

Supporting Information

Effect of cis/trans isomerization on the photochromic performances of triphenylethylene

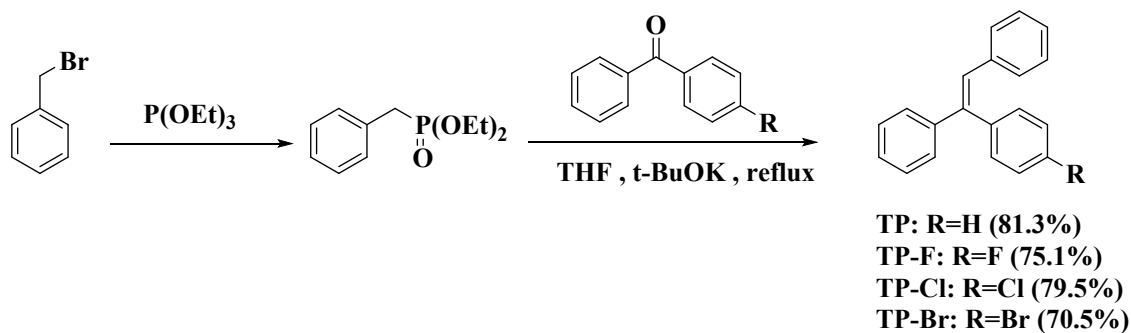
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Scheme S1 Synthesis routes of TP, TP-F, TP-Cl and TP-Br.

Experimental Section

Chemicals and instruments

All solvents and chemical reagents were bought from Shanghai Aladdin reagent Co., Ltd. They were used as received. The ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C using a Qone-WNMR-I 400 MHz spectrometer. Mass spectra were determined with a Thermo Scientific QE plus mass spectrograph. UV-vis absorption spectra were recorded using a Varian Cary 50 spectrophotometer. The time-dependent absorption spectra were conducted with a NOVA-EX optical fiber spectrometer. Single-crystal X-ray diffraction measurements were conducted on an Oxford Diffraction Gemini E diffractometer. The structures were solved by direct methods and refined by a full-matrix least-squares technique on F^2 using SHELX-97 programs.

Synthesis

Diethyl benzylphosphonate

A 100 mL round-bottom flask was charged with benzyl bromide (9.0 g, 53.0 mmol) and triethyl phosphite (7.0 g, 42.0 mmol). The solution was heated at 120 °C for 17 h. The excess triethyl phosphite was evaporated at 160 °C under reduced pressure to obtain a light yellow oil. The product was not purified, and the next reaction was directly carried out.

1,1,2-Triphenylethene (TP)

Under the protection of nitrogen, diethyl benzylphosphonate (5.0 g, 22.0 mmol), benzophenone (3.0 g, 16.5 mmol) and THF (35.0 mL) were added into a Schlenk flask. After cooling to 0 °C, *t*-BuOK (3.2 g, 28.5 mmol) was added in batches. The mixture was allowed to warm to room temperature and stirred for 26 h. The solvent was evaporated under reduced

pressure, and the crude product was purified by flash column chromatography using petroleum ether as eluent to afford a colorless solid (4.4 g, yield 81.3%). ¹H NMR (400 MHz, DMSO-d₆) δ: 7.43~7.39 (m, 2H), 7.38~7.31 (m, 5H), 7.19~7.09 (m, 6H), 7.06~7.01 (m, 3H); ¹³C NMR (101 MHz, DMSO-d₆) δ: 143.05, 140.44, 137.37, 130.25, 129.75, 128.74, 127.99, 127.31. MS (TOF): m/z Found: 257.13 [M+H]⁺, molecular formula C₂₀H₁₆ calculated 256.13.

1-(1,2-Diphenylvinyl)-4-fluorobenzene (TP-F)

The compound TP-F was prepared in a similar procedure as that used for TP from diethyl benzylphosphonate and 4-fluorobenzophenone. Column chromatography (silica gel, petroleum ether) gave TP-F as a colorless solid in 75.1% yield. ¹H NMR (400 MHz, CDCl₃-d₆) δ: 7.26~7.20 (m, 10H), 7.12~7.03 (m, 10H), 6.98~6.93 (m, 7H), 6.92 (s, 1H), 6.89 (s, 1H), 6.83 (s, 1H), ¹³C NMR (101 MHz, CDCl₃-d₆) δ: 141.57, 137.25, 132.19, 130.33, 129.52, 129.27, 128.71, 128.28, 127.67, 126.89, 115.75, 114.96. MS (TOF): m/z Found: 275.12 [M+H]⁺, molecular formula C₂₀H₁₅F calculated 274.12.

1-Chloro-4-(1,2-diphenylvinyl) benzene (TP-Cl)

The compound TP-Cl was prepared in a similar procedure as that used for TP from diethyl benzylphosphonate and 4-chlorobenzophenone. Column chromatography (silica gel, petroleum ether) gave TP-Cl as a colorless solid in 79.5% yield. ¹H NMR (400 MHz, CDCl₃-d₆) δ: 7.28~7.17 (m, 7H), 7.12~7.03 (m, 5H), 6.99~6.94 (m, 2H), 6.89 (s, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ: 142.62, 141.01, 139.22, 137.08, 132.76, 132.22, 129.71, 129.38, 128.84, 128.53, 128.17, 127.57. MS (TOF): m/z Found: 291.09 [M+H]⁺, molecular formula C₂₀H₁₅Cl calculated 290.09.

