Supporting Information

Multinuclear coordination polymers based on Ag···Ag interactions, generated from a novel N-Donor ligand hexakis[2-(1H-pyrazol-3-yl)pyridine-ylmethy1]benzene and different polycarboxylates: syntheses, structures, and luminescent properties

Hua-Yu Shi, Yun-Bo Dong, Ying-Ying Liu* and Jian-Fang Ma*

Key Lab of Polyoxometalate Science, *Department of Chemistry*, *Northeast Normal University*, *Changchun 130024*, *People's Republic of China*

Table S1. Selected bond distances (Å) and angles (°) for **1**.

Ag(1)-O(1)	2.275(3)	Ag(1)-N(2)	2.475(4)
Ag(1)-N(3)	2.554(4)	Ag(1)-N(5)	2.469(3)
Ag(1)-N(6)	2.450(4)	Ag(2)-O(2)	2.152(3)
Ag(2)-N(8)	2.347(3)	Ag(2)-N(9)	2.348(4)
O(1)-Ag(1)-N(2)	101.50(13)	O(1)-Ag(1)-N(3)	104.11(12)
O(1)-Ag(1)-N(5)	141.45(12)	O(1)-Ag(1)-N(6)	116.84(14)
N(2)-Ag(1)-N(3)	68.25(13)	N(5)-Ag(1)-N(2)	91.95(12)
N(6)-Ag(1)-N(2)	138.75(12)	N(5)-Ag(1)-N(3)	114.42(11)
N(6)-Ag(1)-N(3)	87.25(13)	N(6)-Ag(1)-N(5)	67.87(12)
O(2)-Ag(2)-N(8)	139.76(14)	O(2)-Ag(2)-N(9)	130.34(14)
N(8)-Ag(2)-N(9)	71.92(13)		

Table S2. Selected bond distances (Å) and angles (°) for **2**.

Ag(1)-O(1)	2.274(3)	Ag(1)-N(2)	2.395(5)
Ag(1)-N(3)	2.598(6)	Ag(1)-N(5)	2.655(5)

Ag(1)-N(6)	2.359(4)	Ag(2)-O(2)	2.147(4)
Ag(2)-N(8)	2.322(4)	Ag(2)-N(9)	2.339(4)
O(1)-Ag(1)-N(2)	110.19(16)	O(1)-Ag(1)-N(3)	95.90(20)
N(5)-Ag(1)-O(1)	144.59(13)	O(1)-Ag(1)-N(6)	127.08(15)
N(2)-Ag(1)-N(3)	66.78(18)	N(5)-Ag(1)-N(2)	81.23(14)
N(6)-Ag(1)-N(2)	117.48(16)	N(5)-Ag(1)-N(3)	119.03(19)
N(6)-Ag(1)-N(3)	83.23(18)	N(5)-Ag(1)-N(6)	67.18(14)
O(2)-Ag(2)-N(8)	146.14(19)	O(2)-Ag(2)-N(9)	130.49(17)
N(8)-Ag(2)-N(9)	71.93(14)		

Table S3. Selected bond distances (Å) and angles (°) for **3**.

Ag(1)-O(1)	2.237(3)	Ag(1)-O(3)$^{\#1}$	2.411(3)
Ag(1)-O(4)$^{\#1}$	2.720(5)	Ag(1)-N(2)	2.436(3)
Ag(1)-N(3)	2.424(4)	Ag(2)-O(2)	2.209(3)
Ag(2)-N(5)	2.354(3)	Ag(2)-N(6)	2.374(4)
Ag(3)-O(2)	2.366(3)	Ag(3)-O(5)	2.415(5)
Ag(3)-N(8)	2.412(3)	Ag(3)-N(9)	2.291(4)
O(1)-Ag(1)-O(3)$^{\#1}$	116.61(11)	O(1)-Ag(1)-O(4)$^{\#1}$	116.61(12)
O(1)-Ag(1)-N(2)	125.90(12)	O(1)-Ag(1)-N(3)	123.79(13)
O(3)$^{\#1}$-Ag(1)-O(4)$^{\#1}$	50.81(9)	O(3)$^{\#1}$-Ag(1)-N(2)	112.02(11)
O(3)$^{\#1}$-Ag(1)-N(3)	98.36(12)	O(4)$^{\#1}$-Ag(1)-N(2)	78.00(9)
O(4)$^{\#1}$-Ag(1)-N(3)	119.60(11)	N(3)-Ag(1)-N(2)	68.28(11)
O(2)-Ag(2)-N(5)	141.56(12)	O(2)-Ag(2)-N(6)	115.85(13)
N(5)-Ag(2)-N(6)	70.61(12)	O(2)-Ag(3)-O(5)	100.23(15)
O(2)-Ag(3)-N(8)	110.70(11)	N(9)-Ag(3)-O(2)	115.90(13)
N(8)-Ag(3)-O(5)	129.16(14)	N(9)-Ag(3)-O(5)	127.38(16)
N(9)-Ag(3)-N(8)	72.83(12)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y,-z+1.

