Supporting information for

Distinct nonlinear optical responses in three pairs of 2D homochiral Ag(I) enantiomers modulated by dicarboxylic acid ligands

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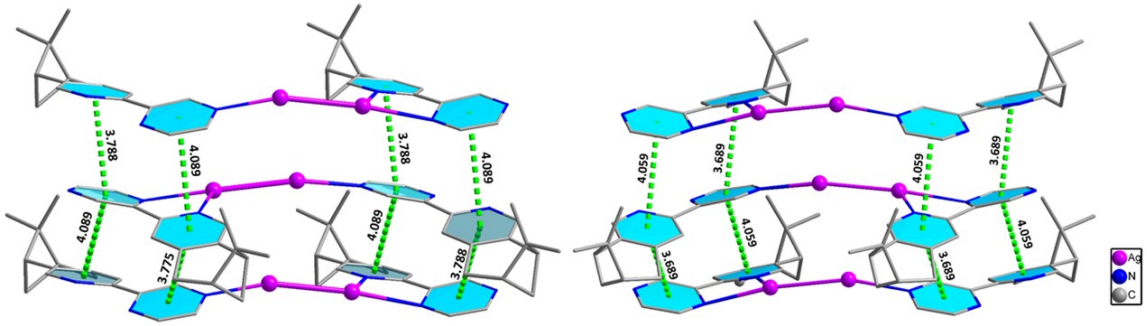

Fig. S1 The π···π interactions for **R1** (left) and **S1** (right).

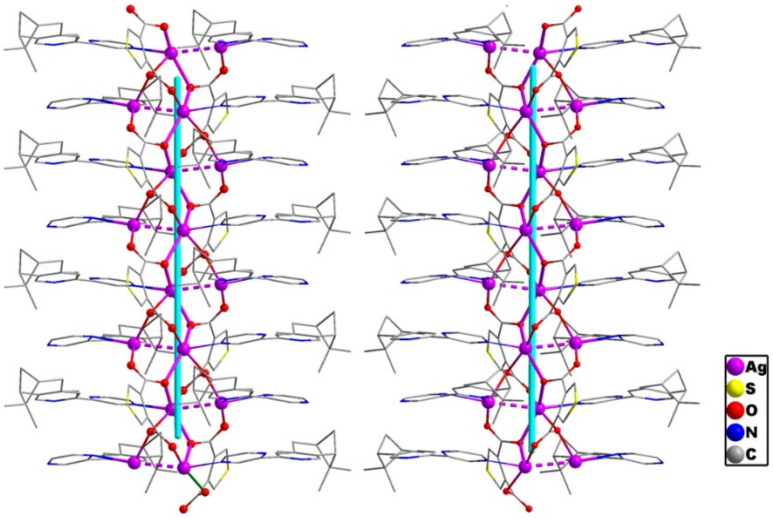

Fig. S2 View of the 1D right-handed (P) and left-handed (M) –Ag2(Ag1)–O– helical chains in **R2** (left) and **S2** (right). H atoms are removed for clarity.

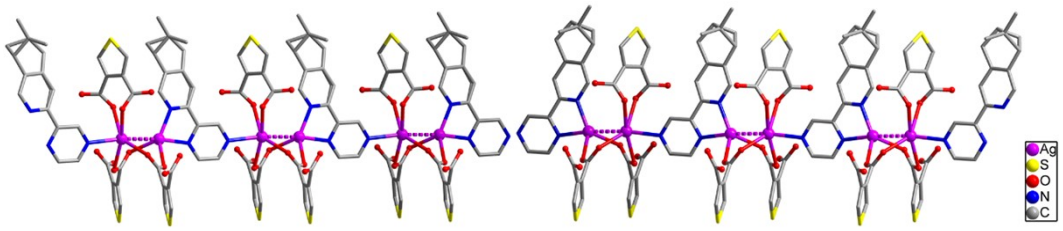

Fig. S3 The bridging of L_R/L_S between Ag2 units along the *a* axis for **R2** (left) and **S2** (right). H atoms are removed for clarity.

