Self-assembled polymers of silver(I) with a chiral diphosphine ligand

Nasser Nasser[a] and Richard J. Puddephatt*[,a]

Supplementary Information

Experimental Details

$[Ag_2(BF_4)_2$(R,R)-1], 3a.

To a solution of **(R,R)-1** (50 mg, 0.0723 mmol) in THF (10 mL) was added a solution of silver tetrafluoroborate (28.2 mg, 0.145 mmol) in THF (5 mL) and H_2O (1 mL). The solution was allowed to stir for 12 h. The solvent was removed and the white product was collected and then purified by reprecipitation from a concentrated acetone solution by addition of n-pentane and dried under vacuum. Yield: 72.2 mg (92.3%). NMR in acetone-d_6: $\delta(^1H)$ = 1.28 (m, 2H), 1.59 (m, 2H), 1.70 (m, 2H), 1.79 (m, 2H), 4.21 (m, 2H; 2 x CHN), 7.10 (m, 2H), 7.37-7.57 (m, 22H), 7.94 (d, J = 7 Hz, 2H; 2 x NH), 8.12 (m, 2H); $\delta(^{31}P)$ = 10.8 at 25˚C; $\delta(^{31}P)$ = 8.92, $^1J(^{31}P\text{-}^{107}Ag)$= 736 Hz, $^1J(^{31}P\text{-}^{109}Ag)$= 843 Hz at -80˚C. Anal. Calcd. for $C_{44}H_{40}Ag_2B_2F_8N_2O_2P_2$: C, 48.93; H, 3.73; N, 2.59. Found: C, 48.92; H, 3.53; N, 2.46%. Single crystals of **3a**.2.5MeOH.0.5H_2O were grown by slow diffusion of n-pentane into a solution of **3a** in chloroform/methanol.

The structure refinement was challenging, and the refinement did not fully converge, due to unresolved disorder in atoms C98, C99 and O6. Hydrogen atoms on O10 were located but refinement was not satisfactory.

$[Ag_2(NO_3)_2$(R,R)-1], 3b.

This was prepared in a similar way using silver nitrate (24.6 mg, 0.145 mmol) and **R,R-1** (50 mg, 0.0723 mmol. Yield : 66.3 mg (88.6 %). NMR in CD_2Cl_2: $\delta(^1H)$ = 1.30 (m, 2H), 1.62-1.85 (m, 4H), 2.12 (m, 2H), 3.97 (m, 2H; 2 x CHN), 7.04 (m, 2H), 7.27-7.51 (m, 22H), 7.59 (m, 2H), 8.05 (d, J = 7 Hz, 2H; 2 x NH), 8.32 (m, 2H); $\delta(^{31}P)$ = 11.92 (at -40˚C) [$^1J(^{31}P\text{-}^{107}Ag)$= 766 Hz, $^1J(^{31}P\text{-}^{109}Ag)$= 885 Hz]. Anal. Calcd. for $C_{44}H_{40}Ag_2N_4O_8P_2(3C_5H_{12})$: C, 56.83; H, 6.14; N, 4.49 %. Found: C, 56.31; H, 6.19; N, 4.58%. Single crystals of complex **3b**.9CH_2Cl_2 were grown by slow diffusion of n-pentane into dichloromethane solution of the compound.

The structure refinement was satisfactory except that the ellipsoid of atom C1J suggests unresolved disorder of this atom.

[$Ag_2(CF_3CO_2)_2$(R,R)-1], 3c.

