Electronic supplementary information

for

Assembling silver(I) coordination polymers of an NS_4-macrocycle via an endo/exocyclic coordination mode

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Experimental

General procedures

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The FT-IR spectra were measured using a Thermo Fisher Scientific Nicolet *i*S 10 FT-IR spectrometer. Each product obtained in this work was dried in a vacuum before elemental analysis, which was carried out on a Thermo Scientific Flash 2000 Series elemental analyser. The powder X-ray diffraction (PXRD) experiments were performed in transmission mode with a Bruker D8 Advance A25 diffractometer equipped with graphite monochromated Cu Kα radiation (λ = 1.54073 Å).

Preparations of $\{[Ag_3L_2](PF_6)_3 \cdot 2CH_2Cl_2\}_n$ (1)

$AgPF_6$ (19.27 mg, 0.076 mmol) in methanol (1.0 mL) was added to a solution of **L** (10.0 mg, 0.025 mmol) in dichloromethane (1.0 mL). Slow evaporation of the solution afforded a colourless crystalline product **1** suitable for X-ray analysis. Yield: 37%; Mp: 168-169 °C. IR: 3005, 2922, 1593, 1573, 1455, 1421, 1269, 1223, 1162, 1087, 1007, 840 (PF_6^-), 714 cm^{-1}. Anal. calc. for $C_{38}H_{46}Ag_3P_3F_{18}N_2S_8$: C, 29.53; H, 3.00; N, 1.81. Found: C, 29.65; H, 3.01; N, 1.89%.

Preparation of $\{[Ag_4L_2(CF_3SO_3)_2](CF_3SO_3)_2 \cdot CH_2Cl_2\}_n$ (2)

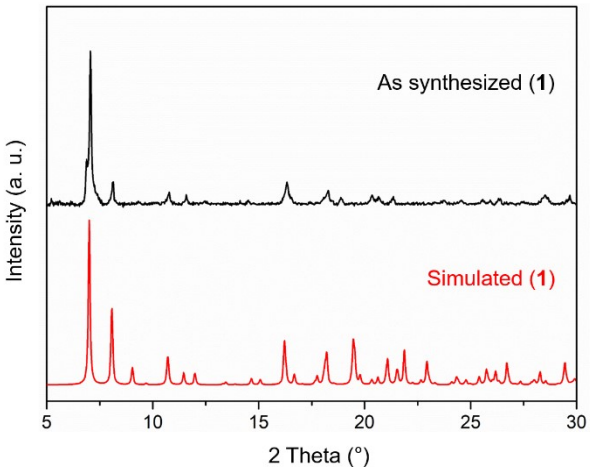
$AgCF_3SO_3$ (19.58 mg, 0.076 mmol) in methanol (1.0 mL) was added to a solution of **L** (10.1 mg, 0.025 mmol) in dichloromethane (1.0 mL). Slow evaporation of the solution afforded a colourless crystalline product **2** suitable for X-ray analysis. Yield: 48%; Mp: 199-200 °C (decomp.) IR: 2992, 2952, 2925, 1629, 1592, 1572, 1455, 1272 ($CF_3SO_3^-$), 1240, 1168, 1093, 1027 ($CF_3SO_3^-$), 897, 808 cm^{-1}. Anal. calc. for $C_{21}H_{23}Ag_2F_6NO_6S_6$: C, 27.79; H, 2.55; N, 1.54. Found: C, 27.84; H, 2.60; N, 1.58%.

