Electronic Supplementary Material (ESI) for Dalton Transactions.

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Photochromic and luminescent switchable iodoargentate hybrids directed by solvated lanthanide cations

Electronic Supplementary Information

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Content

1. Chemical analytical experiment for photoproducts

Dissolve 0.15 mmol powder samples of **1**, **1P**, **2**, **2P**, **3**, **3P**, **4** and **4P** in 4 ml dimethyl sulfoxide containing 1 mmol NaI and 1 mmol $Na_2S_2O_3$, respectively. After several minutes, a spot of black precipitated particles are separated out in the solution of **1P-4P**, then put black precipitated particles washed, drained and treated it with concentrated HNO_3, solution of NaCl and concentrated $NH_3{\cdot}H_2O$ in turn, which further successively confirmed as metal silver. The whole process is carried out in the dark at room temperature.

2. Figures

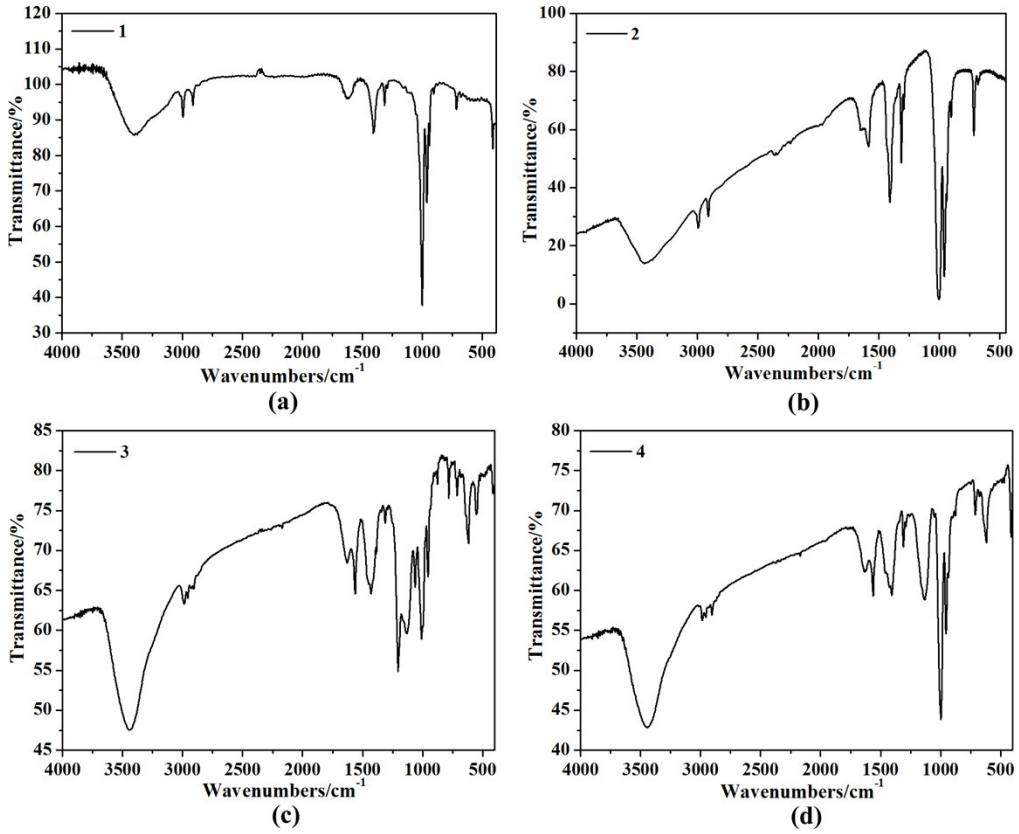

Fig. S1 IR spectra of **1** (a), **2** (b), **3** (c) and **4** (d).

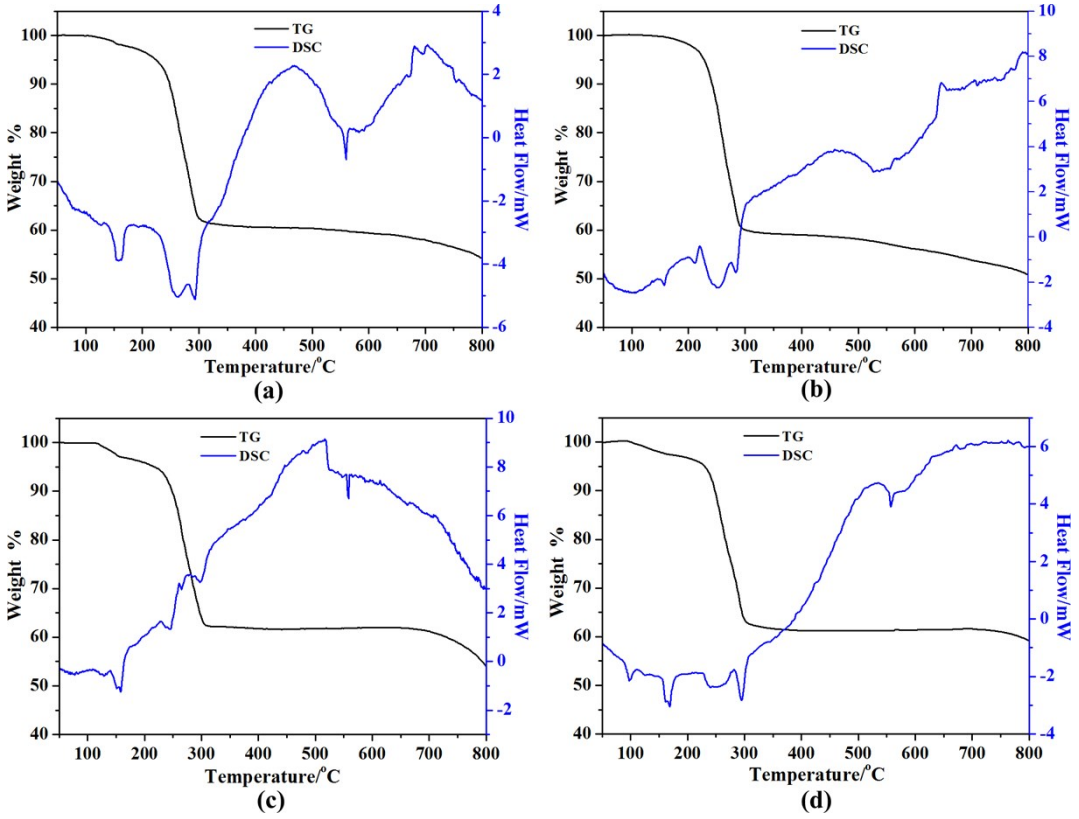

Fig. S2 TG-DSC curve of **1** (a), **2** (b), **3** (c) and **4** (d).

