Electronic Supplementary Material (ESI) for Dalton Transactions.

A fluorescent, photochromic and thermochromic trifunctional material based on a layered metal-viologencomplex

Fang Wan, Li-Xia Qiu, Liang-Liang Zhou, Yan-Qiong Sun* and Yi You
College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, People's Republic of China.

Experimental Section

Materials and General Details.

Commercially available solvents and chemicals were used without further purification. The ligand HBcbpyCl was prepared according to the literature[1]. IR spectra were measured as KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR in the range 400-4000 cm-1. Thermogravimetric data were collected on a Mettler Toledo TGA/SDTA 851e analyzer in flowing nitrogen at a heating rate of 10 ºC/min. Luminescence measurements were made with an Edinburgh Instrument FS920 TCSPC luminescence spectrometer on solution of the compounds. UV–vis diffuse reflectance spectral measurements were carried out using a Perkin–Elmer Lambda 900 spectrometer. The spectrophotometer was calibrated against the surface of $BaSO_4$ for 100% reflectance over the wavelength range under consideration. Electron spin resonance (ESR) signals were recorded with a Bruker A300 spectrometer.

Syntheses of the Compound

$\{(Bcbpy)_2[Zn_2O(N_3)_2].5H_2O)\}_n$ (**1**)

HBcbpyCl (0. 0326 g) was dissolved in 6 mL of the mixed solution of water and methanol with pH = 6, adjusted by 0.5 mol L^{-1}NaOH solution. NaN_3 (0.013 g) was dissolved in 1 mL of water, and the resultant solution was slowly dropped into the solution of NaBcbpyCl with pH= 6. After stirring 15 minutes at room temperature, 2 ml of zinc acetate (0.0219 g) solution was added to the above solution, and the mixture solution was transferred to reflux device, heating reflux for 1 hour with temperature of 50 ℃. The mixture solution was filtered and allowed to stand in the darkness for several days to produce yellow needle crystals of **1** (ca. 11.5% yield based on Zn). Elemental analysis: Calcd (%) for compound **1**: C, 47.95; H, 4.24; N, 15.53; Found(%):C,47.46; H, 4.12; N, 16.41.

Structure determination

The X-ray diffraction data for 1 was collected on a Rigaku Saturn 70 CCD diffractometer with graphite-monochromated Mo-Kα radiation. Empirical absorption corrections were applied using the SADABS program. The structures were solved by the direct method and refined by the full-matrix least-squares method on F2, with all non-hydrogen atoms refined with anisotropic thermal parameters. All of the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. All calculations were carried out with the SHELXTL and OLEX crystallographic software.

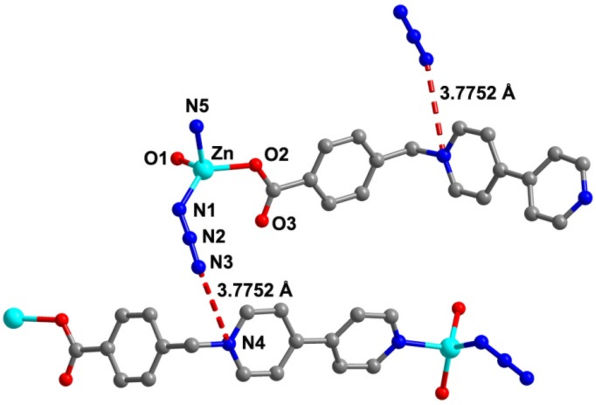

Fig. S1 The purple dotted line shows the distances between the terminal nitrogen atoms of the N_3^- anions and the pyridinium nitrogen atoms.