A mixture of **R,R-1** (50 mg, 0.0723 mmol) and silver trifluoroacetate (31.9 mg, 0.145 mmol) in THF (10 mL) was stirred for 12 h. to give a white precipitate which was collected, washed with n-pentane and diethyl ether and dried under vacuum. Yield : 73.1 mg (89.1 %). NMR in CD_2Cl_2: $\delta(^1H)$ = 1.17-1.33 (m, 4H), 1.64 (m, 2H), 2.01 (m, 2H), 4.04 (m, 2H; 2 x CHN), 7.06 (m, 2H), 7.26-7.57 (m, 24H), 8.12 (m, 2H), 8.18 (br, 2H; 2 x NH); $\delta(^{31}P)$ = 12.22 (at -60°C) [$^1J(^{31}P\text{-}^{107}Ag)$= 763 Hz, $^1J(^{31}P\text{-}^{109}Ag)$= 867 Hz]. Anal. Calcd. for $C_{48}H_{40}Ag_2F_6N_2O_6P_2$: C, 50.91; H, 3.56; N, 2.47 %. Found: C, 50.90; H, 3.42; N, 2.50 %. Single crystals of complex **3c**.C_5H_{12} were grown by slow diffusion of n-pentane into a dichloromethane solution of the compound.

[Ag_2Cl_2(R,R-1)], 3d.

A solution of silver acetate (48.33 mg, 0.2895 mmol) in dichloromethane (10 mL) was added to a solution of **R,R-1** (100 mg, 0.144 mmol) in dichloromethane (10 mL). The mixture was stirred for 12 h. to give a white precipitate which was collected, washed with n-pentane and diethyl ether and dried under vacuum. To a solution of this product [$Ag_2(CH_3CO_2)_2$(R,R-**1**)] (100 mg, 0.0976 mmol) in methanol (10 mL) was added a solution of lithium chloride (8.3 mg, 0.1952 mmol) in methanol (10 mL). The solution was allowed to stir for 24 h., then the solvent was removed to give the product as a white solid. This was dissolved in dichloromethane and the solution was extracted with water to remove inorganic salts. The product was precipitated from dichloromethane solution by addition of n-pentane, then separated and dried under vacuum. Yield: 89.9 mg (94 %). NMR in CD_2Cl_2: $\delta(^1H)$ = 1.04 (m, 2H), 1.26 (m, 2H), 1.61 (m, 2H), 2.11(m, 2H), 3.94 (m, 2H; 2 x CHN), 6.96-7.52 (m, 30H); $\delta(^{31}P)$ = 6.31. Anal. Calcd. for $C_{44}H_{40}Ag_2Cl_2N_2O_2P_2$: C, 54.07; H, 4.13; N, 2.87 %. Found: C, 54.81; H, 4.17; N, 2.64%. Single crystals of complex **3d** were grown by slow diffusion of n-pentane into a solution of the compound in tetrahydrofuran/dichloromethane.

[$Ag_2(CF_3SO_3)_2$(*R,R*-1)], 3e.

A mixture of **(R,R)-1** (50 mg, 0.0723 mmol) and silver triflate (37.2 mg, 0.145 mmol) in THF (10 mL) was stirred for 12 h. to give a white precipitate which was collected, washed with n-pentane and diethyl ether and dried under vacuum. Yield : 80.0 mg (91.7 %). NMR in acetone-d_6: $\delta(^1H)$ = 1.19(m, 2H), 1.50 (m, 2H), 1.62 (m, 2H), 1.71 (m, 2H), 4.13 (m, 2H; 2 x CHN), 7.03 (m, 2H), 7.41-7.59 (m, 24H), 7.89 (m, 2H), 8.24 (br, 2H; 2 x NH); $\delta(^{31}P)$ at -80˚C = 10.48 [$^1J(^{31}P\text{-}^{107}Ag)$= 727 Hz, $^1J(^{31}P\text{-}^{109}Ag)$= 842 Hz].Anal. Calcd. for $C_{46}H_{40}Ag_2F_6N_2O_8P_2S_2$: C, 45.86; H, 3.35; N, 2.33 %. Found: C, 46.11; H, 3.58; N, 2.28 %.

