Supporting Information (SI)

Photochromism and photocatalysis of organic-inorganic hybrid iodoargentates modulated by argentophilic interactions

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Content

1. Chemical analytical experiment for photoproducts

Dissolve 0.20 mmol powder samples of **3**, **3P**, **4** and **4P** in 5 ml dimethyl sulfoxide containing 1 mmol and 1 mmol NaI and $Na_2S_2O_3$, respectively. After several minutes, a small number of black precipitated particles are obtained in the solution of **3P** and **4P**. And then black precipitated particles are washed, dried and treated with concentrated HNO_3, solution of NaCl and concentrated $NH_3{\cdot}H_2O$ in turn, exhibiting the generation of metal silver particles. The above processes are implemented in the dark at room temperature.

2. Figures

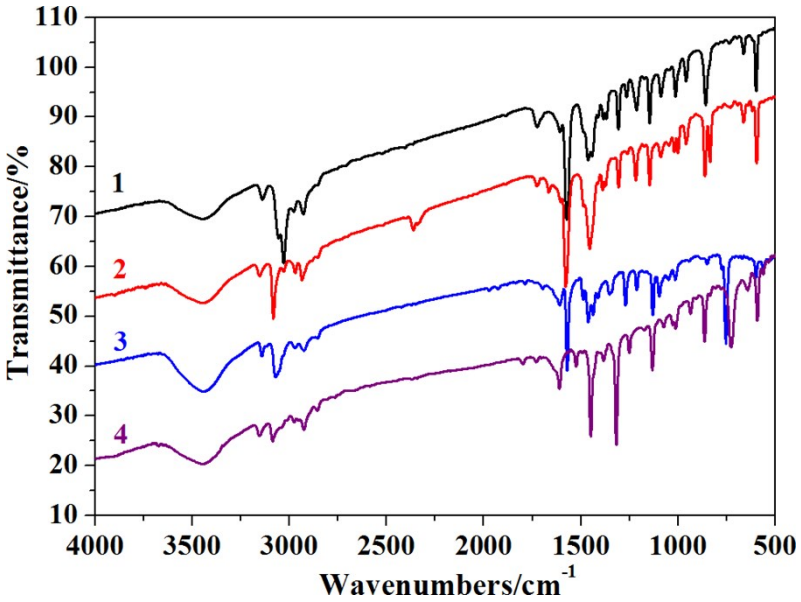

Fig. S1. IR spectra of **1-4**.

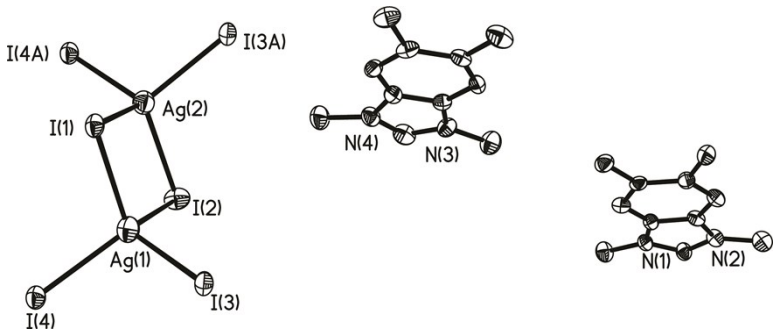

Fig. S2. The asymmetric unit diagram of **1**.

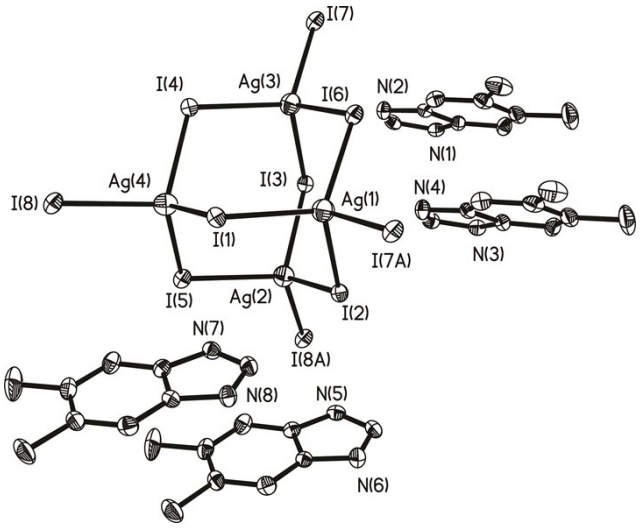

Fig. S3. The asymmetric unit diagram of **2**.

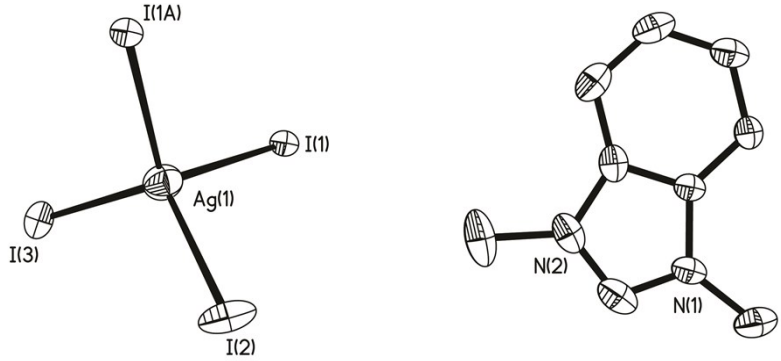

Fig. S4. The asymmetric unit diagram of **3**.