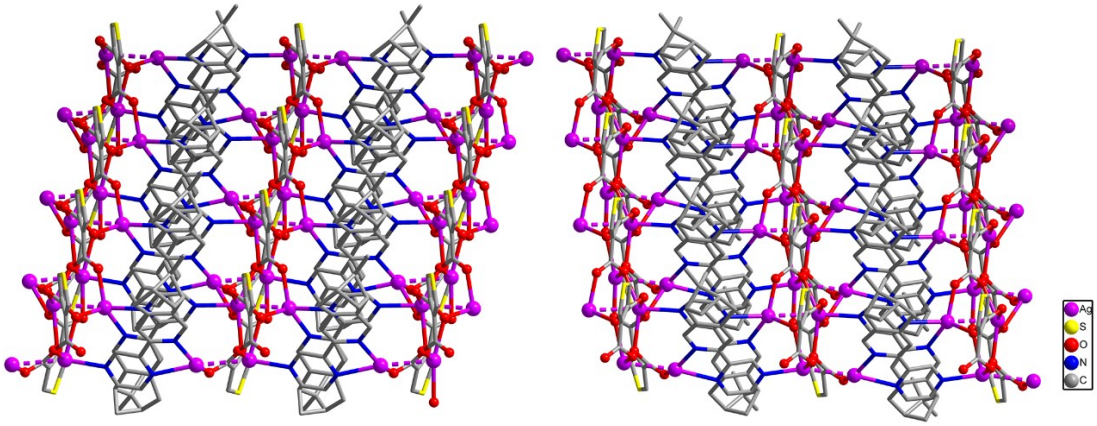

Fig. S4 View of the 2D networks of **R2** (left) and **S2** (right). H atoms are removed for clarity.

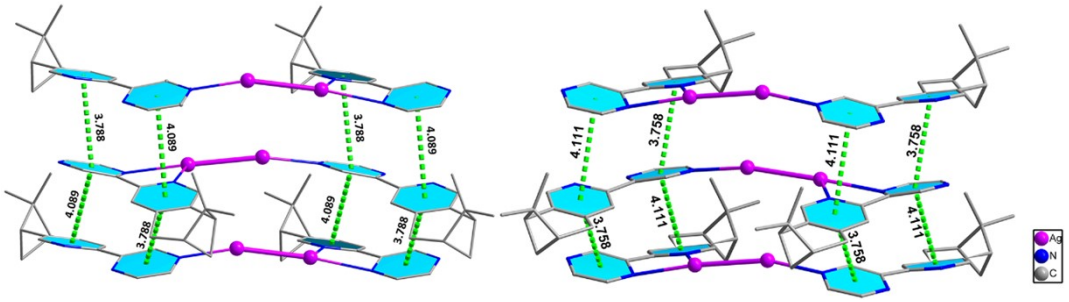

Fig. S5 The $\pi\cdots\pi$ interactions for **R2** (left) and **S2** (right).

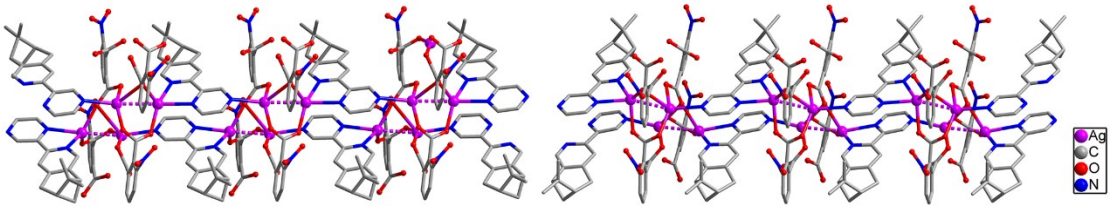

Fig. S6 The bridging of L_R/L_S between Ag4 units along the *b* axis for **R3** (left) and **S3** (right). H atoms are removed for clarity.

