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Hexakis(isopropylthio)-1,5-hexadien-3-yne and its fluorescent Ag(I) coordination polymers: assembly of helicates with thioether sites

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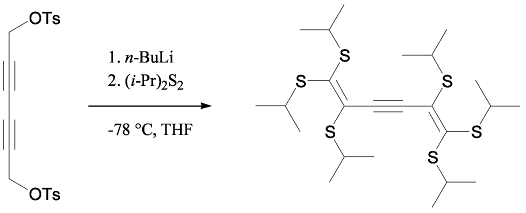
A new thioether-rich ligand with a conjugated dienyne backbone and its fluorescent Ag(I) coordination networks have been synthesized and characterized by single crystal X-ray diffraction studies, which reveal that the supramolecular architectures of the networks contain assembled helicates with thioether sites.

The architectures of supramolecular frameworks formed by metal coordination have been of great interest in the design of new functional materials.[1,2] Many polymeric complexes have been generated by the self-assembly of transition metal centres with a variety of organic spacer ligands.[3,4] Bidentate and multidentate ligands are useful as connecting units for constructing one- to three-dimensional polymers with various topologies.[5,6] We are interested in multidentate thioethers as ligands for the assembly of coordination networks.[7] Many materials based on unsaturated sulfur-containing compounds have been shown to exhibit high electrical conductivity.[8,9] Herein we report the preparation and properties of a new unsaturated polythioether ligand and its Ag(I) supramolecular networks.

Hexakis(isopropylthio)-1,5-hexadien-3-yne (**1**) was prepared by treatment of 1,6-bis(*p*-toluenesulfonyloxy)-2,4-hexadiyne in THF at −78 °C with 4 equivalents of *n*-BuLi, followed by an excess of diisopropyl disulfide (Scheme 1).



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Scheme 1

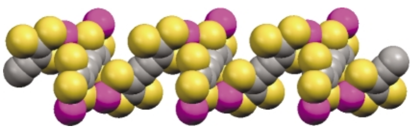

Fig. 1 Segment of helix **2** extended along the *b*-axis. Isopropyl and triflate groups are omitted for clarity.

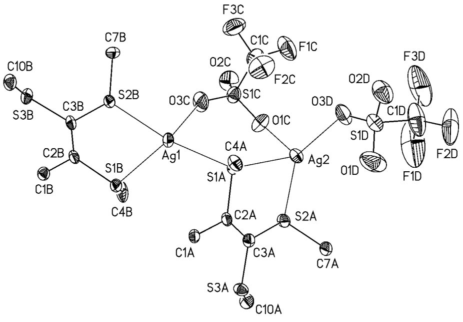

Fig. 2 The coordination environment of the silver atoms in **2**. Displacement ellipsoids are scaled to the 50% probability level.

The reaction of **1** with $AgCF_3SO_3$ in THF gave rise to $[Ag_2(\mathbf{1})(CF_3SO_3)_2]_n$ (**2**). The crystal structure of **2** was found to form a one-dimensional polymeric chain. An interesting structural feature of this network is the assembly of helicates along the *b*-axis (Fig. 1).

The coordination geometry around each silver(I) ion is distorted tetrahedral (Fig. 2). The Ag1–O bond distance is 2.386(4) Å. The Ag1–S distances to the terminal and bridging thioether are quite comparable, ranging from 2.539(1) to 2.557(1) Å. The S1A–Ag1–O3C angle, 89.8(1)°, is slightly pinched and the S1A–Ag1–S2B angle, 138.93(4)°, is significantly greater than expected.†

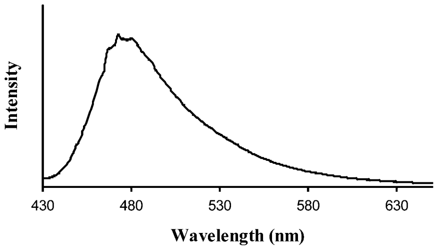

Fig. 3 Solid-state emission spectrum of **2** (λ_{ex} = 385 nm).

