Supporting Information(SI)

Bipyridyltriazolium Chlorobismuthate with Thermo-/Photochromic and Photoluminescent Switching Behaviors Based on ET and CT†

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Section 1. The characterization spectra and data.

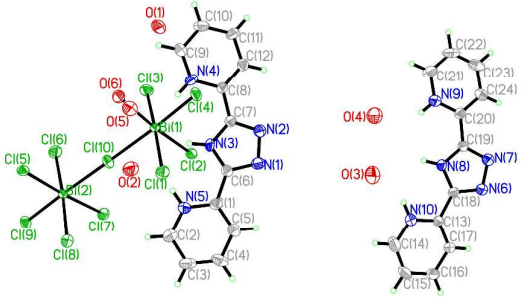

Figure S1. ORTEP16 drawing at 50% probability level of the crystallographically asymmetric unit of **1**.

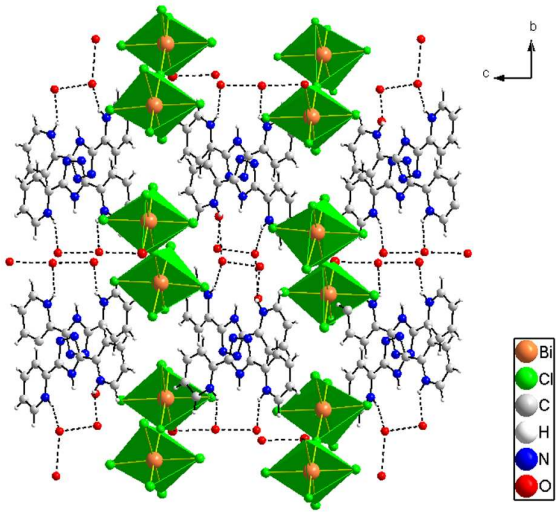

Figure S2. Packing interaction diagram of compound **1** along a-direction and the voids between the cations and anions are occupied by the lattice water molecules in space filling representation and O-H-O and N-H-O hydrogen bonds.

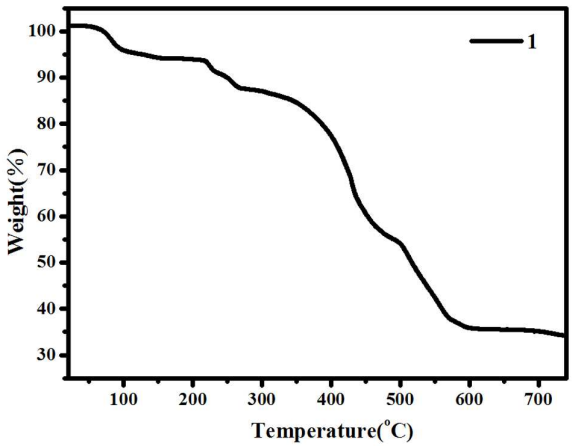

Figure S3. The TGA of title compound **1**.

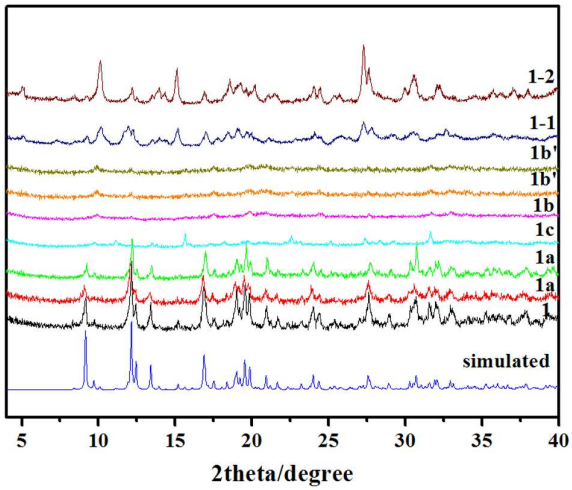

Figure S4. The Powder X-ray diffraction (PXRD) profiles for simulated (blue), experimental (**1**,black), after photoirradiation at room temperature for 30 minutes (**1a**, red) and after heat-treatment for 30 minutes at 54 °C (**1a**, green), 74 °C (**1c**, cyan) and in humid air for 3 days (**1-2,** wine) at room temperature; **1a** after 160 °C in air (**1b**, magenta) and **1b** after photoirradiation for 30 minutes (**1b'**, orange) and heat-treatment at 54 °C for 30 minutes in air (**1b'**, dark yellow) and **1b** in humid air for 5 days at room temperature (**1-1**, dark blue). No obvious spectral changes (**1**,black), (**1-1,** dark blue) and (**1-2**, wine) demonstrate reversible dehydration-rehydration process, the spectrum (**1a**, red) and the spectrum (**1a**, green) demonstrate structure stable after photoirradiation at ambient temperature and 54 °C heat-treatment and are the same compounds. The spectral changes (cyan) and (magenta) demonstrate that the sample takes place significantly phase transformation after dehydration after the heat-treatment at different temperatures.

