Supplementary Information

2-D Silver-thiocyanate Layers Directed by Viologens: Structural Transformations upon Low Pressure Stimuli, Piezochromic Luminescence, Photocurrent Responses and Photocatalytic Properties

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Table S1 Selected Bond Lengths (Å) for 1, 2

			***α*-1**		
Ag(1)-S(1)	2.6746(11)	Ag(1)-S(2)	2.7026(11)	Ag(1)-N(2)	2.248(3)
Ag(1)-N(4)	2.214(3)	Ag(2)-S(1)	2.7353(11)	Ag(2)-S(2)	2.5695(10)
Ag(2)-S(3)	2.5296(11)	Ag(2)-N(3)#1	2.298(3)	Ag(1)-Ag(2)	3.0789(6)
N(4)-Ag(1)-N(2)	128.45(12)	N(4)-Ag(1)-S(1)	111.37(10)	N(2)-Ag(1)-S(1)	99.26(9)
N(4)-Ag(1)-S(2)	109.32(10)	N(2)-Ag(1)-S(2)	98.41(9)	S(1)-Ag(1)-S(2)	108.18(3)
N(3)#1-Ag(2)-S(3)	115.83(8)	N(3)#1-Ag(2)-S(2)	104.09(8)	S(3)-Ag(2)-S(2)	120.66(3)
N(3)#1-Ag(2)-S(1)	98.36(9)	S(3)-Ag(2)-S(1)	105.34(3)	S(2)-Ag(2)-S(1)	110.33(3)
Symmetry code: #1 -x+1,y,-z+3/2					
			***β*-1**		
Ag(1)-S(1)	2.5737(9)	Ag(1)-S(2)	2.7396(10)	Ag(1)-S(3)	2.5316(9)
Ag(1)-N(4)	2.306(3)	Ag(2)-S(1)	2.7055(10)	Ag(2)-S(2)	2.6768(9)
Ag(2)-N(1)#1	2.211(3)	Ag(2)-N(3)	2.245(3)	Ag(1)-Ag(2)	3.0826(5)
N(4)-Ag(1)-S(3)	115.80(8)	N(4)-Ag(1)-S(1)	104.09(8)	S(3)-Ag(1)-S(1)	120.65(3)
N(4)-Ag(1)-S(2)	98.43(9)	S(3)-Ag(1)-S(2)	105.37(3)	S(1)-Ag(1)-S(2)	110.29(3)
N(1)#1-Ag(2)-N(3)	128.47(11)	N(1)#1-Ag(2)-S(2)	111.35(9)	N(3)-Ag(2)-S(2)	99.31(8)
N(1)#1-Ag(2)-S(1)	109.24(10)	N(3)-Ag(2)-S(1)	98.38(9)	S(2)-Ag(2)-S(1)	108.24(3)
Symmetry code: #1 x+1/2,y+1/2,z					
			***α*-2**		
Ag(1)-S(1)	2.5005(13)	Ag(1)-S(2)	2.5476(13)	Ag(1)-S(2)#2	2.7741(13)
Ag(1)-N(3)#1	2.303(4)				
N(3)#1-Ag(1)-S(1)	113.01(11)	N(3)#1-Ag(1)-S(2)	99.31(11)	S(1)-Ag(1)-S(2)	137.07(4)
N(3)#1-Ag(1)-S(2)#2	98.68(11)	S(1)-Ag(1)-S(2)#2	103.97(4)	S(2)-Ag(1)-S(2)#2	97.94(4)
Symmetry codes: #1 x,-y+1/2,z-1/2; #2 -x+2,-y,-z					

***β*-2**					
Ag(1)-S(1)	2.5010(9)	Ag(1)-S(2)	2.5476(9)	Ag(1)-S(2)#1	2.8021(9)
Ag(1)-N(2)	2.302(2)				
N(2)-Ag(1)-S(1)	112.87(7)	N(2)-Ag(1)-S(2)	100.01(7)	S(1)-Ag(1)-S(2)	136.97(3)
N(2)-Ag(1)-S(2)#1	98.80(7)	S(1)-Ag(1)-S(2)#1	103.80(3)	S(2)-Ag(1)-S(2)#1	97.46(2)
Symmetry codes: #1 -x,-y,-z+1					

Table S2 Selected Bond Lengths (Å) for 3, 4

***α*-3**					
Ag(1)-S(1)	2.7294(13)	Ag(1)-S(2)	2.5818(10)	Ag(1)-S(3)	2.5523(11)
Ag(1)-N(4)#1	2.307(3)	Ag(2)-S(1)	2.6437(12)	Ag(2)-S(2)	2.7279(12)
Ag(2)-N(2)	2.186(4)	Ag(2)-N(3)	2.236(4)	Ag(1)-Ag(2)	3.1319(6)
N(4)#1-Ag(1)-S(3)	109.70(9)	N(4)#1-Ag(1)-S(2)	103.85(9)	S(3)-Ag(1)-S(2)	124.10(4)
N(4)#1-Ag(1)-S(1)	101.28(10)	S(3)-Ag(1)-S(1)	106.56(4)	S(2)-Ag(1)-S(1)	109.08(4)
N(2)-Ag(2)-N(3)	126.23(14)	N(2)-Ag(2)-S(1)	115.59(11)	N(3)-Ag(2)-S(1)	103.01(10)
N(2)-Ag(2)-S(2)	101.38(13)	N(3)-Ag(2)-S(2)	101.10(11)	S(1)-Ag(2)-S(2)	107.31(4)
Symmetry code: #1 -x+1,y,-z+1/2					
***β*-3**					
Ag(1)-S(1)	2.7297(10)	Ag(1)-S(2)	2.5536(9)	Ag(1)-S(3)	2.5842(9)
Ag(1)-N(3)	2.306(3)	Ag(2)-S(1)	2.6457(10)	Ag(2)-S(3)	2.7278(10)
Ag(2)-N(2)#1	2.238(3)	Ag(2)-N(4)	2.190(3)	Ag(1)-Ag(2)	3.1311(5)
N(3)-Ag(1)-S(2)	109.71(8)	N(3)-Ag(1)-S(3)	103.86(8)	S(2)-Ag(1)-S(3)	124.16(3)
N(3)-Ag(1)-S(1)	101.18(8)	S(2)-Ag(1)-S(1)	106.50(3)	S(3)-Ag(1)-S(1)	109.12(3)
N(4)-Ag(2)-N(2)#1	126.32(12)	N(4)-Ag(2)-S(1)	115.84(10)	N(2)#1-Ag(2)-S(1)	102.98(9)
N(4)-Ag(2)-S(3)	101.09(11)	N(2)#1-Ag(2)-S(3)	100.94(9)	S(1)-Ag(2)-S(3)	107.38(3)
Symmetry code: #1 -x+1,y,-z+1/2					
4					
Ag(1)-S(1)	2.5827(11)	Ag(1)-S(2)	2.6365(12)	Ag(1)-S(3)	2.5546(10)
Ag(1)-N(6)#1	2.251(3)	Ag(2)-S(3)	2.6241(10)	Ag(2)-S(4)	2.6700(11)
Ag(2)-N(3)#2	2.189(4)	Ag(2)-N(4)	2.243(4)		
N(6)#1-Ag(1)-S(3)	119.23(10)	N(6)#1-Ag(1)-S(1)	104.90(10)	S(3)-Ag(1)-S(1)	110.38(4)
N(6)#1-Ag(1)-S(2)	103.68(9)	S(3)-Ag(1)-S(2)	107.67(4)	S(1)-Ag(1)-S(2)	110.73(4)
N(3)#2-Ag(2)-N(4)	129.28(17)	N(3)#2-Ag(2)-S(3)	115.19(12)	N(4)-Ag(2)-S(3)	95.02(12)
N(3)#2-Ag(2)-S(4)	99.77(11)	N(4)-Ag(2)-S(4)	104.05(10)	S(3)-Ag(2)-S(4)	113.65(3)
Symmetry code: #1 -x+3/2,y+1/2,-z+1/2; #2 x-1,y,z					