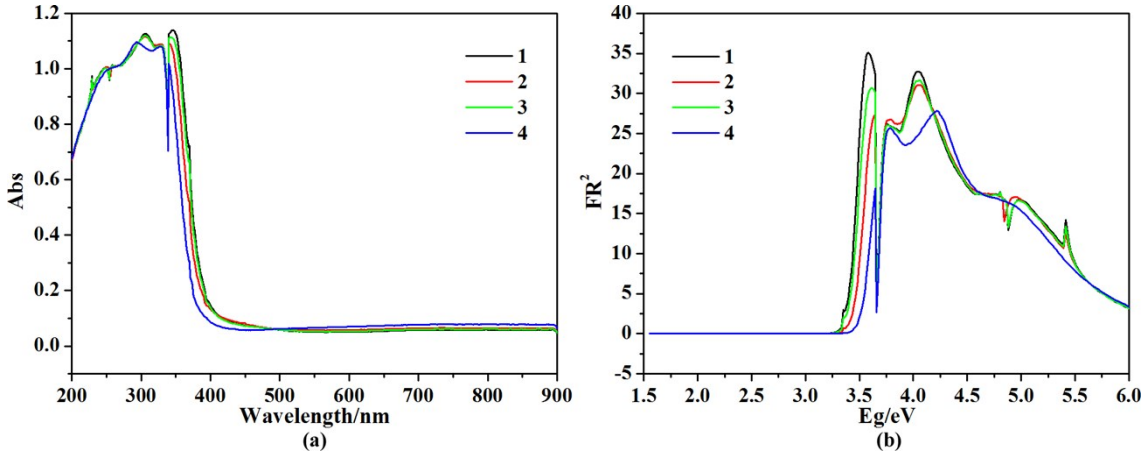

Fig. S3 The UV-vis absorption spectra and band gaps of **1**, **2**, **3** and **4**.

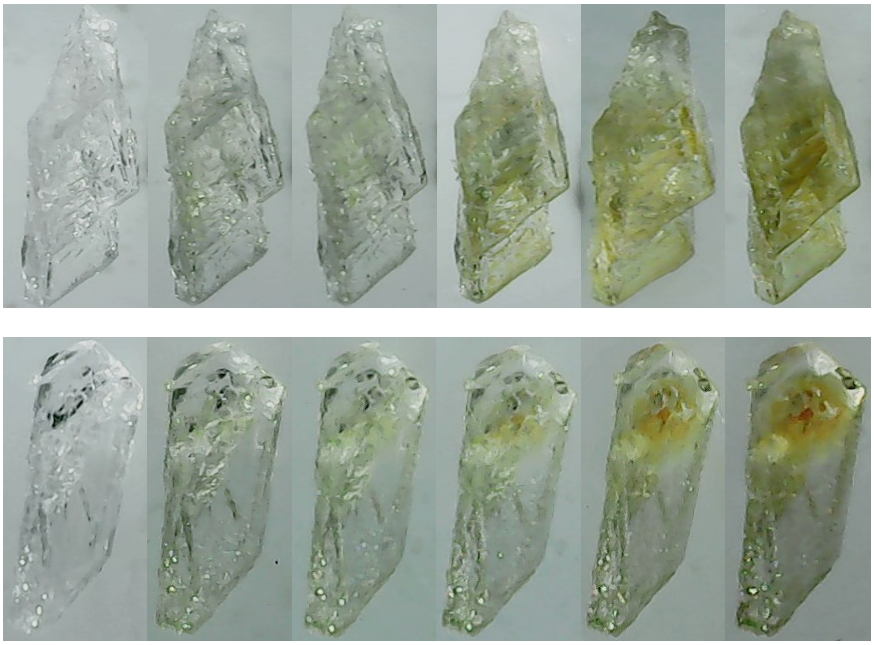

Fig. S4 The coloration process of crystals for **1** (up) and **4** (below).

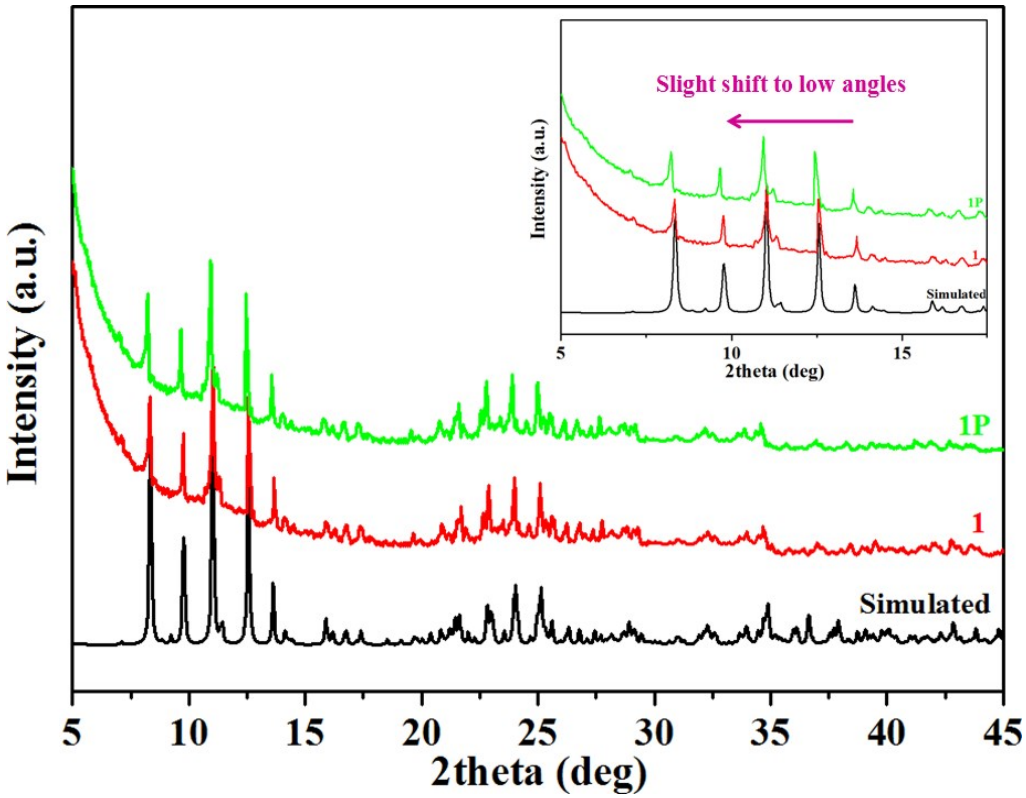

Fig. S5 The comparison of PXRD patterns of **1** and **1P**.

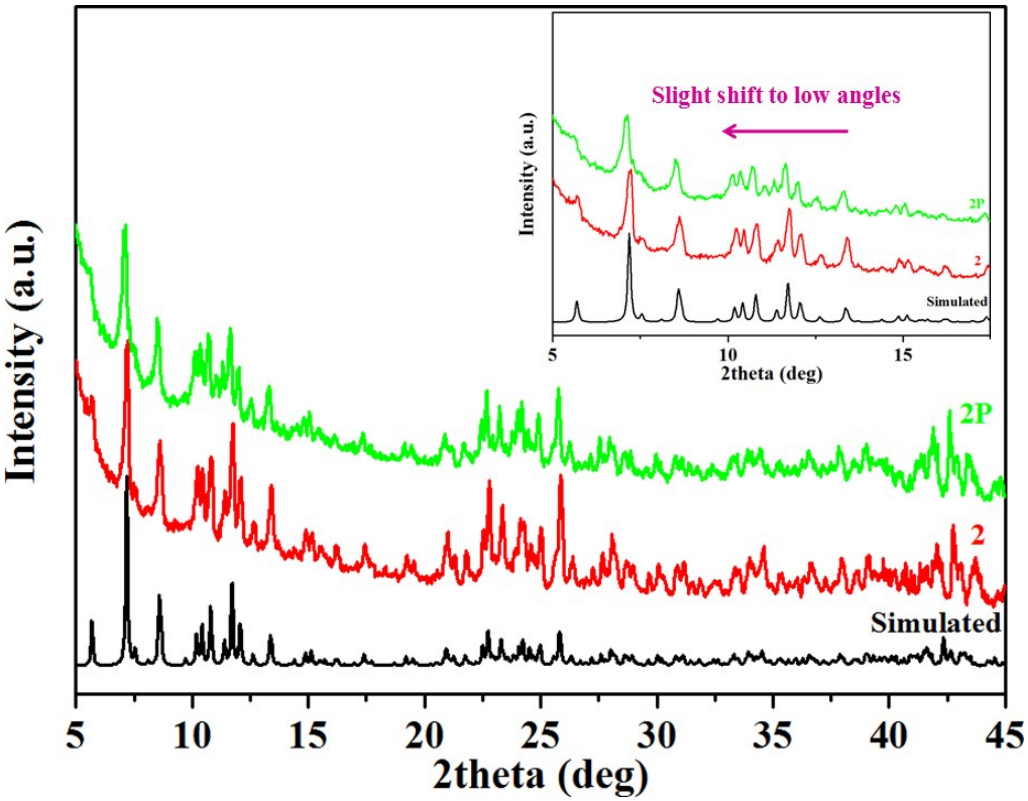

Fig. S6 The comparison of PXRD patterns of **2** and **2P**.

