Supplementary Material (ESI) for Dalton Transactions
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The Key Role of $-CH_3$ Steric Hindrance in Bis(pyrazolyl) Ligand on Polyoxometalate-based Compounds

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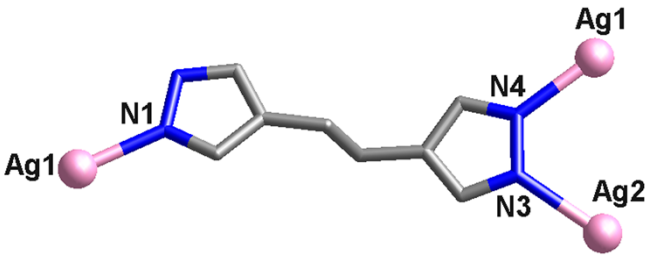

Fig. S1 The coordination mode of Hbhpe in compound **1**.

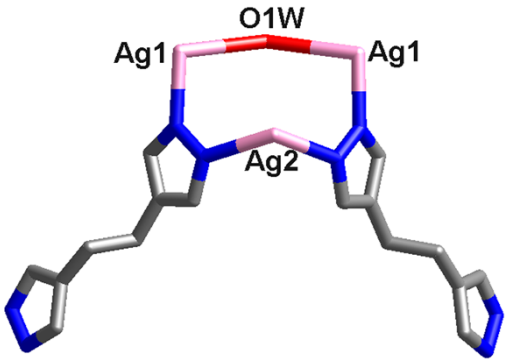

Fig. S2 The tri-nuclear Ag cluster constructed by two adjacent Hbhpe ligands through sharing the same Ag2 ion and the linkage of O1W molecule in compound **1**.

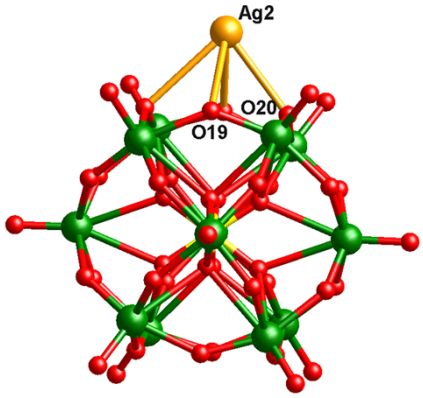

Fig. S3 The PMo_{12} in compound **1** is a single Ag2-capped anion.

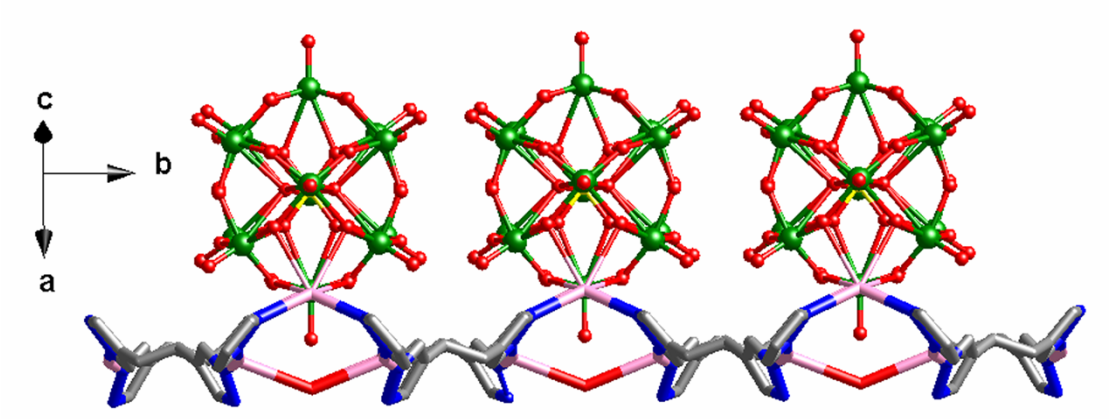

Fig. S4 The PMo_{12} anions float on the large penta-membered Ag cycles in the 2D layer of compound **1**.