Table S4. Selected bond distances (Å) and angles (°) for **4**.

Ag(1)-O(1)$^{\#1}$	2.410(7)	Ag(1)-N(2)	2.386(7)
Ag(1)-N(3)	2.253(9)	Ag(1)-N(19)$^{\#1}$	2.210(7)
Ag(2)-O(1)$^{\#1}$	2.280(6)	Ag(2)-N(5)	2.431(7)
Ag(2)-N(6)	2.368(8)	Ag(2)-N(8)	2.352(7)
Ag(3)-O(2)$^{\#1}$	2.215(7)	Ag(3)-O(3)	2.415(7)
Ag(3)-O(4)	2.609(8)	Ag(3)-N(9)	2.296(7)
Ag(4)-O(5)	2.486(8)	Ag(4)-O(9)	2.631(10)
Ag(4)-N(11)	2.488(7)	Ag(4)-N(12)	2.278(9)
Ag(4)-N(20)	2.267(8)	Ag(5)-O(5)	2.144(7)
Ag(5)-N(14)	2.306(7)	Ag(5)-N(15)	2.346(9)
Ag(6)-O(6)	2.237(7)	Ag(6)-O(7)$^{\#2}$	2.419(7)
Ag(6)-O(8)$^{\#2}$	2.658(8)	Ag(6)-N(17)	2.571(7)
Ag(6)-N(18)	2.282(9)	N(2)-Ag(1)-O(1)$^{\#1}$	108.2(2)
N(3)-Ag(1)-O(1)$^{\#1}$	122.0(3)	N(19)$^{\#1}$-Ag(1)-O(1)$^{\#1}$	71.1(2)
N(3)-Ag(1)-N(2)	72.8(3)	N(19)$^{\#1}$-Ag(1)-N(2)	144.2(3)
N(19)$^{\#1}$-Ag(1)-N(3)	139.4(3)	O(1)$^{\#1}$-Ag(2)-N(5)	121.5(3)
O(1)$^{\#1}$-Ag(2)-N(6)	108.4(3)	O(1)$^{\#1}$-Ag(2)-N(8)	135.0(3)
N(6)-Ag(2)-N(5)	69.9(2)	N(8)-Ag(2)-N(5)	92.3(2)
N(8)-Ag(2)-N(6)	111.0(3)	O(2)$^{\#1}$-Ag(3)-O(3)	111.3(3)
O(2)$^{\#1}$-Ag(3)-O(4)	105.86(30)	O(2)$^{\#1}$-Ag(3)-N(9)	134.7(3)
O(3)-Ag(3)-O(4)	51.64(23)	N(9)-Ag(3)-O(3)	96.8(2)
N(9)-Ag(3)-O(4)	119.39(27)	O(9)-Ag(4)-O(5)	138.10(27)
O(5)-Ag(4)-N(11)	90.6(2)	N(12)-Ag(4)-O(5)	105.7(3)
N(20)-Ag(4)-O(5)	68.3(3)	O(9)-Ag(4)-N(11)	94.97(26)
O(9)-Ag(4)-N(12)	115.40(33)	O(9)-Ag(4)-N(20)	88.90(27)
N(12)-Ag(4)-N(11)	70.9(3)	N(20)-Ag(4)-N(11)	151.1(2)
N(20)-Ag(4)-N(12)	132.4(3)	O(5)-Ag(5)-N(14)	144.6(3)
O(5)-Ag(5)-N(15)	126.0(3)	N(14)-Ag(5)-N(15)	71.0(3)
O(6)-Ag(6)-O(7)$^{\#2}$	109.3(3)	O(8)$^{\#2}$-Ag(6)-O6	101.08(25)

O(6)-Ag(6)-N(17)	128.1(2)	O(6)-Ag(6)-N(18)	133.8(3)
O(8)$^{\#2}$-Ag(6)-O(7)$^{\#2}$	50.51(23)	O(7)$^{\#2}$-Ag(6)-N(17)	92.8(2)
N(18)-Ag(6)-O(7)$^{\#2}$	112.2(3)	O(8)$^{\#2}$-Ag(6)-N(17)	127.98(20)
O(8)$^{\#2}$-Ag(6)-N(18)	90.24(25)	N(18)-Ag(6)-N(17)	69.0(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x,-y+1,-z; $^{\#2}$ -x,-y+1,-z+1.

