Electronic Supplementary Information (ESI) for ChemComm

Synthesis, characterization and property of a mixed-valent Ag^{I}/Ag^{II} coordination polymer

Di Sun, Cheng-Feng Yang, Hao-Ran Xu, Hai-Xia Zhao, Zhan-Hua Wei, Na Zhang, La-Jia Yu, Rong-Bin Huang,* Lan-Sun Zheng

Department of chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China and State key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

Content

(1) Experiment details

Materials and General Methods. All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 740 FTIR Spectrometer at the range of 4000-400 cm^{-1}. Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescence spectra were measured on a Hitachi F-4500 Fluorescence Spectrophotometer (slit width: 2.5 nm; sensitivity: high). X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. UV-Vis measurements (diffuse-reflectance mode) were carried on a Varian Cary5000 UV-VIS-NIR spectrophotometer equipped with an integrating sphere at 298 K. TG curves were measured from 25 to 700 ^{o}C on a SDT Q600 instrument at a heating rate 5 ^{o}C/min under the N_2 atmosphere (100 ml/min). EPR spectrum was taken on a Bruker EMX 10/12 Electron Spin Resonance Spectrometer. Conductivity was measured with a Keithley 2400 SourceMeter.

(2) Table S1: Crystal data for 1 and 2

Compound	**1**	**2**
Empirical formula	$Ag_5C_{20}H_{26}N_{10}O_{18}S_4$	$Ag_2C_8H_{12}N_4O_6S$
Formula weight	1362.14	508.02
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcm*	*C2/c*
a (Å)	7.1428(19)	11.083(2)
b (Å)	14.203(4)	9.0814(18)
c (Å)	35.245(10)	13.803(3)
β (deg)	90	103.24(3)
V(Å^3)	3575.6(17)	1352.4(5)
T(K)	298(2)	173(2)
Z, D_{calcd} (Mg/m^3)	4, 2.527	4, 2.495
F(000)	2628	984
μ(mm^{-1})	3.015	3.083
Ref. collected/unique	15425 / 2897	4670 / 1316
R_{int}	0.0263	0.0257
Parameters	272	97
Final *R* indices[$I > 2\sigma(I)$]	$R_1 = 0.0493$	$R_1 = 0.0197$
	$wR_2 = 0.1096$	$wR_2 = 0.0434$
R indices (all data)	$R_1 = 0.0536$	$R_1 = 0.0212$
	$wR_2 = 0.1124$	$wR_2 = 0.0456$
Max./ min., $\Delta\rho$ (e·Å^{-3})	1.296 / –0.678	0.409 / –0.510

$R_1 = \Sigma| |F_o|-|F_c| | / \Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/ \Sigma w(F_o^2)^2]^{1/2}$

