Letter

A non-interpenetrating 2D coordination polymer from a $(CH_2)_8$ spacer-based highly flexible linear ligand and $AgCF_3CO_2$†

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Reaction of a $(CH_2)_8$ spacer-based ligand, 1,8-bis(8-thioquinolyl)-octane (C8TQ), with $AgCF_3CO_2$ affords a designed non-interpenetrating 2D brick-wall coordination polymer $[Ag_2(C8TQ)(CF_3CO_2)_2]_n$, composed of thio-bridged helical chains racemically aligned and further connected by the $(CH_2)_8$ spacers, while weak F···F interactions between ligated $CF_3CO_2^-$ fabricate the 3D supramolecular architecture.

Synthesis of organic-inorganic hybrid polymeric complexes is a relatively new research area that has evolved rapidly in the last several years. The interest in these systems is justified by the numerous potential applications, such as catalysis,[1] sorption,[2] photochemistry,[3] and magnetism.[4] Molecular self-assembly has been proven to be an effective way of constructing various fascinating polymeric complexes. The basic building blocks recognize each other in a reaction system and aggregate to form the bulk structure.[5] Amongst the synthetic strategies to achieve these multidimensional polymeric complexes, one of the most fruitful choices consists in taking advantage of organic ligands containing two terminal chelating groups that can act as bridging ligands towards transition metal ions.[5b,6] So far a number of one-, two- and three-dimensional infinite frameworks have already been generated with rigid or flexible ligands such as bipyridyl-based systems or derivatized imidazoles.[7] Far less common has been the use of the multidentate ligands with variable aliphatic spacers of the type chelate-spacer-chelate in the construction of extended networks,[8] not to mention sulfur-containing ligands of this type.[8c,8d,8h] (It is well-known that sulfur atoms possess an unusual potential as bridging donors for the construction of coordination architectures.[8h,9]) On the other hand, this approach has attracted much attention from chemists because the flexibility and conformational freedom of such multifunctional ligands offer the possibility of generating unique frameworks unseen before by using them as building blocks.[8] Among the various families of organic sulfur-containing ligands, long chain ligands substituted by 8-thioquinolyl (TQ) often act as bridges to aggregate simple fragments into large molecules after coordination with Ag(I) atoms.[8h,10] In a continuing study of the crystal engineering of complexes constructed by 8-thioquinolyl containing ligands and to challenge the difficulties of incorporating a long spacer, $(CH_2)_8$, with high flexibility to generate multidimensional structures,[8d,8e,8f] we hereby report the synthesis of the new linear ligand 1,8-bis(8-thioquinolyl)octane (C8TQ) and its Ag(I) coordination polymer.

The treatment of C8TQ with $AgCF_3CO_2$ in a 1:2 molar ratio in $CHCl_3$–CH_3CN for 10 min yielded colorless crystalline plate crystals of complex $[Ag_2(C8TQ)(CF_3CO_2)_2]_n$, **1**. The ^1H NMR of **1** in DMSO-d_6 displayed a spectrum similar to that of C8TQ with all proton resonances slightly shifted downfield except for those without a direct connection to the sulfur atoms in the aliphatic spacer. Coupling constants ^3J and ^4J in the ranges 4–8 and 1–1.5 Hz conform to the normal values for ortho and meta protons, respectively, similar to those reported for quinolyl derivative ligated complexes.[8a,10a,11] The infrared spectra of complex **1** exhibits characteristic bands for the C8TQ ligand and trifluoroacetate group. The C=O stretching vibration of the η_1-coordinated trifluoroacetate group appears as a single and strong peak at 1677 cm^{-1}. The groups of weak peaks at 3060–2853 cm^{-1} are attributed to the C–H vibration. The absorptions in the 1488–1597 cm^{-1} and 790–794 cm^{-1} ranges signal the presence of thioquinolyl groups.

Single crystal X-ray diffraction analysis revealed that complex **1** was composed of the neutral dinuclear units $Ag_2(C8TQ)(CF_3CO_2)_2$ in which C8TQ acts both as a bis-bidentate chelating agent to coordinate two symmetry-related Ag atoms in an equivalent manner and as a bridging group with the two sulfur atoms functioning as μ_2 bridges. Each Ag(I) atom is coordinated by NS from one ligand, the sulfur atom from another ligand and the oxygen atom from $CF_3CO^-{}_2$ in a distorted tetrahedral geometry with an S_2NO coordination