Table S3 Selected Bond Lengths (Å) for 5

***α*-5**					
Ag(1)-S(1)	2.6089(9)	Ag(1)-S(2)	2.5385(9)	Ag(1)-S(3)	2.6267(10)
Ag(1)-N(4)#1	2.344(3)	Ag(2)-S(1)	2.7786(9)	Ag(2)-S(3)	2.6188(9)
Ag(2)-N(2)	2.177(3)	Ag(2)-N(3)	2.222(3)	Ag(1)-Ag(2)	3.1098(4)
N(4)#1-Ag(1)-S(2)	102.26(8)	N(4)#1-Ag(1)-S(1)	101.62(10)	S(2)-Ag(1)-S(1)	121.36(3)
N(4)#1-Ag(1)-S(3)	102.99(11)	S(2)-Ag(1)-S(3)	114.60(3)	S(1)-Ag(1)-S(3)	110.80(3)
N(2)-Ag(2)-N(3)	130.33(11)	N(2)-Ag(2)-S(3)	113.22(9)	N(3)-Ag(2)-S(3)	103.59(9)

N(2)-Ag(2)-S(1)	103.13(10)	N(3)-Ag(2)-S(1)	97.27(9)	S(3)-Ag(2)-S(1)	105.93(3)
Symmetry code: #1 -x+1,y,-z+3/2					
		***β*-5**			
Ag(1)-S(1)	2.6363(11)	Ag(1)-S(2)	2.5333(11)	Ag(1)-S(3)	2.6238(11)
Ag(1)-N(1)	2.344(4)	Ag(2)-S(1)	2.6319(11)	Ag(2)-S(3)	2.7887(11)
Ag(2)-N(2)	2.221(4)	Ag(2)-N(3)#1	2.171(4)	Ag(1)-Ag(2)	3.1741(6)
N(1)-Ag(1)-S(2)	101.97(10)	N(1)-Ag(1)-S(3)	100.81(12)	S(2)-Ag(1)-S(3)	122.33(4)
N(1)-Ag(1)-S(1)	104.47(14)	S(2)-Ag(1)-S(1)	114.82(4)	S(3)-Ag(1)-S(1)	109.39(3)
N(3)#1-Ag(2)-N(2)	130.66(14)	N(3)#1-Ag(2)-S(1)	112.24(12)	N(2)-Ag(2)-S(1)	103.84(10)
N(3)#1-Ag(2)-S(3)	104.26(13)	N(2)-Ag(2)-S(3)	97.60(10)	S(1)-Ag(2)-S(3)	104.70(3)
Symmetry code: #1 x+1/2,y+1/2,z					

Table S4 Selected Bond Lengths (Å) for 6, 7

		6			
Ag(1)-S(2)	2.5924(9)	Ag(1)-S(1)	2.6061(9)	Ag(1)-N(3)	2.227(3)
Ag(1)-N(4)	2.260(3)				
N(3)-Ag(1)-N(4)	121.79(13)	N(3)-Ag(1)-S(2)	101.51(9)	N(4)-Ag(1)-S(2)	111.73(9)
N(3)-Ag(1)-S(1)	109.63(9)	N(4)-Ag(1)-S(1)	101.27(8)	S(2)-Ag(1)-S(1)	111.02(3)
		***α*-7**			
Ag(1)-S(1)#1	2.5700(10)	Ag(1)-S(1)	2.6457(10)	Ag(1)-N(3)	2.247(3)
Ag(1)-S(2)	2.5171(10)				
N(3)-Ag(1)-S(2)	120.41(10)	N(3)-Ag(1)-S(1)#1	114.52(10)	S(2)-Ag(1)-S(1)#1	108.61(3)
N(3)-Ag(1)-S(1)	97.62(10)	S(2)-Ag(1)-S(1)	112.67(4)	S(1)#1-Ag(1)-S(1)	100.83(2)
Symmetry code: #1 x+1/2,-y+1/2,z+1/2					
		***β*-7**			
Ag(1)-S(1)#1	2.5686(12)	Ag(1)-S(1)	2.6453(12)	Ag(1)-N(3)	2.249(4)
Ag(1)-S(2)	2.5171(12)				
N(3)-Ag(1)-S(2)	120.31(12)	N(3)-Ag(1)-S(1)#1	114.45(12)	S(2)-Ag(1)-S(1)#1	108.70(4)
N(3)-Ag(1)-S(1)	97.74(12)	S(2)-Ag(1)-S(1)	112.63(4)	S(1)#1-Ag(1)-S(1)	100.85(3)
Symmetry code: #1 x+1/2,-y+1/2,z+1/2					

Table S5 Hydrogen bridging details of 2, 4, 6 and 7

Compound	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/°	Symmetry codes
***α*-2**	C(2)-H(2)···N(2)	0.93	2.56	3.378(6)	147	2-x,1/2+y,1/2-z
	C(4)-H(4)···N(2)	0.93	2.48	3.302(7)	148	x,1/2-y,-1/2+z
	C(5)-H(5)···N(2)	0.93	2.53	3.267(7)	136	3-x,1/2+y,1/2-z
***β*-2**	C(1)-H(1C)···N(3)	0.96	2.49	3.325(4)	146	x,1/2-y,1/2+z
	C(2)-H(2)···N(3)	0.93	2.59	3.313(4)	135	-1-x,-y,1-z
	C(3)-H(3)···N(3)	0.93	2.49	3.313(3)	147	x,y,1+z
	C(5)-H(5)···N(3)	0.93	2.60	3.420(4)	147	-x,-y,1-z
4	C(1)-H(1)···N(5)	0.93	2.58	3.466(6)	160	1/2+x,1/2-y,1/2+z
	C(8)-H(8)···S(4)	0.93	2.78	3.659(3)	158	
	C(11)-H(11A)···S(1)	0.96	2.75	3.525(6)	135	1/2+x,1/2-y,1/2+z

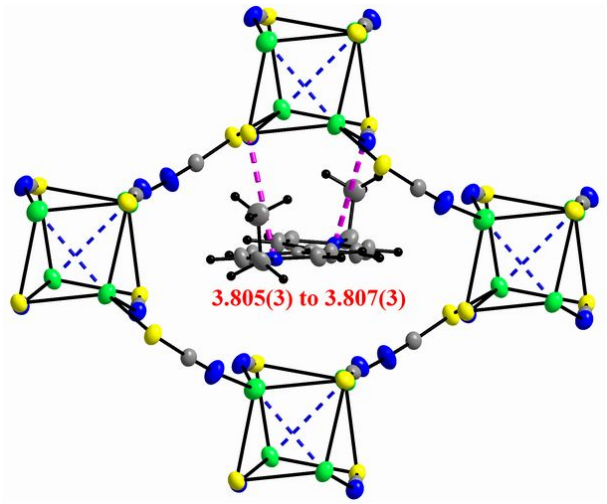
6	C(6)-H(6)···N(2)	0.97	2.60	3.533(4)	160	-x,1/2+y,3/2-z
***α*-7**	C(2)-H(2)···N(2)	0.93	2.37	3.279(6)	165	1+x,y,z
	C(3)-H(3)···N(2)	0.93	2.60	3.476(6)	157	2-x,-y,1-z
***β*-7**	C(4)-H(4)···N(2)	0.93	2.60	3.477(7)	157	1-x,-y,-z
	C(5)-H(5)···N(2)	0.93	2.37	3.280(8)	168	1+x,y,z

Table S6. C–N···π interaction parameters for 7

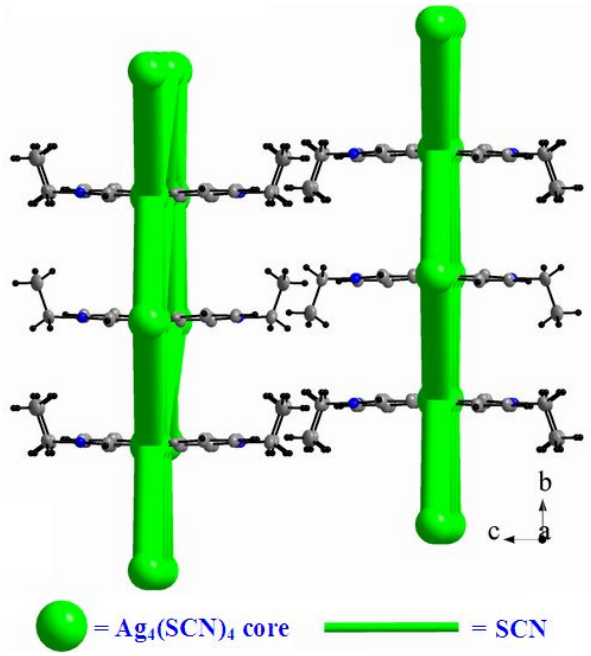
	C–N···π	C···C_g/Å	N···C_g/Å	∠(C–H···C_g)/°	Symmetry transformation
***α*-7**	C(9)–N(2)···C_g(1)	3.676(5)	3.561(4)	75.2(3)	2-x,-y,-z
	C_g(1):N(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				
***β*-7**	C(9)–N(2)···C_g(1)	3.674(6)	3.553	75.4(4)	x,y, z
	C_g(1): N(1)→C(1)→C(2)→ C(3)→C(4)→C(5)→				