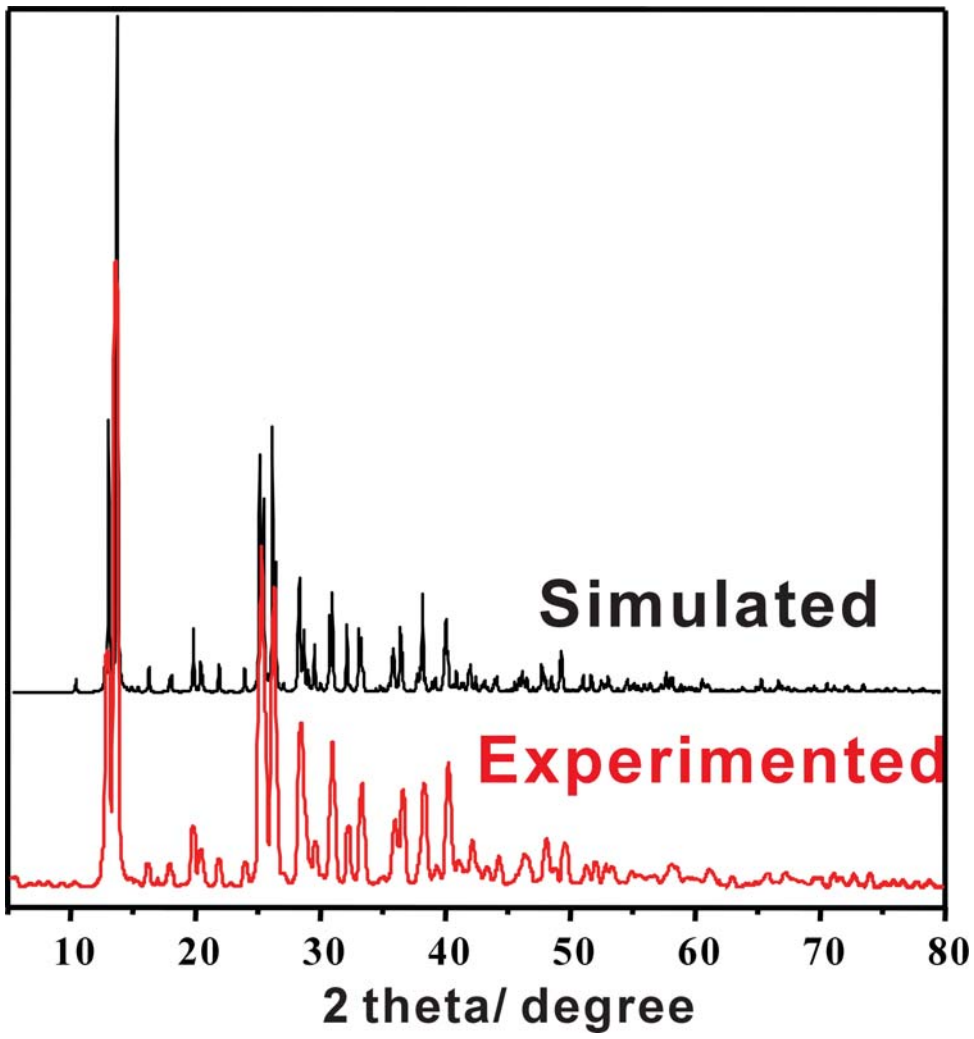
(3) Table S2: The selected bond distances and angles for 1 and 2

Complex 1			
Ag1—N1	2.186(7)	S1—O3	1.476(6)
Ag1—N2^{i}	2.198(6)	S1—O4	1.480(6)
Ag1—O2^{ii}	2.607(6)	Ag3—N5	2.186(5)
Ag1—Ag2	3.3559(11)	Ag3—N6^{iv}	2.197(5)
Ag2—N3	2.181(5)	Ag3—O6	2.594(6)
Ag2—N4^{i}	2.187(5)	S2—O6	1.425(6)
Ag2—O2^{iii}	2.702(6)	S2—O5	1.434(5)
S1—O2	1.426(5)	S2—O7	1.446(5)
S1—O1	1.444(5)	S2—O8	1.549(5)
N1—Ag1—N2^{i}	172.0(3)	N3—Ag2—N4^{i}	172.79(18)
N1—Ag1—O2^{ii}	101.79(19)	N3—Ag2—O2^{iii}	95.21(18)
N2^{i}—Ag1—O2^{ii}	83.61(18)	N4^{i}—Ag2—O2^{iii}	89.36(18)
O2^{ii}—Ag1—O2^{iii}	93.6(3)	N5—Ag3—N6^{iv}	176.57(19)
N6^{iv}—Ag3—O6	94.21(19)	N5—Ag3—O6	88.89(19)
Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y+1/2, -z+1/2$; (iii) $-x+1, y+1/2, z$; (iv) $x+1, y, z$.			
Complex 2			
Ag1—N1	2.194(2)	S1—O1^{iii}	1.4790(18)
Ag1—N2^{i}	2.199(2)	S1—O2	1.4793(17)
Ag1—Ag1^{ii}	3.3485(7)		
N1—Ag1—N2^{i}	172.93(7)	O1^{iii}—S1—O1	109.17(16)
Symmetry codes: (i) $x-1/2, y-1/2, z$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+1, y, -z+3/2$.			

