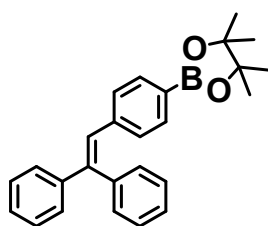


Supporting Information

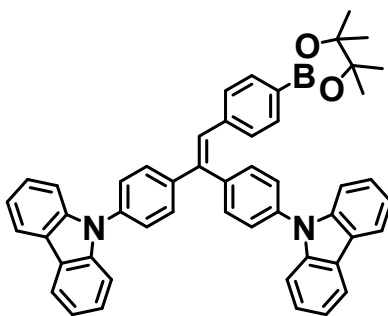
1. Synthesis of TrPEB and TrPEBCar

The details of the synthetic procedures for TrPEB and TrPEBCar are shown below. Compounds (2-(4-bromophenyl)ethene-1,1-diyl)dibenzene and (2-(4-bromophenyl)ethene-1,1-diyl)di(4-carbazole-benzene) were synthesized according to the previous literatures.^[1] The final compounds were characterized by ¹H-NMR spectroscopy, High-resolution EI mass spectroscopy and elemental analysis.



TrPEB

TrPEB. To a two-necked round-bottomed flask containing (2-(4-bromophenyl)ethene-1,1-diyl)dibenzene (3.35 g, 10.0 mmol), potassium acetate (9.81g 100 mmol), bis(pinacolato)diboron (3.81 g, 15.0 mmol) and Pd(PPh₃)₄ were added degassed 1,4-dioxane (30 mL) under an argon atmosphere. Upon refluxing and stirring for 12 hours under an argon atmosphere, the mixture filtered and filtrate was collected. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel (60-230 mesh) with CH₂Cl₂-hexane (2:1, v/v) as eluent. Solvent removal yielded a white solid. Yield: 2.75 g (72 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.13 (s, 12H; -CH₃), 6.94–6.98 (m, 2H; -C₆H₅), 7.02–7.16 (m, 8H; -C₆H₅,), 7.28–7.36 (m, 5H; -C₆H₄- and -CH=); High resolution EI-MS: m/z found: 382.2096 [M]⁺; calcd for C₂₆H₂₇BO₂: 382.2104. Anal. calcd for C₂₆H₂₇BO₂: C 81.68, H 7.12, B 2.83, O 8.37; found: C 81.42, H 7.27.



TrPEBCar

TrPEBCar. The compound was prepared according to the preparation of compound **TrPEB**, except that the (2-(4-bromophenyl)ethene-1,1-diyl)dibenzene (3.35 g, 10.0 mmol) was replaced by (2-(4-bromophenyl)ethene-1,1-diyl)di(4-carbazole-benzene) (6.65 g, 10.0 mmol). Yield: 4.34 g (61 %). ^1H NMR (400 MHz, CD_3Cl , 298 K, relative to Me_4Si): δ = 1.35 (m, 12H, $-\text{CH}_3$), 7.15–7.22 (m, 3H, $-\text{C}_6\text{H}_4-$ and $-\text{CH}=\text{}$), 7.28–7.35 (m, 4H, Carbazole), 7.40–7.56 (m, 10H, $-\text{C}_6\text{H}_4-$), 7.58–7.62 (m, 4H, Carbazole), 7.67–7.71 (m, 4H, Carbazole), 8.17 (d, J = 7.7 Hz, 4H, Carbazole); High resolution EI-MS: m/z found: 712.3251 $[\text{M}]^+$; calcd for $\text{C}_{50}\text{H}_{41}\text{BN}_2\text{O}_2$: 712.3261. Anal. calcd for $\text{C}_{50}\text{H}_{41}\text{BN}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$: C 80.21, H 6.06, B 1.44, N 3.74, O 8.55; found: C 80.55, H 6.32, N 3.88.