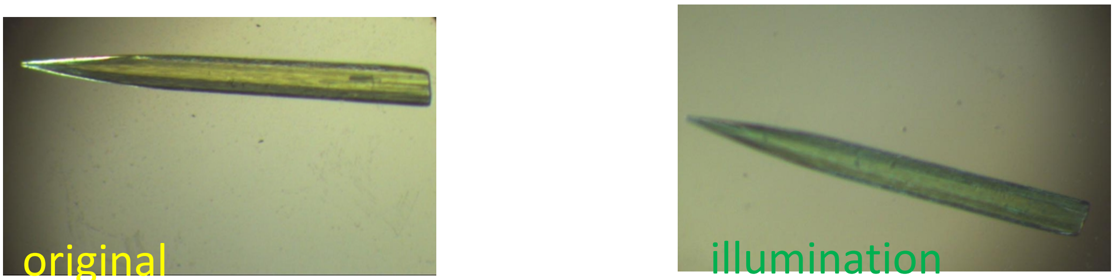

Fig. S2 photochromic effects of single crystal sample shown by photographic images.

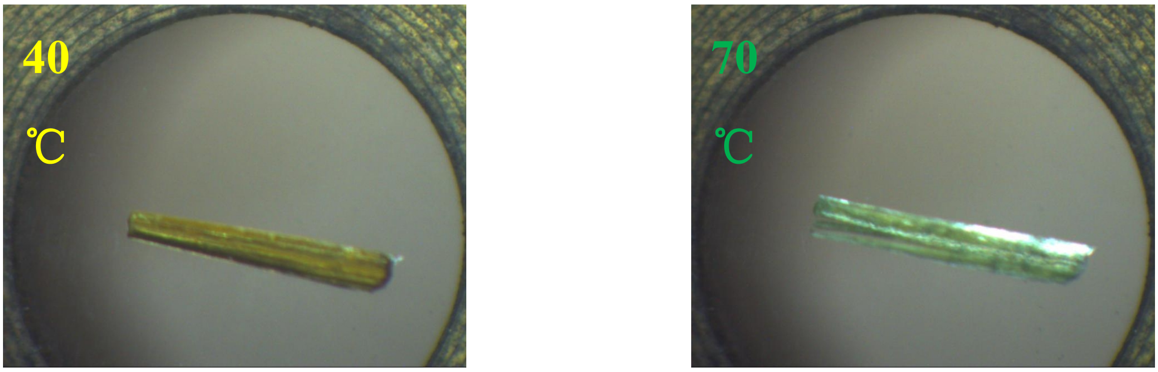

Fig. S3 The thermochromism effects of single crystal samples of **1** shown by photographic images

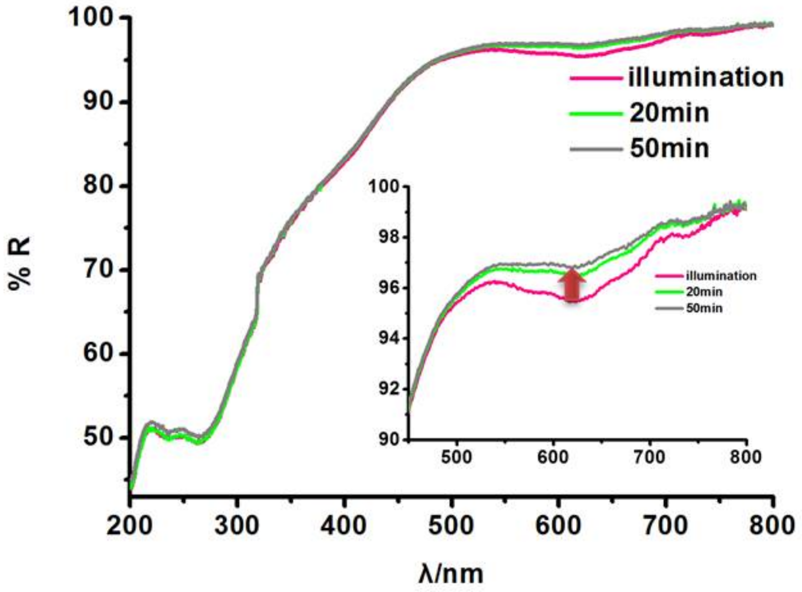

Fig. S4 The diffuse reflectance spectra of **1** after irradiation. The arrow shows a decoloration process in air.