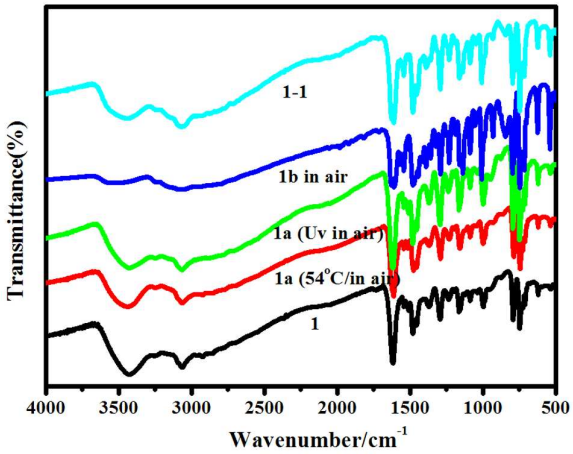

Figure S5. IR spectra of **1** before and after photoirradiation, heat-treatment and dehydration (**1b**, blue) in air for 1h and rehydration (**1-1**, cyan) in air for 5 days, original compound (**1**, black), after heat-treatment for 30 minutes (**1a**, red) and after photoirradiation for 30 minutes (**1a**, green).

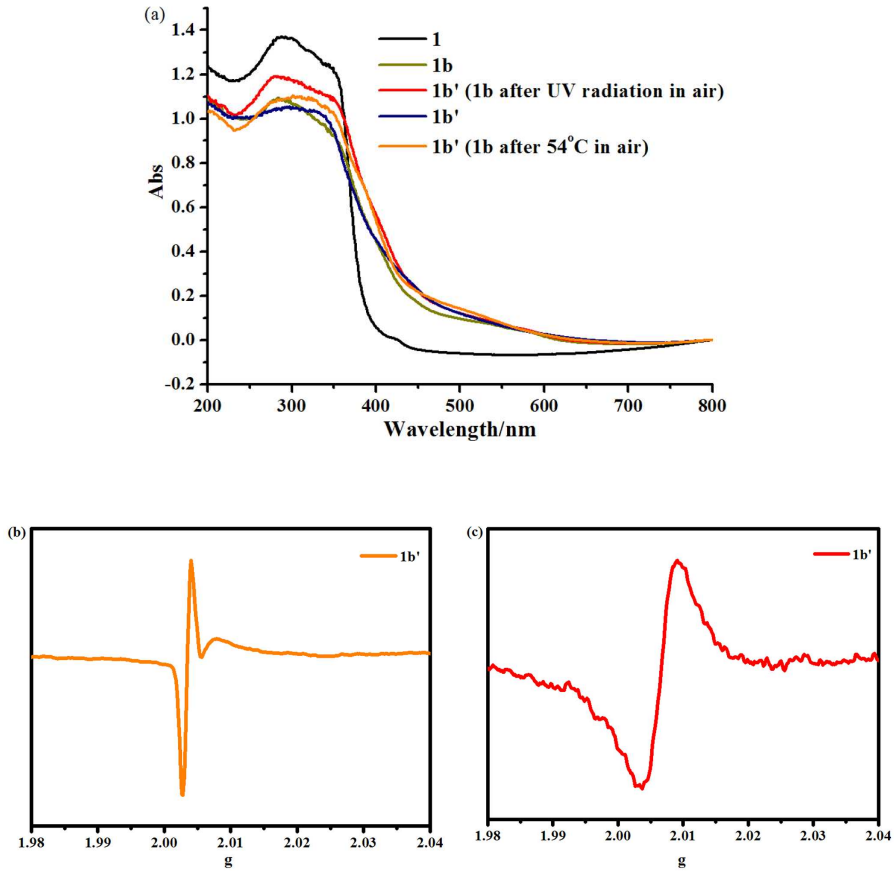

Figure S6. (a) **1b** after 54 °C heat-treatment 30 minutes in air (**1b'**, origion) and UV irradiation 30 minutes in air (**1b'**, red) and **1** after 160 °C heat-treatment in vacuum (**1b'**, navy) and **1** after 160 °C in air (**1b**, dark yellow); (b) The EPR spectrum of **1b'** (**1b** after 54 °C heat-treatment 30 minutes in air); (c) The EPR spectrum of **1b'** (**1b** after UV irradiation 30 minutes in air).

