Electronic supplementary information

for

Preparation of one-dimensional coordination polymers of a flexible tripyridyl disulfide with diverse topologies

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Experimental section

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. NMR spectra were recorded on a Bruker 300 spectrometer (300 MHz). The FT-IR spectra were measured with a Nicolet iS 10 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer. The powder X-ray diffraction (PXRD) experiments were performed in a transmission mode with a Bruker GADDS diffractometer equipped with graphite monochromated CuKα radiation (λ = 1.54073 Å). Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10 K min^{-1} using a TA Instruments TGA-Q50 thermogravimetric analyzer.

CAUTION: The perchlorate-containing complex is potentially explosive and appropriate precautions should be taken during their preparation, handling and storage.

Preparation of $\{[Cu(L)_2(NO_3)_2]\cdot CH_2Cl_2\}_n$ (1). A small amount of toluene was added to a dichloromethane (1 mL) solution of **L** (20.1 mg, 0.061 mmol); then the required copper(II) nitrate (16.0 mg, 0.061 mmol) in acetonitrile was layered on the toluene phase; the (layered) mixture afforded a dark blue crystalline product suitable for X-ray analysis. Mp: 158-161 °C. IR (KBr pellet): 3090, 3035, 2928, 1598, 1535, 1489, 1384 (NO_3^-), 1304, 1226, 1115, 1064, 854, 819, 723 cm^{-1}. Anal. Calcd for [$C_{17.7}H_{15.8}N_4O_3S_2Cu$]: C, 46.20; H, 3.46; N, 12.17; S, 13.93. Found: C, 45.80; H, 3.35; N, 12.20; S, 14.21%.

Preparation of $\{[Ag(L)NO_3]\cdot CH_2Cl_2\}_n$ (2). A small amount of toluene was added to a dichloromethane (1 mL) solution of **L** (20.0 mg, 0.061 mmol); then the required silver(I) nitrate (10.4 mg, 0.061 mmol) in acetonitrile was layered on the toluene phase; the (layered) mixture afforded a colorless crystalline product suitable for X-ray analysis. Mp: 199-203°C (decomp.). IR (KBr pellet): 3057, 2975, 2922, 1589, 1570, 1483, 1348 (NO_3^-), 1216, 1109, 1011, 800, 760, 723, 711 cm^{-1}; Anal. Calcd for [$C_{20.25}H_{21.7}N_4O_4S_2AgCl_{2.3}$]: C, 38.08; H, 3.42; N, 8.77. Found: C, 37.78; H, 3.05; N, 8.42%.

Preparation of $\{[Ag(L)(CH_3CN)]PF_6\}_n$ (3). A small amount of toluene was added to a dichloromethane (1 mL) solution of **L** (20.0 mg, 0.061 mmol); then the required silver(I) hexafluorophosphate (15.5 mg, 0.061 mmol) in acetonitrile was layered on the toluene phase; the (layered) mixture afforded a colorless crystalline product suitable for X-ray analysis. Mp: 205-208 °C (decomp.). IR (KBr pellet): 3089, 3069, 3026, 2977, 1588, 1573, 1483, 1455, 1418,

1273, 1031, 841 (PF_6^-) cm^{-1}. Anal. Calcd for [$C_{19.8}H_{18.7}N_{3.7}S_2AgPF_6$]: C, 38.02; H, 3.01; N, 8.29. Found: C, 37.78; H, 3.05; N, 8.42%.

Preparation of {[Ag(L)ClO_4]·CH_2Cl_2}$_n$ (4). A small amount of toluene was added to a dichloromethane (1 mL) solution of **L** (20.2 mg, 0.062 mmol); then the required silver(I) perchlorate (12.9 mg, 0.062 mmol) in acetonitrile was layered on the toluene phase; the (layered) mixture afforded a colorless crystalline product suitable for X-ray analysis. Mp: 188-191 °C (decomp.). IR (KBr pellet): 3085, 3058, 2908, 1585, 1482, 1449, 1449, 1417, 1107, 1085 (ClO_4^-), 806, 621 (ClO_4^-) cm^{-1}. Anal. Calcd for [$C_{17.8}H_{16.6}AgCl_{2.6}N_3O_4S_2$] as {[Ag(L)$ClO_4$]·0.9$CH_2Cl_2$}$_n$: C, 35.59; H, 2.79; N, 7.00. Found: C, 35.71; H, 2.53; N, 7.16%.