Table S5. Selected bond distances (Å) and angles (°) for **5**.

Ag(1)-O(3)	2.148(4)	Ag(1)-N(2)	2.293(5)
Ag(1)-N(3)	2.377(5)	Ag(2)-O(4)	2.190(4)
Ag(2)-O(7)	2.542(4)	Ag(2)-N(8)	2.339(5)
Ag(2)-N(9)	2.300(5)	Ag(3)-O(7)	2.208(4)
Ag(3)-O(8)$^{\#1}$	2.170(4)	Ag(3)-O(9)$^{\#2}$	2.483(12)
Ag(4)-O(1)	2.188(6)	Ag(4)-O(2)$^{\#3}$	2.252(5)
Ag(4)-O(6)$^{\#4}$	2.313(5)	Ag(4)-O(10)$^{\#6}$	2.696(8)
Ag(5)-O(2)$^{\#2}$	2.598(5)	Ag(5)-O(5)	2.158(4)
Ag(5)-O(10)$^{\#7}$	2.674(10)	Ag(5)-N(6)$^{\#2}$	2.209(5)
O(3)-Ag(1)-N(2)	171.29(18)	O(3)-Ag(1)-N(3)	116.7(2)
N(2)-Ag(1)-N(3)	71.31(17)	O(4)-Ag(2)-O(7)	86.15(14)
O(4)-Ag(2)-N(8)	146.77(16)	O(4)-Ag(2)-N(9)	139.26(18)
N(8)-Ag(2)-O(7)	104.48(15)	N(9)-Ag(2)-O(7)	93.34(16)
N(9)-Ag(2)-N(8)	72.50(18)	O(8)$^{\#1}$-Ag(3)-O(7)	160.21(16)
O(7)-Ag(3)-O(9)$^{\#2}$	83.6(3)	O(8)$^{\#1}$-Ag(3)-O(9)$^{\#2}$	115.6(3)
O(1)-Ag(4)-O(2)$^{\#3}$	139.3(2)	O(1)-Ag(4)-O(6)$^{\#4}$	106.2(2)
O(10)$^{\#6}$-Ag(4)-O1	96.81(22)	O(2)$^{\#3}$-Ag(4)-O(6)$^{\#4}$	113.90(19)
O(10)$^{\#6}$-Ag(4)-O(2)$^{\#3}$	89.41(23)	O(10)$^{\#6}$-Ag(4)-O(6)$^{\#4}$	91.26(21)
O(5)-Ag(5)-O(2)$^{\#2}$	105.71(17)	O(10)$^{\#7}$-Ag(5)-O(2)$^{\#2}$	83.06(21)
N(6)$^{\#2}$-Ag(5)-O(2)$^{\#2}$	99.99(18)	O(10)$^{\#7}$-Ag(5)-O5	101.29(22)
O(5)-Ag(5)-N(6)$^{\#2}$	152.05(18)	O(10)$^{\#7}$-Ag(5)-N6	92.46(24)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+2,-y+1,-z; $^{\#2}$ -x+1,-y,-z; $^{\#3}$ -x,-

y,-z-1; #4 x-1,y,z-1; #5 x+1,y,z+1; #6 1-x,-y,1-z; #7 1+x,y,z.

Table S6. Selected bond distances (Å) and angles (°) for **6**.

Ag(1)-O(1)	2.355(5)	Ag(1)-O(6)#1	2.256(4)
Ag(1)-N(5)	2.388(5)	Ag(1)-N(6)	2.376(5)
Ag(2)-O(5)	2.170(4)	Ag(2)-N(8)	2.353(4)
Ag(2)-N(9)	2.351(4)	O(6)#1-Ag(1)-O(1)	109.7(2)
O(1)-Ag(1)-N(5)	109.18(19)	O(1)-Ag(1)-N(6)	101.8(2)
O(6)#1-Ag(1)-N(5)	132.10(16)	O(6)#1-Ag(1)-N(6)	125.56(18)
N(6)-Ag(1)-N(5)	70.95(15)	O(5)-Ag(2)-N(8)	155.22(18)
O(5)-Ag(2)-N(9)	123.35(18)	N(9)-Ag(2)-N(8)	70.44(15)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z.

