Electronic Supplementary Material (ESI) for Dalton Transactions.

This journal is © The Royal Society of Chemistry 2019

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

*Electronic Supplementary Information*

Pengfei Hao*, Weipin Wang, Junju Shen, Yunlong Fu*

*Key Laboratory of Magnetic Molecules & Magnetic Information Materials Ministry of Education, School of Chemical and Material Science, Shanxi Normal University, Linfen 041004, China*

**Content**

## 1. Figures

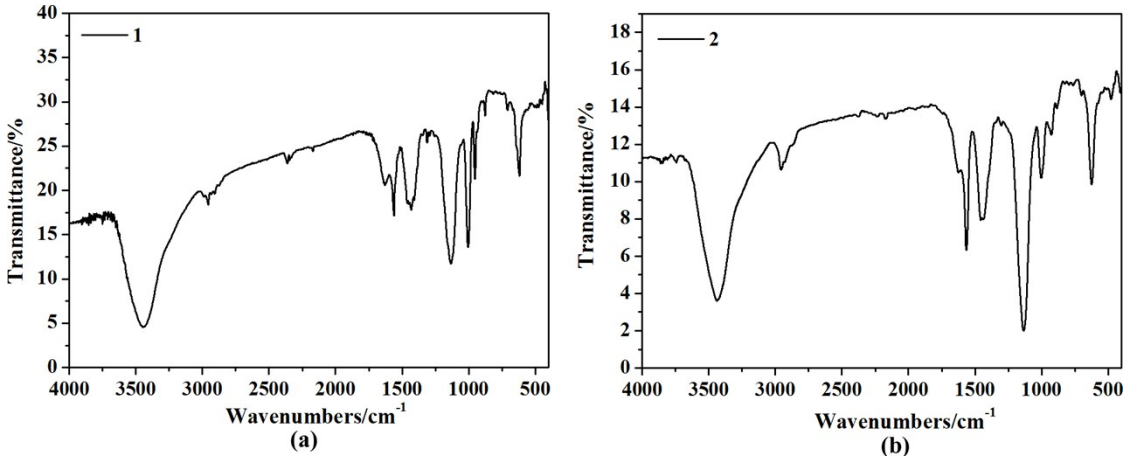


**Fig. S1** IR spectra of **1** and **2**.

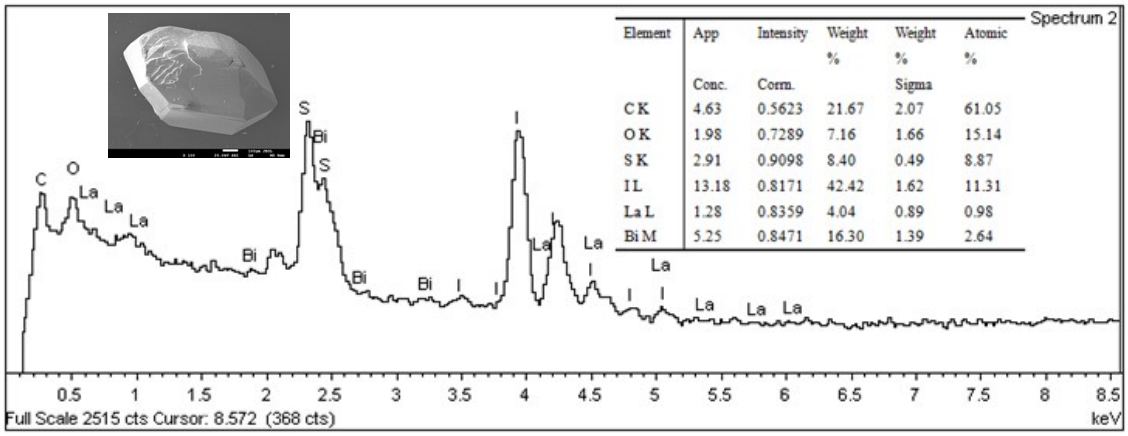


**Fig. S2** The SEM images and EDS pattern of **1**.

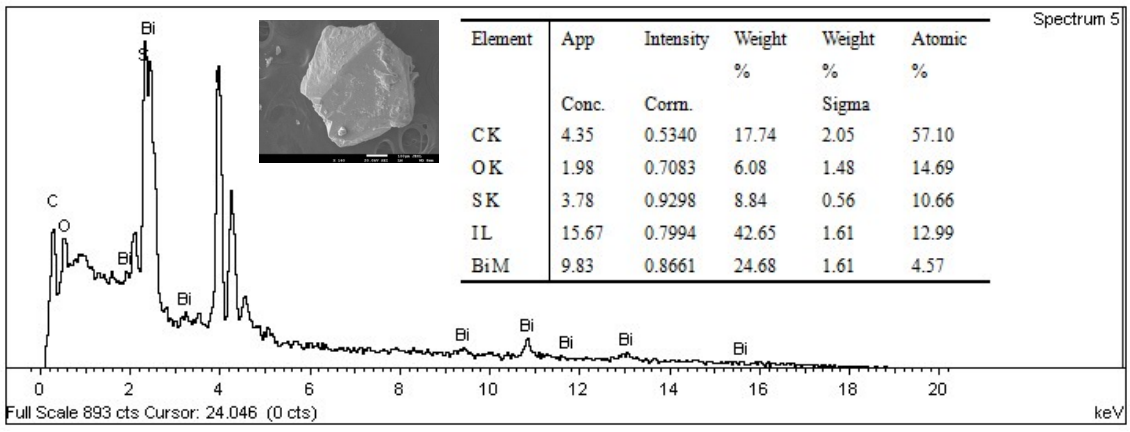


**Fig. S3** The SEM images and EDS pattern of **2**.

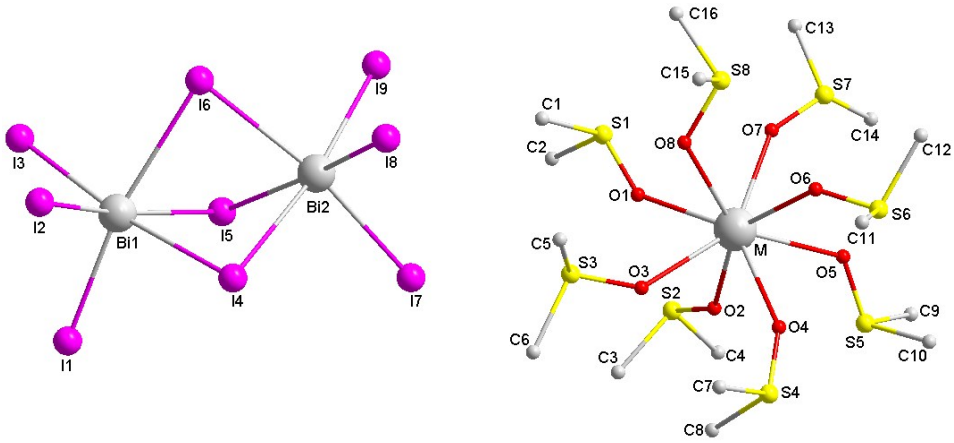


