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Silver(I) and Copper(I) Coordination Polymers Based on Thiaoxa-Macrocycles

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Two S_2O_2-macrocycles with different ring size ($\mathbf{L^1}$: 17- and $\mathbf{L^2}$: 18-membered) were synthesised and structurally characterised by X-ray analysis. Reactions of $\mathbf{L^1}$ and $\mathbf{L^2}$ with silver(I) salts (ClO_4^- and NO_3^-) afforded respective ligand- and/or anion-directed complexes **1**–**4** with different topologies; single-stranded 1D coordination polymer $[Ag\mathbf{L^1}(ClO_4)(DMSO)]_n$ (**1**), double-stranded 1D coordination polymer $\{[Ag_2(\mathbf{L^1})_2(NO_3)_2]\cdot DMSO\}_n$ (**2**), cyclic dimer $[Ag_2(\mathbf{L^2})_2(ClO_4)_2]\cdot CH_2Cl_2\cdot CH_3OH$ (**3**) and 2D polymeric sheet $[Ag(\mathbf{L^2})NO_3]_n$ (**4**). Meanwhile, reactions of these two ligands with copper(I) iodide afforded 1D (**5**) and 2D (**6a**) coordination polymers linked with a rhomboid-type Cu–I_2–Cu unit, respectively. The formation of such discrete and continuous supramolecular complexes is discussed in terms of discrimination of the anion effect, ligand flexibility as well as interligand π-π stacking interaction.

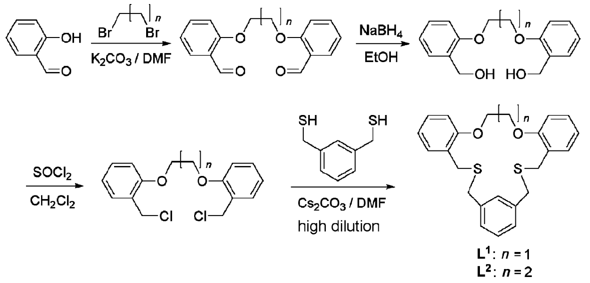
Introduction

The sulfur-bearing crown ethers (thiamacrocycles) show remarkable coordinating ability to form stable complexes with *d*-block metal ions, in many cases forcing the metal ion to adopt an unusual position.[1] Our group[2] and others[3] have proposed the *exo*-coordination behaviour of the thiamacrocycles, which exhibit diverse types of supramolecular complexes with soft metal salts upon varying donor atoms and anions. Recently, we reported that simple tuning of interdonor (S···S) separation in given S_2O_2-macrocycles as a controlling factor is effective to discriminate the products because of the different *exo*-binding mode towards the soft metal ions.[4] Parallel to this, coordination of copper(I) halide with the same ligand system is of particular interest due to the diverse binding mode of copper(I) halide clusters towards the ligand and their unique photophysical properties.[5] On the basis of these considerations, we are interested in extending this approach to the noncoordinating donors of similar ligand systems. Taking these into account, two analogous S_2O_2 macrocycles $\mathbf{L^1}$ (17-membered) and $\mathbf{L^2}$ (18-membered) with variation of flexibility due to the slightly different ring sizes are synthesised. We reasoned that these may trigger discrimination of rigidity-controlled products with soft metal ions, such as silver(I) and copper(I). As a result, we have realised that "small changes in molecular level (*building block*) can induce large differences in supramolecular level (*assembled product*)". For example, in view of both the silver(I) salts and copper(I) iodide system employed, it is becoming apparent that such a small variation of ligand structure plays an important role in the topologies of resulting complexes.

Results and Discussion

Synthesis and Characterisation of Ligands

Synthesis of the ligands began with salicylaldehyde (Scheme 1). Dichloride precursors[6] for cyclisation were prepared through macrocyclisation reactions from corresponding dichlorides and 1,3-phenylenedimethanethiol in the presence of Cs_2CO_3 under high dilution conditions in reasonable yields ($\mathbf{L^1}$: 30% and $\mathbf{L^2}$: 50%).



Scheme 1. Synthesis of ligands $\mathbf{L^1}$ and $\mathbf{L^2}$.

Structures of the macrocycles prepared were also characterised in solid-state by single-crystal X-ray crystallography

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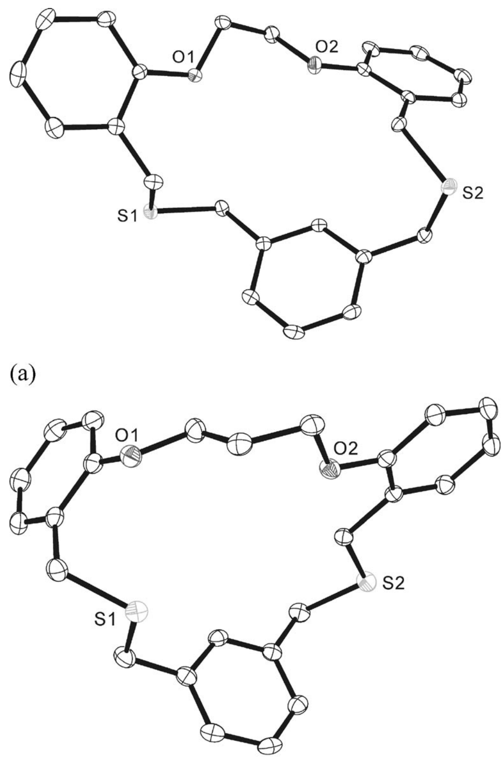
(Figure 1). Colourless crystals of $\mathbf{L^1}$ and $\mathbf{L^2}$ suitable for X-ray analysis were obtained by slow evaporation from the respective solutions of dichloromethane. Without exception, O atoms are oriented in an endodentate fashion, while S atoms are positioned exodentate.[7] The macrocyclic ring of $\mathbf{L^1}$ is slightly twisted and the torsion angle between two O atoms is indicative of a gauche arrangement [O1–C–C–O2 67.2(3)°]. $\mathbf{L^2}$ shows a more twisted configuration due to the flexible nature of the ring cavity than that of $\mathbf{L^1}$. Thus, the O···O distance in $\mathbf{L^2}$ [4.115(3) Å] is longer than that of $\mathbf{L^1}$ [2.870(2) Å], but the S···S distance in $\mathbf{L^2}$ [6.436(1) Å] is shorter than that in $\mathbf{L^1}$ [7.156(1) Å], indicating the flexible nature of $\mathbf{L^2}$.



