Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information

A dual-stimuli responsive small molecule organic material with tunable multi-state response showing turn-on luminescence and photocoloration**

Ya-Jun Zhang,[ac] Cheng Chen,[a] Bin Tan,[a] Li-Xuan Cai,[a] Xiao-Dong Yang,[a] and Jie Zhang*[ab]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, E-mail: zhangjie@fjirsm.ac.cn

[b] Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/ Electrophotonic Conversion Materials, School of Chemistry, Beijing Institute of Technology, Beijing, 100081, P. R. China, E-mail: zhangjie68@bit.edu.cn

[c] University of the Chinese Academy of Sciences, Beijing, 100049, P. R. China.

****

Section 1. Materials and General Procedures

1.1 Materials and instruments

All chemicals were purchased from commercial sources and were used without further purification. Elemental analyses of C, H, and N were taken on a Vario EL III CHNOS elemental analyzer. ^{1}H NMR spectra were performed on a Bruker AV-400 NMR spectrometer. Power X-ray diffraction (PXRD) were recorded on a Rigaku MiniFlex 600 diffractometer using Cu Kα radiation with a scan speed of 2 °min^{-1} in the angular rage of 2θ = 5°-55°. UV-Vis diffuse reflectance spectra were taken on a Pekin-Elmer Model Lambda 950 spectrometer with $BaSO_4$ as a reference. Electron spin resonance (ESR) signals were determined by a Bruker A300 EPR spectrometer. The infrared spectra were carried out on a Bomem MB-102 IR spectrometer with samples as KBr pellets in the range of 4000-400 cm^{-1}.

1.2 Synthesis

Synthesis of crystal 1 (DBCAbpe·Br·H_2O)**:** 5-(bromomethyl)-1,3-benzenedicarboxylate (2.871 g, 10 mmol) was dissolved in 15 mL acetonitrile and then dropwise added into a stirred solution of 4,4′-vinylenedipyridine (2.733 g, 15 mmol) in 10 mL acetonitrile, and the temperature remained 90 °C for 6 h. Light yellow precipitate was obtained by filtration and washed with acetonitrile for three times. The precipitate was dried in a vacuum, giving the product as light brown powder, then recrystallized in water to obtain a bright yellow crystal **1** (yield 50%). ^{1}H NMR (400 MHz, DMSO-D_6): δ 3.92 (s, 2H), 5.96 (s, 2H), 7.66-7.68 (m, 2H), 7.66-7.68 (d, J = 16.41 Hz, 1H), 7.77-7.81 (d, J = 16.42 Hz, 1H), 8.34-8.35 (d, 2H), 8.48 (d, 2H), 8.51 (m, 1H), 8.69-8.71 (m, 2H), 9.21-9.23 (d, 2H). Elemental analysis: calc. for $C_{23}H_{23}N_2O_5Br$: C, 56.67; H, 4.72; N, 5.74. Found: C, 56.76; H, 4.63; N, 5.80%. Powdered crystalline **1** (10 mg) was continuously irradiated by 365nm UV light for 48 h, then dissolved in a distilled water. The colorless crystals **1′** suitable for X-ray diffraction analysis were obtained after a few days.

Synthesis of crystal 2 (DBCAbpe·PF_6)**:** KPF_6 (0.552g, 3 mmol) in 25mL acetonitrile was added into 25 mL aqueous solution containing crystals **1** (0.469g, 1 mmol) to yield a lot of precipitation at once. After being continuously stirred for 10 min under 70 °C, the precipitation dissolved gradually. The solution was allowed to stand at room temperature in the dark for slow evaporation. Colorless block crystals of **2** were obtained after a few days (yield: 50%). Elemental analysis: calc. for $C_{23}H_{21}N_2O_4PF_6$: C, 51.69; H, 3.93; N, 5.23. Found: C, 51.63; H, 4.12; N, 5.33%.

1.3 X-ray crystallography

The X-ray diffraction data for crystal **1** and crystal **2** were collected on an Agilent Diffraction SuperNova dual diffractometer with Cu Kα radiation (λ = 1.54178 Å). A multi-scan method was used for absorption corrections. **1′** was collected on Rigaku Saturn 724+ MicroMax 007 with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The CrystalClear program was used for the absorption correction. The structure was solved using direct methods with SHELXS-97 and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on carbon atoms were placed in a calculated position with isotropic displacement parameters. The hydrogen atoms of lattice water molecule had not been included in final refinement.

