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Stepwise assembly of two 3d–4d heterometallic coordination polymers based on a hexanuclear silver(I) metalloligand

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(1) Experiment details

Materials and General Methods. All chemicals and solvents used in the syntheses were of analytical grade and used without further purification (2, 2'-bipyridine, ethylenediamine and 2-mercaptonicotinic acid were purchased from Alfa Aesar). 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 of **1** and **2** were measured on a Hitachi F-7000 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. Energy dispersive X-ray spectra were obtained on HITACHI S-4800 scanning electron microscope, which is equipped with an HORIBA EDS unit. 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).

(2) X-ray Crystallography

Single crystals of the complex **1** – **2** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer with graphite-monochromated Mo Kα radiation source (λ= 0.71073 Å) operating at 50 kV and 90 mA in ω scan mode for **1** – **2**. A total of 44 × 5.00° oscillation images was collected, each being exposed for 5.0 min. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.[1] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97[2] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[3] Atoms were located from iterative examination of difference *F*-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 – 1.5 times U_{eq} of the attached C or N atoms. The hydrogen atoms attached to oxygen were refined with O–H = 0.85 Å, and $U_{iso}(H) = 1.2U_{eq}(O)$. All structures were examined using the Addsym subroutine of PLATON[4] to assure that no additional symmetry could be applied to the models.

(1) T. Higashi, *ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation*, Rigaku Corporation, Tokyo, 1995.

(2) G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

(3) G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

(4) A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

(3) Synthesis of 1 and 2

In this work, not only the stepwise self-assembly approach but also liquid/liquid diffusion method in the last step are very crucial for forming heterometallic networks. Both directly mixing two pre-synthezied solution and one-pot synthetic route result in the formation of touchier precipitation. To circumvent this synthetic issue, we have sought to employ a diffusion approach to slow the speed of reaction which readily leads to satisfactory crystalline products with high yields (>80%).

Synthesis of **1**:

First step: preparation of a solution of $[Ag_6(mna)_6]^{6-}$ metalloligand

Solution A: mixture of $AgNO_3$ (167 mg, 1 mmol) and H_2mna (155 mg, 1 mmol) were add to water (6 mL) in conical flask under ultrasonic treatment (160 W, 40 KHz) for 20 min at room temperature. The precipitation was dissolved by dropwise addition of aqueous solution of NH_3 (25%, 8 drops) to give a clear yellow solution.

Second step: preparation of a solution of cationic metalloligand containing 3d metal centers

Solution B: a mixture of $Cu(OAc)_2{\cdot}2H_2O$ (199 mg, 1 mmol) and bipy (156 mg, 1mmol) were add to water-ethanol (8 mL, v:v = 2:1) in conical flask under ultrasonic treatment (160 W, 40 KHz) for 20 min at room temperature to give a clear blue solution.

Third step: self-assembly of two pre-prepared metalloligands using liquid/liquid diffusion method

Then, the solution B was carefully layered on the top of solution A in the tube (15 cm). After the solutions were allowed to stand for about two days, purple block crystals **1** were formed. The crystals were filtered off and washed with ethanol and dried in air. Yield: *Ca*. 85% based on Ag. Elemental analysis: Anal. Calc. for $Ag_{12}Cu_6C_{132}H_{150}N_{24}O_{57}S_{12}$: C 31.42, H 3.00, N 6.66%. Found: C 31.39, H 3.11, N 6.59%. Selected IR peaks (cm^{-1}): 3436 (s), 2973 (w), 2918 (w), 1586 (s), 1497 (w), 1476 (w), 1445 (m), 1384 (s), 1156 (w), 1129 (w), 1080 (m), 1049 (w), 772 (w), 732 (w).

Synthesis of **2**: This process is similar to that of **1**, but with different solution B. Solution B: a mixture of $Zn(OAc)_2 \cdot 2H_2O$ (220 mg, 1 mmol) and eda (1 mL) were add to water-ethanol (8 mL, v:v = 2:1) in conical flask under ultrasonic treatment (160 W, 40 KHz) for 20 min at room temperature to give a clear colorless solution. Then, the solution B was carefully layered on the top of solution A in the tube (15 cm). After the solutions were allowed to stand for about four days, colorless block crystals **2** were formed. The crystals were filtered off and washed with ethanol and dried in air. Yield: *Ca*. 90% based on Ag. Elemental analysis: Anal. Calc. for $Ag_6Zn_3C_{42}H_{66}N_{12}O_{24}S_6$: C 23.37, H 3.08, N 7.79%. Found: C 23.28, H 3.15, N 7.85%. Selected IR peaks (cm^{-1}): 3439 (s), 3345 (s), 3259 (s), 2930 (w), 1564 (s), 1443 (w), 1385 (s), 1299 (m), 1275 (m), 1159 (w), 1132 (w), 1080 (m), 1052 (w), 1028 (w), 991 (w), 848 (w), 815 (w), 787 (w), 735 (w), 665 (w), 510 (w), 476 (w).

(4) Table S1:Comparison of Selected Bond Distances (Å) in the $\{[Ag_6(mna)_6]^{6-}\}$ (L_{Ag}) with different cationic parts