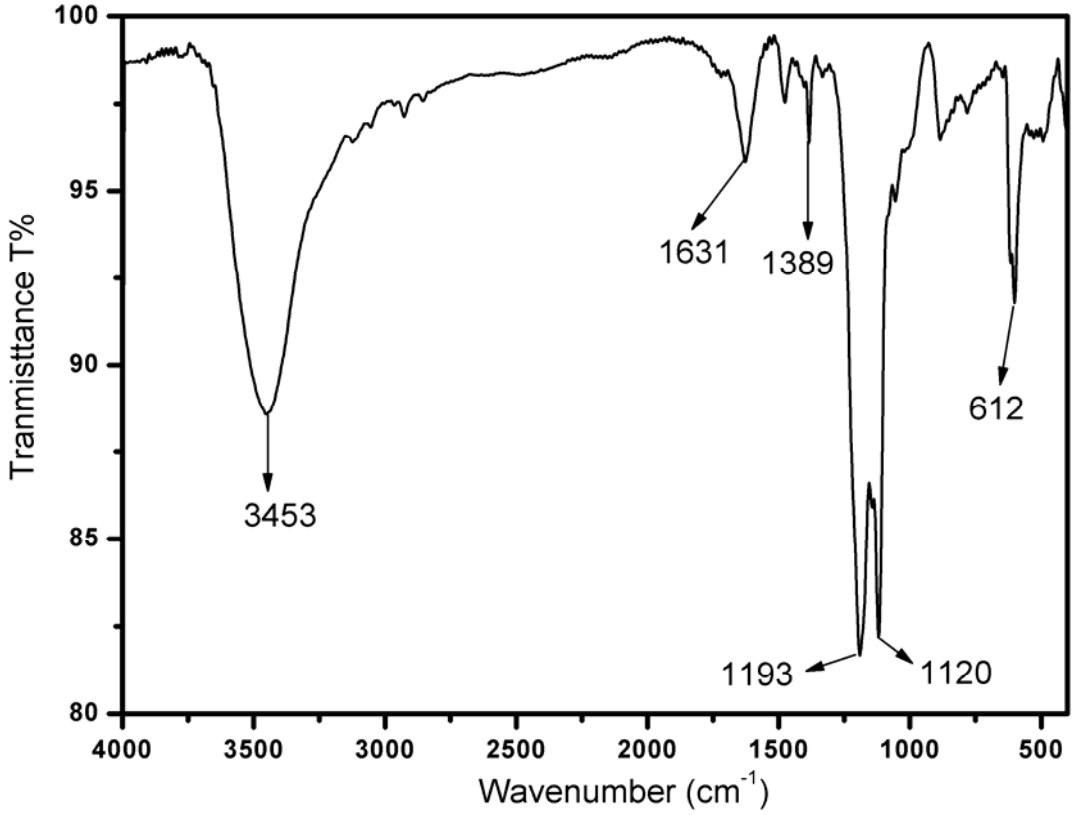
(4) Table S3: The hydrogen bonds geometries for 1 and 2

Complex 1				
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8B···O1W	0.85	1.93	2.641(7)	140
O1W—H1WA···O1	0.85	2.02	2.770(7)	148
O1W—H1WB···O7^{i}	0.85	1.96	2.796(7)	168
Symmetry codes: (i) $x-1, y, z$.				
Complex 2				
O1W—H1WA···O1	0.85	1.94	2.789(2)	173
O1W—H1WB···O2^{iv}	0.85	1.92	2.763(3)	172
Symmetry codes: (iv) $x+1/2, y-1/2, z$				

