Electronic Supplementary Information (ESI) for

Direction of topological isomers of silver(I) coordination polymers induced by solvent, and selective anion-exchange of a class of PtS-type host frameworks

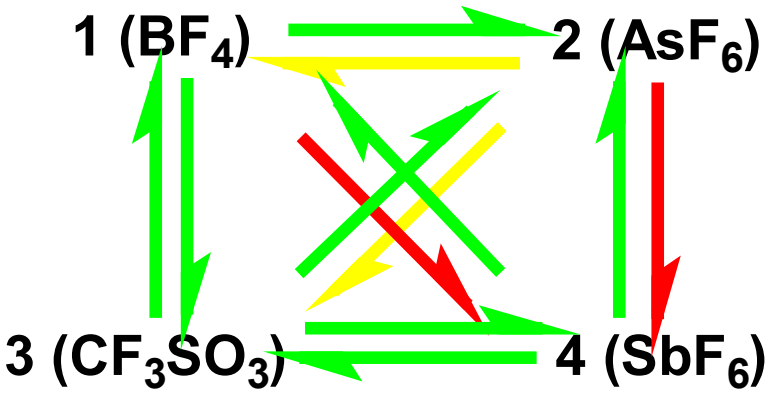
Miao Du,* Xiao-Jun Zhao, Jian-Hua Guo, Stuart R. Batten*

Experimental Section

Materials and General Methods. With the exception of the new bridging ligand 2,5-bis(4-pyrazine)-1,3,4-oxadiazole (bpzo), all of the starting materials and solvents were obtained commercially and used as received without further purification. Fourier transform (FT)-IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer. Elemental (Carbon, Hydrogen and Nitrogen) analyses were performed on a CE-440 (Leemanlabs) analyzer. ^{1}H NMR spectra were recorded on a Bruker AC-P 300 spectrometer (300 MHz) at 25 °C with tetramethylsilane as the internal reference. X-ray powder diffraction data (XRPD) were collected on a Rigaku RU200 diffractometer.

Single-Crystal X-ray Diffraction Determination and Refinement. Semi-empirical absorption corrections were applied using SADABS program and the program SAINT was used for integration of the diffraction profiles (Bruker AXS, *SAINT Software Reference Manual*, Madison, WI, 1998). All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL (G. M. Sheldrick, *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures,* University of Göttingen, Germany, 1997). The final refinement was performed by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all the non-H atoms. H atoms bonded to the ligand were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times U_{eq} of the atoms to which they are attached. H atoms of water solvents in **1** and hydroxide ion in **1a** cannot be located.

General Procedure of Anion Exchange Reaction. A well-ground polycrystalline sample of the coordination polymer (ca. 0.2 mmol) was suspended in an aqua solution containing the anion (NaX, ca. 0.3 mmol) to be used for the exchange, at room temperature. Normally, the exchange reaction is complete within 8 hours under stirring and 48 hours for the cases of no exchange or partial exchange. The product of the exchange was filtered, washed with water and then dried in vacuum. The results of the anion exchange are illustrated in the following scheme. The results of the transformation were testified by IR spectroscopy, elemental analysis (C, H and N) and XRPD. Obviously, the XRPD patterns of **1**–**4** and all exchange products are extraordinary similar due to their isostructural nature (rietveld refinement and the simulated patterns depending on single-crystal reflection data were performed using the PowderCell 2.4 software, see W. Kraus and G. J. Nolze, *Appl. Cryst.,* 1996, **29**, 301-303), however, they can prove that the PtS host frameworks are kept in all the cases. Details for the characterization of these exchange products are listed below. In the cases of complete exchange (or no exchange), products of exchange have IR spectra identical to those of the corresponding complexes synthesized from the silver(I) salt and ligand, and satisfactory elemental analysis. For the cases of partial exchange, the products exhibit the characteristic absorbed bands of two types of counter anions, and a mediate result of elementary analysis.



