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Supporting Information

A fast-response photochromic host-guest coordination polymer with close-packed stacking structure

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Experimental Section

General: 1, 1'-diphenyl-4, 4'-bipyridinium dichloride was synthesized according to the reported procedure[S1], and all of the other reagents were purchased from commercial channels and used without further purification; ATA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the thermogravimetric analysis (TGA) curve in N_2 100 ml·min^{-1} at a rate of 10 ^{o}C·min^{-1}. The X-ray powder diffraction (XRD) data were collected in the angular range of 2θ = 5^{o}-60^{o} with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ=1.5406 Å). UV-Vis diffuse reflectance spectral measurements were carried out using a HITACHI U-3010 spectrometer, and a $BaSO_4$ plate was used as a 100% reflectance standard. IR spectra were characterized by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. Electron spin resonance (ESR) signals were recorded at room temperature with a Bruker EMX-10/12 Electron Spin Resonance Spectrometer, using 1, 1 -diphenyl-2-picrylhydrazyl as reference. The C, H and N elemental analyses (EA) were performed on a Vario EL III elemental analyzer.

References:

S1 M. Freitag, L. Gundlach, P. Piotrowiak, E. Galoppini, *J. Am. Chem. Soc*. 2012, **134**, 3358-3366.

Synthesis of $[Zn_3(m\text{-}BDC)_4]\cdot(PV)\cdot H_2O$ (1): $Zn(NO_3)_2\cdot 6H_2O$ (89mg, 0.3mmol) 1,1'-diphenyl-4,4'-bipyridinium dichloride (38.1mg, 0.1mmol) and m-H_2BDC (66.4 mg,

0.4 mmol) were added to a mixed solvent of H_2O (2 mL), C_2H_5OH (5 mL) and DMF (5 mL). The mixture was stirred 5min until completely dissolved, then sealed in a 25ml Teflon-lined steel bomb and kept at 85 °C for 48 h. The solution was allowed to cool at a rate of 5 °C/h. Block-shaped yellow crystals were collected by filtration, washed by water (3×10ml) and ethanol (3×10ml), dried at room temperature (0.067 mmol, 79.6mg, 67% yield based on $Zn(NO_3)_2{\cdot}6H_2O$). IR (KBr): ν=3695(w), 3485(w), 3429(w), 3103(m), 3034(m), 1620(vs), 1578(s), 1550(s), 1485(m), 1430(s), 1394(vs), 1344(vs), 1271(m), 1224(w), 1166(w), 1101(w), 1074(w), 997(w), 951(w), 920(w), 832(m), 748(s), 720(s), 692(m), 661(w), 613(w), 576(w), 536(m), 511(w), 457(m) cm^{-1}. Elemental analysis calcd. (%) for $C_{54}H_{36}N_2O_{17}Zn_3$ (M = 1180.96): C 54.92, H 3.07, N 2.37; found: C 54.87, H 2.98, N 2.38.

X-ray single crystal diffraction

The data were measured on a Rigaku R-AXIS SPIDER CCD diffractometer with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å). Data were collected at 293K, using the ω- and φ-scans to a maximum θ value of 25.68°. Absorption corrections were performed using a multi-scan method. The structure was solved by direct methods and refined by full-matrix least squares methods with SHELXL. Non-hydrogen atoms were all refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and thermal parameters were fixed during structural refinement. CCDC 1470520 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ukf/data_request/cif.

Crystal data for **1**: $C_{54}H_{36}N_2O_{17}Zn_3$, *fw* = 1180.96 g · mol^{-1}, monoclinic, space group $P2_1$, a = 9.422 (2) Å, b = 10.196 (2) Å, c = 25.032(5) Å, β = 96.37 (3) °, V = 2389.9(8) $Å^3$, Z = 2, ρ_{calcd} = 1.641 g·cm^{-3}, F(000) = 1200, final R_1 = 0.0593 and wR_2 = 0.1062 for 8987 independent reflections [I > 2σ(I)].