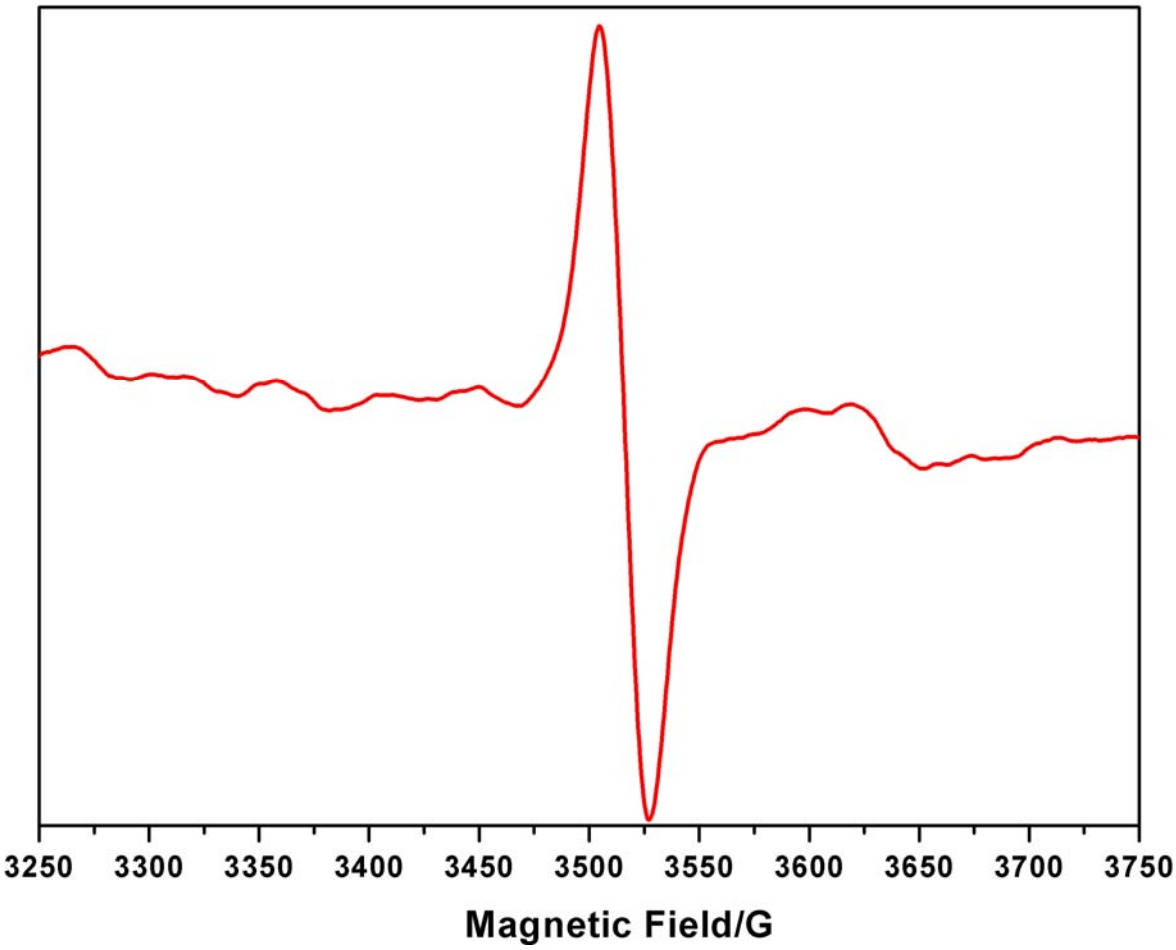
(5) Fig. S1: XRD spectrum of 1



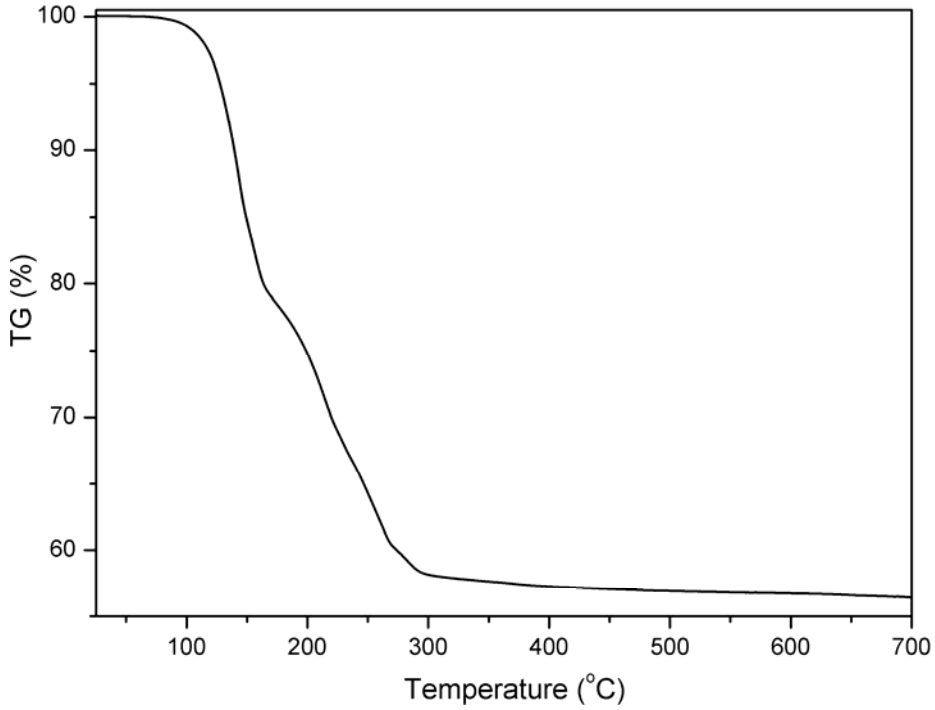