1-Bromo-4-(1,2-diphenylvinyl) benzene (TP-Br)

The compound TP-Br was prepared in a similar procedure as that used for TP from diethyl benzylphosphonate and 4-bromo-benzophenone. Column chromatography (silica gel, petroleum ether) gave TP-Br as a colorless solid in 70.5% yield. ¹H NMR (400 MHz, CDCl₃-d₆) δ: 7.40~7.35 (d, 2H), 7.27~7.19 (m, 5H), 7.12~7.05 (m, 3H), 7.03~6.93 (m, 4H), 6.89 (s, 1H); ¹³C NMR (101 MHz, CDCl₃-d₆) δ: 143.00, 141.40, 139.33, 137.06, 132.26, 131.85, 129.54, 128.78, 128.15, 127.67, 127.02, 126.53. MS (TOF): m/z Found: 335.04 [M+H]⁺, molecular formula C₂₀H₁₅Br calculated 334.04.

Preparation of triphenylethylene-doped PMMA films

The photochromic material (5 wt%) and polymethylmethacrylate (PMMA) (95 wt%) were completely dissolved in dichloromethane. Then pour the mixed solution into a clean and dry glass mold, place it in dark and slowly evaporate to obtain a transparent uniform film.

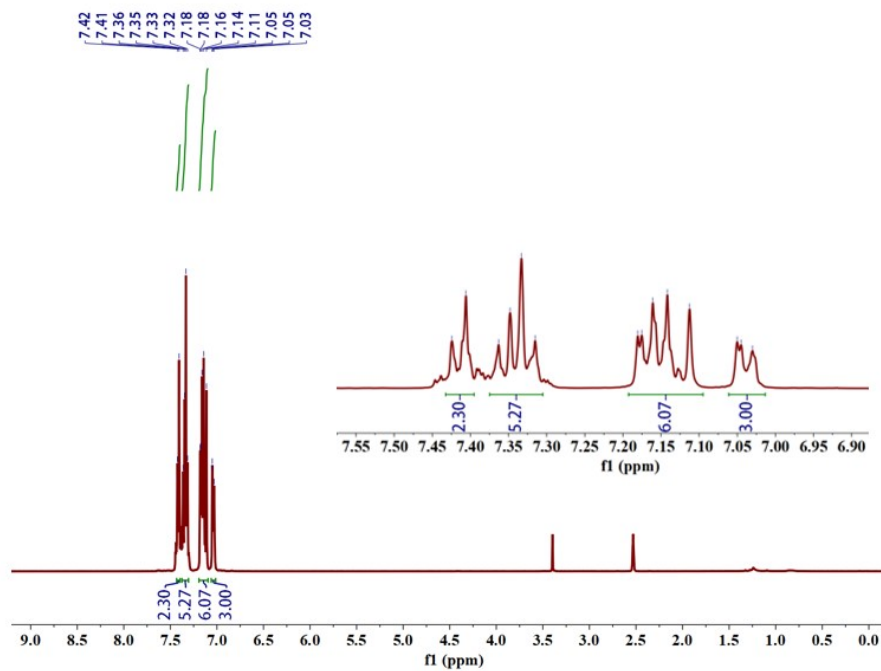


Fig. S1 ^1H NMR spectrum of TP.

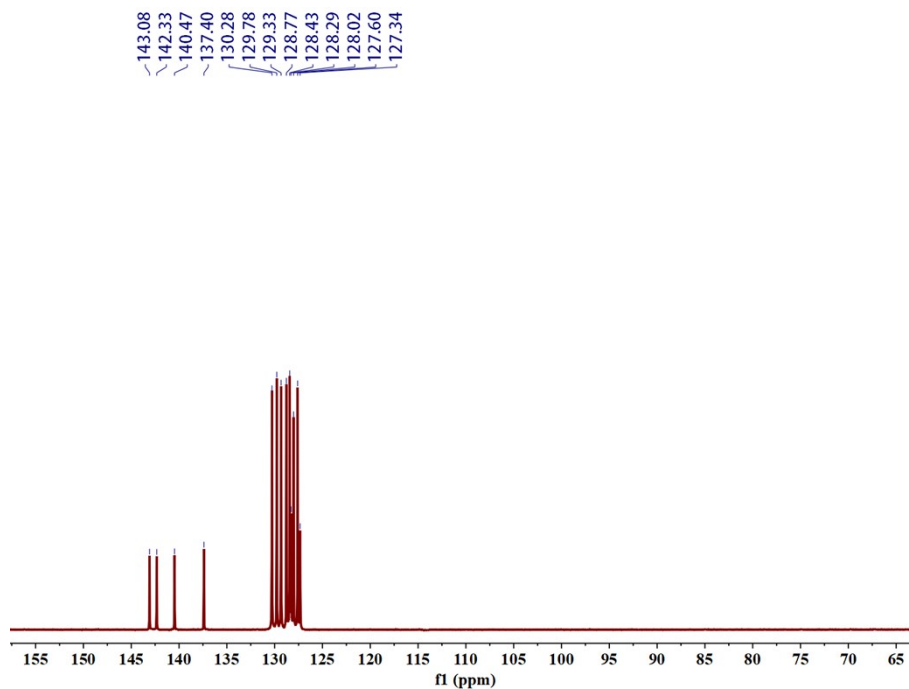


Fig. S2 ^{13}C NMR spectrum of TP.