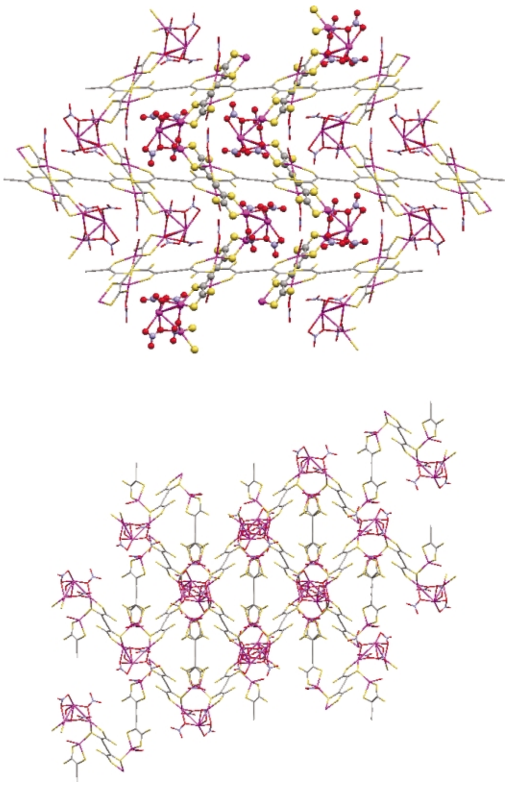

Fig. 4 View of three-dimensional polymeric structure of **3** along the *a*-axis (top); along the *c*-axis (bottom). Isopropyl groups are omitted for clarity.

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The Ag2 ion is bound by two oxygen atoms from the bridging and terminal trifluoromethanesulfonate ligands and two sulfur atoms from one thioether ligand. The S1A–Ag2–O1C angle, 88.54(9)°, is slightly pinched and the S2A–Ag2–O3D angle, 142.6(1)°, is significantly greater than expected. The Ag2–O3D bond distance, 2.230(4) Å, is shorter than that of Ag2–O1C, 2.428(3) Å. The Ag2–S bond distances are 2.520(1) and 2.622(1) Å.

The emission spectrum of **2** is shown in Fig. 3. A strong fluorescence band with $\lambda_{\mathrm{F,max}} \approx 473$ nm was seen.

Yellow crystals of $[\mathrm{Ag_5}(\mathbf{1})_2(\mathrm{H_2O})(\mathrm{NO_3})_5]_n$ (**3**) were obtained by layering an aqueous solution of $AgNO_3$ with a solution of **1** in THF. The crystal structure of **3** is shown in Fig. 4 and reveals a three-dimensional reticulated structure. An interesting structural feature of this network is the assembly of cylindrical helices. When viewed along the *a*-axis, parallel helices in layers are formed as shown in Fig. 4 (top). Fig. 4 (bottom) shows the grid feature with the view along the *c*-axis.

The Ag1 ion is bound by a nitrate ion, two chelating sulfur atoms from a single thioether ligand (**1**) and a bridging sulfur, S(2), from a second molecule of **1** (Fig. 5). The Ag3 ion has a similar coordination environment to that of Ag1 except the nitrate ions are replaced by H_2O molecules. The Ag4–Ag5 distance of 3.3504(5) Å is less than the sum of the van der Waals radii of two silver atoms, 3.44 Å.[10]

The emission spectrum of **3** is shown in Fig. 6. A strong fluorescence band with $\lambda_{\mathrm{F,max}} \approx 480$ nm was detected, which is close to that of **2**.

The cyclic voltammogram of **2** in CH_3CN solution containing 0.1 M $[(n\text{-Bu})_4\mathrm{N}]\mathrm{PF_6}$ exhibited one reversible oxidation wave at a half-wave potential of +0.65 V *vs.* Ag wire. For the cyclic voltammogram of **3** in CH_3CN solution containing 0.1 M $[(n\text{-Bu})_4\mathrm{N}]\mathrm{PF_6}$, two oxidation waves were observed; one irreversible wave with a peak potential of 0.72 V *vs.* Ag wire and another reversible wave with a half-wave potential of +0.60 V *vs.* Ag wire.