X-ray crystallographic analysis. Crystal data for **L** and **1-4** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames). Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of 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 except coordinated water molecules 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 **1-4** are summarised in Tables 1-5.

References

S1. Bruker, *APEX2 Version 2009.1-0 Data Collection and Processing Software*; Bruker AXS Inc.: Madison, WI, 2008.

S2. Bruker, *SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc.: Madison, WI, 2001.

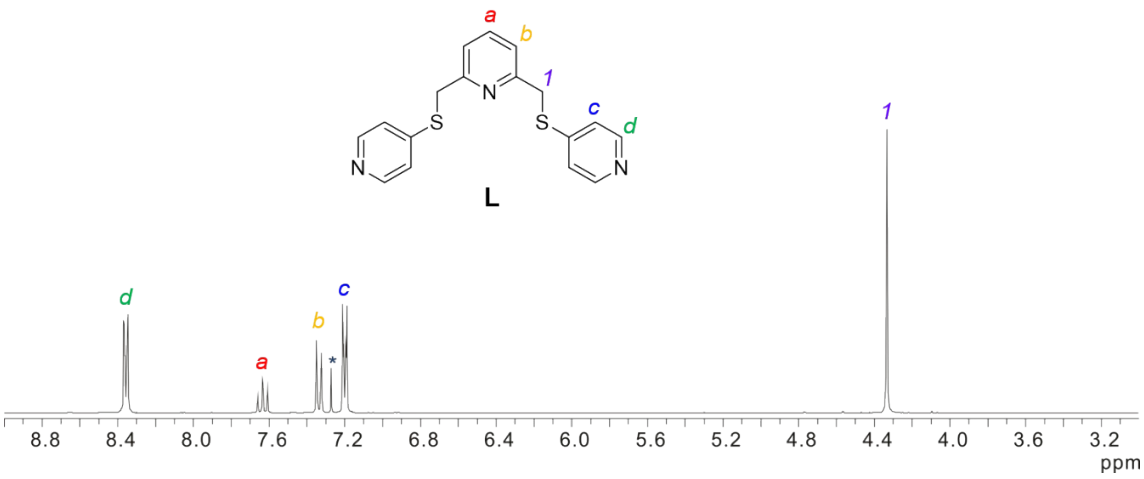

Fig. S1 ^{1}H NMR spectrum of **L** in $CDCl_3$.

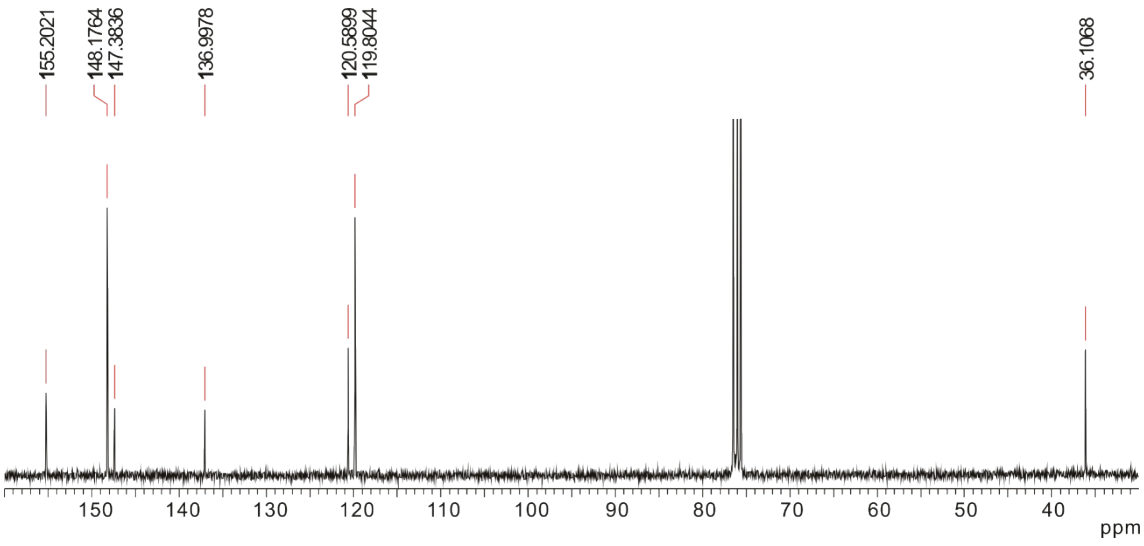

Fig. S2 ^{13}C NMR spectrum of **L** in $CDCl_3$.