2404178698-1TP #10-64 RT: 0.05-0.29 AV: 27 SB: 17 0.75-0.90 NL: 8.59E7
T: FTMS + p APCI corona Full ms [50.0000-750.0000]

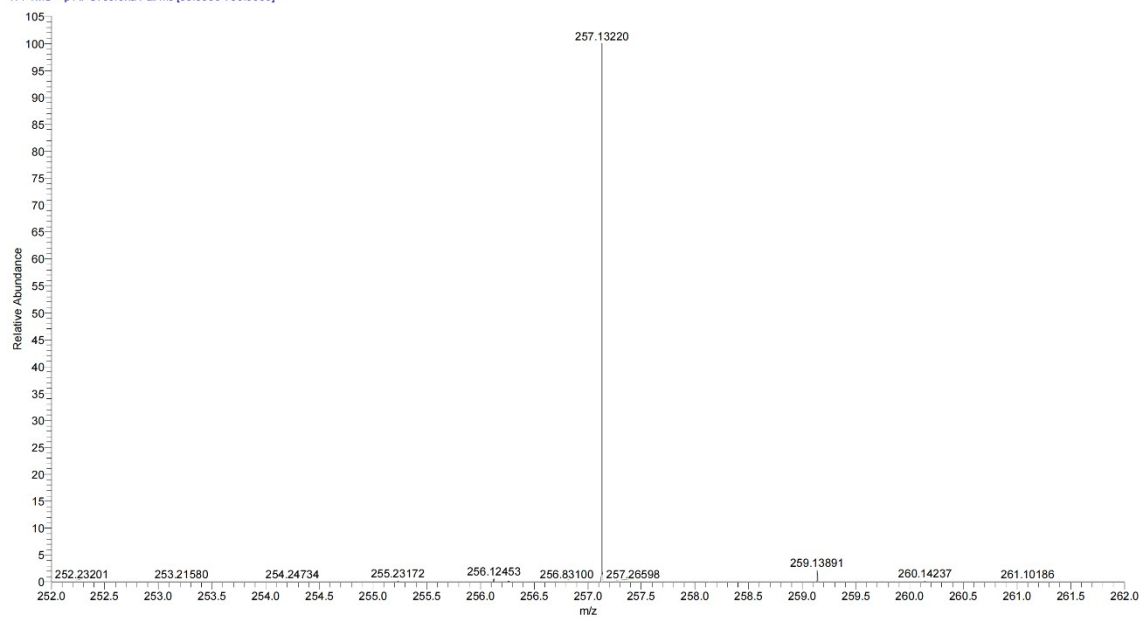


Fig. S3 Mass spectrum of TP.

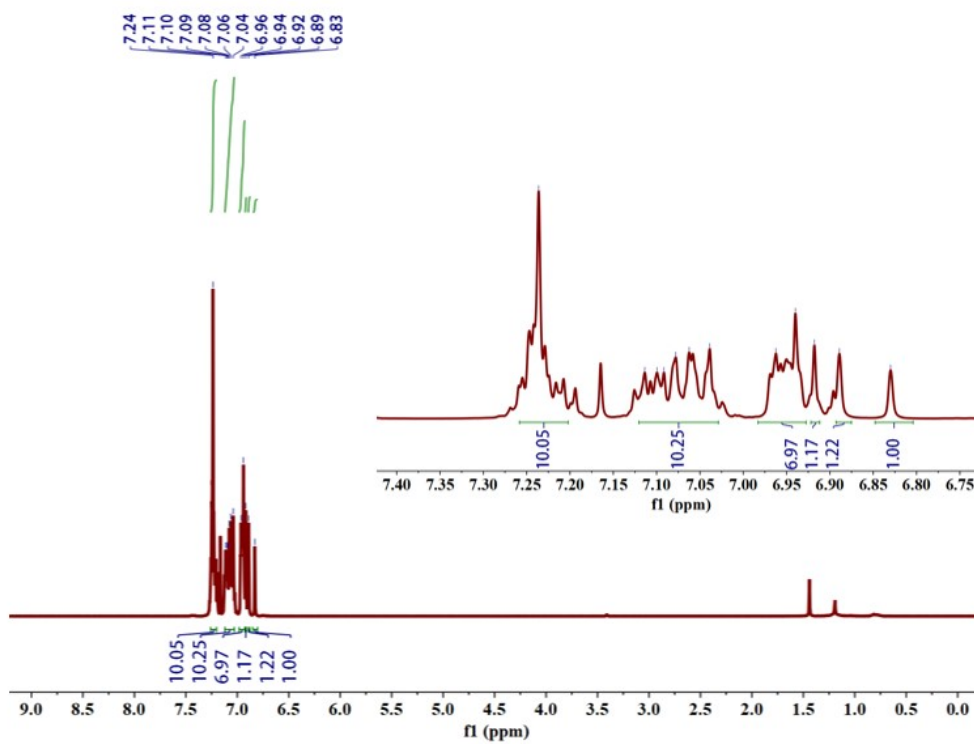


Fig. S4 ^1H NMR spectrum of TP-F.