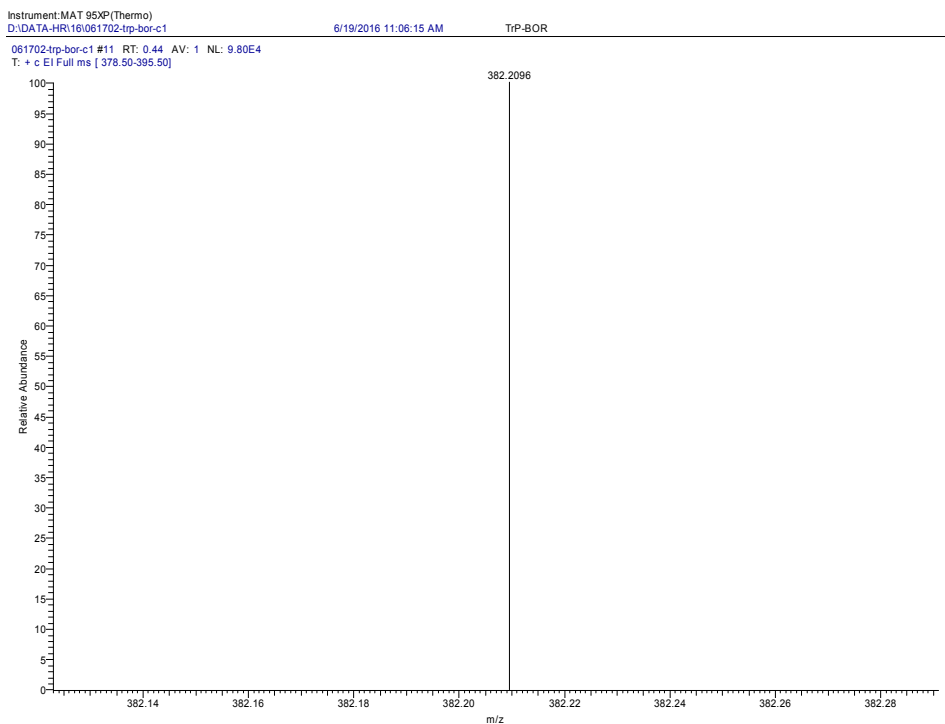


Figure S1. High Resolution EI mass spectrum of TrPEB.

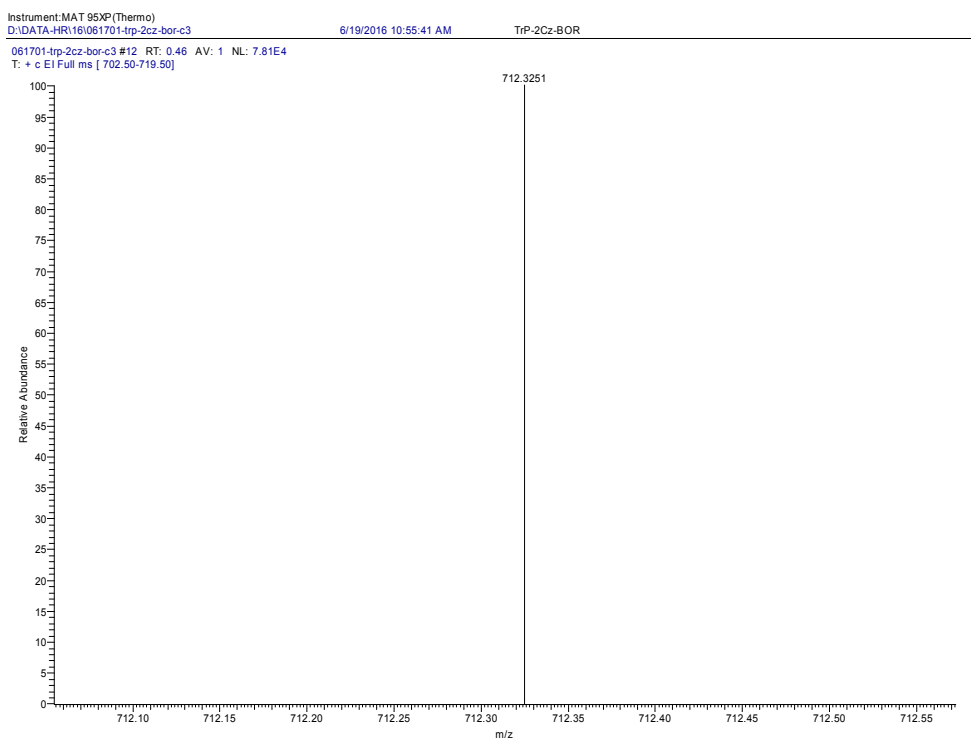


Figure S2. High Resolution EI mass spectrum of TrPEBCar.