**Fig. S4** The asymmetric unit of **1** and **2** (M = La (**1**), Bi (**2**)).

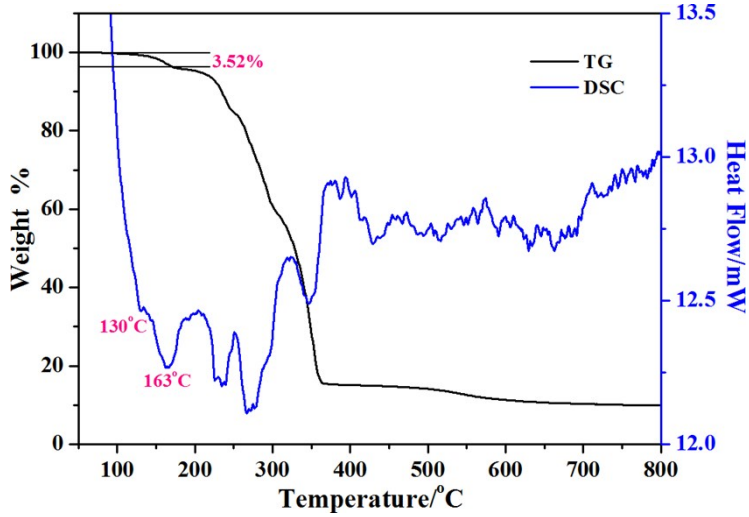


**Fig. S5** TG-DSC curve of **1**.

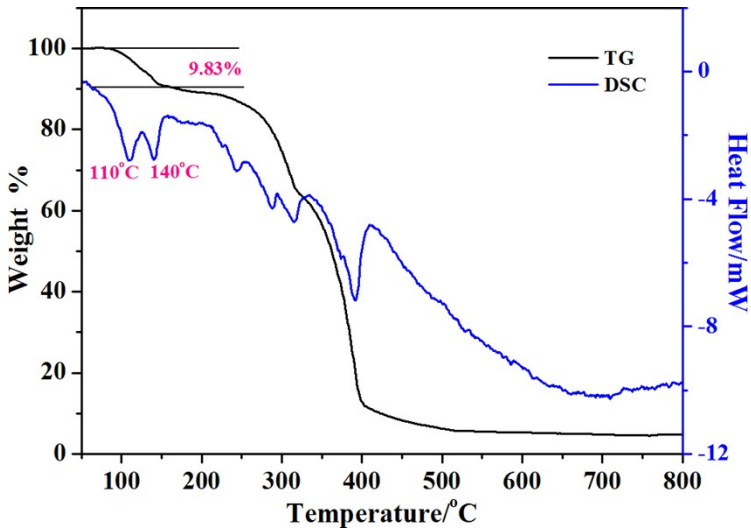


**Fig. S6** TG-DSC curve of **2**.

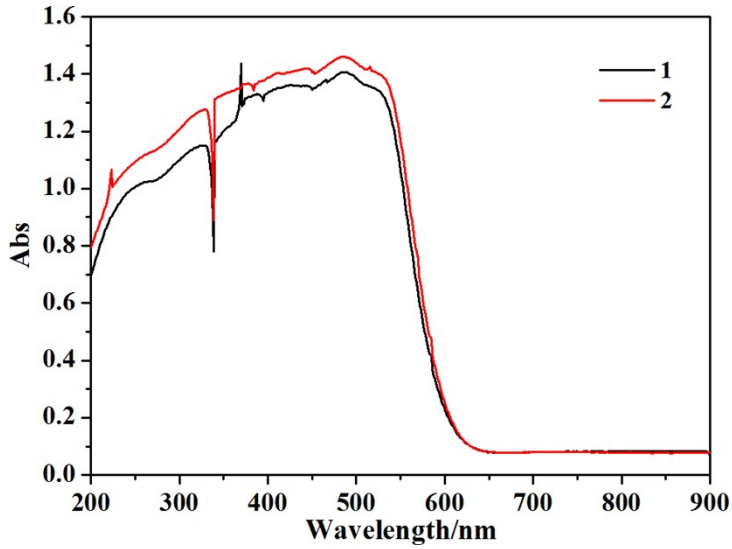


**Fig. S7** The comparison of UV-vis absorption spectra for **1** and **2**.

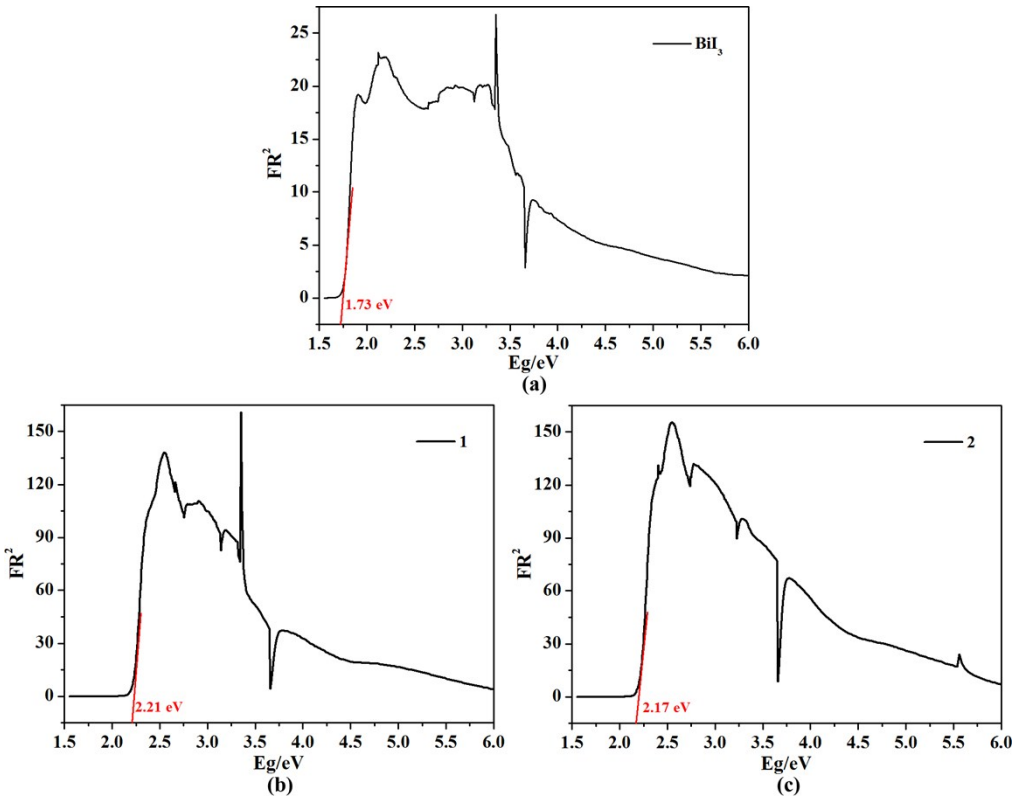