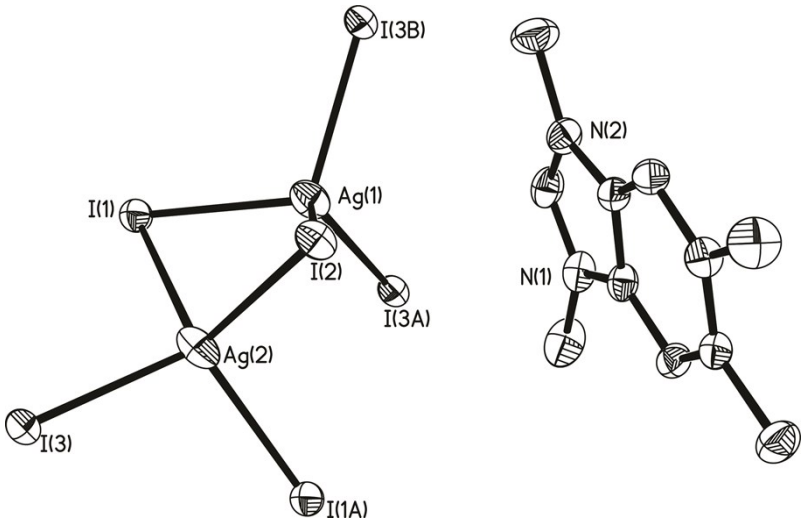

Fig. S5. The asymmetric unit diagram of **4**.

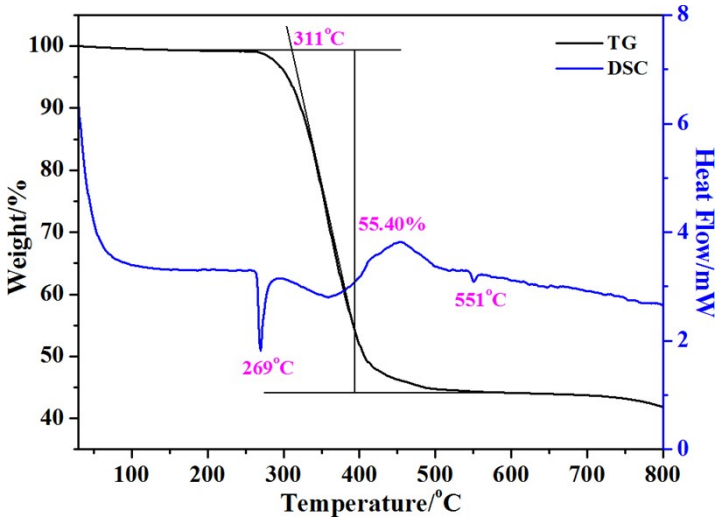

Fig. S6. Thermo-gravimetric (TG) and differential scanning calorimetry (DSC) curves of **1**.

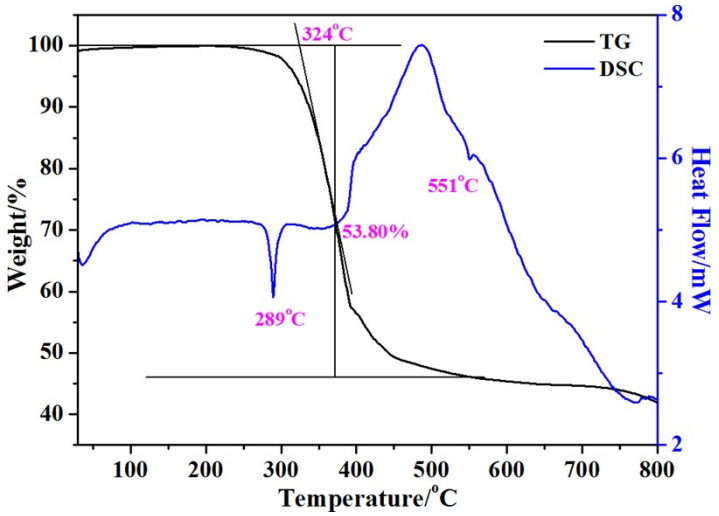

Fig. S7. Thermo-gravimetric (TG) and differential scanning calorimetry (DSC) curves of **2**.

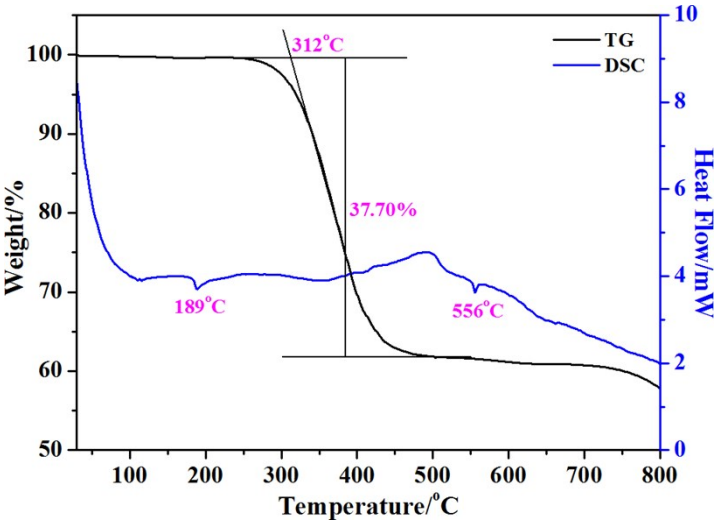

Fig. S8. Thermo-gravimetric (TG) and differential scanning calorimetry (DSC) curves of **3**.