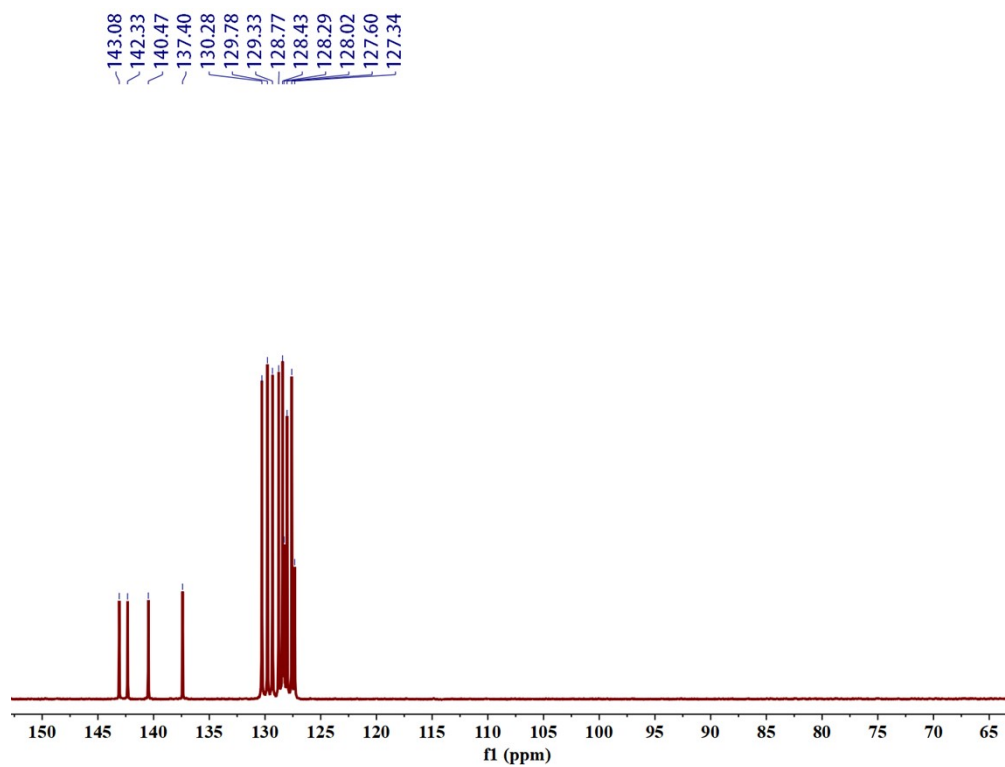


Fig. S5 ^{13}C NMR spectrum of TP-F.

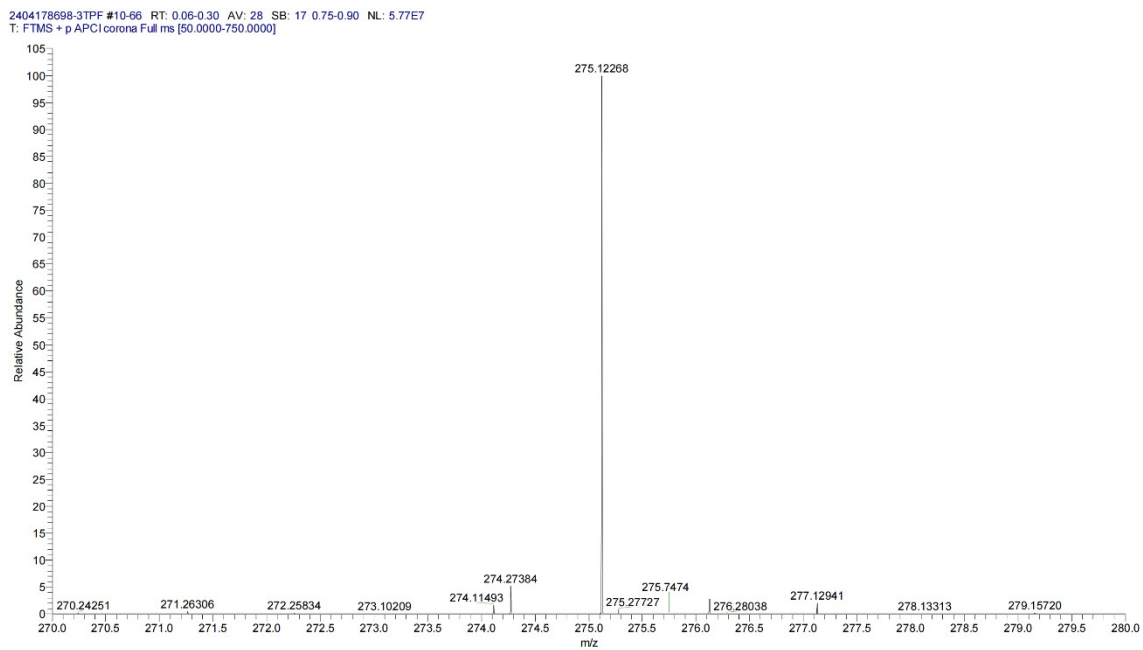


Fig. S6 Mass spectrum of TP-F.