Preparations of $\{[Ag_4L_2(CF_3CO_2)_2](CF_3CO_2)_2 \cdot 4CH_3OH\}_n$ (3)

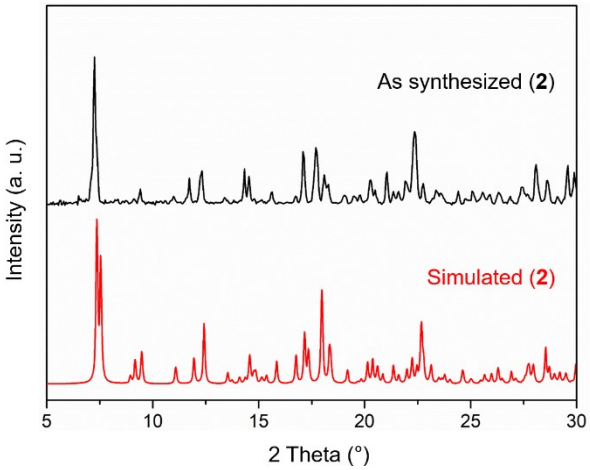
$AgCF_3CO_2$ (16.83 mg, 0.076 mmol) in methanol (1.0 mL) was added to a solution of **L** (10.0 mg, 0.025 mmol) in dichloromethane (1.0 mL). Slow evaporation of the solution afforded a colourless crystalline product **3** suitable for X-ray analysis. Yield: 43%; Mp: 178-179 °C (decomp.). IR: 3097, 2913, 1663 ($CF_3CO_2^-$), 1590, 1451, 1435, 1211 ($CF_3CO_2^-$), 1133, 839, 807, 724 cm^{-1}. Anal. calc. for $C_{23}H_{23}Ag_2F_6NO_4S_4$: C, 33.07; H, 2.78; N, 1.68. Found: C, 33.19; H, 2.80; N, 1.81%.

Anion exchange

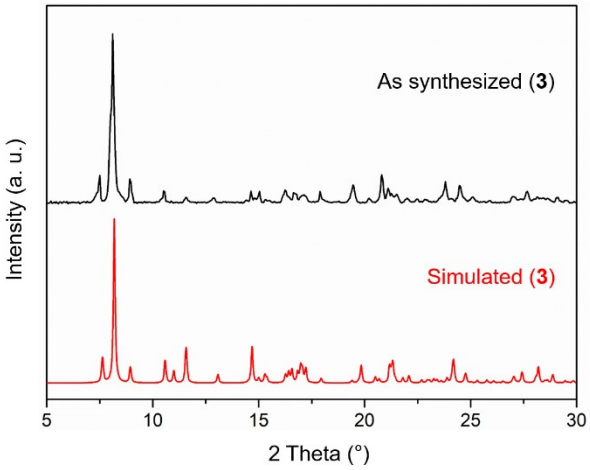
The anion exchange experiments were performed with products **1**-**3** (5 mg) by immersing in 3 M aqueous solution (2.0 mL) of each sodium salt and leaving undisturbed at room temperature. Each solid sample was periodically collected by filtration, washed several times with distilled water, and then dried in air.



(a)

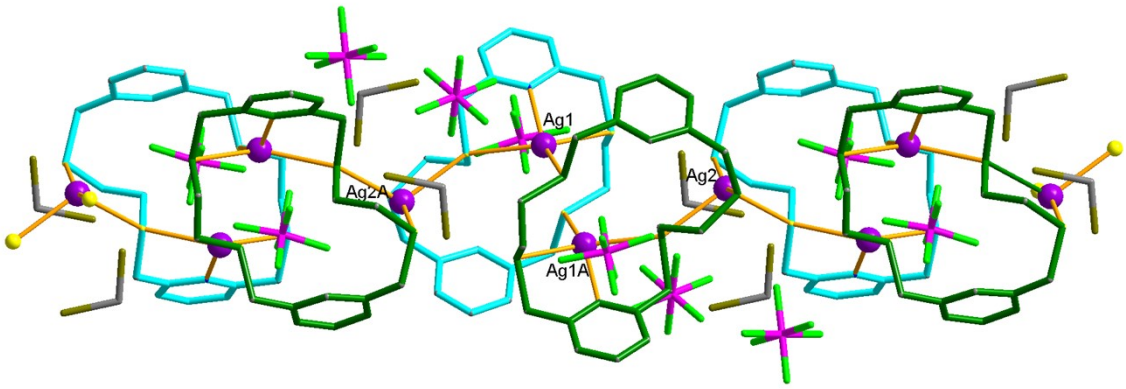


(b)