Table S7 Summary of S···N, S···S distances and dihedral angle in viologens

Compound	S···N/Å	S···S interaction/Å	Dihedral angle in viologen/°
***α*-1**	3.856(2)	3.730(1)	9.76
***β*-1**	3.860(3)	3.736(1)	10.26
***α*-2**	3.650(4)	4.191(5)	0.000
***β*-2**	3.682(2)/3.760(2)	4.255(2)	0.050
***α*-3**	3.805(3)	4.184(2)	8.74
***β*-3**	3.807(3)	4.184(1)	8.74
4	3.695(3)/3.828(4)	5.984(6)	14.6
***α*-5**	4.050(1)	4.462(3)	0.029
***β*-5**	4.115(1)	4.563(1)	10.83
6	3.644(2)	4.133(2)	0.050

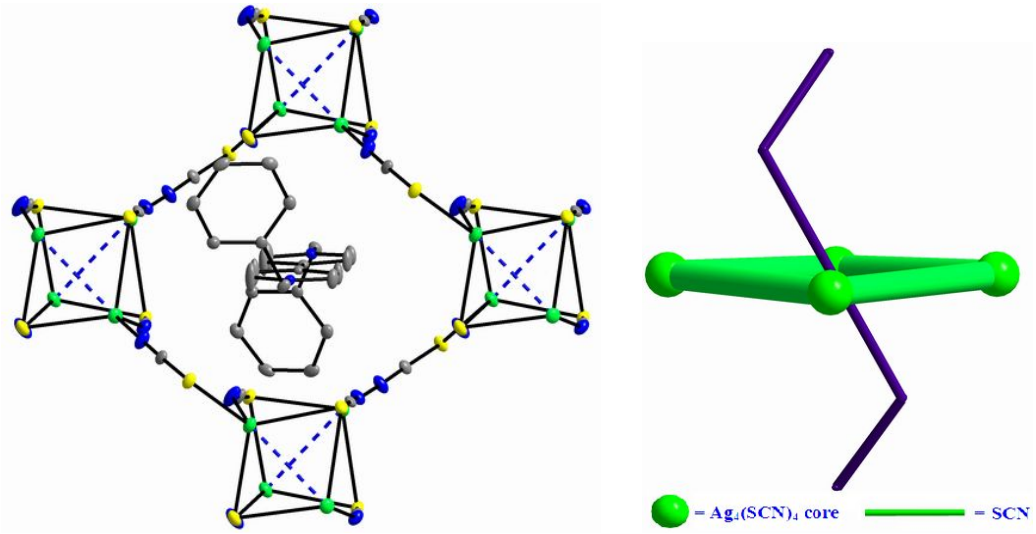


(a)

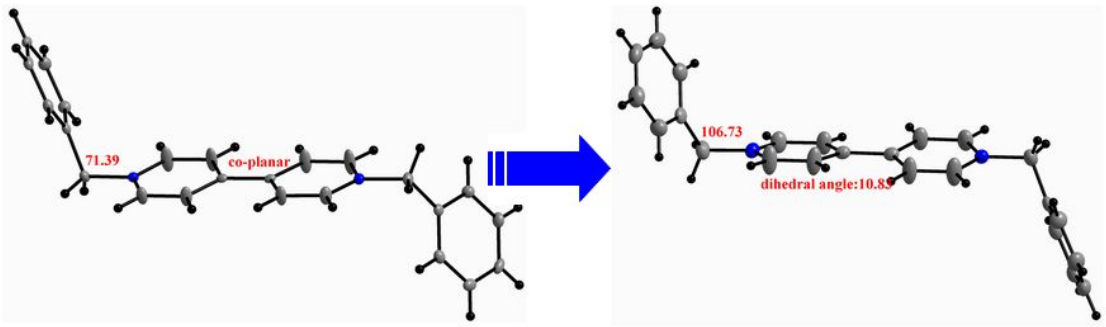


(b)

Fig. S1 (a) EV^{2+} cation confined in the $Ag_{16}(SCN)_{20}$ elliptic box showing weakened S···MV^{2+} interaction from α-3 to β-3 upon pressure; (b) Packing diagram illustrating configurations of EV^{2+}



(a)



(b)

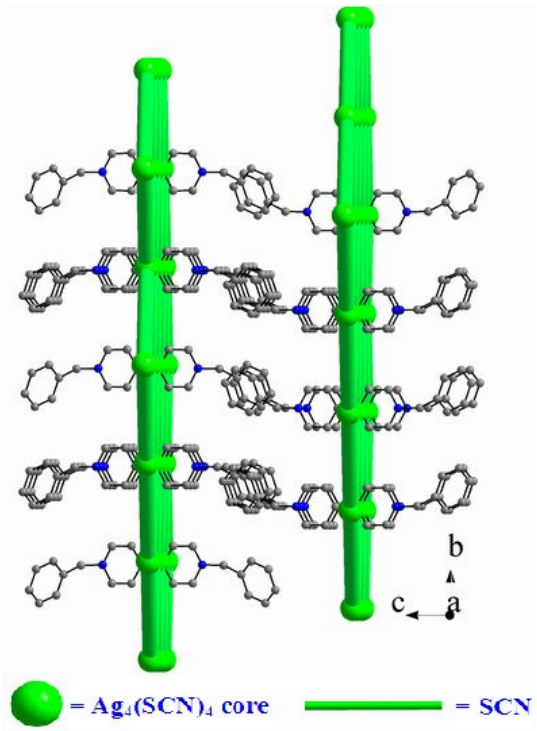
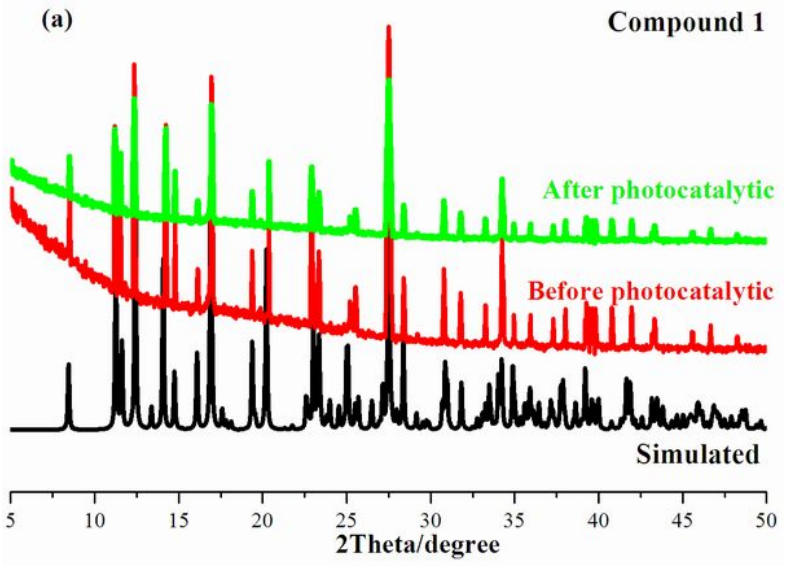
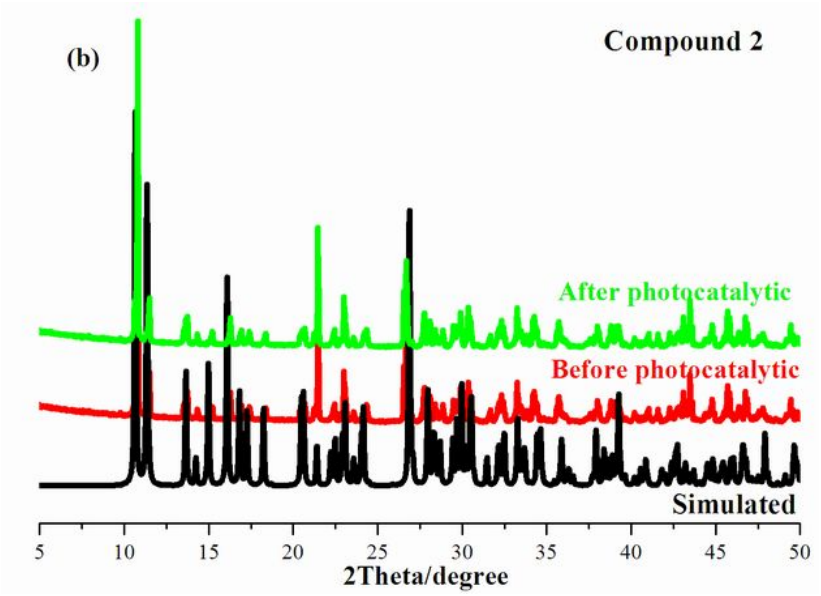
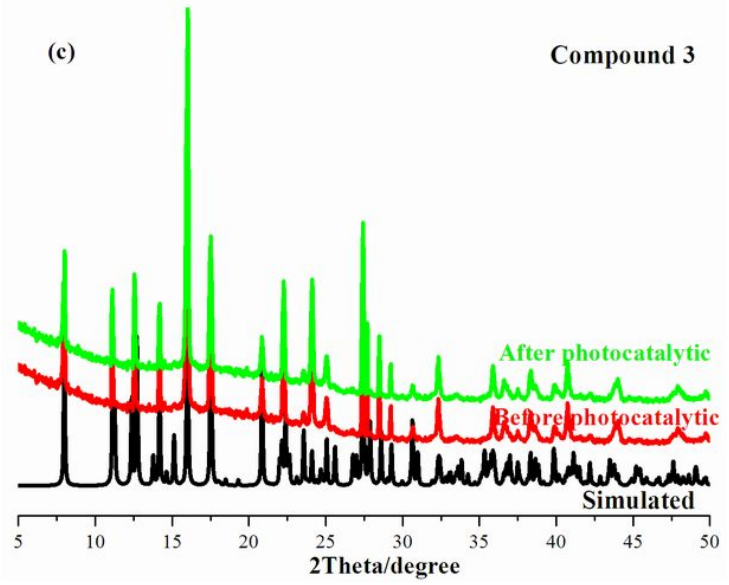
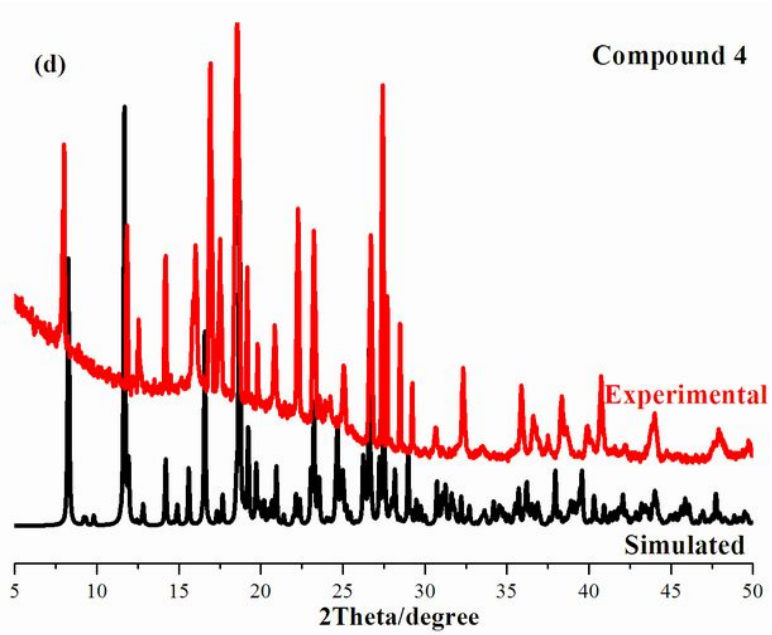