Scheme. The results of the anion exchange (red arrow refers to no exchange, yellow to partial exchange and green to complete exchange)

Table S1 Bond geometries of the coordination sphere of Ag(I) in all complexes

Bond lengths*

	$Ag–N_{pyz1}$	$Ag–N_{pyz2}$	$Ag–N_{oxa}$
1	2.379(2)	2.728(2)	2.597(2)
1a	2.436(11)	2.708(9)	2.565(9)
2	2.351(6)	2.717(4)	2.499(5)
3	2.354(4)	2.722(3)	2.520(3)
4	2.371(7)	2.726(6)	2.518(6)

Bond angles**

	$N_{pyz1}–Ag–N_{pyz1}$	$N_{pyz1}–Ag–N_{oxa}$	$N_{oxa}–Ag–N_{oxa}$
1	154.36(11)	106.93(8) and 92.51(7)	81.99(10)
1a	82.8(14)	105.6(6) and 144.6(6)	48.8(4)
2	151.1(3)	100.67(10) and 100.67(10)	84.3(3)
3	150.10(18)	101.00(6) and 101.00(6)	84.63(16)
4	153.1(3)	100.06(12) and 100.06(12)	82.8(3)

* N_{pyz1} refers to the nitrogen donor of pyrazine ring coordinating to Ag^I in a monodentate fashion; N_{pyz2} refers to the pyrazine nitrogen chelated to Ag^I together with the oxadiazole system; N_{oxa} refers to the oxadiazole nitrogen. ** Only the bond parameters can reflect the geometries of the Ag^I nodes are listed.

Color versions of figures 1-3 in this communication

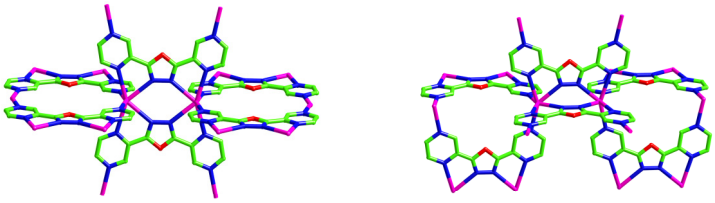


Fig. 1 Local coordination geometries of ligand and metal in the structures of **1**–**4** (left) and **1a** (right).

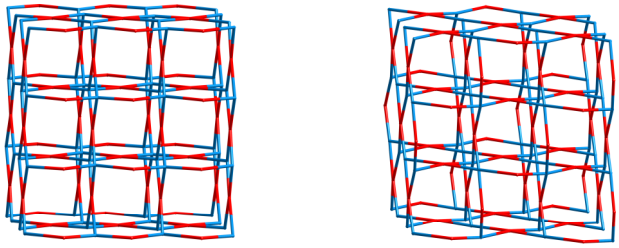


Fig. 2 Network topologies in **1**–**4** (left, PtS) and **1a** (right, lvt). Silver nodes are represented in blue, ligand nodes are red.

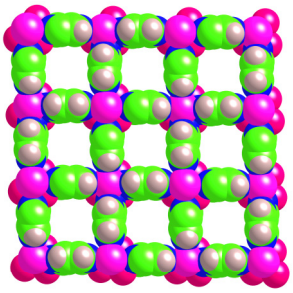
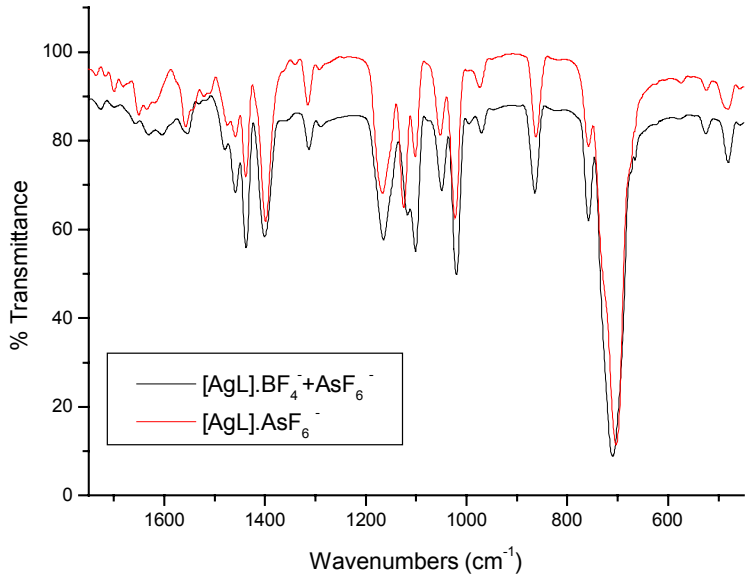