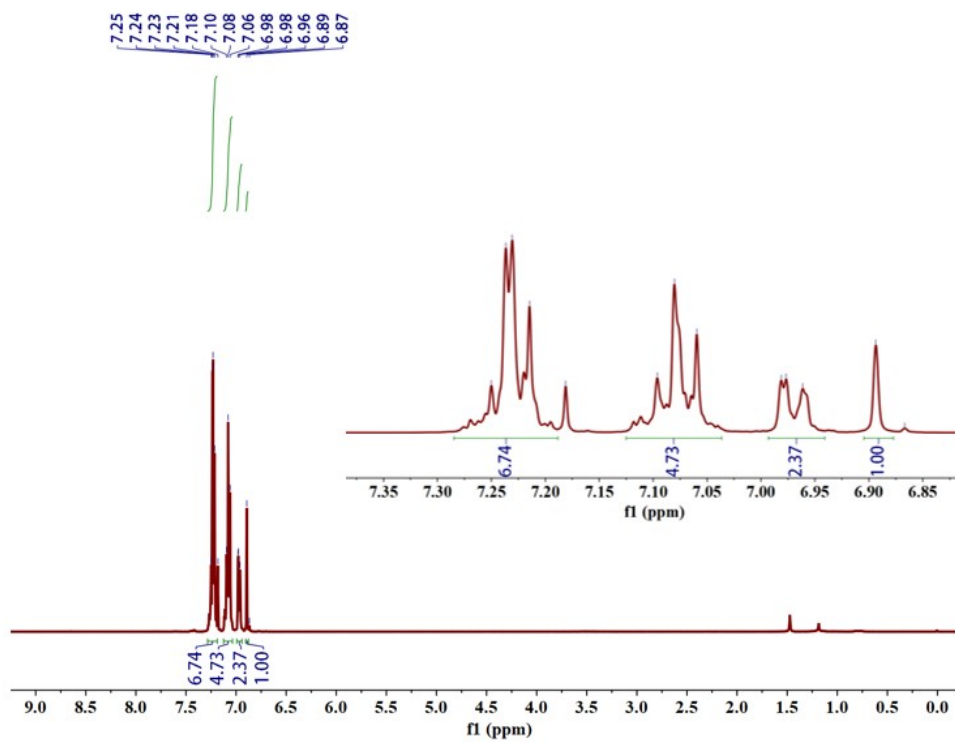


Fig. S7 ^1H NMR spectrum of TP-Cl.

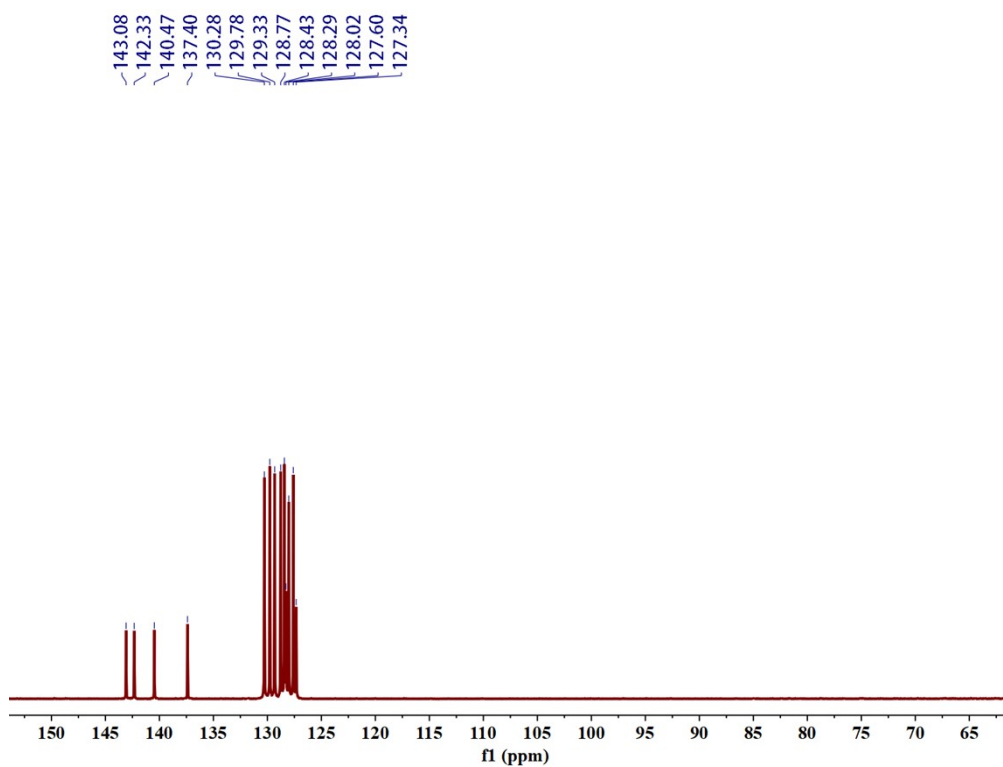


Fig. S8 ^{13}C NMR spectrum of TP-Cl.

2404178698-2TPCL #10-65 RT: 0.05-0.30 AV: 28 SB: 17 0.75-0.90 NL: 1.95E7
T: FTMS + p APCI corona Full ms [50.0000-750.0000]

