

Electronic Supplementary Material (ESI) for Dalton Transactions.

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Non-transient Thermo-/Photochromism of Iodobismuthate Hybrids Directed by Solvated Metal Cations

Electronic Supplementary Information

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1. Figures

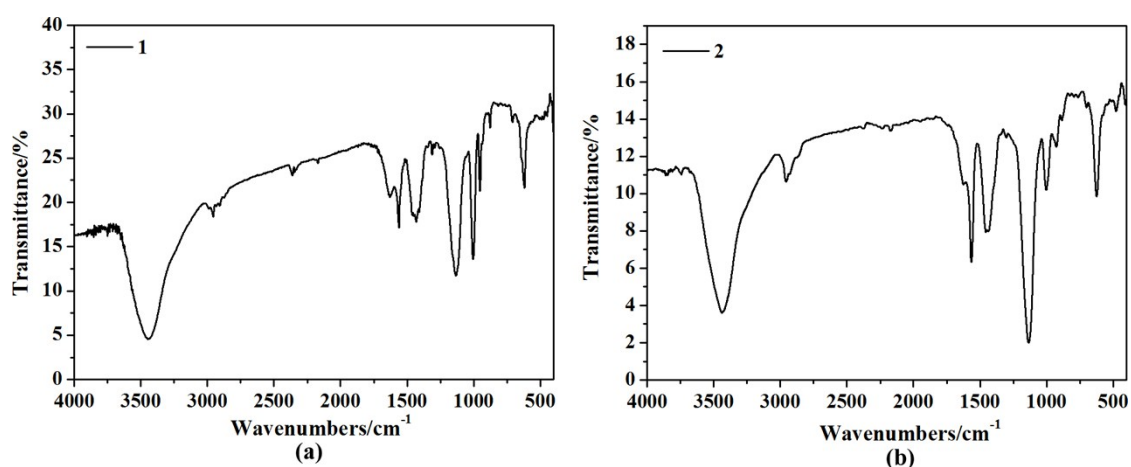


Fig. S1 IR spectra of 1 and 2.

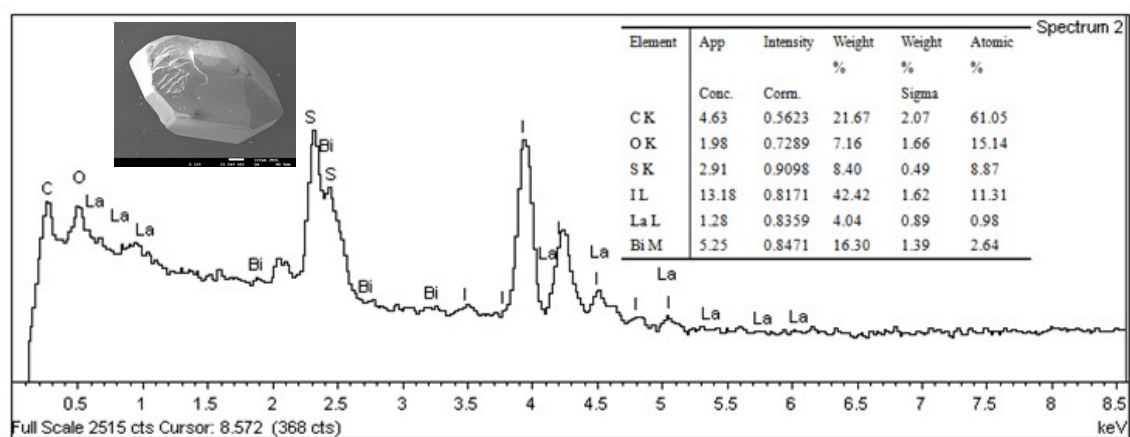


Fig. S2 The SEM images and EDS pattern of 1.