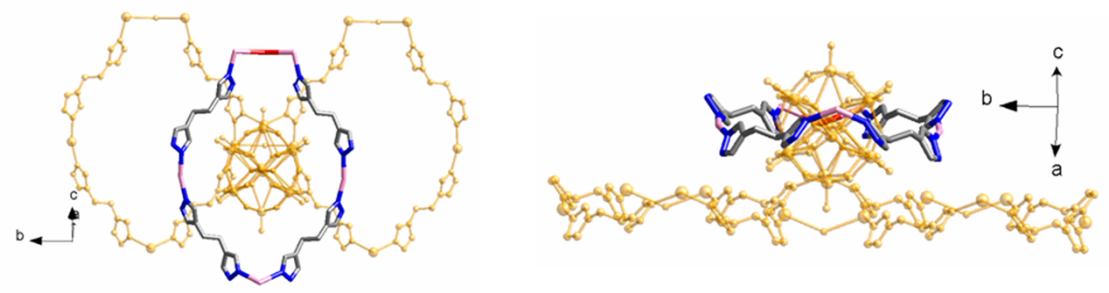

Fig. S5 The anions insert into the cycles in adjacent 2D layers in compound **1**.

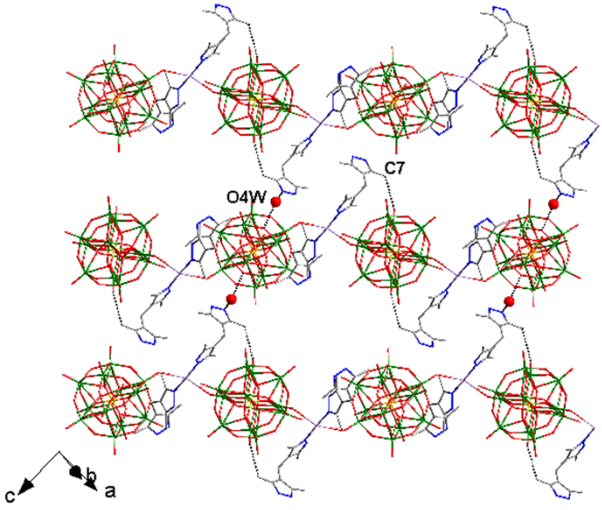

Fig. S6 The 2D supramolecular layer of **2** induced by hydrogen bonding interactions between water molecules, H_2bdpm ligands and anions.

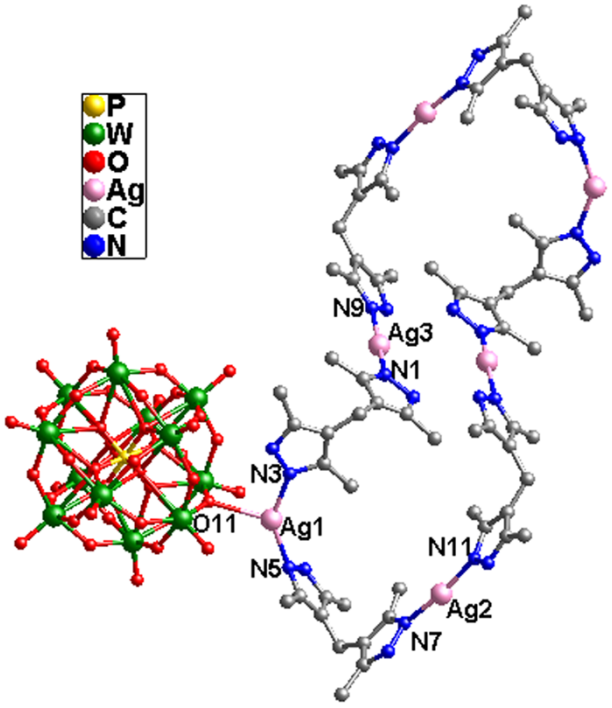

Fig. S7 Ball/stick view of the asymmetric unit of **3**. The hydrogen atoms and crystal water molecules are omitted for clarity.

