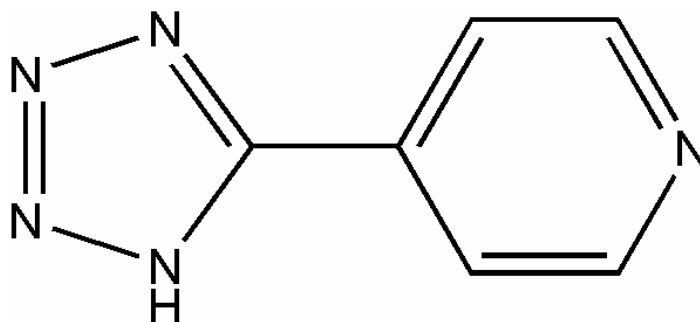


**Three 3D Metal-Organic Frameworks Constructed from
Keggin Polyanions and Multi-nuclear Ag^I Clusters:
Assembly, Structures and Properties**

Xiu-Li Wang, Na Li, Ai-Xiang Tian, Jun Ying, Guo-Cheng Liu, Hong-Yan Lin, and
Dan Zhao

*Department of Chemistry, Bohai University, Liaoning Province Silicon Materials
Engineering Technology Research Center, Jinzhou 121013, P. R. China.*



Scheme S1. The rigid N-donor ligand 5-(4-pyridyl)-tetrazole (ptzH).

Supporting information

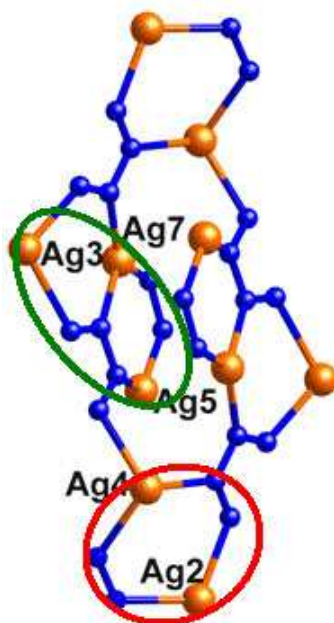


Fig. S1. The multi-nuclear subunit containing a pair of tri-nuclear subunits [$\text{Ag}_3(\text{ptz})_3$] (in green cycle) and a pair of binuclear subunits [$\text{Ag}_2(\text{ptz})_2$] (in red cycle).

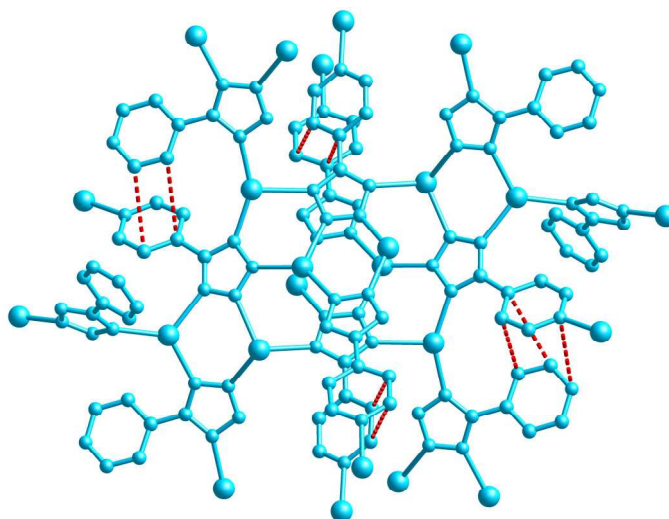


Fig. S2. The π - π stacking interactions between the corresponding pyridyl groups in the multi-nuclear unit (π - π interaction distances: 3.581 to 3.9 Å).