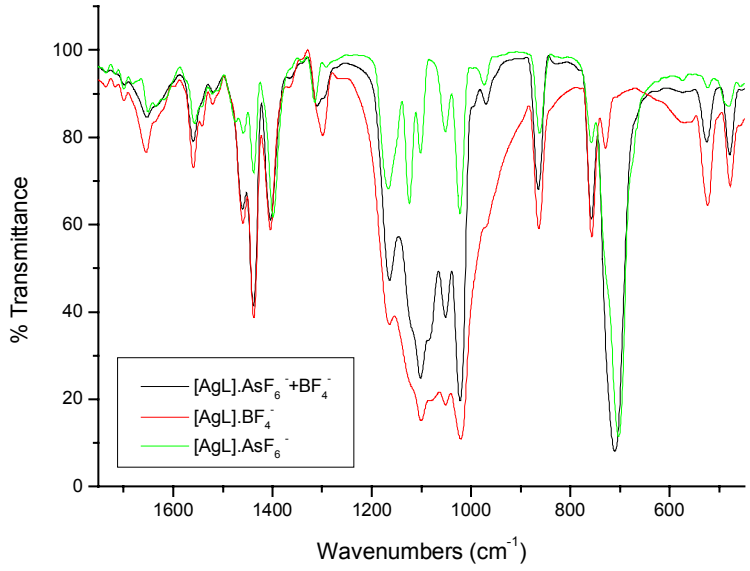
Fig. 3 Space-filling view of the square channels running parallel to *a* axis in **1a**. The structures of **1**–**4** have similar channels along *c* axis.

Fig. S1 IR Spectrum of the Exchange Product (From 1 to 2)



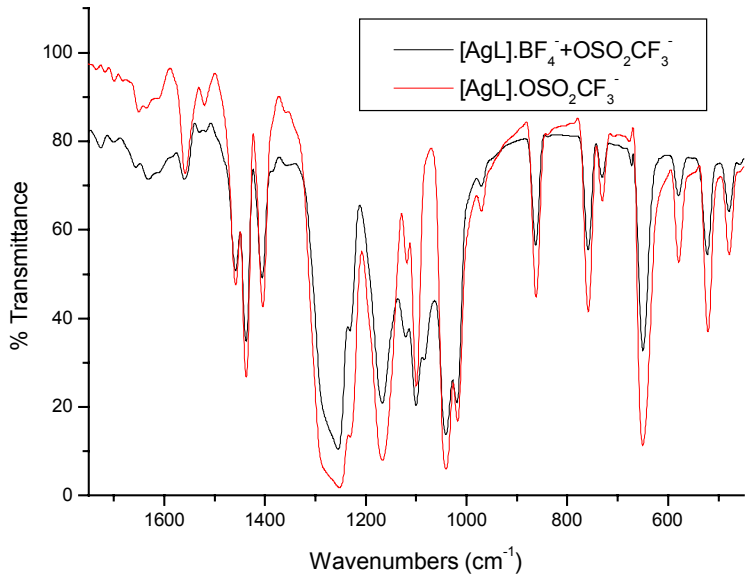
Elemental analysis of the exchange product: Found: C, 22.66; H, 1.51; N, 15.77%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**): C, 22.96; H, 1.16; N, 16.06%.

Fig. S2 IR Spectrum of the Exchange Product (From 2 to 1)