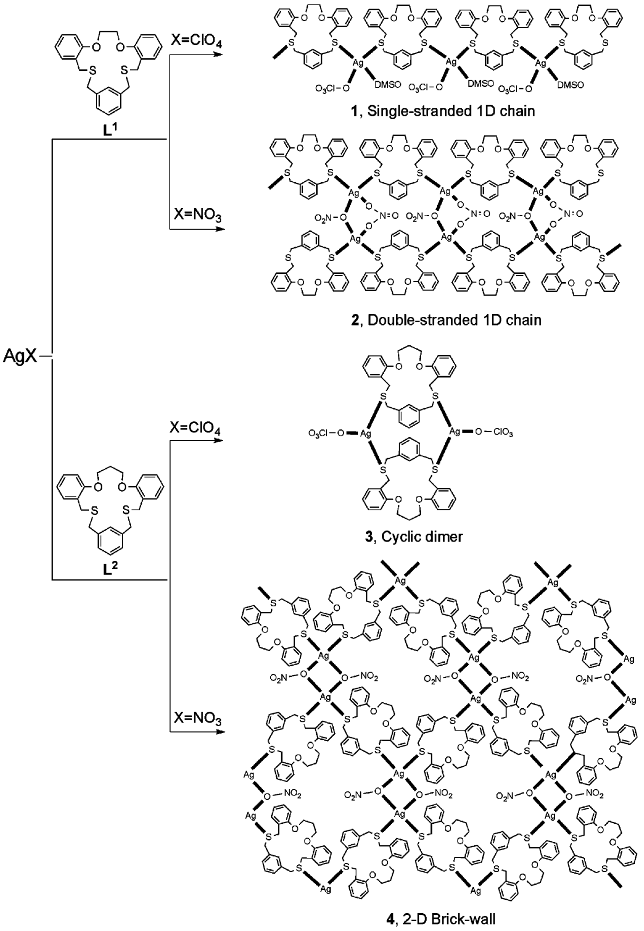
(a)

(b)

Figure 1. Molecular structures of (a) $\mathbf{L^1}$, and (b) $\mathbf{L^2}$.

Syntheses of Silver(I) Complexes and Structural Description

In complexation with silver(I), perchlorate and nitrate were used to examine the anion effect on resulting complexes. Using these reaction systems, we obtained four supramolecular complexes **1**–**4** with different topologies (Scheme 2), and their structures were characterised by X-ray analysis (Figures 2, 3, 4 and 6).



Scheme 2. Silver(I) complexes prepared.

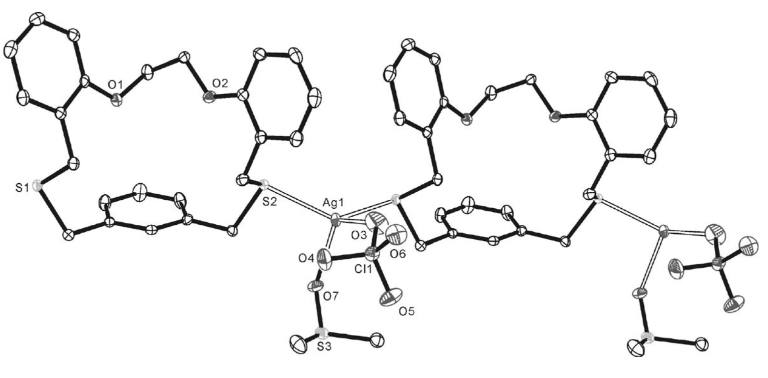


Figure 2. Single-stranded 1D polymeric structure of **1**, $[\mathrm{Ag}(\mathbf{L^1})(\mathrm{ClO_4})(\mathrm{DMSO})]_n$. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–O7 2.347(3), Ag1–O3 2.448(4), Ag1–S1A 2.478(1), Ag1–S2 2.487(1), O7–Ag1–O3 115.5(1), O7–Ag1–S1A 103.0(1), O3–Ag1–S1A 96.8(1), O7–Ag1–S2 99.9(1), O3–Ag1–S2 113.0(1), S1A–Ag1–S2 129.3(4). Symmetry operation: A: x, $y + 1$, z.

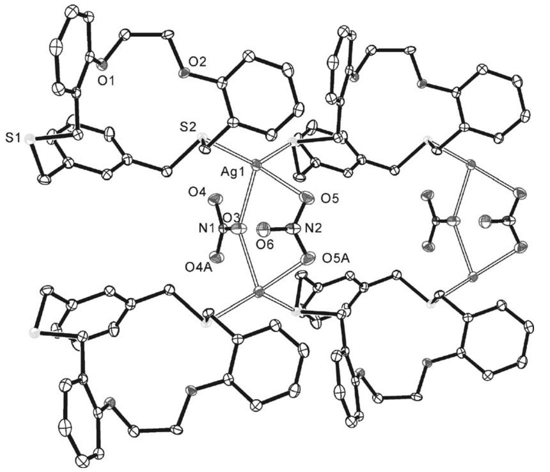


Figure 3. Double-stranded 1D polymeric structure of **2**, $\{[Ag_2(\mathbf{L^1})_2(NO_3)_2]\cdot DMSO\}_n$. Hydrogen atoms and noncoordinating solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–O3 2.454(2), Ag1–S2 2.463(1), Ag1–S1A 2.476(1), Ag1–O5 2.501(4), O3–Ag1–S2 105.8(1), O3–Ag1–S1A 108.0(1), S2–Ag1–S1A 132.1(4), O3–Ag1–O5 82.3(1), S2–Ag1–O5 119.0(1), S1A–Ag1–O5 98.7(1). Symmetry operation: A: *x*, *y*, *z* – 1.