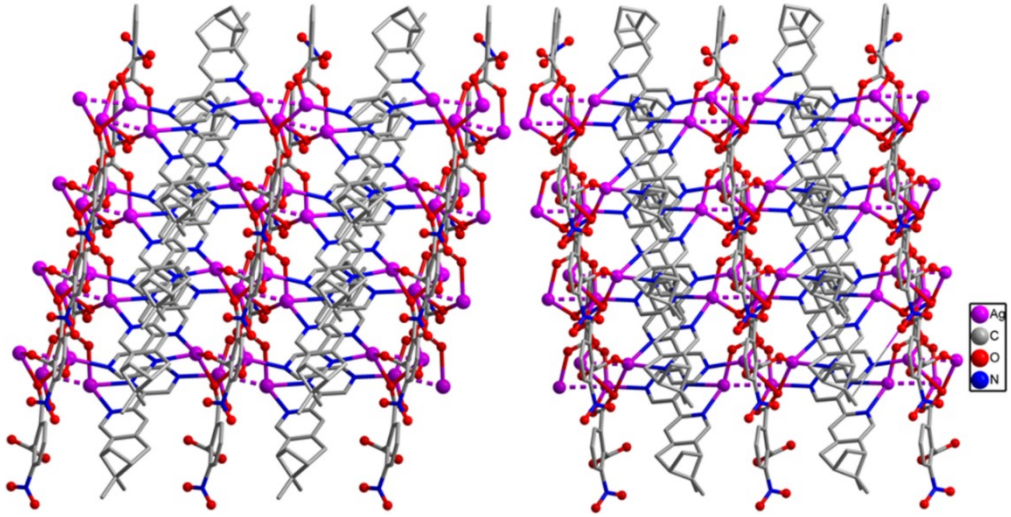

Fig. S7 The 2D networks of **R3** (left) and **S3** (right). H atoms are removed for clarity.

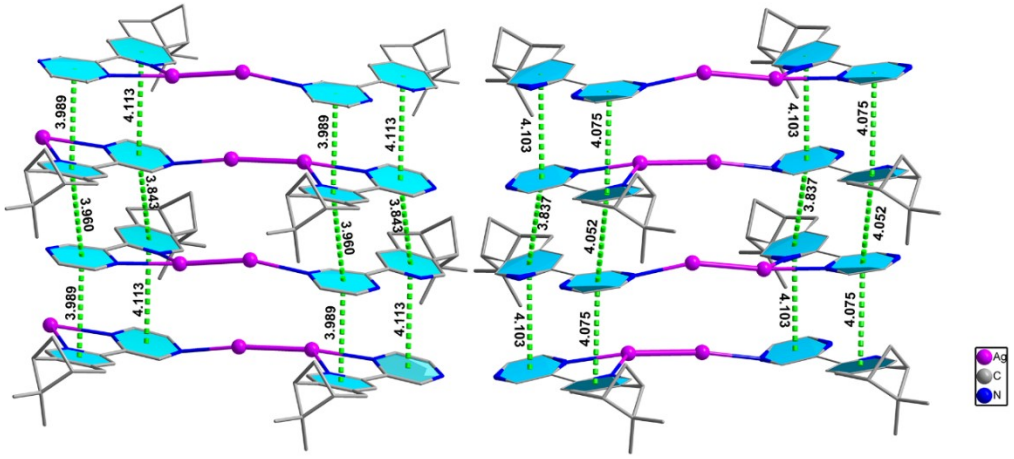

Fig. S8 The $\pi\cdots\pi$ interactions for **R3** (left) and **S3** (right).

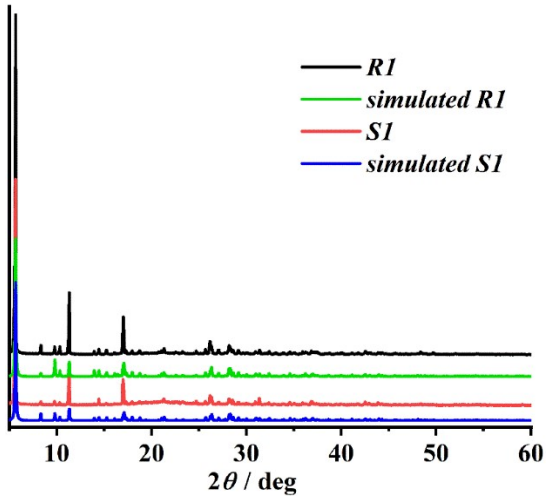

Fig. S9 The powder XRD patterns and the simulated ones from the single-crystal diffraction data for **R1** and **S1**.

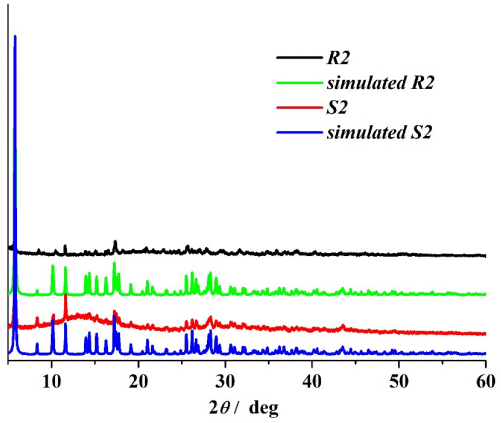

Fig. S10 The powder XRD patterns and the simulated ones from the single-crystal diffraction data for **R2** and **S2**.