PXRD Analysis

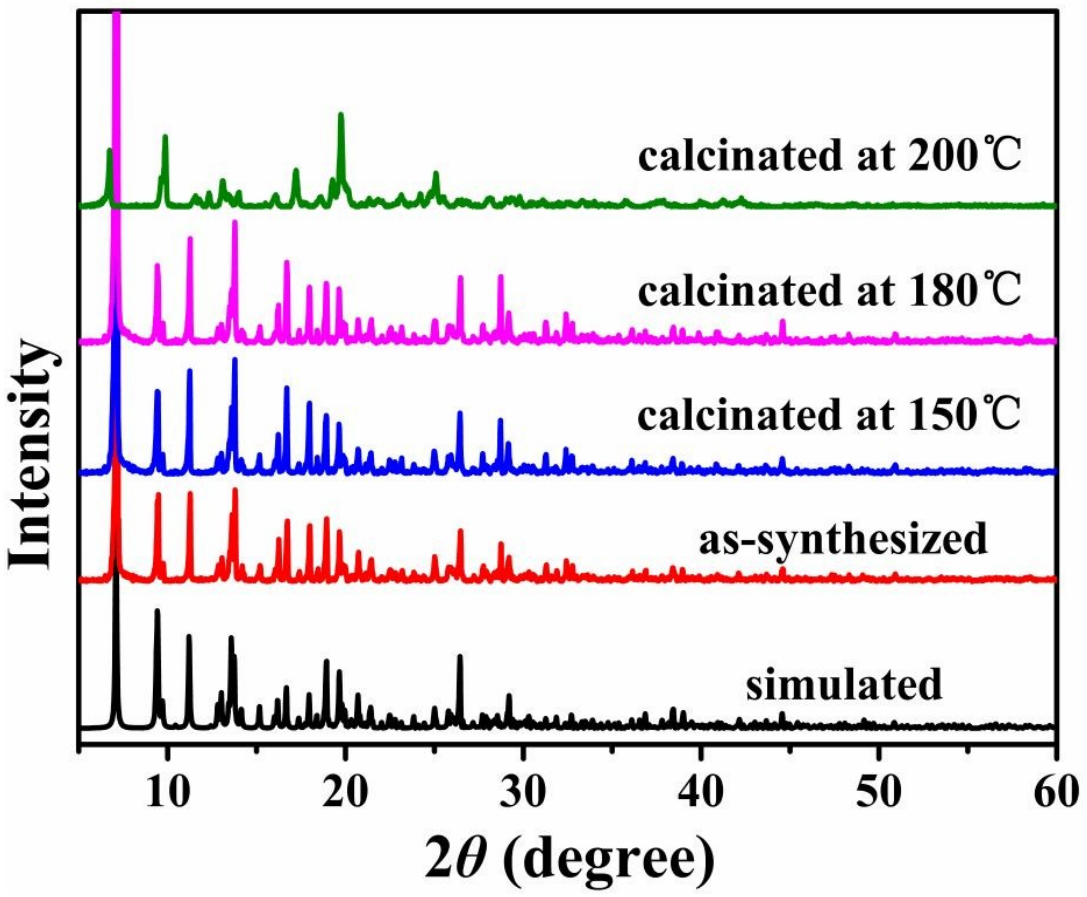

Fig. S1 The powder X-ray diffraction patterns of compound **1**.