Table S7. Selected bond distances (Å) and angles (°) for **7**.

Ag(1)-O(2)	2.655(6)	Ag(1)-O(5)#1	2.458(6)
Ag(1)-O(6)#1	2.475(7)	Ag(1)-N(2)	2.280(4)
Ag(1)-N(3)	2.371(5)	Ag(2)-O(2)	2.202(3)
Ag(2)-N(5)	2.310(4)	Ag(2)-N(6)	2.370(4)
Ag(3)-O(7)	2.188(3)	Ag(3)-N(8)	2.568(4)
Ag(3)-N(9)	2.218(4)	O(2)-Ag(1)-O(5)#1	98.46(20)
O(2)-Ag(1)-O(6)#1	97.06(25)	O(2)-Ag(1)-N(2)	98.70(17)
O(2)-Ag(1)-N(3)	105.35(24)	O(5)#1-Ag(1)-O(6)#1	51.6(2)
N(2)-Ag(1)-O(5)#1	155.30(19)	N(3)-Ag(1)-O(5)#1	86.6(2)
N(2)-Ag(1)-O(6)#1	142.46(19)	N(3)-Ag(1)-O(6)#1	135.40(19)
N(2)-Ag(1)-N(3)	71.89(16)	O(2)-Ag(2)-N(5)	157.08(14)
O(2)-Ag(2)-N(6)	130.34(14)	N(5)-Ag(2)-N(6)	71.50(14)
O(7)-Ag(3)-N(8)	138.06(13)	O(7)-Ag(3)-N(9)	147.61(15)
N(9)-Ag(3)-N(8)	70.28(14)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1.

Table S8. Selected bond distances (Å) and angles (°) for **8**.

Ag(1)-O(1)	2.289(7)	Ag(1)-O(8)$^{\#1}$	2.306(6)
Ag(1)-N(2)	2.388(7)	Ag(1)-N(3)	2.245(8)
Ag(2)-O(5)$^{\#4}$	2.678(7)	Ag(2)-O(6)	2.341(6)
Ag(2)-O(6)$^{\#4}$	2.610(7)	Ag(2)-N(5)	2.459(6)
Ag(2)-N(6)	2.345(8)	Ag(3)-O(7)	2.516(7)
Ag(3)-O(8)	2.493(6)	Ag(3)-N(8)	2.373(6)
Ag(3)-N(9)	2.361(7)	O(1)-Ag(1)-O(8)$^{\#1}$	99.0(2)
O(1)-Ag(1)-N(2)	123.1(2)	N(3)-Ag(1)-O(1)	119.4(3)
O(8)$^{\#1}$-Ag(1)-N(2)	115.7(2)	N(3)-Ag(1)-O(8)$^{\#1}$	127.0(2)
N(3)-Ag(1)-N(2)	73.7(3)	O(5)$^{\#4}$-Ag(2)-O(6)	96.71(22)
O(5)$^{\#4}$-Ag(2)-O(6)$^{\#4}$	48.82(20)	O(5)$^{\#4}$-Ag(2)-N(5)	82.61(23)
O(5)$^{\#4}$-Ag(2)-N(6)	122.48(24)	O(6)$^{\#4}$-Ag(2)-O6	90.99(21)
O(6)-Ag(2)-N(5)	146.8(2)	O(6)-Ag(2)-N(6)	133.4(2)
O(6)$^{\#4}$-Ag(2)-N(5)	112.04(21)	O(6)$^{\#4}$-Ag(2)-N(6)	96.67(21)
N(6)-Ag(2)-N(5)	69.5(2)	O(8)-Ag(3)-O(7)	50.7(2)
N(8)-Ag(3)-O(7)	160.7(3)	N(9)-Ag(3)-O(7)	94.4(3)
N(8)-Ag(3)-O(8)	148.0(2)	N(9)-Ag(3)-O(8)	126.1(2)
N(9)-Ag(3)-N(8)	69.8(2)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y+1,-z+1; $^{\#4}$ -x,1-y,1-z.