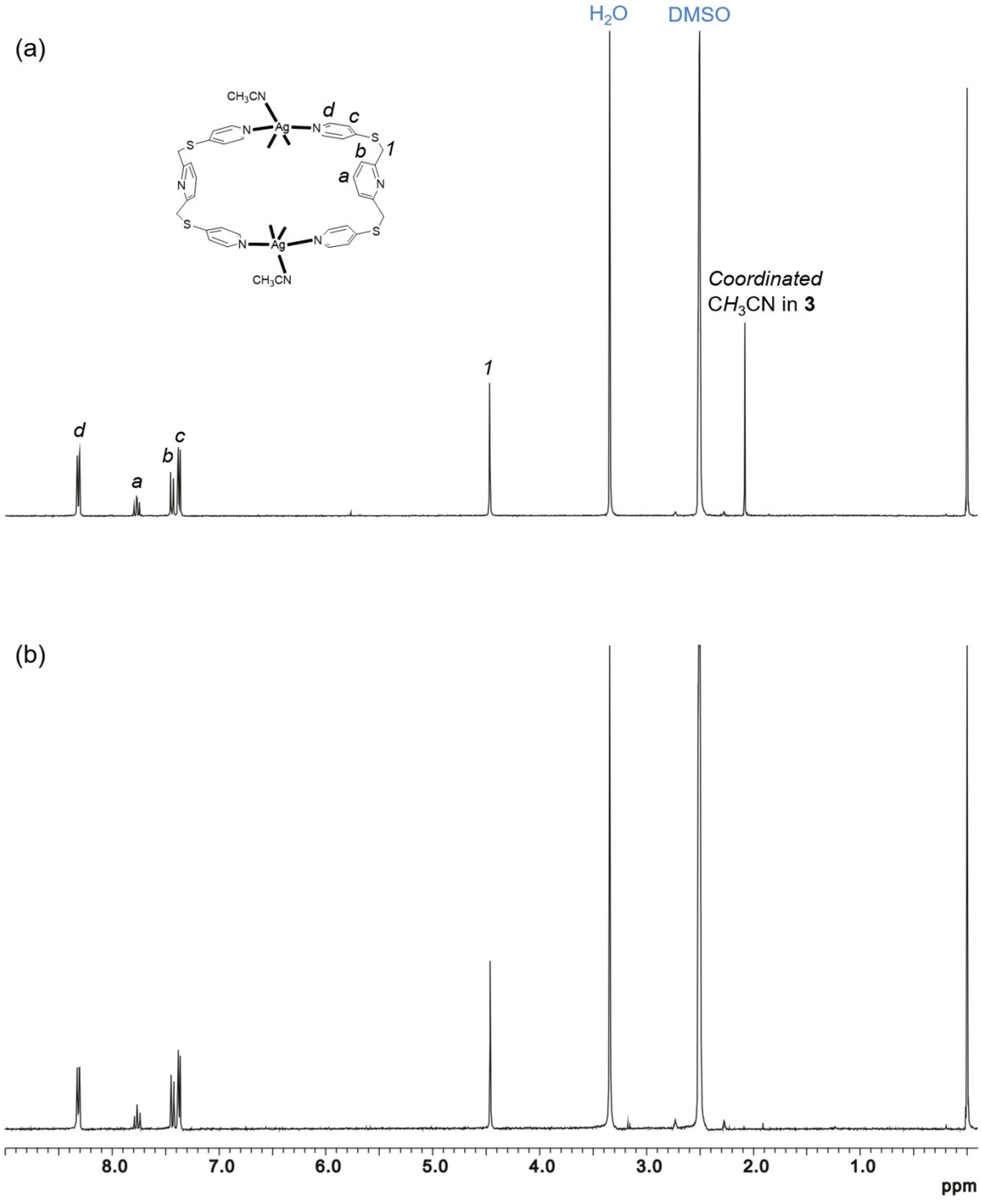

Fig. S3 NMR spectra of (a) **3** (PF_6-form) and (b) its anion-exchanged product [PF_6^- by NO_3^-] obtained after 48 h showing the removal of the coordinated acetonitrile molecules (singlet at 2.10 ppm).