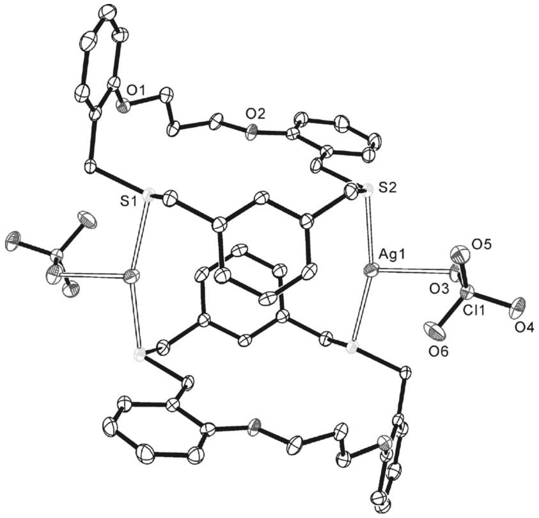


Figure 4. Cyclic dimer structure of **3**, $[Ag_2(\mathbf{L^2})_2(ClO_4)_2]\cdot CH_2Cl_2\cdot CH_3OH$. Hydrogen atoms and noncoordinating solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–S1A 2.420(1), Ag1–S2 2.426(1), Ag1–O3 2.636(3), S1A–Ag1–S2 161.8(1), S1–Ag1–O3 86.2(1), S1A–Ag1–O3 107.0(1). Symmetry operation: A: –*x* + 1, –*y* + 1, –*z* + 1.

From the reactions of $\mathbf{L^1}$ with silver(I) salts (**1**: ClO_4^- and **2**: NO_3^-), two complexes **1** and **2** were prepared as follows. Each colourless precipitate was obtained from $\mathbf{L^1}$ with the corresponding silver(I) salts in CH_2Cl_2/CH_3OH and single crystals of the respective complexes suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into the DMSO solution. The X-ray analysis revealed that **1** is a unique single-stranded 1D polymeric array of formula $[Ag\mathbf{L^1}(ClO_4)(DMSO)]_n$ with a –$\mathbf{L^1}$–Ag–$\mathbf{L^1}$–Ag pattern (Figure 2). Thus, the asymmetric unit of **1** contains one $\mathbf{L^1}$, one Ag atom, one perchlorate ion and one DMSO molecule. The structural unit shown in Figure 2 is generated through the continual symmetry operations. The Ag1 atom which links two macrocycles via Ag–S bonds shows distorted tetrahedral coordination composed of two S donor atoms from two $\mathbf{L^1}$, one monodentate ClO_4^- and one DMSO molecule. Two O donor atoms in the ring cavity remain uncoordinated. The largest deviations from tetrahedral coordination around Ag involve the angles O6–Ag–S1A [96.8(1)°] and S2–Ag1–S1A [129.3(4)°]. The conformation of $\mathbf{L^1}$ in **1** is not significantly different from that in free $\mathbf{L^1}$, suggesting that the ligand is relatively well preorganised. It is also noteworthy that the coordinated macrocycles are arranged side by side showing the interligand π-π stacking (dashed lines in Figure S1; see Supporting Information) between two benzo-groups in adjacent ligands. The preference for the 1D array, in this case, is probably due to the interligand π-π stacking observed for all of the $\mathbf{L^1}$ complexes in this work (see below).

To examine the role of anions in the formation of $\mathbf{L^1}$ complexes, the reaction was repeated with $AgNO_3$. Reaction of $\mathbf{L^1}$ and $AgNO_3$ in CH_2Cl_2/CH_3OH afforded a precipitate immediately. The precipitate was filtered and collected. The colourless crystalline product **2** was grown by vapour diffusion of diethyl ether into DMF/DMSO solution of the complex. The structure of **2** is more interesting. The X-ray analysis revealed that **2** is a double-stranded 1D array of formula $\{[Ag_2(\mathbf{L^1})_2(NO_3)_2]\cdot DMSO\}_n$ (Figure 3). The asymmetric unit contains one $\mathbf{L^1}$, one Ag atom, a half of a monodentate nitrate ion and a half of a bidentate nitrate ion. Each Ag atom outside the cavity is four-coordinate by two S atoms from two adjacent $\mathbf{L^1}$ forming an Ag–$\mathbf{L^1}$–Ag–$\mathbf{L^1}$ array. The remaining sites are occupied by one mono- and one bidentate nitrate ion which bridge two arrays via Ag–O(NO)O–Ag and Ag–O(NO_2)–Ag bonds. In other words, the Ag–$(NO_3)_2$–Ag bridging units are located at the centre of four $\mathbf{L^1}$ and each Ag atom is tetrahedrally coordinated by two S donors from two adjacent $\mathbf{L^1}$ by Ag–S bonds and two O atoms from two bridging nitrate ions forming an infinite poly(cyclic dimer) structure. Unlike the case of **1**, one DMSO molecule was found uncoordinated in the cavity. The S2–Ag–S1A angle for the different macrocycles is 132.1(4)° and the S2–Ag–O3 and S1A–Ag–O5 angles are 105.8(1) and 98.7(1)°, respectively. Some discrete and polymeric species linked with the square-dimer Ag–$(NO_3)_2$–Ag unit have been reported.[8] To the best of our knowledge, this is the first characterised example of a disilver system doubly bridged by one mono- and one bidentate nitrate ion. The interligand π-π stacking (dashed lines in Figure S2) between two benzo groups in adjacent ligands is also observed. As a result, the nitrate ions as the second coordinating species and interligand π-π stacking both show an influence on the assembled structure of **2**.

Having successfully obtained $\mathbf{L^1}$ complexes (**1** and **2**), we proceeded with the preparation of $\mathbf{L^2}$ complexes (**3** and **4**). Colourless crystalline complex **3** was obtained by slow concentration of the reaction mixture of $\mathbf{L^2}$ and $AgClO_4$ in CH_2Cl_2/CH_3OH at room temperature. The X-ray analysis revealed that **3** is a discrete-type cyclic dimer of formula $[Ag_2(\mathbf{L^2})_2(ClO_4)_2]\cdot CH_2Cl_2\cdot CH_3OH$ (Figure 4). The asymmetric unit contains one $\mathbf{L^2}$, one Ag atom, one perchlorate ion and two noncoordinating solvent molecules (not shown). The structural unit shown in Figure 4 is generated through an inversion symmetry. Each three-coordinate Ag atom that lies outside the cavity bridges two S donors from two facing macrocycles. The coordination geometry of the Ag atom is trigonal planar with two coordination sites being occupied by the S atoms and the third site occupied by a monodentate perchlorate ion. The trigonal planar silver(I) is considerably distorted from the regular one to give a T-shaped geometry: the bond angles for S2–Ag1–S1A, S2–Ag1–O3 and S1A–Ag1–O3 are 161.8(1)°, 86.2(1)° and 107.0(1)°, respectively. The difference in the bond angles around the Ag centre is caused by the steric hindrance of the macrocycles.