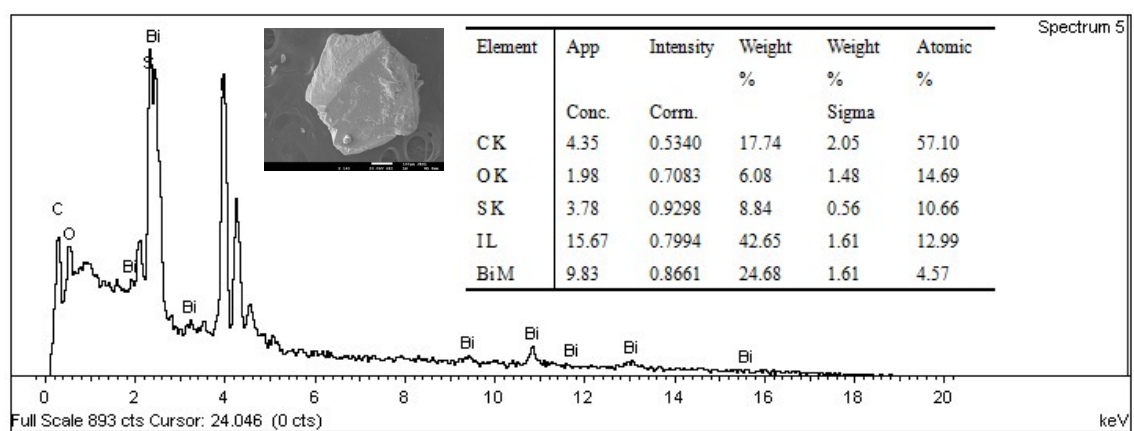


Fig. S3 The SEM images and EDS pattern of 2.

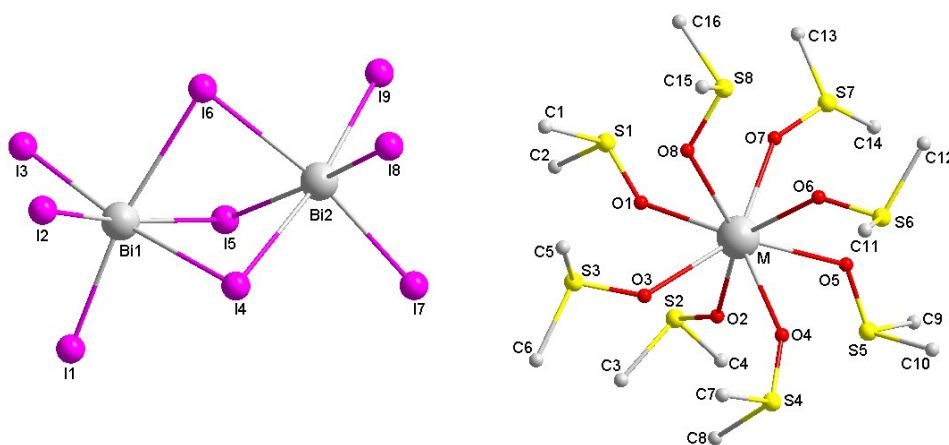


Fig. S4 The asymmetric unit of **1** and **2** (M = La (**1**), Bi (**2**)).

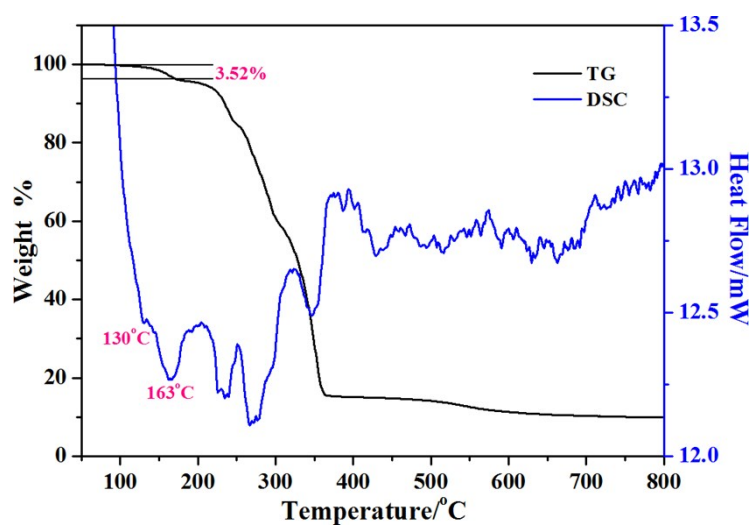


Fig. S5 TG-DSC curve of **1**.