2. Physical Measurements and Instrumentations

^1H -NMR spectra were recorded using a Varian Mercury-Plus 300 Nuclear Magnetic Resonance Spectrometer with chemical shifts recorded relative to tetramethylsilane (Me_4Si). Positive ion EI mass spectra were performed using a Thermo MAT95XP high resolution mass spectrometer. UV-vis reflectance spectra were carried out using an Ocean Optic Maya2000PRO spectrometer with Ocean Optic reflection probes R600-125F. Steady state emission spectra were recorded using a Shimadzu RF-5301pc spectrofluorometer and low-temperature emission studies were conducted with the same spectrofluorometer equipped with a Cryocon 22C temperature controller. The elemental analysis was performed using a Vario EL analyzer. The particle size distribution (dynamic light scattering) was measured on a EliteSizer nanoparticle size-zeta potential and molecular weight analyzer. SEM images were obtained using a HITACHI S-4800 field-emission scanning electron microscope operated at 10 kV.

3 DSC scans and UV-vis Absorption/Reflectance Spectra

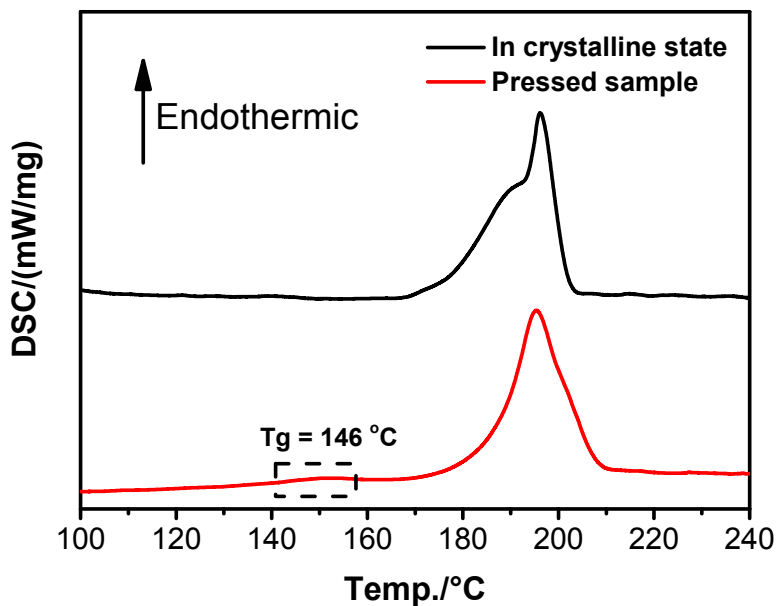


Figure S3. The first heating DSC scans of TrPEBCar in the crystalline state before and after pressing.

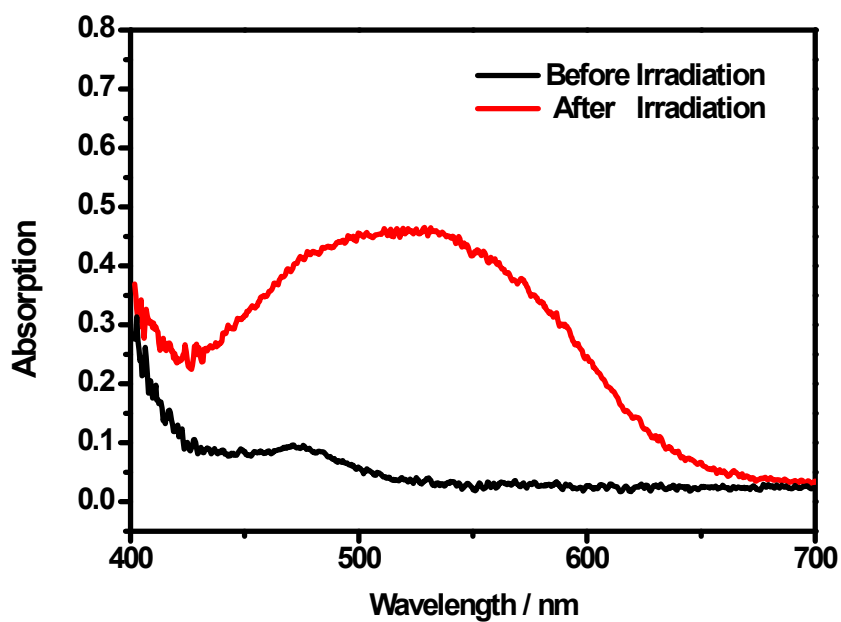


Figure S4. UV-vis reflectance spectra of compound TrPEB in the crystalline state before and after UV-light irradiation.