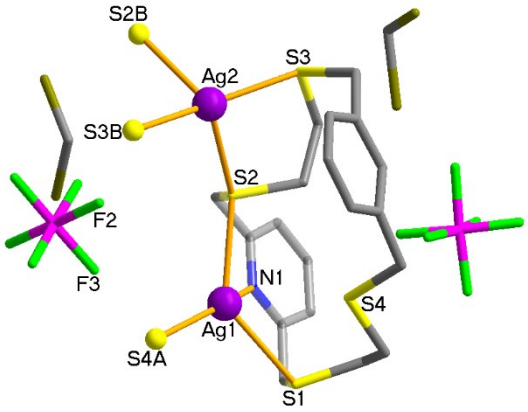


(c)

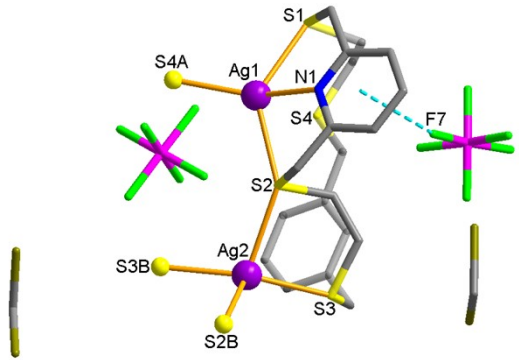
Fig. S1 PXRD patterns for (a) **1**, (b) **2** and (c) **3**: (top) as synthesised and (bottom) simulated from the single crystal X-ray data.



(a)

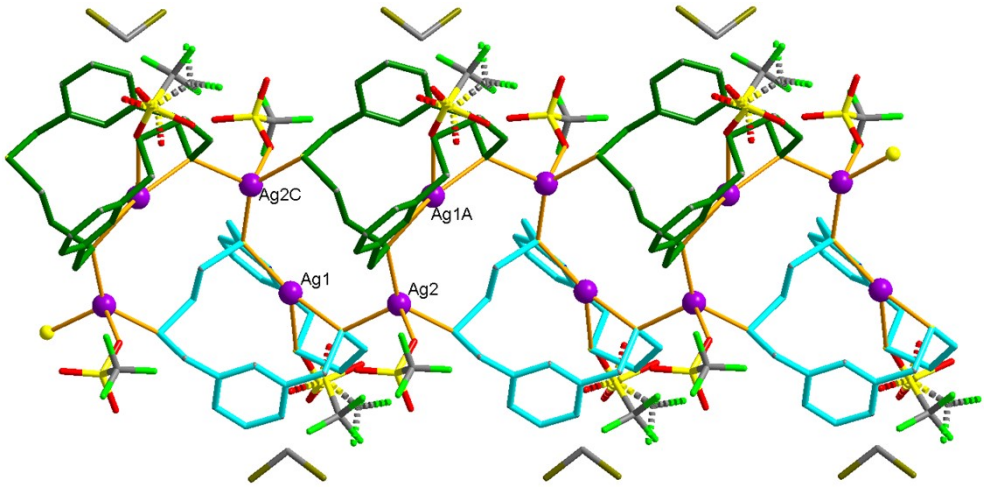


(b)

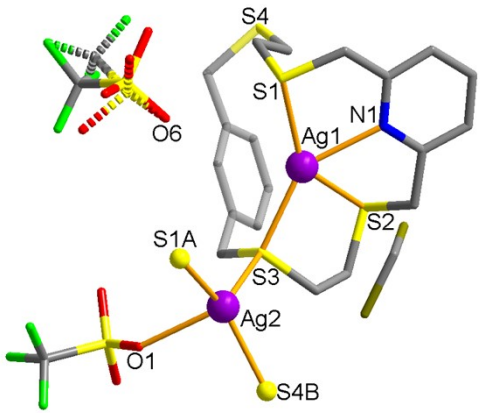


(c)

Fig. S2 Crystal structure of **1** (PF_6^- form) showing non-coordinated anions and solvent molecules: (a) 1D polymeric array, (b) asymmetric unit and (c) anion-π interaction between one PF_6^- and the pyridyl moiety (green dashed line; F7···centroid 3.316 Å). The shortest distance between Ag(I) and anion; Ag1···F3 3.767 Å.