Fig. S2 (a) BV^{2+} cation confined in the $Ag_{16}(SCN)_{20}$ elliptic box showing the configuration of BV^{2+};(b) confirmation change of BV^{2+} upon pressure; (c) Packing diagram illustrating configurations of BV^{2+} in 5




(b)
Compound 2
After photocatalytic
Before photocatalytic
Simulated
5
10
15
20
25
30
35
40
45
50
2Theta/degree


(c)
Compound 3
After photocatalytic
Before photocatalytic
Simulated
5
10
15
20
25
30
35
40
45
50
2Theta/degree


(d)
Compound 4
Experimental
Simulated
5
10
15
20
25
30
35
40
45
50
2Theta/degree

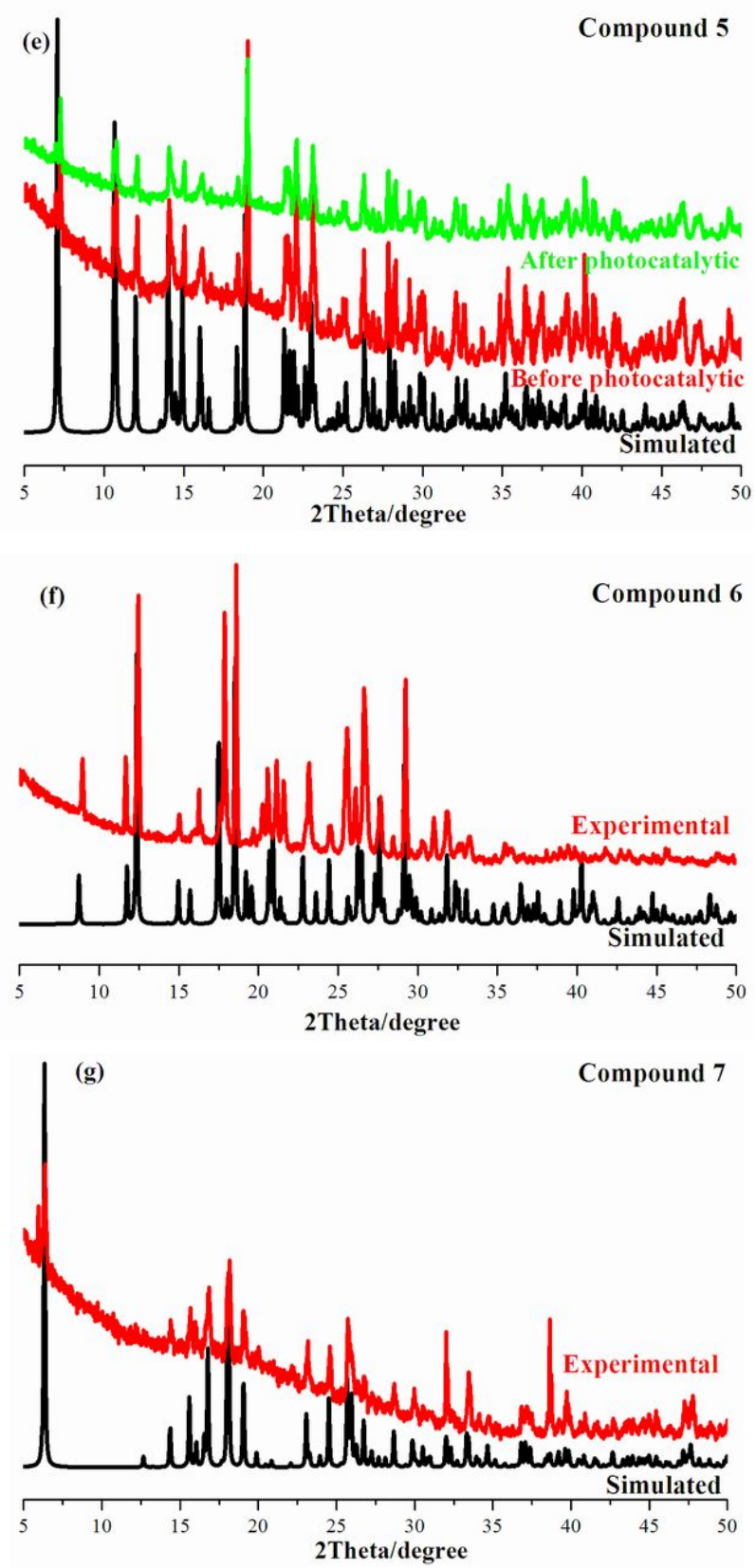
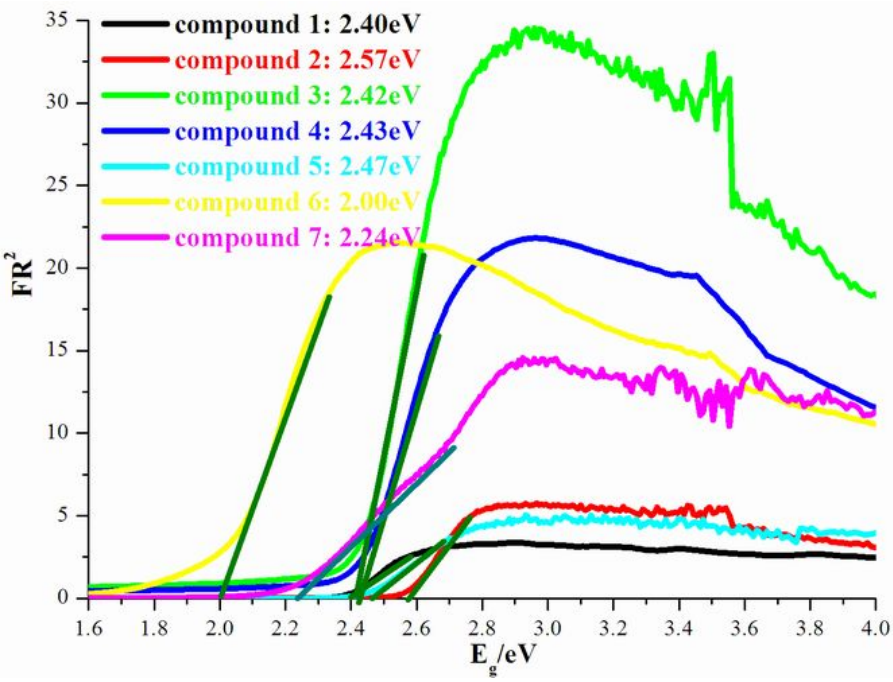
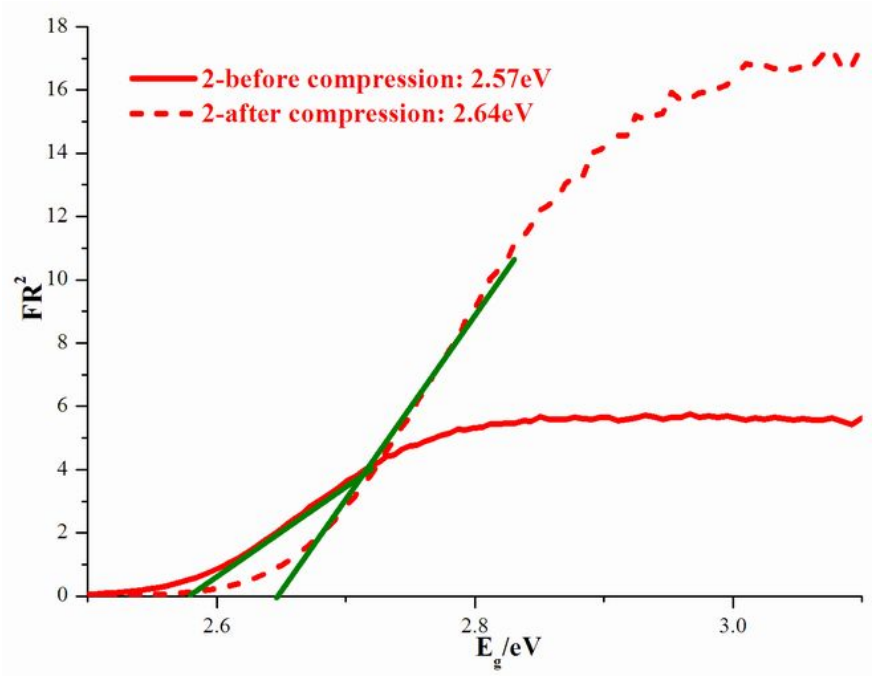