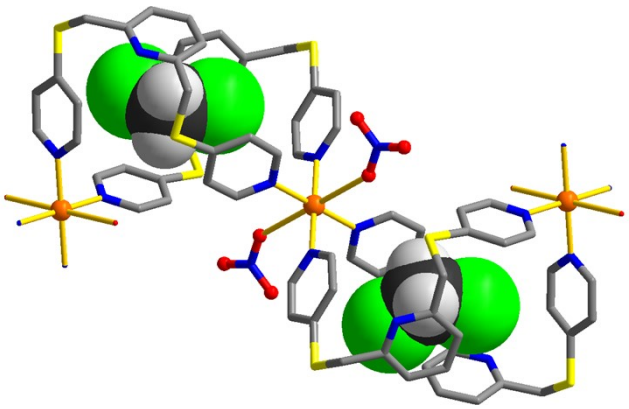

Fig. S4 Single crystal X-ray structure of **1**, $\{[Cu(\mathbf{L})_2(NO_3)_2]\cdot CH_2Cl_2\}_n$.

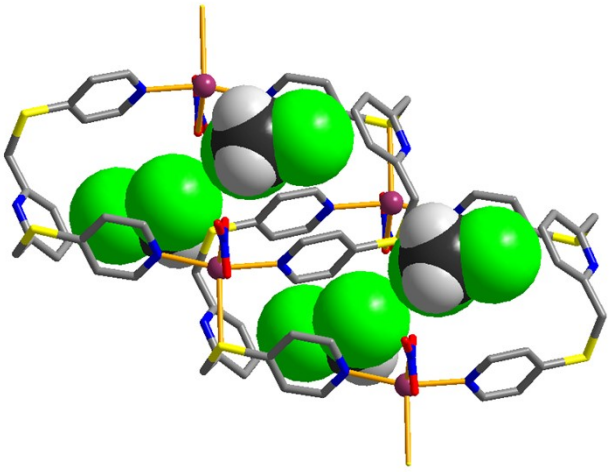

Fig. S5 Single crystal X-ray structure of **2**, $\{[Ag(\mathbf{L})NO_3]\cdot CH_2Cl_2\}_n$.

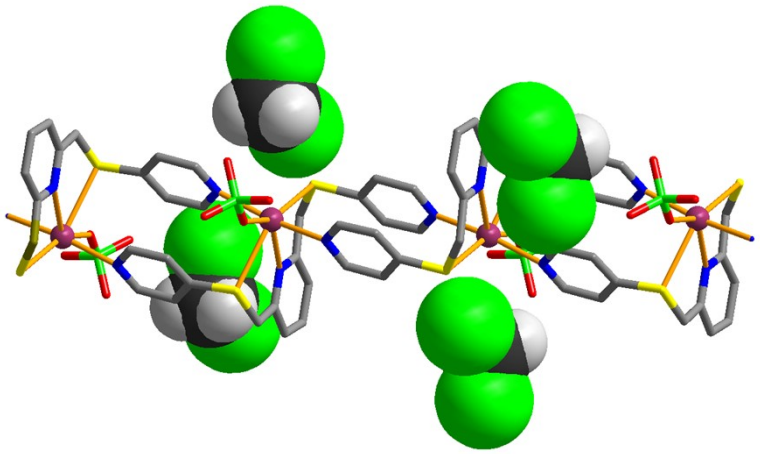

Fig. S6 Single crystal X-ray structure of **4**, $\{[Ag(\mathbf{L})ClO_4]\cdot CH_2Cl_2\}_n$.