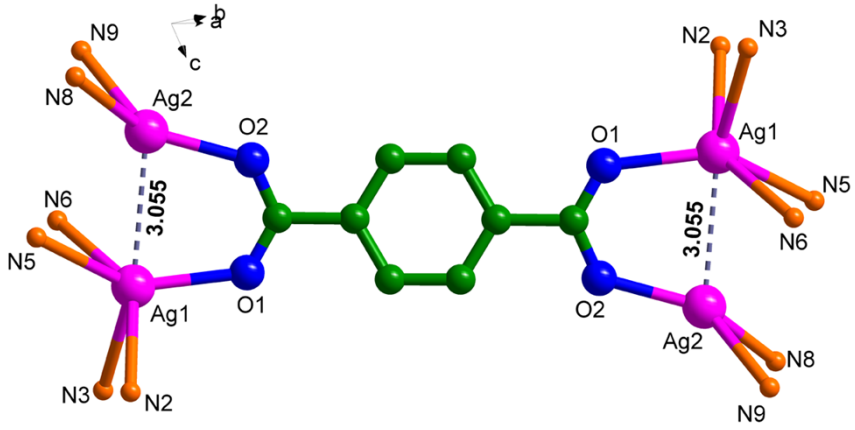


Fig. S1 Binuclear Ag(I) unit of compound **1** (the connected hpyb ligand were omitted for clarity, the same below).

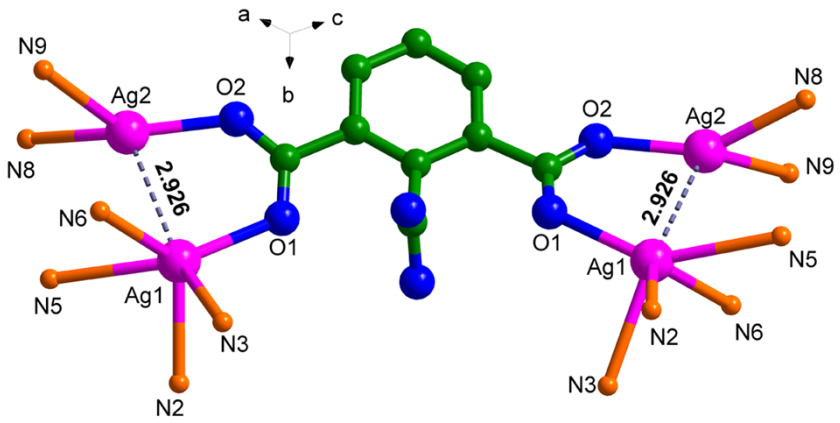


Fig. S2 Binuclear Ag(I) unit of compound **2**.

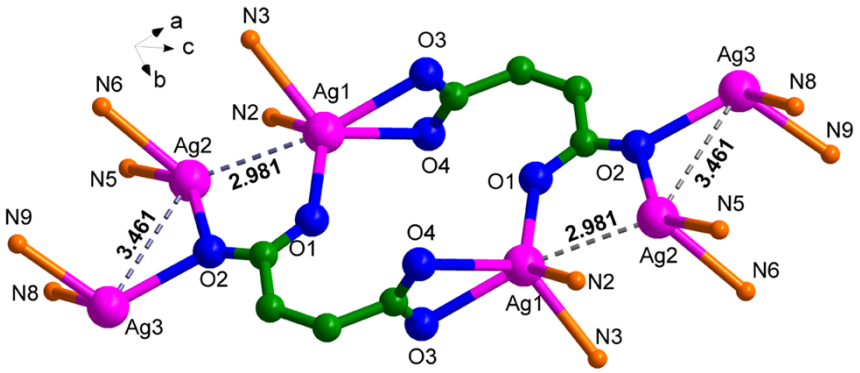


Fig. S3 Trinuclear Ag(I) cluster of compound **3**.