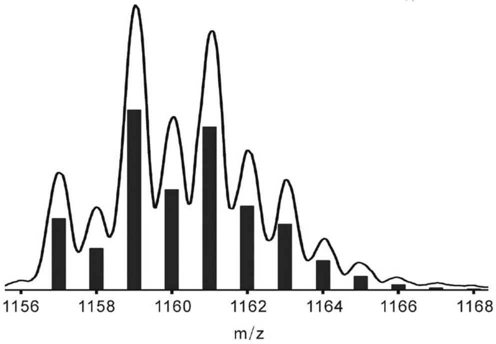
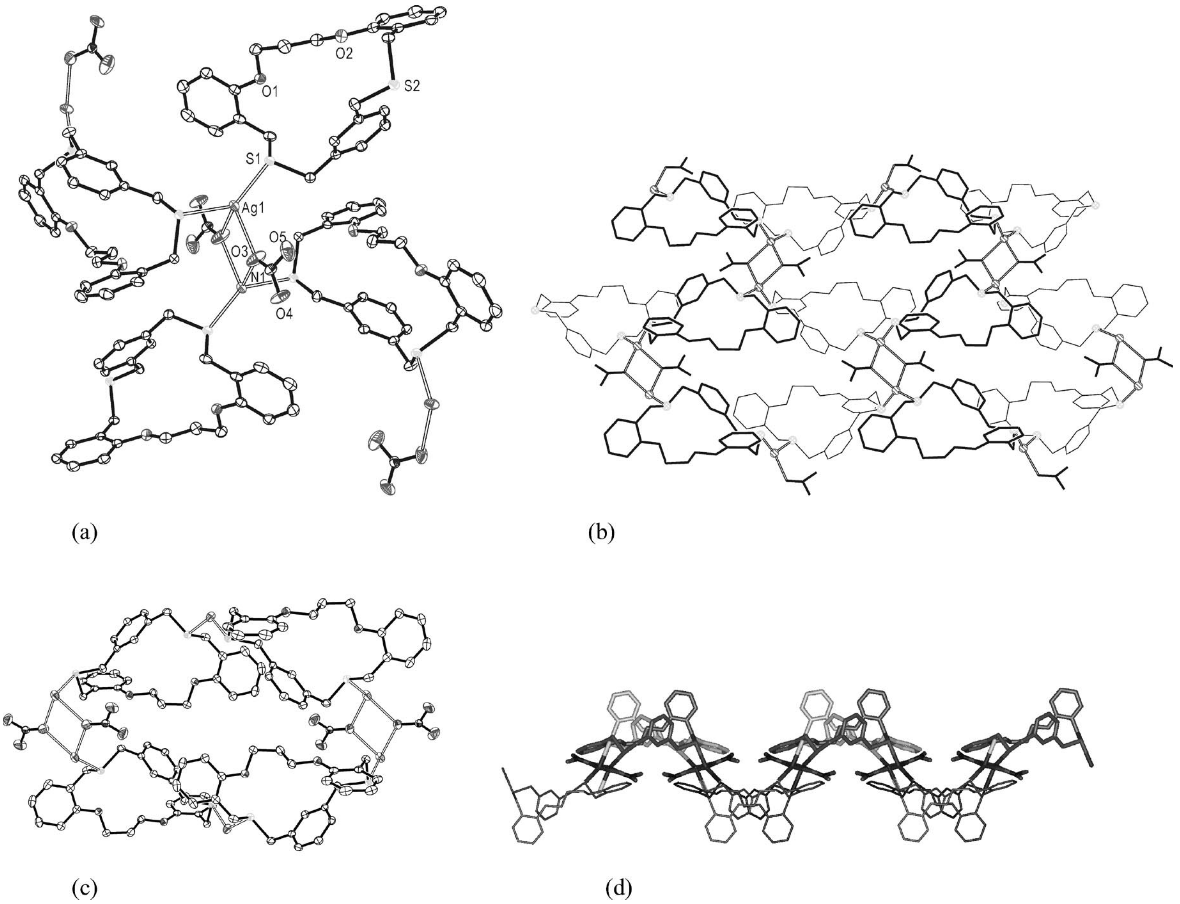


Figure 5. Observed isotopic distribution for $[Ag_2(\mathbf{L^2})_2(ClO_4)]^+$ in the FAB mass spectrum of **3**. The bars represent the predicted mass spectral distribution for this ion.

The FAB mass spectrum of **3** contains a peak at *m*/*z* 1159, which corresponds to $[Ag_2(\mathbf{L^2})_2(ClO_4)]^+$, according to its isotope pattern (Figure 5).

Colourless crystalline complex **4** was obtained by slow concentration of a reaction mixture of $\mathbf{L^2}$ and $AgNO_3$ in CH_2Cl_2/CH_3OH at room temperature. The X-ray analysis revealed that **4** is a 2D polymeric array of formula $[Ag\mathbf{L}(\mu\text{-}NO_3)]_n$ (Figure 6). The 2D network of **4** basically contains an Ag–$(\mu\text{-}NO_3)_2$–Ag rhomboid core bonded to four ligands via Ag–S bonds (Figure 6, a). The Ag atom is tetrahedrally coordinated by two S donors from two adjacent ligands and two monodentate μ_2-NO_3 ions. The Ag–S [2.416(1) and 2.514(1) Å] and Ag–O [2.391(2) and 2.444(2) Å] bond lengths are reasonably similar to those in other complexes.[9] The gross geometry of **4** can be described as an infinite brick-wall pattern (Figure 6, b). The asymmetric unit of **4**



(a)