$\{[Cu_3(bipy)_3(H_2O)_5][L_{Ag}]]\cdot 12H_2O\}_n$		$\{[Zn_3(eda)_3(H_2O)_4][L_{Ag}]\cdot 8H_2O\}_n$		$\{Na_4[(HOCH_2)_3CNH_3]_2\}[L_{Ag}]\cdot 10H_2O$	
Ag1—N1	2.303(9)	Ag1—N3	2.280(3)	Ag1—Ag2’	2.9373(4)
Ag1—S3^{i}	2.472(3)	Ag1—S1	2.4976(8)	Ag1—Ag3’	2.9884(5)
Ag1—S1	2.475(3)	Ag1—S2	2.5137(8)	Ag2—Ag3	3.3485(5)
Ag1—Ag2	2.9163(12)	Ag1—Ag2	2.9484(4)	Ag3—N3	2.292(3)
Ag1—Ag3	2.9828(12)	Ag1—Ag3	2.9672(3)	Ag1—N1’	2.293(3)
Ag1—Ag2^{i}	3.3086(12)	Ag2—N2	2.259(3)	Ag2—N2	2.298(3)
Ag2—N2^{i}	2.305(10)	Ag2—S3	2.4752(8)	Ag1—S2	2.4682(9)
Ag2—S2	2.478(3)	Ag2—S1^{i}	2.4806(8)	Ag1—S3	2.4773(9)
Ag2—S1^{i}	2.479(3)	Ag2—Ag3^{i}	3.0522(4)	Ag2—S3	2.4742(9)
Ag2—Ag3^{i}	3.0175(13)	Ag3—N1	2.289(3)	Ag2—S1	2.5175(9)
Ag2—Ag1^{i}	3.3086(12)	Ag3—S2^{i}	2.4973(8)	Ag3—S2	2.4795(9)
Ag3—N3	2.297(10)	Ag3—S3	2.4982(8)	Ag3—S1	2.5180(9)
Ag3—S3	2.483(3)	Ag3—Ag2^{i}	3.0522(4)		
Ag3—S2	2.498(3)				
Ag3—Ag2^{i}	3.0175(13)				
Ag4—N6	2.260(9)				
Ag4—S4	2.462(3)				
Ag4—S5	2.481(3)				
Ag4—Ag5	2.9275(13)				
Ag4—Ag6	2.9279(13)				
Ag5—N5	2.275(10)				
Ag5—S4^{ii}	2.463(3)				
Ag5—S6	2.480(3)				
Ag5—Ag6^{ii}	3.0841(14)				
Ag6—N4	2.296(10)				
Ag6—S5^{ii}	2.519(3)				
Ag6—S6	2.519(3)				
Ag6—Ag5^{ii}	3.0841(14)				
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(5) Table S2: The selected bond distances and angles for 1 and 2

Complex 1

Ag1—N1	2.303 (9)	Ag5—S6	2.480 (3)
Ag1—S3^{i}	2.472 (3)	Ag5—Ag6^{ii}	3.0841 (14)
Ag1—S1	2.475 (3)	Ag6—N4	2.296 (10)
Ag1—Ag2	2.9163 (12)	Ag6—S5^{ii}	2.519 (3)
Ag1—Ag3	2.9828 (12)	Ag6—S6	2.519 (3)
Ag1—Ag2^{i}	3.3086 (12)	Ag6—Ag5^{ii}	3.0841 (14)
Ag2—N2^{i}	2.305 (10)	Cu1—O17W	2.021 (11)
Ag2—S2	2.478 (3)	Cu1—N8	2.025 (11)
Ag2—S1^{i}	2.479 (3)	Cu1—O14W	2.034 (10)
Ag2—Ag3^{i}	3.0175 (13)	Cu1—N7	2.051 (12)
Ag2—Ag1^{i}	3.3086 (12)	Cu1—O16W	2.197 (10)
Ag3—N3	2.297 (10)	Cu2—O3	1.970 (8)
Ag3—S3	2.483 (3)	Cu2—O13W	1.983 (12)
Ag3—S2	2.498 (3)	Cu2—N9	2.013 (10)
Ag3—Ag2^{i}	3.0175 (13)	Cu2—N10	2.026 (9)
Ag4—N6	2.260 (9)	Cu2—O7^{i}	2.209 (10)
Ag4—S4	2.462 (3)	Cu3—O6	1.958 (9)
Ag4—S5	2.481 (3)	Cu3—O9W	1.973 (11)
Ag4—Ag5	2.9275 (13)	Cu3—N12	2.008 (11)
Ag4—Ag6	2.9279 (13)	Cu3—N11	2.027 (9)
Ag5—N5	2.275 (10)	Cu3—O12	2.305 (9)
Ag5—S4^{ii}	2.463 (3)		
N1—Ag1—S3^{i}	118.7 (3)	N5—Ag5—S4^{ii}	119.1 (3)
N1—Ag1—S1	112.5 (2)	N5—Ag5—S6	124.8 (3)
S3^{i}—Ag1—S1	117.61 (10)	S4^{ii}—Ag5—S6	110.00 (10)
N1—Ag1—Ag2	91.2 (2)	N5—Ag5—Ag4	89.6 (3)
S3^{i}—Ag1—Ag2	75.47 (7)	S4^{ii}—Ag5—Ag4	133.58 (9)
S1—Ag1—Ag2	136.85 (7)	S6—Ag5—Ag4	72.86 (7)
N1—Ag1—Ag3	86.1 (2)	N5—Ag5—Ag6^{ii}	83.8 (2)
S3^{i}—Ag1—Ag3	138.69 (7)	S4^{ii}—Ag5—Ag6^{ii}	71.58 (8)
S1—Ag1—Ag3	74.79 (7)	S6—Ag5—Ag6^{ii}	137.32 (8)
Ag2—Ag1—Ag3	71.30 (3)	Ag4—Ag5—Ag6^{ii}	76.88 (3)
N1—Ag1—Ag2^{i}	140.2 (2)	N4—Ag6—S5^{ii}	120.1 (2)
S3^{i}—Ag1—Ag2^{i}	100.10 (7)	N4—Ag6—S6	129.0 (2)
S1—Ag1—Ag2^{i}	48.16 (7)	S5^{ii}—Ag6—S6	109.02 (10)
Ag2—Ag1—Ag2^{i}	90.45 (3)	N4—Ag6—Ag4	87.2 (2)
Ag3—Ag1—Ag2^{i}	57.04 (3)	S5^{ii}—Ag6—Ag4	127.71 (8)
N2^{i}—Ag2—S2	118.6 (2)	S6—Ag6—Ag4	72.34 (7)