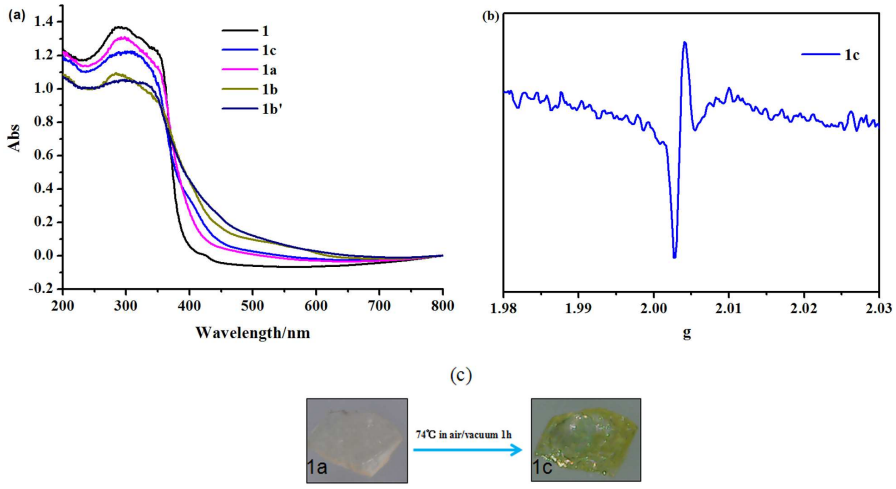

Figure S7. (a) **1** (black) after 54 °C in air (**1a**, magenta), 74 °C in air (**1c**, blue), 160 °C in air (**1b**, dark yellow) and 160 °C in vacuum (**1b'**, navy). (b) The EPR spectrum of **1c** (**1** after 74 °C in air). (c) Thermochromic behaviors of polyphase shown by photographic images.**1** (left) after 54 °C in air or in vacuum for 1h turns to yellow green **1c** (right).

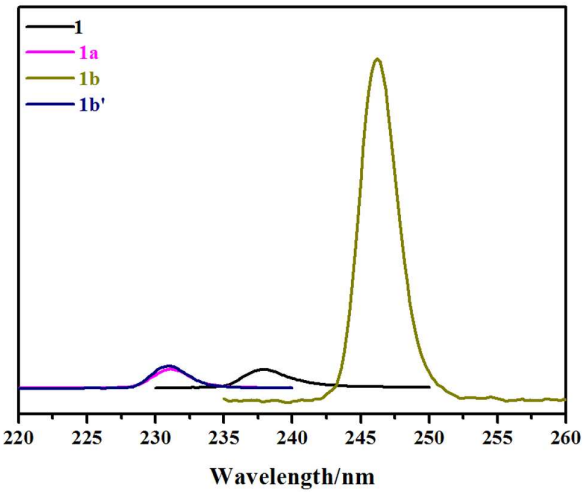

Figure S8. Normalized solid-state excitation spectra of **1** (black) and after photoirradiation (**1a**, magenta); after 160 °C heat-treatment in air (**1b**, dark yellow) and after photoirradiation (**1b'**, navy).

Section 2. The detailed experiment process about photochromism and thermochromism.

Under thermal treatment at any temperature in the range from 54 °C to 60 °C (in thermostatic waterbath) in air or in vacuum for 1 h, the colorless **1** turns to yellow **1a**. **1a** is reversible and stable in air and can return to initial colorless **1** in the dark air for 3 days or in black box at ozone atmosphere for 8 h. **1** (place **1** on the cooling fin) also turns from colorless to yellow **1a** under continuous irradiation using

Hg lamp (300w, 365nm) in air or in vacuum at room temperature within 30 min. The photoinduced yellow **1a** is also stable in air and can undergo reversible transformation to colorless **1** in the dark in air for 3 days.

