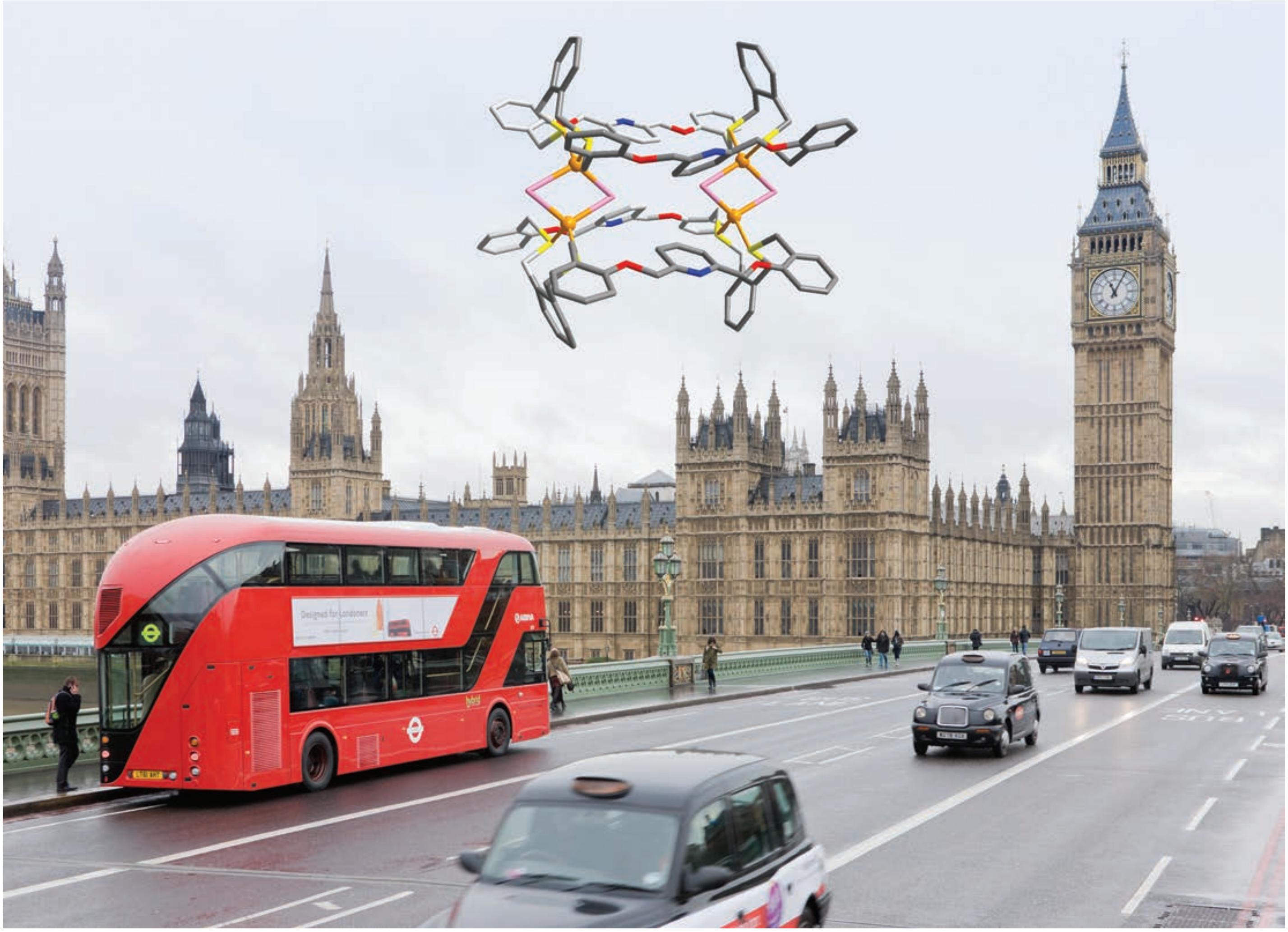

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Title: A double decker type complex: copper(I) iodide complexation with mixed donor macrocycles *via* [1 : 1] and [2 : 2] cyclisations

A 38-membered macrocycle obtained from the [2 : 2] cyclisation reacts with CuI to form a double decker type complex which shows a sliding upon removal of the lattice solvents in an SCSC manner.