TG Analysis

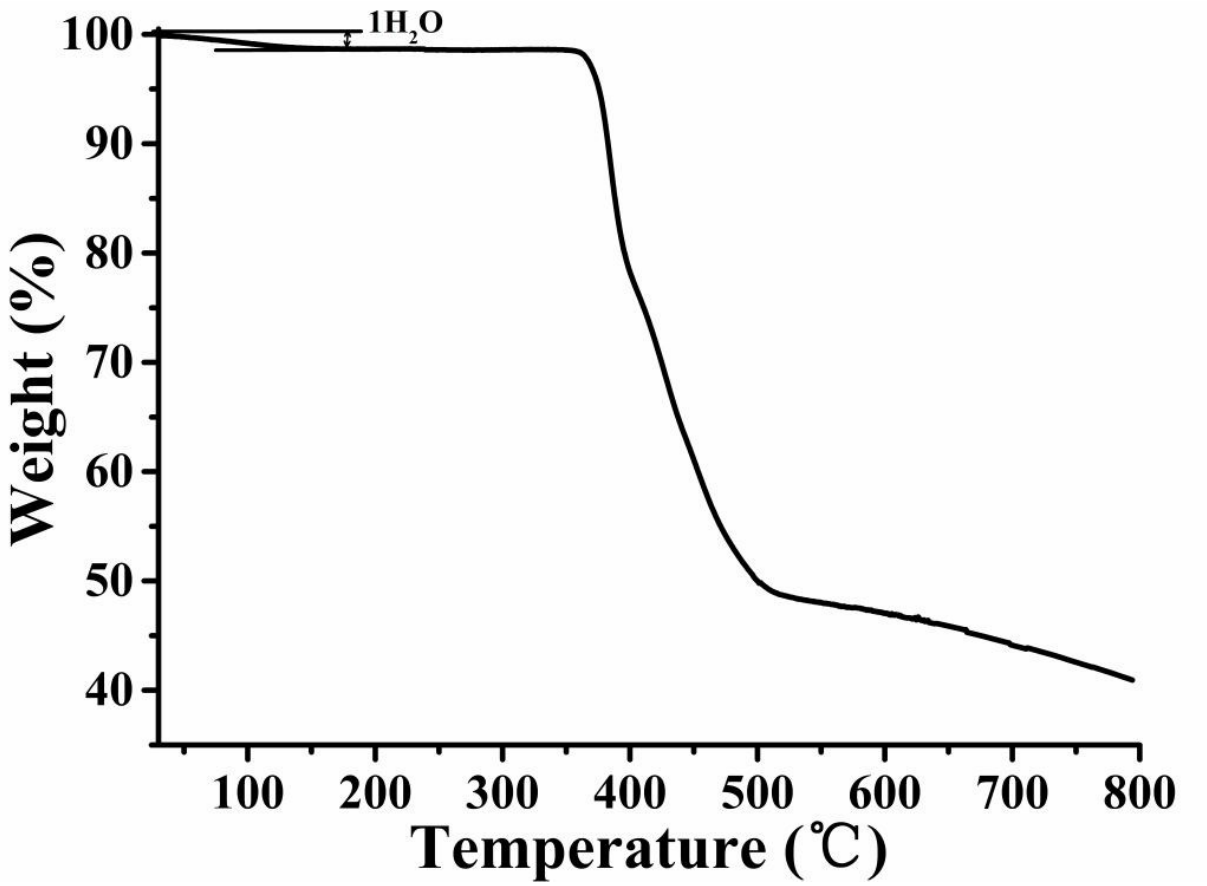

Fig. S2 Thermal gravimetric curve of compound **1**.