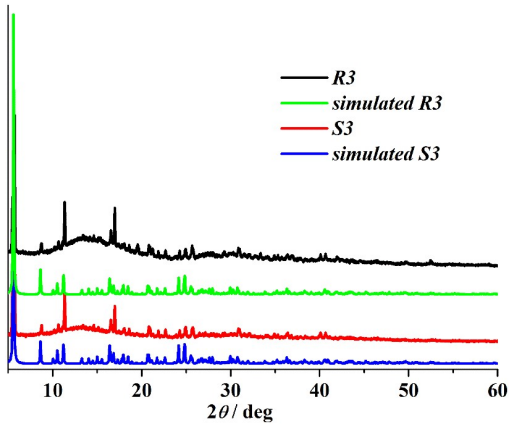

Fig. S11 The powder XRD patterns and the simulated ones from the single-crystal diffraction data for **R3** and **S3**.

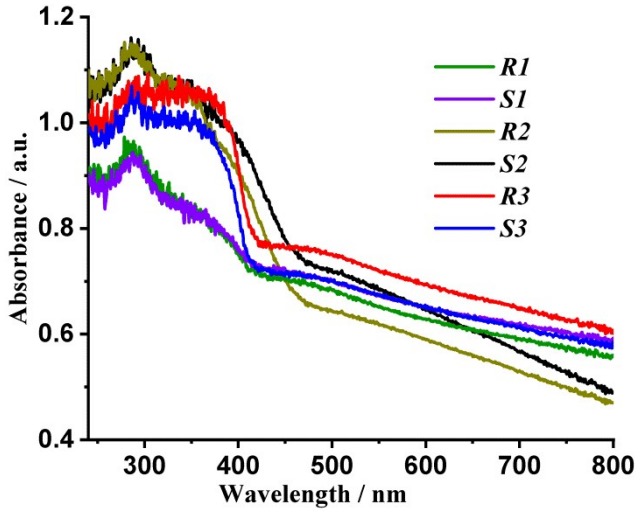

Fig. S12 The UV-vis diffuse reflectance spectra of **R1**/**S1**, **R2**/**S2** and **R3**/**S3**.

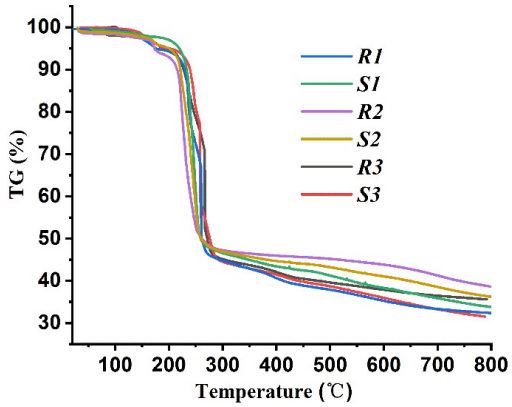

Fig. S13 TG plots of **R1**/**S1**, **R2**/**S2** and **R3**/**S3**.

Table S1. Crystallographic data and structure refinement parameters for **R1**/**S1**, **R2**/**S2** and **R3**/**S3**.