Supporting information

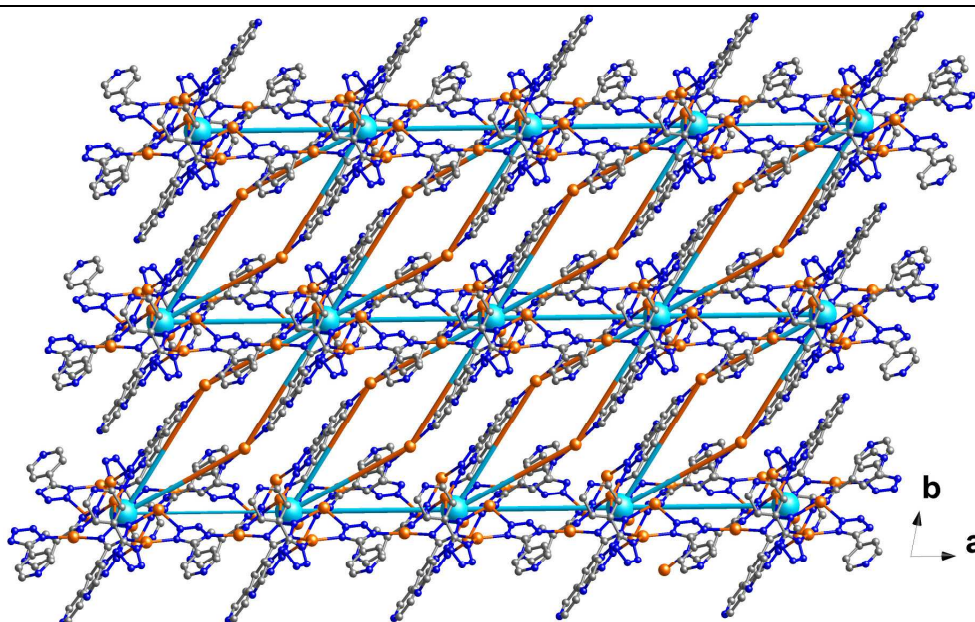


Fig. S3. Illustration of the 2D network of compound 1.

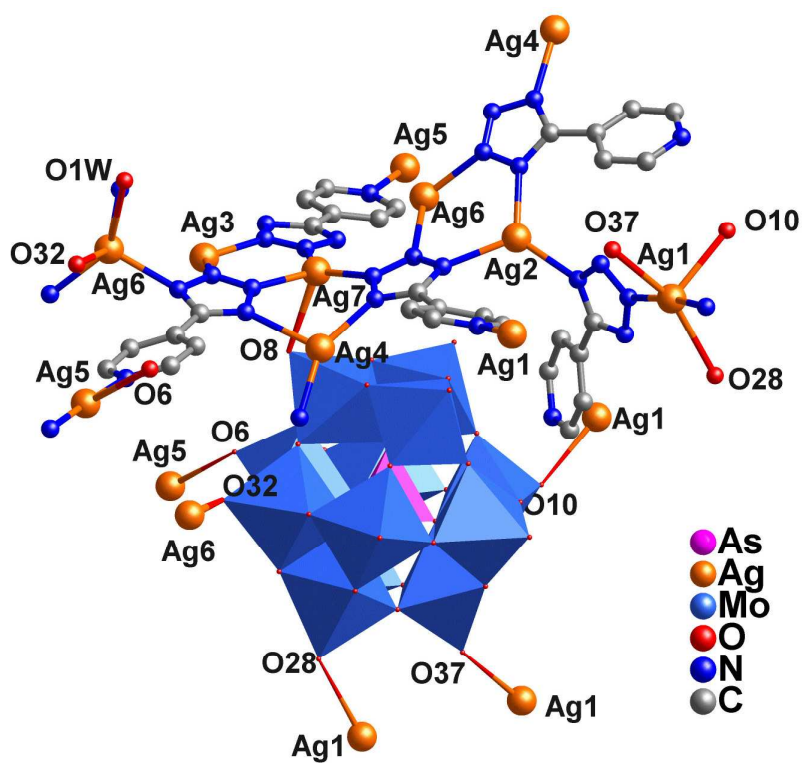


Fig. S4. Ball-and-stick and polyhedral representation of the structural unit of compound 3 and the coordination environment of the Ag^{I} cations (H atoms were omitted for clarity).