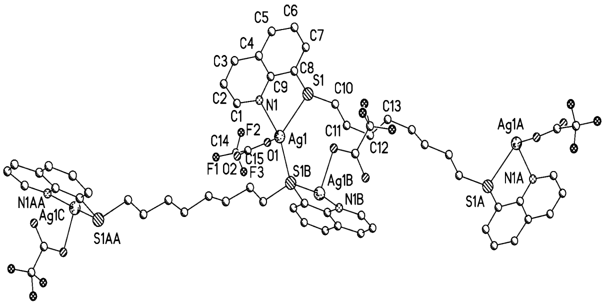

Fig. 1 Coordination environment around the silver(I) atom in **1**. Selected bond lengths (Å) and angles (°): Ag1–O1 = 2.319(4), Ag1–N1 = 2.319(4), Ag1–S1′ = 2.510(2), Ag1–S1 = 2.605(1), O1–Ag1–N1 = 111.17(14), O1–Ag1–S1′ = 112.72(12), N1–Ag1–S1′ = 124.00(10), O1–Ag1–S1 = 107.65(12), N1–Ag1–S1 = 75.38(9), S1–Ag1–S1′ = 120.24(3).

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† Electronic supplementary information (ESI) available: ^1H NMR spectra and data for C8TQ and complex **1** and the 3-D structure of complex **1**. See http://www.rsc.org/suppdata/nj/b3/b301777j

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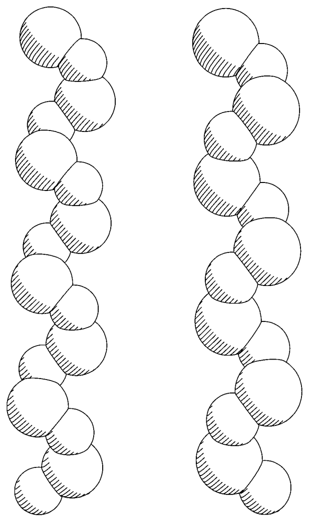

a) left-handed (Λ) b) right-handed (Δ)

Fig. 2 Space-filling plots of the left-handed (a) and right-handed (b) helical $[\mathrm{AgTQ}]_n$ chains. Quinoline groups and H atoms are omitted for clarity.

sphere, as shown in Fig. 1. The two quinoline rings coordinated to the same silver(I) atom have a significant angle (dihedral angle 45.2°). The μ_2-S atom acts as a bridge to coordinate with silver(I) atoms in an offset way, resulting in right (Δ)- or left (Λ)-handed helical $[\mathrm{AgTQ}]_n$ chains, as shown in Fig. 2, running along the *b* axis. Owing to the fact that two TQ moieties of the same ligand are from two adjacent helical chains of different chirality and that the $(\mathrm{CH_2})_8$ spacers cross the chains to form a rectangle, a 2D brick-wall coordination polymer is thus formed in a predictable way in the *ab* plane, as shown in Fig. 3. The two adjacent chains construct a series of 26-membered macrometallacyclic units with dimensions of 7.87 × 11.30 Å^2 (calculated by considering the four sulfur atoms at the corners of the macrocycles), while η_1-coordinated $\mathrm{CF_3CO^-_2}$ anions are alternatively located on opposite sides of the plane. In these macrocycles, two adjacent quinolyl groups are stacked with weak $\pi\cdots\pi$ interactions (centroid-centroid distances in the range of 3.96–4.05 Å), the presence of which maybe the key in the generation of such non-interpenetrating structures. This result suggests that $(\mathrm{CH_2})_8$ spacer-based ligands can also be used in the assembly of non-interpenetrating coordination polymers through ligand modification.

Interestingly, it should be noted that these 2D brick walls can be further stacked into a 3D network *via* weak F···F interactions, in which two of the F atoms from each $\mathrm{CF_3CO^-_2}$ anion form two pairs of weak F···F interactions with other two anions of an adjacent layer, with the shortest F–F distance being *ca.* 2.68 Å.[12] To our knowledge, non-interpenetrating porous structures assembled with flexible $(\mathrm{CH_2})_n$ $(n \geq 4)$ spacer-based ligands as building block have been seldom investigated.[8b,8d,8k] The present study provides the first example of a non-interpenetrating, covalently bonded 2D structure self-assembled by the reaction of a flexible ligand with a long aliphatic spacer, $(\mathrm{CH_2})_8$, with a Ag(I) salt, while the 3D network is further constructed from the repeating basic unit with dimensions of 7.87 × 11.30 × 10.59 Å^3 (S···S × S···S × Ag···Ag).

Experimental

Synthesis

C8TQ was prepared from NaTQ and 1,8-dibromoctane in 66% yield, similar to the literature.[13] Anal. calcd. for $\mathrm{C_{26}H_{28}N_2S_2}$: C, 72.18; H, 6.52; N, 6.47; found: C, 72.35; H, 6.50; N, 6.50%.

