Electronic Supplementary Information

Dual structure evolution of a Ag(I) supramolecular framework triggered by anion-exchange: replacement of terminal ligand and switching of network interpenetration degree

Cheng-Peng Li, Si Wang, Wei Guo, Yan Yan and Miao Du*

College of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China

* Corresponding author. E-mail: dumiao@public.tpt.tj.cn

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Experimental section

Materials and methods. All starting materials and solvents were obtained commercially and used as received. The ligand L^{424} was synthesized according to a literature procedure.[1] Fourier transform (FT) IR spectra (KBr pellets) were recorded in 400−4000 cm^{-1} on an AVATAR-370 (Nicolet) spectrometer. Elemental analysis of C, H, and N was taken on a Leemanlabs CE-440 analyzer. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 1.5406 Å), with a step size of 0.02° in 2θ and a scan speed of 2 °/min. The simulated PXRD patterns were calculated from the single-crystal X-ray diffraction data.

$[Ag(L^{424})(H_2O)](NO_3)$ (1⊃NO_3). A CH_3OH solution (4 mL) of L^{424} (30.1 mg, 0.1 mmol) was carefully layered onto a buffer of ethyl acetate (4 mL), below which a H_2O solution (4 mL) of $AgNO_3$ (17.0 mg, 0.1 mmol) was placed in a straight glass tube. The tube was left to stand at room temperature in darkness. Colourless block crystals were observed on the tube wall after ca. three days. Yield: 51% (based on L^{424}). Anal. Calcd for $C_{17}H_{14}AgN_7O_4$ (**1⊃NO_3**): C, 41.82; H, 2.89; N, 20.08%. Found: C, 41.55; H, 2.99; N, 20.11%. IR (cm^{-1}): 3463b, 1640s, 1602m, 1563w, 1526w, 1444m, 1385vs, 1121m, 990w, 904w, 828m, 804w, 720m, 610m, 523m.

$[Ag(L^{424})(NO_2)](H_2O)_{1.5}$ (1⊃NO_2). The single-crystal sample of **1⊃NO_3** was immersed in an aqueous solution (5 mL) of excess $NaNO_2$ (0.1 M) at room temperature. The solution was left to quietly stand for about ten days. The resulting colourless block crystals were determined as $[Ag(L^{424})(NO_2)](H_2O)_{1.5}$ by single-crystal diffraction. IR (cm^{-1}): 3434b, 1595s, 1515w, 1467s,

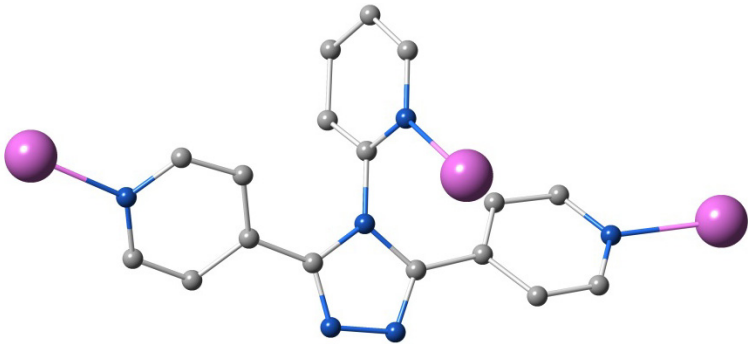
1441s, 1270vs, 1067w, 1014w, 864w, 827s, 804m, 750w, 721s, 665w, 613m, 521w, 464w.

[Ag(L^{424})(CF_3COO)](H_2O) (1⊃CF_3COO). The same procedure as that for **1⊃NO_2** was used except that $NaNO_2$ was replaced with CF_3COONa, forming colourless block single crystals of [Ag(L^{424})(CF_3COO)](H_2O) as revealed by single-crystal diffraction. IR (cm^{-1}): 3456b, 1666vs, 1604s, 1472m, 1449m, 1187s, 1129s, 1067m, 1005w, 832s, 794s, 753w, 719s, 662w, 613m, 522w, 468w.