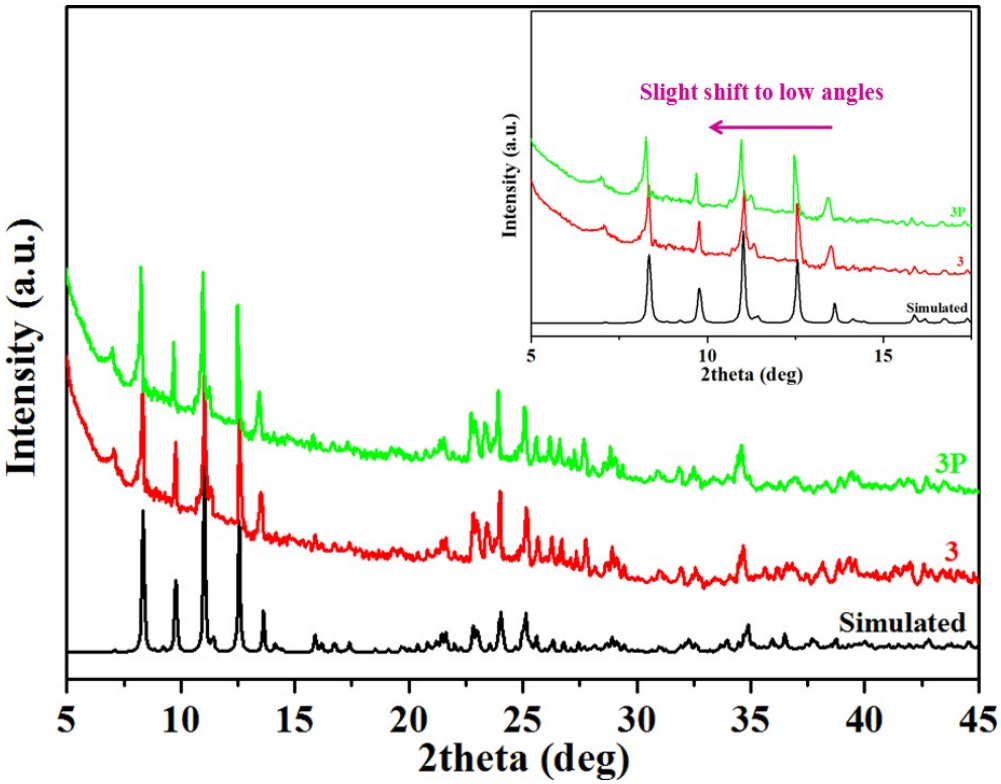

Fig. S7 The comparison of PXRD patterns of **3** and **3P**.

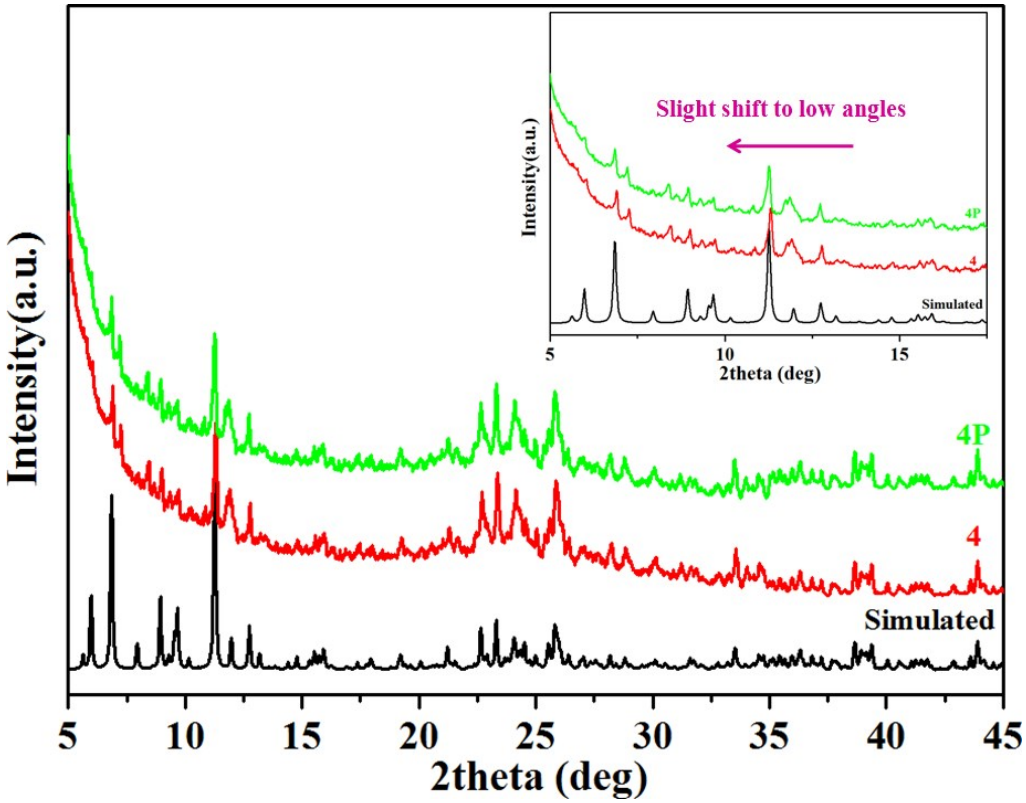

Fig. S8 The comparison of PXRD patterns of **4** and **4P**.