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# A double decker type complex: copper(I) iodide complexation with mixed donor macrocycles *via* [1 : 1] and [2 : 2] cyclisations†

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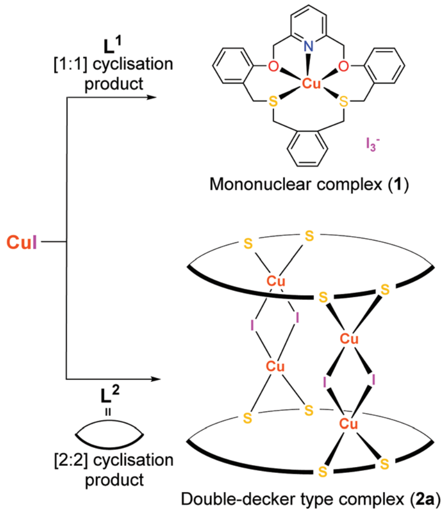
19-membered and a 38-membered macrocycles obtained as a mixture *via* respective [1 : 1] and [2 : 2] cyclisations were separated and their coordination behaviours with copper(I) iodide were investigated. One of the notable products isolated is a tetranuclear bis(macrocycle) complex with the larger macrocycle adopting a double decker type structure. Furthermore, removal of the lattice solvent molecules in the above complex in air motivates the displacement of the double decker units along the *a*-axis by sliding in a single-crystal-to-single-crystal manner.

## Introduction

A macrocyclic ligand synthesised *via* a [2 : 2] cyclisation has a large cavity which can bind two metal ions in the defined position.[1–3] Since most reported large macrocycles based on [2 : 2] cyclisation are the Schiff base type, their dinuclear complexes have been focused on the transition metal ions.[1] Thus, the reported dinuclear soft metal complexes of such larger macrocycles are relatively rare.[2]

As an approach to obtain non-Schiff base type large thiamacrocycles, a coupling cyclisation reaction between a dithiol and a dihalide (or a ditosylate) in the presence of a weak inorganic base such as $Cs_2CO_3$ yields not only the [1 : 1] cyclisation ligand but also the [2 : 2] cyclised product by working at higher concentration.[3] The authors of this paper have already reported such a [2 : 2] cyclisation-based 24-membered $N_2S_6$ macrocycle and its disilver(I) complex.[4] We have also been interested in preparing new types of dinuclear macrocyclic complexes of sulfur-containing mixed-donor macrocycles such as large macrocycles,[3a] linked macrocycles,[5] and calix-bis-crowns.[6] Recently, we have reported the isolation of a 40-membered $N_4O_4S_4$ macrocycle *via* [2 : 2] cyclisation and its dimercury(II)[3a] and disilver(I)[3b] complexes.



Scheme 1 Copper(I) iodide complexes of $\mathbf{L}^1$ and $\mathbf{L}^2$.

In the course of our ongoing works to explore new types of di- or oligonuclear complexes with large macrocycles based on [2 : 2] cyclisation, we were successful in isolating a unique double decker type copper(I) iodide complex as depicted in Scheme 1. In addition, the double decker type complex showed a sliding in a single-crystal-to-single-crystal (SCSC) manner when the solvent molecules in the lattice were removed in air. The details of our investigations are described.