Crystal data for **1**: $C_{23}H_{23}N_2O_5Br$; *Mr* = 487.34; monoclinic P2(1)/n; *a* = 14.4012(6), *b* = 10.1201(5), *c* = 15.5792(7) Å, α = 90.0, β = 97.623(4), γ = 90.0°, *V* = 2250.47(18) Å^3; *T* = 173(2) K; *Z* = 4; *Dc* = 1.438 g cm^{-1}; μ(Cu Kα) = 2.799 mm^{-1}; *F*(000) = 1000; 9010 reflections collected, of which 4483 unique (R_{int} = 0.0211); GOF = 1.050; R_1 = 0.0450 and wR_2 = 0.1247 [$I > 2\sigma(I)$]. CCDC 1429578.

Crystal data for **1′**: $C_{46}H_{58}Br_2N_4O_6$; *Mr* = 1082.78; Triclinic C2/c; *a* = 27.25(5), *b* = 13.662(16), *c* = 17.30(2) Å, α = 90.0, β = 110.040(18), γ = 90.0°, *V* = 6051(15) Å^3; *T* = 173(2) K; *Z* = 4; *Dc* = 1.189 g cm^{-1}; μ(Mo Kα) = 1.399 mm^{-1}; *F*(000) = 2240; 21961 reflections collected, of which 6872 unique(R_{int} = 0.1044); GOF = 0.926; R_1 = 0.1069 and wR_2 = 0.3012[$I > 2\sigma(I)$]. CCDC 1429579.

Crystal data for **2**: $C_{23}H_{21}N_2O_4PF_6$; *Mr* = 534.39; Monoclinic P2(1)/c; *a* = 6.8210(6), *b* = 17.801(2), *c* = 19.7701(18) Å, α = 90.0, β = 98.215(8), γ = 90.0°, *V* = 2375.8(4) Å^3; *T* = 296(2) K; *Z* = 4; *Dc* = 1.494 g cm^{-1}; μ(Cu Kα) = 1.770 mm^{-1}; *F*(000) = 1096; 8711 reflections collected, of which 4704 unique (R_{int} = 0.0289); GOF = 1.092; R_1 = 0.0822 and wR_2 = 0.1623 [$I > 2\sigma(I)$]. CCDC 1429580.

Section 2. Additional Data

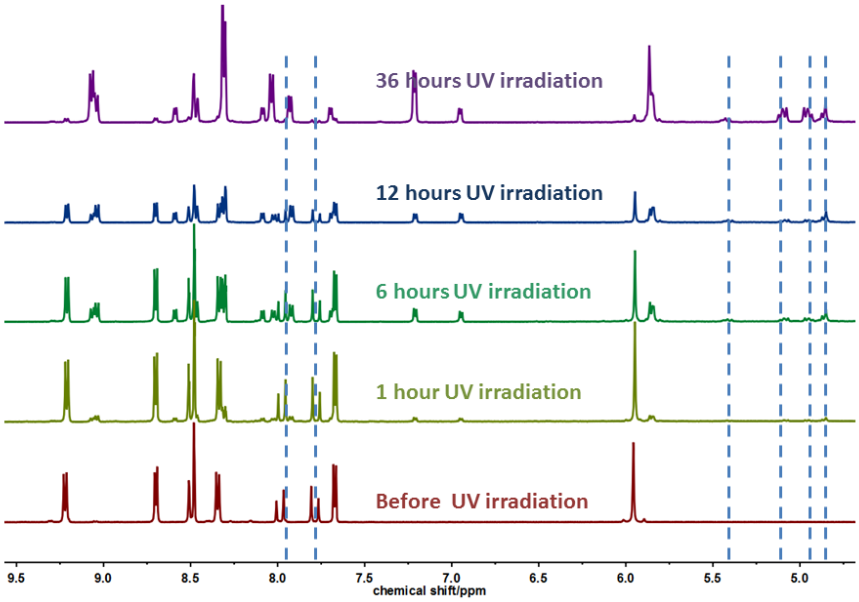

Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6) spectra showing the photocycloaddition of crystal **1** under 365 nm UV light irradiation.