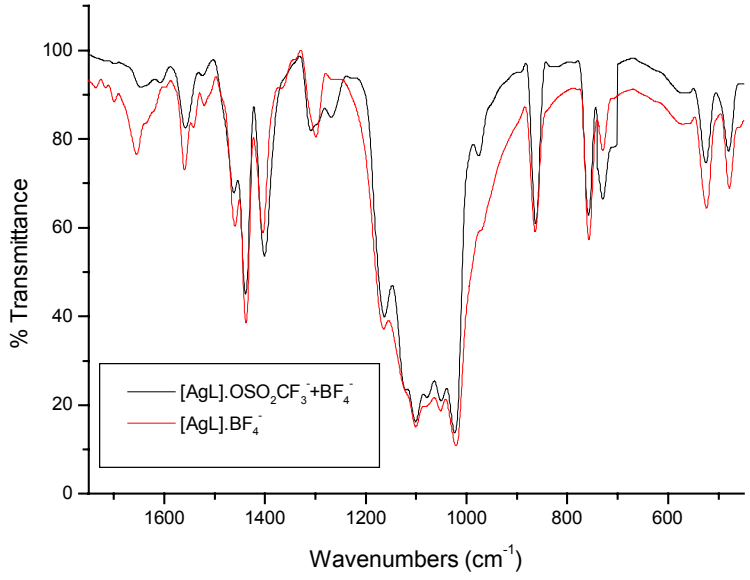
Elemental analysis of the exchange product: Found: C, 24.85; H, 1.67; N, 17.57%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**): C, 22.96; H, 1.16; N, 16.06%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](BF_4)\cdot 1.5H_2O$ (**1**): C, 26.81; H, 2.03; N, 18.75%.

Fig. S3 IR Spectrum of the Exchange Product (From 1 to 3)



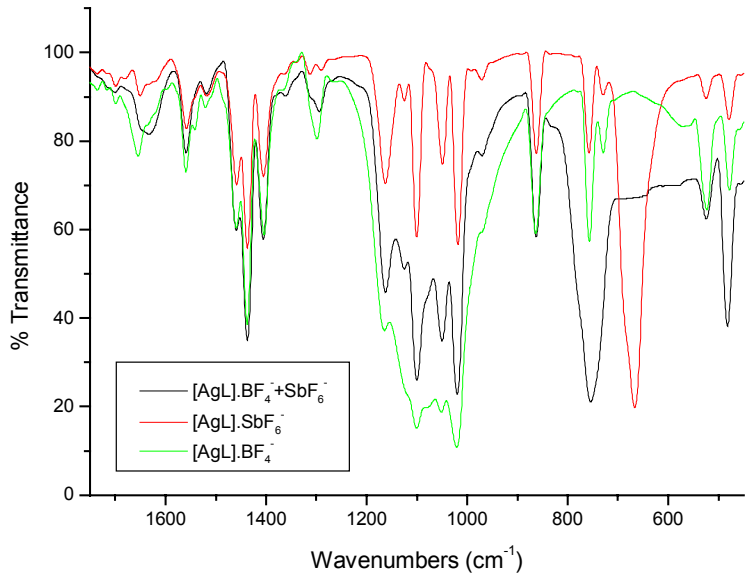
Elemental analysis of the exchange product: Found: C, 27.05; H, 1.07; N, 17.44%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](CF_3SO_3)$ (**3**): C, 27.34; H, 1.25; N, 17.39%.

Fig. S4 IR Spectrum of the Exchange Product (From 3 to 1)



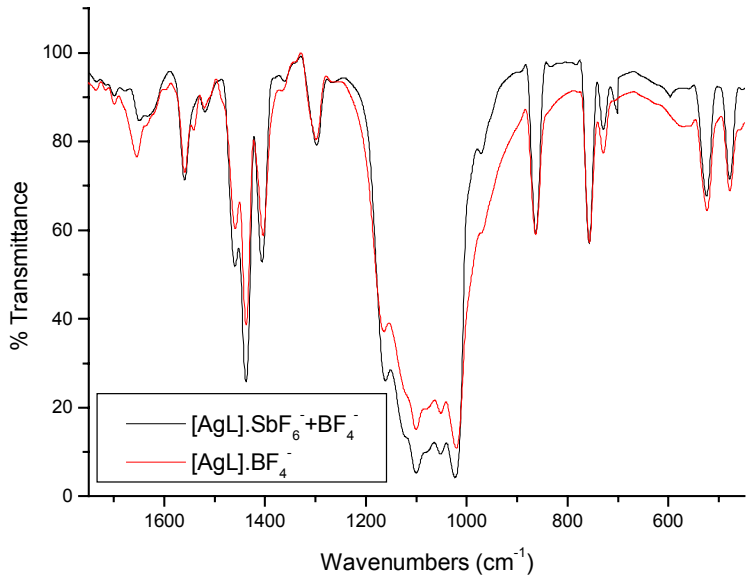
Elemental analysis of the exchange product: Found: C, 26.55; H, 1.91; N, 18.98%. $[Ag(C_{10}H_6N_6O)](BF_4)\cdot 1.5H_2O$ (**1**): C, 26.81; H, 2.03; N, 18.75%.