## Results and discussion

A mixture of 19-membered ($\mathbf{L}^1$) and 38-membered ($\mathbf{L}^2$) macrocycles was obtained through [1 : 1] and [2 : 2] cyclisation

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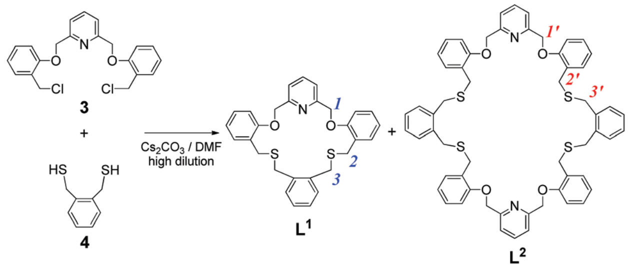
† Electronic supplementary information (ESI) available: NMR spectra, photographs of crystals, simulated PXRD patterns, crystal structures. CCDC 1417219 (**1**), 1417220 (**2a**) and 1417221 (**2b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03751d



**Scheme 2** Syntheses of $L^1$ and $L^2$ *via* [1 : 1] and [2 : 2] cyclisations, respectively.

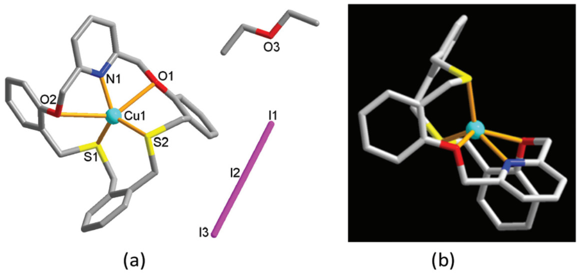


**Fig. 2** Mononuclear complex $[Cu(L^1)]I_3$·ether (**1**): (a) general view and (b) side view (non-coordinated solvent and anion are omitted).

reactions utilising dichloride precursor **3** and dithiol **4** in the presence of $Cs_2CO_3$ in dimethylformamide (DMF) (Scheme 2). The dichloride precursor **3** was prepared through the corresponding dialdehyde and dialcohol using the known procedure.[7]

For the separation of each macrocycle, the crude product mixture dissolved in ethyl acetate/*n*-hexane was eluted through column chromatography on silica-gel to remove the polar impurities. The $^1H$ NMR spectrum of this crude product mixture revealed the presence of two macrocycles in an 8 : 1 ($L^1 : L^2$) ratio (Fig. 1b). The [2 : 2] cyclised $L^2$ as a minor product shows a general downfield shift compared to the spectrum of the 1 : 1 cyclisation product $L^1$. The column chromatography on silica-gel allows the separation of $L^1$ as a colourless pure solid in 36% yield. However, the fraction of the purified $L^2$ still contains a small amount of $L^1$ which was then removed completely by washing the fine ground powder with 30% ethyl acetate/*n*-hexane on filter paper to obtain the pure $L^2$ as a colourless solid in 4% yield (Fig. 1a). The $^1H$ NMR spectra of $L^1$ and $L^2$ clearly show the successful separation of two macrocycles from the mixed product. The $^{13}C$ NMR and mass spectra were also clearly in agreement with the proposed structures (Fig. S1–S4†).

Copper(I) iodide was employed in the complexation of $L^1$ and $L^2$. Each species was prepared under slightly different conditions, giving rise to **1** and **2a** with different stoichiometries and coordination modes, respectively. Their structures were characterised by X-ray analysis (Table S1†).

As mentioned, the complexation of $L^1$ with CuI in dichloromethane/acetonitrile afforded a crystalline product **1**. Single crystal X-ray analysis revealed that **1** crystallises in a monoclinic system with the formula $[Cu(L^1)]I_3$·ether adopting a typical mononuclear structure in which the metal ion accommodates in the ring cavity (Fig. 2). The Cu(I) centre in **1** is five-coordinate, being bound to the O1, O2, N1 and S1 donors of the macrocycle defining a square plane, with the remaining site occupied by the S2 donor adopting an overall distorted square pyramidal geometry ($\tau = 0.31$).[8] The Cu1–N1 [2.038(2) Å] in **1** is consistent with the typical strong coordination between copper(I) and the pyridine nitrogen. The Cu–S bond distances [Cu1–S1 2.2660(8), Cu1–S2 2.2996(8) Å] are typical and the Cu–O bond distances [Cu1–O1 2.610(2), Cu1–O2 2.726(2) Å] are also within the normal literature range for this bond type.[9]

