Electronic Supplementary Information

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

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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. 1H 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 BaSO₄ 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-H₂O): 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%). 1H NMR (400 MHz, DMSO-D₆): 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 C₂₃H₂₃N₂O₅Br: 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-PF₆): KPF₆(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 C₂₃H₂₁N₂O₄PF₆: 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 ($\lambda = 1.54178$ 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 ($\lambda = 0.71073$ 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$_2$O$_5$Br; $Mr = 487.34$; monoclinic P2(1)/n; $a = 14.4012(6)$, $b = 10.1201(5)$, $c = 15.5792(7)$ Å, $\alpha = 90.0$, $\beta = 97.623(4)$, $\gamma = 90.0^\circ$, $V = 2250.47(18)$ Å$^3$; $T = 173(2)$ K; $Z = 4$; $D_c = 1.438$ g cm$^{-1}$; $\mu$(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$_2$N$_4$O$_6$; $Mr = 1082.78$; triclinic C2/c; $a = 27.25(5)$, $b = 13.662(16)$, $c = 17.30(2)$ Å, $\alpha = 90.0$, $\beta = 110.040(18)$, $\gamma = 90.0^\circ$, $V = 6051(15)$ Å$^3$; $T = 173(2)$ K; $Z = 4$; $D_c = 1.189$ g cm$^{-1}$; $\mu$(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$_2$O$_4$PF$_6$; $Mr = 534.39$; monoclinic P2(1)/c; $a = 6.8210(6)$, $b = 17.801(2)$, $c = 19.7701(18)$ Å, $\alpha = 90.0$, $\beta = 98.215(8)$, $\gamma = 90.0^\circ$, $V = 2375.8(4)$ Å$^3$; $T = 296(2)$ K; $Z = 4$; $D_c = 1.494$ g cm$^{-1}$; $\mu$(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 rett-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 (λ = 365 nm); Bottom panel: The emission spectra of the irradiated sample 1, λ<sub>ex</sub> = 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; θ<sub>3</sub> is the angle between the >C=C< and C=C-C=C Planes). The corresponding geometrical parameters θ<sub>1</sub>, θ<sub>2</sub>, θ<sub>3</sub>, D1 and D2 in crystal 1 are 0°, 89.960°, 76.255°, 0.003 Å and 3.866 Å.

Fig. S7  <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) 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.