Supporting information

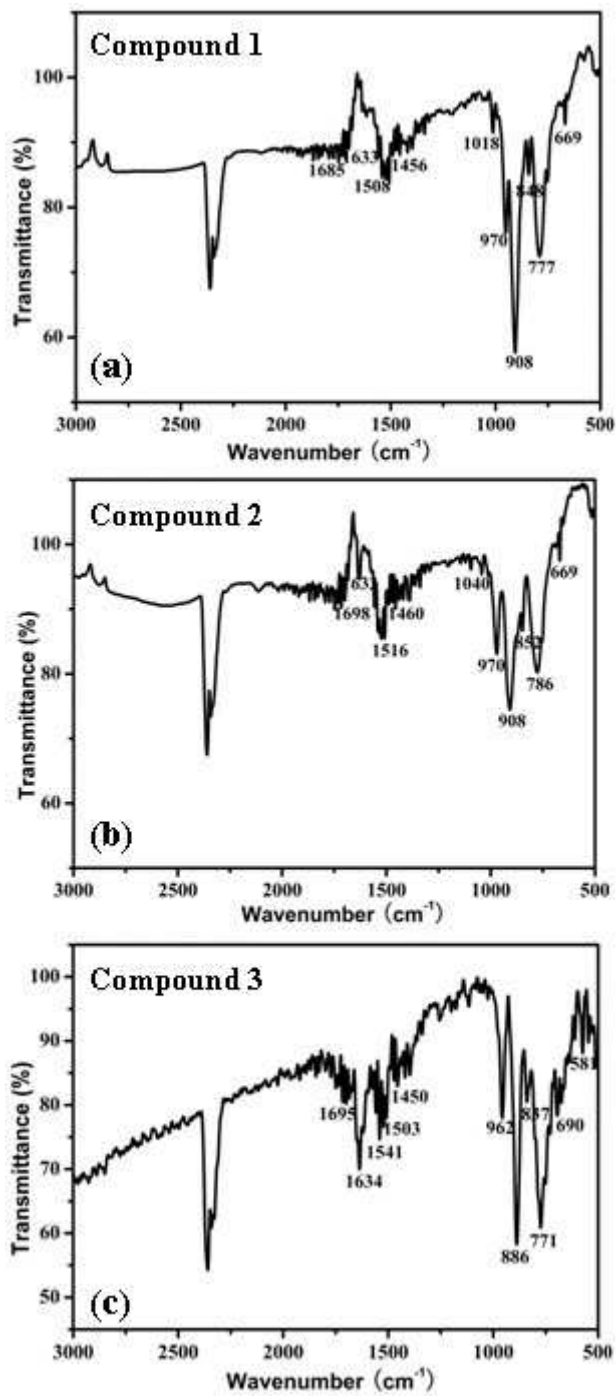


Fig. S5. IR spectra of compounds 1–3.

Supporting information

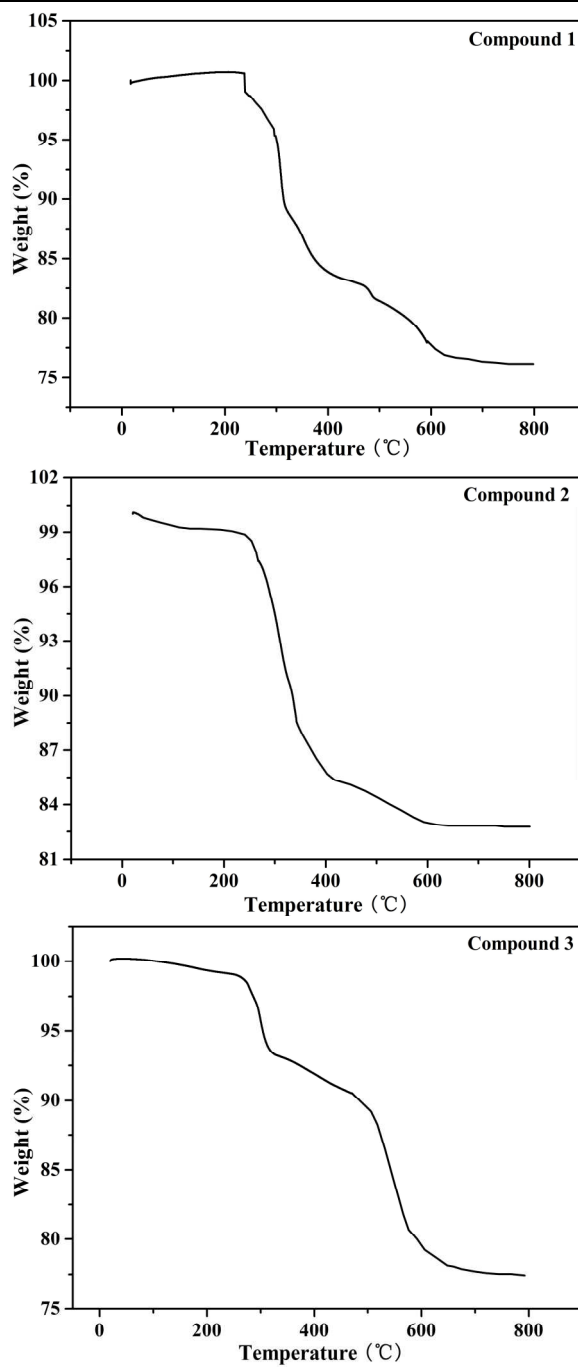


Fig. S6. The TG curves of compounds 1–3.