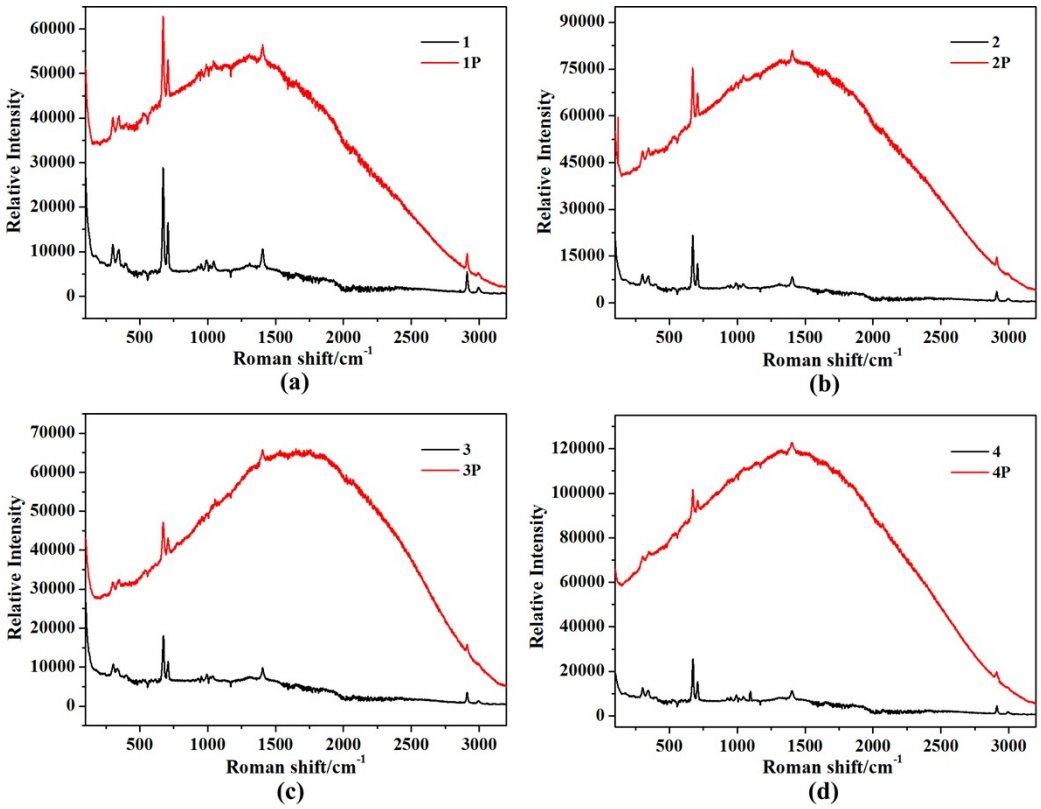

Fig. S9 The SER spectra of **1**, **1P**, **2**, **2P**, **3**, **3P**, **4** and **4P**.

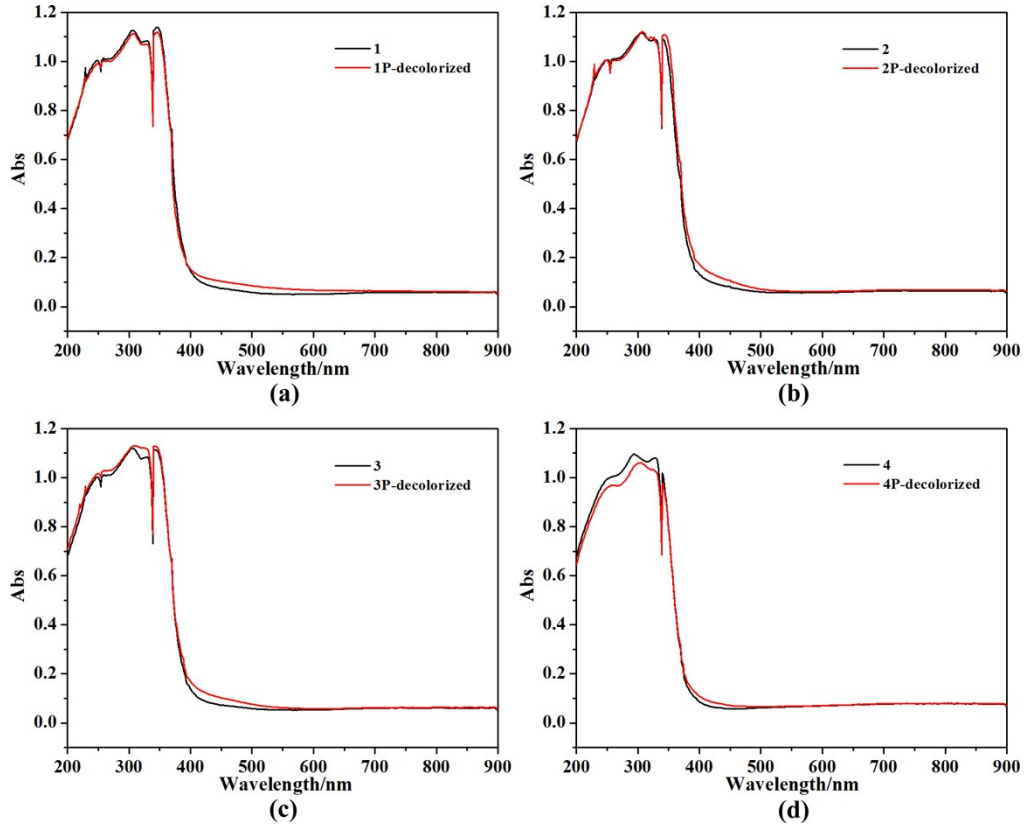

Fig. S10 The comparison of UV-vis absorption spectra of **1**, **1P**-decolorized, **2**, **2P**-decolorized, **3**, **3P**-decolorized, **4** and **4P**-decolorized.

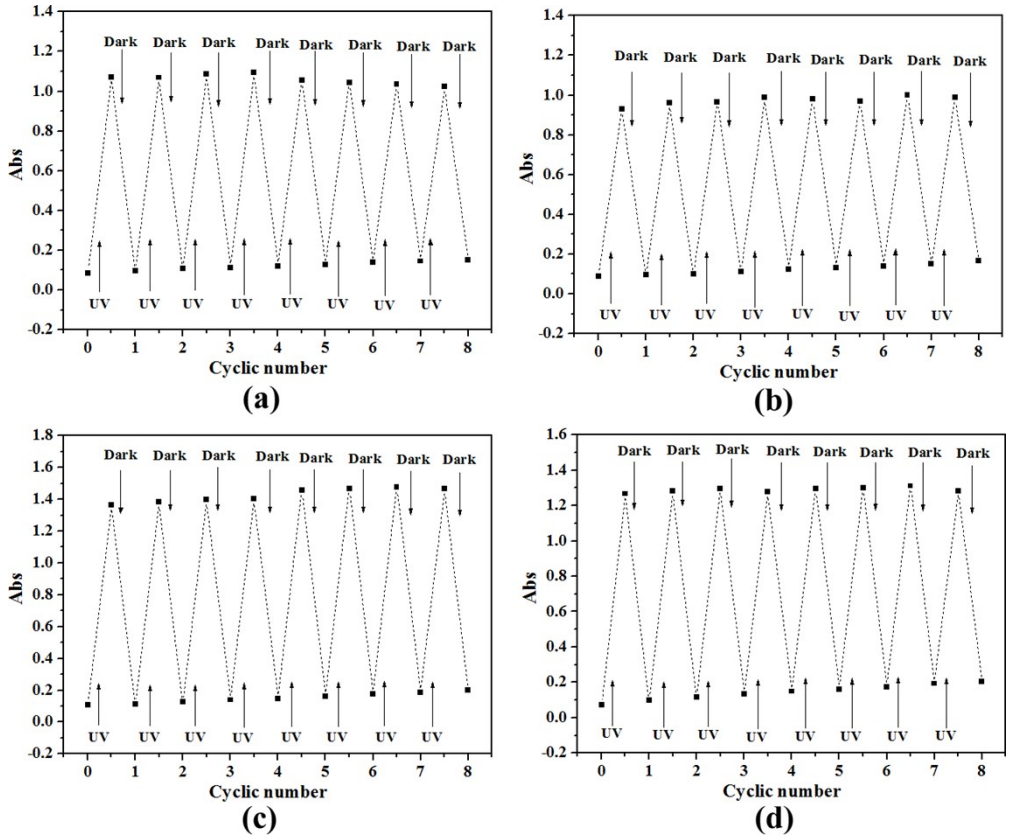

Fig. S11 The switching cycles of coloration-decoloration processes of **1**, **2**, **3** and **4** upon alternating UV light irradiation and dark treatment.