[{Ag(μ-1)}$_n$](CF$_3$SO$_3$)$_n$, 4

A solution with stoichiometry $(AgO_3SCF_3)_3$(*R,R*-**1**)$_2$ (midway between **2d** and **3e**) was prepared in acetone-d_6 solution. The ^{31}P NMR spectrum at room temperature contained only a sharp singlet resonance at $\delta(^{31}P)$ = 10.32, with no ^1J(AgP) coupling, indicating rapid exchange. At -60^{o}C, the spectrum was very broad but no separate signals for either **2d** or **3e** were resolved. Pure compound **2d** gave a well resolved spectrum at room temperature [$\delta(^{31}P)$ = 12.05, $^1J(^{107}AgP)$ = 541 Hz, $^1J(^{109}AgP)$ = 622 Hz] and **3e** gave a broad singlet at room temperature [$\delta(^{31}P)$ = 9] and partly resolved spectrum at -60^{o}C [$\delta(^{31}P)$ = 8.80, ^1J(AgP)(average) = 780 Hz]. These data are interpreted in terms of the presence of a dynamic mixture with **2d** and **3e** in rapid equilibrium with oligomers [(XAg)(μ-**1**-Ag)$_n$(μ-**1**-AgX)], X = triflate, n = 1,2.., in solution, the exchange being faster than for either component **2d** or **3e** alone.

Single crystals of polymeric complex **4** (n = 4) were grown by slow diffusion of n-pentane into a solution containing silver triflate and *R,R*-**1** in close to 1:2 ratio in a mixture of acetone, chloroform and methanol.