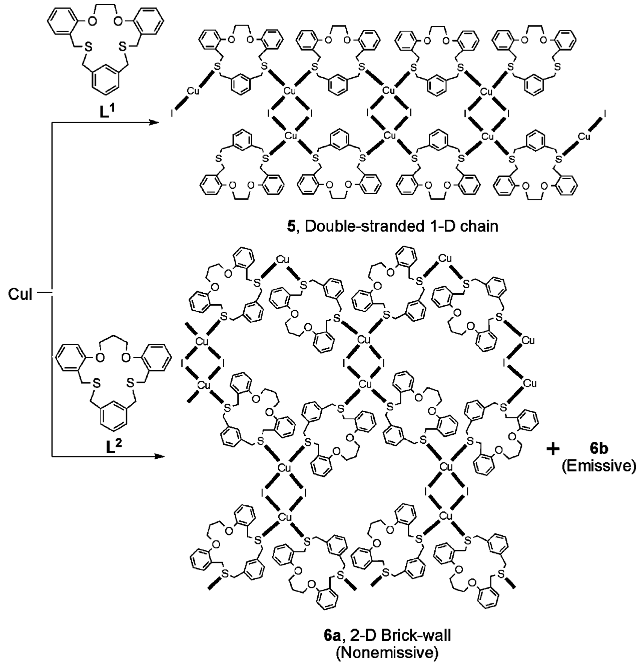
(b)

(c)

(d)

Figure 6. (a) Coordination environment of **4**, $[Ag(\mathbf{L^2})NO_3]_n$, (b) brick-wall type 2D polymeric network, (c) a single brick unit in **4** generated through four $\mathbf{L^2}$ and four Ag–$(\mu\text{-}NO_3)_2$–Ag rhomboid cores and (d) side view of wavy 2D network. Selected bond lengths [Å] and angles [°]: Ag1–O3 2.391(2), Ag1–S1 2.416(1), Ag1–O3A 2.444(2), Ag1–S2B 2.514(1), O3–Ag1–S1 117.3(1), O3–Ag1–O3A 71.1(1), S1–Ag1–O3A 134.3(1), O3–Ag1–S2B 100.1(1), S1–Ag1–S2B 127.3(2), O3A–Ag1–S2B 91.0(1). Symmetry operations: A: $-x + 2$, $-y + 2$, $-z + 1$, B: $-x + 3/2$, $y + 1/2$, $-z + 3/2$.

contains one L^2, one Ag atom and one nitrate ion. A single brick unit of **4** contains four asymmetric units where each ligand is interconnected by the Ag–(μ-NO_3)$_2$–Ag linkers alternately (Figure 6, c). In this case, the preference for the 2D polymeric scaffold is probably due to the flexible nature of L^2 together with the steric effect (hindrance) between the macrocycles.



Scheme 3. Copper(I) iodide coordination polymers prepared.

Syntheses of Copper(I) Iodide Complexes and Structural Description

As mentioned, the ligand-directed products **5** and **6a** with different topologies were obtained by the assembly reactions of each ligand with copper(I) iodide as depicted in Scheme 3.

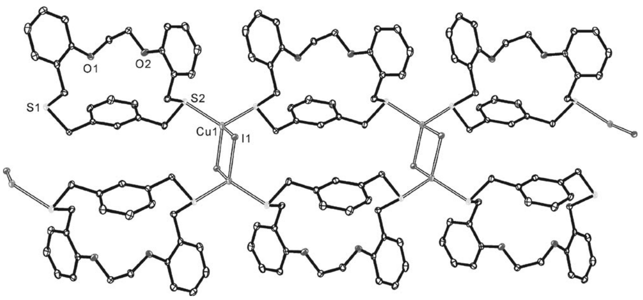


Figure 7. Double-stranded 1D polymeric structure of **5**, $[(Cu_2I_2)(\mathbf{L}^1)_2]_n$. Selected bond lengths [Å] and angles [°]: Cu1–S1A 2.332(2), Cu1–S2 2.371(2), Cu1–I1 2.617(1), Cu1–I1B 2.677(1), S1A–Cu1–S2 112.1(1), S1A–Cu1–I1 109.8(1), S2–Cu1–I1 112.7(1), S1A–Cu1–I1B 103.5(1), S2–Cu1–I1B 109.3(1), I1–Cu1–I1B 109.1(1), Cu1–I1–Cu1B 70.9(1). Symmetry operations: A: x, $y + 1$, z, B: $-x + 1$, $-y + 2$, $-z + 1$.