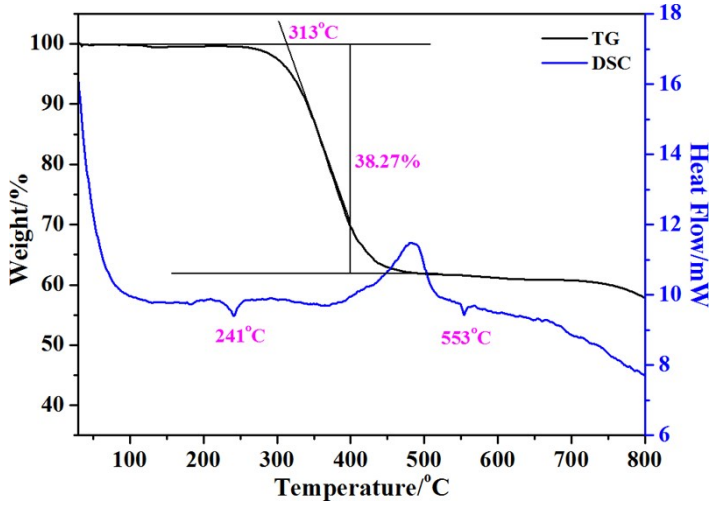

Fig. S9. Thermo-gravimetric (TG) and differential scanning calorimetry (DSC) curves of **4**.

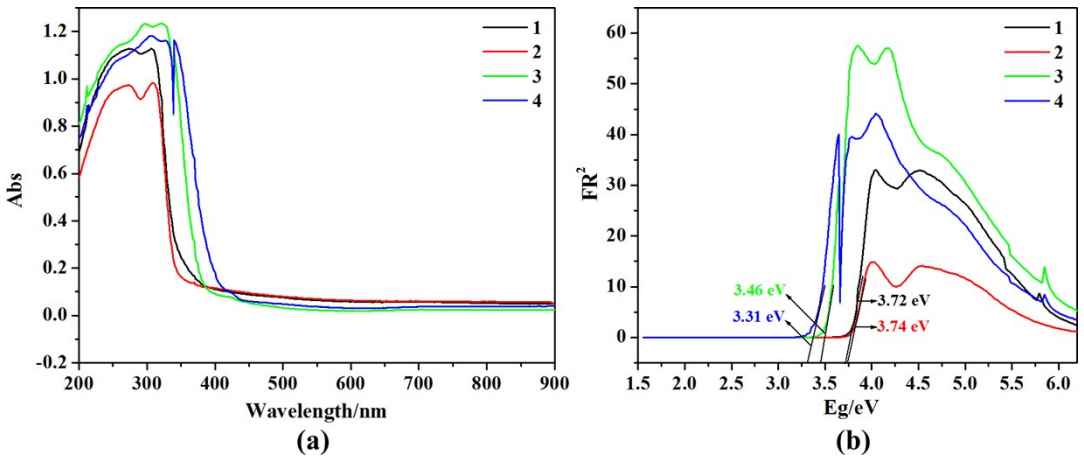

Fig. S10. The UV-vis absorption spectra (a) and band gaps (b) for **1**, **2**, **3** and **4**.

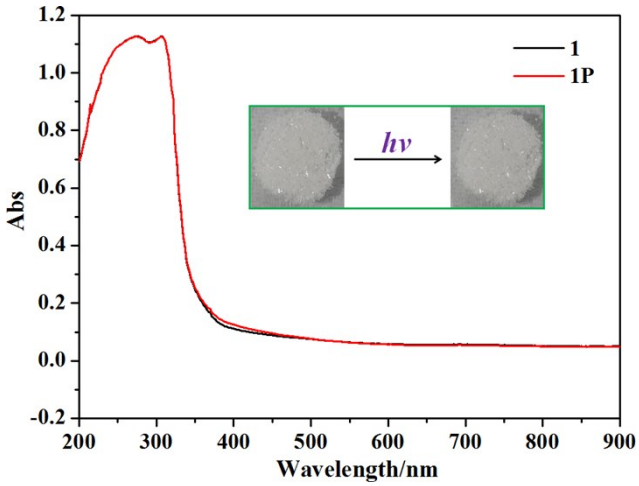

Fig. S11. UV-vis absorption spectra of **1** before and after UV light irradiation. The inset showing the photochromic behavior of **1**.

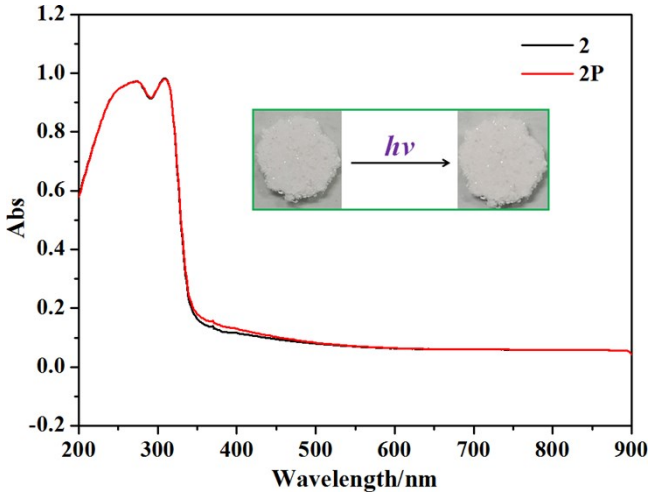

Fig. S12. UV-vis absorption spectra of **2** before and after UV light irradiation. The inset showing the photochromic behavior of **2**.