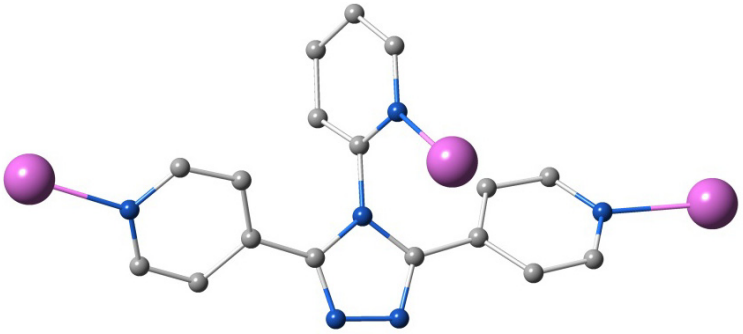
Single-crystal X-ray diffraction. Data collection was carried out on a Bruker Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature. A semi-empirical absorption correction (SADABS) was applied in each case and the SAINT program was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS program of SHELXTL and refined using SHELXL by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-H atoms. In general, H atoms were determined geometrically and refined as ridings with isotropic displacement parameters. Further crystallographic details and selected bond parameters are listed in Table S1 and Table S2, respectively.

Reference

1. M. H. Klingele and S. Brooker, *Eur. J. Org. Chem.*, 2004, 3422–3434.



(a)



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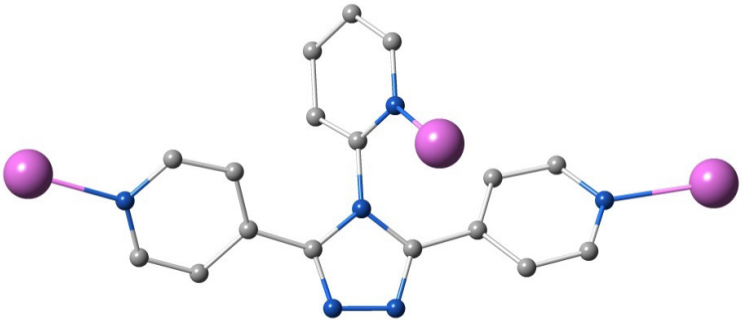
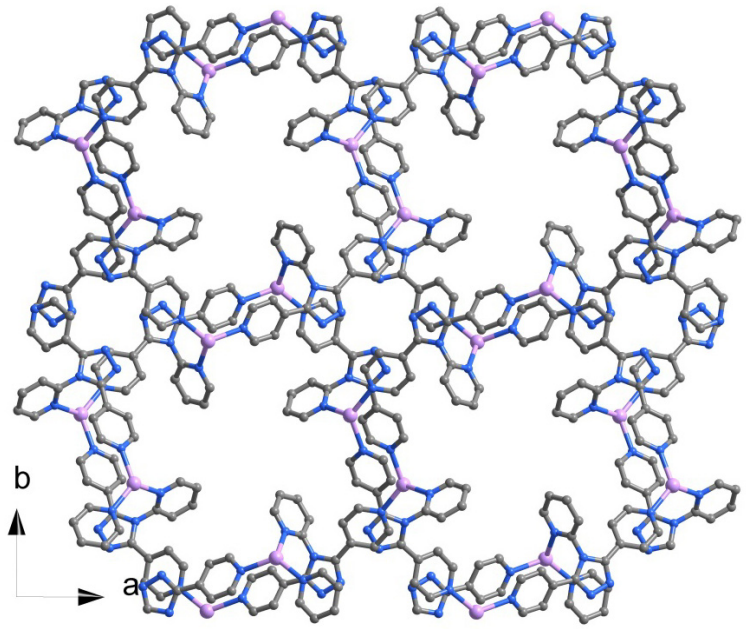
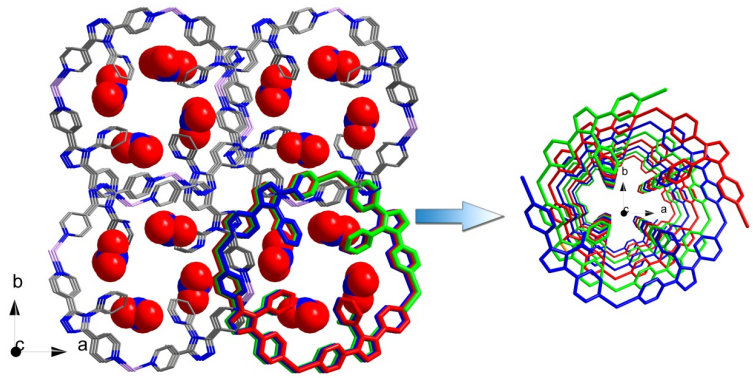