Fig. S5 IR Spectrum of the Exchange Product (From 1 to 4)



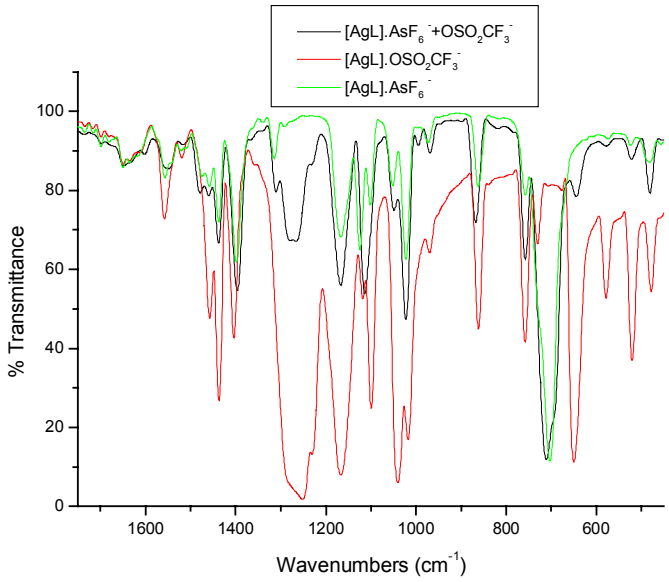
Elemental analysis of the exchange product: Found: C, 27.02; H, 1.69; N, 18.59%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](BF_4)\cdot 1.5H_2O$ (**1**): C, 26.81; H, 2.03; N, 18.75%.

Fig. S6 IR Spectrum of the Exchange Product (From 4 to 1)



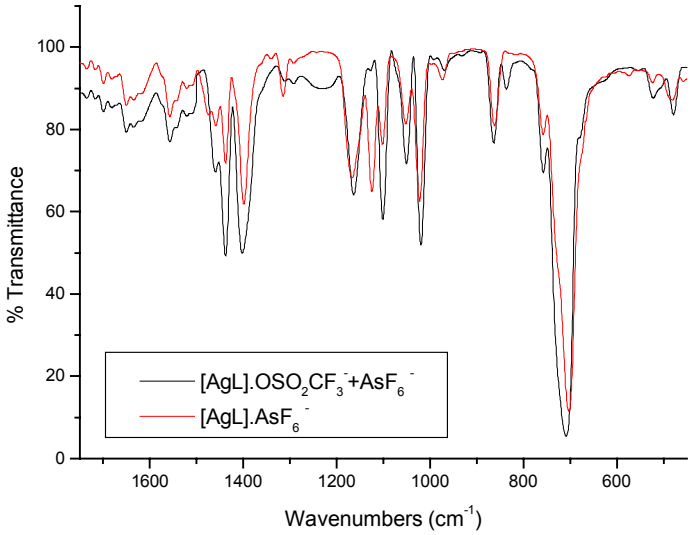
Elemental analysis of the exchange product: Found: C, 26.59; H, 1.87; N, 18.34%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](BF_4)\cdot 1.5H_2O$ (**1**): C, 26.81; H, 2.03; N, 18.75%.

Fig. S7 IR Spectrum of the Exchange Product (From 2 to 3)