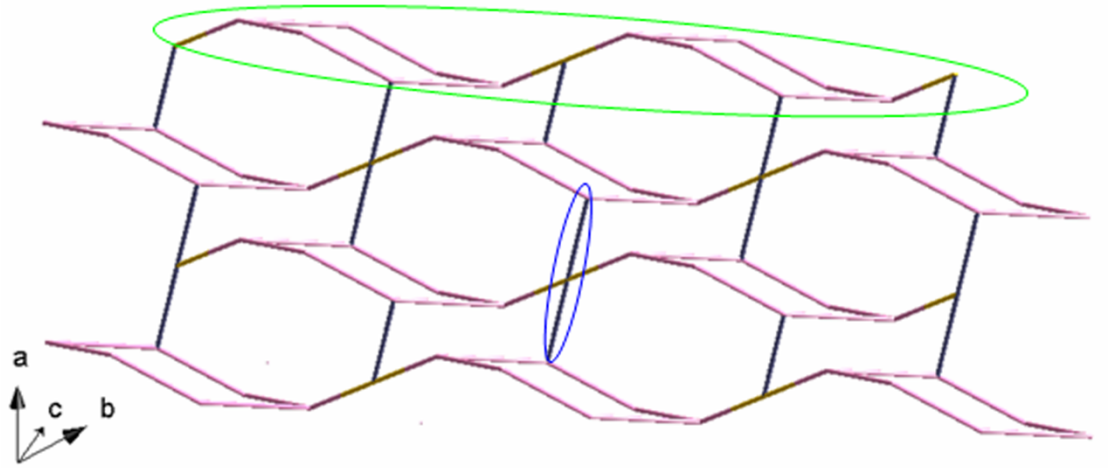

Fig. S8 The 1D chains (in green cycle) are fused by Ag3-O bonds (in blue cycle) to form a 2D layer of compound **3**.

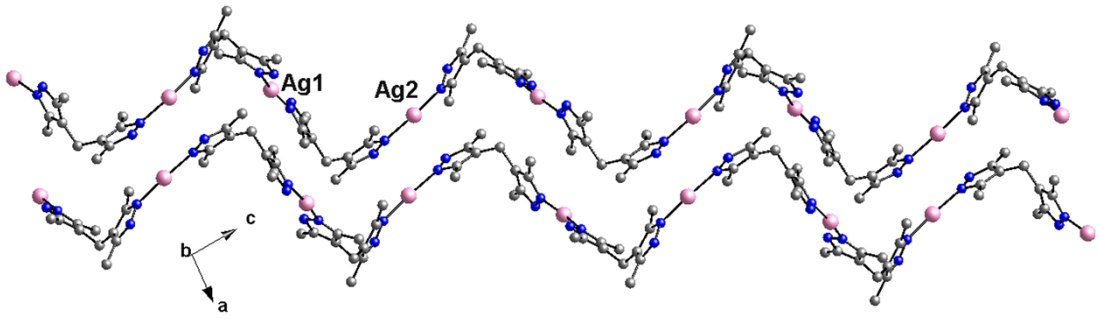

Fig. S9 The wavy double-track chain in compound **4** containing two $[Ag(H_2bdpm)]_n^{n+}$ lines.