Supporting information

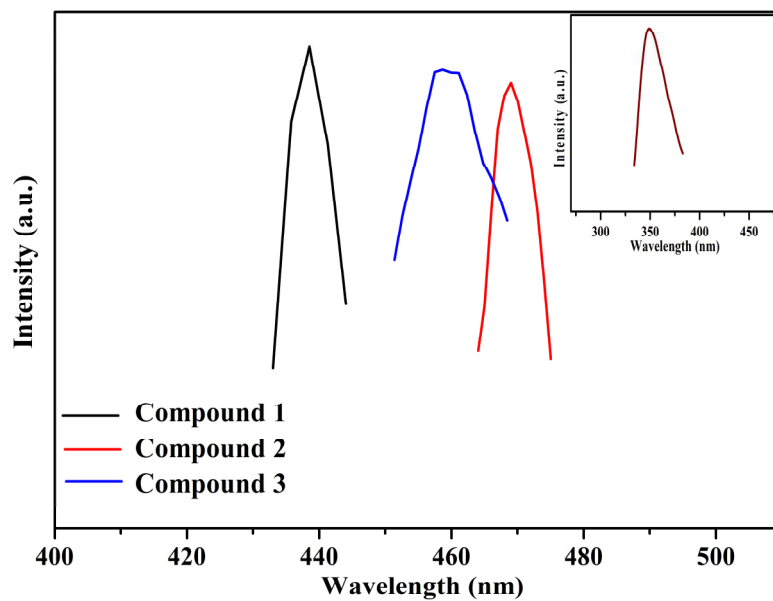


Fig. S7. The emission spectra of compounds 1–3, and the free ptzH ligand (inset).

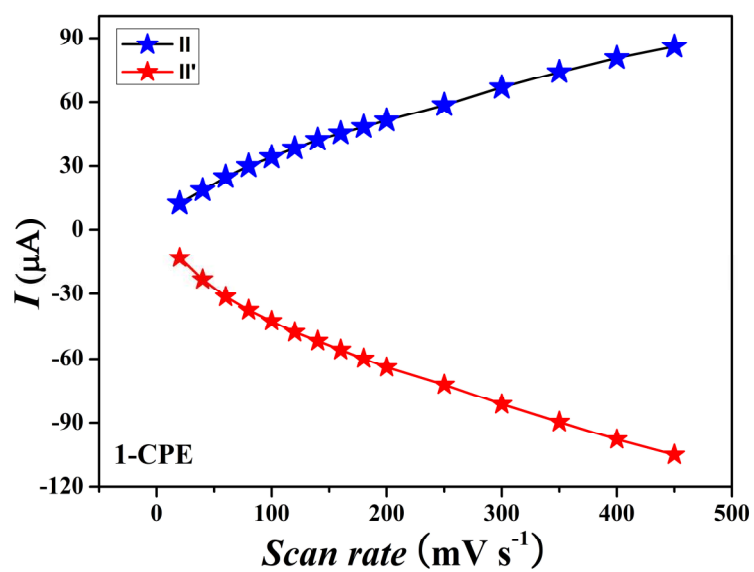


Fig. S8. The plot of the cathodic/anodic peak currents vs. scan rates of the 1-CPE.

Supporting information

Table S1. Selected bond distances (Å) and angles (°) for compounds **1–3**.