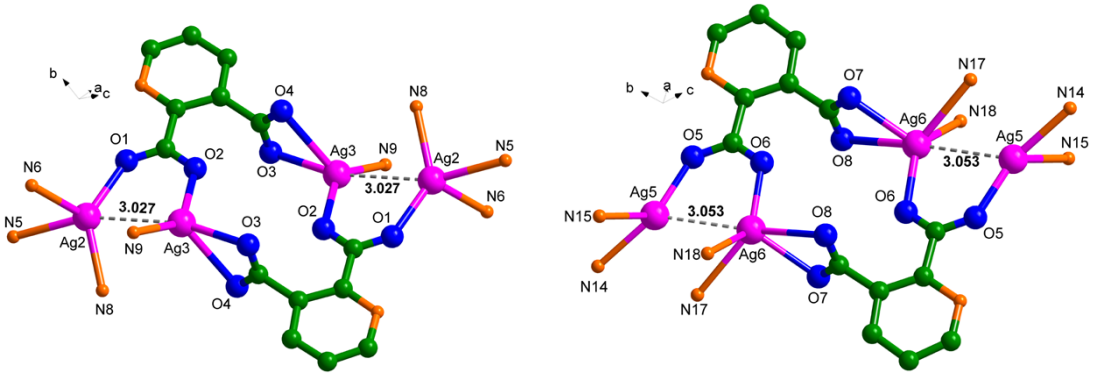
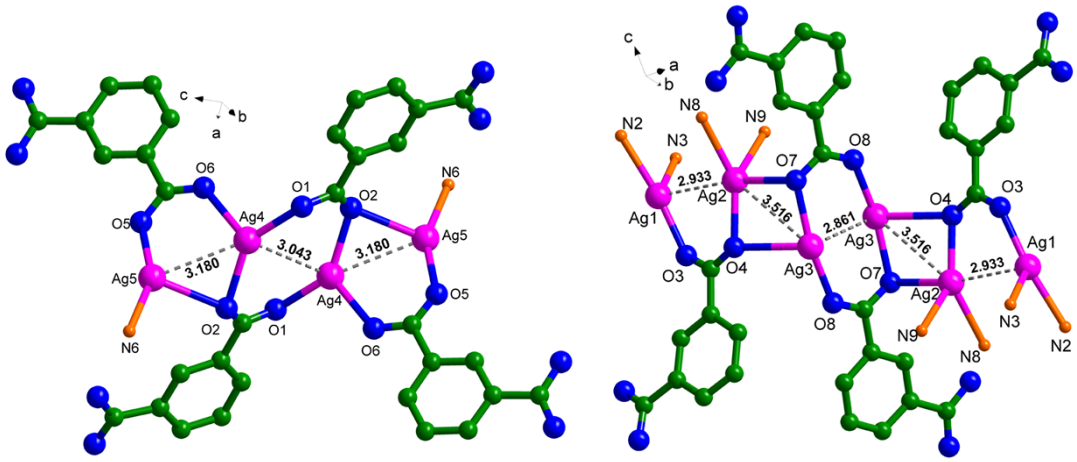
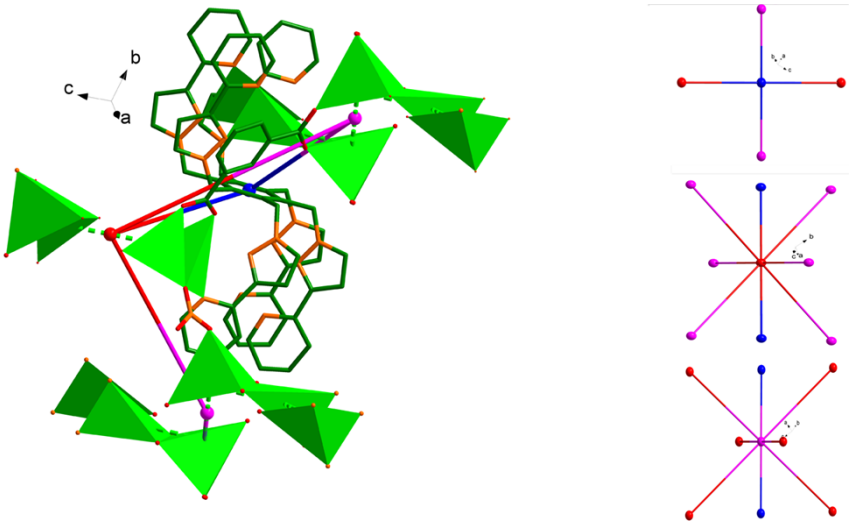


Fig. S4 Binuclear Ag(I) units of compound **4**.



(a)



(b)

Fig. S5 (a) Tetranuclear and hexanuclear Ag(I) clusters of compound **5**. (b) Schematic views of the 4- and 8-connected nodes of **5**.