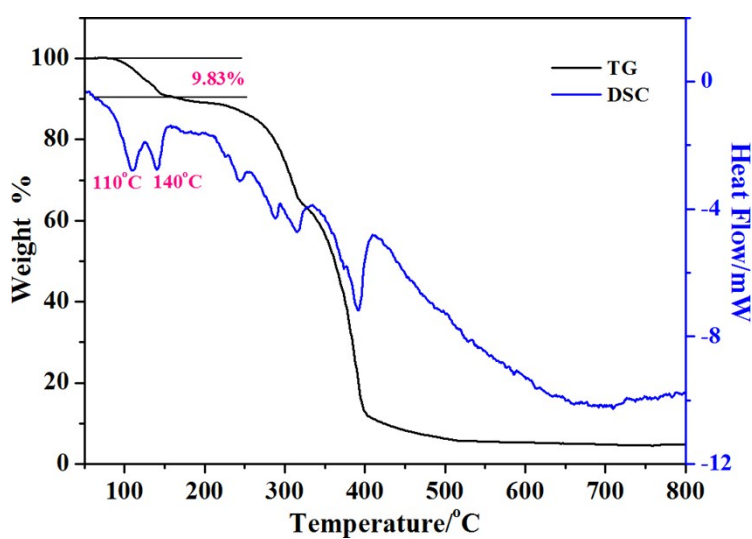


Fig. S6 TG-DSC curve of **2**.

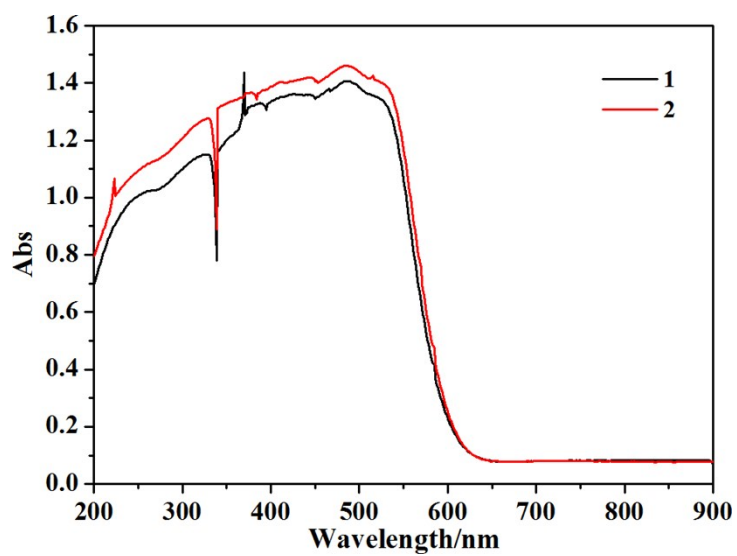


Fig. S7 The comparison of UV-vis absorption spectra for **1** and **2**.

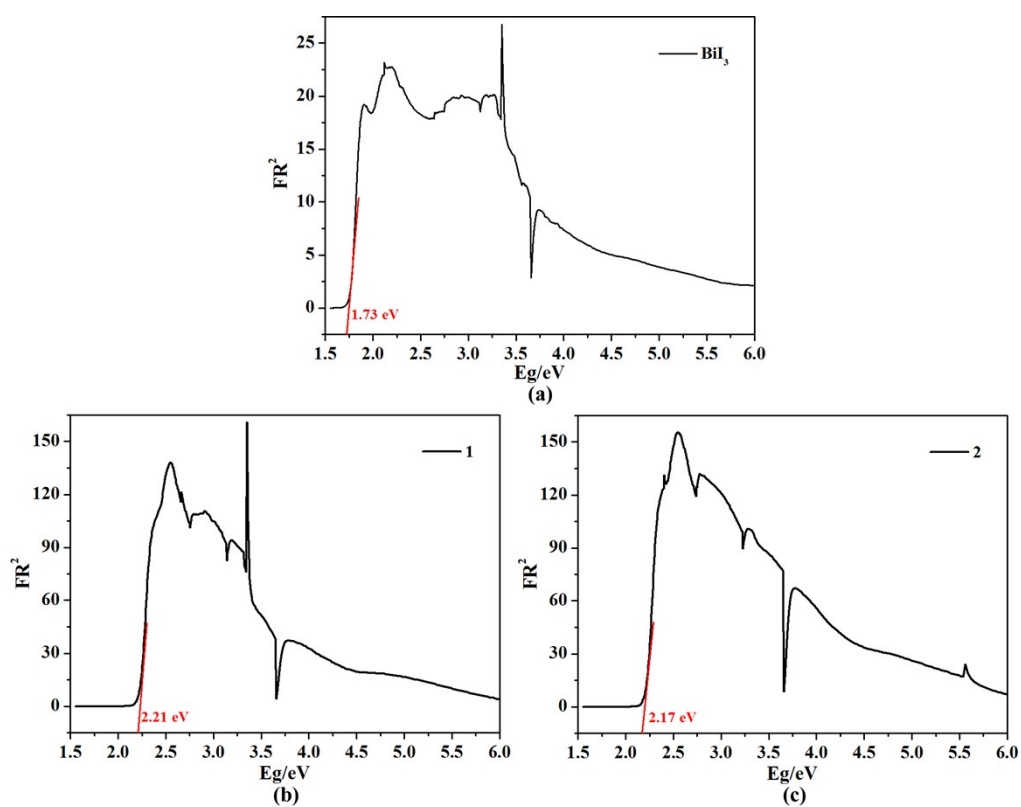


Fig. S8 The comparison of energy gaps for **1** and **2**.