Notably, a triiodide ion ($I_3^-$) was found in **1** as a separated anion part (Fig. 2a). In the presence of surplus $I^-$, the formed $I_2$ would be converted to $I_3^-$ assuming the presence of atmospheric $O_2$ as an oxidant.[10] As shown in Fig. 2, the macrocycle twists considerably such that an unsymmetrical but apparently favourable cavity with a 3D-like *tight-and-twisted* conformation is formed, preventing the coordination of the anion or solvent. The preferred anion-free coordination mode in **1** reflects the

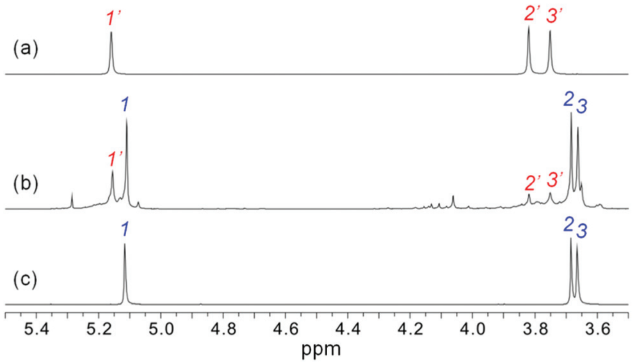


**Fig. 1** $^1H$ NMR spectra of the aliphatic region for (a) $L^2$, (b) the crude product containing a mixture of $L^1$ and $L^2$ (after removing polar impurities with column chromatography on silica-gel) and (c) $L^1$ in $CDCl_3$.

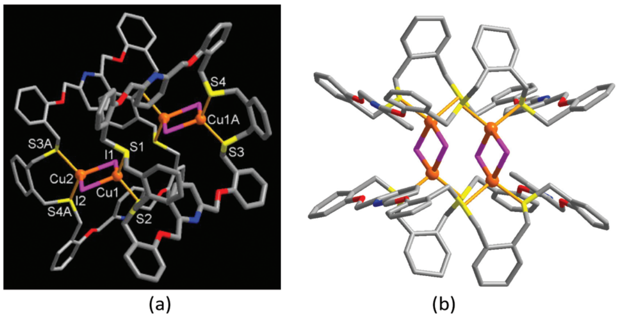


**Fig. 3** Tetranuclear bis(macrocycle) complex $[(Cu_2I_2)_2(L^2)_2]$·$2CH_3CN$·2-toluene (**2a**): (a) general view and (b) side view showing the double decker structure. Symmetry code: (A) −*x* + 1, −*y*, −*z* + 1. Non-coordinated solvent molecules are omitted.

synergic contribution of the hetero-donors especially sulfur and nitrogen atoms towards the metal centre.

To our surprise, the reaction of $\mathbf{L}^2$ with copper(I) iodide in dichloromethane/toluene/acetonitrile afforded the double decker type complex **2a**. The complex **2a** crystallises in the triclinic space group $P\bar{1}$ adopting a tetranuclear bis(macrocycle) species with the formula $[(\mathrm{Cu_2I_2})_2(\mathbf{L}^2)_2]\cdot 2\mathrm{CH_3CN}\cdot 2$toluene (Fig. 3). The selected geometric parameters of **2a** are presented in Table S3.† The asymmetric unit of the suprastructure in **2a** contains two Cu atoms, two iodide atoms and one ligand. So, the structure in Fig. 3 is generated through an inversion symmetry.