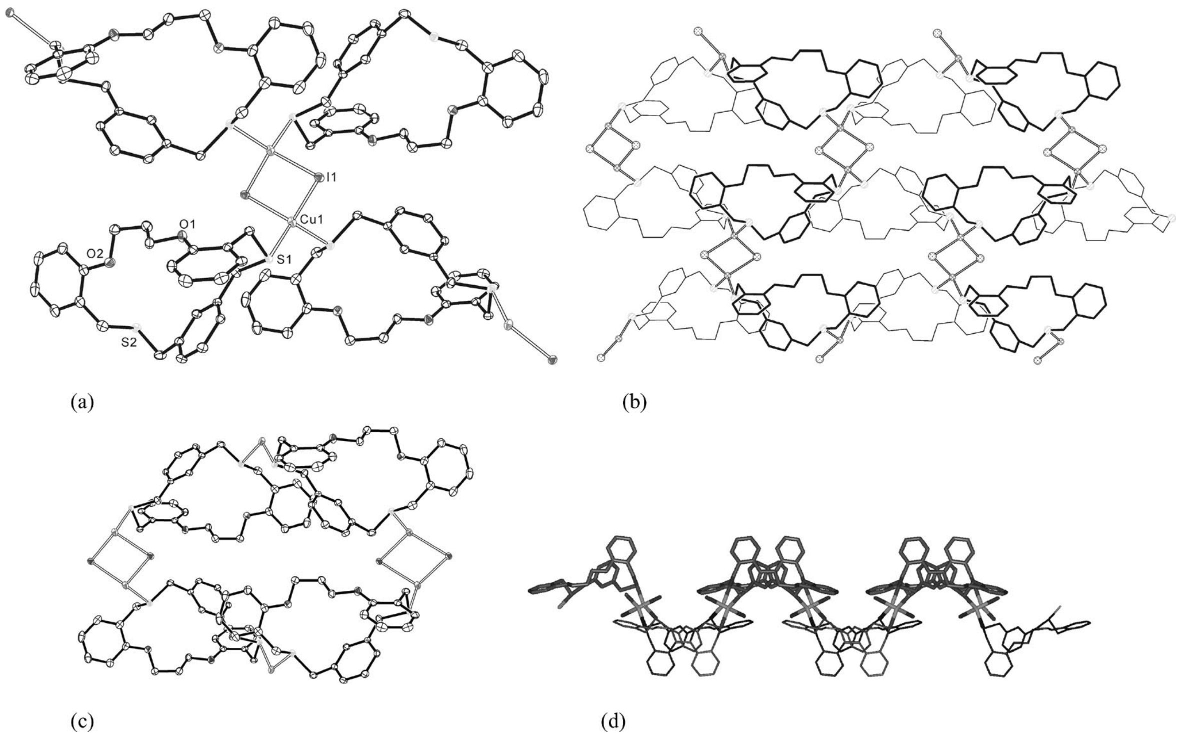


Figure 8. (a) Coordination environment of **6a**, $[(Cu_2I_2)(\mathbf{L}^2)_2]_n$, (b) brick-wall-type 2D polymeric network, (c) a single brick unit in **6a** generated through four L^2 and four Cu–I_2–Cu rhomboid cores. Selected bond lengths [Å] and angles [°]: Cu1–S2A 2.307(1), Cu1–S1 2.352(1), Cu1–I1 2.646(1), Cu1–I1B 2.674(1), I1–Cu1B 2.674(1), S2A–Cu1–S1 111.1(4), S2A–Cu1–I1 108.5(3), S1–Cu1–I1 104.7(3), S2A–Cu1–I1B 118.8(3), S1–Cu1–I1B 105.9(3), I1–Cu1–I1B 106.9(2), Cu1–I1–Cu1B 73.1(2). Symmetry operations: A: $-x + 1/2$, $y + 1/2$, $-z + 1/2$, B: $-x$, $-y + 2$, $-z + 1$.

Slow diffusion of dichloromethane solution of **L^1** into an acetonitrile solution of CuI afforded pale yellow crystalline product **5**. Complex **5** features a double-stranded 1D polymer with formula $[(Cu_2I_2)(\mathbf{L^1})_2]_n$ (Figure 7). Each **L^1** is linked with the Cu–I_2–Cu rhomboid unit via Cu–S bonds. The copper(I) coordination sphere is a distorted tetrahedral shape, with the tetrahedral angles falling in the range 103.5(1)–112.7(1)°. Only two examples of thia-macrocycles yielding coordination polymers incorporating a double-stranded 1D copper(I) halide coordination polymer are reported.[10]

The reaction of **L^2** with CuI afforded a mixed product (**6a** and **6b**) with a pale-yellow colour which can be separated manually into two pure species under an optical microscope; block crystals of **6a** and powdered **6b** were thus obtained. The X-ray analysis revealed that **6a** is a 2D polymeric array of formula $[(Cu_2I_2)(\mathbf{L^2})_2]_n$ (Figure 8). The 2D network of **6a** contains a Cu–I_2–Cu rhomboid core bonded to four ligands via Cu–S bonds (Figure 8, a). So, the infinite brick-wall-type gross geometry of **6a** is similar to that of **4** (Figure 6, b and Figure 8, b). The asymmetric unit of **6a** contains one **L^2**, one Cu atom and one I atom. A single brick unit of **6a** contains four asymmetric units where each ligand is interconnected by the Cu–I_2–Cu linking units alternately but no solvent molecule is included inside (Figure 8, c). Consequently, the flexible nature of **L^2** together with the steric effect (hindrance) between the macrocycles may, in part, produce the sheet-type polymeric scaffold. Some other examples of layered copper(I) halide complexes with thiamacrocycles have been reported by our group[11] and others.[12] Figure 9 shows the emission spectra of **6a** and **6b** at room temperature in the solid state. In contrast to **6a**, **6b** exhibits a broad band with bright-yellow emission maxima at 570 nm arising from the cluster-centred excited state with mixed halide-to-metal charge transfer character.[5]

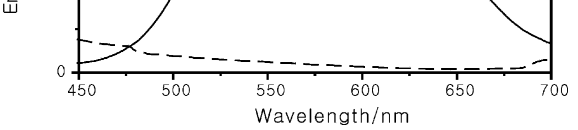


Figure 9. Solid-state emission spectra of **6a** (dashed line) and **6b** (solid line) at room temperature excited at 360 nm.

Conclusions

In summary, two analogous dithiamacrocycles **L^1** (17-membered) and **L^2** (18-membered) with variation of flexibility due to the different ring sizes were synthesised and structurally characterised. Five coordination polymers and one metallo-cyclic dimer were obtained from the assembly reactions of the macrocycles with the silver salts (perchlorate and nitrate) and copper(I) iodide. The versatility of results has been discussed with emphasis placed on the influences of the ring flexibility of the macrocycles, variation of anions and interligand π-π stacking of the respective supramolecular complexes.

Experimental Section

General Remarks: Chemical reagents and solvents were purchased commercially and used as received without further purification. Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer, and the NMR spectra were recorded with a Bruker 300 MHz spectrometer. Mass spectra were obtained with an Applied Biosystems QTRAP-3200 (ESI) or JEOL JMS-700 (FAB) spectrometer at the Central Laboratory of Gyeongsang National University.

Synthesis and Characterisation of L^1: Cs_2CO_3 (9.78 g, 30.0 mmol) was dissolved in DMF (1 L) in a flask; also a syringe was filled with 2,2′-(ethylenedioxy)bis(benzyl chloride) (4.65 g, 15.0 mmol) and 1,3-phenylenedimethanethiol (2.55 g, 15.0 mmol) dissolved in DMF (30 mL). Under a nitrogen atmosphere, the content of the syringe was added at regular speed (0.6 mL/h) into the DMF solution maintaining 45–50 °C. After cooling to room temperature the reaction mixture was filtered and the solvent was removed. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2. Flash column chromatography on silica gel using dichloromethane/*n*-hexane gave **L^1** as a white solid. Yield 1.97 g (30%); m.p. 137–139 °C (decomp.). $C_{24}H_{24}O_2S_2$ (408.58): calcd. C 70.55, H 5.92, S 15.70; found C 70.40, H 6.02, S 15.68. IR (KBr): $\tilde{\nu}$ = 2935, 2363, 2330, 1588, 1487, 1447, 1102, 1064, 940, 715 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74–7.50 (m, 12 H, Ar), 4.19 (s, 4 H, OCH_2), 3.68 (s, 4 H, $OArCH_2S$), 3.66 (s, 4 H, $ArCH_2S$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 156.0, 137.3, 130.5, 128.1, 126.6, 121.1, 121.0, 111.5, 66.2, 38.0, 29.7 ppm. MS: *m*/*z* 408 $[C_{24}H_{24}O_2S_2]^+$.