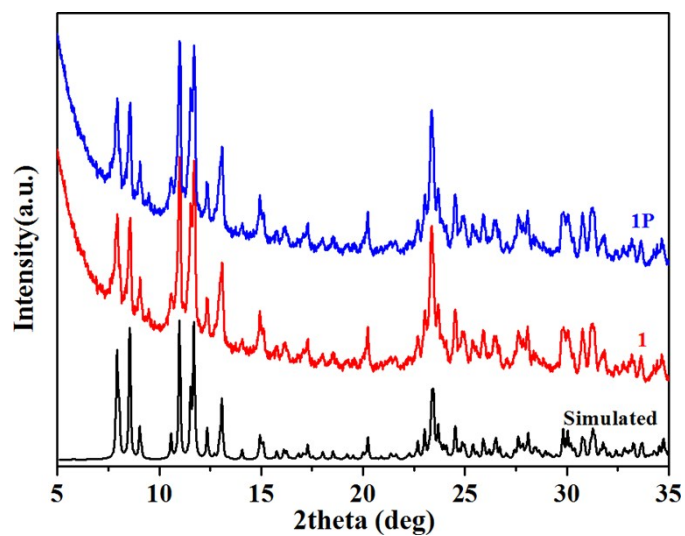


Fig. S9 UV-vis absorption spectra of **1** before and after light illumination.

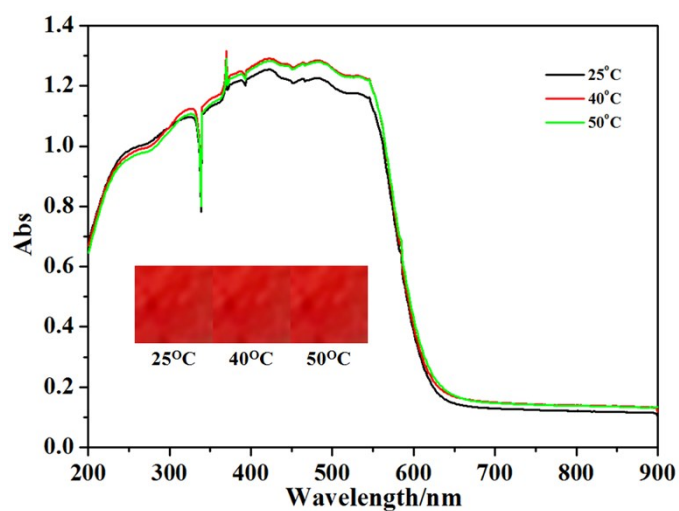


Fig. S10 Temperature-dependent UV-vis absorption spectra of **2** heated at the temperature range of 25–50°C for 15 min.

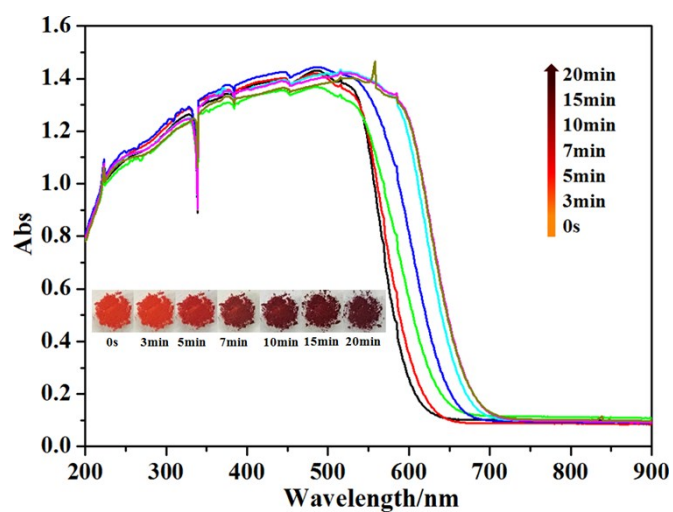


Fig. S11 Time-dependent UV-vis absorption spectra and photographs for the thermo-induced coloration process of **2**.