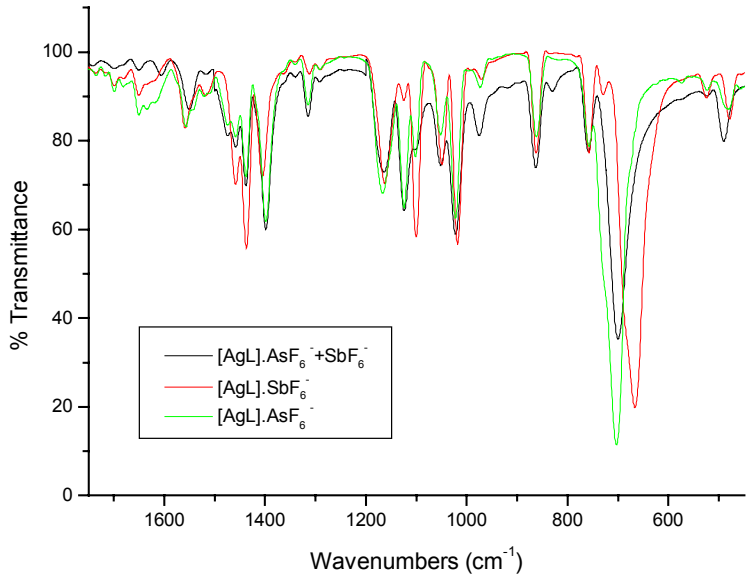
Elemental analysis of the exchange product: Found: C, 24.28; H, 1.13; N, 16.71%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**): C, 22.96; H, 1.16; N, 16.06%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](CF_3SO_3)$ (**3**): C, 27.34; H, 1.25; N, 17.39%.

Fig. S8 IR Spectrum of the Exchange Product (From 3 to 2)



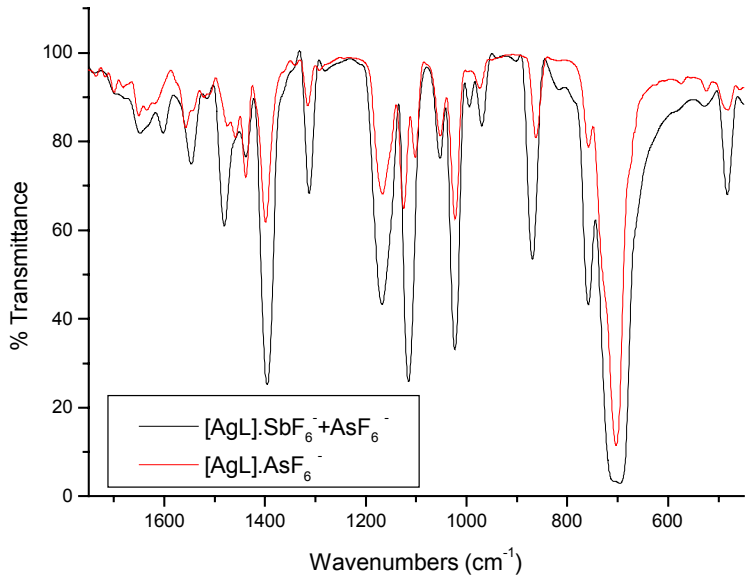
Elemental analysis of the exchange product: Found: C, 22.78; H, 1.29; N, 15.63%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**): C, 22.96; H, 1.16; N, 16.06%.

Fig. S9 IR Spectrum of the Exchange Product (From 2 to 4)



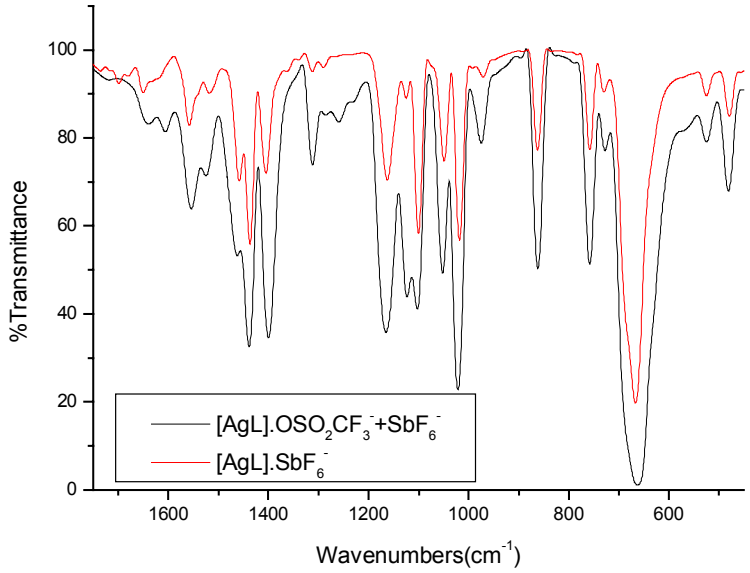
Elemental analysis of the exchange product: Found: C, 22.81; H, 1.55; N, 16.24%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**): C, 22.96; H, 1.16; N, 16.06%.