**Fig. S8** The comparison of energy gaps for **1** and **2**.

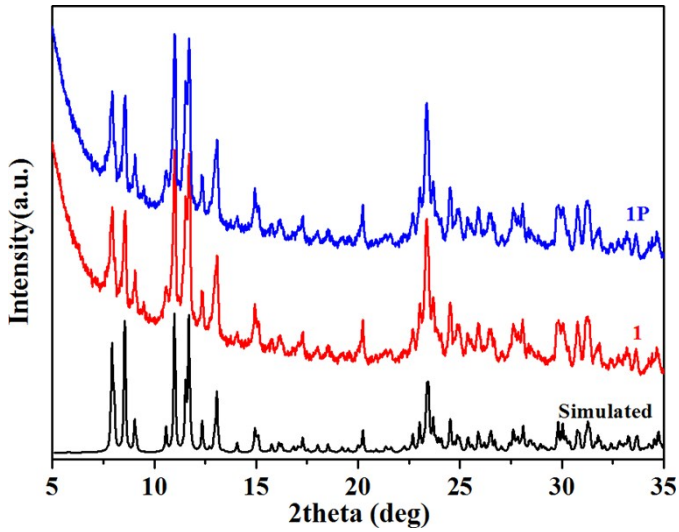


**Fig. S9** UV-vis absorption spectra of **1** before and after light illumination.

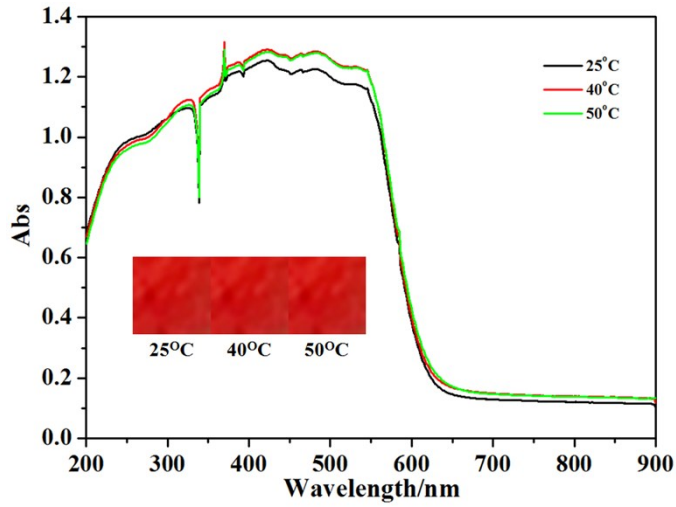


**Fig. S10** Temperature-dependent UV-vis absorption spectra of **2** heated at the temperature range of 25-50°C for 15 min.