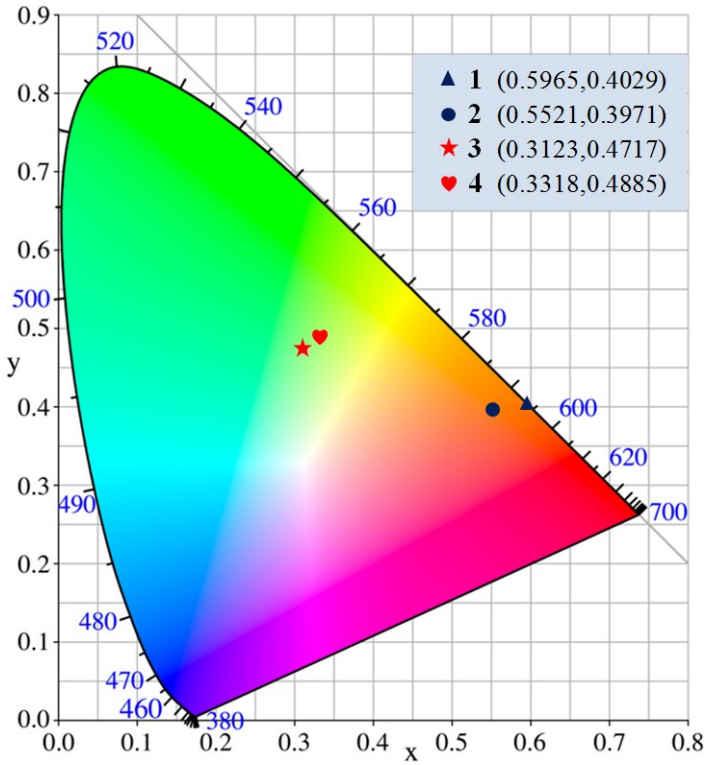

Fig. S12 The CIE for **1**, **2**, **3** and **4**.

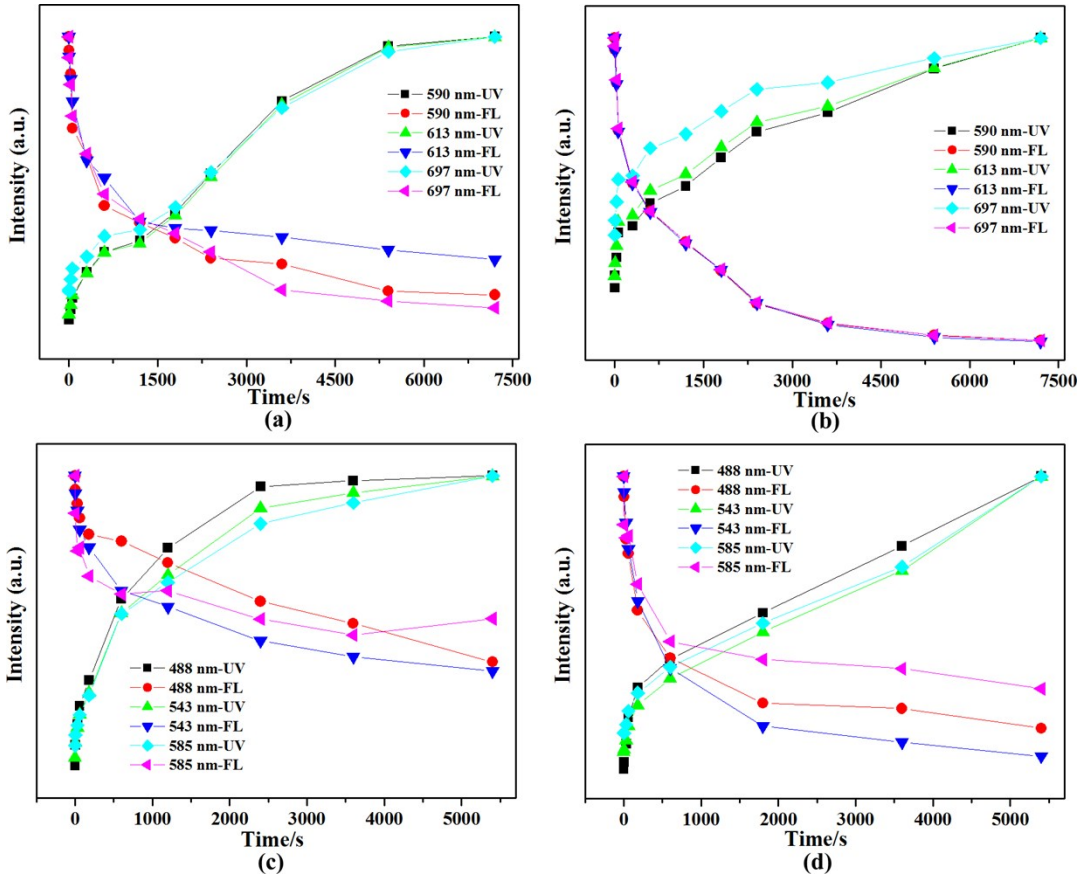

Fig. S13 The comparison of coloration rate and fluorescence quenching rate of **1** (a), **2** (b), **3** (c) and **4** (d).

3. Tables

Table S1 Crystal data and structure refinement for compounds **1**-**4**.

Compounds	**1**	**2**
CCDC code	1976991	1976992
Empirical formula	$C_{32}H_{76}Ag_7Eu_2I_{13}O_{16}S_{16}$	$C_{16}H_{48}Ag_7EuI_{10}O_8S_8$
Formula weight	3938.62	2801.07
Crystal size (mm)	0.20 × 0.09 × 0.08	0.20 × 0.10 × 0.08
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
a(Å)	43.352(7)	12.4723(4)
b(Å)	12.991(2)	23.4245(10)
c (Å)	18.555(3)	21.0231(8)
α (°)	90	90
β(°)	101.839(4)	99.650(3)
γ(°)	90	90
Volume (Å^3)	10228(3)	6055.1(4)
Z	4	4
D_c(g cm^{-3})	2.558	3.073
F(000)	7184	5032
μ (mm^{-1})	6.807	8.637
ϑ range (°)	2.24 to 28.35	2.91 to 25.00
Reflections collected	71499	26150
Unique reflections	12786	10646
R_{int}	0.0470	0.0290
Goodness-of-fit on F^2	1.033	1.065
R_1/wR_2, $[I \geq 2\sigma(I)]^{a,b}$	0.0944 / 0.2588	0.0550 / 0.1309
R_1/wR_2, (all data)	0.1122 / 0.2740	0.0841 / 0.1423
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	4.493 / -5.850	3.994 / -1.677

Compounds	**3**	**4**
CCDC code	1976993	1976999
Empirical formula	$C_{32}H_{92}Ag_7I_{13}O_{16}S_{16}Tb_2$	$C_{16}H_{48}Ag_6I_9O_8S_8Tb$
Formula weight	3968.65	2573.26
Crystal size (mm)	0.20 × 0.09 × 0.08	0.20 × 0.07 × 0.06
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a(Å)	43.485(16)	31.7458(16)
b(Å)	13.005(5)	19.7768(11)
c (Å)	18.690(7)	22.4989(10)
α (°)	90	90
β(°)	102.214(10)	125.6640(10)
γ(°)	90	90
Volume (Å^3)	10331(7)	11476.2(10)
Z	4	8
D_c(g cm^{-3})	2.552	2.979
F(000)	7264	9280
μ (mm^{-1})	6.895	8.383
ϑ range (°)	2.25 to 25.00	2.20 to 28.38
Reflections collected	111386	84529
Unique reflections	8997	14307
R_{int}	0.1095	0.0636
Goodness-of-fit on F^2	1.063	1.081
R_1/wR_2, [$I \geq 2\sigma(I)$][a,b]	0.1035 / 0.2720	0.0611 / 0.1442
R_1/wR_2, (all data)	0.1182 / 0.2900	0.0840 / 0.1543
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	3.311 / -3.731	3.585 / -3.526

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

Table S2 Selected bond lengths (Å) and angles (°) for compounds **1**-**4**.