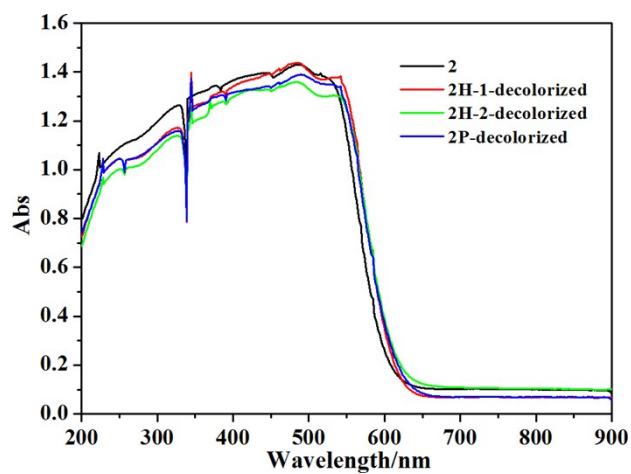


Fig. S12 The comparison of UV-vis absorption spectra of **2**, **2H-1-decolorized**, **2H-2-decolorized** and **2P-decolorized**.

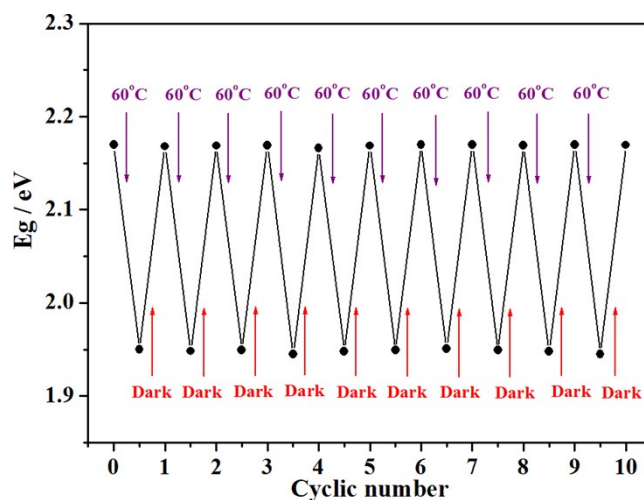


Fig. S13 The switching cycles of coloration-decoloration processes of **2** upon alternating thermal (60°C) and dark treatment.

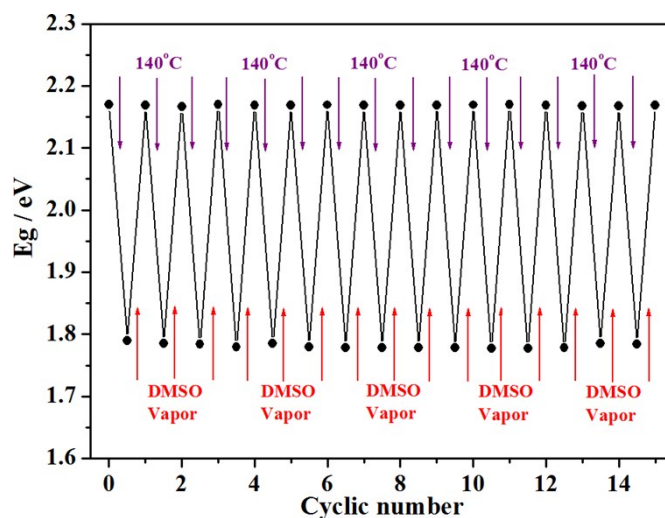


Fig. S14 The switching cycles of coloration-decoloration processes of **2** upon alternating thermal treatment (140°C) and exposing in the DMSO vapor.

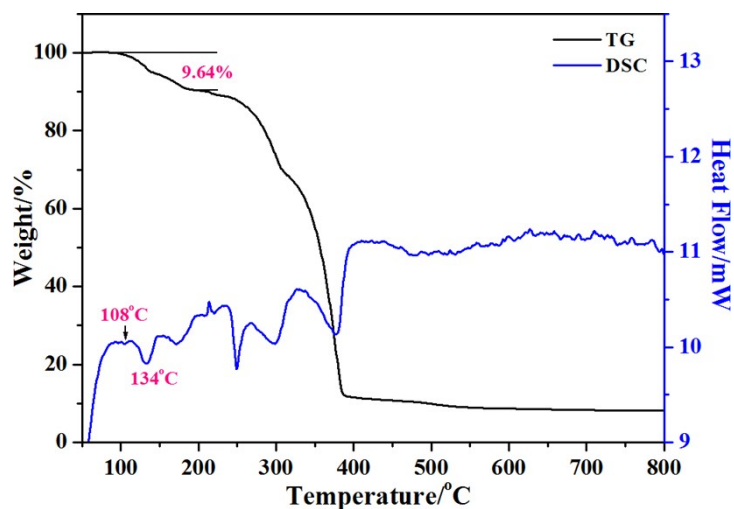


Fig. S15 TG-DSC curve of 2H-1.