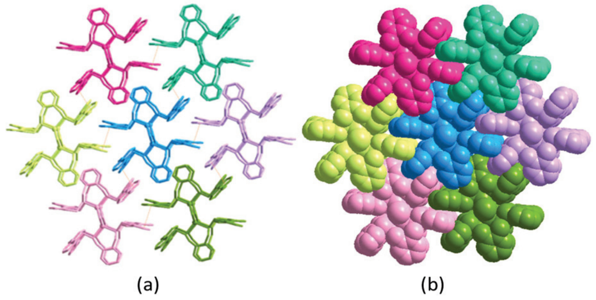


**Fig. 4** Packing structure of **2a**: (a) ball-stick representation and (b) space-filling presentation showing intermolecular π–π stacking between star-shaped molecules *via* aromatic interactions.

In **2a**, two square $\mathrm{Cu_2I_2}$ clusters link two facing $\mathbf{L}^2$ molecules perpendicularly as pillars *via* Cu–S bonds to form a double decker type product. Each Cu(I) centre in **2a** has a distorted tetrahedral coordination environment with the coordination sites occupied by two sulfur donors from $\mathbf{L}^2$ and two bridging iodide atoms. The bridging Cu–S bonds in **2a** [2.311(5)–2.345(4) Å, av. 2.332(9) Å] are slightly longer than those in **1** [av. 2.283(1) Å], probably due to the repulsive force between the two facing macrocycles, but both are within the normal range.

The large macrocyclic cavity in **2a** has a rectangular configuration with one nanometer square area (dimension *ca.* 10.5 × 9.5 Å) (Fig. S5†). However its aromatic subunits show different orientations: two pyridines direct inside, four phenoxy-rings at the corners direct outside and two benzo-rings near sulfur donors direct upward. Accordingly, the macrocyclic plane is considerably puckered probably to minimise the interligand repulsion showing an overall star-shaped structure of each complex unit (Fig. 4). It is notable that the packing structure shows face-to-face π–π stacking interactions between the star-shaped complexes with a centroid–centroid distance of 4.46 Å which stabilises a pseudo 2D layer (Fig. 4 and S4†).

Consideration of the bisulfur binding site in the large cavity of $\mathbf{L}^2$ along with the nature of copper(I) iodide clusters indicates that the sulfur-to-sulfur distances (S1⋯S2 3.742(5), S3⋯S4 3.745(6) Å) in the binding site might induce the formation of the square $\mathrm{Cu_2I_2}$ clusters as a pillar which leads to