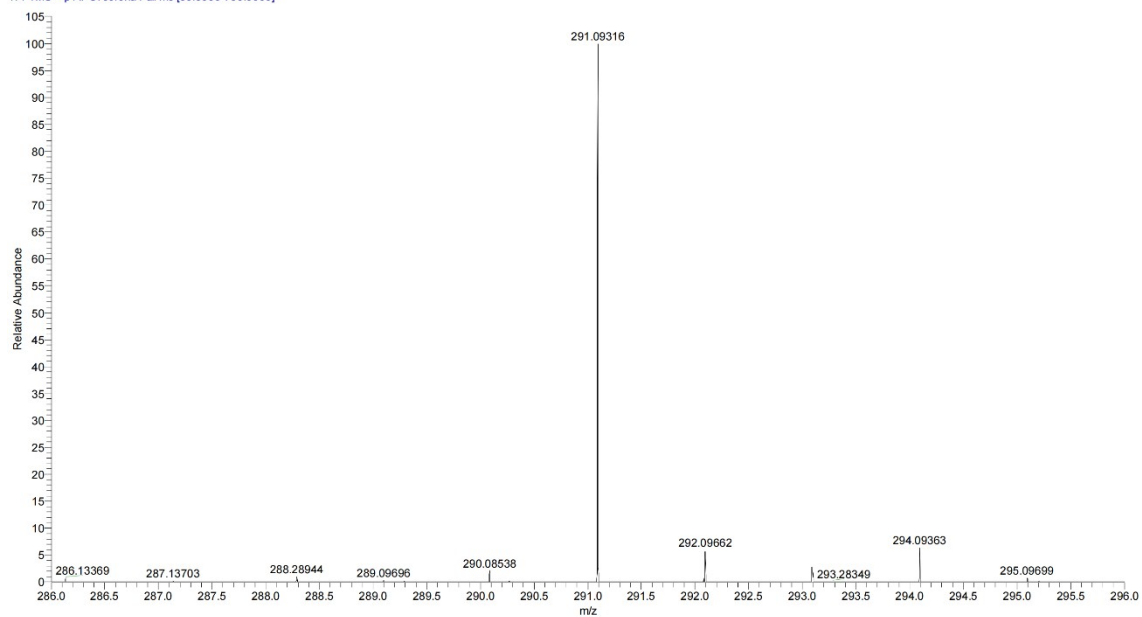


Fig. S9 Mass spectrum of TP-Cl.

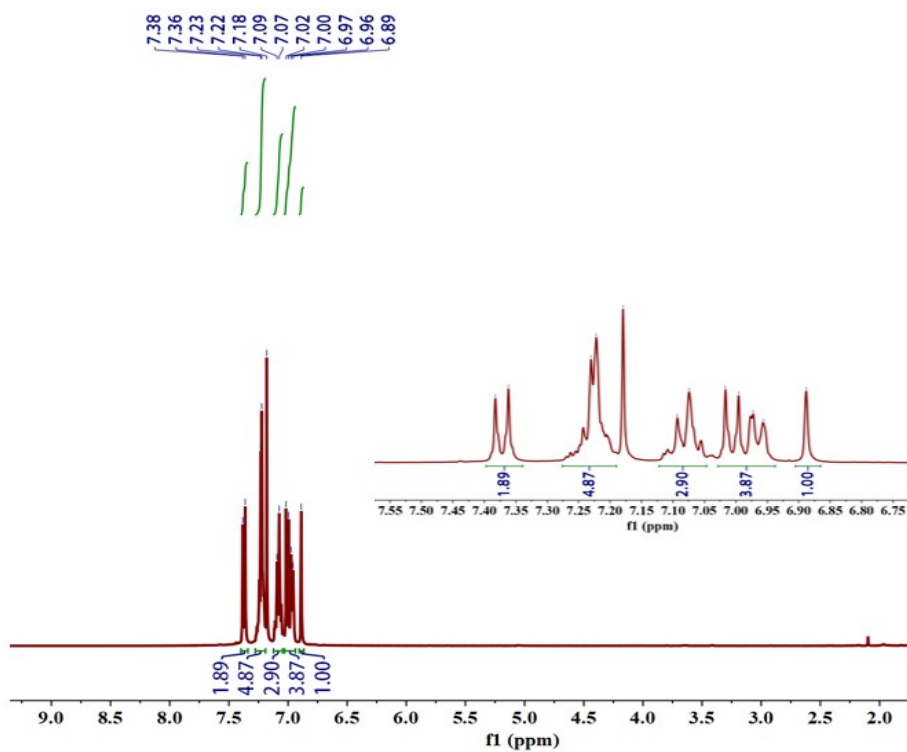


Fig. S10 ^1H NMR spectrum of TP-Br.