Visible-light induced photochromism

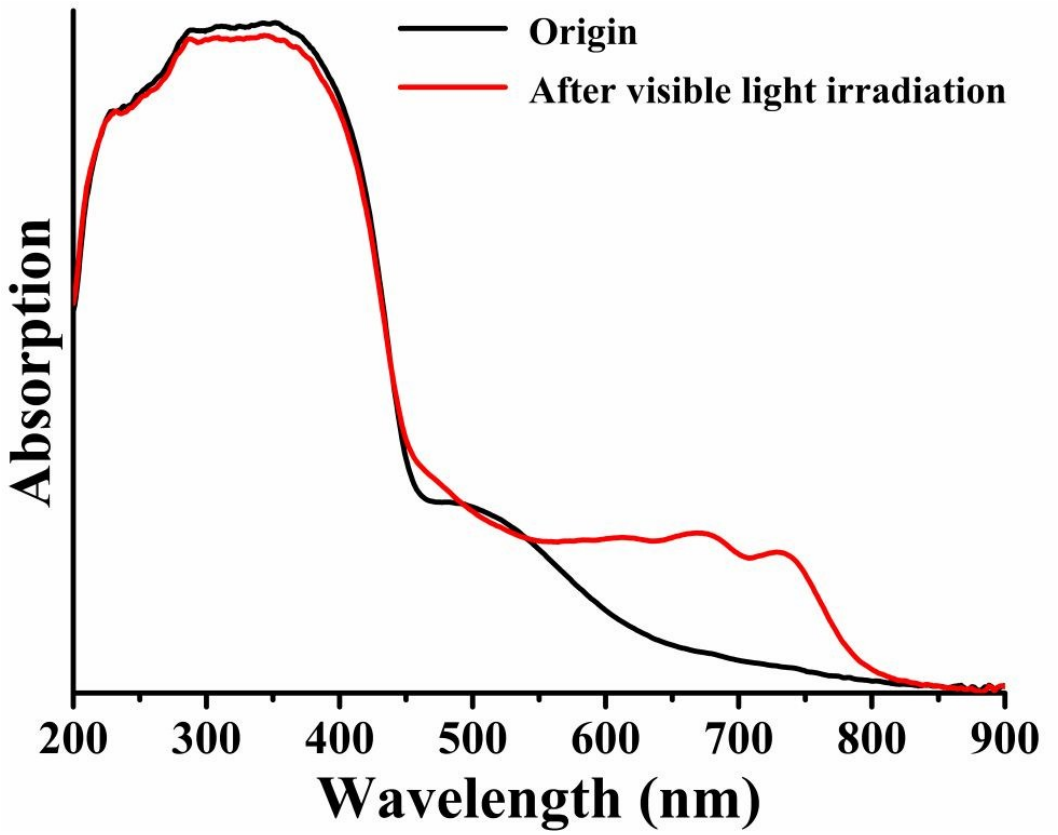

Fig. S3 Diffuse reflectance spectral changes of the sample after visible light irradiation (controlled by an edge filter, $\lambda > 400$ nm) for 50 s.