Compound 1			
Ag(1)–N(9)	2.126(5)	Ag(1)–N(5)	2.132(5)
Ag(1)–Ag(5)#1	3.3079(8)	Ag(2)–N(14)	2.234(5)
Ag(2)–N(18)	2.245(5)	Ag(2)–N(23)#2	2.305(5)
N(23)–Ag(2)#2	2.305(5)	Ag(3)–N(22)	2.203(5)
Ag(3)–N(20)#3	2.190(5)	N(20)–Ag(3)#3	2.190(5)
Ag(3)–N(4)	2.444(5)	Ag(4)–N(7)#2	2.297(5)
Ag(4)–N(12)#4	2.343(5)	Ag(4)–N(16)	2.390(5)
N(7)–Ag(4)#2	2.297(5)	N(12)–Ag(4)#4	2.343(5)
Ag(4)–O(2W)	2.409(10)	Ag(5)–N(1)#5	2.187(6)
Ag(5)–N(21)	2.234(5)	Ag(5)–O(1W)	2.393(12)
N(1)–Ag(5)#7	2.187(6)	Ag(5)–Ag(1)#1	3.3079(8)
Ag(6)–O(39)	2.598(4)	Ag(6)–N(10)	2.136(5)
Ag(6)–N(25)	2.161(5)	Ag(6)–O(4)	2.586(4)
N(15)–Ag(7)#7	2.210(6)	Ag(7)–N(15)#5	2.210(6)
Ag(7)–N(17)	2.242(5)	Ag(7)–N(19)	2.377(5)
Ag(7)–O(3)	2.552(4)	N(9)–Ag(1)–N(5)	174.3(2)
N(9)–Ag(1)–Ag(5)#1	89.47(16)	N(5)–Ag(1)–Ag(5)#1	94.15(16)
C(10)–N(5)–Ag(1)	123.7(4)	C(12)–N(9)–Ag(1)	122.1(4)
C(6)–N(5)–Ag(1)	117.4(5)	C(2)–N(9)–Ag(1)	120.3(4)
N(14)–Ag(2)–N(18)	126.09(18)	N(14)–Ag(2)–N(23)#2	120.75(18)
C(4)–N(14)–Ag(2)	136.0(4)	N(3)–N(14)–Ag(2)	116.7(4)
C(3)–N(18)–Ag(2)	135.9(4)	C(19)–N(23)–Ag(2)#2	139.2(4)
N(7)–N(18)–Ag(2)	118.4(4)	N(16)–N(23)–Ag(2)#2	115.7(4)
N(18)–Ag(2)–N(23)#2	113.10(17)	N(20)#3–Ag(3)–N(22)	148.84(19)
N(20)#3–Ag(3)–N(4)	104.47(17)	N(22)–Ag(3)–N(4)	106.49(18)
N(19)–N(4)–Ag(3)	110.7(4)	C(15)–N(4)–Ag(3)	142.8(4)
N(24)–N(20)–Ag(3)#3	115.1(4)	N(17)–N(22)–Ag(3)	118.0(4)

Supporting information

C(3)–N(20)–Ag(3)#3	138.4(4)	C(19)–N(22)–Ag(3)	135.6(4)
N(18)–N(7)–Ag(4)#2	125.5(4)	N(17)–N(16)–Ag(4)	123.6(4)
C(15)–N(12)–Ag(4)#4	134.9(4)	N(21)–N(12)–Ag(4)#4	114.8(4)
N(23)–N(16)–Ag(4)	125.5(4)	N(24)–N(7)–Ag(4)#2	121.6(4)
N(7)#2–Ag(4)–N(12)#4	111.22(18)	N(7)#2–Ag(4)–N(16)	105.31(18)
N(12)#4–Ag(4)–N(16)	106.60(18)	N(7)#2–Ag(4)–O(2W)	138.5(3)
N(12)#4–Ag(4)–O(2W)	106.6(3)	N(16)–Ag(4)–O(2W)	78.8(3)
N(11)–N(1)–Ag(5)#7	132.7(6)	O(1W)–Ag(5)–Ag(1)#1	68.2(2)
N(15)–N(1)–Ag(5)#7	117.3(4)	N(12)–N(21)–Ag(5)	127.2(4)
N(19)–N(21)–Ag(5)	118.8(4)	N(21)–Ag(5)–Ag(1)#1	102.14(13)
N(1)#5–Ag(5)–N(21)	124.3(2)	N(1)#5–Ag(5)–O(1W)	129.3(3)
N(21)–Ag(5)–O(1W)	103.7(3)	N(1)#5–Ag(5)–Ag(1)#1	85.41(16)
N(13)–N(10)–Ag(6)	120.9(4)	N(3)–N(10)–Ag(6)	127.1(4)
C(8)–N(25)–Ag(6)	123.5(4)	C(16)–N(25)–Ag(6)	118.8(4)
N(10)–Ag(6)–N(25)	169.9(2)	N(10)–Ag(6)–O(4)	90.49(17)
N(25)–Ag(6)–O(4)	85.42(17)	N(10)–Ag(6)–O(39)	98.16(18)
N(25)–Ag(6)–O(39)	91.57(18)	Mo(12)#3–O(39)–Ag(6)	136.0(2)
N(15)#5–Ag(7)–N(17)	141.1(2)	N(15)#5–Ag(7)–N(19)	119.7(2)
N(17)–Ag(7)–N(19)	97.95(18)	N(15)#5–Ag(7)–O(3)	91.97(18)
N(17)–Ag(7)–O(3)	109.98(17)	N(19)–Ag(7)–O(3)	72.01(16)
N(1)–N(15)–Ag(7)#7	120.9(5)	N(2)–N(15)–Ag(7)#7	129.5(6)
N(22)–N(17)–Ag(7)	131.6(4)	N(21)–N(19)–Ag(7)	116.4(4)
N(4)–N(19)–Ag(7)	133.7(4)	N(16)–N(17)–Ag(7)	118.4(4)