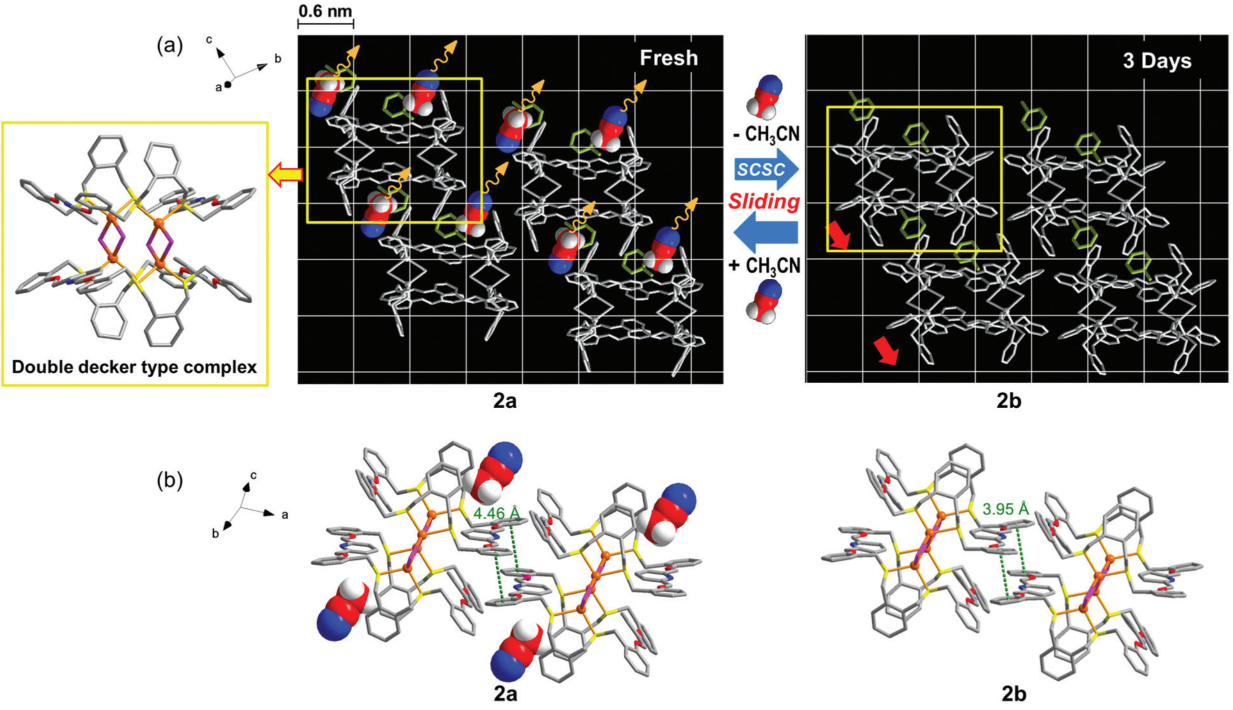


**Fig. 5** (a) The removal of the acetonitrile molecules (space filling representation) in **2a** by *sublimation* in air followed by the *sliding* (red arrows) of the double decker units to **2b**, $[(\mathrm{Cu_2I_2})_2(\mathbf{L}^2)_2]\cdot 2$toluene *via* SCSC transformation. (b) The π–π stacking interactions showing the changes in the centroid–centroid distances of the aromatic rings between double decker units upon removal of the acetonitrile molecules and sliding (the toluene molecules in the lattice are omitted).

the preferred formation of the double decker type complex. Several coordination networks of thiamacrocycles linked by different types of copper(I) iodide clusters *via* exocyclic coordination modes were reported by us.[11] As far as we are aware, this is the first example of complexes with large [2 : 2] cyclisation macrocycles exhibiting such structure and stoichiometry.

In **2a**, two toluene and two acetonitrile solvent molecules are trapped in the lattice (left in Fig. 5a). Interestingly, we found that the acetonitrile molecules in **2a** were removed under ambient conditions and this removal induced the sliding of the double decker complex units *via* an SCSC transformation. The details of the observed SCSC transformation upon solvent removal are discussed below.

When the colourless crystals of **2a** were kept in the air, the removal of the acetonitrile molecules by sublimation (orange arrows in Fig. 5a) within 3 days was confirmed and the sample colour changed slightly to pale yellow (termed **2b**, $[(Cu_2I_2)_2(\mathbf{L}^2)_2]\cdot$2toluene, see Fig. S7†). We also found that the removal of the acetonitrile solvents induced a change in the π–π stacking between the double decker complexes: the closest intercentroid distance in **2a** is 4.46 Å, while it is 3.95 Å in **2b** (Fig. 5b). The displacement of the double decker units along the *a*-axis occurred by sliding (red arrows in Fig. 5a). Such a sliding rearrangement is considered to stabilise the packing structure with the optimised intercentroid distance. Due to the sublimation of the acetonitrile molecules followed by the sliding rearrangement, **2a** and **2b** show high $R_1$ values. The removal of the acetonitrile solvent molecules in air was also confirmed by the comparative $^1$H NMR spectra (Fig. S8†). The powder X-ray diffraction (PXRD) patterns of the acetonitrile-free sample **2b** after immersing in acetonitrile for 10 min (termed **2a′** in Fig. S11†) is identical to that for the original crystals of **2a**: both are colourless, indicating that the sublimation/absorption process of the acetonitrile solvent molecules and the accompanying sliding occurs reversibly.