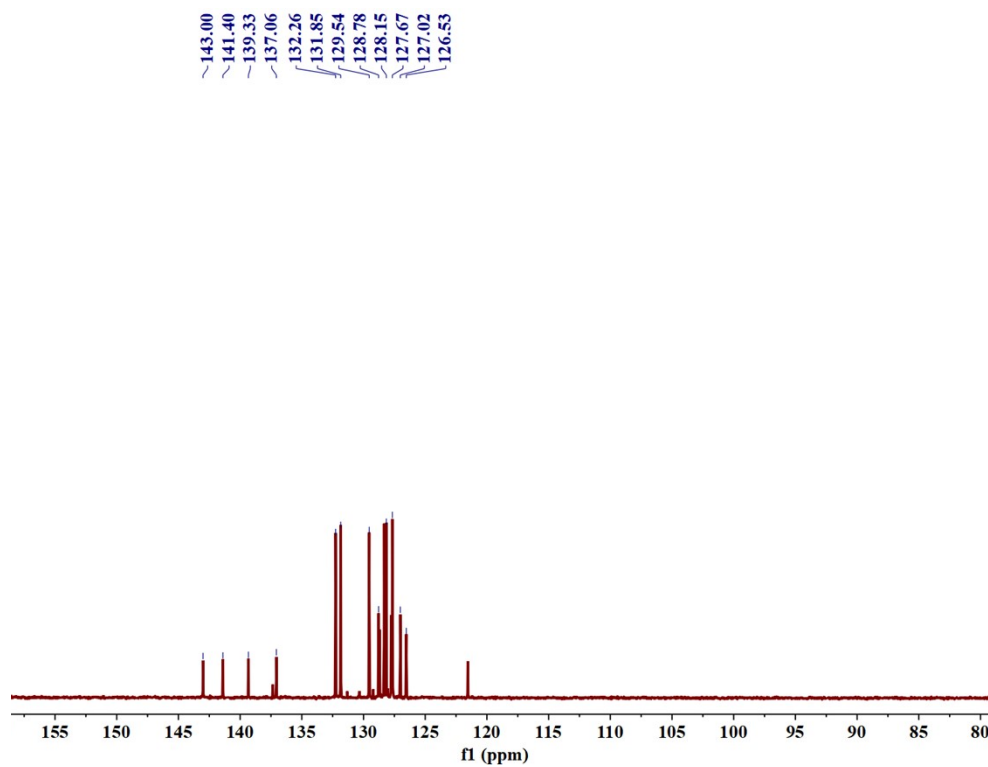


Fig. S11 ^{13}C NMR spectrum of TP-Br.

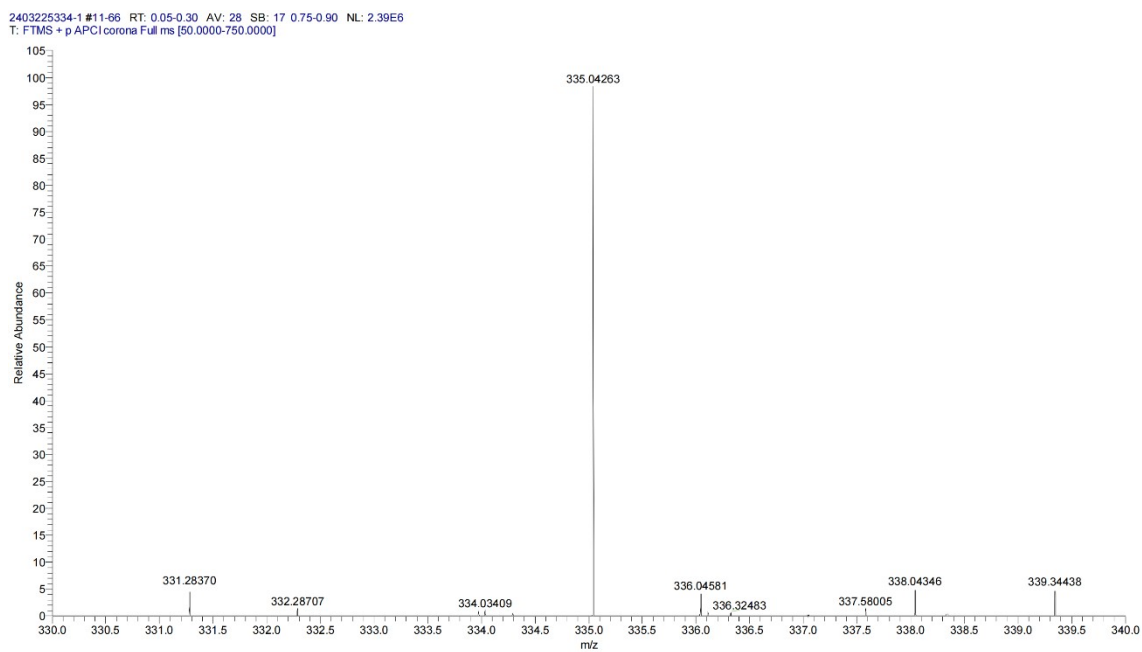


Fig. S12 Mass spectrum of TP-Br.

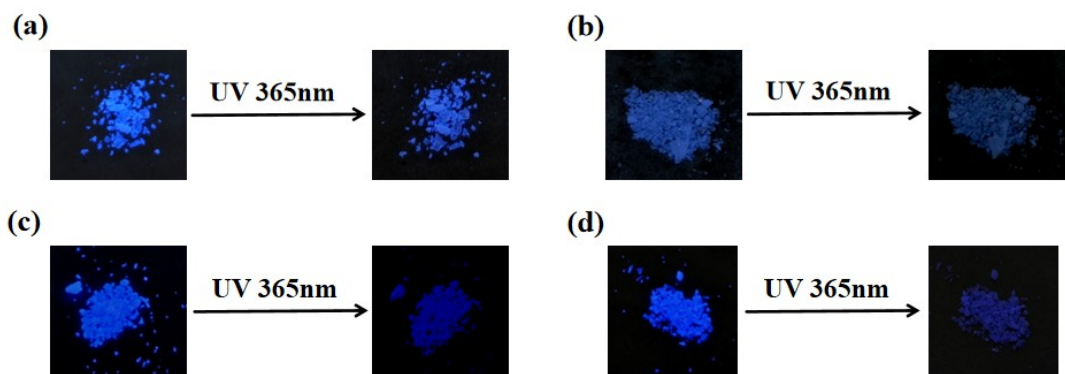


Fig. S13 Changes of PL image of TP (a), TP-F (b), TP-Cl (c) and TP-Br (d) before and after UV irradiation at 365 nm.