Supporting Figures

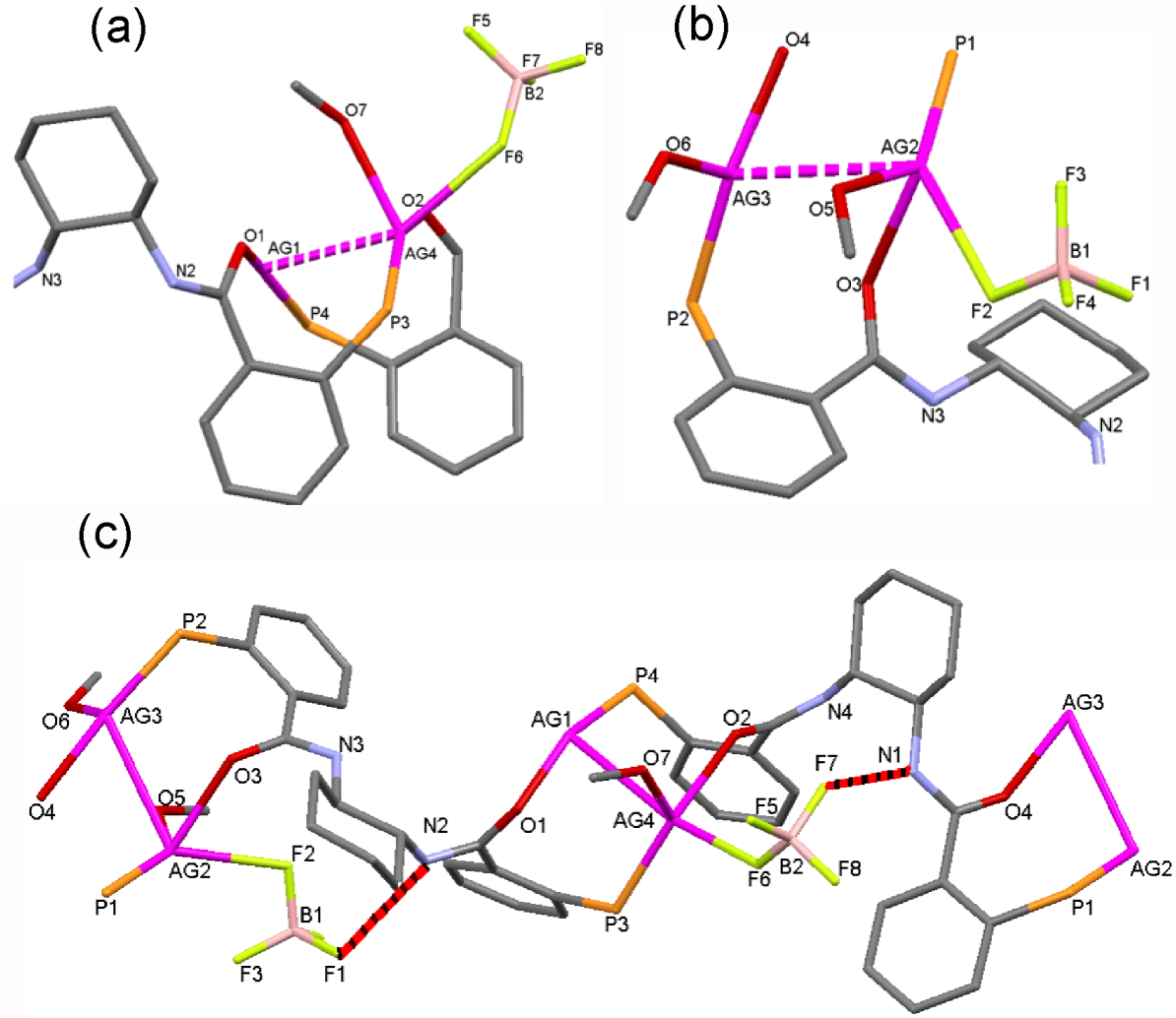

Figure S1. Views of the structure of complex **3a**: (a) the coordination of the Ag(1)..Ag(4) unit showing weak coordination of a methanol molecule and tetrafluoroborate anion to Ag(4); (b) the coordination of the Ag(2)..Ag(3) unit showing weak coordination of a methanol molecule to Ag(3) and a methanol molecule and tetrafluoroborate anion to Ag(2); (c) part of the polymer chain with methanol molecules and tetrafluoroborate anions included, along with some NH..F hydrogen-bonding interactions.