## Conclusions

In summary, we have demonstrated the formation of supramolecular copper(I) iodide complexes with 19-membered and the 38-membered macrocycles obtained *via* [1 : 1] and [2 : 2] cyclisation reactions, respectively. The smaller macrocycle forms an anion-free mononuclear complex in which all the heterodonors in the ring cavity cooperatively bind to the central metal ion. While the use of the larger macrocycle leads the generation of a highly organised tetranuclear bis(macrocycle) complex featuring the double decker type suprastructure. In obtaining this outcome, the bisulfur binding site appears to be important to induce the formation of the square type $Cu_2I_2$ clusters as pillars. The reversible sliding of the double decker complex molecule *via* the SCSC transformation triggered by the sublimation of the lattice solvent molecules in air was also observed. Investigations on the large macrocycle to obtain new bi-complexes of oligonuclear species as well as supramolecular coordination networks are in progress.

## Experimental section

### General procedures

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. NMR spectra were recorded using a Bruker DRX 300 and a DRX 500 spectrometer. The FT-IR spectra were measured with a Nicolet *i*S 10 spectrometer. The electrospray ionisation (ESI) mass spectra were obtained using a Thermo Scientific LCQ Fleet spectrometer. The microanalysis was carried out with a LECO CHNS-932 elemental analyser.

### Synthetic procedures

**Syntheses, separation and characterisation of $\mathbf{L^1}$ and $\mathbf{L^2}$.** Cesium carbonate (8.57 g, 26.3 mmol) was dissolved in DMF (2000 mL) in a 3 L round-bottom flask. Dithiol **4** (3.20 g, 18.7 mmol) and dichloride **3** (7.30 g, 18.8 mmol) were dissolved in DMF (300 mL), and this solution was added to a dropping funnel. The contents in the dropping funnel were added dropwise into a DMF solution of $Cs_2CO_3$ at 50–60 °C for 5 h. The reaction mixture was rapidly stirred for a further 24 h, allowed to cool to room temperature, and then filtered. The filtrate was evaporated, and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. The crude solid mixture was dissolved in 30% ethyl acetate/hexane and eluted through column chromatography on silica-gel to remove the polar impurities. The resulting solid was later shown to contain a mixture of $\mathbf{L^1}$ (major, 89%) and $\mathbf{L^2}$ (minor, 11%) by $^1$H NMR. The $\mathbf{L^1}$ and $\mathbf{L^2}$ were separated by MPLC on silica-gel by using 0–30% ethyl acetate/*n*-hexane. A small amount of $\mathbf{L^1}$ content in $\mathbf{L^2}$ was removed by washing the fine ground powder of the sample with 30% ethyl acetate/*n*-hexane on filter paper.

$\mathbf{L^1}$: Yield 36%. Mp 153–155 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.96–7.79 (m, 15 H), 5.14 (s, 4 H), 3.70 (s, 4 H), 3.68 (s, 4 H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 156.6, 156.0, 137.4, 136.4, 130.7, 130.0, 128.3, 126.9, 123.2, 121.6, 112.9, 72.3, 34.1, 31.1. IR (KBr, pellet): 3069, 3017, 2922, 2853, 1720, 1655, 1597, 1561, 1544, 1492, 1450, 1239, 1188, 1161, 1095, 1047, 1007, 847, 751, 706, cm$^{-1}$. MS (ESI) *m*/*z*: 486.24 (M + 1)$^+$. Anal. Calcd for $[C_{29}H_{27}NO_2S_2]$: C, 71.72; H, 5.60; N, 2.88; S, 13.20. Found: C, 71.93; H, 5.57; N, 2.95; S, 12.82%.