N2^{i}—Ag2—S1^{i}	112.1 (2)	N4—Ag6—Ag5^{ii}	83.2 (2)
S2—Ag2—S1^{i}	121.59 (10)	S5^{ii}—Ag6—Ag5^{ii}	68.16 (7)
N2^{i}—Ag2—Ag1	89.2 (2)	S6—Ag6—Ag5^{ii}	130.07 (8)
S2—Ag2—Ag1	72.69 (7)	Ag4—Ag6—Ag5^{ii}	72.79 (3)
S1^{i}—Ag2—Ag1	135.88 (8)	O17W—Cu1—N8	95.4 (5)
N2^{i}—Ag2—Ag3^{i}	82.5 (2)	O17W—Cu1—O14W	86.7 (4)
S2—Ag2—Ag3^{i}	137.42 (7)	N8—Cu1—O14W	177.9 (5)
S1^{i}—Ag2—Ag3^{i}	74.08 (7)	O17W—Cu1—N7	158.1 (5)
Ag1—Ag2—Ag3^{i}	71.01 (3)	N8—Cu1—N7	80.6 (5)
N2^{i}—Ag2—Ag1^{i}	136.3 (2)	O14W—Cu1—N7	97.5 (5)
S2—Ag2—Ag1^{i}	102.62 (7)	O17W—Cu1—O16W	104.6 (5)
S1^{i}—Ag2—Ag1^{i}	48.05 (7)	N8—Cu1—O16W	89.5 (4)
Ag1—Ag2—Ag1^{i}	89.55 (3)	O14W—Cu1—O16W	89.9 (4)
Ag3^{i}—Ag2—Ag1^{i}	56.04 (3)	N7—Cu1—O16W	97.0 (4)
N3—Ag3—S3	117.2 (2)	O3—Cu2—O13W	94.6 (4)
N3—Ag3—S2	119.9 (2)	O3—Cu2—N9	89.4 (4)
S3—Ag3—S2	118.71 (9)	O13W—Cu2—N9	173.4 (5)
N3—Ag3—Ag1	88.6 (2)	O3—Cu2—N10	156.8 (4)
S3—Ag3—Ag1	130.37 (8)	O13W—Cu2—N10	94.6 (5)
S2—Ag3—Ag1	71.24 (7)	N9—Cu2—N10	79.8 (4)
N3—Ag3—Ag2^{i}	85.5 (2)	O3—Cu2—O7^{i}	104.5 (4)
S3—Ag3—Ag2^{i}	73.43 (7)	O13W—Cu2—O7^{i}	90.9 (6)
S2—Ag3—Ag2^{i}	129.96 (8)	N9—Cu2—O7^{i}	93.3 (4)
Ag1—Ag3—Ag2^{i}	66.92 (3)	N10—Cu2—O7^{i}	96.7 (4)
N6—Ag4—S4	124.2 (2)	O6—Cu3—O9W	92.4 (5)
N6—Ag4—S5	122.9 (2)	O6—Cu3—N12	91.5 (4)
S4—Ag4—S5	107.07 (10)	O9W—Cu3—N12	176.0 (4)
N6—Ag4—Ag5	88.1 (2)	O6—Cu3—N11	162.3 (4)
S4—Ag4—Ag5	133.42 (8)	O9W—Cu3—N11	94.6 (4)
S5—Ag4—Ag5	71.34 (7)	N12—Cu3—N11	81.4 (4)
N6—Ag4—Ag6	85.6 (2)	O6—Cu3—O12	85.8 (4)
S4—Ag4—Ag6	74.48 (7)	O9W—Cu3—O12	94.0 (4)
S5—Ag4—Ag6	134.77 (8)	N12—Cu3—O12	87.4 (4)
Ag5—Ag4—Ag6	76.05 (3)	N11—Cu3—O12	109.9 (4)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*+2, −*y*+2, −*z*+3.

Complex 2

Ag1—N3	2.280 (3)	Ag3—Ag2^{i}	3.0522 (4)
Ag1—S1	2.4976 (8)	Zn1—N5	2.111 (3)
Ag1—S2	2.5137 (8)	Zn1—N5^{ii}	2.111 (3)
Ag1—Ag2	2.9484 (4)	Zn1—N4^{ii}	2.128 (3)
Ag1—Ag3	2.9672 (3)	Zn1—N4	2.128 (3)
Ag2—N2	2.259 (3)	Zn1—O6	2.246 (2)
Ag2—S3	2.4752 (8)	Zn1—O6^{ii}	2.246 (2)
Ag2—S1^{i}	2.4806 (8)	Zn2—O3	1.976 (2)

Ag2—Ag3^{i}	3.0522 (4)	Zn2—O3W	2.016 (3)
Ag3—N1	2.289 (3)	Zn2—O6W	2.022 (3)
Ag3—S2^{i}	2.4973 (8)	Zn2—N6	2.029 (3)
Ag3—S3	2.4982 (8)		
N3—Ag1—S1	124.16 (7)	N1—Ag3—Ag2^{i}	86.29 (6)
N3—Ag1—S2	126.49 (7)	S2^{i}—Ag3—Ag2^{i}	71.569 (18)
S1—Ag1—S2	104.93 (3)	S3—Ag3—Ag2^{i}	135.84 (2)
N3—Ag1—Ag2	87.58 (7)	Ag1—Ag3—Ag2^{i}	78.325 (11)
S1—Ag1—Ag2	131.21 (2)	N5—Zn1—N5^{ii}	180.00 (11)
S2—Ag1—Ag2	73.223 (19)	N5—Zn1—N4^{ii}	96.95 (10)
N3—Ag1—Ag3	87.64 (7)	N5^{ii}—Zn1—N4^{ii}	83.05 (10)
S1—Ag1—Ag3	70.573 (19)	N5—Zn1—N4	83.05 (10)
S2—Ag1—Ag3	131.56 (2)	N5^{ii}—Zn1—N4	96.95 (10)
Ag2—Ag1—Ag3	75.605 (10)	N4^{ii}—Zn1—N4	180.0 (2)
N2—Ag2—S3	125.94 (6)	N5—Zn1—O6	88.14 (9)
N2—Ag2—S1^{i}	124.31 (7)	N5^{ii}—Zn1—O6	91.86 (9)
S3—Ag2—S1^{i}	107.36 (3)	N4^{ii}—Zn1—O6	89.62 (9)
N2—Ag2—Ag1	86.23 (7)	N4—Zn1—O6	90.38 (9)
S3—Ag2—Ag1	71.446 (19)	N5—Zn1—O6^{ii}	91.86 (9)
S1^{i}—Ag2—Ag1	129.04 (2)	N5^{ii}—Zn1—O6^{ii}	88.14 (9)
N2—Ag2—Ag3^{i}	85.85 (6)	N4^{ii}—Zn1—O6^{ii}	90.38 (9)
S3—Ag2—Ag3^{i}	130.26 (2)	N4—Zn1—O6^{ii}	89.62 (9)
S1^{i}—Ag2—Ag3^{i}	69.281 (19)	O6—Zn1—O6^{ii}	180.00 (17)
Ag1—Ag2—Ag3^{i}	74.402 (10)	O3—Zn2—O3W	108.36 (10)
N1—Ag3—S2^{i}	123.45 (7)	O3—Zn2—O6W	115.18 (11)
N1—Ag3—S3	120.80 (7)	O3W—Zn2—O6W	108.94 (12)
S2^{i}—Ag3—S3	110.54 (3)	O3—Zn2—N6	101.08 (10)
N1—Ag3—Ag1	85.34 (7)	O3W—Zn2—N6	114.06 (12)
S2^{i}—Ag3—Ag1	135.55 (2)	O6W—Zn2—N6	109.21 (11)
S3—Ag3—Ag1	70.823 (19)		

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+2, -y+1, -z-1$.