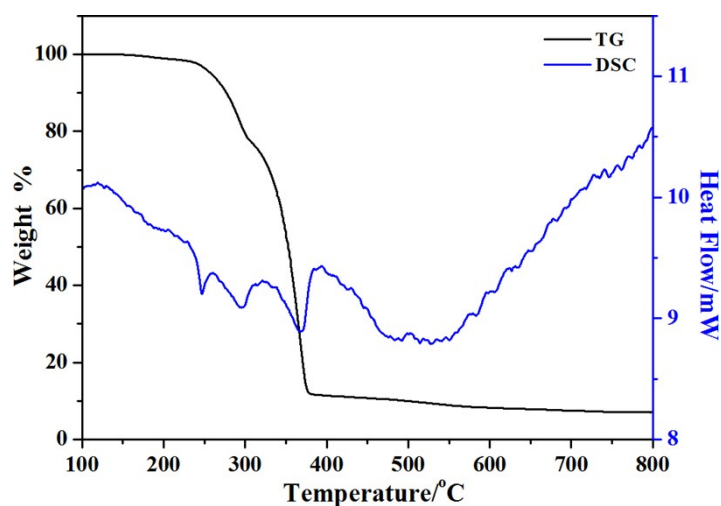


Fig. S16 TG-DSC curve of 2H-2.

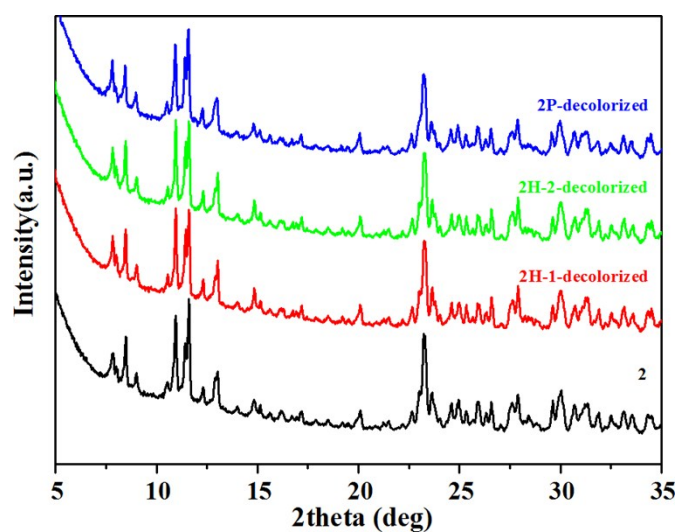


Fig. S17 The comparison of PXRD patterns of **2**, **2H-1-decolorized**, **2H-2-decolorized** and **2P-decolorized**.

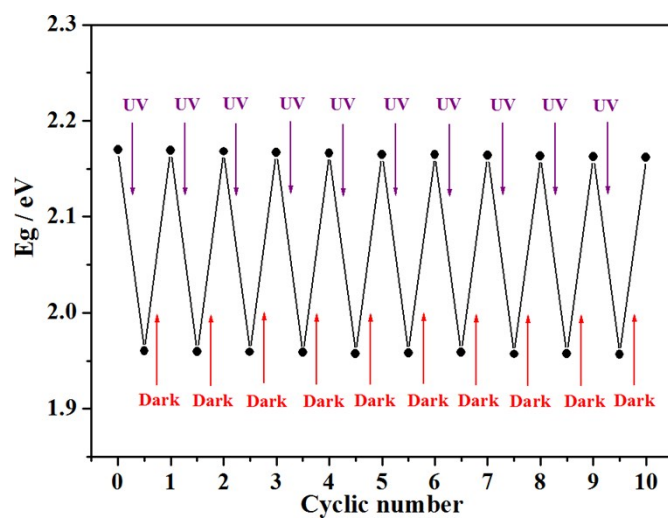


Fig. S18 The switching cycles of coloration-decoloration processes of **2** upon UV light irradiation and dark treatment.

2. Tables

Table S1 Crystallographic data and refinement parameters of compounds **1** and **2**.