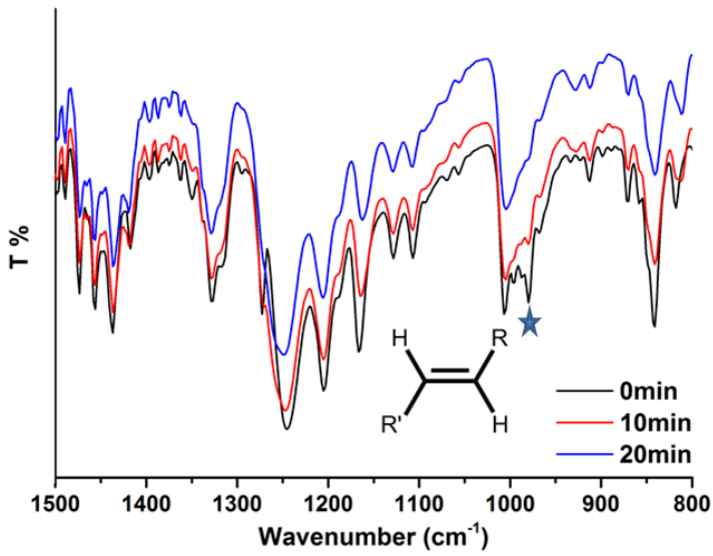

Fig. S2 In-situ IR spectra of crystal **1** under 365 nm UV light irradiation.

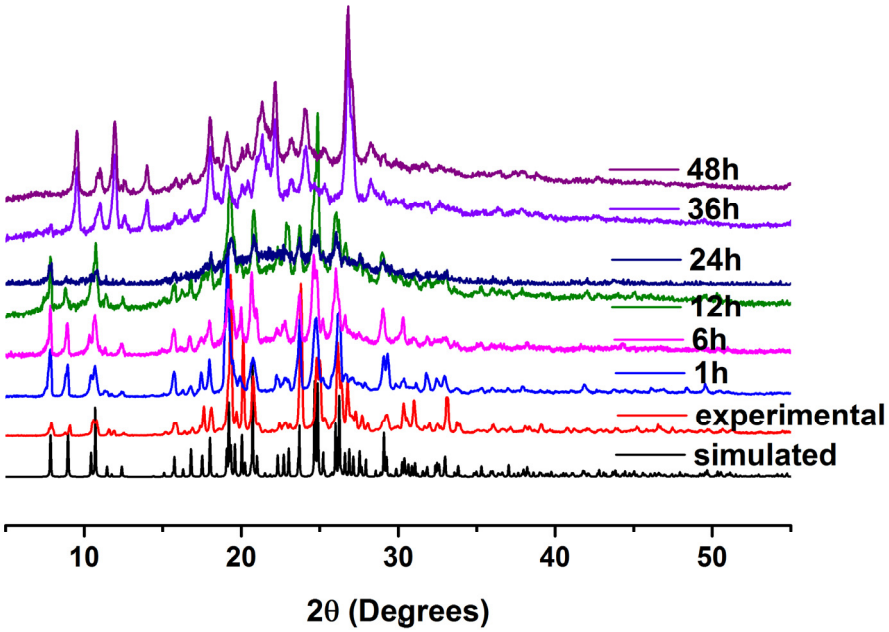

Fig. S3 The PXRD patterns of compounds **1** under 365 UV light irradiation.

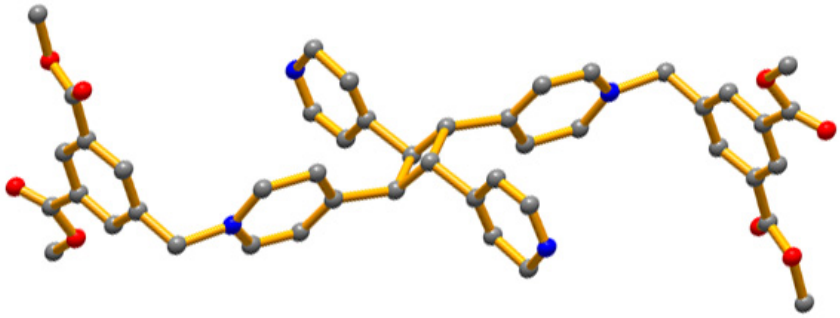

Fig. S4 The molecular conformation of rctt-type dimer **1′** obtained by recrystallization of the photoirradiated sample **1** from the distilled water (C, grey; N, blue; O, red). Hydrogen atoms are omitted for clarity.