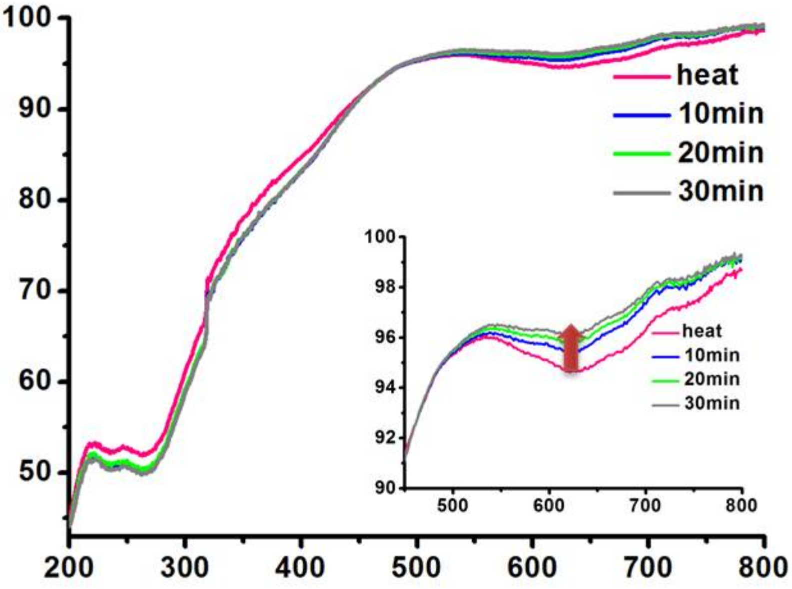

Fig. S5 The diffuse reflectance spectra of **1** after heat. The arrow shows a decoloration process in air.

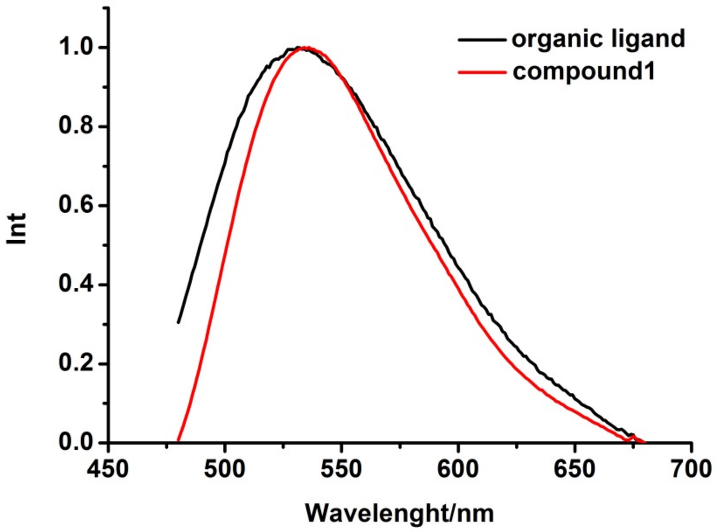

Fig. S6 The fluorescent spectra of organic $H_2BcbpyCl_2$ ligand (black) and compound **1**(red).

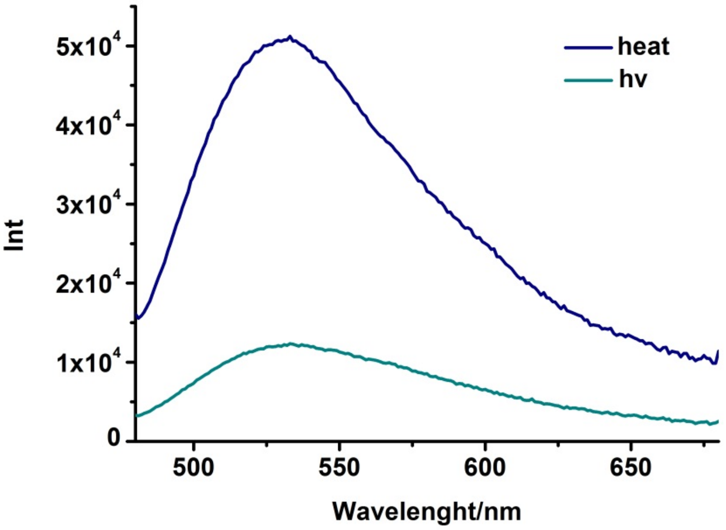

Fig. S7 The fluorescent spectral of 1. blue lines: after heat, green lines: after irradiation.