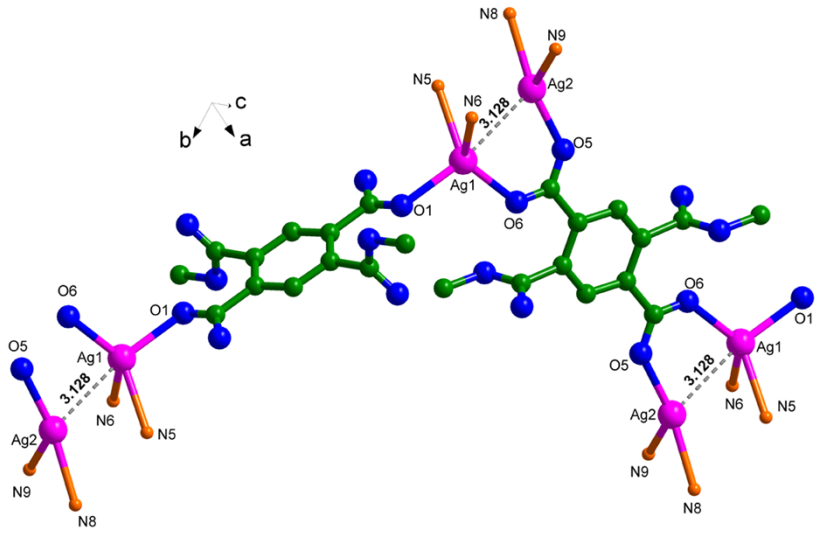
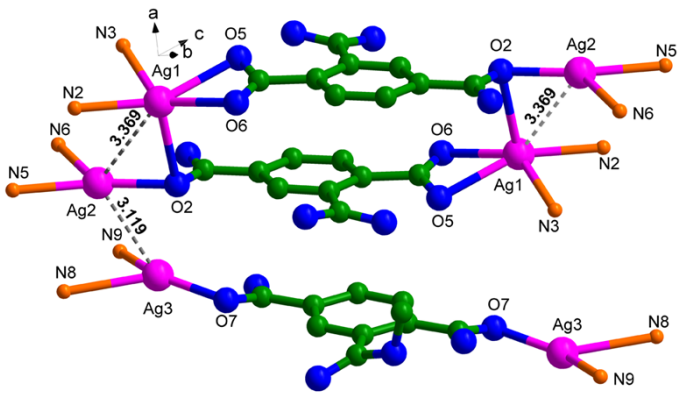
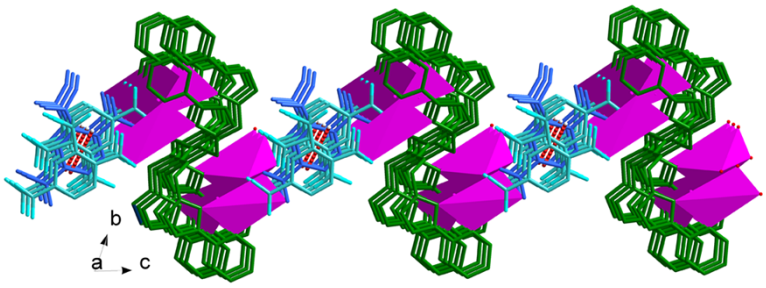


Fig. S6 Binuclear Ag(I) units of compound **6**.



(a)



(b)

Fig. S7 (a) Trinuclear Ag(I) cluster of compound **7**. (b) The 2D wave like layer of compound **7.**

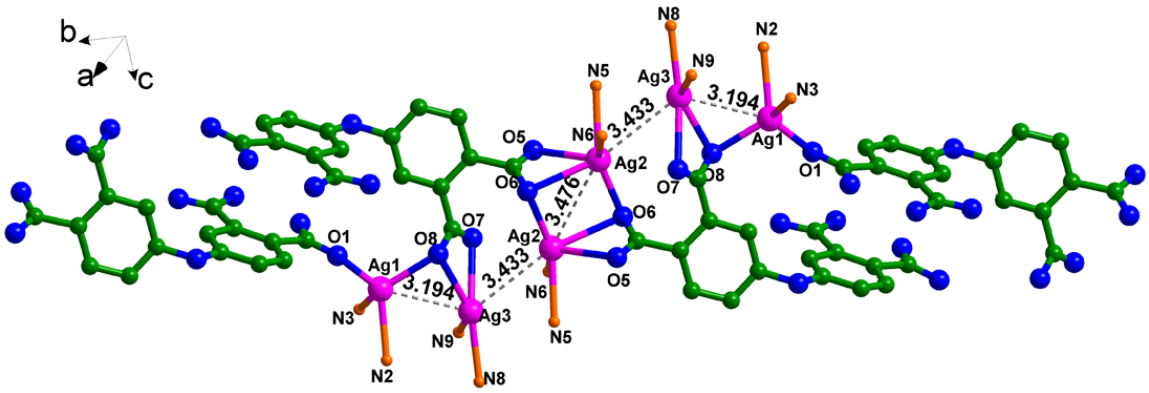


Fig. S8 Hexanuclear Ag(I) cluster of compound **8**.