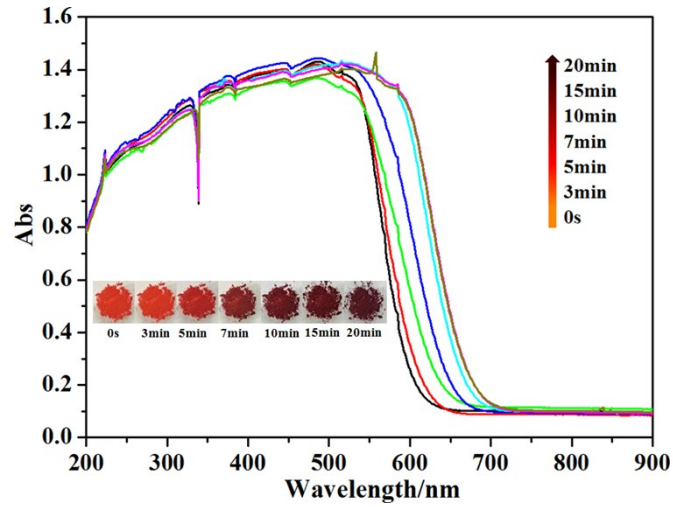


**Fig. S11** Time-dependent UV-vis absorption spectra and photographs for the thermo-induced coloration process of **2**.

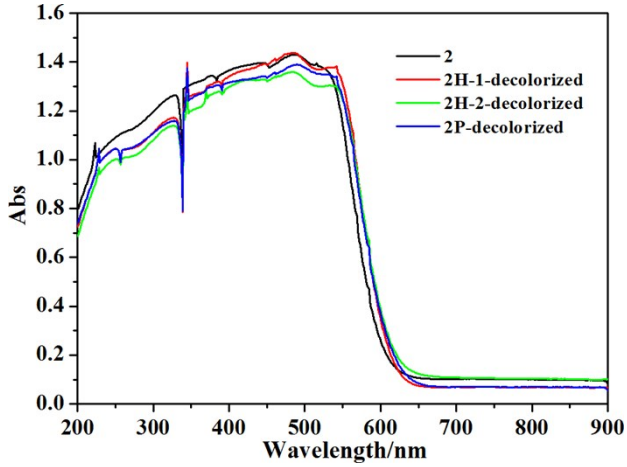


**Fig. S12** The comparison of UV-vis absorption spectra of **2**, **2H**-**1**-decolorized, **2H**-**2**-decolorized and **2P**-decolorized.

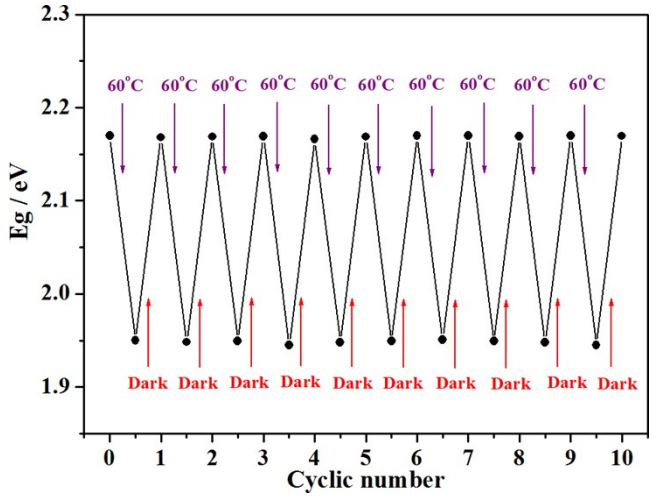


**Fig. S13** The switching cycles of coloration-decoloration processes of **2** upon alternating thermal (60°C) and dark treatment.