Preparation of complex 1. $[\mathrm{Ag_2(C_{26}H_{28}N_2S_2)(CF_3CO_2)_2}]_n$. To a solution of C8TQ (21.6 mg, 0.05 mmol) in $\mathrm{CH_3Cl}$ (3 mL) was added dropwise a solution of $\mathrm{AgCF_3CO_2}$ (22.1 mg, 0.10 mmol) in $\mathrm{CH_3CN}$ (3 mL) at room temperature to give a clear solution. The complex was crystallized by slow diffusion of diethyl ether vapor into the reaction mixture. X-Ray quality colorless crystals formed after several days in *ca.* 65% yield. Anal. calcd. for $\mathrm{Ag_2(C_{26}H_{28}N_2S_2)(CF_3CO_2)_2}$: C, 41.21; H, 3.23; N, 3.20; found: C, 40.95; H, 3.17; N, 3.20%.

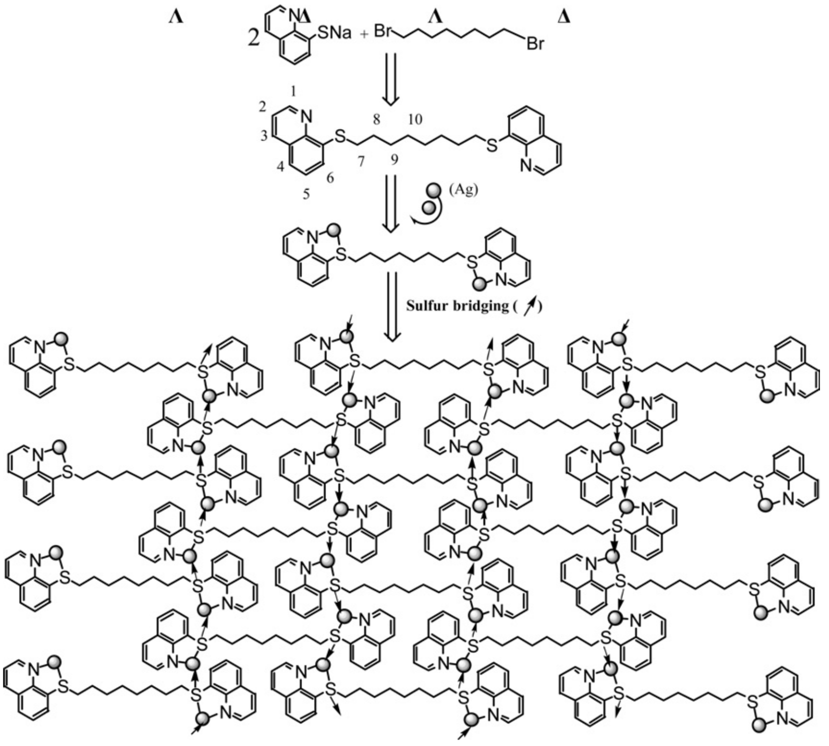

Fig. 3 Syntheses of the ligand C8TQ and the complex **1** in a predictable way, with labeled proton positions for ^{1}H NMR assignments.

X-Ray crystallography

Data were collected on a Bruker SMART CCD diffractometer at 293 K by the ω scan technique using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied to both complexes using the SADABS program. The structures were solved by direct methods (SHELXS-97) and refined on F^2 using the full-matrix least-squares method (SHELXL-97). The two middle C atoms in the aliphatic spacer are disordered.

Crystal data for 1. $C_{30}H_{28}Ag_2F_6N_2O_4S_2$, $M = 874.42$, monoclinic, space group $P2(1)/n$, $a = 11.888(6)$, $b = 7.870(4)$, $c = 17.378(9)$ Å, $\gamma = 100.736(9)°$, $U = 1597.4(14)$ Å^3, $T = 293(2)$ K, $\lambda = 0.71073$ Å, $Z = 4$, μ(Mo-Kα) $= 1.430$ mm^{-1}, 9516 reflections measured, 3472 independent reflections ($R_{\text{int}} = 0.027$), $R_1 = 4.2\%$, $wR_2 = 11.8\%$ [$I > 2\sigma(I)$], $R_1 = 5.7\%$, $wR_2 = 13.0\%$ (all data) GOF $= 1.06$. CCDC reference number 200968. See http://www.rsc.org/suppdata/nj/b3/b301777j/ for crystallographic files in CIF or other electronic format.

Acknowledgements

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