Complex	**R1**	**S1**	**R2**	**S2**	**R3**	**S3**
Chemical formula	$C_{24}H_{21}Ag_2N_3O_4$	$C_{24}H_{21}Ag_2N_3O_4$	$C_{22}H_{21}Ag_2N_3O_5S$	$C_{22}H_{21}Ag_2N_3O_5S$	$C_{48}H_{40}Ag_4N_8O_{12}$	$C_{48}H_{40}Ag_4N_8O_{12}$
Formula weight	629.16	631.18	653.20	653.70	1349.33	1352.36
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P1$	$P1$
a (Å)	10.6317(3)	10.6396(4)	10.5999(2)	10.5969(3)	7.4073(4)	7.4052(7)
b (Å)	6.9314(2)	6.9241(3)	6.9785(2)	6.9791(2)	10.3055(5)	10.3072(10)
c (Å)	15.6461(5)	15.6239(12)	15.2396(3)	15.2394(4)	15.7862(8)	15.8000(10)
α (deg)	90	90	90	90	92.756(4)	92.830(7)
β (deg)	93.261(3)	93.242(4)	90.403(2)	90.369(2)	90.02	90.07
γ (deg)	90	90	90	90	95.853(4)	95.982(8)
V(Å^3)	1151.13(6)	1149.17(11)	1127.27(4)	1127.03(5)	1197.37(11)	1197.91(18)
Z	2	2	2	2	1	1
D_c(g cm^{-3})	1.815	1.824	1.924	1.926	1.871	1.875
μ (mm^{-1})	13.952	13.976	15.152	15.155	13.544	13.538
F(000)	620.0	624.0	644.0	645.0	665.0	668.0
Reflections collected	10094	4035	4390	4287	6115	7780
Independent reflections	4054	3040	3222	3244	4084	5431
Data/restraints/parameters	4054/58/327	3040/1/300	3222/154/336	3244/66/327	4084/3/653	5431/78/662
GOF	1.043	1.102	1.056	1.084	0.932	1.069
R_1[I > = 2σ (I)][a]	0.0514	0.0731	0.0627	0.0626	0.0433	0.0961
wR_2 [I > = 2σ (I)][b]	0.1437	0.0648	0.1605	0.1762	0.1153	0.2419
Flack parameter	0.006(11)	-0.01(4)	-0.02(3)	-0.03(3)	0.020(13)	-0.03(3)

Table S2. Selected bond lengths (Å) and angle (°) for **R1**/**S1**, **R2**/**S2** and **R3**/**S3**.

R1		**S1**	
Ag2-Ag1A	3.0456(10)	Ag2-Ag1A	3.0447(17)
Ag2-O3B	2.546(10)	Ag2-O3B	2.571(16)
Ag2-O2A	2.411(9)	Ag2-O2A	2.397(13)
Ag2-O2B	2.613(8)	Ag2-O2B	2.629(13)
Ag2-N3C	2.423(9)	Ag2-N3C	2.428(16)
Ag2-O4	2.358(10)	Ag2-O4	2.36(2)
Ag1-O1	2.236(9)	Ag1-O1	2.235(16)
Ag1-O3D	2.365(8)	Ag1-O3D	2.336(15)
Ag1-N1	2.223(8)	Ag1-N1	2.216(13)
Ag1-N2	2.569(9)	Ag1-N2	2.572(15)
A: +X, –1+Y, +Z; B: –X, –1/2+Y, 1–Z; C: –1+X, –1+Y, +Z; D: +X, 1+Y, +Z.		A: +X, 1+Y,+Z; B: 2–X, 1/2+Y, 1–Z; C: 1+X, 1+Y, +Z; D: +X, –1+Y, +Z.	
O2A-Ag2-O2B	142.72(18)	O2A-Ag2-O2B	143.1(4)
O2A-Ag2-N3C	114.0(3)	O2B-Ag2-N3C	114.5(6)
O2A-Ag2-O3B	93.6(3)	O2B-Ag2-O3A	93.4(5)
O4-Ag2-O2A	94.6(3)	O4-Ag2-O2B	94.5(6)
O4-Ag2-O2B	110.1(4)	O4-Ag2-O2A	109.4(5)
O4-Ag2-N3C	82.4(3)	O4-Ag2-N3C	82.9(5)
O4-Ag2-O3B	163.9(3)	O4-Ag2-O3A	164.2(5)
N3C-Ag2-O2B	97.1(3)	N3C-Ag2-O2A	96.3（4）
N3C-Ag2-O3B	81.6(3)	N3C-Ag2-O3A	81.4(5)
O3B-Ag2-O2B	70.2(3)	O2A-Ag2-O3A	70.8(4)
O1-Ag1-N2	99.3(3)	O1-Ag1-N2	99.1(5)
O1-Ag1-O3D	95.8(3)	O1-Ag1-O3D	95.1(6)
N1-Ag1-O1	145.4(4)	N1-Ag1-O1	145.5(6)
N1-Ag1-N2	70.4(3)	N1-Ag1-N2	70.2(5)
N1-Ag1-O3D	118.5(3)	N1-Ag1-O3D	119.1(6)
O3D-Ag1-N2	103.3(3)	O3D-Ag1-N2	103.4(5)
A: +X, –1+Y, +Z; B: –X, –1/2+Y, 1–Z; C: –1+X, –1+Y, +Z; D: +X, 1+Y, +Z.		A: 2–X, 1/2+Y, 1–Z; B: +X, 1+Y, +Z; C: 1+X, 1+Y, +Z; D: +X, –1+Y, +Z.	
R2		**S2**	
Ag2-Ag1A	3.0288(13)	Ag2-Ag1	3.0306(14)
Ag2-O4B	2.420(13)	Ag2-O4C	2.407(13)
Ag2-O2C	2.537(10)	Ag2-O2A	2.541(11)
Ag2-O2A	2.416(10)	Ag2-O2	2.404(11)
Ag2-N3	2.395(11)	Ag2-N3B	2.388(11)
Ag2-O3C	2.552(12)	Ag2-O3A	2.543(14)
Ag1-O1	2.244(12)	Ag1-O1	2.241(12)
Ag1-O3D	2.373(12)	Ag1-O3C	2.390(12)
Ag1-N2	2.542(12)	Ag1-N1	2.207(6)