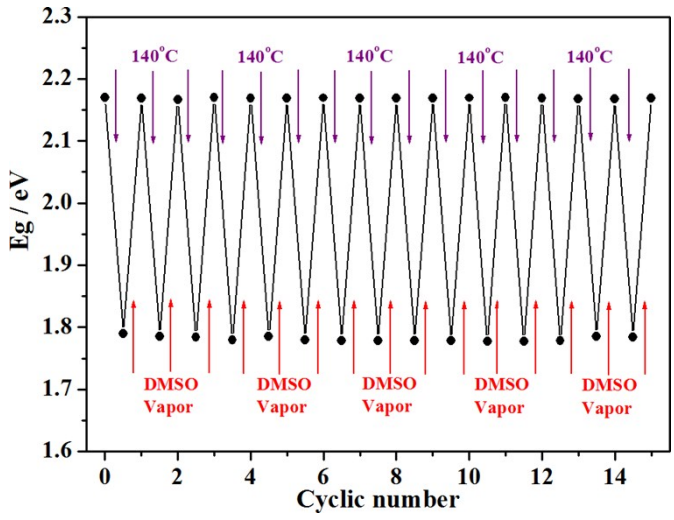


**Fig. S14** The switching cycles of coloration-decoloration processes of **2** upon alternating thermal treatment (140°C) and exposing in the DMSO vapor.