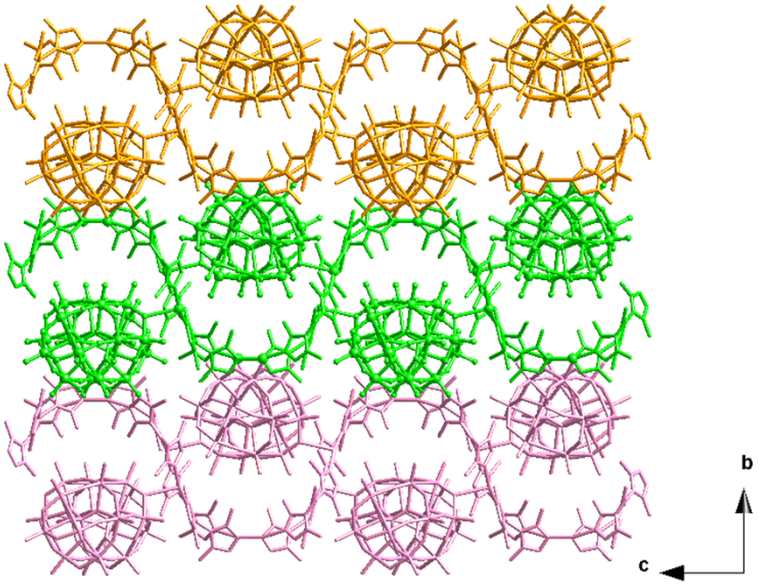

Fig. S10 The adjacent chains are parallel to form a 2D supramolecular structure of compound **4**.

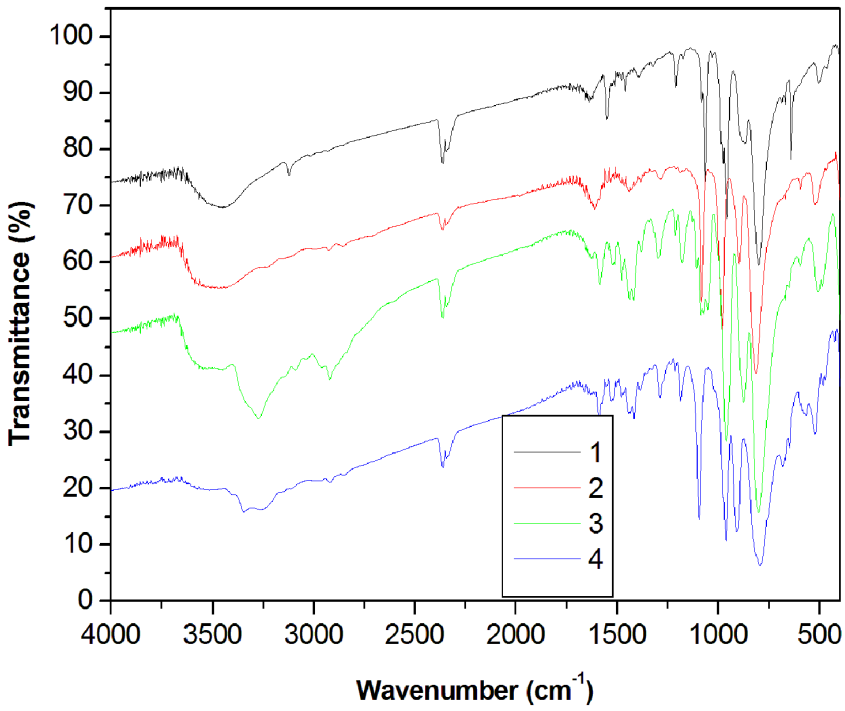

Fig. S11 The IR spectra of compounds **1**–**4**.