Symmetry codes: #1 $-x+2, -y+1, -z+1$; #2 $-x+1, -y+2, -z$; #3 $-x+2, -y+2, -z$; #4 $-x+1, -y+1, -z+1$; #5 $x-1, y-1, z$; #6 $-x+2, -y+1, -z$; #7 $x+1, y+1, z$

Compound 2

O(1W)–Ag(1)	2.26(2)	Ag(1)–N(20)	2.22(2)
Ag(1)–Ag(5)	3.061(4)	N(11)–Ag(2)	2.200(16)
N(24)–Ag(2)#3	2.135(15)	O(3)–Ag(2)#4	2.584(12)

Supporting information

Ag(2)–N(24)#3	2.135(16)	Ag(2)–O(3)#4	2.584(12)
N(3)–Ag(3)	2.305(15)	N(7)–Ag(3)	2.257(15)
N(9)–Ag(3)	2.239(13)	N(6)–Ag(4)	2.219(14)
N(13)–Ag(4)	2.198(15)	N(15)–Ag(4)	2.341(15)
Ag(4)–O(5)	2.577(14)	Ag(5)–N(10)#2	2.277(14)
N(5)–Ag(5)	2.232(16)	N(8)–Ag(5)	2.342(15)
N(10)–Ag(5)#2	2.277(14)	N(4)–Ag(6)	2.129(16)
N(25)–Ag(6)	2.140(17)	Ag(6)–Ag(8)#6	3.374(3)
N(2)–Ag(7)#1	2.181(14)	N(12)–Ag(7)	2.535(15)
N(14)–Ag(7)	2.209(15)	Ag(7)–N(2)#7	2.181(14)
N(17)–Ag(8)	2.220(18)	O(2W)–Ag(8)	2.377(19)
N(19)–Ag(8)	2.215(18)	Ag(8)–Ag(6)#6	3.374(3)
N(20)–Ag(1)–O(1W)	163.6(7)	N(13)–N(20)–Ag(1)	113.5(13)
N(20)–Ag(1)–Ag(5)	98.7(5)	C(1)–N(20)–Ag(1)	139.9(15)
O(1W)–Ag(1)–Ag(5)	68.6(5)	N(5)–Ag(5)–Ag(1)	132.5(4)
N(8)–Ag(5)–Ag(1)	81.3(4)	N(10)#2–Ag(5)–Ag(1)	93.7(4)
N(1)–N(24)–Ag(2)#3	122.1(12)	N(24)#3–Ag(2)–N(11)	169.9(7)
N(21)–N(24)–Ag(2)#3	126.2(13)	N(24)#3–Ag(2)–O(3)#4	92.4(5)
W(11)–O(3)–Ag(2)#4	145.6(8)	N(11)–Ag(2)–O(3)#4	84.0(6)
C(27)–N(11)–Ag(2)	121.7(14)	C(7)–N(11)–Ag(2)	118.9(13)
C(12)–N(3)–Ag(3)	137.9(11)	C(18)–N(7)–Ag(3)	138.2(16)
N(8)–N(3)–Ag(3)	118.4(11)	N(21)–N(7)–Ag(3)	113.7(12)
N(5)–N(9)–Ag(3)	118.9(11)	N(9)–Ag(3)–N(7)	126.8(6)
C(23)–N(9)–Ag(3)	135.2(11)	N(9)–Ag(3)–N(3)	113.3(5)
N(7)–Ag(3)–N(3)	119.9(6)	N(20)–N(13)–Ag(4)	128.6(15)
N(8)–N(6)–Ag(4)	120.6(11)	N(19)–N(13)–Ag(4)	122.1(13)
N(14)–N(6)–Ag(4)	127.9(11)	N(17)–N(15)–Ag(4)	116.2(12)
N(12)–N(15)–Ag(4)	132.0(12)	N(13)–Ag(4)–O(5)	84.9(6)
N(13)–Ag(4)–N(6)	136.5(7)	N(6)–Ag(4)–O(5)	116.7(5)