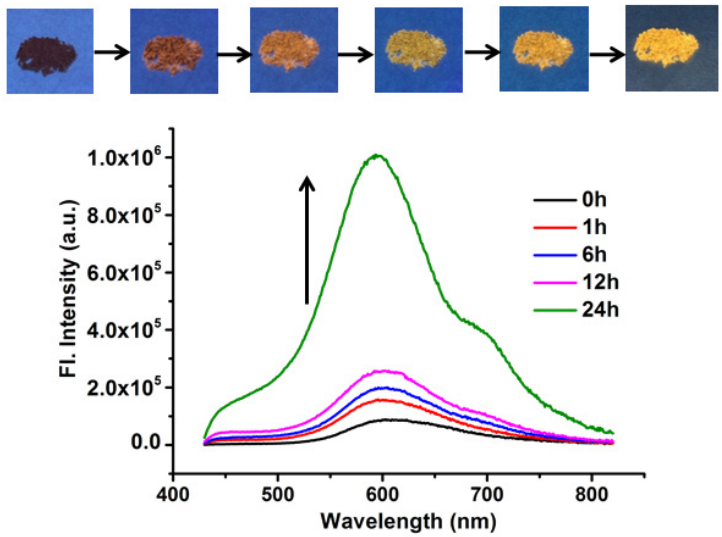

Fig. S5 Top panel: Fluorescence image of powdered crystal **1** upon UV irradiation ($\lambda = 365$nm); Bottom panel: The emission spectra of the irradiated sample **1**, $\lambda_{ex} = 395$nm.

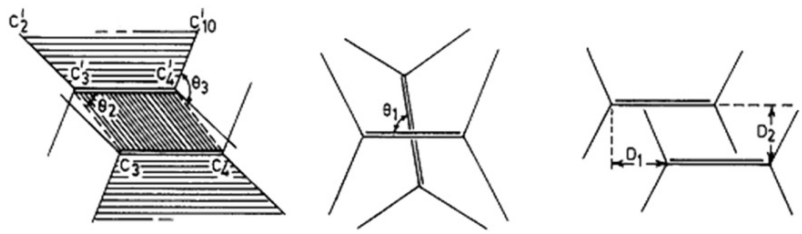

Fig.S6 Definition of the parameters usually considered to be geometric criteria for [2+2] photodimerization of double bonds (According to Ref: V. Ramamurthy, and K. Venkatesan, *Chem. Rev.*, 1987, 87, 433–481; θ3 is the angle between the >C=C< and C=C-C=C Planes). The corresponding geometrical parameters θ_1, θ_2, θ_3, D1 and D2 in crystal **1** are 0°, 89.960°, 76.255°, 0.003 Å and 3.866 Å.

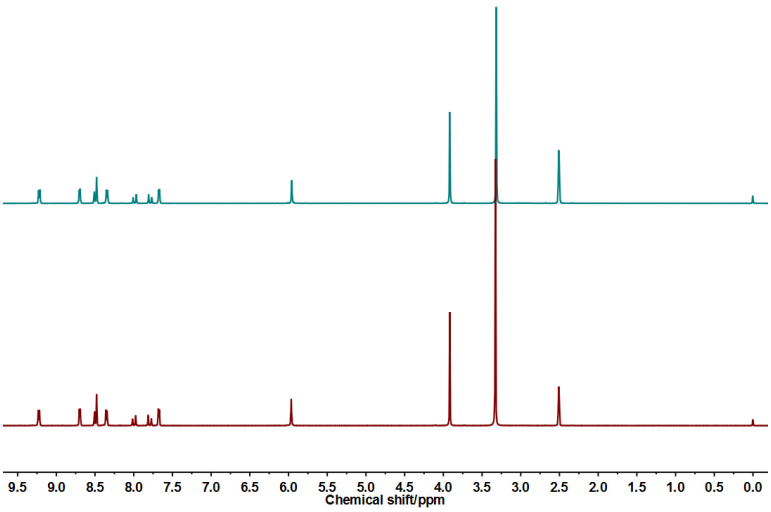

Fig. S7 ^{1}H NMR (400 MHz, DMSO-d_6) spectra of crystal **1** under visible light irradiation showing no photocycloaddition product.