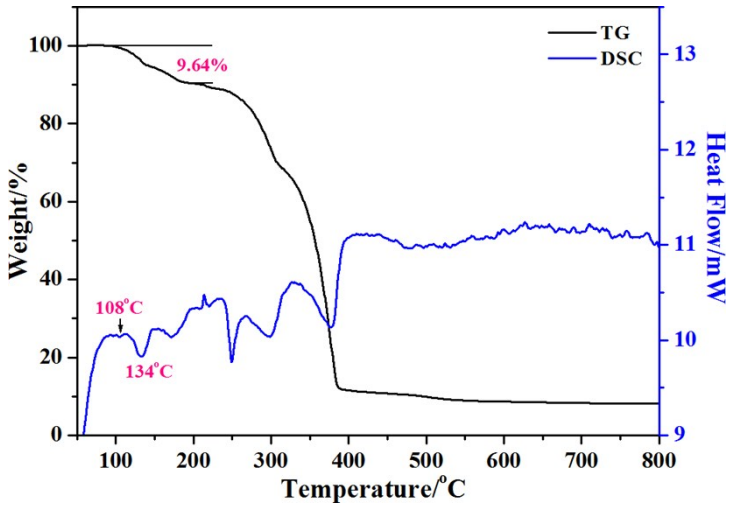


**Fig. S15** TG-DSC curve of **2H-1**.

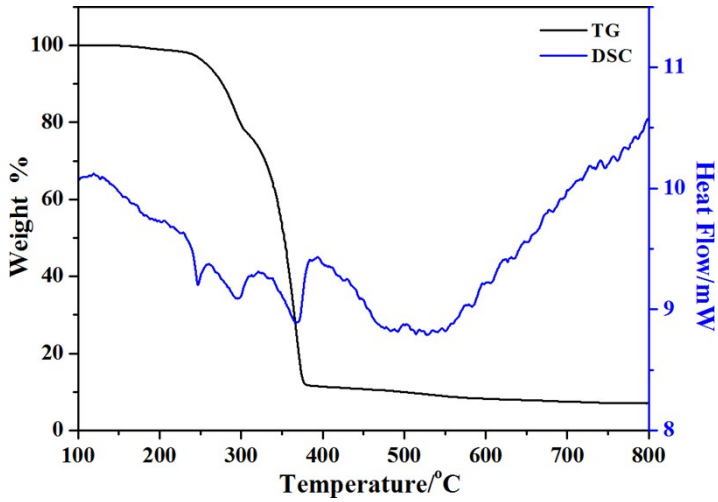


**Fig. S16** TG-DSC curve of **2H-2**.

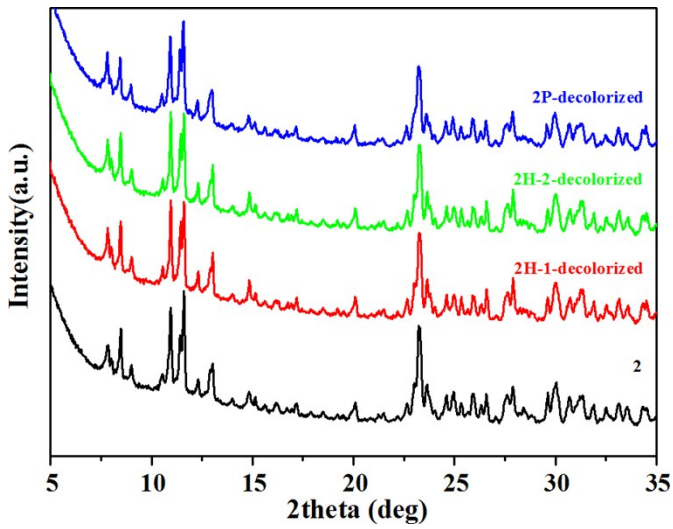


**Fig. S17** The comparison of PXRD patterns of **2**, **2H**-**1**-decolorized, **2H**-**2**-decolorized and **2P**-decolorized.

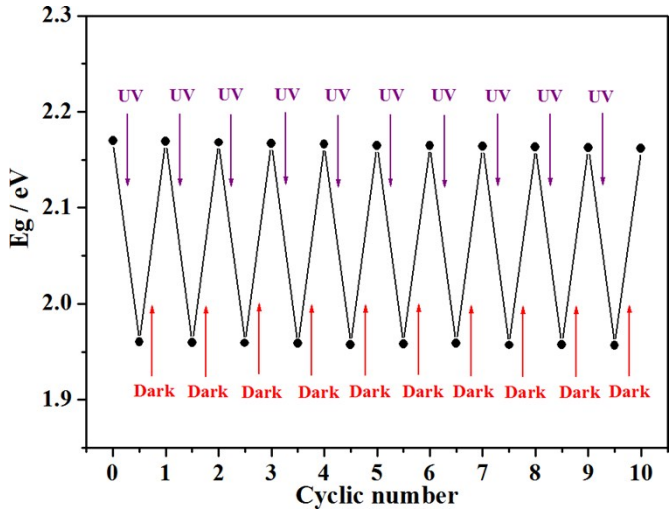


**Fig. S18** The switching cycles of coloration-decoloration processes of **2** upon UV light irradiation and dark treatment.

## 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 | $C_{16}H_{45}O_8S_8LaBi_2I_9$ | $C_{16}H_{36}O_8S_8Bi_3I_9$ |
| Formula weight | 2320.97 | 2381.97 |
| Crystal size (mm) | 0.122x0.07x0.028 | 0.18x0.14x0.09 |
| Crystal system | Triclinic | Triclinic |
| Space group | *P-1* | *P-1* |
| *a* (Å) | 12.0219(14) | 11.958(3) |
| *b* (Å) | 15.8042(19) | 15.817(4) |
| *c* (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) |
| *V* (Å$^3$) | 2843.5(6) | 2831.1(13) |
| *Z* | 2 | 2 |
| $D_c$ (g cm$^{-3}$) | 2.711 | 2.794 |
| *F*(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 |
| $R_{int}$ | 0.0624 | 0.0834 |
| Goodness-of-fit on $F^2$ | 1.059 | 1.036 |
| $R_1/wR_2$, $[I \geq 2\sigma(I)]$[a,b] | 0.0635/0.1663 | 0.1541/0.3401 |
| $R_1/wR_2$, (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 (Eg) of **2** with the decrease of I···I distancebased on DFT calculation.

| I···I distance (Å) | LUMO (eV) | HOMO (eV) | Eg (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 |