Supporting information

N(13)–Ag(4)–N(15)	118.3(7)	N(15)–Ag(4)–O(5)	74.6(5)
N(6)–Ag(4)–N(15)	104.2(6)	W(6)–O(5)–Ag(4)	114.4(7)
N(18)–N(5)–Ag(5)	120.9(11)	N(5)–Ag(5)–N(10)#2	121.4(6)
N(9)–N(5)–Ag(5)	126.7(12)	N(5)–Ag(5)–N(8)	111.0(5)
N(6)–N(8)–Ag(5)	125.7(11)	N(10)#2–Ag(5)–N(8)	109.7(5)
N(3)–N(8)–Ag(5)	121.6(11)	N(17)–N(10)–Ag(5)#2	112.6(12)
C(5)–N(10)–Ag(5)#2	138.1(11)	C(30)–N(4)–Ag(6)	122.6(14)
C(26)–N(25)–Ag(6)	125.1(14)	C(20)–N(4)–Ag(6)	119.9(13)
C(24)–N(25)–Ag(6)	117.5(17)	N(4)–Ag(6)–Ag(8)#6	86.8(5)
N(4)–Ag(6)–N(25)	174.3(7)	N(25)–Ag(6)–Ag(8)#6	92.8(5)
C(23)–N(2)–Ag(7)#1	137.4(12)	N(2)#7–Ag(7)–N(14)	149.7(5)
N(18)–N(2)–Ag(7)#1	113.8(10)	N(2)#7–Ag(7)–N(12)	102.3(5)
N(15)–N(12)–Ag(7)	108.6(11)	N(14)–Ag(7)–N(12)	107.9(5)
C(5)–N(12)–Ag(7)	144.6(11)	N(6)–N(14)–Ag(7)	117.9(11)
C(12)–N(14)–Ag(7)	135.5(11)	N(10)–N(17)–Ag(8)	127.1(15)
N(17)–Ag(8)–O(2W)	106.6(7)	N(15)–N(17)–Ag(8)	120.9(13)
N(19)–Ag(8)–Ag(6)#6	85.3(6)	N(22)–N(19)–Ag(8)	130.5(15)
N(17)–Ag(8)–Ag(6)#6	104.2(7)	N(13)–N(19)–Ag(8)	119.1(12)
O(2W)–Ag(8)–Ag(6)#6	70.7(5)	N(19)–Ag(8)–N(17)	119.7(7)
N(19)–Ag(8)–O(2W)	131.9(6)		

Symmetry codes: #1 $x+1, y, z$; #2 $-x+3, -y, -z+2$; #3 $-x+4, -y+1, -z+3$; #4 $-x+3, -y, -z+3$
 #5 $x+1, y-1, z$; #6 $-x+2, -y, -z+2$; #7 $x-1, y, z$; #8 $x-1, y+1, z$

Compound 3

Ag(1)–N(24)	2.144(11)	Ag(1)–N(1)	2.172(12)
Ag(2)–N(18)#1	2.251(12)	Ag(2)–N(3)	2.253(10)
N(18)–Ag(2)#1	2.251(12)	Ag(2)–N(5)	2.316(11)
Ag(3)–Ag(5)#2	3.375(2)	Ag(3)–N(25)	2.230(17)
Ag(3)–N(8)	2.238(12)	N(4)–Ag(4)#5	2.210(11)
Ag(4)–N(4)#3	2.210(11)	Ag(4)–N(20)	2.217(11)