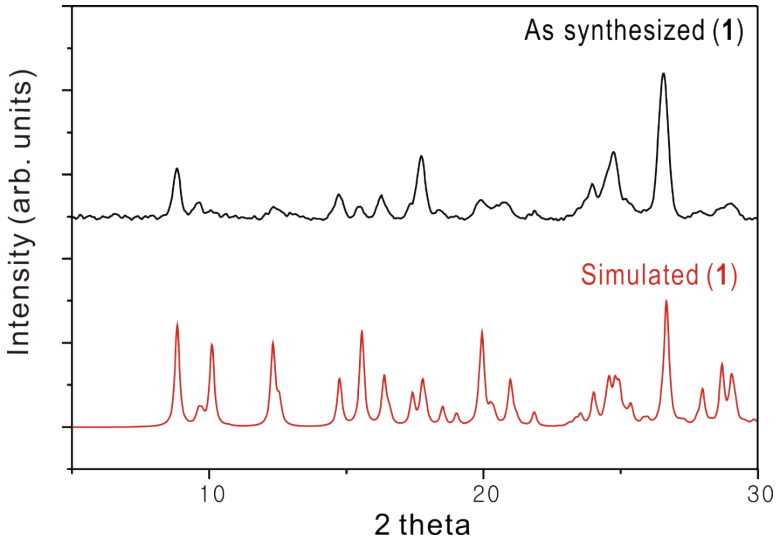

Fig. S7 PXRD patterns for **1**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The discrepancies in the intensities may be due to preferred orientations of the powder or partial removal of solvents during grinding.

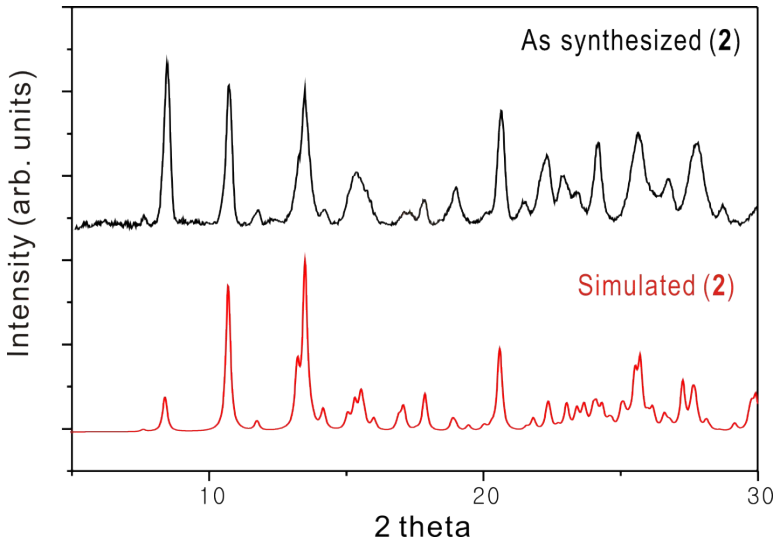

Fig. S8 PXRD patterns for **2**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The discrepancies in the intensities may be due to preferred orientations of the powder or partial removal of solvents during grinding.

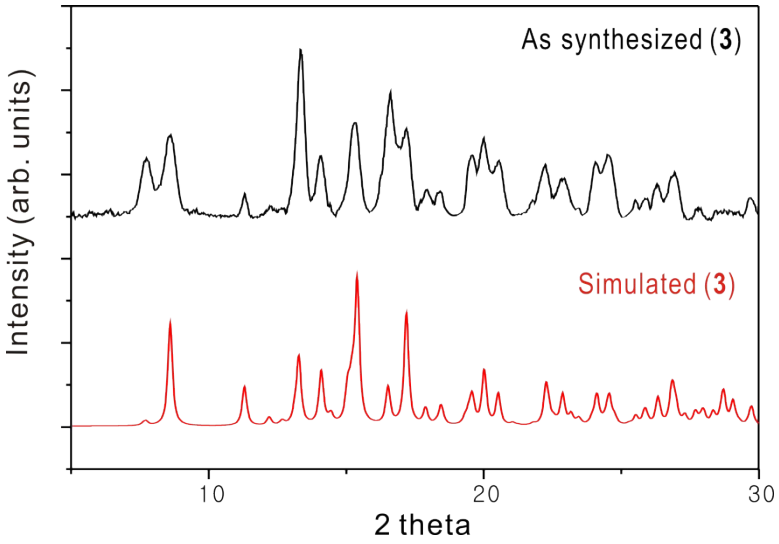

Fig. S9 PXRD patterns for **3**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The discrepancies in the intensities may be due to preferred orientations of the powder or partial removal of solvents during grinding.