(6) Fig. S2: IR spectrum of 1



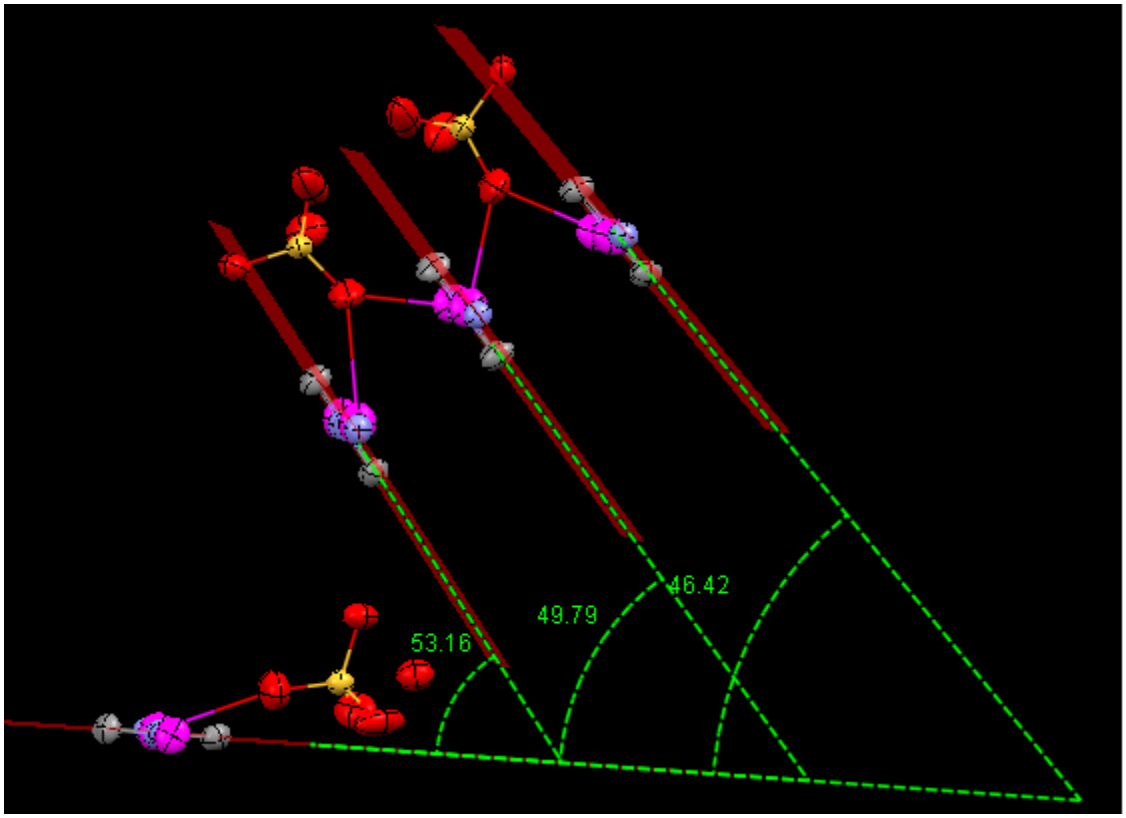
(7) Fig. S3: ESR spectrum at room temperature