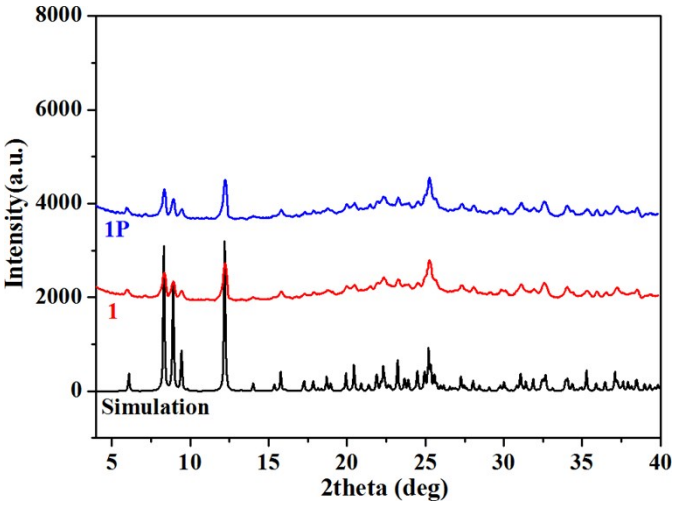

Fig. S13. Powder X-ray diffraction (PXRD) patterns of **1** and **1P** at room temperature.

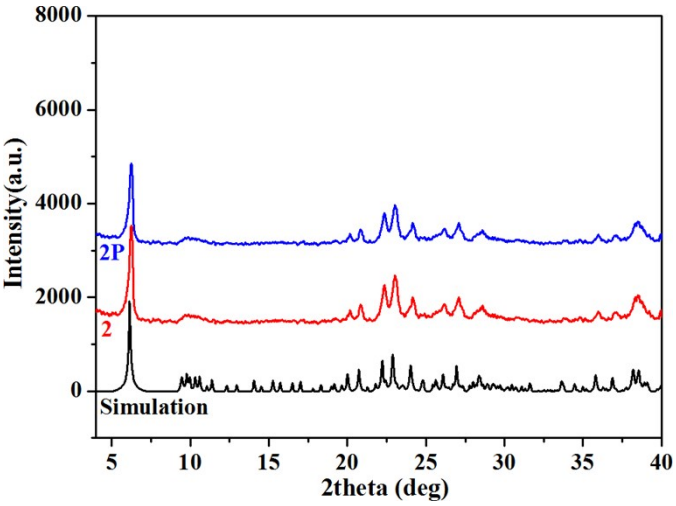

Fig. S14. Powder X-ray diffraction (PXRD) patterns of **2** and **2P** at room temperature.

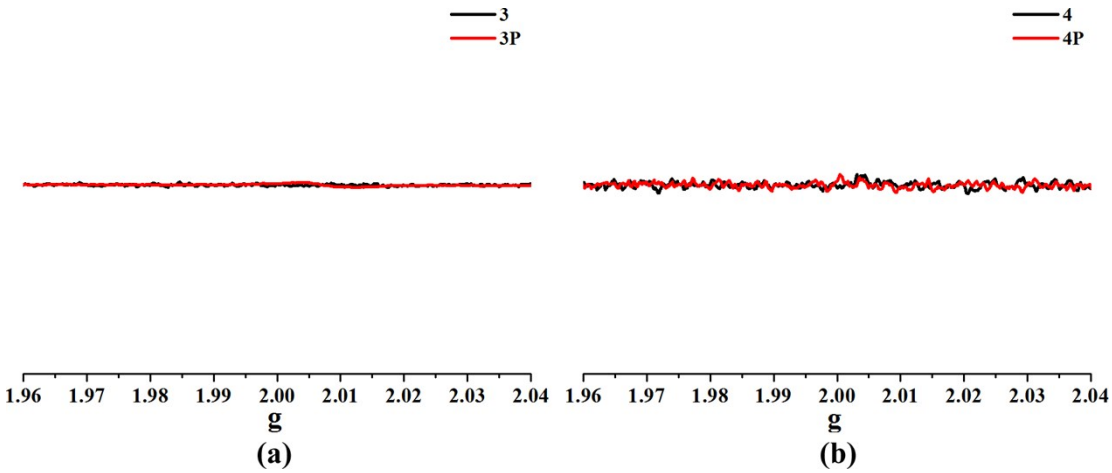

Fig. S15. The EPR spectra of **3** and **3P** (a), and **4** and **4P** (b)

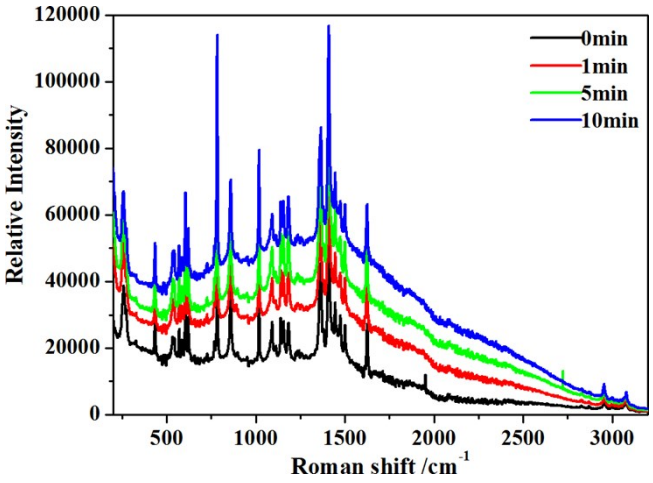

Fig. S16. The surface enhanced raman spectra (SERS) of **4** upon UV light irradiation.