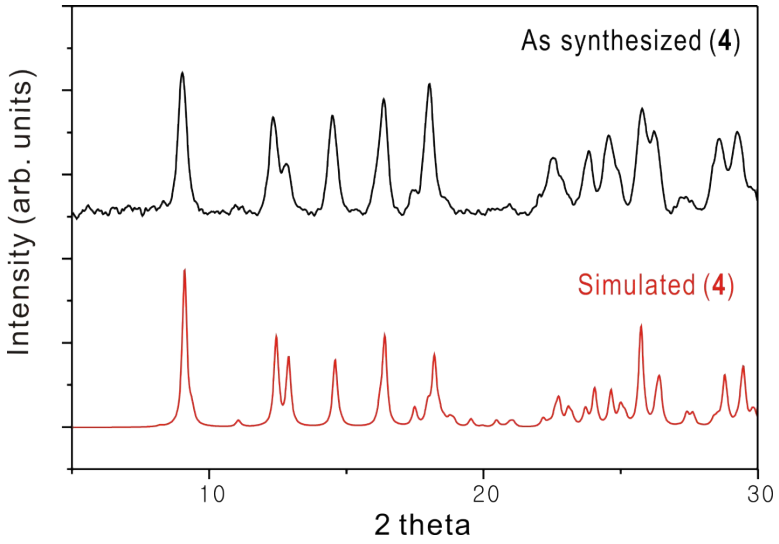

Fig. S10 PXRD patterns for **4**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The discrepancies in the intensities may be due to preferred orientations of the powder or partial removal of solvents during grinding.

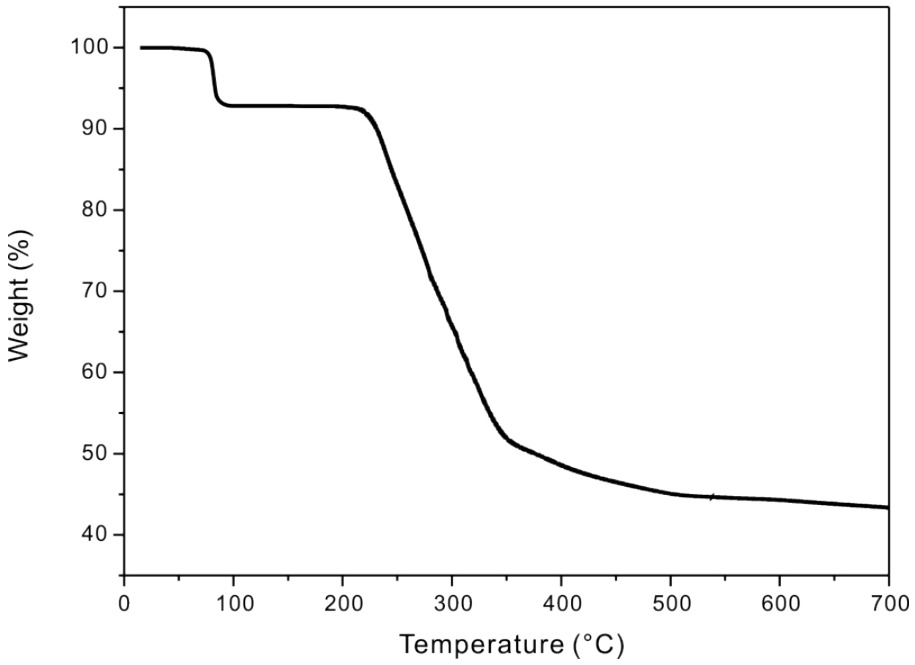

Fig. S11 TGA curve of **1**.