Compound **1**			
Ag(1)-I(2)	2.801(2)	Ag(1)-I(4)	2.859(2)
Ag(1)-I(3)	2.891(2)	Ag(1)-I(1)	2.900(2)
Ag(2)-I(2)#2	2.803(2)	Ag(2)-I(3)	2.866(2)
Ag(2)-I(1)#1	2.889(2)	Ag(2)-I(4)	2.897(2)
Ag(3)-I(5)	2.7240(19)	Ag(3)-I(6)	2.944(2)
Ag(3)-I(7)#3	2.972(2)	Ag(3)-I(7)	2.978(2)
Ag(4)-I(4)	2.972(4)	Ag(4)-I(1)	2.990(4)
Ag(4)-I(3)#1	3.008(4)	Ag(4)-I(1)#1	3.022(4)
Eu(1)-O(6)	2.353(13)	Eu(1)-O(2)	2.358(11)
Eu(1)-O(1)	2.372(12)	Eu(1)-O(4)	2.376(11)
Eu(1)-O(3)	2.380(12)	Eu(1)-O(5)	2.393(11)
Eu(1)-O(7)	2.399(11)	Eu(1)-O(8)	2.412(10)
Ag(1)-Ag(2)	3.055(2)	Ag(2)-Ag(4)	3.053(4)
Ag(1)-Ag(4)	3.167(4)	Ag(4)-Ag(4)#1	1.761(10)
Ag(1)-Ag(4)#1	3.186(4)	Ag(4)-Ag(2)#1	3.031(4)
Ag(2)-Ag(4)#1	3.031(4)	Ag(4)-Ag(1)#1	3.186(4)
I(2)-Ag(1)-I(4)	115.92(7)	I(5)-Ag(3)-I(6)	120.17(7)
I(2)-Ag(1)-I(3)	108.81(7)	I(5)-Ag(3)-I(7)#3	117.34(7)
I(4)-Ag(1)-I(3)	116.10(7)	I(6)-Ag(3)-I(7)#3	99.14(6)
I(2)-Ag(1)-I(1)	109.75(7)	I(5)-Ag(3)-I(7)	117.61(7)
I(4)-Ag(1)-I(1)	102.19(7)	I(6)-Ag(3)-I(7)	99.01(6)
I(3)-Ag(1)-I(1)	102.90(7)	I(7)#3-Ag(3)-I(7)	99.70(7)
I(2)#2-Ag(2)-I(3)	115.69(7)	I(4)-Ag(4)-I(1)	97.49(11)
I(2)#2-Ag(2)-I(1)#1	112.31(7)	I(4)-Ag(4)-I(3)#1	117.16(16)
I(3)-Ag(2)-I(1)#1	106.11(7)	I(1)-Ag(4)-I(3)#1	100.14(12)

I(2)#2-Ag(2)-I(4)	101.52(7)	I(4)-Ag(4)-I(1)#1	100.16(12)
I(3)-Ag(2)-I(4)	115.69(7)	I(1)-Ag(4)-I(1)#1	145.93(18)
I(1)#1-Ag(2)-I(4)	105.21(7)	I(3)#1-Ag(4)-I(1)#1	97.37(11)
O(6)-Eu(1)-O(2)	107.1(6)	O(3)-Eu(1)-O(5)	73.6(5)
O(6)-Eu(1)-O(1)	142.6(6)	O(6)-Eu(1)-O(7)	76.9(6)
O(2)-Eu(1)-O(1)	86.0(6)	O(2)-Eu(1)-O(7)	144.2(5)
O(6)-Eu(1)-O(4)	70.2(6)	O(1)-Eu(1)-O(7)	72.9(6)
O(2)-Eu(1)-O(4)	73.2(5)	O(4)-Eu(1)-O(7)	137.4(6)
O(1)-Eu(1)-O(4)	146.5(6)	O(3)-Eu(1)-O(7)	120.6(6)
O(6)-Eu(1)-O(3)	145.0(6)	O(5)-Eu(1)-O(7)	73.3(5)
O(2)-Eu(1)-O(3)	77.0(6)	O(6)-Eu(1)-O(8)	75.3(5)
O(1)-Eu(1)-O(3)	71.4(5)	O(2)-Eu(1)-O(8)	73.2(4)
O(4)-Eu(1)-O(3)	78.3(6)	O(1)-Eu(1)-O(8)	75.4(4)
O(6)-Eu(1)-O(5)	84.7(6)	O(4)-Eu(1)-O(8)	120.9(4)
O(2)-Eu(1)-O(5)	141.8(5)	O(3)-Eu(1)-O(8)	136.4(5)
O(1)-Eu(1)-O(5)	106.8(5)	O(5)-Eu(1)-O(8)	144.4(5)
O(4)-Eu(1)-O(5)	77.3(5)	O(7)-Eu(1)-O(8)	73.7(4)

Symmetry code:

1: #1 -x+1/2,-y+3/2,-z #2 -x+1/2,y-1/2,-z+1/2 #3 -x+2,y,-z+3/2 #4 -x+1/2,y+1/2,-z+1/2

Compound 2

Ag(1)-I(3)	2.7472(15)	Ag(4)-I(6)	2.9146(15)
Ag(1)-I(1)	2.9163(19)	Ag(4)-I(9)	2.9331(17)
Ag(1)-I(2)	2.9303(17)	Ag(5)-I(10)	2.7579(17)
Ag(1)-I(8)#1	2.9947(17)	Ag(5)-I(6)	2.8745(18)
Ag(2)-I(3)	2.7680(17)	Ag(5)-I(5)	2.8771(17)
Ag(2)-I(7)	2.7972(17)	Ag(5)-I(9)	2.9968(18)
Ag(2)-I(4)	2.8720(17)	Ag(6)-I(4)#2	2.8278(18)
Ag(2)-I(6)	2.9823(16)	Ag(6)-I(9)#2	2.8584(17)
Ag(3)-I(2)	2.7433(18)	Ag(6)-I(5)#2	2.8904(17)
Ag(3)-I(4)	2.8389(17)	Ag(6)-I(9)	2.9960(18)