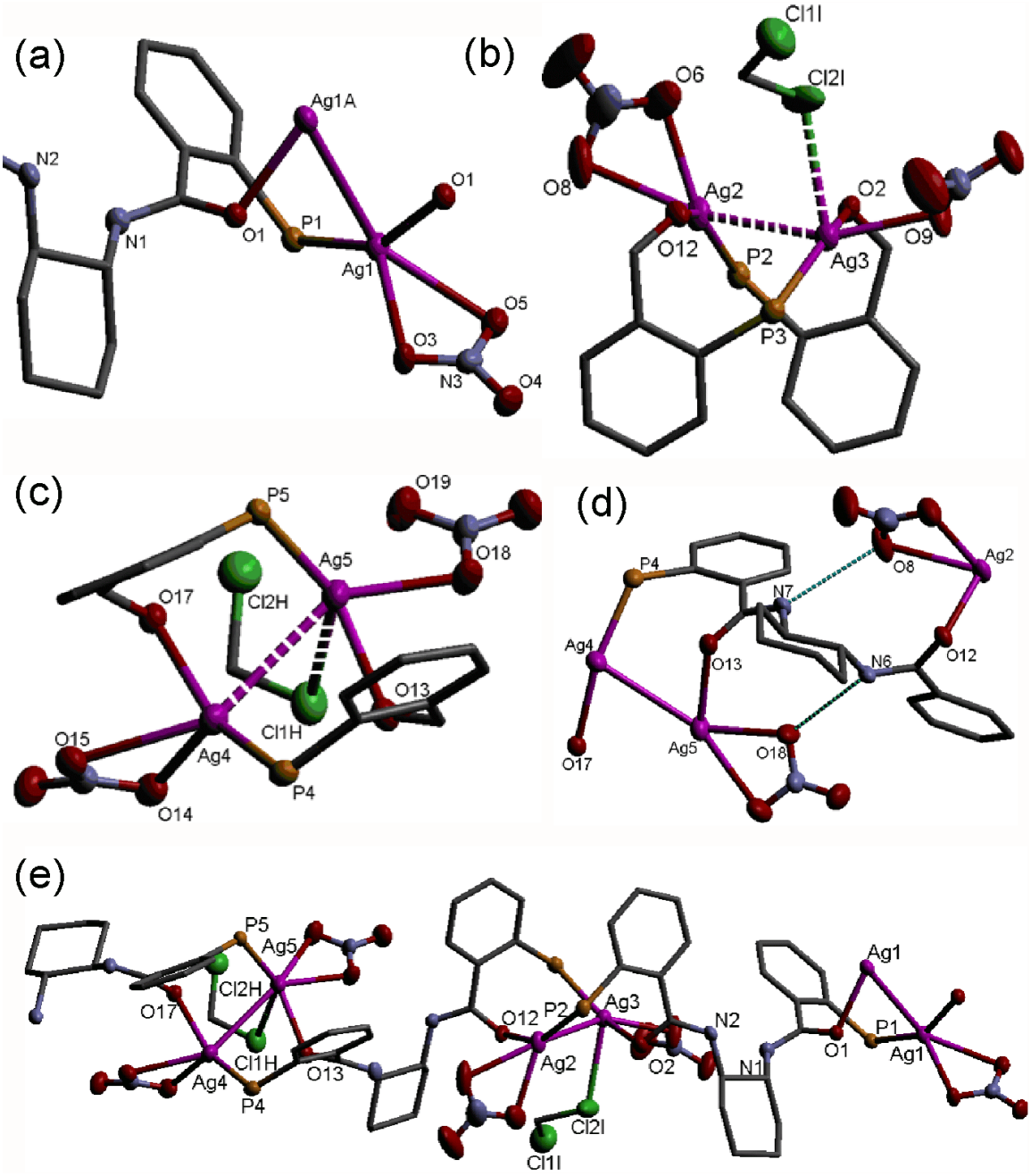

Figure S2. Views of the structure of complex **3b**: (a) the Ag(1)..Ag(1A) unit, showing weak coordination of a nitrate anion; (b) the Ag(2)..Ag(3) unit showing coordination of nitrate anions to Ag(2) and Ag(3) and a dichloromethane molecule to Ag(3); (c) the Ag(4)..Ag(5) unit showing coordination of nitrate anions to Ag(4) and Ag(5) and a dichloromethane molecule to Ag(5); (d) some NH..O hydrogen bonding interactions; (e) part of the polymer chain with nitrate and dichloromethane units included.