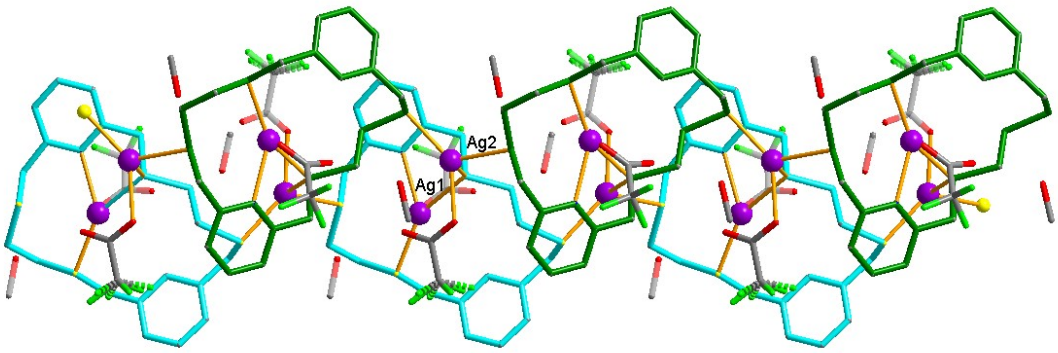


(a)

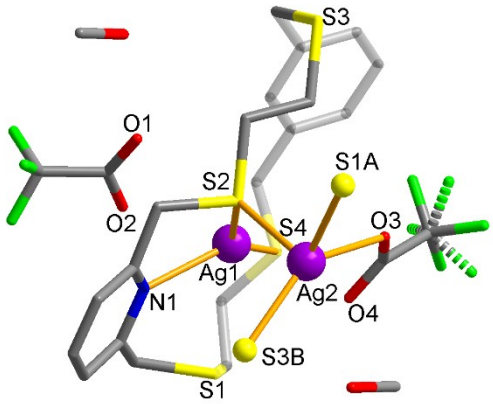


(b)

Fig. S3 Crystal structure of **2** ($CF_3SO_3^-$ form) showing non-coordinated anions and solvent molecules: (a) 1D polymeric array and (b) asymmetric unit. The non-coordinated trifluorosulfonate ion is disordered (60:40). The shortest distance between Ag(I) and the non-coordinated anion; Ag1···O6 3.896 Å.

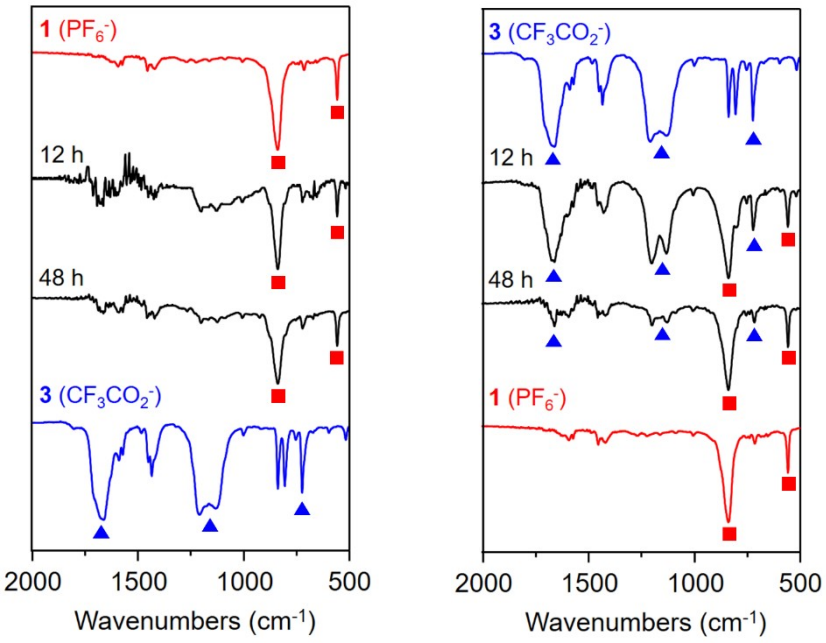


(a)