Ag(3)-I(6)	2.8911(17)	Ag(7)-I(10)	2.7132(16)
Ag(3)-I(5)	2.987(2)	Ag(7)-I(1)#3	2.828(2)
Ag(4)-I(7)	2.8111(17)	Ag(7)-I(8)	2.8458(18)
Ag(4)-I(8)	2.8255(16)	Eu(1)-O(8)	2.331(10)
Eu(1)-O(4)	2.363(9)	Eu(1)-O(6)	2.416(10)
Eu(1)-O(7)	2.373(10)	Eu(1)-O(5)	2.428(8)
Eu(1)-O(1)	2.399(11)	Eu(1)-O(3)	2.432(12)
Eu(1)-O(2)	2.406(10)		
Ag(1)-Ag(7)#1	2.9584(19)	Ag(5)-Ag(6)#2	3.093(2)
Ag(2)-Ag(4)	3.1452(18)	Ag(6)-Ag(5)#2	3.093(2)
Ag(3)-Ag(6)#2	3.365(2)	Ag(6)-Ag(3)#2	3.365(2)
Ag(4)-Ag(5)	3.3332(19)	Ag(7)-Ag(1)#3	2.9584(19)
I(3)-Ag(1)-I(1)	114.19(6)	I(2)-Ag(3)-I(5)	114.79(6)
I(3)-Ag(1)-I(2)	131.05(6)	I(4)-Ag(3)-I(5)	101.90(6)
I(1)-Ag(1)-I(2)	96.37(5)	I(6)-Ag(3)-I(5)	102.57(6)
I(3)-Ag(1)-I(8)#1	112.33(6)	I(7)-Ag(4)-I(8)	112.89(5)
I(1)-Ag(1)-I(8)#1	99.87(5)	I(7)-Ag(4)-I(6)	112.51(5)
I(2)-Ag(1)-I(8)#1	97.89(5)	I(8)-Ag(4)-I(6)	94.82(5)
I(3)-Ag(2)-I(7)	118.08(6)	I(7)-Ag(4)-I(9)	107.70(5)
I(3)-Ag(2)-I(4)	112.51(5)	I(8)-Ag(4)-I(9)	120.05(6)
I(7)-Ag(2)-I(4)	110.19(6)	I(6)-Ag(4)-I(9)	108.28(5)
I(3)-Ag(2)-I(6)	102.66(5)	I(10)-Ag(5)-I(6)	108.50(6)
I(7)-Ag(2)-I(6)	110.90(5)	I(10)-Ag(5)-I(5)	118.24(6)
I(4)-Ag(2)-I(6)	100.85(5)	I(6)-Ag(5)-I(5)	105.78(5)
I(2)-Ag(3)-I(4)	122.74(7)	I(10)-Ag(5)-I(9)	108.12(6)
I(2)-Ag(3)-I(6)	108.68(6)	I(6)-Ag(5)-I(9)	107.63(5)
I(4)-Ag(3)-I(6)	103.92(5)	I(5)-Ag(5)-I(9)	108.13(5)

I(4)#2-Ag(6)-I(9)#2	121.19(6)	I(5)#2-Ag(6)-I(9)	106.77(6)
I(4)#2-Ag(6)-I(5)#2	104.63(6)	I(10)-Ag(7)-I(1)#3	124.05(7)
I(9)#2-Ag(6)-I(5)#2	111.66(5)	I(10)-Ag(7)-I(8)	126.93(7)
I(4)#2-Ag(6)-I(9)	110.46(5)	I(1)#3-Ag(7)-I(8)	105.75(5)
I(9)#2-Ag(6)-I(9)	101.47(5)	O(8)-Eu(1)-O(4)	100.0(4)
O(8)-Eu(1)-O(7)	89.4(5)	O(8)-Eu(1)-O(5)	148.3(4)
O(4)-Eu(1)-O(7)	141.3(3)	O(4)-Eu(1)-O(5)	76.3(3)
O(8)-Eu(1)-O(1)	75.2(5)	O(7)-Eu(1)-O(5)	76.3(3)
O(4)-Eu(1)-O(1)	148.0(3)	O(1)-Eu(1)-O(5)	124.0(4)
O(7)-Eu(1)-O(1)	70.7(3)	O(2)-Eu(1)-O(5)	131.5(4)
O(8)-Eu(1)-O(2)	74.0(5)	O(6)-Eu(1)-O(5)	76.2(4)
O(4)-Eu(1)-O(2)	72.0(3)	O(8)-Eu(1)-O(3)	139.3(5)
O(7)-Eu(1)-O(2)	145.9(3)	O(4)-Eu(1)-O(3)	89.2(4)
O(1)-Eu(1)-O(2)	76.4(4)	O(7)-Eu(1)-O(3)	107.8(4)
O(8)-Eu(1)-O(6)	72.6(4)	O(1)-Eu(1)-O(3)	76.4(4)
O(4)-Eu(1)-O(6)	73.8(3)	O(2)-Eu(1)-O(3)	71.4(5)
O(7)-Eu(1)-O(6)	73.5(3)	O(6)-Eu(1)-O(3)	147.0(4)
O(1)-Eu(1)-O(6)	131.3(4)	O(5)-Eu(1)-O(3)	72.4(4)
O(2)-Eu(1)-O(6)	126.3(4)		
Symmetry code:			
2: #1 x,-y+3/2,z-1/2	#2 -x,-y+2,-z+1	#3 x,-y+3/2,z+1/2	

Compound 3			
Ag(1)-I(1)	2.810(2)	Ag(3)-I(4)	2.970(5)
Ag(1)-I(4)#1	2.875(3)	Ag(3)-I(3)#3	3.008(5)
Ag(1)-I(2)#1	2.910(3)	Ag(3)-I(3)	3.023(5)
Ag(1)-I(3)#2	2.913(3)	Ag(3)-I(2)#3	3.026(5)
Ag(2)-I(1)	2.819(2)	Ag(4)-I(7)	2.741(2)
Ag(2)-I(2)	2.881(3)	Ag(4)-I(5)	2.949(3)
Ag(2)-I(3)	2.906(3)	Ag(4)-I(6)	2.989(3)
Ag(2)-I(4)	2.914(3)	Ag(4)-I(6)#6	2.992(3)

Tb(1)-O(3)	2.329(16)	Tb(1)-O(8)	2.380(12)
Tb(1)-O(5)	2.364(14)	Tb(1)-O(6)	2.384(13)
Tb(1)-O(1)	2.369(14)	Tb(1)-O(2)	2.388(13)
Tb(1)-O(7)	2.370(11)	Tb(1)-O(4)	2.389(13)
Ag(1)-Ag(2)#1	3.082(3)	Ag(2)-Ag(1)#4	3.082(3)
Ag(1)-Ag(3)#1	3.215(5)	Ag(3)-Ag(3)#3	1.790(12)
Ag(1)-Ag(3)#2	3.233(5)	Ag(3)-Ag(2)#3	3.039(5)
Ag(2)-Ag(3)#3	3.039(5)	Ag(3)-Ag(1)#4	3.215(5)
Ag(2)-Ag(3)	3.057(5)	Ag(3)-Ag(1)#5	3.233(5)
Ag(4)-Ag(4)#6	2.821(4)		
I(1)-Ag(1)-I(4)#1	115.70(9)	I(4)-Ag(3)-I(3)#3	97.19(13)
I(1)-Ag(1)-I(2)#1	109.03(8)	I(4)-Ag(3)-I(3)	100.67(13)
I(4)#1-Ag(1)-I(2)#1	115.84(9)	I(3)#3-Ag(3)-I(3)	145.5(2)
I(1)-Ag(1)-I(3)#2	111.53(9)	I(4)-Ag(3)-I(2)#3	117.5(2)
I(4)#1-Ag(1)-I(3)#2	101.54(8)	I(3)#3-Ag(3)-I(2)#3	100.65(13)
I(2)#1-Ag(1)-I(3)#2	102.08(8)	I(3)-Ag(3)-I(2)#3	96.93(12)
I(1)-Ag(2)-I(2)	115.68(8)	I(7)-Ag(4)-I(5)	120.18(8)
I(1)-Ag(2)-I(3)	111.73(9)	I(7)-Ag(4)-I(6)	117.23(9)
I(2)-Ag(2)-I(3)	106.74(9)	I(5)-Ag(4)-I(6)	99.11(7)
I(1)-Ag(2)-I(4)	101.86(8)	I(7)-Ag(4)-I(6)#6	117.47(9)
I(2)-Ag(2)-I(4)	115.52(8)	I(5)-Ag(4)-I(6)#6	99.05(7)
I(3)-Ag(2)-I(4)	104.90(8)	I(6)-Ag(4)-I(6)#6	99.99(8)
O(3)-Tb(1)-O(5)	70.1(7)	O(8)-Tb(1)-O(6)	70.2(5)
O(3)-Tb(1)-O(1)	78.3(7)	O(3)-Tb(1)-O(2)	75.5(8)
O(5)-Tb(1)-O(1)	120.2(6)	O(5)-Tb(1)-O(2)	138.0(5)
O(3)-Tb(1)-O(7)	110.8(8)	O(1)-Tb(1)-O(2)	73.8(5)
O(5)-Tb(1)-O(7)	73.4(5)	O(5)-Tb(1)-O(2)	138.0(5)