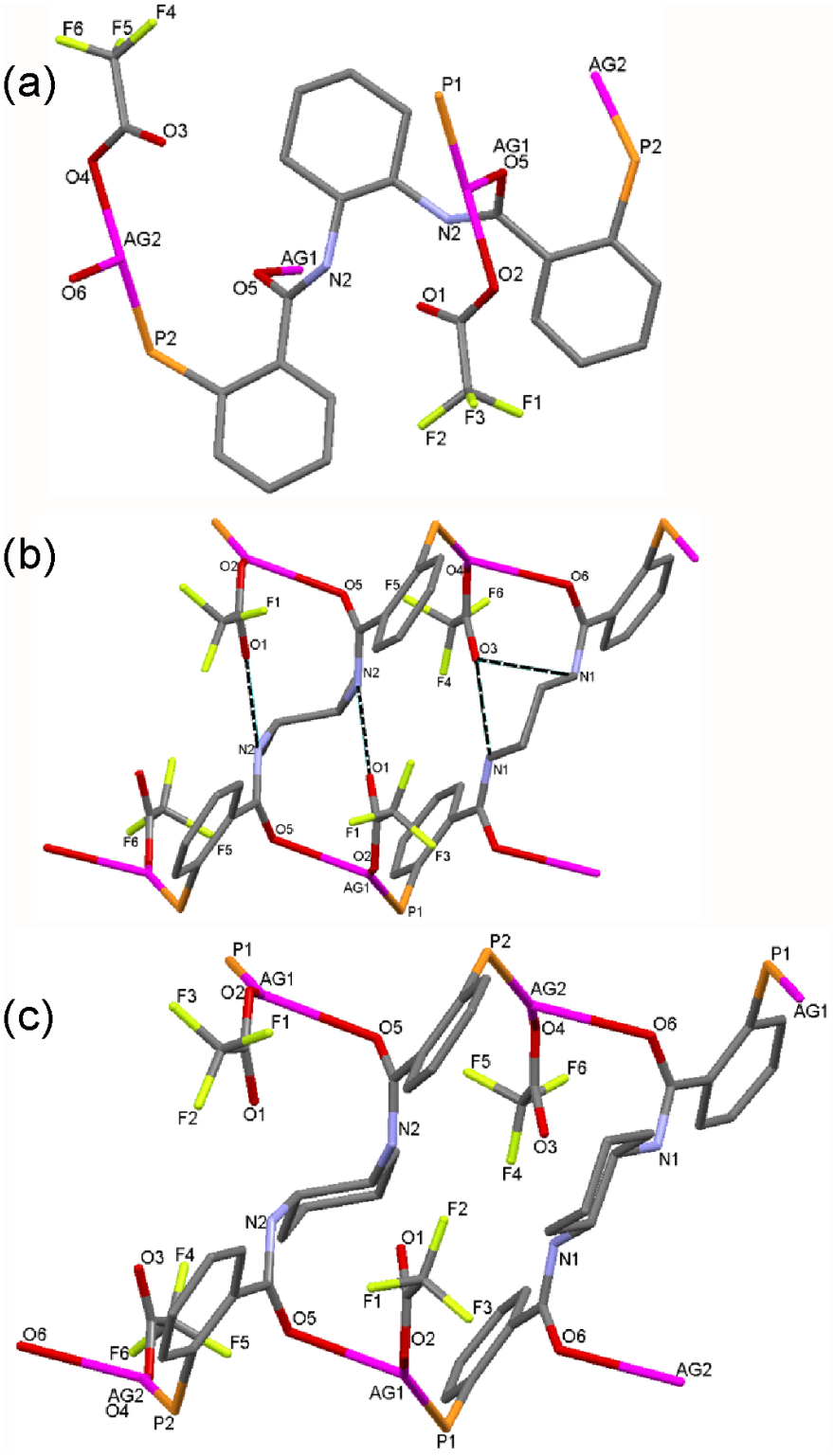
(a)
F6
F5
F4
O3
O4
AG2
O6
P2
AG1
O5
N2
P1
AG2
P2
AG1
O5
N2
O2
O1
F1
F3
F2
(b)
O2
O5
F5
O4
O6
F1
F6
O1
O3
N2
F4
N1
N2
O1
N1
F6
F5
O5
F1
O2
F3
AG1
P1
(c)
P1
AG1
F3
O2
F1
O5
F2
O1
P2
AG2
O4
O6
P1
AG1
F5
F6
N2
O3
F4
N1
N2
F2
O1
O3
F4
N1
F1
F3
O5
O2
O6
O6
F6
F5
AG2
AG2
O4
P2
AG1
P1

Figure S3. Views of the structure of complex **3c**: (a) the T-shaped coordination of Ag(1) and Ag(2); (b) some NH..O hydrogen-bonding interactions; (c) part of the ribbon polymer chain.

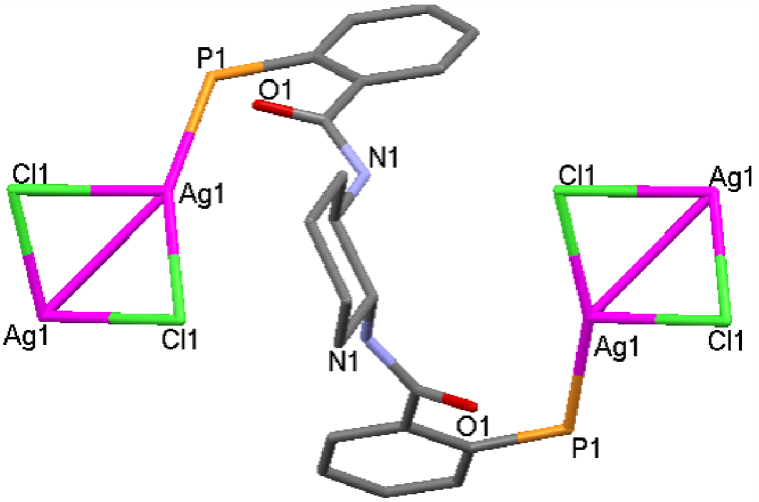

Figure S4. Part of the polymeric structure of complex **3d**.

