhibits a broad blue-fluorescent emission around 480 nm (lifetime $\tau = 3.15$ ns) upon excitation at 394 nm, which is quite similar to that of ligand L1 (emission maximum

The luminescent spectra of complexes **3** and **4** as well as ligand L2 in the solid state at room temperature are shown in Fig. 6. Complex **3** exhibits an intense broad photoluminescence with maximum emission at *ca.* 462 nm ($\tau = 1.36$ ns) upon excitation at 394 nm, which is near to the maximum emission at 459 nm ($\tau = 1.56$ ns) of the free ligand L2 under the same conditions. Therefore the luminescence observed in **3** is attributed to the intraligand luminescent emission. In contrast to the very similar emission maximum and lifetime of complex **3** and L2, complex **2** showed blue-shifted emission with short lifetime

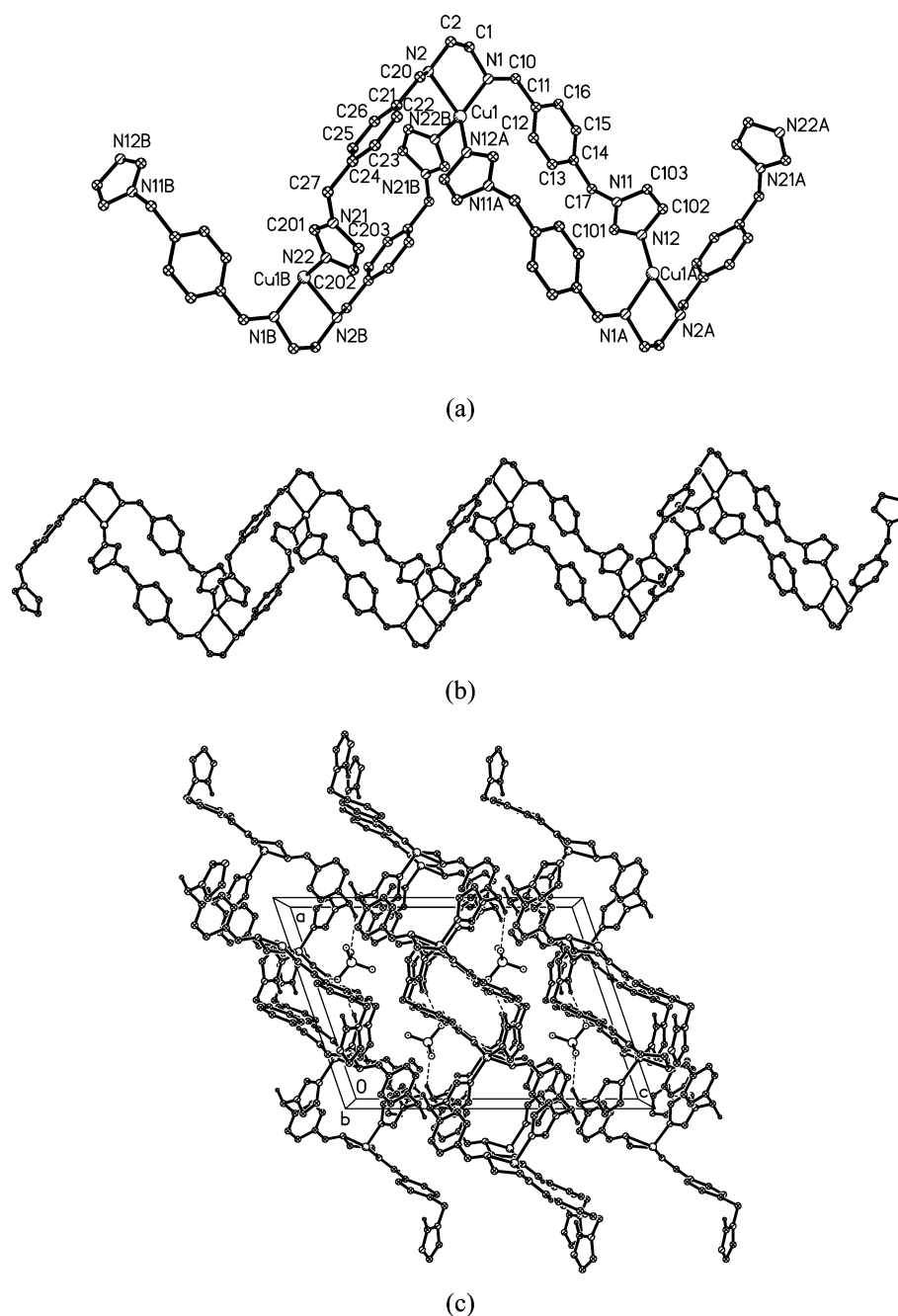


Fig. 4 (a) The coordination environment around the copper(I) atom in $[\text{Cu}(\text{L}2)]\text{ClO}_4$ (**4**); hydrogen atoms were omitted for clarity. (b) An infinite zigzag chain structure in **4**. (c) The crystal packing diagram of **4** with hydrogen bonds indicated by dashed lines.

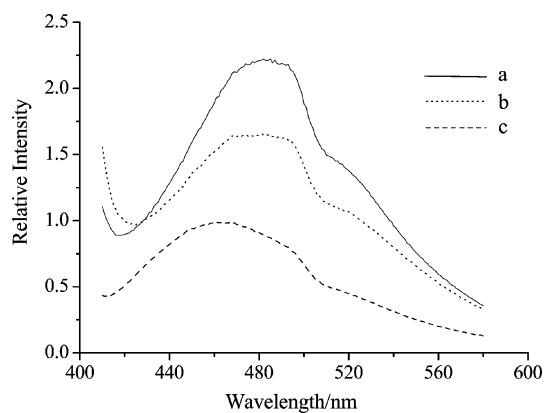


Fig. 5 The emission spectra of (a) ligand L1, (b) complex **1** and (c) complex **2** in the solid state at room temperature, $\lambda_{\text{exc}} = 394$ nm.