Synthesis and Characterisation of L^2: Synthetic procedure was almost the same as for **L^1** except for the use of 2,2′-(propylenedioxy)-bis(benzyl chloride). The flash column chromatography (SiO_2; dichloromethane/*n*-hexane, 1:3) afforded the product as a white solid in 50% yield; m.p. 120–123 °C (decomp.). $C_{25}H_{26}O_2S_2$ (422.60): calcd. C 71.05, H 6.20, S 15.18; found C 71.17, H 6.24, S 15.11. IR (KBr): $\tilde{\nu}$ = 3070, 3033, 2916, 2865, 2361, 2339, 1587, 1500, 1448, 1237, 1098, 1025, 755, 711, 670 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.81–7.31 (m, 12 H, Ar), 4.15 (t, 4 H, OCH_2), 3.73 (s, 4 H, $OArCH_2S$), 3.64 (s, 4 H, $ArCH_2S$), 2.15 (m, 2 H, OCH_2CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 139.0, 130.8, 128.7, 128.3, 127.0, 126.9, 120.7, 112.0, 64.6, 36.0, 30.7, 28.4 ppm. MS: *m*/*z* 423.2 $[C_{25}H_{26}O_2S_2]^+$.

$[Ag(L^1)(ClO_4)(DMSO)]_n$ (1): $AgClO_4$ (15.0 mg, 0.074 mmol) was dissolved in methanol (2 mL) and added to a solution of **L^1** (30.0 mg, 0.074 mmol) in dichloromethane. The white precipitate (41.0 mg, 0.067 mmol) in 92% yield formed immediately. The precipitate was filtered off, washed with methanol and diethyl ether and dried in vacuo. Single crystals suitable for X-ray analysis were obtained by vapour diffusion with diethyl ether into DMSO solution (2 mL); m.p. 198–200 °C (decomp.). $C_{26}H_{30}AgClO_7S_3$ (694.03): calcd. C 45.00, H 4.36, S 13.86; found C 45.20, H 4.41, S

14.00. IR (KBr): ṽ = 2937, 1595, 1487, 1448, 1244, 1229, 1148, 1113, 1103, 1080, 1065, 941, 752, 710, 625 cm^{-1}.

{[Ag$_2$(L^1)$_2$(NO$_3$)$_2$]·DMSO}$_n$ (2): AgNO$_3$ (13.0 mg, 0.074 mmol) was dissolved in methanol (2 mL) and added to a solution of **L^1** (30.0 mg, 0.074 mmol) in dichloromethane. A white precipitate (39.0 mg, 0.067 mmol) was formed immediately, 90% yield. The precipitate was filtered off, washed with methanol and diethyl ether and dried in vacuo. Single crystals suitable for X-ray analysis were obtained by vapour diffusion with diethyl ether into DMSO and DMF solution (2 mL); m.p. 196–198 °C (decomp.). $C_{50}H_{54}Ag_2N_2O_{11}S_5$ (1235.03): calcd. C 48.63, H 4.41, N 2.27, S 12.98; found C 48.48, H 4.52, N 2.30, S 13.01. IR (KBr): ṽ = 2941, 2343, 1591, 1491, 1439, 1410, 1385, 1362, 1317, 1292, 1252, 1225, 1188, 1103, 1045, 931, 754, 714 cm^{-1}.

[Ag$_2$(L^2)$_2$(ClO$_4$)$_2$]·CH$_2$Cl$_2$·CH$_3$OH (3): AgClO$_4$ (8.01 mg, 0.038 mmol) was dissolved in methanol (2 mL) and added to a solution of **L^2** (15.0 mg, 0.035 mmol) in dichloromethane. Single crystals suitable for X-ray analysis were obtained by slow concentration. Yield ca. 50%; m.p. 180–184 °C (decomp.). $C_{25}H_{26}AgClO_6S_2$ (629.92): calcd. C 47.67, H 4.16, S 10.18; found C 47.53, H 4.19, S 10.20. IR (KBr): ṽ = 3064, 3041, 2955, 2932, 2878, 2360, 2343, 1596, 1585, 1491, 1455, 1243, 1101, 1056, 953, 750, 711, 620 cm^{-1}. MS: *m/z* 1159.07 [$C_{25}H_{26}O_2S_2$]$^+$. MS: *m/z* 1159 [Ag$_2$(**L^2**)$_2$(ClO$_4$)]$^+$.

[Ag(L^2)NO$_3$]$_n$ (4): AgNO$_3$ (7.01 mg, 0.041 mmol) was dissolved in methanol (2 mL) and added to a solution of **L^2** (15.0 mg, 0.035 mmol) in dichloromethane. Single crystals suitable for X-ray analysis were obtained by slow concentration. Yield ca. 50%; m.p. 160–165 °C (decomp.). $C_{25}H_{26}AgNO_5S_2$ (592.48): calcd. C 50.68, H 4.42, N 2.36, S 10.82; found C 50.83, H 4.37, N 2.57, S 10.74. IR (KBr): ṽ = 3067, 3024, 2955, 2933, 2882, 2867, 2360, 2340, 1652, 1635, 1554, 1543, 1492, 1454, 1425, 1384, 1281, 1241, 1102, 1019, 760, 717, 668 cm^{-1}.