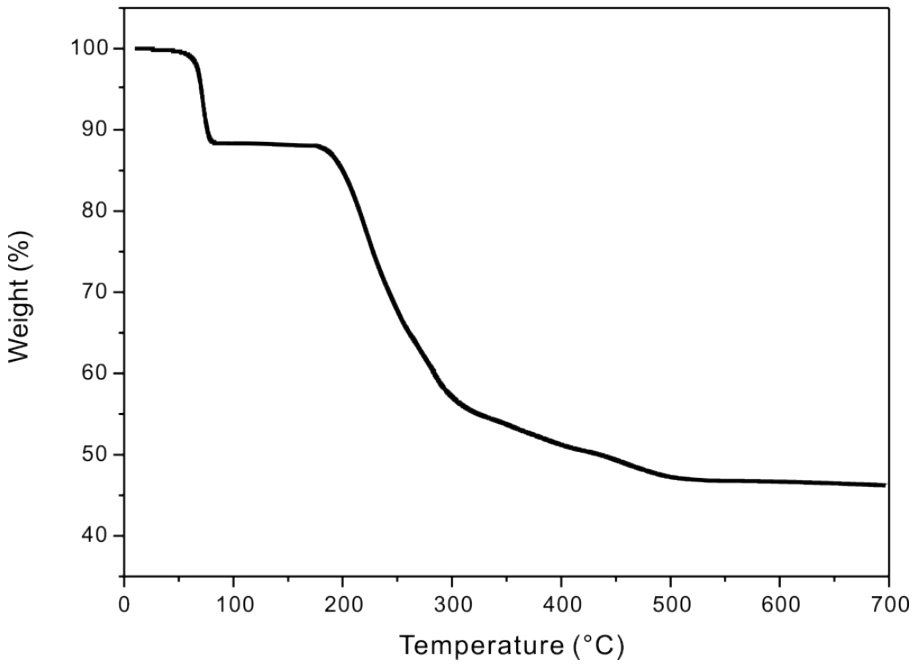

Fig. S12 TGA curve of **2**.

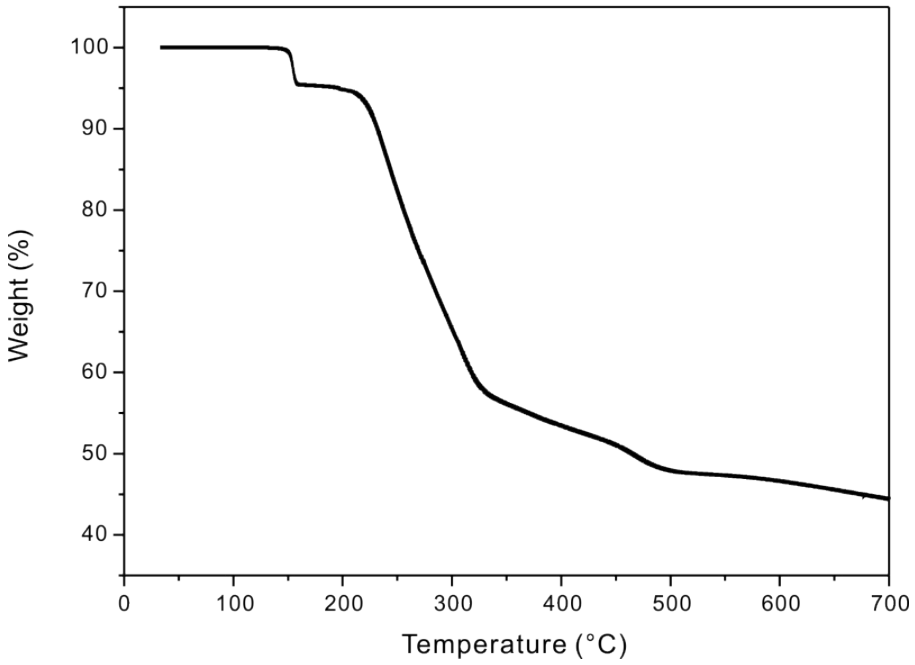

Fig. S13 TGA curve of **3**.