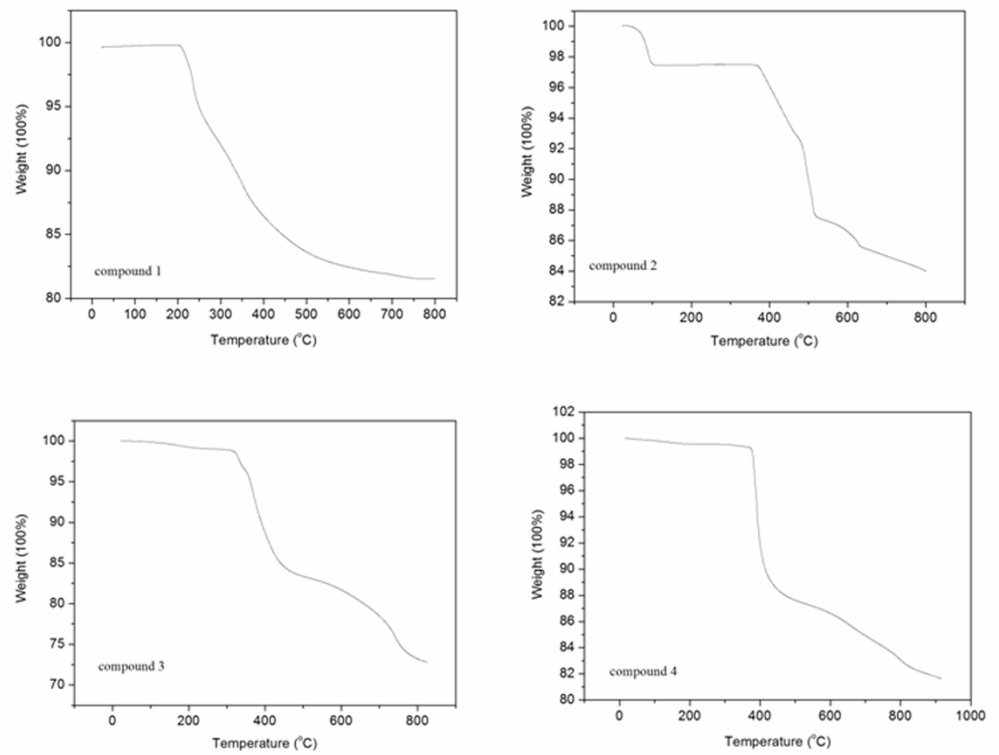

Fig. S12 The TGA curves of compounds **1**–**4**.

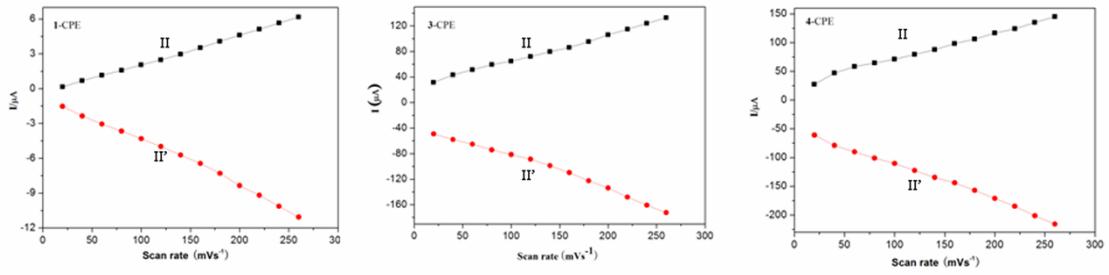

Fig. S13 The dependence of anodic peak (II) and cathodic peak (II') currents of **1**–, **3**– and **4**–CPEs on scan rates.

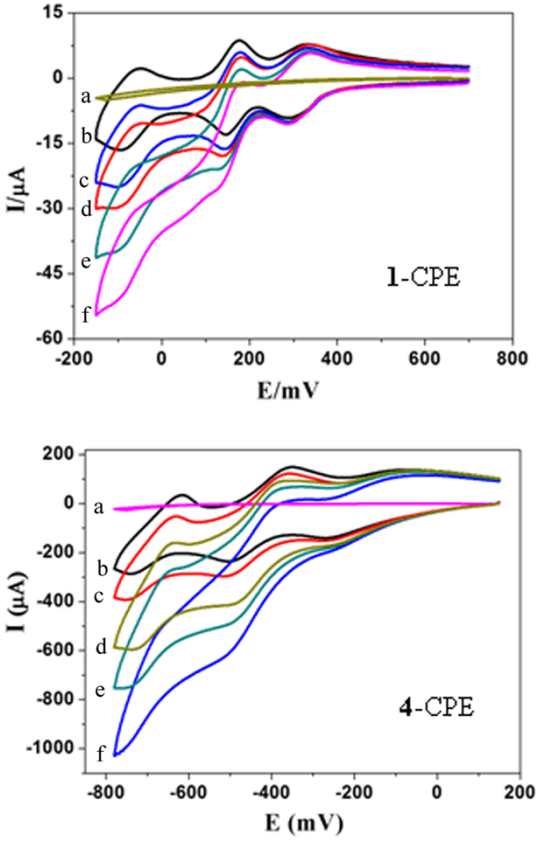

Fig. S14 Cyclic voltammograms of the **1**– and **4**–CPEs in 0.1M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution containing 0(b); 2(c); 4(d); 6(e) and 8(f) mM H_2O_2 and a bare CPE (a) in a 4.0 mM H_2O_2 + 0.1M H_2SO_4 + 0.5M Na_2SO_4 solution. Scan rate: 200 $mV \cdot s^{-1}$.