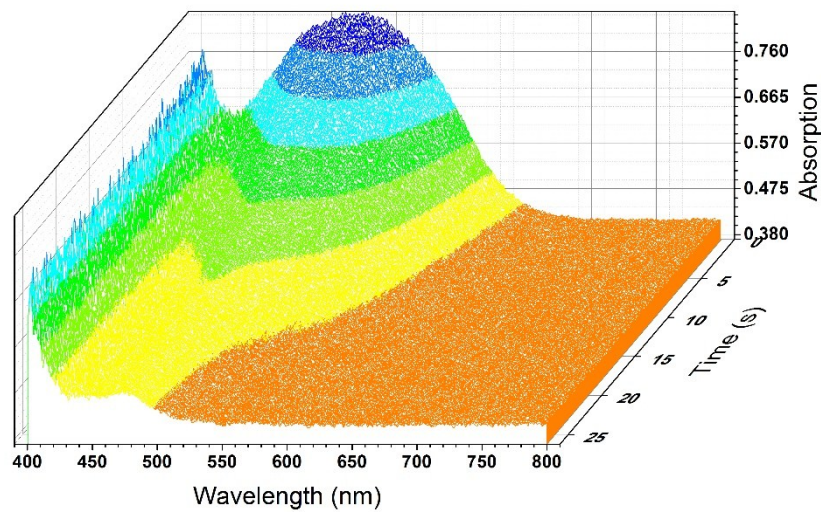


Figure S5. Time dependent UV-vis reflectance spectra of compound TrPEB in the crystalline state during the reverse ring-opening process (after stopping UV-light irradiation).

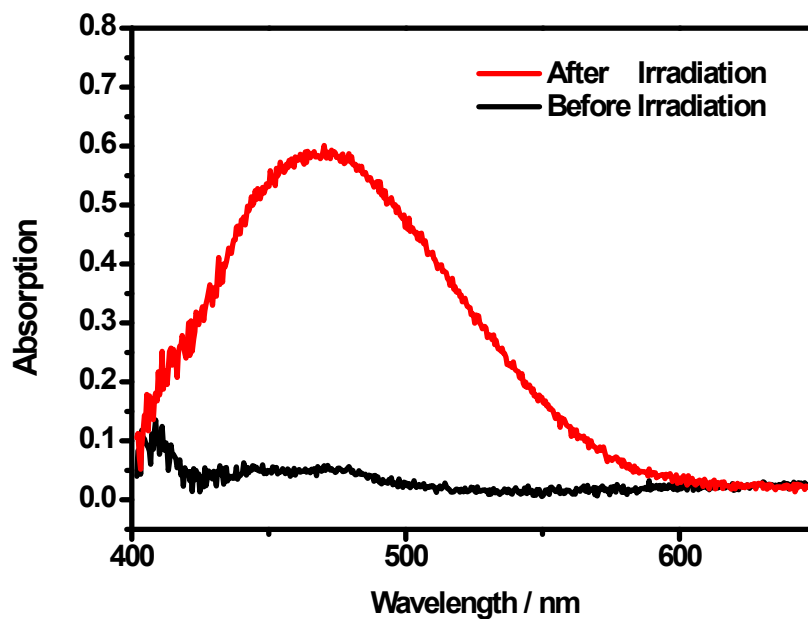


Figure S6. UV-vis reflectance spectra of compound TrPEB in the crystalline state before and after the UV-light irradiation process.

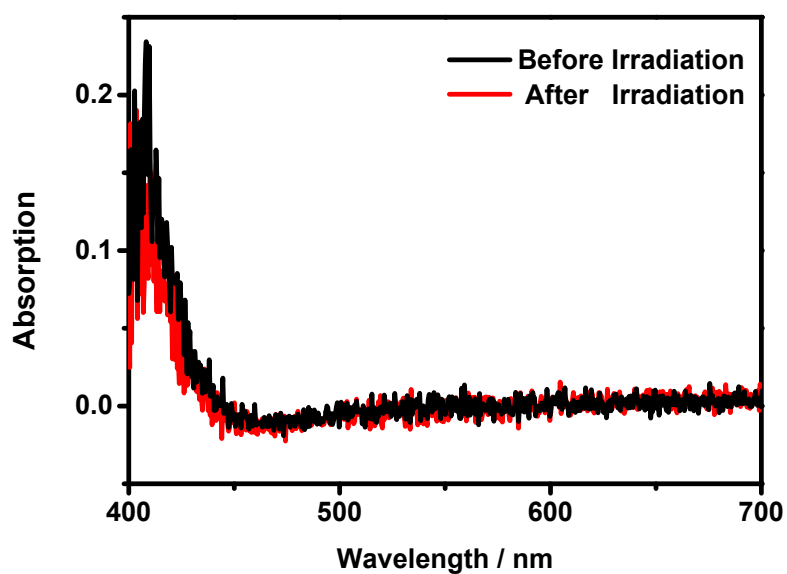


Figure S7. UV-vis reflectance spectra of compound TrPEBCar in the amorphous state before and after the UV-light irradiation process.