Ag1-N1	2.216(6)	Ag1-N1	2.207(6)
A: –1+X, +Y, +Z; B: –1+X, 1+Y, +Z; C: 1–X, 1/2+Y, 1–Z; D: +X, 1+Y, +Z.		A: 2–X, –1/2+Y, 1–Z; B: 1+X, +Y, +Z; C: +X, –1+Y, +Z.	
O4A-Ag2-O2C	115.1(4)	O4B-Ag2-O2A	115.1(5)
O4A-Ag2-O3C	165.1(4)	O4B-Ag2-O3A	165.7(4)
O2B-Ag2-O4A	91.4(4)	O2-Ag2-O4B	91.2(5)
O2B-Ag2-O2C	143.3(2)	O2-Ag2-O2A	143.4(2)
O2B-Ag2-O3C	89.2(4)	O2-Ag2-O3A	89.1(4)
O2C-Ag2-O3C	71.5(3)	O2A-Ag2-O3A	71.7(4)
N3-Ag2-O4A	83.2(4)	N3C-Ag2-O4B	83.0(4)
N3-Ag2-O2C	94.0(4)	N3C-Ag2-O2A	93.8(4)
N3-Ag2-O2B	114.9(4)	N3C-Ag2-O2	115.3(5)
N3-Ag2-O3C	83.1(4)	N3C-Ag2-O3A	84.0(5)
O1-Ag1-$O3^5$	93.1(5)	O1-Ag1-O3B	93.1(5)
O1-Ag1-N2	98.8(4)	O1-Ag1-N2	99.3(4)
$O3^5$-Ag1-N2	110.2(5)	O3B-Ag1-N2	110.7(5)
N1-Ag1-O1	144.7(4)	N1-Ag1-O1	145.4(5)
N1-Ag1-$O3^5$	122.2(4)	N1-Ag1-O3B	121.5(4)
N1-Ag1-N2	70.8(3)	N1-Ag1-N2	70.5(4)
A: –1+X, 1+Y, +Z; B: –1+X, +Y, +Z; C: 1–X, 1/2+Y, 1–Z.		A: 2–X, –1/2+Y, 1–Z; B: +X, –1+Y, +Z; C: 1+X, +Y, +Z.	
R3		**S3**	
Ag1-O4D	2.346(7)	Ag1-O4	2.225(15)
Ag1-O6	2.267(14)	Ag1-O6B	2.43(2)
Ag1-N2	2.439(12)	Ag1-N2	2.45(2)
Ag1-N1	2.319(9)	Ag1-N1	2.29(2)
Ag2-N3C	2.366(10)	Ag2-N3A	2.40(3)
Ag2-O6B	2.874(13)	Ag2-O6B	2.59(2)
Ag2-O3	2.235(6)	Ag2-O3	2.265(15)
Ag2-O8B	2.278(8)	Ag2-O8B	2.256(19)
Ag3-O5	2.219(9)	Ag3-O5	2.228(15)
Ag3-O7B	2.635（11）	Ag3-O7B	2.857(30)
Ag3-O10	2.260(7)	Ag3-O10	2.219(13)
Ag3-N6	2.391(11)	Ag3-N6	2.37(2)
Ag4-N4A	2.286(9)	Ag4-N4A	2.320(17)
Ag4-N5A	2.409(10)	Ag4-N5A	2.42(2)
Ag4-O7B	2.419(9)	Ag4-O7B	2.23(2)
Ag4-O9	2.240(7)	Ag4-O9	2.329(17)
Ag2-Ag1B	2.8916(13)	Ag1-Ag2	2.910(3)
A: +X, –1+Y, +Z; B: 1+X, +Y, +Z; C: 1+X, –1+Y, +Z; D: –1+X, +Y, +Z.		A: +X, –1+Y, +Z; B: –1+X, +Y, +Z.	
O4D-Ag1-N2	89.7(3)	O4-Ag1-N2	102.7(7)
O6-Ag1-O4D	108.9(4)	O4-Ag1-O6B	107.9(7)