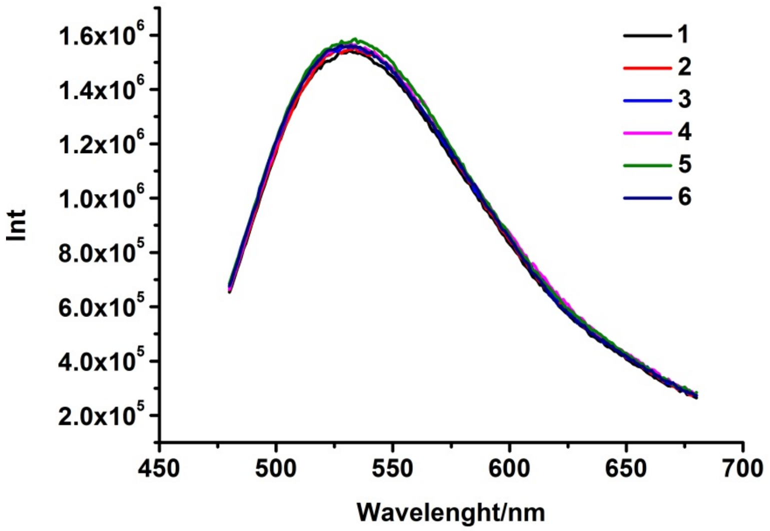

Fig. S8 The fluorescent spectral changes of organic HBcbpyCl ligand upon visible light (465 nm) irradiation in the solid state at room temperature.

XRD analysis

The diffraction peaks of the experimental and simulated X-ray powder diffraction pattern of compound **1** agree well in position, indicating that the as-synthesized samples have high phase purity (Fig.S9).

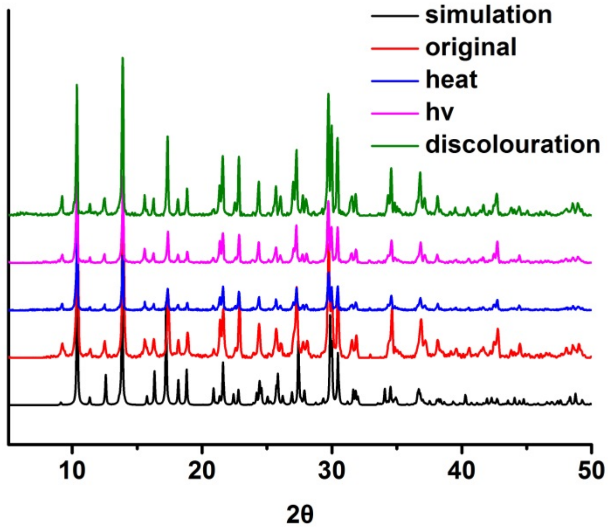

Fig. S9 XRPD patterns show the illumination, heating and discolouration processes.