Table S1 Crystallographic data and refinement parameters of **1-4**

	1	**2**	**3**	**4**
Formula	$C_{70}H_{64}Cl_4Cu_2N_{16}O_{12}S_8$	$C_{18}H_{17}AgCl_2N_4O_3S_2$	$C_{19}H_{18}AgF_6N_4PS_2$	$C_{18}H_{17}AgCl_3N_3O_4S_2$
Formula weight	1846.73	580.24	619.33	617.68
Temperature	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	$P2_1$/n	*P*-1	*P*-1
a /Å	18.6359(6)	7.9319(3)	8.05010(10)	9.8728(8)
b /Å	11.9828(6)	23.0680(10)	12.5630(2)	10.2889(9)
c /Å	17.9652(7)	11.7359(5)	12.6704(2)	10.9536(9)
α /deg	90	90	68.6860(10)	80.721(5)
β /deg	103.225(3)	91.872(2)	78.0620(10)	87.251(5)
γ /deg	90	90	89.6740(10)	73.377(4)
V /Å^3	3905.4(3)	2146.21(15)	1164.54(3)	1052.22(15)
Z	2	4	2	2
D_{calc} /(g/cm^3)	1.570	1.796	1.766	1.950
μ (mm^{-1})	0.967	1.412	1.177	1.571
$2\theta_{max}$ (deg)	52	52	52.00	52.00
Reflections collected	31014	19736	19065	16013
Independent reflections	3842 [R_{int} = 0.0815]	4197 [R_{int} = 0.0820]	4589 [R_{int} = 0.0256]	4122 [R_{int} = 0.0442]
Goodness-of-fit on *F*2	1.042	1.029	1.039	1.009
R_1, wR_2 [$I > 2\sigma(I)$]	0.0437, 0.1027	0.1014, 0.2508	0.0293, 0.0678	0.1429, 0.4537
R_1, wR_2 [all data]	0.0641, 0.1122	0.1231, 0.2663	0.0358, 0.0705	0.1505, 0.4768

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

Cu1-N1	2.018(2)	Cu1-N3A	2.034(2)
Cu1- O1	2.885(7)		
N1B-Cu1-N1	180.000(1)	N1B-Cu1-N3C	90.00(10)
N1-Cu1-N3A	90.00(10)	N1B-Cu1-N3C	90.00(10)
N1-Cu1-N3C	90.00(10)	N3A-Cu1-N3C	180.000(1)
N1B-Cu1-O1	89.9(2)	N1-Cu1-O1	90.1(2)
N3C-Cu1-O1	88.6(2)	N3B-Cu1-O1	91.4(2)

[a]Symmetry operations: (A) 1-x, y, 1.5-z; (B) 1-x, 1-y, 1-z; (C) x, 1-y, -0.5+z.

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

Ag1-N1	2.220(6)	Ag1-N3A	2.205(6)
Ag1-O1	2.683(8)	Ag1-S2B	2.886(2)
N1-Ag1-O1	91.2(3)	N1-Ag1-S2B	95.37(16)
N3A-Ag1-O1	88.3(3)	N3A-Ag1-S2B	104.06(17)
N3A-Ag1-N1	159.1(2)	O1-Ag1-S2B	112.71(18)

[a]Symmetry operations: (A) 2-x, 2-y, -z; (B) 1-x, 2-y, -z.

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

Ag1-N3A	2.270(2)	Ag1-N1B	2.280(2)
Ag1-N4	2.595(3)	Ag1-S2	2.7428(7)
Ag1-N2	2.786(2)		
N4-Ag1-N2	160.92(8)	S2-Ag1-N2	72.85(5)
N4-Ag1-S2	88.53(7)	N3A-Ag1-N4	92.65(9)
N3A-Ag1-N2	89.09(7)	N3A-Ag1-S2	107.306)
N3A-Ag1-N1B	155.48(8)	N1B-Ag1-N2	94.87(7)
N1B-Ag1-N4	91.40(9)	N1B-Ag1-S2	96.97(6)

[a] Symmetry operations: (A) 1+x, y, z; (B) 1-x, 2-y, 1-z.

Table S5 Selected bond lengths (Å) and bond Angles (°) for **4**[a]

Ag1-S1	2.865(3)	Ag1-S2	2.832(3)
Ag1-N2	2.744(9)	Ag1-N1A	2.297(10)
Ag1-O1	2.914(11)	Ag1-N3B	2.276(10)
N3B-Ag1-N1A	169.6(3)	N3B-Ag1-N2	96.2(3)
N1A-Ag1-N2	94.2(3)	N3B-Ag1-S2	94.7(2)
N1A-Ag1-S2	89.9(2)	N2-Ag1-S2	69.2(2)
N3B-Ag1-S1	89.7(3)	N1A-Ag1-S1	93.0(2)
N2-Ag1-S1	69.5(2)	S2-Ag1-S1	138.69(8)
N3B-Ag1-O1	83.2(4)	N1A-Ag1-O1	87.2(4)
N2-Ag1-O1	161.6(4)	S2-Ag1-O1	92.5(3)
S1-Ag1-O1	128.8(3)		

[a]Symmetry operations: (A) -x, -y, 1-z; (B) 1-x, -y, 2-z.