$\mathbf{L^2}$: Yield 4%. Mp 151–154 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.86–7.61 (m, 30 H), 5.18 (s, 4 H), 3.84 (s, 4H), 3.77 (s, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 156.7, 155.9, 137.7, 136.5, 130.6, 130.5, 128.5, 126.9, 121.0, 119.8, 111.8, 77.2, 70.3, 33.8, 31.3. IR (KBr, pellet): 3061, 2922, 2854, 1720, 1655, 1598, 1561, 1544, 1492, 1448, 1243, 1085, 778 cm$^{-1}$. MS (ESI) *m*/*z*: 971.44 (M + 1)$^+$. Anal. Calcd for $[C_{58}H_{54}N_2O_4S_4]$: C, 71.72; H, 5.60; N, 2.88; S, 13.20. Found: C, 71.38; H, 5.52; N, 2.86; S, 13.58%.

**Preparation of 1, $[\mathbf{Cu(L^1)}]\mathbf{I_3}$·ether.** To a stirring solution of $\mathbf{L^1}$ (10.0 mg, 0.021 mmol) in dichloromethane (1 mL) CuI (11.8 mg, 0.062 mmol) in acetonitrile was added. After filtration, the volume of the filtrate was reduced and ethyl ether was added. After 2 h, a needle-shaped light brown-coloured crystalline product **1** suitable for X-ray analysis was isolated. Yield: 70%. Mp 240–242 °C. IR (KBr pellet) 2968, 2927, 2877, 1745, 1701, 1655, 1638, 1601, 1561, 1491, 1459, 1400, 1378, 1342, 1320, 1295, 1249, 1222, 1102, 1030, 961, 897, 829, 792, 750 $cm^{-1}$. Anal. Calcd for $[C_{33}H_{37}CuI_3NO_3S_2]$: C, 39.48; H, 3.71; N, 1.40; S, 6.39. Found: C, 39.74; H, 3.55; N, 1.64; S, 6.41. MS (ESI) *m*/*z*: 548.36 $[Cu(\mathbf{L}^1)]^+$.

**Preparation of 2a, $[(Cu_2I_2)_2(L^2)_2]\cdot$2toluene$\cdot 2CH_3CN$.** Toluene (2.6 mL) was added to a dichloromethane (0.2 mL) solution of $\mathbf{L}^2$ (2.0 mg, 0.004 mmol); then CuI (0.4 mg, 0.002 mmol) in acetonitrile (0.2 mL) was layered on the toluene phase; the (layered) mixture afforded a block-shaped colourless crystalline product **2a** suitable for X-ray analysis. Mp 223–225 °C. IR (KBr, pellet): 3022, 2925, 1719, 1702, 1674, 1654, 1638, 1627, 1544, 1509, 1492, 1449, 1336, 1245, 1106, 1560, 1106, 1060, 992, 851, 751 $cm^{-1}$. Anal. Calcd for $[C_{67}H_{65}Cu_2I_2N_3O_4S_4]$: C, 54.17; H, 4.41; N, 2.83; S, 8.63. Found: C, 54.39; H, 4.36; N, 2.51; S, 8.77. MS (ESI) *m*/*z*: 1033.25 $[Cu(\mathbf{L}^2)]^+$.

### X-ray crystallographic analysis

Crystal data for **1**, **2a** and **2b** were collected using a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames). Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2.[12] All of the calculations for the structure determination were carried out using the SHELXTL package.[13] In all cases, all non-hydrogen atoms except in the toluene and acetonitrile molecules were refined anisotropically and all hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. **2a** and **2b** show high $R_1$ values because of the solvent loss and the structural rearrangement. Since the lattice solvent molecules in **2a** and **2b** are highly disordered, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.[14] The relevant crystal data collection and refinement data for the crystal structures of **1**, **2a** and **2b** are summarised in Table S1.†

## Acknowledgements

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