Compounds	1	2
CCDC code	1958253	1958251
Temperature (K)	293(2)	293(2)
Empirical formula	C ₁₆ H ₄₅ O ₈ S ₈ LaBi ₂ I ₉	C ₁₆ H ₃₆ O ₈ S ₈ Bi ₃ I ₉
Formula weight	2320.97	2381.97
Crystal size (mm)	0.122x0.07x0.028	0.18x0.14x0.09
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	12.0219(14)	11.958(3)
<i>b</i> (Å)	15.8042(19)	15.817(4)
<i>c</i> (Å)	16.282(2)	16.280(5)
α (°)	82.124(3)	82.222(6)
β (°)	69.973(3)	69.979(6)
γ (°)	78.890(3)	78.914(6)
<i>V</i> (Å ³)	2843.5(6)	2831.1(13)
<i>Z</i>	2	2
<i>D_c</i> (g cm ⁻³)	2.711	2.794
<i>F</i> (000)	2066	2100
μ (mm ⁻¹)	12.119	14.531
ϑ range (°)	2.51 to 28.36	2.63 to 28.42
Reflections collected	40936	21701
Unique reflections	14207	14222
<i>R</i> _{int}	0.0624	0.0834
Goodness-of-fit on <i>F</i> ²	1.059	1.036
<i>R</i> ₁ / <i>wR</i> ₂ , [<i>I</i> ≥ 2σ(<i>I</i>)] ^{a,b}	0.0635/0.1663	0.1541/0.3401
<i>R</i> ₁ / <i>wR</i> ₂ , (all data)	0.1031/0.1928	0.2368/0.3981
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	3.395/-3.578	5.872/-5.024

Table S2 Selected bond lengths (Å) and angles (°) for **1** and **2**.

Compound 1			
Bi(1)-I(1)	2.9144(11)	Bi(2)-I(8)	2.9369(12)
Bi(1)-I(2)	2.9459(10)	Bi(2)-I(9)	2.9951(10)
Bi(1)-I(3)	2.9493(13)	Bi(2)-I(7)	3.0104(12)
Bi(1)-I(5)	3.2002(10)	Bi(2)-I(6)	3.1386(11)
Bi(1)-I(4)	3.2345(11)	Bi(2)-I(4)	3.1895(10)
Bi(1)-I(6)	3.3072(11)	Bi(2)-I(5)	3.2577(11)
La(1)-O(7)	2.448(9)	La(1)-O(2)	2.468(9)
La(1)-O(1)	2.476(8)	La(1)-O(6)	2.484(10)
La(1)-O(8)	2.490(9)	La(1)-O(5)	2.500(8)
La(1)-O(4)	2.501(9)	La(1)-O(3)	2.540(9)
I(1)-Bi(1)-I(2)	95.52(3)	I(8)-Bi(2)-I(9)	93.48(4)
I(1)-Bi(1)-I(3)	95.54(4)	I(8)-Bi(2)-I(7)	95.07(4)
I(2)-Bi(1)-I(3)	91.32(4)	I(9)-Bi(2)-I(7)	96.56(3)
I(1)-Bi(1)-I(5)	93.06(3)	I(8)-Bi(2)-I(6)	92.71(4)
I(2)-Bi(1)-I(5)	169.34(3)	I(9)-Bi(2)-I(6)	88.80(3)
I(3)-Bi(1)-I(5)	94.14(4)	I(7)-Bi(2)-I(6)	170.26(3)
I(1)-Bi(1)-I(4)	91.62(3)	I(8)-Bi(2)-I(4)	90.24(3)
I(2)-Bi(1)-I(4)	88.78(3)	I(9)-Bi(2)-I(4)	171.68(3)
I(3)-Bi(1)-I(4)	172.79(4)	I(7)-Bi(2)-I(4)	90.52(3)
I(5)-Bi(1)-I(4)	84.66(3)	I(6)-Bi(2)-I(4)	83.58(3)
I(1)-Bi(1)-I(6)	169.69(3)	I(8)-Bi(2)-I(5)	172.60(3)
I(2)-Bi(1)-I(6)	90.71(3)	I(9)-Bi(2)-I(5)	91.13(3)
I(3)-Bi(1)-I(6)	92.52(4)	I(7)-Bi(2)-I(5)	90.14(3)
I(5)-Bi(1)-I(6)	79.92(3)	I(6)-Bi(2)-I(5)	81.60(3)
I(4)-Bi(1)-I(6)	80.28(3)	I(4)-Bi(2)-I(5)	84.45(3)
Compound 2			