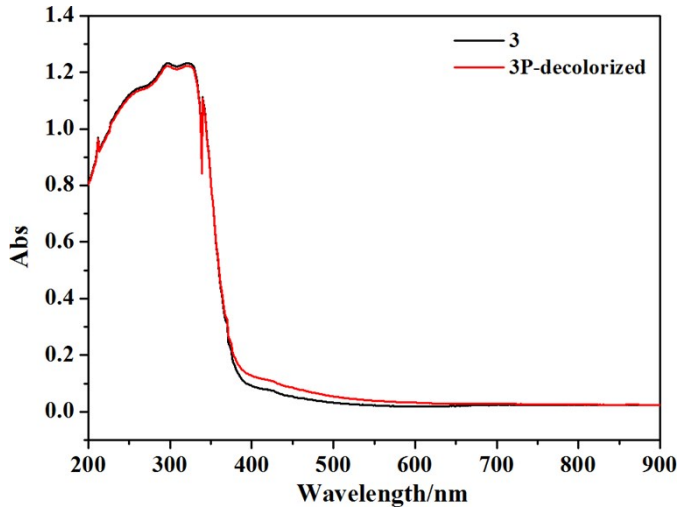

Fig. S17. UV-vis absorption spectra of **3** and **3P**-decolorized.

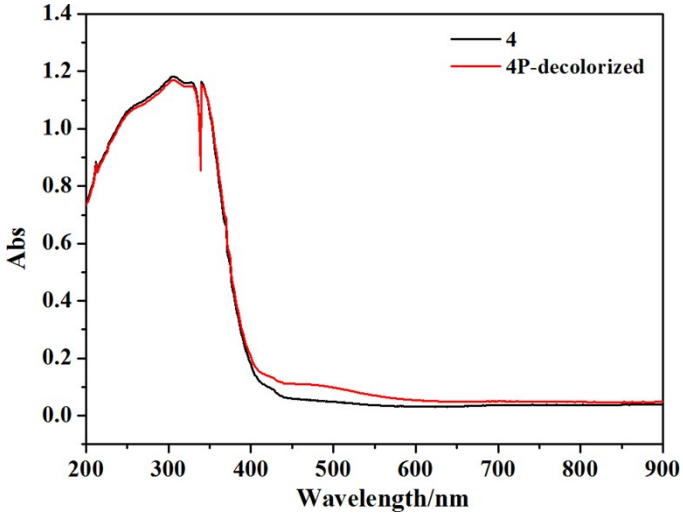

Fig. S18. UV-vis absorption spectra of **4** and **4P**-decolorized.

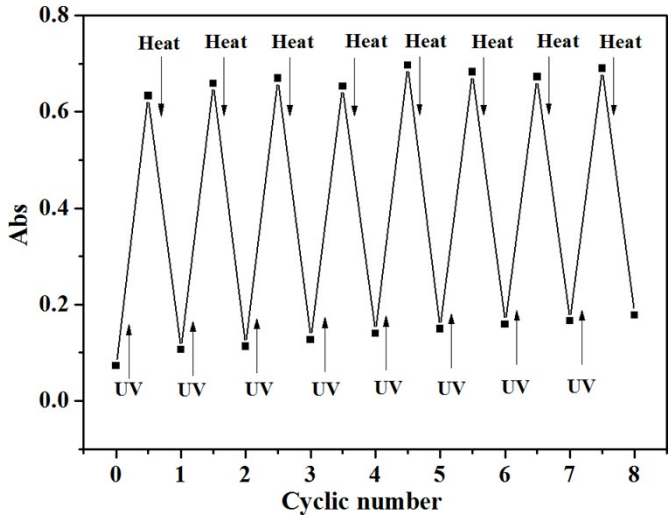

Fig. S19. The coloration-decoloration processes with repeated UV irradiation/heating of **3**.

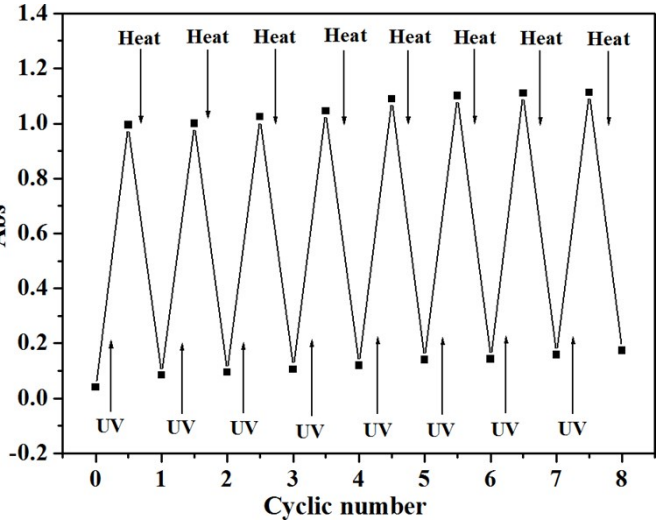

Fig. S20. The coloration-decoloration processes with repeated UV irradiation/heating of **3**.

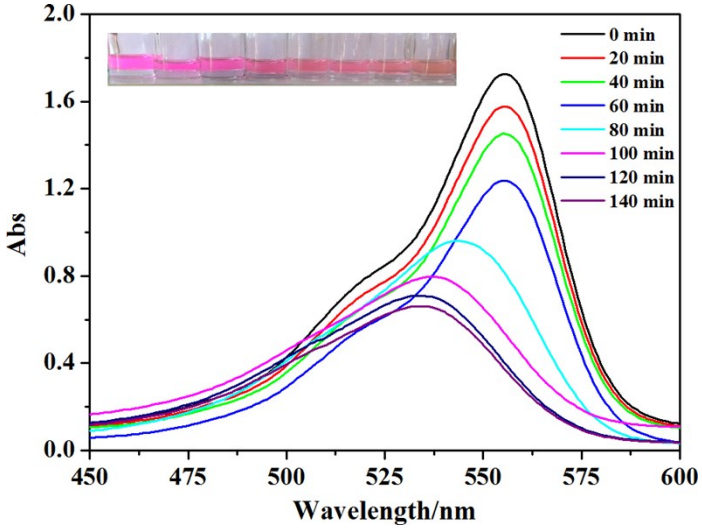

Fig. S21. UV-vis absorption spectra of the RhB solution in the presence of **3** upon light irradiation.