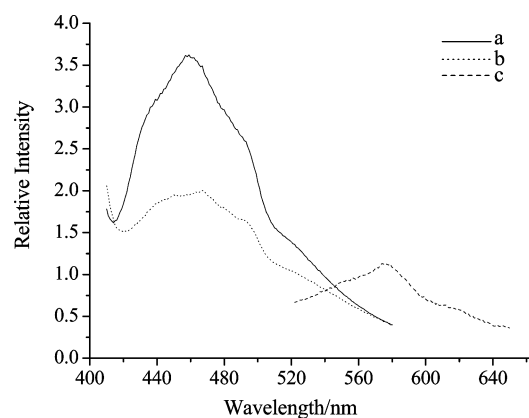


Fig. 6 The emission spectra of (a) ligand L2, (b) complex **3**, (c) complex **4** in the solid state at room temperature, $\lambda_{\text{exc}} = 394$ nm for L2 and **3** and $\lambda_{\text{exc}} = 250$ nm for **4**.

compared with those of ligand L1 as mentioned above. Such differences in maximum emission and lifetime between complex **2** and L1 may probably be caused by Ag \cdots Ag interactions in **2**, since no such interactions were found in **3** as revealed by crystal structure analyses. It has been suggested that Ag \cdots Ag interactions may have impact on the emissions.²⁶

In the emission spectrum of complex **4** (Fig. 6c), a weak photoluminescence with maximum emission at *ca.* 574 nm was observed upon excitation at 250 nm. Similar photoluminescence has been reported for the 2D layered Cu(I) coordination polymer with maximum emission at *ca.* 580 nm (*ca.* τ = 1.06 ns, λ_{ex} = 250 nm).²⁷ The UV-vis spectrum of complex **4** exhibits a low-energy band at *ca.* 402 nm in the solid state, which corresponds to the metal-to-ligand charge transfer (MLCT).²⁸ However, the metal center d to s orbital transition could not be completely ruled out.²⁷ It is well known that low-energy emissions of [Cu(NN)₂]⁺ (NN = 2,9-disubstituted-1,10-phenanthroline) systems are usually assigned to the metal-to-ligand d– π^* charge transfer (MLCT) and hence the observed luminescence of **4** can be ascribed to the MLCT emission similar to the reported Cu(I) complexes.^{29–31}

During the past decades, the photoluminescence properties of copper(I) complexes, especially with 2,9-disubstituted-1,10-phenanthroline ligands, have been extensively examined.²⁹ The results showed that the emission behavior of these Cu(I) complexes, *e.g.* emission wavelength, excited state lifetime, is quite changeable depending on the chemical nature, size, and position of substituents and distortions of the structure. To inhibit the flattening distortion of the excited state, bulky substituents in the ligands were introduced, and as a result, fluorescent properties of their Cu(I) complexes were improved.²⁹ On the other hand, McMillin *et al.* reported the luminescent property of a bis(phenanthroline)copper(I) complex without such steric substituents in the solid state.^{31a} The observation of this luminescence is ascribed to the small flattening distortion probably due to the packing interactions in the crystal, which prevent further distortion in the photoexcited state. Compared with these [Cu(NN)₂]⁺ complexes, the coordination polymer **4**, in which the coordinated N atoms are of mixed types (two imino Ns and two imidazole Ns), shows both flattening and rocking distortions in the solid.³² The flattening distortion is demonstrated by a dihedral angle of 98.7° between the planes defined by Cu(1), N(1), N(2) and by Cu(1), N(12A), N(22B) (Fig. 4a), and the rocking distortion is reflected by a long Cu(1)–N(2) bond length [2.335(3) Å] compared with other three bonds (Table 2) and an approximately pyramidal coordination geometry around the copper(I) atom. Such distortions in the crystal are probably induced by crystal packing interactions that may also oppose further distortion in the excited state,^{31a} and as a consequence the coordination polymer **4** shows a weak, short-lived emission (*ca.* τ = 1.7 ns) in the solid.

Conclusion

The present study shows that the reactions of new long-chain ligands L1 and L2 with various metal salts can afford a variety of fascinating self-assembled polymeric frameworks. The difference between ligands L1 and L2 is that the former is more flexible than the latter. Flexible ligand L1 can adjust its conformations to fit with the geometrical needs of transition metal ions. In complex **1**, ligand L1 adopts the compressed W-shape to give a 2D rhombic grid network when it reacted with cadmium(II) bromide. In the reaction with Ag(I) salt, long-chain ligand L1 adopts conformations of U- and W-shapes to meet the geometric need of four-coordinated and two-coordinated Ag(I) atoms to form an infinite wandering 1D chain in complex **2** (Scheme 2). The relatively rigid ligand L2 only adopts a U-shape conformation in complexes **3**, **4** and **5** and its complexes all exhibit an infinite zigzag 1D chain structures (Scheme 2). On the other hand, the coordination mode of silver(I) atoms

in complex **2** is very different from that in complex **3**. In complex **2**, the silver(I) atoms have two types, namely, four- and two-coordinate, while the complex **3** only contains four-coordinated silver(I) atoms. The results are assigned to the different flexibility of long chain ligands L1 and L2 and demonstrate the important role of the nature of ligand on the assembly.

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