(c)

Fig. S1 Coordination fashions of L^{424} ligands in (a) **1⊃NO$_3$**, (b) **1⊃NO$_2$** and (c) **1⊃CF$_3$COO**.



(a)



(b)

Fig. S2 Crystal structure of **1⊃NO$_3$**. (a) One independent 3D open network. (b) Left: 3-fold interpenetrated framework with included nitrate anions shown in space-filling model. Right: Highlight of three entangled helical chains viewed along the *c* axis.

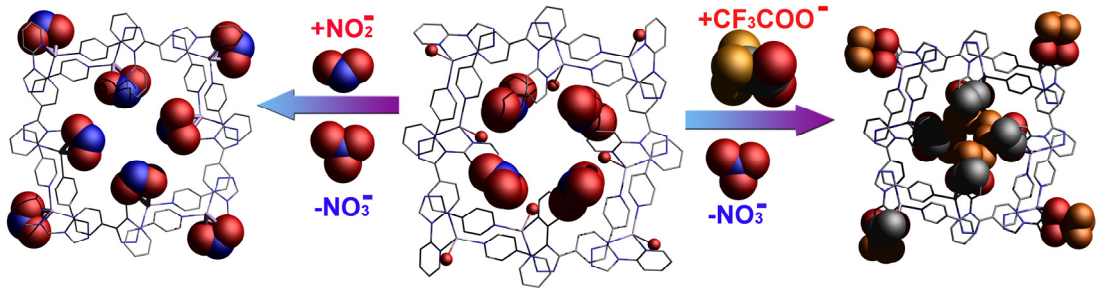


Fig. S3 Dual SC-SC transformations between **1⊃NO$_3$** and **1⊃NO$_2$** or **1⊃CF$_3$COO**.

