Supplementary Information

Experimental

General

All reagents were used as received without further purification. Samples for elemental analysis were
dried under high vacuum. Elemental analysis for carbon, hydrogen and nitrogen was carried out by the
Elemental Analysis Service at Durham. Powder diffraction was performed on a Siemens D5000 X-Ray
Diffractometer using CuKα radiation at a wavelength of 1.5406 Å.

Planar Complex (2)

\(N,N''\)-pentane-1,5-diylbis(3-pyridin-3-ylurea) (90 mg, 0.26 mmol) was dissolved in a 1:1:1 mixture of
MeOH, CHCl₃ and MeCN (4.5 mL) and added to AgNO₃ (45 mg, 0.26 mmol). Crystals formed upon
slow evaporation of the solvent. Samples for elemental analysis were dried in air resulting in some loss
of water. Samples dried under high vacuum proved to absorb moisture from the atmosphere upon
exposure. Yield 79 mg, 0.14 mmol, 55 %. Calc. for C₁₇H₂₂N₇O₅Ag(MeCN)(H₂O)₁.₂₅: C 39.53, H 4.83,

Quintuple Helix (3)

\(N,N''\)-pentane-1,5-diylbis(3-pyridin-3-ylurea) (90 mg, 0.26 mmol) was dissolved in a 3:2 mixture of
THF and water (6 mL) and added to AgBF₄ (51 mg, 0.26 mmol). Crystals formed upon slow
evaporation of the solvent. The material proved highly unstable in the atmosphere rapidly losing solvent and as a result samples for elemental analysis were dried under high vacuum however varying amounts of solvent remained. Yield 29 mg, 0.05 mmol, 19 %. Calc. for C_{17}H_{22}BN_{6}O_{2}F_{4}Ag(C_{4}H_{8}O)_{0.25}: C 38.94, H 4.36, N 15.14; Found: C 39.90, H 4.44, N 15.75. Two separate crystals were analysed by X-ray crystallography at low temperature under nitrogen and both gave the same structure.

**Powder X-ray Data**

The bulk phase purity of the samples was examined by PXRD. In the case of 2 the dehydration procedure causes loss of crystallinity (Fig. S1). In the case of 3 the PXRD pattern for the dried material superficially resemble that calculated from the single crystal structure (Fig. S2), however the instability of the crystals upon exposure to atmosphere makes comparison between the single crystal and powder data very difficult.

![Figure S1: PXRD data for 2](image-url)
Experiments with further anions.

Reaction of the ligand with Ag(CH₃CO₃) in thf/water in the same way as outlined for 3 results in the formation of a powdery sample from which just a few single crystals can be isolated. These crystals are of the acetate salt [Ag(1)](CH₃CO₂)·nH₂O containing large water filled channels. The geometry of the ligand and the [Ag(1)]⁺ chain is essentially non-helical, closely related to the found in 2 consistent with the planarity of the acetate anion, but with a slight helical twist of the ligand (Fig. S3). The acetate anion is disordered and hence work is in progress on the full characterisation of this material.
Fig S3: Preliminary X-ray crystal structure of [Ag(I)](CH₃CO₂)·nH₂O