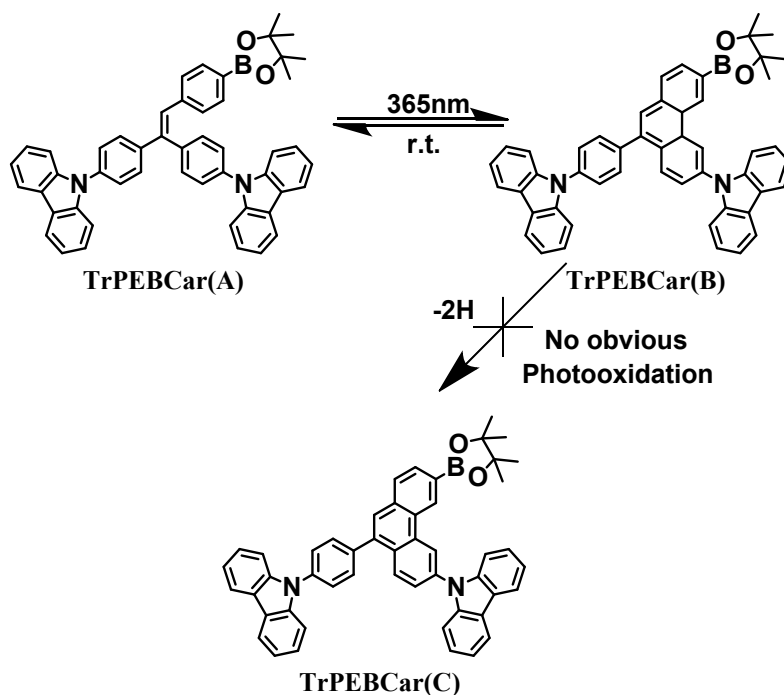


Figure S8. Mechanism of the photochromic process.

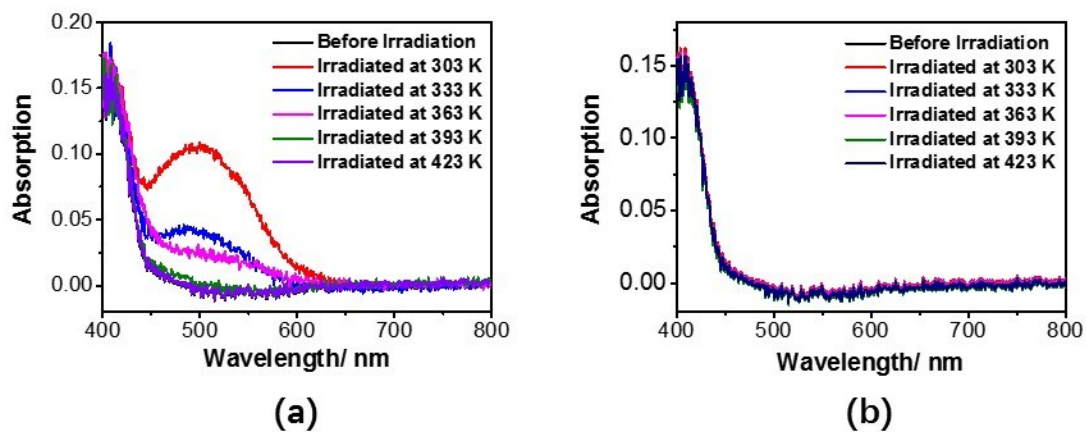


Figure S9. (a) Temperature-dependent UV-vis reflectance spectra of compound TrPEBCar in the crystalline state before and after the UV-light irradiation process, (b) Temperature-dependent UV-vis reflectance spectra of compound TrPEBCar in the amorphous state before and after the UV-light irradiation process.

Reference:

- [1] Z. Yang, Z. Chi, T. Yu, X. Zhang, M. Chen, B. Xu, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2009, **19**, 5541; (b) H. Li, Z. Chi, B. Xu, X. Zhang, Z. Yang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2010, **20**, 6103