Continuously heating from 60 ^{o}C to 160 ^{o}C or directly heating at 160 ^{o}C (in thermostatic waterbath), the yellow **1a** also changes to the deep green **1b** in vacuum. Moreover, When **1** directly heated at 160 ^{o}C, **1** also turns to deep green sample **1b** in air or **1b'** in vacuum for 1 hour. The deep green sample **1b** and **1b'** can turn to colorless **1** in humid air for 5 days. Moreover, **1b** can turn to **1b'** after thermotreatment between 54 ^{o}C and 74 ^{o}C or photoirradiation by Hg lamp (300w, 365nm) for 30 min at ambient temperature in dry air.

As a reference, colorless **1** changes into yellow green **1c** (figure S7) by directly heating at 74 ^{o}C in air or in vacuum 1 hour. Because the part of lattice water molecules lose, **1** takes place significant phase transition (figure S3, S4).

Section 3. Crystallographic data tables.

Table S1. Selected bond lengths (Å) and angles (°) for **1**.

Bi(1)-Cl(2)	2.5277(18)	Bi(2)-Cl(9)	2.5487(17)
Bi(1)-Cl(4)	2.5541(17)	Bi(2)-Cl(5)	2.6170(18)
Bi(1)-Cl(3)	2.6433(18)	Bi(2)-Cl(6)	2.676(2)
Bi(1)-O(6)	2.678(5)	Bi(2)-Cl(8)	2.782(2)
Bi(1)-Cl(1)	2.7515(18)	Bi(2)-Cl(7)	2.788(2)
Bi(1)-Cl(10)	2.9135(18)	Bi(2)-Cl(10)	2.9593(18)
Cl(2)-Bi(1)-Cl(4)	90.60(6)	Cl(9)-Bi(2)-Cl(5)	92.83(6)
Cl(2)-Bi(1)-Cl(3)	90.22(6)	Cl(9)-Bi(2)-Cl(6)	90.08(7)
Cl(4)-Bi(1)-Cl(3)	89.84(6)	Cl(5)-Bi(2)-Cl(6)	88.65(6)
Cl(2)-Bi(1)-O(6)	173.60(12)	Cl(9)-Bi(2)-Cl(8)	86.46(6)
Cl(4)-Bi(1)-O(6)	83.48(12)	Cl(5)-Bi(2)-Cl(8)	89.97(6)
Cl(3)-Bi(1)-O(6)	92.20(12)	Cl(6)-Bi(2)-Cl(8)	176.21(7)
Cl(2)-Bi(1)-Cl(1)	88.25(6)	Cl(9)-Bi(2)-Cl(7)	89.53(6)
Cl(4)-Bi(1)-Cl(1)	93.52(6)	Cl(5)-Bi(2)-Cl(7)	176.42(6)
Cl(3)-Bi(1)-Cl(1)	176.31(6)	Cl(6)-Bi(2)-Cl(7)	88.65(6)
O(6)-Bi(1)-Cl(1)	89.68(12)	Cl(8)-Bi(2)-Cl(7)	92.87(6)
Cl(2)-Bi(1)-Cl(10)	90.58(6)	Cl(9)-Bi(2)-Cl(10)	177.89(6)
Cl(4)-Bi(1)-Cl(10)	176.83(6)	Cl(5)-Bi(2)-Cl(10)	87.99(6)
Cl(3)-Bi(1)-Cl(10)	87.21(6)	Cl(6)-Bi(2)-Cl(10)	91.89(6)
O(6)-Bi(1)-Cl(10)	95.46(11)	Cl(8)-Bi(2)-Cl(10)	91.59(6)
Cl(1)-Bi(1)-Cl(10)	89.45(6)	Cl(7)-Bi(2)-Cl(10)	89.76(6)

Bi(1)-Cl(10)-Bi(2)	178.89(9)

Table S2. Hydrogen-bond parameters in compound **1.**

D-H...A	d(D-H)(Å)	d(H...A)(Å)	d(D...A)(Å)	<(DHA)(°)
N(10)-H(13)...O(3)	0.86	1.98	2.776(9)	153.7
N(9)-H(26)...O(4)	0.86	2.07	2.811(9)	143.2
N(5)-H(6)...O(2)	0.86	2.06	2.832(8)	148.6
N(4)-H(7)...O(5)	0.86	2.09	2.829(8)	144.0