Optical band gap

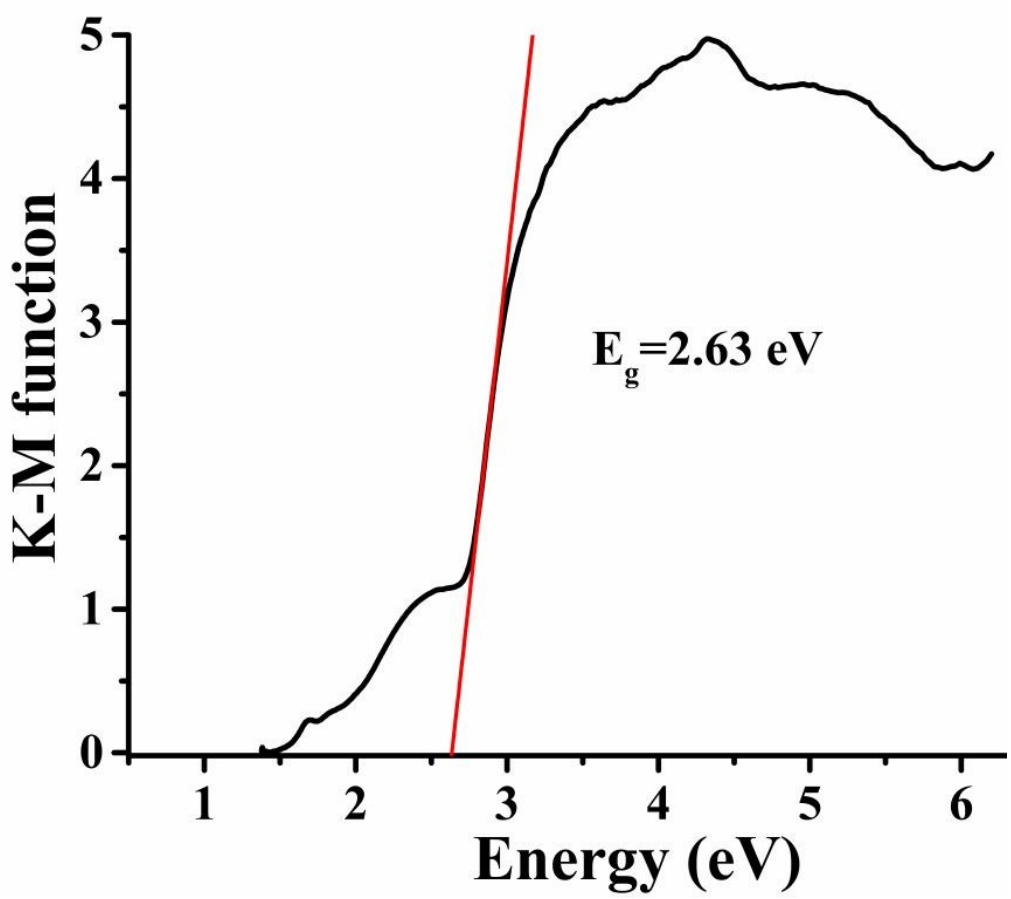

Fig. S4 Optical band gap energy of compound **1**.

IR spectrum

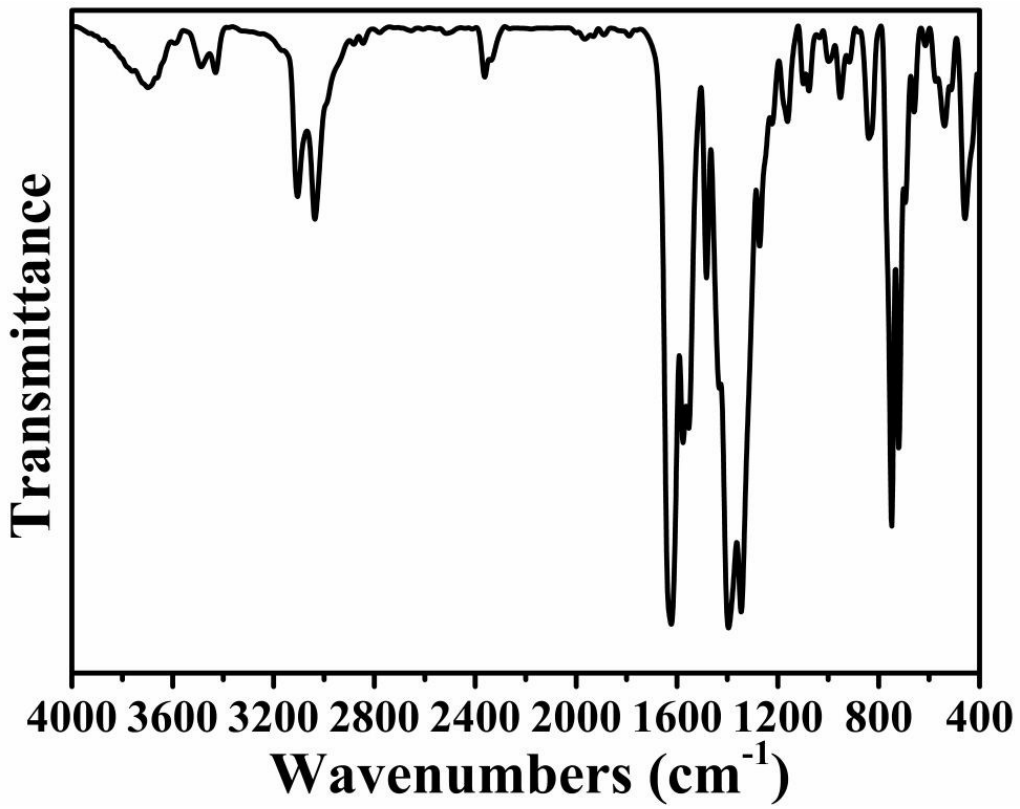

Fig. S5 IR spectrum of compound **1**.