O(1)-Tb(1)-O(7)	72.5(5)	O(1)-Tb(1)-O(2)	73.8(5)
O(3)-Tb(1)-O(8)	144.2(7)	O(7)-Tb(1)-O(2)	143.3(5)
O(5)-Tb(1)-O(8)	145.1(6)	O(8)-Tb(1)-O(2)	74.3(6)
O(1)-Tb(1)-O(8)	75.3(6)	O(6)-Tb(1)-O(2)	120.8(6)
O(7)-Tb(1)-O(8)	83.6(6)	O(3)-Tb(1)-O(4)	82.5(8)
O(3)-Tb(1)-O(6)	143.7(6)	O(5)-Tb(1)-O(4)	78.0(5)
O(5)-Tb(1)-O(6)v	78.9(6)	O(1)-Tb(1)-O(4)	145.9(5)
O(1)-Tb(1)-O(6)	135.4(5)	O(7)-Tb(1)-O(4)	141.3(5)
O(7)-Tb(1)-O(6)	76.4(5)	O(8)-Tb(1)-O(4)	107.0(6)
O(6)-Tb(1)-O(4)	73.0(6)	O(2)-Tb(1)-O(4)	74.3(6)

Symmetry code:

3: #1 -x+1/2,y+1/2,-z+1/2 #2 x,-y+1,z+1/2 #3 -x+1/2,-y+1/2,-z

#4 -x+1/2,y-1/2,-z+1/2 #5 x,-y+1,z-1/2 #6 -x+2,y,-z+1/2

Compound 4

Ag(1)-I(1)	2.8106(13)	Ag(4)-I(7)	2.7550(13)
Ag(1)-I(3)	2.8515(12)	Ag(4)-I(5)	2.8792(13)
Ag(1)-I(2)	2.8724(13)	Ag(4)-I(4)	2.8880(13)
Ag(1)-I(6)	2.9633(12)	Ag(4)-I(6)	2.9276(13)
Ag(2)-I(1)#1	2.7708(13)	Ag(5)-I(8)	2.8032(13)
Ag(2)-I(3)	2.8430(13)	Ag(5)-I(2)	2.8373(12)
Ag(2)-I(6)	2.9217(13)	Ag(5)-I(5)	2.8467(13)
Ag(2)-I(4)	3.0143(15)	Ag(5)-I(6)	3.0023(14)
Ag(3)-I(9)#2	2.8267(15)	Ag(6)-I(7)	2.7615(17)
Ag(3)-I(3)	2.8605(13)	Ag(6)-I(9)	2.7655(18)
Ag(3)-I(5)	2.8907(14)	Ag(6)-I(8)	2.7661(15)
Ag(3)-I(4)	2.9381(14)	Tb(1)-O(2)	2.324(7)
Tb(1)-O(6)	2.344(7)	Tb(1)-O(4)	2.392(8)
Tb(1)-O(7)	2.362(7)	Tb(1)-O(8)	2.394(7)
Tb(1)-O(3)	2.366(7)	Tb(1)-O(1)	2.401(7)
Tb(1)-O(5)	2.373(7)		

I(1)-Ag(1)-I(3)	122.57(4)	I(5)-Ag(3)-I(4)	102.81(4)
I(1)-Ag(1)-I(2)	106.02(4)	I(7)-Ag(4)-I(5)	114.59(5)
I(3)-Ag(1)-I(2)	110.86(4)	I(7)-Ag(4)-I(4)	104.98(4)
I(1)-Ag(1)-I(6)	104.95(4)	I(5)-Ag(4)-I(4)	104.36(4)
I(3)-Ag(1)-I(6)	103.07(4)	I(7)-Ag(4)-I(6)	106.98(4)
I(2)-Ag(1)-I(6)	108.58(4)	I(5)-Ag(4)-I(6)	111.29(4)
I(1)#1-Ag(2)-I(3)	120.74(5)	I(4)-Ag(4)-I(6)	114.68(4)
I(1)#1-Ag(2)-I(6)	112.58(4)	I(8)-Ag(5)-I(2)	122.30(4)
I(3)-Ag(2)-I(6)	104.34(4)	I(8)-Ag(5)-I(5)	115.37(5)
I(1)#1-Ag(2)-I(4)	103.03(4)	I(2)-Ag(5)-I(5)	101.53(4)
I(3)-Ag(2)-I(4)	104.73(4)	I(8)-Ag(5)-I(6)	98.89(4)
I(6)-Ag(2)-I(4)	111.13(4)	I(2)-Ag(5)-I(6)	108.45(4)
I(9)#2-Ag(3)-I(3)	113.22(4)	I(5)-Ag(5)-I(6)	110.07(4)
I(9)#2-Ag(3)-I(5)	107.02(5)	I(7)-Ag(6)-I(9)	114.41(5)
I(3)-Ag(3)-I(5)	112.22(4)	I(7)-Ag(6)-I(8)	115.23(6)
I(9)#2-Ag(3)-I(4)	114.91(4)	I(9)-Ag(6)-I(8)	128.31(6)
I(3)-Ag(3)-I(4)	106.28(4)	O(2)-Tb(1)-O(6)	144.0(3)
O(6)-Tb(1)-O(7)	82.1(3)	O(3)-Tb(1)-O(4)	76.5(3)
O(2)-Tb(1)-O(3)	88.9(3)	O(5)-Tb(1)-O(4)	74.5(3)
O(6)-Tb(1)-O(3)	143.1(3)	O(2)-Tb(1)-O(8)	73.4(3)
O(7)-Tb(1)-O(3)	108.0(3)	O(6)-Tb(1)-O(8)	70.8(3)
O(2)-Tb(1)-O(5)	144.0(3)	O(7)-Tb(1)-O(8)	75.2(2)
O(6)-Tb(1)-O(5)	75.0(3)	O(3)-Tb(1)-O(8)	145.7(3)
O(7)-Tb(1)-O(5)	71.9(3)	O(5)-Tb(1)-O(8)	135.0(3)
O(3)-Tb(1)-O(5)	74.9(3)	O(4)-Tb(1)-O(8)	122.0(3)
O(2)-Tb(1)-O(4)	70.5(3)	O(2)-Tb(1)-O(1)	74.3(3)
O(6)-Tb(1)-O(4)	75.3(3)	O(6)-Tb(1)-O(1)	143.7(3)
O(7)-Tb(1)-O(4)	143.3(3)	O(7)-Tb(1)-O(1)	80.6(3)

O(3)-Tb(1)-O(1)	73.0(3)	O(4)-Tb(1)-O(1)	133.2(3)
O(5)-Tb(1)-O(1)	128.0(3)	O(8)-Tb(1)-O(1)	74.0(3)

Symmetry code:

4: #1 -x+3/2,-y+1/2,-z+1 #2 x,-y,z+1/2 #3 x,-y,z-1/2

Table S3 Synthesis conditions for compounds **1**, **2**, **3** and **4**.

Entry	Lanthanide nitrate (mmol)	AgI (mmol)	KI (mmol)	DMSO (mL)	Ag/I	Products
1	0.25	0.5	1.5	4	1:4	**1**
2	0.25	0.5	1.0	4	1:3	**1** and **2**
3	0.25	2.0	2.0	4	1:2	**2**
4	0.25	0.5	1.5	4	1:4	**3**
5	0.25	0.5	1.0	4	1:3	**3** and **4**
6	0.25	3.0	3.0	4	1:2	**4**