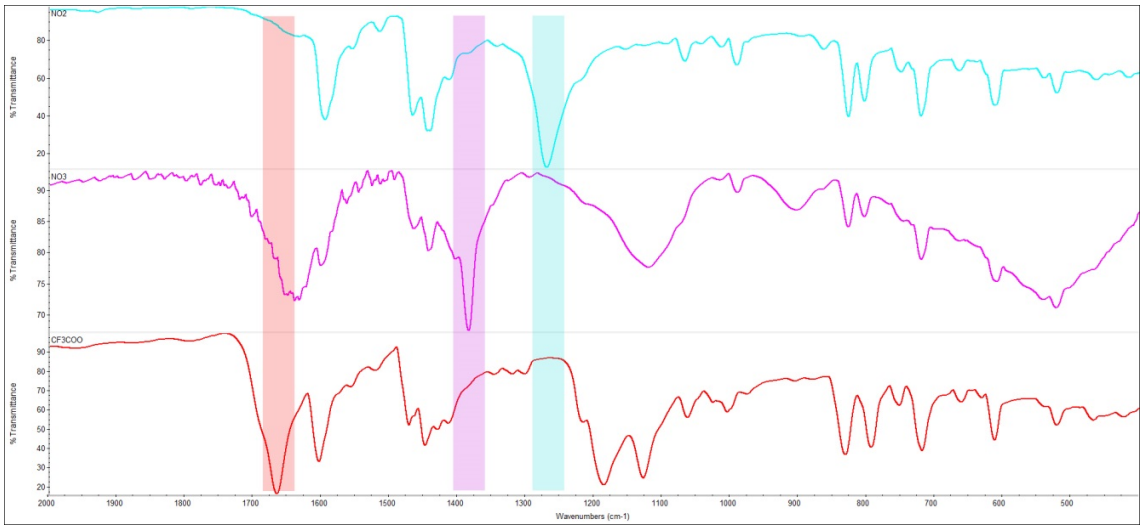
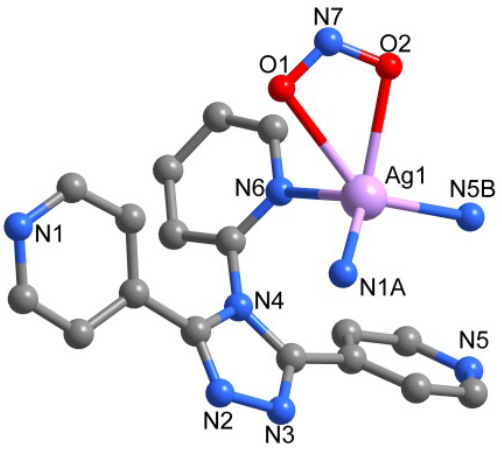
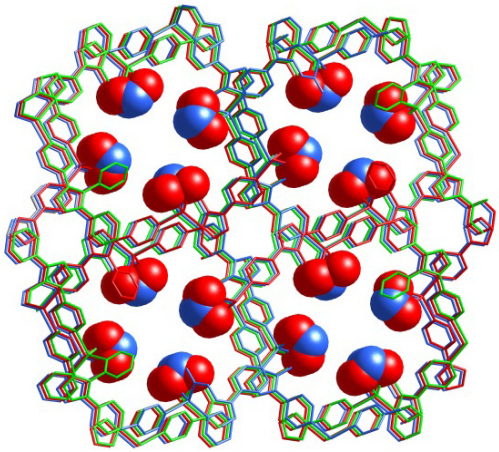


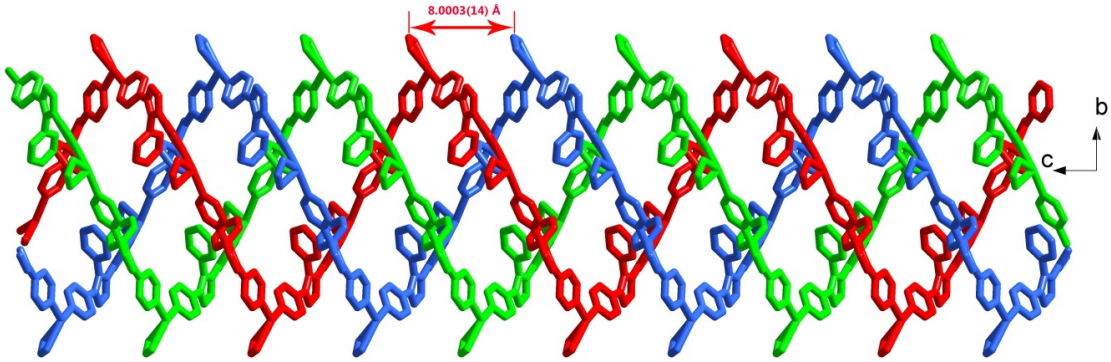
Fig. S4 IR spectra of **1⊃NO$_2$**, **1⊃NO$_3$** and **1⊃CF$_3$COO** (from top to bottom), in which the characteristic peaks of NO_2^- (1270 cm^{-1}), NO_3^- (1385 cm^{-1}) and CF_3COO^- (1666 cm^{-1}) are highlighted with cyan, purple, and pink column, respectively.