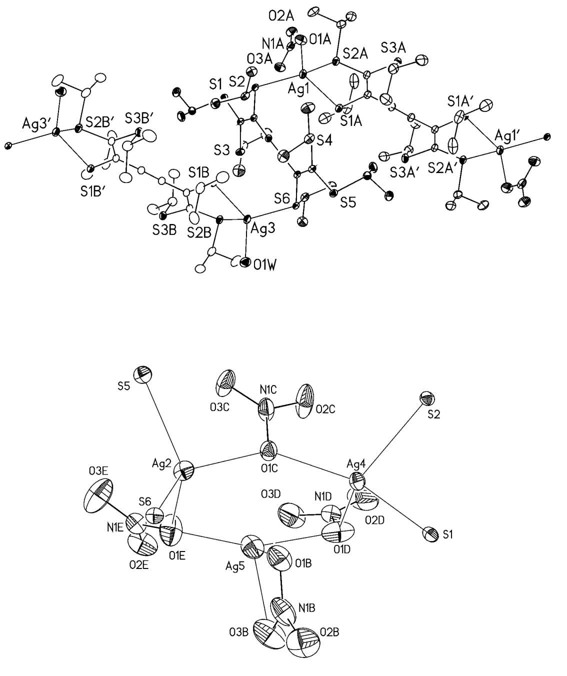

Fig. 5 The coordination environment of the silver atoms in **3**. Displacement ellipsoids are scaled to the 30% probability level.†

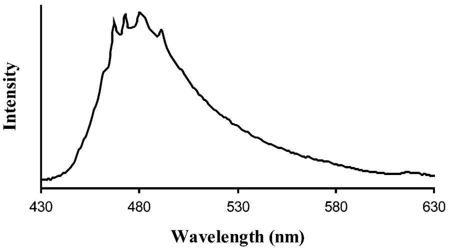

Fig. 6 Solid-state emission spectrum of **3** ($\lambda_{\mathrm{ex}} = 345$ nm).

In conclusion two interesting supramolecular networks have been formed by use of a new thioether-rich ligand. These coordination polymers show interesting electronic properties and may have potential application to optoelectronic devices.

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Notes and references

† Crystal data for **2**: $\mathrm{C_{26}H_{42}Ag_2F_6O_6S_8}$, $M = 1036.82$, triclinic, space group $P\bar{1}$, $a = 12.5105(2)$, $b = 12.7713(2)$, $c = 12.9300(2)$ Å, $\alpha = 87.501(1)$, $\beta = 77.200(1)$, $\gamma = 82.947(1)°$, $V = 1999.03(5)$ Å^3, $Z = 2$, $D_c = 1.723$ g cm^{-3}, μ(Mo-Kα) = 1.461 mm^{-1}, $T = 153(2)$ K, $\lambda = 0.71073$ Å, 13090 reflections collected, 9048 independent reflections ($R_{\mathrm{int}} = 0.0277$), $R_1 = 0.0457$, $wR_2 = 0.1105$ [$I > 2\sigma(I)$]. Crystal data for **3**: $\mathrm{C_{48}H_{86}Ag_5N_5O_{16}S_{12}}$, $M = 1913.29$, monoclinic, space group $P2_1/n$ (No. 14), $a = 18.5580(1)$, $b = 18.6065(1)$, $c = 21.9358(1)$ Å, $\beta = 107.995(1)$, $V = 7203.90(6)$ Å^3, $Z = 4$, $D_c = 1.764$ g cm^{-3}, μ(Mo-Kα) = 1.744 mm^{-1}, $T = 153(2)$ K, $\lambda = 0.71073$ Å, 97906 reflections collected, 16489 independent reflections ($R_{\mathrm{int}} = 0.0426$), $R_1 = 0.0356$, $wR_2 = 0.0900$ [$I > 2\sigma(I)$]. CCDC 224823 and 224824. See http://www.rsc.org/suppdata/cc/b3/b314292b/ for crystallographic data in .cif format.

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