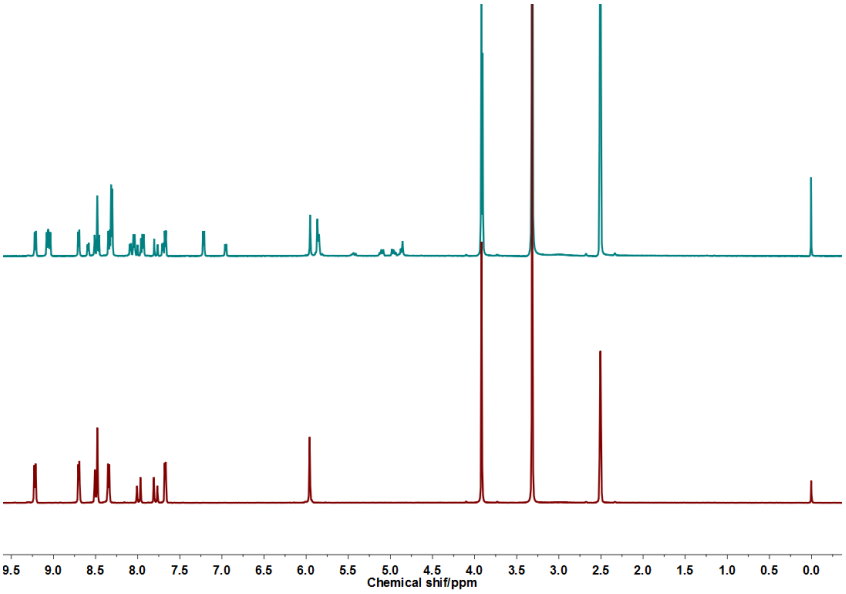

Fig. S8 ^{1}H NMR (400 MHz, DMSO-d_6) spectra of crystal **1-Vis** under 365 nm UV light irradiation showing that photocycloaddition reaction can be restarted in **1-Vis** by re-exposing to the UV light.

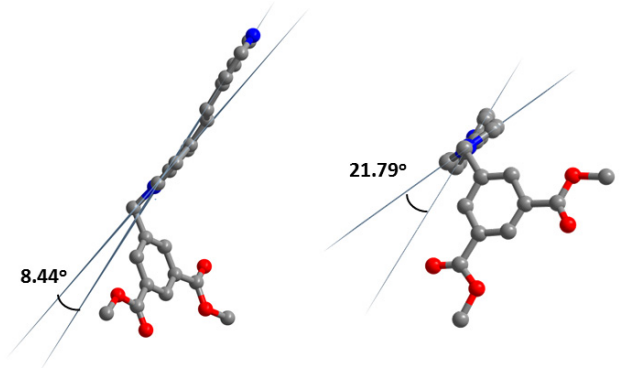

Fig. S9 The corresponding angles between the pyridinium and pyridine rings in crystal **1** (left) and crystal **2** (right). Hydrogen atoms are omitted for clarity.

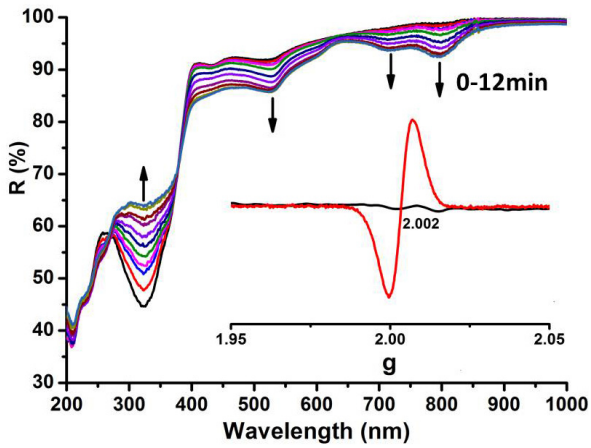

Fig. S10 The diffuse reflectance spectra of crystal **2** under Xenon lamp. Insert: the ESR spectra of crystal **2** before (black) and after (red) Xenon lamp irradiation for 1 h.