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

Complex 1

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WA···O10W	0.85	2.00	2.80 (2)	158
O1W—H1WB···O6W^{iii}	0.85	2.01	2.81 (2)	157
O2W—H2WA···O10	0.85	1.86	2.709 (19)	173
O2W—H2WB···O1W^{iv}	0.85	2.01	2.86 (2)	173
O3W—H3WA···O2W	0.85	1.74	2.59 (3)	177
O3W—H3WB···O4W^{v}	0.85	1.82	2.67 (3)	177
O4W—H4WA···O9	0.85	1.60	2.42 (3)	161
O4W—H4WB···O5W^{ii}	0.85	1.71	2.53 (4)	164
O5W—H5WA···O8W	0.85	1.70	2.52 (4)	164
O5W—H5WB···O6W	0.85	1.94	2.77 (4)	169
O6W—H6WA···O12	0.85	2.09	2.874 (15)	154
O6W—H6WB···O7W^{i}	0.85	2.06	2.85 (2)	154
O7W—H7WA···O1	0.85	1.92	2.725 (18)	157
O7W—H7WB···O8W^{i}	0.85	1.92	2.71 (3)	155
O8W—H8WB···O8^{vi}	0.85	2.01	2.82 (3)	159
O9W—H9WA···O11	0.85	2.04	2.829 (14)	154
O9W—H9WB···O2^{viii}	0.85	2.34	3.004 (15)	135
O10W—H10A···O15W^{vii}	0.85	1.88	2.717 (16)	168
O10W—H10B···O5^{i}	0.85	2.16	2.99 (2)	168
O12W—H12B···O2	0.85	1.98	2.825 (18)	178
O13W—H13B···O4	0.85	2.07	2.826 (15)	148
O13W—H13C···O9^{viii}	0.85	2.41	3.100 (17)	139
O14W—H14B···O8^{ix}	0.85	2.53	3.075 (14)	123
O14W—H14A···O11^{x}	0.85	2.15	2.995 (13)	179
O15W—H15A···O10	0.85	1.92	2.749 (19)	165
O15W—H15B···O4^{viii}	0.85	1.97	2.793 (13)	164
O16W—H16A···O1^{xi}	0.85	1.88	2.723 (13)	170
O17W—H17B···O2W^{i}	0.85	2.51	3.257 (19)	147
O17W—H17A···O8^{ix}	0.85	2.01	2.843 (14)	167

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*+2, −*y*+2, −*z*+3; (iii) *x*, *y*+1, *z*; (iv) *x*+1, *y*, *z*; (v) −*x*+3, −*y*+3, −*z*+3; (vi) −*x*+1, −*y*+2, −*z*+3; (vii) *x*−1, *y*, *z*; (viii) −*x*+2, −*y*+2, −*z*+2; (ix) *x*−1, *y*−1, *z*−1; (x) −*x*+1, −*y*+1, −*z*+2; (xi) *x*−1, *y*−1, *z*.

Complex 2

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WA···O1	0.85	1.93	2.780 (4)	176
O1W—H1WB···O2^{iii}	0.85	2.03	2.883 (4)	176

O2W—H2WA···O1	0.85	2.29	3.063	(5)	152
O2W—H2WB···O4W^{iv}	0.85	1.98	2.788	(4)	157
O3W—H3WB···O2^{v}	0.85	2.12	2.964	(4)	174
O4W—H4WA···O3	0.85	1.99	2.831	(3)	169
O4W—H4WB···O5W	0.85	1.94	2.775	(4)	169
O5W—H5WA···O1W^{vi}	0.85	1.85	2.702	(4)	179
O5W—H5WB···O5^{vii}	0.85	1.96	2.806	(3)	179
O6W—H6WA···O5^{viii}	0.85	2.21	3.022	(3)	160
O6W—H6WB···O4^{vi}	0.85	2.08	2.927	(4)	173

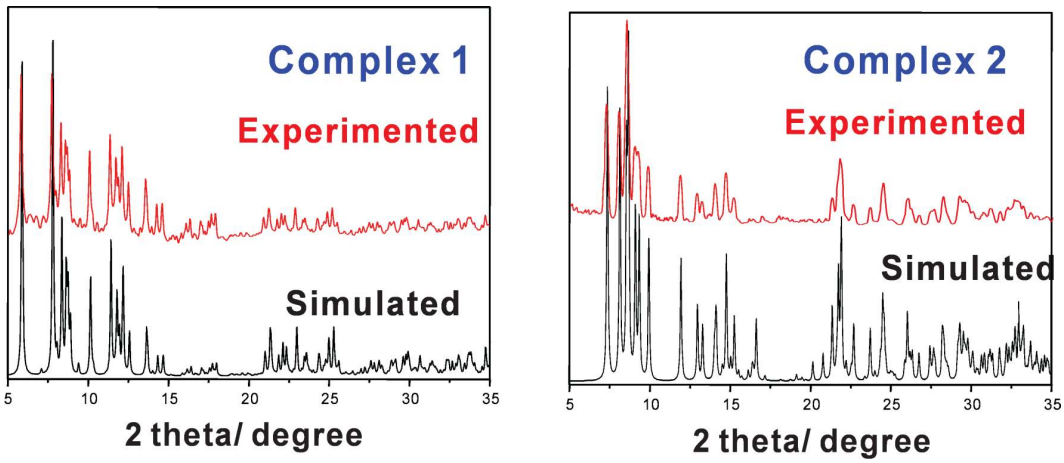
Symmetry codes: (iii) $-x+1, -y+2, -z+1$; (iv) $x+1, y-1, z$; (v) $x-1, y, z$; (vi) $-x, -y+2, -z+1$; (vii) $-x, -y+2, -z$; (viii) $x-1, y+1, z+1$.