(a)



(b)



(c)

Fig. S5 Crystal structure of **1⊃NO$_2$**. (a) Coordination geometry of Ag^{I} ion. (b) 3-fold interpenetrated structure with three independent networks shown in different colors and nitrite anions in space filling model. (c) Three entangled Ag–L^{424} helical chains with a separation of 8.0003(14) Å, being equal to the length of *c* axis.

Table S1 Crystallography data for **1⊃NO$_3$**, **1⊃NO$_2$** and **1⊃CF$_3$COO**.

Compound reference	**1⊃NO$_3$**	**1⊃NO$_2$**	**1⊃CF$_3$COO**
Chemical formula	$C_{17}H_{14}AgN_7O_4$	$C_{17}H_{15}AgN_7O_{3.50}$	$C_{19}H_{14}AgF_3N_6O_3$
Formula mass	488.22	481.23	539.23
Crystal system	Tetragonal	Tetragonal	Tetragonal
a/Å	31.370(3)	31.065(3)	22.8131(6)
b/Å	31.370(3)	31.065(3)	22.8131(6)
c/Å	7.8467(13)	8.0003(14)	7.7879(4)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
Unit cell volume/Å^3	7721.8(16)	7720.4(17)	4053.1(3)
Temperature/K	296(2)	296(2)	296(2)
Space group	$I4_1/a$	$I4_1/a$	$P4_2/n$
Z	16	16	8
Absorption coefficient, μ/mm^{-1}	1.084	1.081	1.057
No. of reflections measured	18793	19218	20158
No. of independent reflections	3381	3428	3588
R_{int}	0.0248	0.0357	0.0509
Final R_1 values ($I > 2\sigma(I)$)	0.0379	0.0309	0.0400
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1165	0.0853	0.0876
Final R_1 values (all data)	0.0476	0.0423	0.0798
Final $wR(F^2)$ values (all data)	0.1310	0.0917	0.1110
Goodness of fit on F^2	1.094	1.051	1.026

Table S2 Selective bond lengths (Å) and angles (°) for **1⊃NO$_3$**, **1⊃NO$_2$** and **1⊃CF$_3$COO**.

		1⊃NO$_3$	
Ag1–N5	2.235(3)	Ag1–N1	2.291(3)
Ag1–N6	2.358(3)	Ag1–O1	2.414(4)
N5–Ag1–N1	124.70(13)	N5–Ag1–N6	120.71(11)
N1–Ag1–N6	101.18(12)	N5–Ag1–O1	102.96(15)
N1–Ag1–O1	112.63(14)	N6–Ag1–O1	89.25(13)
		1⊃NO$_2$	
Ag1–N1A	2.256(3)	Ag1–N5B	2.353(3)
Ag1–N6	2.432(3)	Ag1–O2	2.476(3)
Ag–O1	2.607(4)		
N1A–Ag1–N5B	116.46(10)	N1A–Ag1–N6	120.45(9)
N5B–Ag1–N6	97.82(10)	N1A–Ag1–O2	125.18(12)
N5B–Ag1–O2	92.32(11)	N6–Ag1–O2	98.19(11)
O1–Ag1–O2	47.98(12)	O1–Ag1–N5B	137.58(11)
O1–Ag1–N1A	101.18(11)	O1–Ag1–N6	77.65(11)
		1⊃CF$_3$COO	
Ag1–N1	2.231(4)	Ag1–N5	2.346(4)
Ag1–N6	2.447(4)	Ag1–O2	2.356(5)
N1–Ag1–N5	115.80(15)	N1–Ag1–N6	118.92(14)
N5–Ag1–N6	100.64(15)	N1–Ag1–O2	128.63(18)
N5–Ag1–O2	95.05(19)	N6–Ag1–O2	91.78(16)

Symmetry codes for **1⊃NO$_2$**: A = y – 1/4, $–x$ + 1/4, $–z$ + 9/4; B = $–x$ + 1/2, $–y$ + 1/2, $–z$ + 3/2.