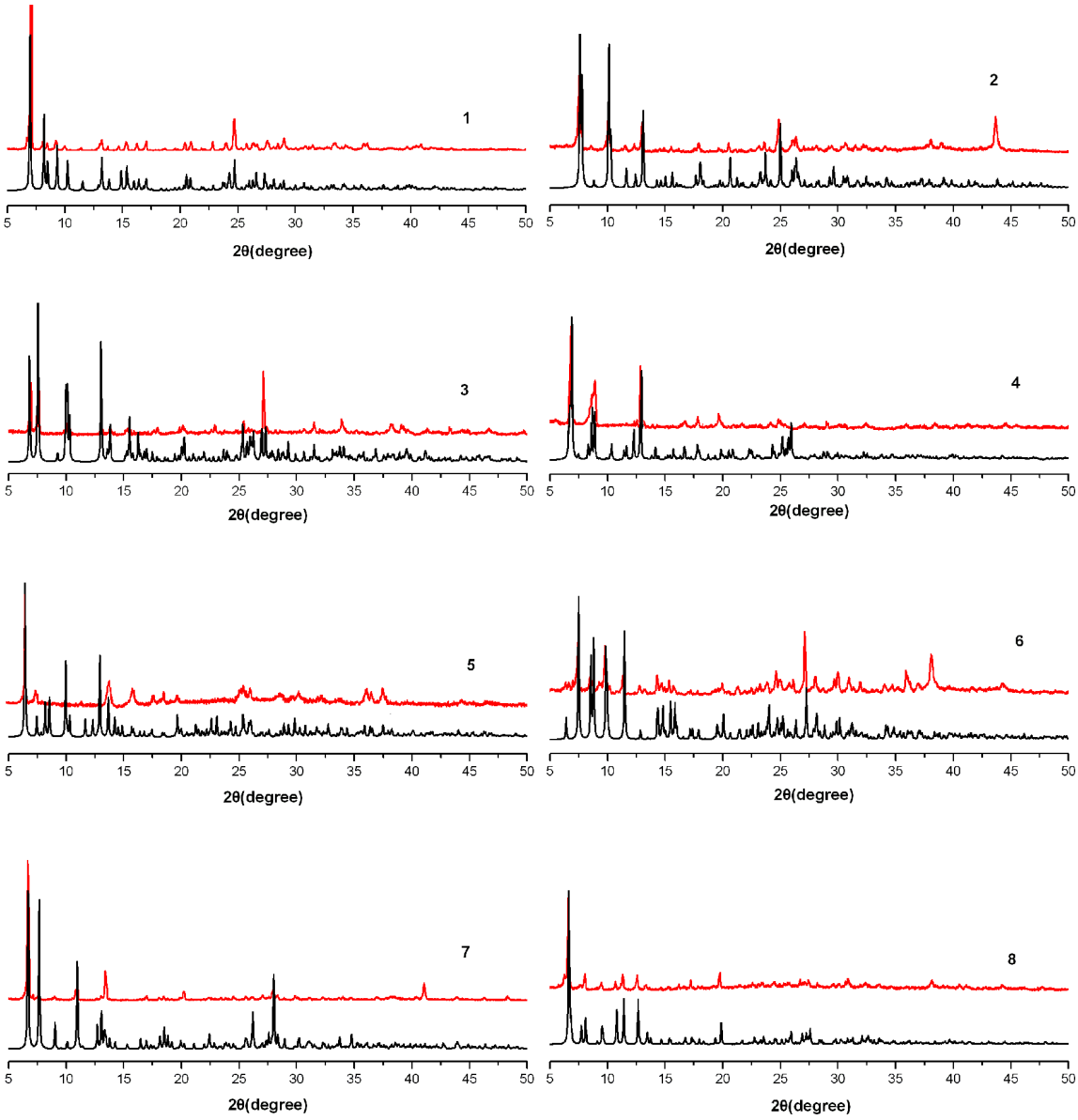


Fig. S9 Simulated (black) and experimental (red) PXRD patterns of **1**-**8**.