Fig. S3 Powder X-ray diffraction (PXRD) patterns of compounds 1-7

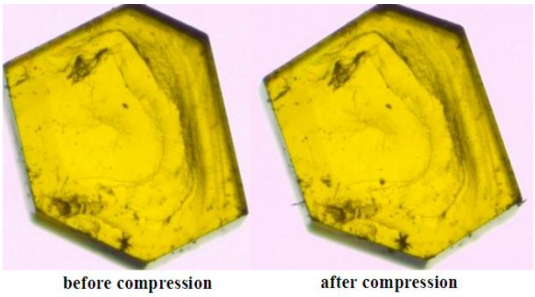


(a)

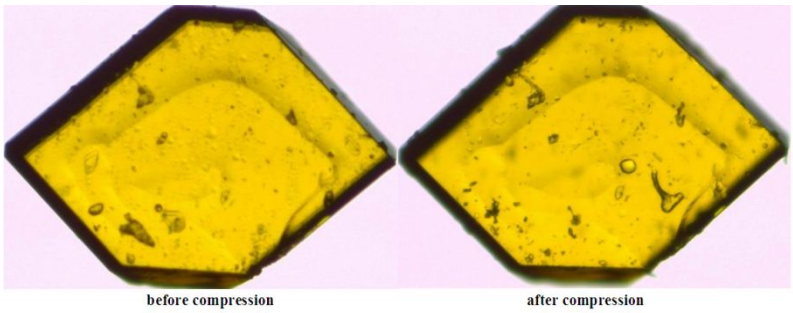


(b)

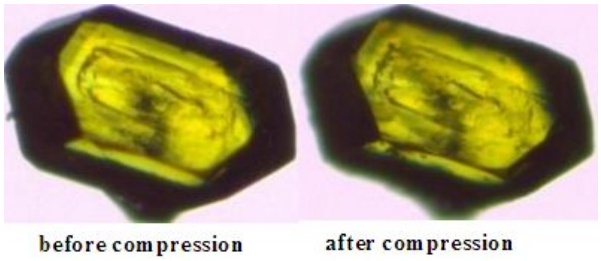
Fig. S4 (a) optical diffuse reflectance spectra for 1-7; (b) optical gap of 2 before and after compression



(a)



(b)



(c)