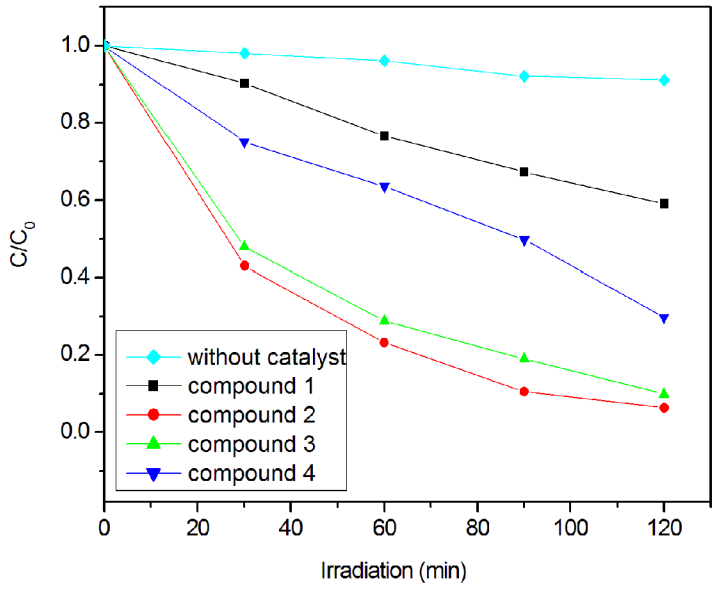

Fig. S15 Photocatalytic decomposition rate of the MB solution under UV irradiation with the use of the title compounds and no catalyst in the same conditions.

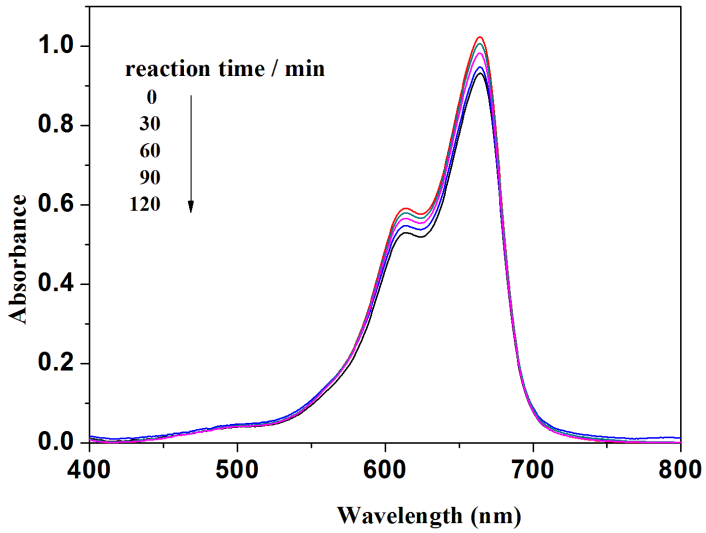

Fig. S16 Absorption spectra of the MB solution during the decomposition reaction under UV irradiation without the presence of any title compounds.