[(Cu$_2$I$_2$)(L^1)$_2$]$_n$ (5): A dichloromethane (2 mL) solution of **L^1** (30.1 mg, 0.074 mmol) was allowed to diffuse slowly to an acetonitrile (2 mL) solution of CuI (14.0 mg, 0.074 mmol) in a capillary tube (i.d. 5 mm). The pale yellow single crystals suitable for X-ray analysis were obtained in the tube. Yield ca. 50%; m.p. 197–198 °C (decomp.). $C_{24}H_{24}CuIO_2S_2$ (599.03): calcd. C 48.12, H 4.04, S 10.71; found C 48.36, H 4.11, S 10.82. IR (KBr): ṽ = 2923, 1587, 1491, 1454, 1292, 1250, 1222, 1103, 1053, 937, 750, 710 cm^{-1}.

[(Cu$_2$I$_2$)(L^2)$_2$]$_n$ (6a) and [(Cu$_4$I$_4$)(L^2)$_2$]$_n$ (6b): A dichloromethane (2 mL) solution of **L^2** (15.0 mg, 0.035 mmol) was allowed to diffuse slowly to an acetonitrile (2 mL) solution of CuI (8.01 mg,

Table 1. Relevant crystal data collection and refinement data for the crystal structures of **L^1**, **L^2**, and **1**–**6a**.

	L^1	**L^2**	**1**	**2**
Empirical formula	$C_{24}H_{24}O_2S_2$	$C_{25}H_{26}O_2S_2$	$C_{26}H_{30}AgClO_7S_3$	$C_{50}H_{54}Ag_2N_2O_{11}S_5$
Formula mass	408.55	422.58	694.00	1234.99
Temperature [K]	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	*P*2$_1$/*c*	*P*-1	*P*-1	*P*2$_1$/*m*
Z	4	2	2	2
a [Å]	8.7931(5)	8.1852(8)	8.5370(8)	8.4446(4)
b [Å]	23.8008(14)	10.1526(9)	11.2691(10)	27.3965(14)
c [Å]	10.2176(6)	13.3760(12)	15.0738(14)	11.2232(6)
α [°]	90	93.562(2)	94.712(2)	90
β [°]	106.4270(10)	90.205(2)	94.964(2)	98.8290(10)
γ [°]	90	96.644(2)	100.500(2)	90
V [Å^3]	2051.1(2)	1101.90(18)	1413.4(2)	2565.7(2)
D_x [g cm^{-3}]	1.323	1.274	1.072	1.599
$2\theta_{max}$ [°]	54.00	52.00	53.00	55.00
R	0.0558	0.0456	0.0410	0.0487
wR	0.1148	0.1043	0.0898	0.0893
No. of reflections used [$I > 2\sigma(I)$]	4448 [*R*(int) = 0.0470]	4250 [*R*(int) = 0.0517]	5746 [*R*(int) = 0.0279]	5849 [*R*(int) = 0.0469]
	3	**4**	**5**	**6**
Empirical formula	$C_{52}H_{57.6}Ag_2Cl_{4.4}O_{12.8}S_4$	$C_{25}H_{26}AgNO_5S_2$	$C_{49}H_{50}Cl_2Cu_2I_2O_4S_4$	$C_{25}H_{26}CuIO_2S_2$
Formula mass	1387.34	592.46	1282.91	613.02
Temperature [K]	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*n*	$P\bar{1}$	*P*2$_1$/*n*
Z	2	4	1	4
a [Å]	14.0598(8)	10.6473(4)	8.4742(9)	11.4183(5)
b [Å]	9.6617(5)	17.7381(6)	11.0406(11)	17.1126(7)
c [Å]	22.2090(12)	13.0668(4)	13.8713(14)	12.1539(5)
α [°]	90	90	105.921(2)	90
β [°]	104.5720(10)	90.2700(10)	92.628(2)	91.0480(10)
γ [°]	90	90	100.479(2)	90
V [Å^3]	2919.9(3)	2467.81(15)	1220.9(2)	2374.38(17)
D_x [g cm^{-3}]	1.578	1.595	1.745	1.715
$2\theta_{max}$ [°]	54.00	54.00	52.00	53.98
R	0.0436	0.0305	0.0507	0.0301
wR	0.1156	0.0747	0.1268	0.0651
No. of reflections used [$I > 2\sigma(I)$]	6353 [*R*(int) = 0.0259]	5387 [*R*(int) = 0.0230]	4683 [*R*(int) = 0.0193]	5140 [*R*(int) = 0.0304]

0.042 mmol) in a capillary tube (i.d. 5 mm). A mixture of the pale-yellow X-ray-quality crystals (**6a**) and pale-yellow powder (**6b**) were obtained in the tube. The mixture was separated into two pure species manually under an optical microscope. **6a**: Yield ca. 20%; m.p. 225–228 °C (decomp.). $C_{25}H_{26}CuIO_2S_2$ (613.05): calcd. C 44.88, H 4.27, S 10.46; found C 44.79, H 4.37, S 10.49. IR (KBr): $\tilde{\nu}$ = 3064, 3040, 2951, 2912, 2873, 1597, 1586, 1494, 1452, 1241, 1099, 1062, 1028, 960, 757, 717, 666 cm^{-1}. **6b**: Yield ca. 40%; m.p. 270–272 °C (decomp.). $C_{25}H_{26}Cu_2I_2O_2S_2$: calcd. C 37.37, H 3.26, S 7.98; found C 37.55, H 3.29, S 7.97. IR (KBr): $\tilde{\nu}$ = 3056, 3037, 2956, 2914, 2867, 2349, 1597, 1585, 1493, 1452, 1244, 1101, 1060, 1022, 958, 748, 719, 700 cm^{-1}.

CAUTION! Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

X-ray Crystallography: All data were collected with a Bruker Smart diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation source and a CCD detector. The 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT program.[13] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 for all data using SHELXTL software.[14] The non-hydrogen atoms were refined anisotropically. Relevant crystal data collection and refinement data for the crystal structures of **L**^{1}, **L**^{2}, and **1**–**6a** are summarised in Table 1.

CCDC-679188 (for **1**), -679189 (for **2**), -679190 (for **3**), -679191 (for **4**), -679192 (for **5**), -679193 (for **6a**), -679194 (for **L**^{1}), -679195 (for **L**^{2}) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Figures S1–S3; crystal structures of **1**–**3** showing π-π stacking, Figure S4; mass spectrum of **3**, Figures S5–S6; NMR spectra of **L**^{1} and **L**^{2}, Figures S7 and S8; packing structures of **4** and **6a**.

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