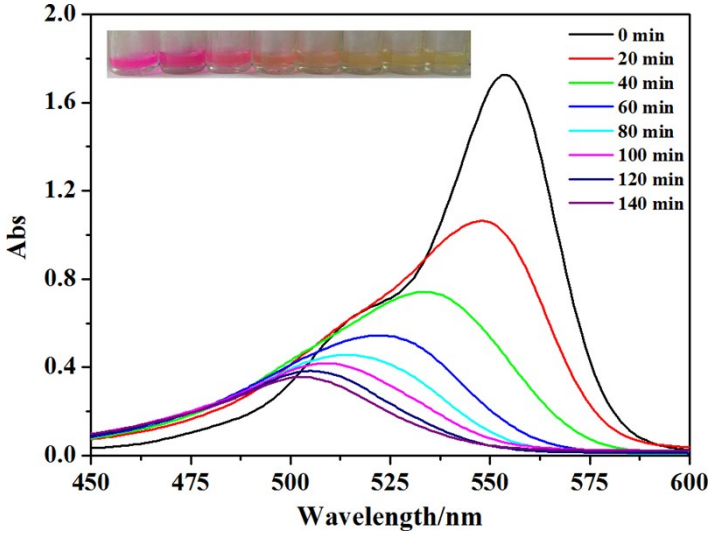

Fig. S22. UV-vis absorption spectra of the RhB solution in the presence of **4** upon light irradiation.

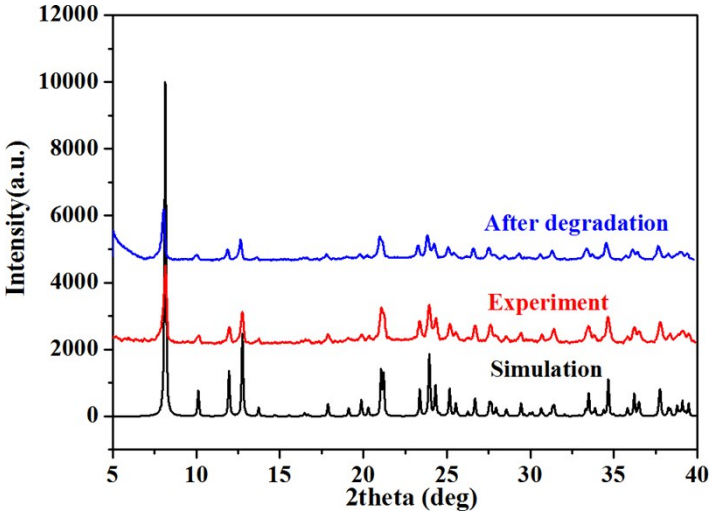

Fig. S23. The PXRD patterns of **3** before and after photodegradation.

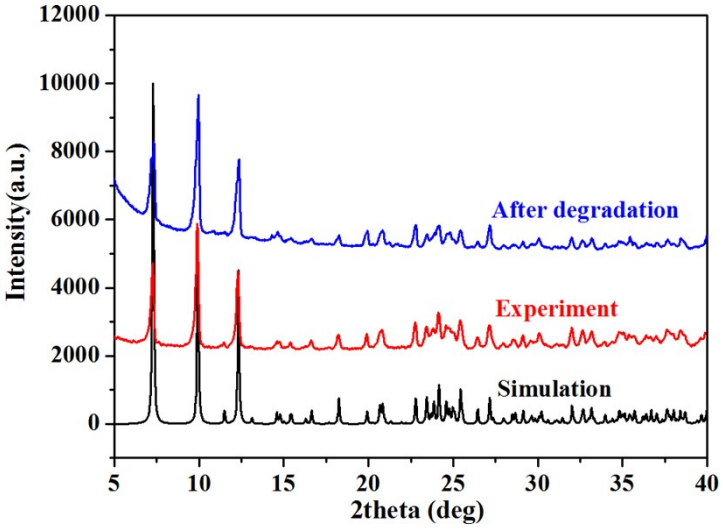

Fig. S24. The PXRD patterns of **4** before and after photodegradation.

3. Tables

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

Compounds	**1**	**2**	**3**	**4**
CCDC code	2003491	2003492	2003493	2003494
Empirical formula	$C_{22}H_{30}N_4Ag_2I_4$	$C_{36}H_{44}N_8Ag_4I_8$	$C_9H_{11}N_2Ag_2I_3$	$C_{11}H_{15}N_2Ag_2I_3$
Formula weight	1073.84	2035.47	743.64	771.69
Crystal size (mm)	0.05×0.05×0.4	0.35×0.22×0.0	0.07×0.03×0.0	0.29×0.12×0.1
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	P-1	$Pnma$	$P2_1/c$
a (Å)	7.0674(4)	9.4556(14)	17.4877(15)	8.9078(7)
b (Å)	19.8103(10)	9.4596(14)	6.6760(6)	24.2649(18)
c (Å)	21.2365(12)	29.009(4)	13.8701(12)	8.1079(6)
α (°)	90	87.486(3)	90	90
β (°)	92.976	87.279(3)	90	91.485(2)
γ (°)	90	84.662(3)	90	90
V (Å^3)	2969.3(3)	2558.8(7)	1619.3(2)	1751.9(2)
Z	4	2	4	4
D_c (g cm^{-3})	2.402	2.642	3.050	2.926
F (000)	1984	1856	1328	1392
μ (mm^{-1})	5.495	6.369	8.117	7.508
Reflections collected	43180	37987	20906	23273
Unique reflections	7394	12463	2169	4289
R_{int}	0.0404	0.0340	0.0229	0.0340
Goodness-of-fit on F^2	1.194	1.156	1.175	1.258
R_1/wR_2, $[I\geq 2\sigma(I)]^{a,b}$	0.0433, 0.1273	0.0442, 0.1350	0.0426, 0.1278	0.0405,0.1139
R_1/wR_2, (all data)	0.0566, 0.1420	0.0563, 0.1537	0.0521, 0.1518	0.0462,0.1232
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.164,-1.966	1.916, -2.403	2.714, -2.561	2.820,-2.595