Fig. S5 Photographs of 1(a), 5(b) and 7(c) before and after compression

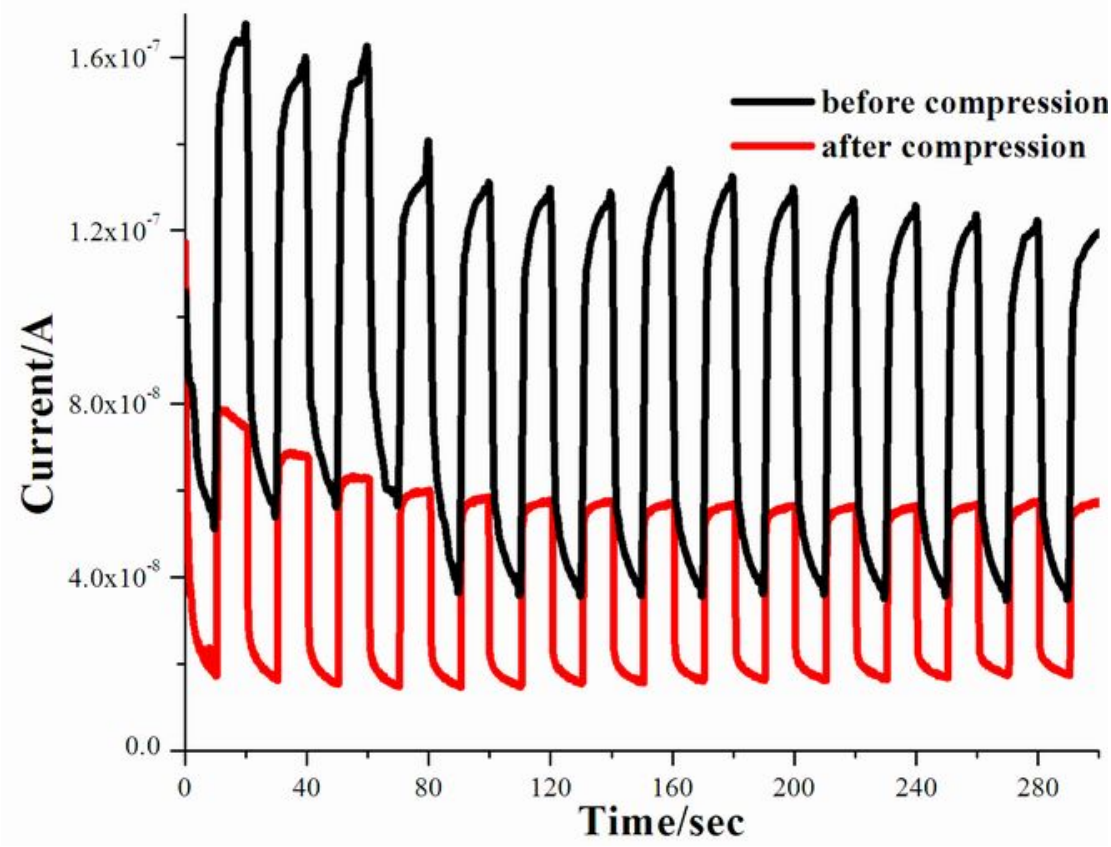
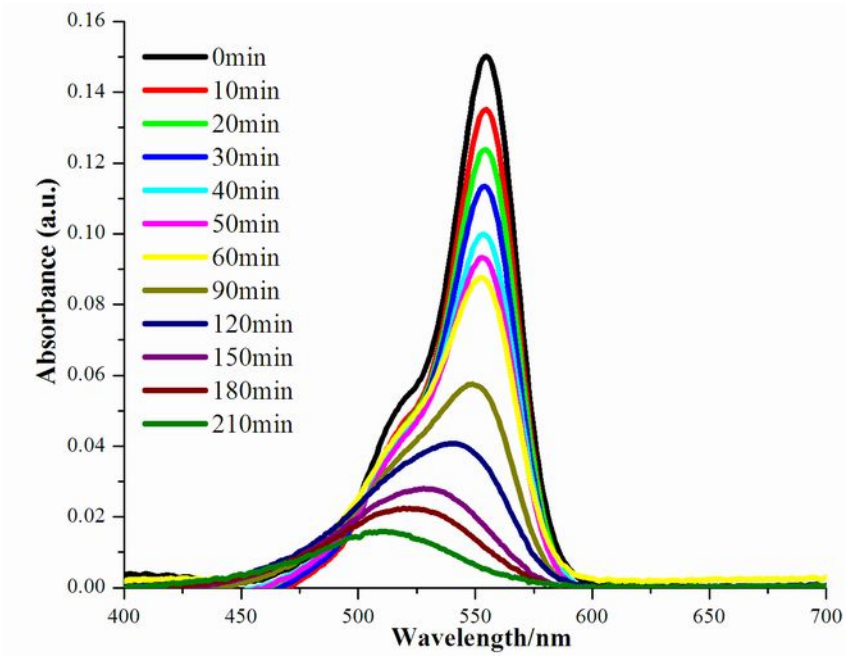
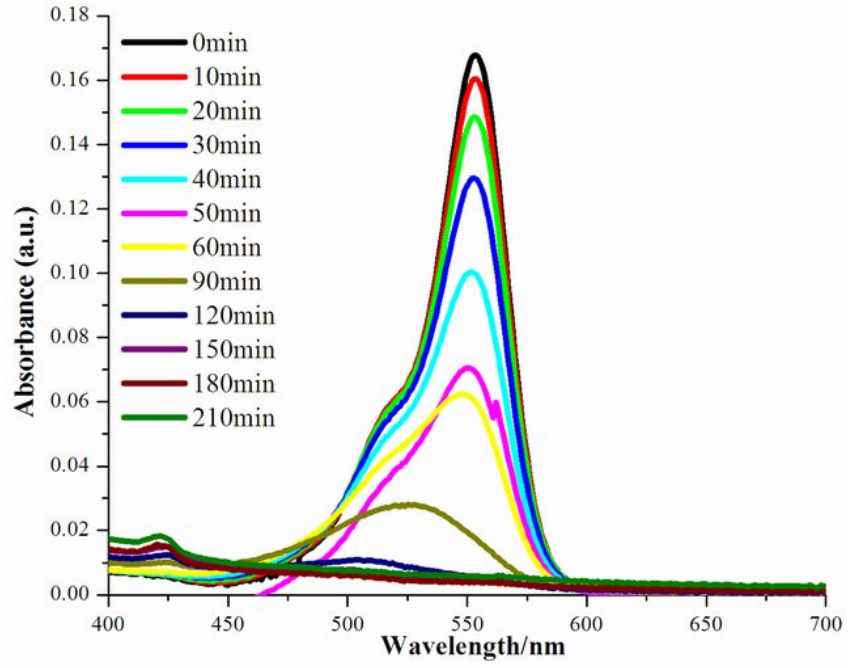


Fig. S10 Photocurrent of 3 before and after compression

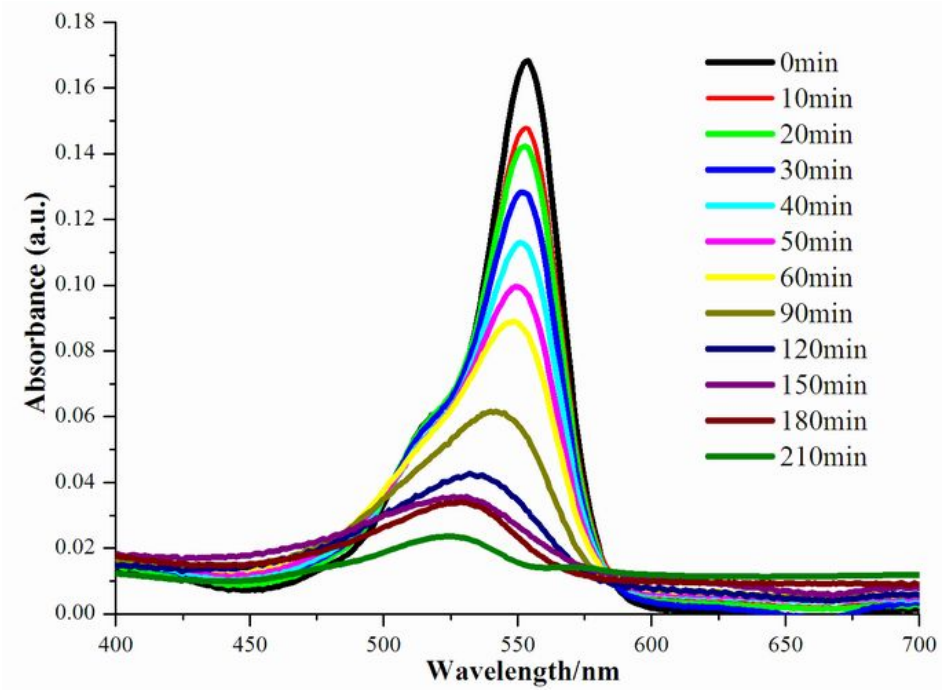


(a)

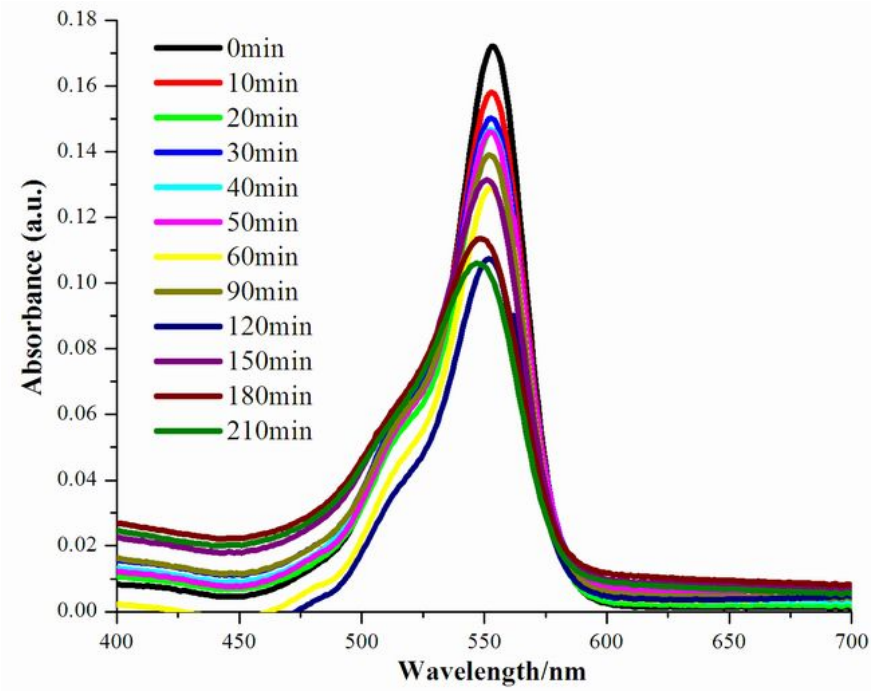

0min
10min
20min
30min
40min
50min
60min
90min
120min
150min
180min
210min
Absorbance (a.u.)
Wavelength/nm
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
400
450
500
550
600
650
700