(7) Table S4: Crystal data for 1 and 2

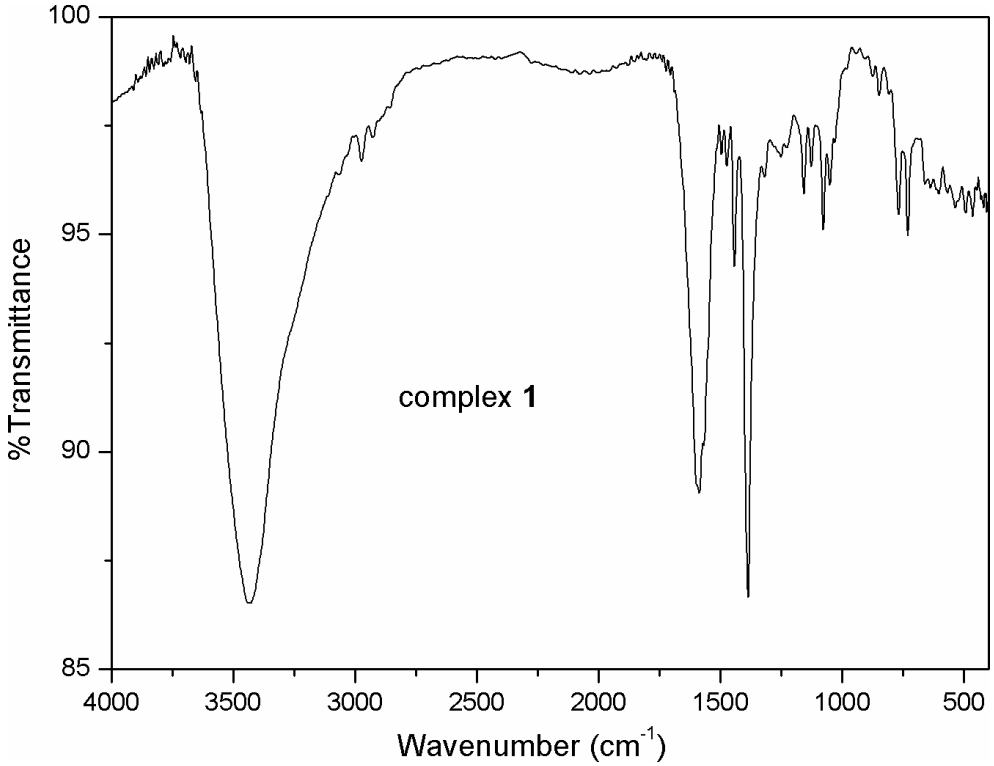
Compound	**1**	**2**
Empirical formula	$Ag_{12}Cu_6C_{132}H_{150}N_{24}O_{57}S_{12}$	$Ag_6Zn_3C_{42}H_{66}N_{12}O_{24}S_6$
Formula weight	5045.16	2158.76
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a (Å)	12.8443(4)	12.5619(3)
b (Å)	15.9047(6)	12.6722(3)
c (Å)	21.8952(8)	13.559(3)
α (deg)	103.901(1)	85.830(1)
β (deg)	93.249(1)	64.096(1)
γ (deg)	102.625(1)	60.566(1)
V(Å^3)	4208.6(3)	1663.0(4)
T(K)	173(2)	173(2)
Z, D_{calcd} (Mg/m^3)	1, 1.991	1, 2.156
F(000)	2496	1062
μ(mm^{-1})	2.341	3.059
Ref. collected/unique	33055/14750	14346/6466
R_{int}	0.0463	0.0348
Parameters	1081	421
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0771$	$R_1 = 0.0279$
	$wR_2 = 0.1688$	$wR_2 = 0.0683$
R indices (all data)	$R_1 = 0.0990$	$R_1 = 0.0313$
	$wR_2 = 0.1841$	$Wr_2 = 0.0704$
GOF	1.069	1.028
Max./ min., $\Delta\rho$ (e·Å^{-3})	2.310 / –1.305	1.251 / –1.103

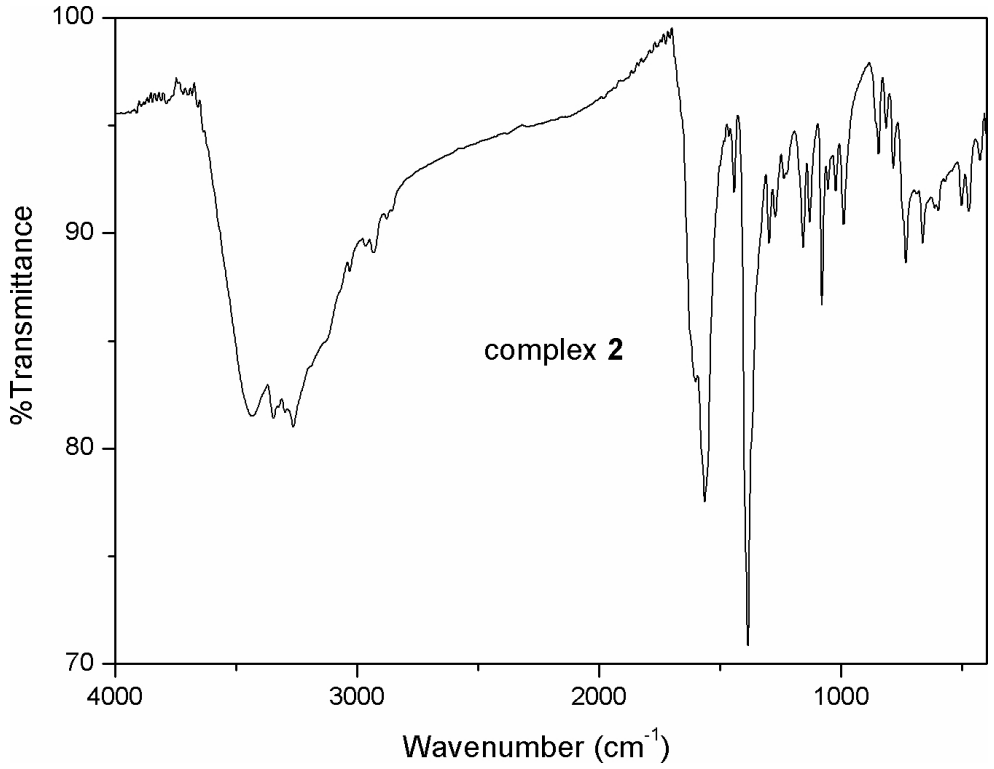
$R_1 = \Sigma| |F_o|-|F_c| | / \Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/ \Sigma w(F_o^2)^2]^{1/2}$