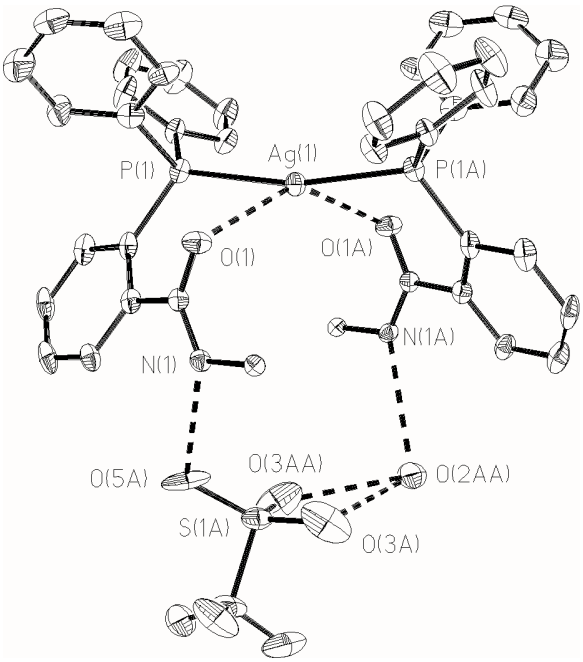

Figure S5. The hydrogen bonding interactions of the triflate ion and water molecule in polymeric complex **4**. There is a C_2 symmetry axis which passes through Ag(1) and the midpoint of O(3A) and O(3AA), leading to 50:50 disorder of triflate and water positions.

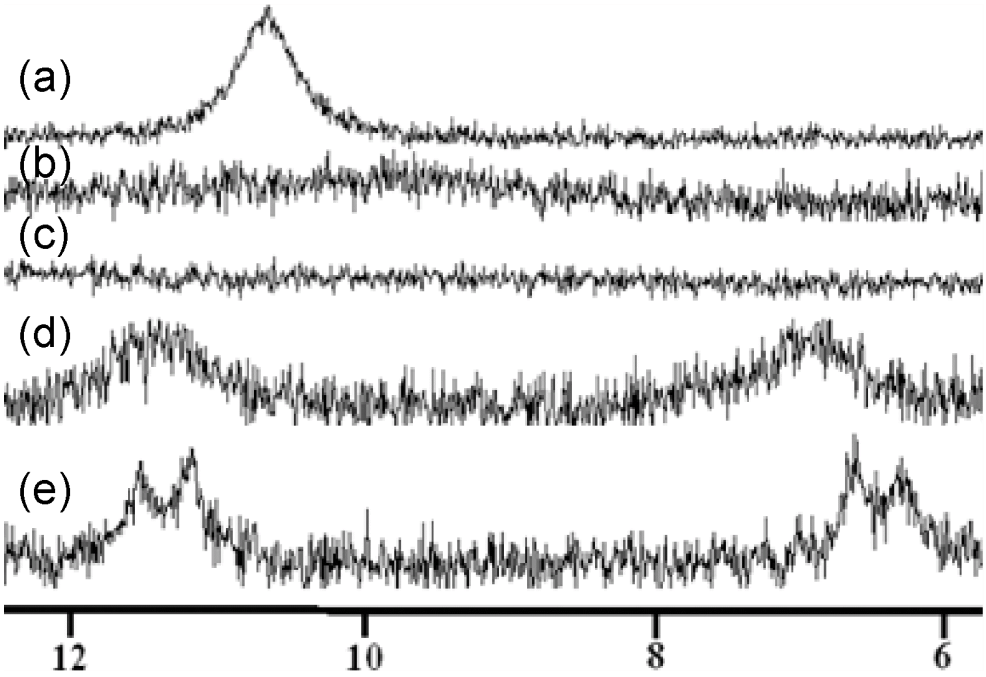

Figure S6. Variable temperature ^{31}P NMR spectra (162 MHz) for complex **3a** at (a) 25^{o}C; (b) -20^{o}C; (c) -40^{o}C; (d) -40^{o}C; (e) -80^{o}C.