[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 **1-4**

Compound **1**			
Ag(1)-I(2)	2.8201(8)	Ag(2)-I(3)#1	2.8478(8)
Ag(1)-I(3)	2.8482(8)	Ag(2)-I(4)#1	2.8839(9)
Ag(1)-I(4)	2.8770(8)	Ag(2)-I(1)	2.9176(8)
Ag(1)-I(1)	2.9175(8)	Ag(2)-I(2)	2.8271(9)
I(2)-Ag(1)-I(3)	110.19(3)	I(3)#1-Ag(2)-I(4)#1	106.45(3)
I(2)-Ag(1)-I(4)	118.13(3)	I(2)-Ag(2)-I(1)	100.89(3)
I(3)-Ag(1)-I(4)	106.63(3)	I(3)#1-Ag(2)-I(1)	111.43(3)
I(2)-Ag(1)-I(1)	101.06(3)	I(4)#1-Ag(2)-I(1)	108.28(2)
I(3)-Ag(1)-I(1)	111.78(3)	I(2)-Ag(2)-I(3)#1	111.14(3)
I(4)-Ag(1)-I(1)	109.08(2)	I(2)-Ag(2)-I(4)#1	118.58(3)
Symmetry code: #1 x-1,y,z; 2 x+1,y,z; #1 x,y,z-1; #2 -x+1,-y+1,-z+1; #3 x,y,z+1			
Compound **2**			
Ag(1)-I(1)	2.8297(8)	Ag(1)-I(2)	2.8487(9)
Ag(1)-I(6)	2.8577(9)	Ag(1)-I(7)#1	2.9249(9)
Ag(2)-I(3)	2.8488(9)	Ag(2)-I(2)	2.8548(9)
Ag(2)-I(5)	2.8608(9)	Ag(2)-I(8)#2	2.8794(9)
Ag(3)-I(3)	2.8483(9)	Ag(3)-I(4)	2.8545(8)
Ag(3)-I(6)	2.8597(9)	Ag(3)-I(7)	2.8753(9)
Ag(4)-I(1)	2.8298(9)	Ag(4)-I(4)	2.8500(9)
Ag(4)-I(5)	2.8586(9)	Ag(4)-I(8)	2.9251(9)
I(1)-Ag(1)-I(2)	109.18(3)	I(1)-Ag(1)-I(6)	117.71(3)
I(2)-Ag(1)-I(6)	110.57(3)	I(1)-Ag(1)-I(7)#1	102.79(2)
I(2)-Ag(1)-I(7)#1	107.21(3)	I(6)-Ag(1)-I(7)#1	108.66(3)
I(3)-Ag(2)-I(2)	108.97(3)	I(3)-Ag(2)-I(5)	108.75(3)
I(2)-Ag(2)-I(5)	105.51(2)	I(3)-Ag(2)-I(8)#2	105.41(3)
I(2)-Ag(2)-I(8)#2	115.78(3)	I(5)-Ag(2)-I(8)#2	112.28(3)
I(3)-Ag(3)-I(4)	108.47(3)	I(3)-Ag(3)-I(6)	108.90(3)
I(4)-Ag(3)-I(6)	105.39(2)	I(3)-Ag(3)-I(7)	105.81(2)
I(4)-Ag(3)-I(7)	115.87(3)	I(6)-Ag(3)-I(7)	112.25(3)
I(1)-Ag(4)-I(4)	109.31(3)	I(1)-Ag(4)-I(5)	117.82(3)

I(4)-Ag(4)-I(5)	110.44(3)	I(1)-Ag(4)-I(8)	102.81(2)
I(4)-Ag(4)-I(8)	107.12(3)	I(5)-Ag(4)-I(8)	108.62(3)

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

Compound **3**

Ag(1)-I(3)	2.7990(9)	Ag(1)-I(2)	2.8011(9)
Ag(1)-I(1)#1	2.8979(8)	Ag(1)-I(1)	2.9508(9)
Ag(1)-Ag(1)#2	3.1268(15)		
I(3)-Ag(1)-I(2)	114.86(3)	I(3)-Ag(1)-I(1)#1	111.73(3)
I(2)-Ag(1)-I(1)#1	112.95(3)	I(3)-Ag(1)-I(1)	103.68(3)
I(2)-Ag(1)-I(1)	104.93(3)	I(1)#1-Ag(1)-I(1)	107.74(2)