(8) Fig. S1: XRD spectrum of 1 and 2

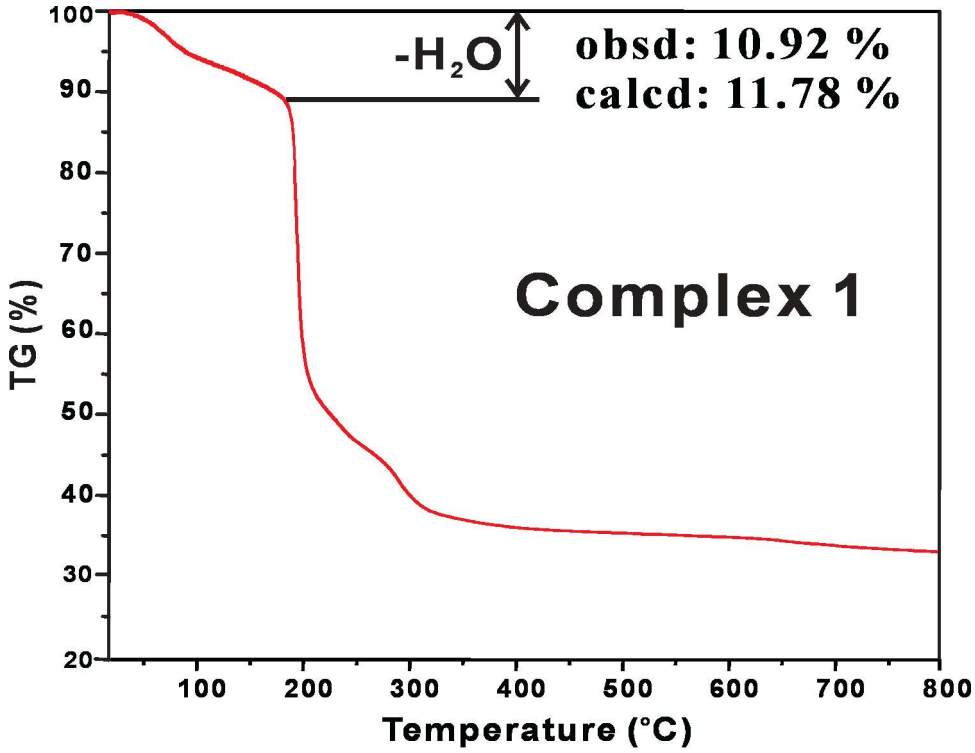


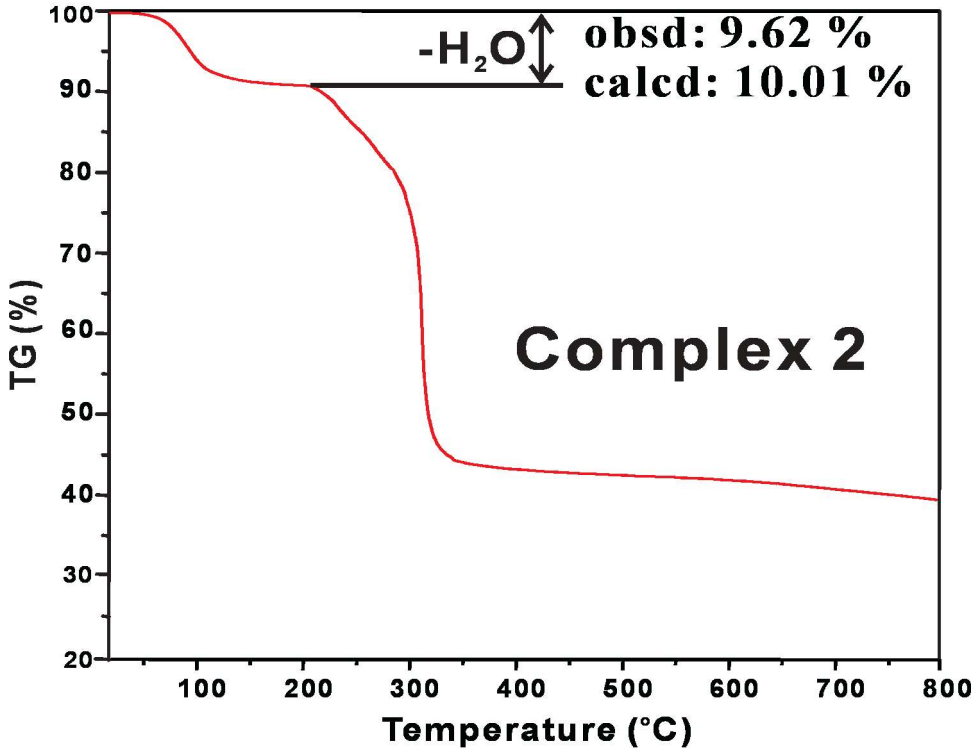
(9) Fig. S2: IR spectrum of 1 and 2



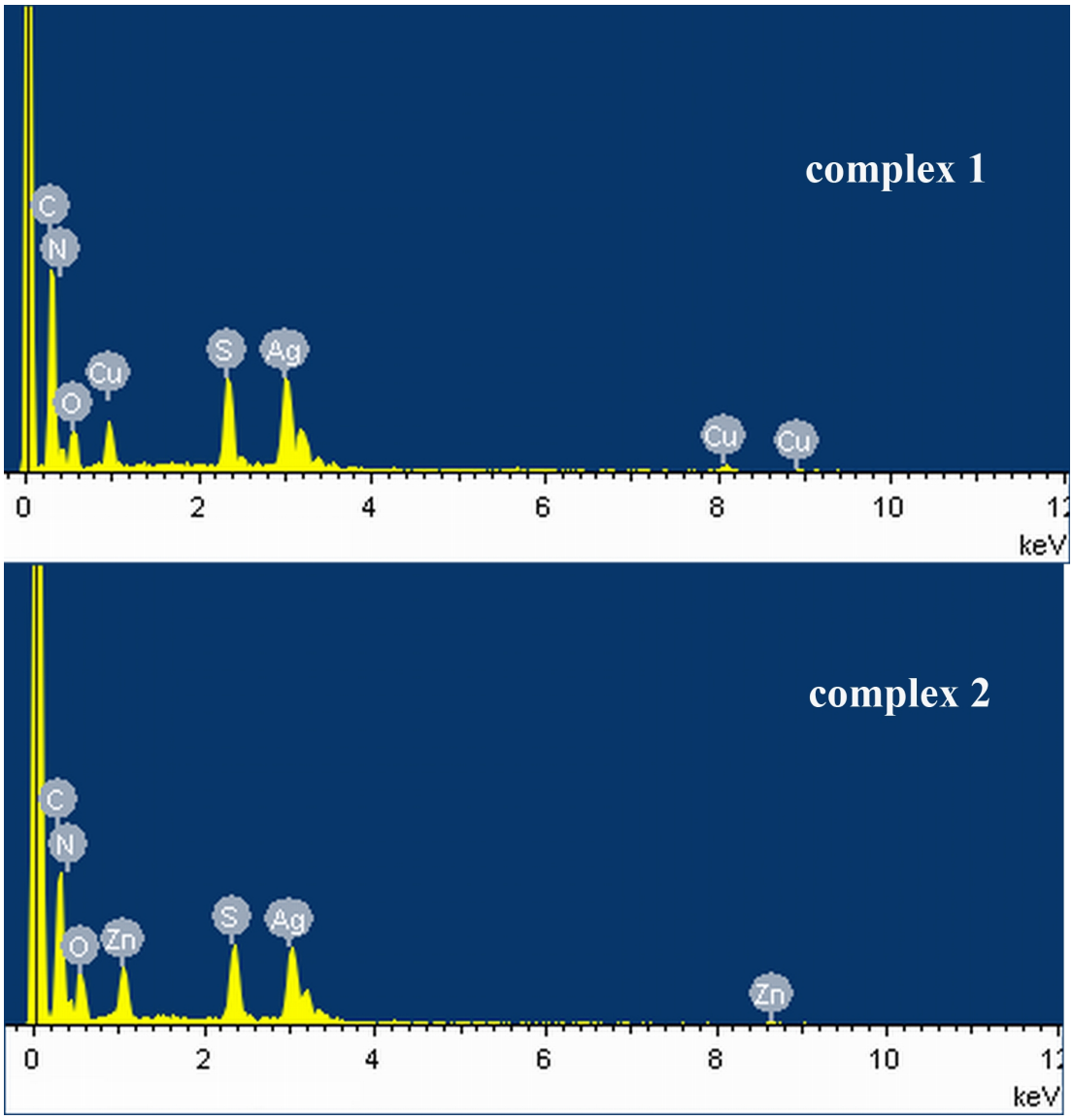


(10) Fig. S3: The TGA curves of 1 and 2

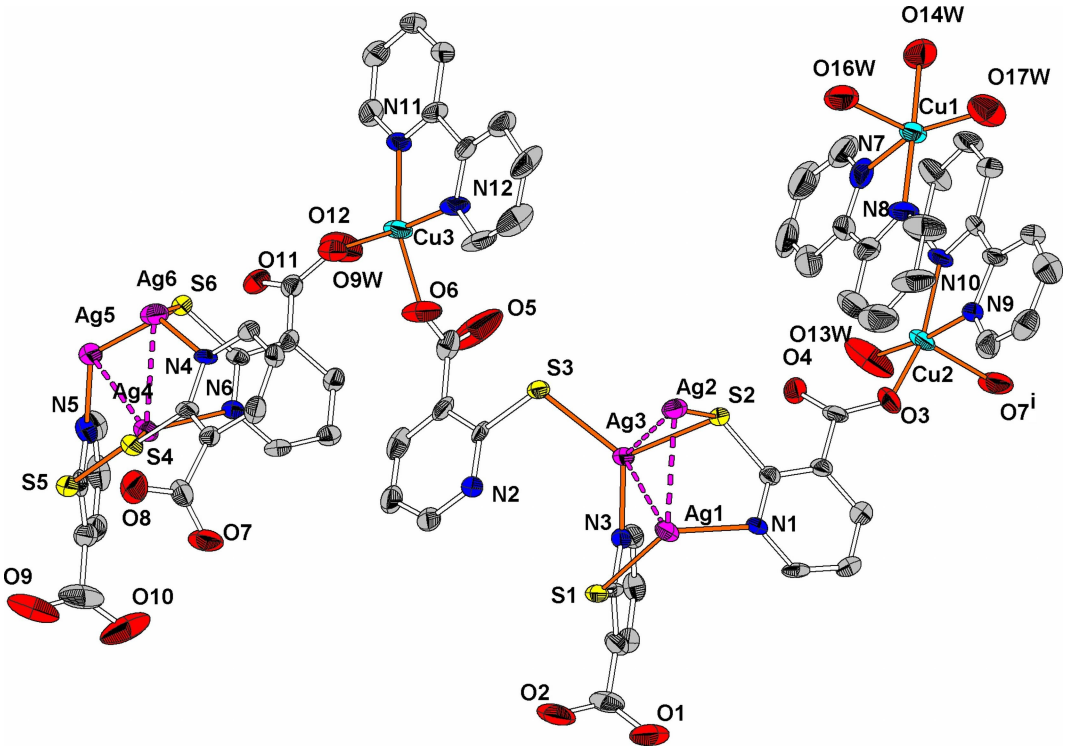




(11) Fig. S4:Energy dispersive X-ray spectroscopy (EDS) data for 1 and 2



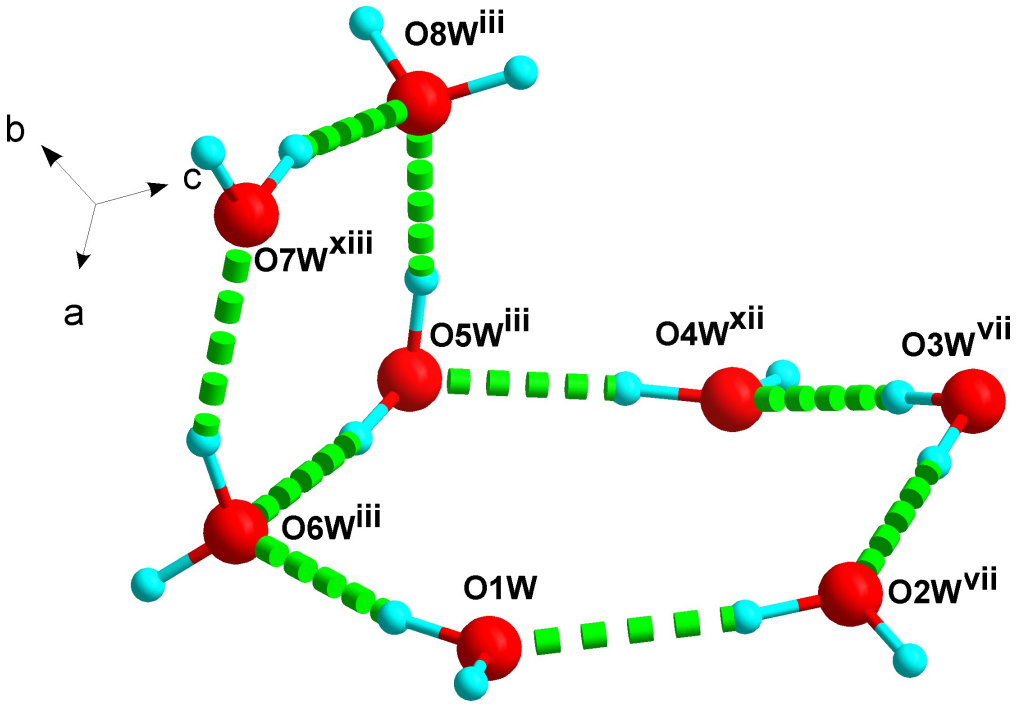