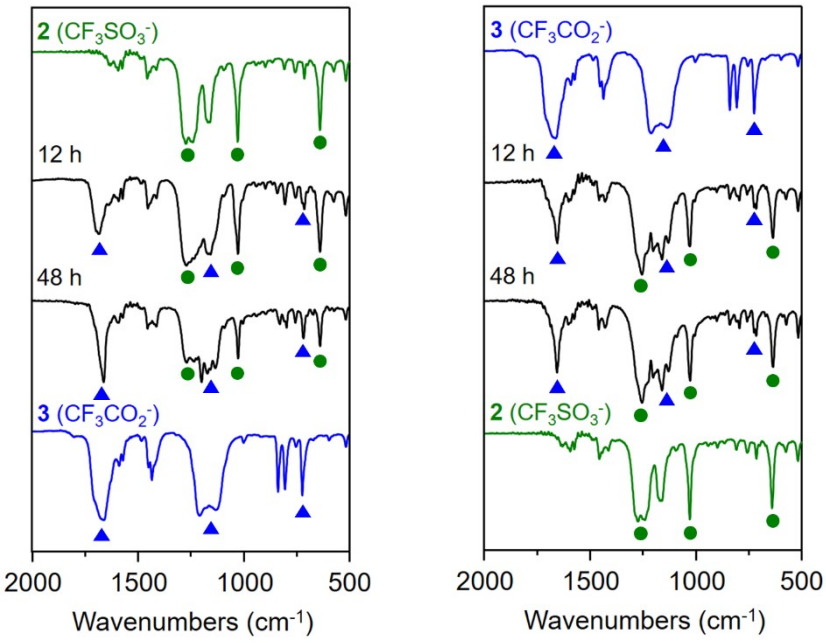
(b)

Fig. S4 Crystal structure of **3** ($CF_3CO_2^-$ form) showing anions and solvent molecules. (a) 1D polymeric array and (b) asymmetric unit. The coordinated trifluoroacetate ion is disordered (86:14). The Ag1 atom weakly interacts with the other anion (Ag1···O1 3.117, Ag1···O2 3.033 Å).



(a) (b)

Fig. S5 IR spectra for (a) **1** (PF_6^- form) and (b) **3** ($CF_3CO_2^-$ form) after anion exchanges (for 12 h and 48 h) with 3 M $NaCF_3CO_2$ and 3 M $NaPF_6$ aqueous solution, respectively.



(a) (b)

Fig. S6 IR spectra for (a) **2** ($CF_3SO_3^-$ form) and (b) **3** ($CF_3CO_2^-$ form) after anion exchanges (for 12 h and 48 h) with 3 M $NaCF_3CO_2$ and 3 M $NaCF_3SO_3$ aqueous solution, respectively.

X-ray crystallographic analysis

All data were collected on a Bruker SMART APEX2 ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.[S1] All of the calculations for the structure determination were carried out using the SHELXTL package.[S2] In all cases, all nonhydrogen atoms 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. Relevant crystal data collection and refinement data for the crystal structures of **1**-**3** are summarised in Table S1.

References

S1. *Bruker, APEX2 Version 2009.1-0 Data collection and Processing Software,* Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

S2. *Bruker, SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures,* Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