Fig. S10 IR Spectrum of the Exchange Product (From 4 to 2)



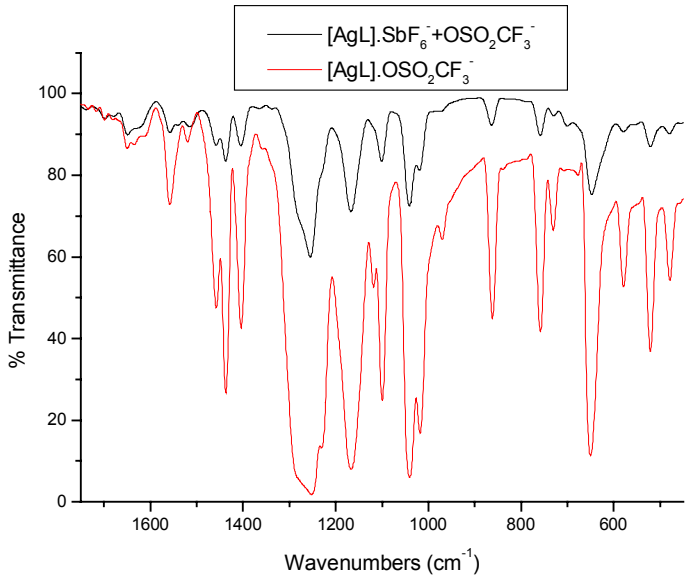
Elemental analysis of the exchange product: Found: C, 23.26; H, 0.90; N, 16.19%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**): C, 22.96; H, 1.16; N, 16.06%.

Fig. S11 IR Spectrum of the Exchange Product (From 3 to 4)



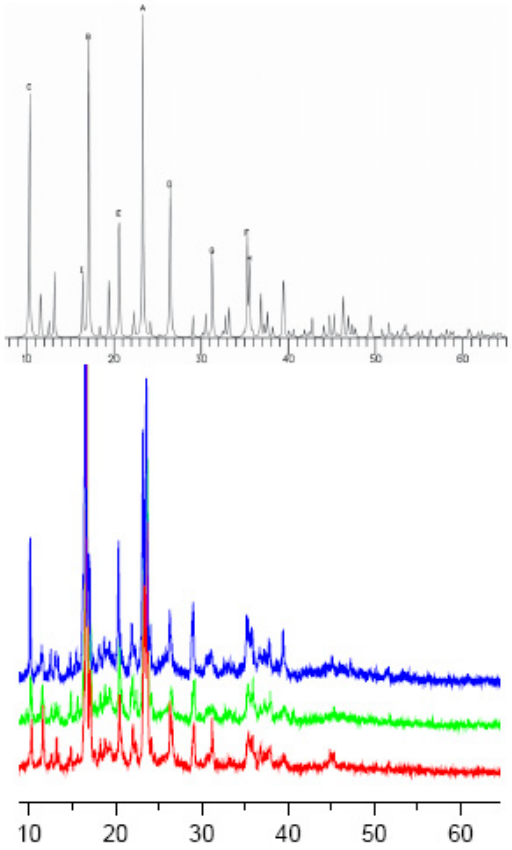
Elemental analysis of the exchange product: Found: C, 20.89; H, 1.42; N, 14.95%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](SbF_6)$ (**4**): C, 21.08; H, 1.06; N, 14.74%.

Fig. S12 IR Spectrum of the Exchange Product (From 4 to 3)



Elemental analysis of the exchange product: Found: C, 27.15; H, 0.86; N, 17.02%. *Anal.* Calcd for $[Ag(C_{10}H_6N_6O)](CF_3SO_3)$ (**3**): C, 27.34; H, 1.25; N, 17.39%.

XRPD patterns for complexes 1–4 (isostructural, simulated from the single crystal data, black); and the exchange products (red) complete exchange, (green) no exchange (blue) partial exchange.



A quantitative comparison of the experimental (black) and simulated (red) XRPD patterns using the software PowderCell (the difference of them is shown in green)