(12) Fig. S5: The Oak Ridge Thermal Ellipsoid Plot (ORTEP) and atom numbering schemes of asymmetric unit of 1



Water molecules and hydrogen atoms are omitted for clarity

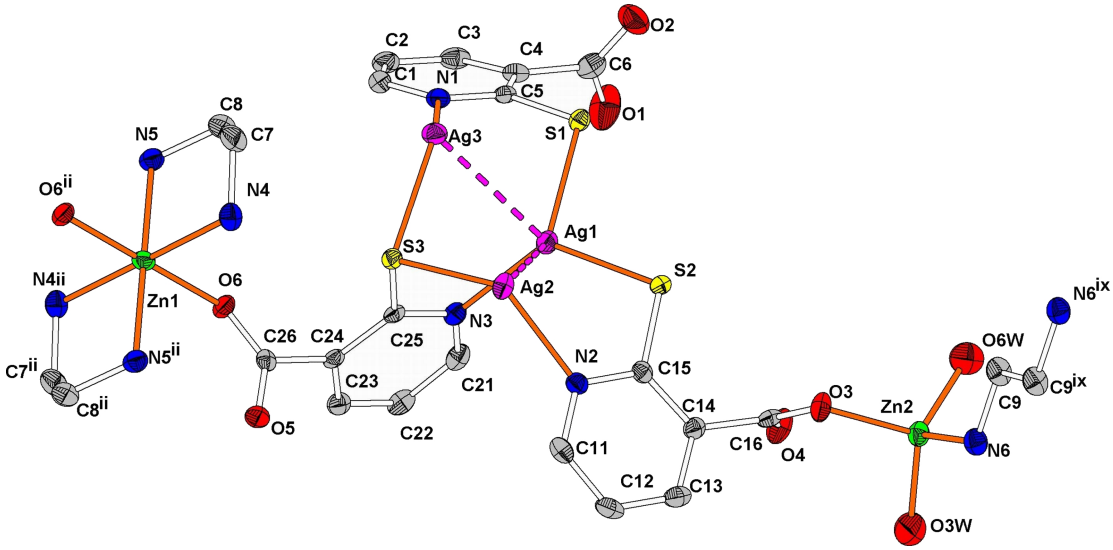
Symmetry codes (i) $-x+1, -y+2, -z+2$

(13) Fig. S6: The octamer water cluster in 1



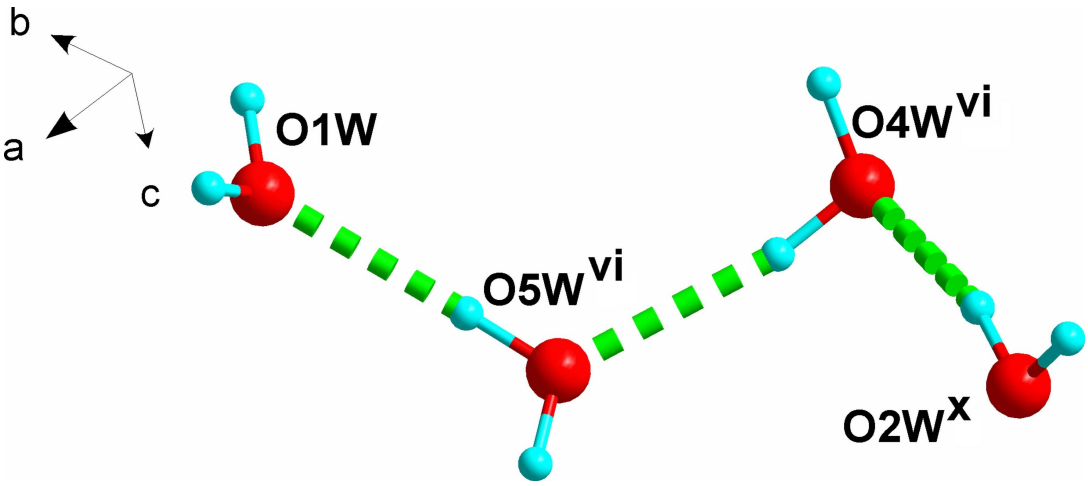
Symmetry codes: (iii) x, y+1, z; (vii) x−1, y, z; (xi) x−1, y−1, z; (xii) −x+2, −y+3, −z+3; (xiii) −x+1, −y+3, −z+2.

(14) Fig. S7: The Oak Ridge Thermal Ellipsoid Plot (ORTEP) and atom numbering schemes of asymmetric unit of 2



Water molecules and hydrogen atoms are omitted for clarity
Symmetry codes: (ii) −*x*+2, −*y*+1, −*z*−1; (ix) −*x*−1, −*y*+3, −*z*+1

(15) Fig. S8: The finite water chain in 2



Symmetry codes: (vi) −*x*, −*y*+2, −*z*+1; (x) −*x*+1, −*y*+1, −*z*+1

(16) Fig. S9: The UV-Vis spectra of 1 and 2