0min
10min
20min
30min
40min
50min
60min
90min
120min
150min
180min
210min

(b)

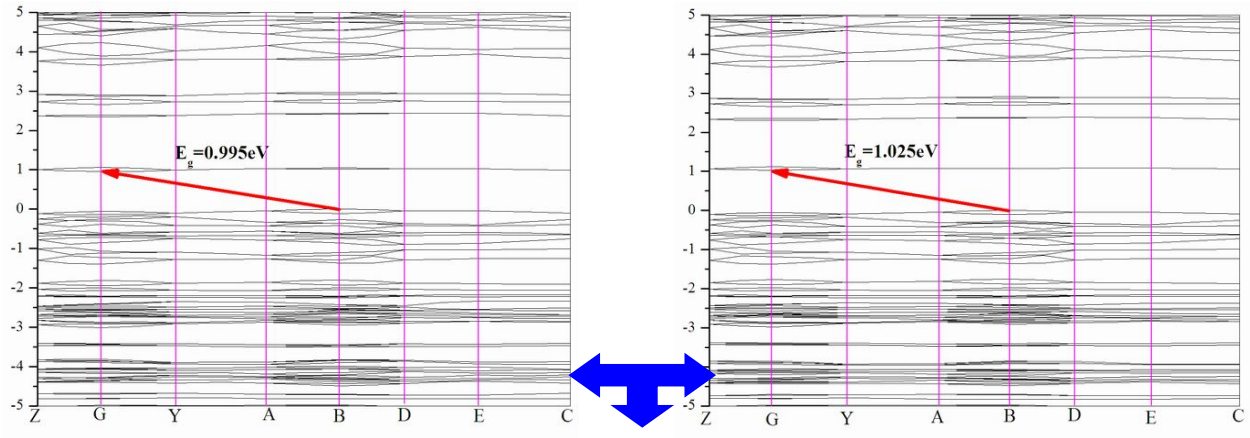

0min
10min
20min
30min
40min
50min
60min
90min
120min
150min
180min
210min
Absorbance (a.u.)
Wavelength/nm
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
400
450
500
550
600
650
700

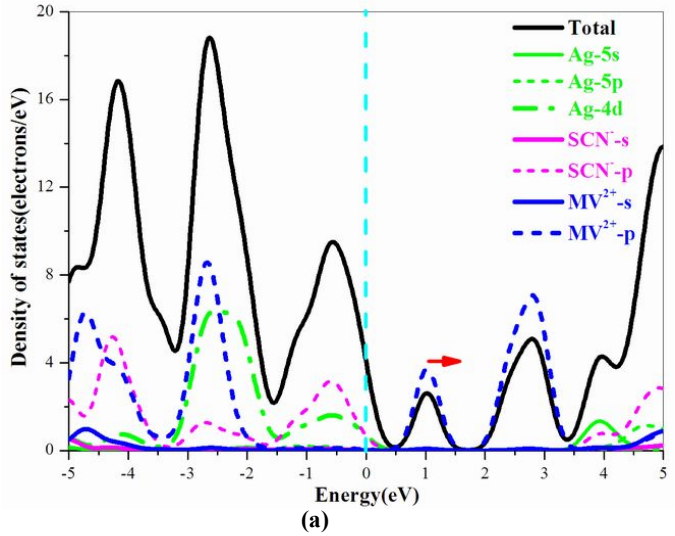
(c)



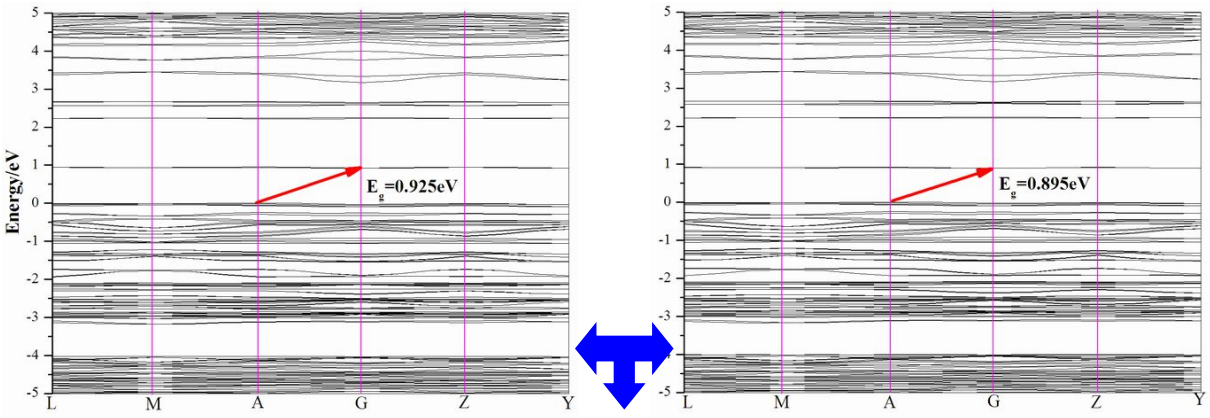
(d)

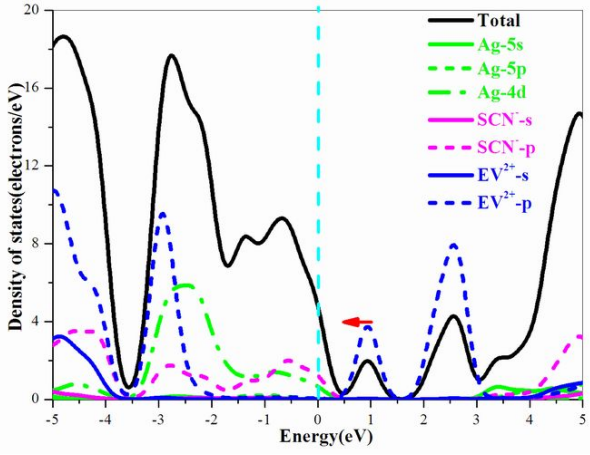
Fig. S11 Time-dependent UV−Vis spectra and photographs of RhB with the presence of 1 (a), 2 (b), 3 (c) and 5(d) under the irradiation of xenon-lamp


E_g=0.995eV
E_g=1.025eV
Z G Y A B D E C

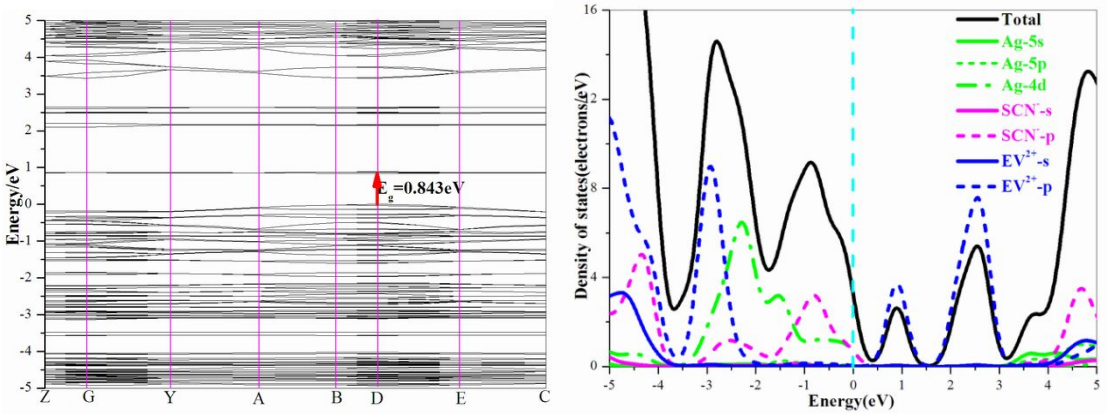

Total
Ag-5s
Ag-5p
Ag-4d
SCN⁻-s
SCN⁻-p
MV²⁺-s
MV²⁺-p
Density of states(electrons/eV)
Energy(eV)

(a)