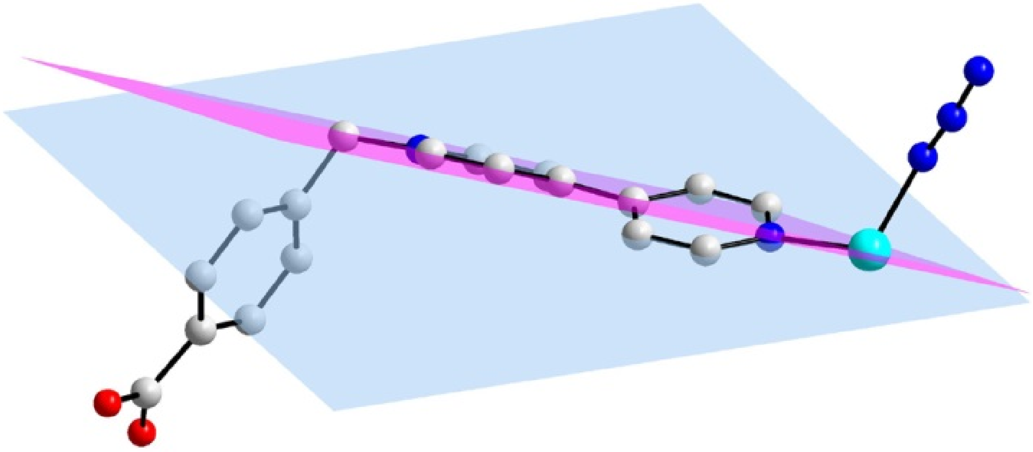

Fig. S10 The dihedral angle between the pyridine rings in compound **1**.

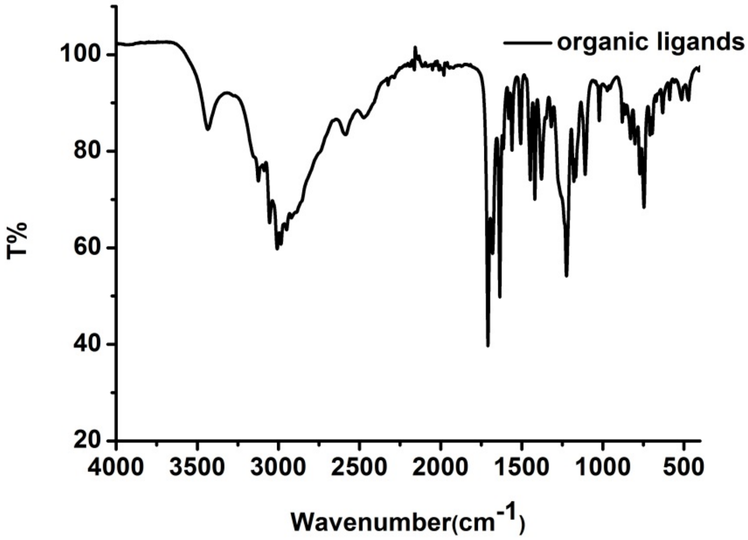

Fig. S11 The FTIR spectrum of HBpybcCl ligand.

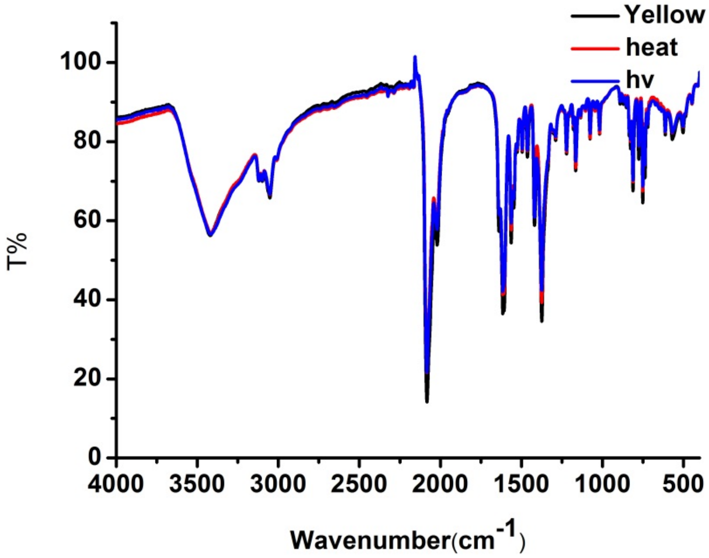

Fig. S12 IR spectrum of the original compounds **1**, red line :after heat, blue line: after irradiation

The FT-IR spectrum of HBpybcCl presents broad bands around 3000-3450 cm^{-1} due to the stretching vibrations of the OH, CH_2, and CH groups. The weak bands at 2598 and 2474 cm^{-1} can be assigned to overtones and combination bands (due to OH bend and C-O stretch) enhanced by Fermi resonance with the broad OH stretch band. The characteristic C=O stretching vibrations of carboxylic acid appear at 1705 cm^{-1}. The strong band at 1643 cm^{-1} can be attributed to the typical C=N and C=C stretching vibrations of bipyridinium. The C-OH in-plane bending and C-O stretching vibrations are observed at 1424 and 1273 cm^{-1}, respectively (Fig. S11). In the IR spectrum of **1** (Fig. S12), The appearance of new band at 2083 cm^{-1} attributed to the asymmetric stretching vibrations of the N_3^- ions is consistent with the single crystal structure analysis.