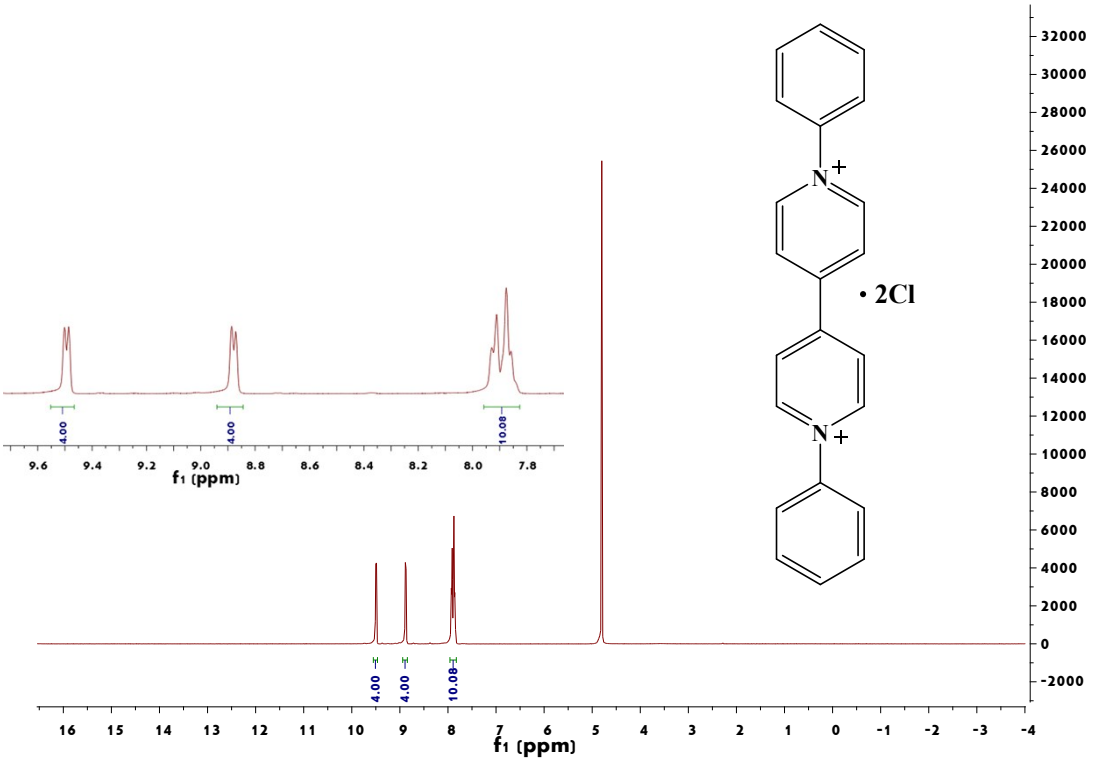

Fig. S6 NMR observation of 1,1'-diphenyl-4,4'-bipyridinium dichloride 9.49 (d, 4H, Ar-H), 8.88 (d, 4H, Ar-H), 7.89 (m, 10H, Ar-H).

Elemental analysis calcd. (%) for $C_{22}H_{18}N_2Cl_2$ (M = 381.30): C 69.30, H 4.76, N 7.35; found: C 69.19, H 4.91, N 7.27.