Supporting information

Ag(4)–N(7)	2.502(11)	Ag(5)–N(16)	2.143(12)
Ag(5)–N(19)	2.147(12)	Ag(5)–Ag(3)#2	3.376(2)
Ag(6)–N(2)	2.290(12)	Ag(6)–N(12)#4	2.331(12)
N(12)–Ag(6)#4	2.331(12)	Ag(6)–N(6)	2.378(11)
Ag(7)–O(8)	2.572(10)	Ag(7)–N(13)	2.200(14)
Ag(7)–N(11)	2.240(11)	Ag(7)–N(21)	2.333(11)
N(23)–N(24)–Ag(1)	120.2(9)	N(9)–N(24)–Ag(1)	127.1(9)
C(10)–N(1)–Ag(1)	119.0(11)	C(8)–N(1)–Ag(1)	123.7(10)
N(24)–Ag(1)–N(1)	170.1(5)	N(18)#1–Ag(2)–N(3)	125.3(4)
N(18)#1–Ag(2)–N(5)	121.3(4)	N(3)–Ag(2)–N(5)	113.4(4)
C(7)–N(3)–Ag(2)	136.5(9)	N(2)–N(3)–Ag(2)	117.9(8)
N(6)–N(5)–Ag(2)	116.9(8)	C(17)–N(5)–Ag(2)	137.6(9)
N(9)–N(18)–Ag(2)#1	116.3(9)	C(15)–N(18)–Ag(2)#1	136.0(9)
N(25)–Ag(3)–N(8)	121.0(5)	N(25)–Ag(3)–Ag(5)#2	85.2(4)
N(21)–N(8)–Ag(3)	119.1(8)	N(12)–N(8)–Ag(3)	126.4(9)
N(8)–Ag(3)–Ag(5)#2	102.5(3)	N(4)#3–Ag(4)–N(20)	149.3(4)
N(4)#3–Ag(4)–N(7)	103.8(4)	N(20)–Ag(4)–N(7)	106.8(4)
C(16)–N(7)–Ag(4)	144.2(9)	N(21)–N(7)–Ag(4)	108.8(8)
N(11)–N(20)–Ag(4)	118.5(8)	C(17)–N(20)–Ag(4)	133.3(9)
C(7)–N(4)–Ag(4)#5	140.0(9)	N(10)–N(4)–Ag(4)#5	113.2(8)
N(16)–Ag(5)–N(19)	175.6(6)	N(16)–Ag(5)–Ag(3)#2	94.9(4)
N(19)–Ag(5)–Ag(3)#2	85.9(4)	C(5)–N(16)–Ag(5)	124.4(12)
C(2)–N(16)–Ag(5)	116.6(13)	C(11)–N(19)–Ag(5)	121.5(10)
C(30)–N(19)–Ag(5)	121.1(10)	N(2)–Ag(6)–N(12)#4	113.1(4)
N(2)–Ag(6)–N(6)	107.4(4)	N(12)#4–Ag(6)–N(6)	107.9(4)
N(10)–N(2)–Ag(6)	121.9(9)	N(3)–N(2)–Ag(6)	126.2(8)
N(5)–N(6)–Ag(6)	124.3(8)	N(11)–N(6)–Ag(6)	124.9(8)
C(16)–N(12)–Ag(6)#4	136.4(9)	N(8)–N(12)–Ag(6)#4	115.1(8)
N(13)–Ag(7)–N(11)	139.4(5)	N(13)–Ag(7)–N(21)	118.5(5)

Supporting information

N(11)–Ag(7)–N(21)	101.5(4)	N(13)–Ag(7)–O(8)	88.1(5)
N(11)–Ag(7)–O(8)	111.1(4)	N(21)–Ag(7)–O(8)	73.9(4)
N(20)–N(11)–Ag(7)	130.8(9)	N(6)–N(11)–Ag(7)	118.3(8)
N(25)–N(13)–Ag(7)	122.4(12)	N(22)–N(13)–Ag(7)	129.5(13)
N(8)–N(21)–Ag(7)	117.9(8)	N(7)–N(21)–Ag(7)	133.5(9)

Symmetry codes: #1 $-x+3, -y+2, -z$; #2 $-x+1, -y+1, -z-1$; #3 $x-1, y, z$; #4 $-x+2, -y+1, -z-1$

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