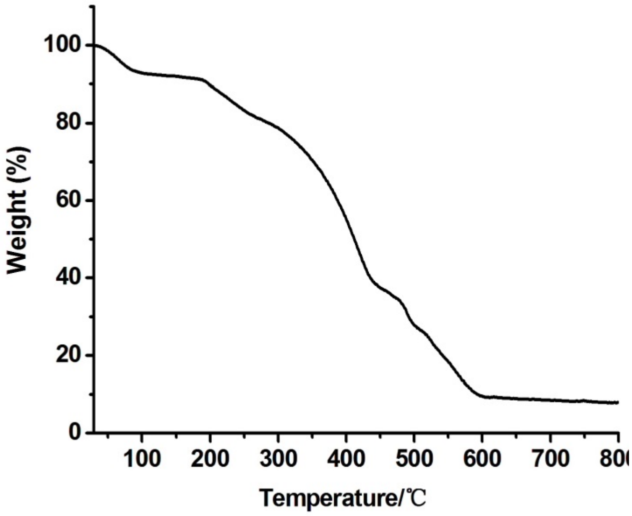

Fig. S13 TG curve under N2 atmosphere for 1.

TG analysis

The thermogravimetric analysis (TGA) of compounds 1 was carried out under N2 atmosphere with a heating rate of 10 ° C/min (Fig. S13). For compound 1, a weight loss of 9.17% (calcd, 9.97

%) is observed from 30 to 190°C due to the release of five free water molecules. The decomposition of BCbpy molecule was observed after from 190°C.

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Table S1 Crystal Date Collection and Structure Refinement for **1** (yellow) and **1**P (green).

Compounds	**1 (yellow)**	**1P(green)**
Empirical formula	$C_{36}H_{38}N_{10}O_{10}Zn_2$	$C_{36}H_{38}N_{10}O_{10}Zn_2$
Formula weight	901.42	901.42
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
space group	*Pccn*	*Pccn*
a(Å)	22.471(4) A	22.479(5) A
b(Å)	8.7703(17) A	8.7660(19) A
c(Å)	19.775(3) A	19.770(4) A
α(°)	90	90
β(°)	90	90
γ(°)	90	90
Volume (Å^3), Z	3897.2(12), 4	3895.7(14), 4
D_c (Mg/m^3)	1.519	1.520
F(000)	1816	1816
Limiting indices	$-23 \le h \le 26$;	$-26 \le h \le 21$;
	$-9 \le k \le 10$;	$-10 \le k \le 10$;
	$-22 \le l \le 23$	$-21 \le l \le 23$
Reflections collected	13805	14405
Goodness–of-fit on F^2	1.057	1.049
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	$R_1 = 0.0687$, $wR_2 = 0.2216$	$R_1 = 0.0635$, $wR_2 = 0.1874$
R_1, wR_2 (all data)	$R_1 = 0.0870$ $wR_2 = 0.2441$	$R_1 = 0.0728$, $wR_2 = 0.1987$
$\Delta\rho_{max}$ (e·Å^{-3})	1.502	1.325
$\Delta\rho_{min}$ (e·Å^{-3})	–0.689	-0.612

[a] $R_1 = \sum \lvert \lvert F_0 \rvert - \lvert F_c \rvert \rvert / \sum \lvert F_0 \rvert$. [b] $wR_2 = \{\sum[w(F_0^2 - F_c)^2] / \sum[w(F_0^2)^2]\}^{1/2}$

Table S2. Comparison of bond lengths (Å) between **1** (yellow) and **1'**(green)