Bi(1)-I(3)	2.913(3)	Bi(2)-I(8)	2.934(3)
Bi(1)-I(2)	2.943(3)	Bi(2)-I(9)	3.000(3)
Bi(1)-I(1)	2.962(3)	Bi(2)-I(7)	3.022(3)
Bi(1)-I(5)	3.196(3)	Bi(2)-I(6)	3.135(3)
Bi(1)-I(4)	3.231(3)	Bi(2)-I(4)	3.186(3)
Bi(1)-I(6)	3.329(3)	Bi(2)-I(5)	3.253(3)
Bi(3)-O(7)	2.40(2)	Bi(3)-O(3)	2.42(3)
Bi(3)-O(8)	2.45(3)	Bi(3)-O(1)	2.45(3)
Bi(3)-O(6)	2.47(3)	Bi(3)-O(5)	2.48(3)
Bi(3)-O(4)	2.53(3)	Bi(3)-O(2)	2.53(3)
I(3)-Bi(1)-I(2)	95.66(11)	I(8)-Bi(2)-I(9)	93.69(10)
I(3)-Bi(1)-I(1)	95.61(12)	I(8)-Bi(2)-I(7)	94.73(12)
I(2)-Bi(1)-I(1)	91.27(12)	I(9)-Bi(2)-I(7)	96.65(10)
I(3)-Bi(1)-I(5)	92.85(10)	I(8)-Bi(2)-I(6)	92.86(12)
I(2)-Bi(1)-I(5)	169.59(10)	I(9)-Bi(2)-I(6)	88.43(9)
I(1)-Bi(1)-I(5)	93.88(11)	I(7)-Bi(2)-I(6)	170.58(9)
I(3)-Bi(1)-I(4)	91.60(9)	I(8)-Bi(2)-I(4)	90.09(10)
I(2)-Bi(1)-I(4)	89.02(10)	I(9)-Bi(2)-I(4)	171.55(8)
I(1)-Bi(1)-I(4)	172.73(11)	I(7)-Bi(2)-I(4)	90.56(9)
I(5)-Bi(1)-I(4)	84.73(8)	I(6)-Bi(2)-I(4)	83.84(8)
I(3)-Bi(1)-I(6)	169.29(9)	I(8)-Bi(2)-I(5)	172.77(11)
I(2)-Bi(1)-I(6)	91.02(10)	I(9)-Bi(2)-I(5)	91.02(9)
I(1)-Bi(1)-I(6)	92.60(11)	I(7)-Bi(2)-I(5)	90.17(9)
I(5)-Bi(1)-I(6)	79.72(8)	I(6)-Bi(2)-I(5)	81.78(9)
I(4)-Bi(1)-I(6)	80.13(8)	I(4)-Bi(2)-I(5)	84.53(8)

Table S3 The relative stability of solvated metal cations in **1** and **2** based on DFT calculation.

	La(DMSO) ₈ ³⁺	La(DMSO) ₇ ³⁺	DMSO
Energy (Hartree)	-4454.6023118	-3901.5622148	-552.9660428
ΔE(kcal/mol)	[(-4454.6023118)-(-3901.5622148)-(-552.9660428)]*627.5095 = -46.4697140149		
	Bi(DMSO) ₈ ³⁺	Bi(DMSO) ₇ ³⁺	DMSO
Energy (Hartree)	-4428.679145	-3875.5981133	-553.0125036
ΔE(kcal/mol)	[(-4428.679145)-(-3875.5981133)-(-553.0125036)]*627.5095 = -43.00203376695		

Table S4 The band gap (E_g) of **2** with the decrease of I···I distance based on DFT calculation.

I···I distance (Å)	LUMO (eV)	HOMO (eV)	E _g (eV)
3.78614	18.78973	16.70126	2.088473
3.73614	18.78783	16.70942	2.078405
3.68614	18.8164	16.79241	2.023982
3.63614	18.81395	16.80303	2.010921
3.58614	18.84306	16.8901	1.952961
3.53614	18.84878	16.9018	1.946974
3.48614	18.86973	16.99541	1.87432
3.43614	18.86674	17.01228	1.854456
3.38614	18.89667	17.10997	1.786699
3.33614	18.89313	17.13092	1.762209
3.28614	18.92361	17.23542	1.688194
3.23614	18.91953	17.26099	1.658534
3.18614	18.95082	17.37229	1.578532
3.13614	18.94592	17.40249	1.543429
3.08614	18.97858	17.52086	1.457714
3.03614	18.97286	17.55678	1.41608