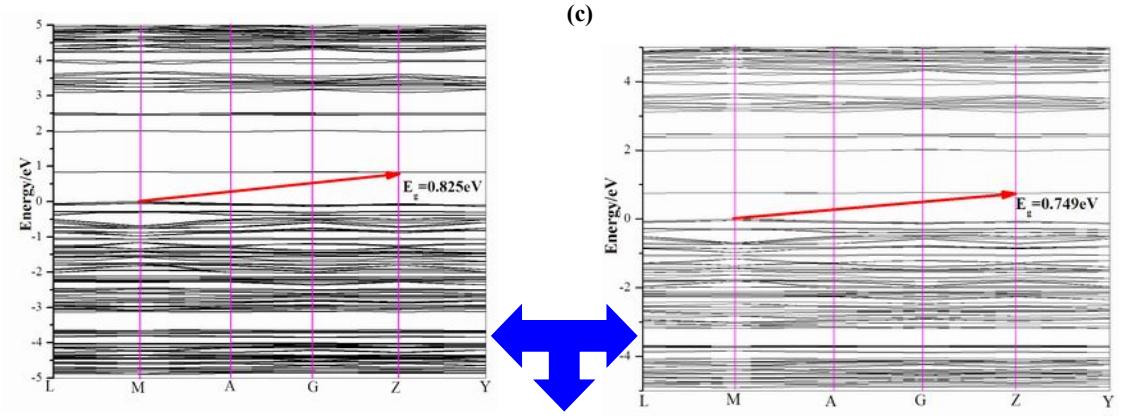

E_g=0.925eV
E_g=0.895eV
Energy/eV
L M A G Z Y

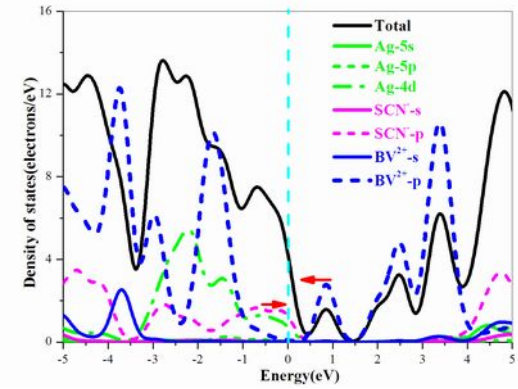

Total
Ag-5s
Ag-5p
Ag-4d
SCN⁻-s
SCN⁻-p
EV²⁺-s
EV²⁺-p
Density of states(electrons/eV)
Energy(eV)

3(b)

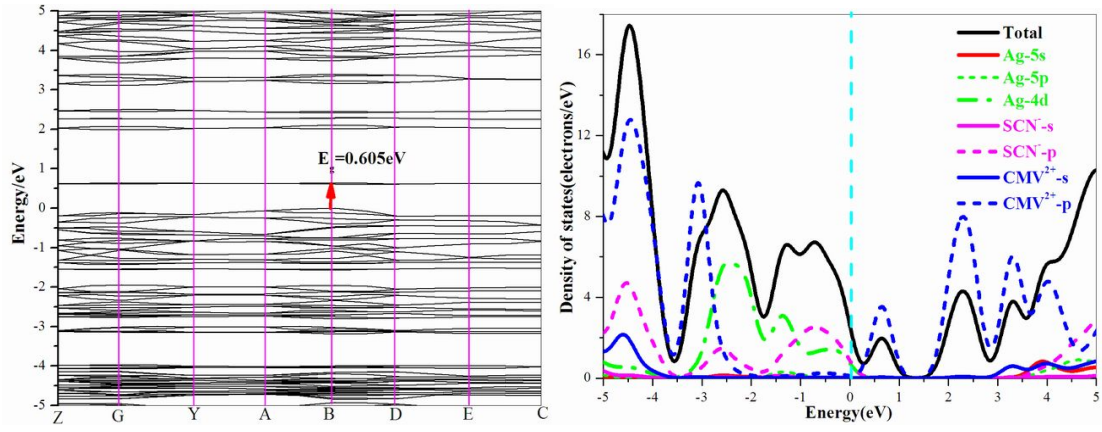

Energy/eV
Z G Y A B D E C
E_g=0.843eV
Density of states(electrons/eV)
Energy(eV)
Total
Ag-5s
Ag-5p
Ag-4d
SCN⁻-s
SCN⁻-p
EV²⁺-s
EV²⁺-p

(c)

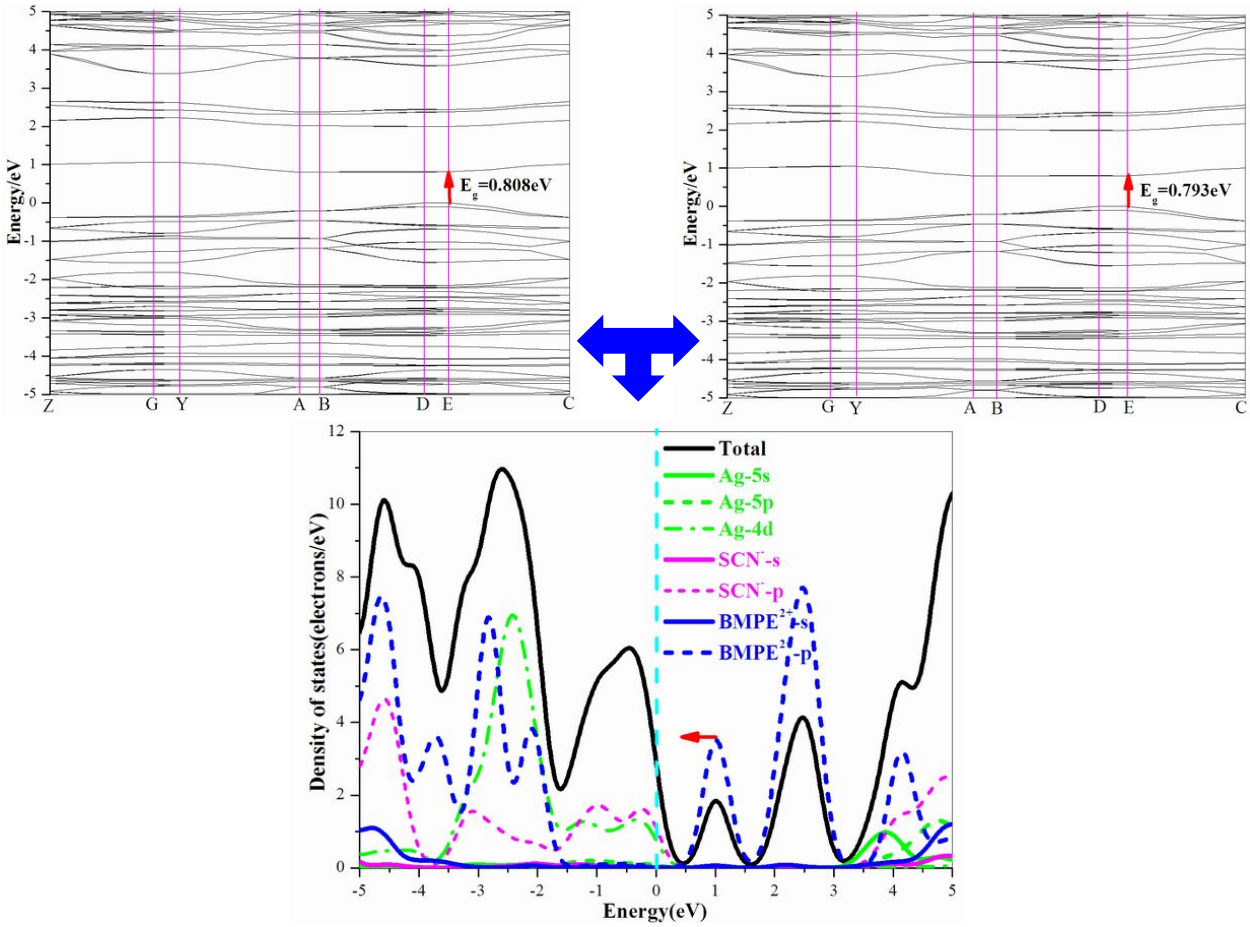

Energy/eV
L M A G Z Y
E_g=0.825eV
E_g=0.749eV


Density of states(electrons/eV)
Energy(eV)
Total
Ag-5s
Ag-5p
Ag-4d
SCN⁻-s
SCN⁻-p
BV²⁺-s
BV²⁺-p

(d)


Energy/eV
Z G Y A B D E C
E_g=0.605eV
Density of states(electrons/eV)
Energy(eV)
Total
Ag-5s
Ag-5p
Ag-4d
SCN⁻-s
SCN⁻-p
CMV²⁺-s
CMV²⁺-p

(e)



(f)

Fig. S12 Band structure correlation diagram (before compression: left; after compression: right) and DOS (bottom) of 2 (a), 3(b), 5(d), 7(f) and band structure (left) and DOS (right) of 4(c), 6(e)