Symmetry code: 1 -x+1,-y,-z+1; x,-y+1/2,z; -x+1,y-1/2,-z+1; x,-y-1/2,z

Compound **4**

Ag(1)-I(1)	2.8544(8)	Ag(2)-I(3)	2.8155(8)
Ag(1)-I(3)#1	2.8577(8)	Ag(2)-I(1)#2	2.9263(9)
Ag(1)-I(2)	2.8620(8)	Ag(2)-I(1)	3.0727(9)
Ag(1)-I(3)#2	2.9375(8)	Ag(2)-I(2)	2.7737(7)
Ag(1)-Ag(2)#2	3.1846(8)	Ag(2)-Ag(1)#2	3.1846(8)
Ag(1)-Ag(2)	3.0664(9)	Ag(2)-Ag(2)#2	2.8909(13)
I(1)-Ag(1)-I(3)#1	109.61(3)	I(2)-Ag(2)-I(1)	102.28(2)
I(1)-Ag(1)-I(2)	105.71(3)	I(3)-Ag(2)-I(1)	95.62(3)
I(3)#1-Ag(1)-I(2)	104.01(2)	I(1)#2-Ag(2)-I(1)	122.44(2)
I(1)-Ag(1)-I(3)#2	102.13(2)	I(2)-Ag(2)-I(3)	131.36(3)
I(3)#1-Ag(1)-I(3)#2	108.58(2)	I(2)-Ag(2)-I(1)#2	104.12(3)
I(2)-Ag(1)-I(3)#2	126.19(3)	I(3)-Ag(2)-I(1)#2	103.37(2)

Symmetry code: #1 x,y,z-1; #2 -x+1,-y+1,-z+1; #3 x,y,z+1

Table S3. Hydrogen bonds of for compounds **1**-**4** (Å and °).

Compound **1**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(1)-H(1)···I(3)#1	0.930	3.094	3.946	153.17
C(2)-H(2C)···I(4)#1	0.960	3.231	4.147	160.20
C(4)-H(4)···I(2)#2	0.930	3.067	3.992	173.26
C(10)-H(10A)···I(3)#1	0.960	3.209	4.123	159.83
C(10)-H(10B)···I(3)#3	0.960	3.252	4.185	164.53
C(12)-H(12)···I(1)#2	0.930	2.877	3.760	159.01
C(13)-H(13A)···I(1)#2	0.960	3.271	4.146	152.32
C(15)-H(15)···I(3)#1	0.930	3.078	4.000	171.57
C(20)-H(20)···I(4)#4	0.930	3.288	4.202	168.19
#1 x-1, y, z-1; #2 x-1/2, -y+1/2, z-1/2; #3 -x+2, -y+1, -z+1; #4 -x+3/2, y+1/2, -z+3/2				
Compound **2**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(1)-H(1)···I(1)#1	0.930	3.083	3.771	132.17
C(1)-H(1)···I(2)#2	0.930	3.110	3.724	125.15
C(10)-H(10)···I(3)	0.930	3.106	3.703	123.62
C(10)-H(10)···I(4)#3	0.930	3.004	3.684	131.20
C(19)-H(19)···I(1)#3	0.930	3.064	3.758	132.79
C(19)-H(19)···I(4)#4	0.930	3.126	3.736	124.76
C(28)-H(28)···I(2)	0.930	2.991	3.682	132.38
C(28)-H(28)···I(3)#5	0.930	3.127	3.720	123.34
N(1)-H(1A)···I(7)#3	0.860	2.845	3.643	155.11
N(2)-H(2A)···I(2)#2	0.860	3.292	3.796	119.96
N(2)-H(2A)···I(3)	0.860	3.231	3.691	116.09
N(2)-H(2A)···I(7)	0.860	3.212	3.865	134.69
N(3)-H(3)···I(6)#3	0.860	2.894	3.678	152.47
N(4)-H(4)···I(2)	0.860	3.141	3.599	115.68
N(4)-H(4)···I(3)	0.860	3.245	3.753	120.33
N(4)-H(4)···I(6)	0.860	3.253	3.889	132.81
N(5)-H(5A)···I(8)#3	0.860	2.847	3.643	154.57
N(6)-H(6)···I(3)#5	0.860	3.225	3.686	116.17
N(6)-H(6)···I(4)#4	0.860	3.289	3.793	120.06

N(6)-H(6)···I(8)#4	0.860	3.216	3.866	134.33
N(7)-H(7)···I5	0.860	3.216	3.676	152.37
N(8)-H(8)···I(3)#5	0.860	3.249	3.757	120.38
N(8)-H(8)···I(4)#5	0.860	3.127	3.593	116.39
N(8)-H(8)···I(5)#5	0.860	3.261	3.893	132.39

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

Compound **3**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(2)-H(2)···I(1)#1	0.930	3.190	3.839	128.53
C(5)-H(5)···I(3)#2	0.930	3.008	3.899	160.95
C(8)-H(8)···I(3)#3	0.930	3.202	4.043	151.40
C(9)-H(9A)···I(1)#3	0.960	3.175	4.088	159.36
C(9)-H(9B)···I(3)	0.960	3.311	4.236	162.32

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

Compound **4**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(1)-H(1C)···I(3)#1	0.960	2.998	3.915	160.18
C(1)-H(1A)···I(3)#2	0.960	3.215	4.079	150.54
C(2)-H(2)···I(1)#3	0.930	3.297	3.909	125.33
C(3)-H(3A)···I(3)#3	0.960	3.178	4.101	161.72
C(6)-H(6)···I(2)	0.930	3.192	4.111	170.03

#1 x-1, y, z-1; #2 -x+1, -y+1, -z+1; #3 -x+1, -y+1, -z; #4 x, y, z-1; #5 x, -y+1/2, z-1/2

Table S4. Synthesis conditions for compounds **1**-**4**.

Entry	DMBI/BI (mmol)	AgI (mmol)	NaI·2H_2O (mmol)	HI (mL)	Methanol (mL)	Acetonitrile (mL)	Product
1	0.6	0.6	2	0.2	2	3	**1**
2	0.6	0.6	2	0.2	5	0	**2**
3	0.6	1.2	2	0.2	2	3	**3**
4	0.6	1.2	2	0.2	2	3	**4**