O6-Ag1-N2	114.1(4)	N2-Ag1-O6B	109.0(7)
O6-Ag1-N1	124.9(4)	N1-Ag1-O6B	104.8(7)
N1-Ag1-O4D	126.2(3)	O4-Ag1-N1	146.8(7)
N1-Ag1-N2	69.4(3)	N1-Ag1-N2	71.1(7)
N3C-Ag2-O6B	116.6(4)	N3A-Ag2-O6B	120.2(7)
O3-Ag2-N3C	107.7(3)	O3-Ag2-N3A	96.9(6)
O3-Ag2-O6B	88.5(3)	O3-Ag2-O6B	92.7(7)
O3-Ag2-O8B	150.0(3)	O8B-Ag2-O3	148.4(7)
O8B-Ag2-N3C	101.1(3)	O8B-Ag2-N3A	108.6(8)
O8B-Ag2-O6B	86.1(4)	O8B-Ag2-O6B	90.4(9)
O7B-Ag3-O10	91.9(3)	O7B-Ag3-O10	87.7(7)
O5-Ag3-N6	107.7(3)	O5-Ag3-N6	102.8(9)
O7B-Ag3-N6	119.5(3)	O7B-Ag3-N6	118.4(9)
O5-Ag3-O7B	92.1(3)	O5-Ag3-O7B	84.2(9)
O10-Ag3-N6	97.3(3)	O10-Ag3-N6	107.0(7)
O10-Ag3-O5	148.5(3)	O10-Ag3-O5	149.4(8)
N4A-Ag4-N5A	71.0(3)	N4A-Ag4-N5A	69.0(7)
N4A-Ag4-O7B	104.6(3)	O7B-Ag4-N4A	125.0(9)
N5A-Ag4-O7B	108.0(4)	O7B-Ag4-N5A	114.0(12)
O9-Ag4-N4A	147.1(3)	N4A-Ag4-O9	125.9(7)
O9-Ag4-N5A	103.2(3)	O9-Ag4-N5A	90.0(8)
O9-Ag4-O7B	107.9(3)	O7B-Ag4-O9	109.1(9)
A: +X, –1+Y, +Z; B: 1+X, +Y, +Z; C: 1+X, –1+Y, +Z; D: –1+X, +Y, +Z.		A: +X, –1+Y, +Z; B: –1+X, +Y, +Z; C: +X, 1+Y, +Z; D: 1+X, +Y, +Z.	

Table S3. Four-Coordinate τ_4 Parameters[a] for **R1**/**S1**, **R2**/**S2** and **R3**/**S3**.

Silver	τ_4	α	β
Ag1 in **R1**	0.68	145.4(4)	118.5(3)
Ag2 in **R1**	0.56	163.9(3)	114.0(3)
Ag1 in **S1**	0.68	146.5(8)	117.4(8)
Ag2 in **S1**	0.59	162.9(6)	113.8(7)
Ag1 in **R2**	0.66	144.7	122.2
Ag1 in **S2**	0.66	145.4	121.5
Ag1 in **R3**	0.72	148.6(8)	109.9(10)
Ag2 in **R3**	0.63	150.4(7)	120.4(8)
Ag4 in **R3**	0.78	126.7(7)	124.0(8)
Ag1 in **S3**	0.74	146.7(7)	109.1(8)
Ag2 in **S3**	0.65	148.3(7)	120.3(7)

[a]$\tau_4 = [360 - (\alpha+\beta)]/141$, where α and β are the largest angles around the metal centers. For a perfect square-planar geometry, τ_4 equals 0, and a perfect tetrahedral geometry is described when $\tau_4 = 1$.