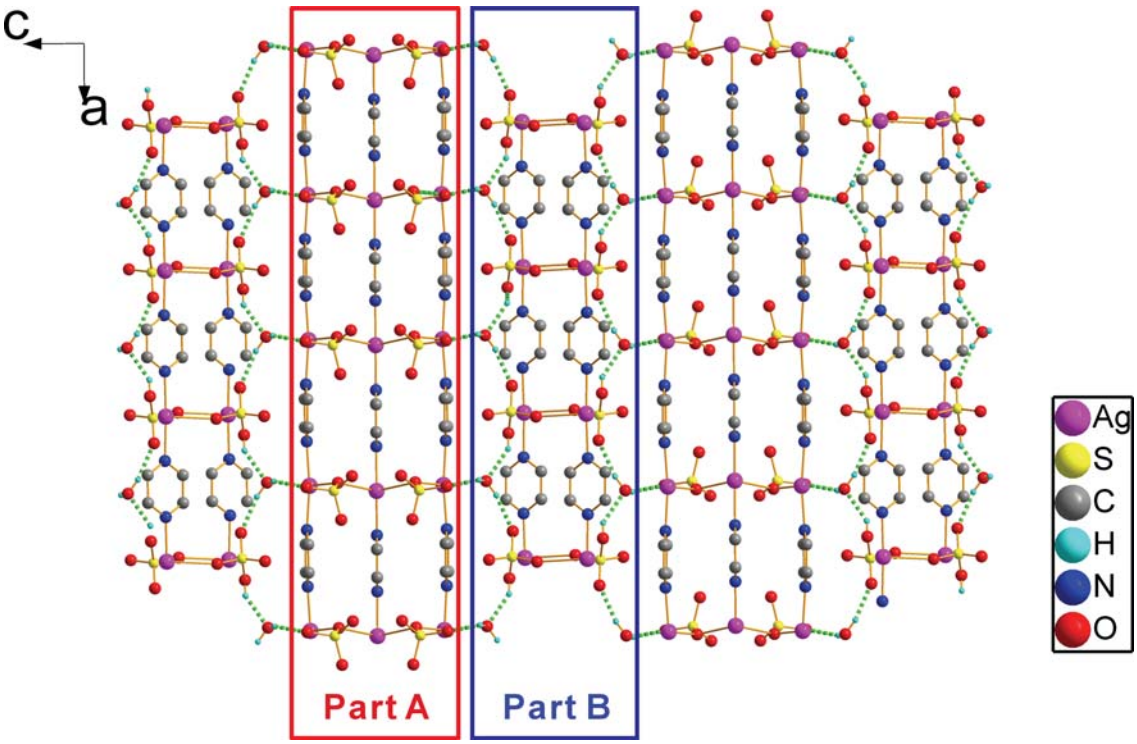
(8) Fig. S4: The TGA curve of 1



(9) Fig. S5: The dihedral angles between pyz rings in part A and B



(10) Fig. S6: The 2D supramolecular sheet constructed from alternate part A and B viewed along the *ac* plane



(11) Synthesis of $\{[Ag^{I}(SO_4)_{0.5}(pyz)]\cdot H_2O\}_n$ (2)

Reaction of $AgNO_3$ (167 mg, 1 mmol), $Na_2SO_4\cdot 10H_2O$ (322 mg, 1 mmol) and pyz (80 mg, 1mmol) in acetonitrile/H_2O media (10 ml, *v/v* = 1:1) in air under ultrasonic treatment (160W, 40 KHz, 20 min) at 50 ^{o}C. The resultant colorless solution was allowed slowly to evaporate at room temperature for three days to give colorless block crystals of **2**. The crystals were isolated by filtration and washed by deionized water and dried in air. Yield: *Ca*. 74% based on Ag. Elemental analysis: Anal. Calc. for $Ag_2C_8H_{12}N_4O_6S$: C 18.91, H 2.38, N 11.03%. Found: C 18.86, H 2.43, N 10.96%. Selected IR peaks (cm^{-1}): 3440(s), 1635(m), 1395(s), 1190(s), 1118(s), 608(w).

Crystal data for **2**: $Ag_2C_8H_{12}N_4O_6S$, fw = 508.02 g mol^{-1}, monoclinic, space group $C2/c$, Z = 4. T = 173(2) K, a = 11.083(2) Å, b = 9.0814(18), c = 13.803(3) Å, β = 103.24(3)^{o} V = 1352.4(5) $Å^3$, D_c = 2.495 g cm^{-3}, R_1 = 0.0197, wR_2 = 0.0434, μ = 3.083 mm^{-1}, S = 1.140. X-Ray crystallographic data of **2** were collected with a Mo Kα radiation source (λ = 0.71073 Å) by using Rigaku IP diffractometer equipped with graphite monochromator. The structures were solved by direct methods and refined by fullmatrix least-squares calculations ($F2$) by using the SHELXTL-97 software. All non-H atoms were refined in the anisotropic approximation against $F2$ for all reflections. The positions of the water H atoms were assigned to calculated positions with isotropic thermal parameters and refined with the O–H bond length restrained to 0.85 Å.