Bond or Bond angles	**1(yellow)**	**1'(green)**	**Different**
Zn(1)-O(1)	1.903(3)Å	1.902(2) Å	-0.001(1) Å
Zn(1)-N(1)	1.951(6) Å	1.946(5) Å	-0.005(1) Å
Zn(1)-N(5)	2.056(5) Å	2.056(4) Å	0(1) Å
Zn(1)-O(3)	1.954(4) Å	1.953 (3)Å	-0.001(1) Å
N(3)…N(4)	3.7752 Å	3.7736 Å	-0.0016 Å
O(2)-C(1)	1.223(7) Å	1.221(6) Å	-0.002(1) Å
O(3)-C(1)	1.270(7) Å	1.277 (6)Å	0.007(1) Å
N(1)-N(2)	1.147(8) Å	1.149(7) Å	-0.002(1) Å
N(2)-N(3)	1.160(9) Å	1.167(7) Å	-0.007(2) Å
∠N(1)-N(2) -N(3)	172.985°	173.423°	0.438°
N(4)-C(10)	1.348(7) Å	1.346(6) Å	-0.002(1) Å
C(10)-C(12)	1.347(8) Å	1.358(7) Å	0.011(1) Å
N(4)-C(8)	1.486(7) Å	1.490(5) Å	0.004(2) Å
N(4)-C(9)	1.340(7)	1.340(6) Å	0(1)
N(5)-C(17)	1.330(8) Å	1.332(7) Å	0.002(1) Å
N(5)-C(18)	1.335(8) Å	1.338(7) Å	0.003(1) Å
C(1)-C(2)	1.490(8) Å	1.498(6) Å	0.008(2) Å
C(2)-C(3)	1.385(8) Å	1.392(6) Å	0.007(2) Å
C(2)-C(4)	1.392(8) Å	1.386(6) Å	-0.006(2) Å
C(3)-C(5)	1.385(8) Å	1.376 (7)Å	-0.009(1) Å
C(4)-C(6)	1.377(9) Å	1.376 (7)Å	-0.001(2) Å
C(5)-C(7)	1.380(8) Å	1.386(7) Å	0.006(1) Å
C(6)-C(7)	1.374(9) Å	1.375(7) Å	0.001(2) Å
C(7)-C(8)	1.503(8) Å	1.506(6) Å	0.003(2) Å
C(9)-C(11)	1.378(8) Å	1.377(6) Å	-0.001(2) Å
C(11)-C(13)	1.399(7) Å	1.397 (6)Å	-0.002(1) Å
C(12)-C(13)	1.397(8) Å	1.392 (6)Å	-0.005(2) Å
C(13)-C(14)	1.476(7) Å	1.472 (6)Å	-0.004(1) Å
C(14)-C(16)	1.381(8) Å	1.382 (6)Å	0.001(2) Å
C(14)-C(15)	1.385(8) Å	1.385 (6)Å	0 (2) Å
C(15)-C(17)	1.381(8) Å	1.387 (7)Å	0.006(1) Å
C(16)-C(18)	1.365(9) Å	1.369 (7)Å	0.004(2) Å

Because the crystals of **1** after illumination are good enough for single-crystal X-ray diffraction, we take the crystal structures of **1** and **1P** as examples for photocrystallographic analyses (Table S1, ESI†). Their structures are very similar and there are only minor differences in molecular geometry. The bigger changes were that the Zn–N1 (N1 atom from N_3^- anion) was shortened by 0.005 Å, and that the N2-N3 distances of N_3^- anion are lengthened by 0.002 and 0.007 Å, respectively(Table S2, ESI†). When **1** is converted to **1P** after illumination, this suggests that the N_3^- anion acts as an electron-donating group because the zinc(II) atom is too stable to be changed. As mentioned above, the Bcbpy ligand forms a radical species after photo-coloration. A smaller change in the bond lengths of Bcbpy between **1** and **1P** is observed for N4–C10, N4–C8 and C10–C12 bonds with values of 0.002, 0.004 and 0.011 Å, respectively (Table S2, ESI†). These data demonstrates that the electron transfer from the N_3^- anion to the Bcbpy ligand contributes to the photo-coloration of **1**.