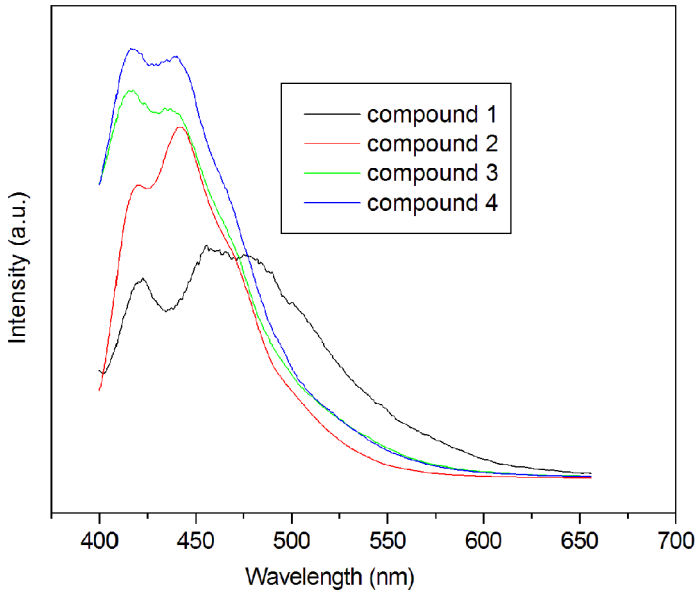

Fig. S17 Photoluminescent spectra of **1**–**4** dissolved in DMSO at room temperature. Photoluminescence spectra of **1**–**4** dissolved in DMSO at room temperature are shown in Fig. S17. Two prominent emission peaks are observed at about 421 and 456 nm for **1**, 419 and 441 nm for **2**, 416 and 436 nm for **3** and 417 and 439 nm for **4** (excitation at 340 nm). The emission peak would be assigned to ligand-to-metal charge transfer (LMCT).

Table S1 Selected Bond Lengths (Å) and Bond Angles (°) for Compounds **1**–**4**.

Compound **1**			
Ag1-N1	2.126(8)	Ag1-N4	2.124(7)
Ag1-O1W	2.730(6)	Ag2-N3	2.278(6)
Ag2-O20	2.697(7)	Ag2-O5	2.908(6)
N1-Ag1-N4	163.9(3)	N1-Ag1-O1W	98.55(2)
N4-Ag1-O1W	98.70(5)	N3-Ag2-N3	112.1(3)
Symmetry codes for **1**: #1 x,-y,z #2 x-1/2,-y-1/2,z-1 #3 x+1/2,-y-1/2,z+1			
Compound **2**			
Ag1-N3	2.12(2)	Ag1-N4	2.12(2)
Ag1-O12	2.755(5)	Ag1-O29	2.803(2)
N3-Ag1-N4	176.5(12)	O12-Ag1-O29	146.30(13)
Symmetry codes for **2**: #1 -x-1,-y,-z #2 -x,-y+1,-z-1			
Compound **3**			
Ag1-O11	2.53(2)	Ag1-N3	2.12(3)
Ag1-N5	2.12(2)	Ag2-N7	2.090(18)
Ag2-N11	2.090(17)	Ag2-O14	2.743(10)
Ag3-N1	2.070(2)	Ag3-N9	2.114(19)
Ag3-O13	2.838(15)	Ag3-O20	2.853(10)
N3-Ag1-N5	142.4(9)	N3-Ag1-O11	94.6(8)
N5-Ag1-O11	123.0(8)	N7-Ag2-N11	172.2(8)
N11-Ag2-O14	82.05(9)	N7-Ag2-O14	104.59(8)
N1-Ag3-N9	170.2(8)	N9-Ag3-O13	111.85(5)
N1-Ag3-O13	77.76(8)	N9-Ag3-O20	82.32(6)
Symmetry codes for **3**: #1 -x+1,-y-1,-z+1 #2 -x,-y+1,-z+1			
Compound **4**			
Ag1-N8	2.056(15)	Ag1-N1	2.108(17)
Ag1-O17	2.883(15)	Ag2-N3	2.078(16)
Ag2-N5	2.091(16)	N8-Ag1-N1	166.2(7)
N8-Ag1-O17	99.88(6)	N1-Ag1-O17	90.41(7)
N3-Ag2-N5	163.7(6)		
Symmetry codes for **4**: #1 -x+2,y,-z+1/2 #2 x-1/2,-y+1/2,z-1/2 #3 x+1/2,-y+1/2,z+1/2			