(12) Table S4: Reported semiconducting silver coordination polymers

Coordination Polymer	σ/S cm^{-1} (298K)	method	Reference and Note
$[Ag_2(2\text{-cyanopyridine})_2(NO_3)_2]_n$	3.1×10^{-7}	pellet	S1
$[Ag_4(3\text{-cyanopyridine})_8(SiF_6)_2(H_2O)_2]_n$	2.7×10^{-7}		
$[Ag(3\text{-cyanopyridine})_2(NO_3)]_n$	$\sim10^{-11}$		
$[Ag(\text{pyridine-3,4-dicarbonitrile})_2(NO_3)]_n$	7.4×10^{-6}		
$[Ag_2(sb)]_n$	4.08×10^{-6}	pellet	S2 (sb = 2-sulfobenzoate dianion, bipy=4,4'-bipyridine, bpe=1,2-bis(4-pyridyl)ethylene)
$\{[Ag_2(sb)(bipy)_2(H_2O)]\cdot(H_2O)_2\}_n$	3.93×10^{-6}		
$\{[Ag_4(sb)_2(bpe)_4](H_2O)_9\}_n$	2.34×10^{-6}		
$[Ag(\text{pyridine-2-thiolate})]_n$	2.04×10^{-5}	pellet	S3
$[Ag_4(2\text{-mba})_2\cdot(H_2O)_2]_n$	3.24×10^{-5}	pellet	S4, 2-H_2mba = 2-mercaptobenzoic acid)
$[Ag_6(BTC)_2(APYZ)_6\cdot9H_2O]_n$	5.56×10^{-7}	pellet	S5, H_3BTC=benzene-1,3,5-tricarboxylic acid APYZ=2-aminopyrazine
$[Ag_7(NHpyz)_6(ClO_4)]_n$	6.78×10^{-6}	pellet	S6, NH_2pyz = 2-aminopyrazine
$\{[Ag_4(hmt)_2(3\text{-sb})_2(H_2O)_2]\cdot2H_2O\}_n$	3.54×10^{-5}	pellet	S7, sb = sulfobenzoate, hmt = hexamethylenetetramine
$\{[Ag_3(hmt)_2(4\text{-sb})(NO_3)(H_2O)]\cdot3H_2O\}_n$	5.52×10^{-7}	pellet	
$[Ag_3(H_2BTC)_2(HBTC)]_n$	1.06×10^{-6}	pellet	S8, H_3BTC=benzene-1,3,5-tricarboxylic acid
$[Ag_2(CA)]_n$	5×10^{-3} parallel to Ag sheet 2×10^{-5} perpendicular to Ag sheet	single crystal	S9

References:

(S1) P. Lin, R. A. Henderson, R. W. Harrington, W. Clegg, C.-D. Wu and X.-T. Wu, *Inorg. Chem.,* 2004, **43**, 181.

(S2) X. F. Zheng and L. G. Zhu, *Cryst. Growth Des.* 2009, **9**, 4407.

(S3) W. Su, M. Hong, J. Weng, R. Cao and S. Lu, *Angew. Chem. Int. Ed.,* 2000**, 39**, 2911.

(S4) D. Sun, G. G. Luo, N. Zhang, Q. J. Xu, Y. C. Jin, Z. H. Wei, C. F. Yang, L. R. Lin, R. B. Huang and L. S. Zheng, *Inorg. Chem. Comm.* 2010, **13**, 306.

(S5) D. Sun, G. G. Luo, Q. J. Xu, N. Zhang, Y. C. Jin, H. X. Zhao, L. R. Lin, R. B. Huang and L. S. Zheng, *Inorg. Chem. Comm.* 2009, **12**, 782.

(S6) D. Sun, G. G. Luo, N. Zhang, Q. J. Xu, C. F. Yang, Z. H. Wei, Y. C. Jin, L. R. Lin, R. B. Huang and L. S. Zheng, *Inorg. Chem. Comm.* 2010, **13**, 290.

(S7) X. F. Zheng and L. G. Zhu, *CrystEngComm* 2010, DOI: 10.1039/c000028k

(S8) D. F. Sun, R. Cao, J. Weng, M. Hong and Y. C. Liang, *J. Chem. Soc., Dalton Trans.,*2002, 291.

(S9) C. N. R. Rao, A. Ranganathan, V. R. Pedireddi, A. R. Raju, *Chem. Comm.* 2000, 39.