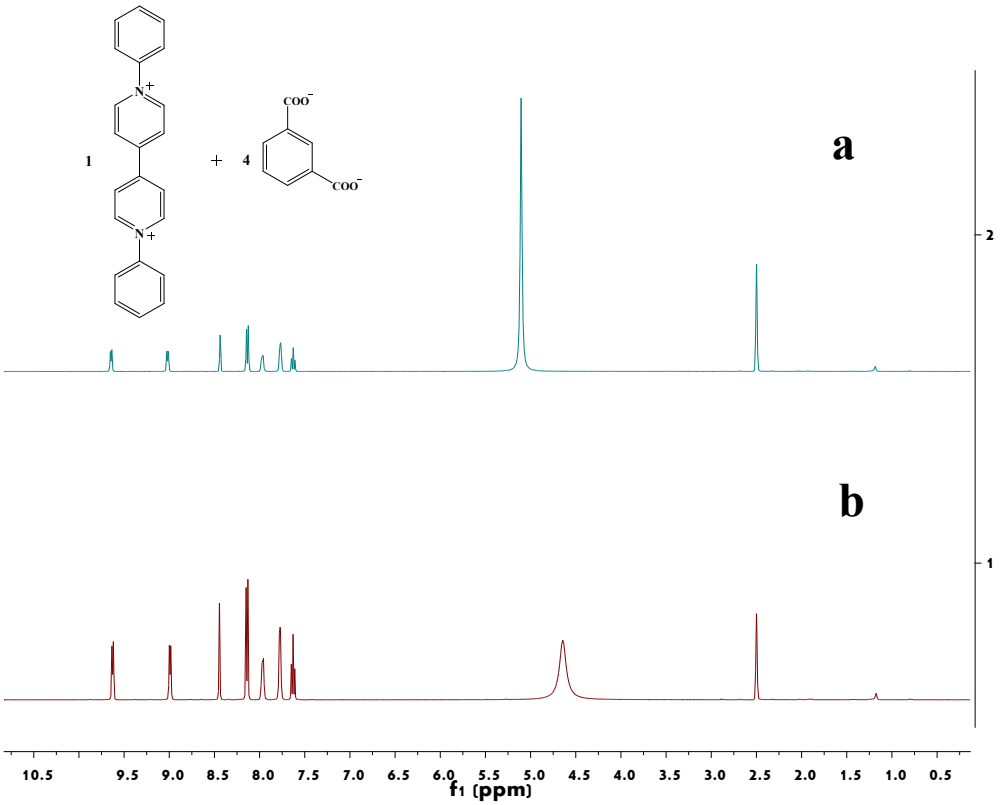

Fig. S7 NMR observation of the sample that was used for the photo response reaction decomposed in deuterated DMSO (DCl digested) before (a) and after (b) the experiment.

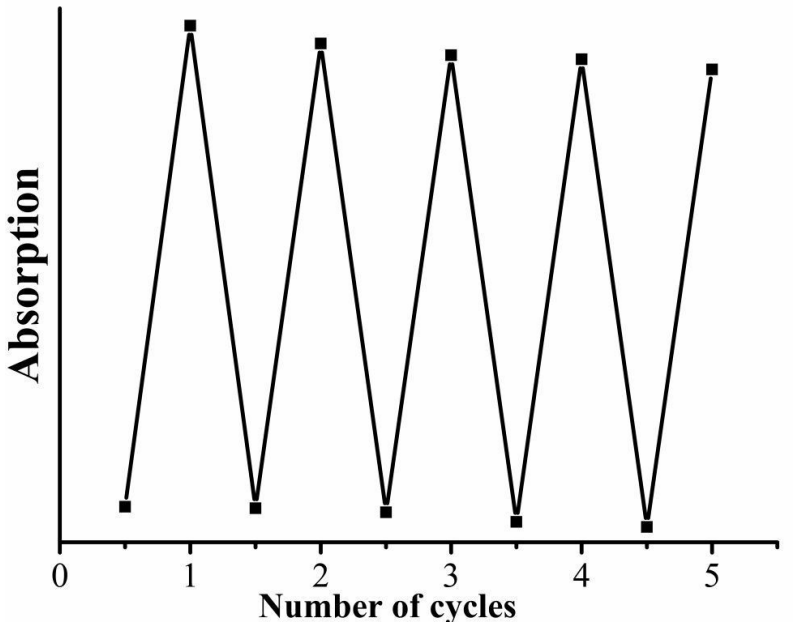

Fig. S8 on alternate excitation by photoirradiation and stored in the dark at room temperature for 12 h five cycles in air.