CCDC 2290290 (**1**), 2290291 (**2**) and 2290292 (**3**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic data and refinement parameters of **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{40}H_{50}Ag_3Cl_4F_{18}N_2P_3S_8$	$C_{43}H_{48}Ag_4Cl_2F_{12}N_2O_{12}S_{12}$	$C_{25}H_{31}Ag_2F_6NO_6S_4$
Formula weight	1715.62	1899.93	899.49
Temperature	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbcm*	*C*2/*c*	$P2_1$
Z	4	4	2
a (Å)	10.9437(2)	24.3861(9)	11.5778(7)
b (Å)	21.7335(3)	10.5716(4)	12.0547(7)
c (Å)	25.2207(4)	24.9876(9)	12.4212(8)
α (°)	90	90	90
β (°)	90	106.300(2)	111.230(4)
γ (°)	90	90	90
V (Å^3)	5998.62(17)	6182.9(4)	1615.94(17)
D_{calc} (g/cm^3)	1.900	2.041	1.849
$2\theta_{max}$ (°)	52.00	52.00	52.00
R_1, wR_2 [$I > 2\sigma(I)$]	0.0608, 0.1562	0.0365, 0.0921	0.0321, 0.0660
R_1, wR_2 [all data]	0.0732, 0.1647	0.0438, 0.0970	0.0349, 0.0676
Goodness-of-fit on F^2	1.045	1.030	1.030
No. of reflection used [>2σ(*I*)]	6041 [R_{int} = 0.0543]	6081 [R_{int} = 0.0451]	5811 [R_{int} = 0.0314]
Refinement	full-matrix	full-matrix	full-matrix

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**

Ag1-N1	2.332(6)	Ag2-S2	2.726(2)
Ag1-S1	2.715(2)	Ag2-S3	2.498(2)
Ag1-S2	2.699(2)	Ag2-S2B	2.726(2)
Ag1-S4A	2.461(2)	Ag2-S3B	2.498(2)
N1-Ag1-S1	76.6(1)	S2-Ag2-S3	86.0(1)
N1-Ag1-S2	75.9(1)	S2-Ag2-S2B	116.5(1)
N1-Ag1-S4A	148.7(1)	S2-Ag2-S3B	104.5(1)
S1-Ag1-S2	132.8(1)	S3-Ag2-S2B	104.5(1)
S1-Ag1-S4A	107.3(1)	S3-Ag2-S3B	160.3(1)
S2-Ag1-S4A	116.1(1)		

Symmetry operations: (A) -x+1, -y, -z+1 (B) x, -y+0.5, -z+1

Table S3 Selected bond lengths (Å) and bond angles (°) for **2**

Ag1-N1	2.398(3)	Ag2-S1A	2.525(1)
Ag1-S1	2.584(1)	Ag2-S3	2.546(3)
Ag1-S2	2.846(1)	Ag2-S4B	2.507(1)
Ag1-S3	2.504(1)	Ag2-O1	2.596(1)
N1-Ag1-S1	75.8(1)	S1A-Ag2-S3	116.3(1)
N1-Ag1-S2	72.3(1)	S1A-Ag2-S4B	136.0(1)
N1-Ag1-S3	142.2(1)	S1A-Ag2-O1	90.3(1)
S1-Ag1-S2	137.4(1)	S3-Ag2-S4B	104.0(1)
S1-Ag1-S3	140.0(1)	S3-Ag2-O1	112.1(1)
S2-Ag1-S3	79.7(1)	S4B-Ag2-O1	90.4(1)

Symmetry operations: (A) x, y+1, z (B) -x+0.5, y+0.5, -z+0.5

Table S4 Selected bond lengths (Å) and bond angles (°) for **3**

Ag1-N1	2.484(3)	Ag2-S2	2.658(1)
Ag1-S2	2.516(1)	Ag2-S3B	2.483(1)
Ag1-S4	2.467(1)	Ag2-O3	2.332(3)
Ag2-S1A	2.584(1)		
N1-Ag1-S2	74.9(1)	S1A-Ag2-S2	107.3(1)
N1-Ag1-S4	137.2(1)	S1A-Ag2-S3B	119.2(1)
S2-Ag1-S4	147.8(1)	S1A-Ag2-O3	92.8(1)
S2-Ag2-S3B	105.6(1)	S3B-Ag2-O3	140.2(1)
S2-Ag2-O3	84.2(1)		

Symmetry operations: (A) -x-1, y+0.5, -z-2 (B) -x-1, y-0.5, -z-2