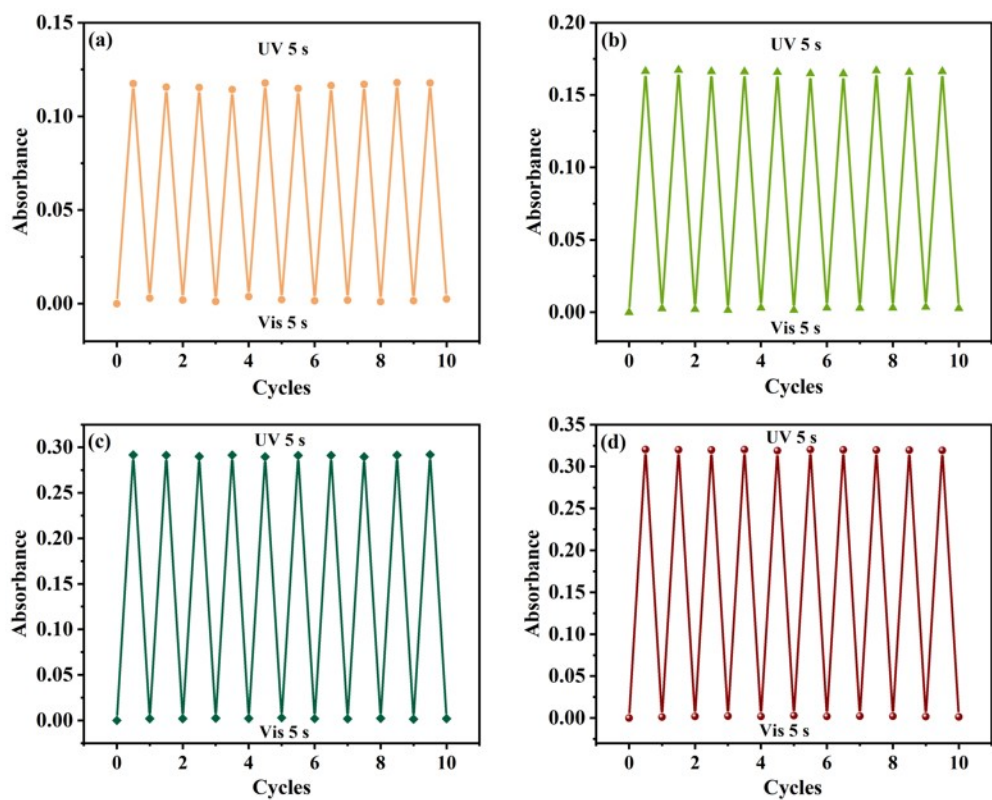
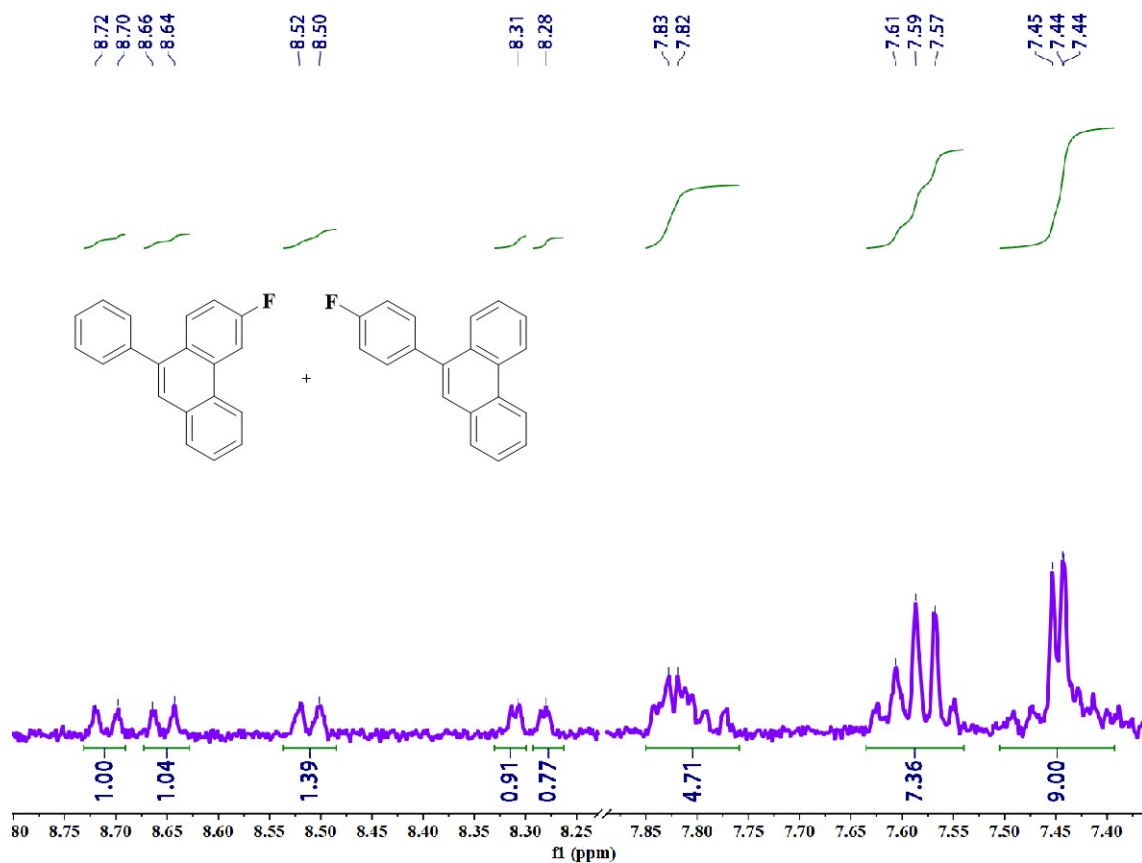


Fig. S14 Recycling of the photochromic processes of solid TP-F (a), TP-Cl (b) and TP-Br (c) as a function of exposure to UV-light and white-light in air, respectively.

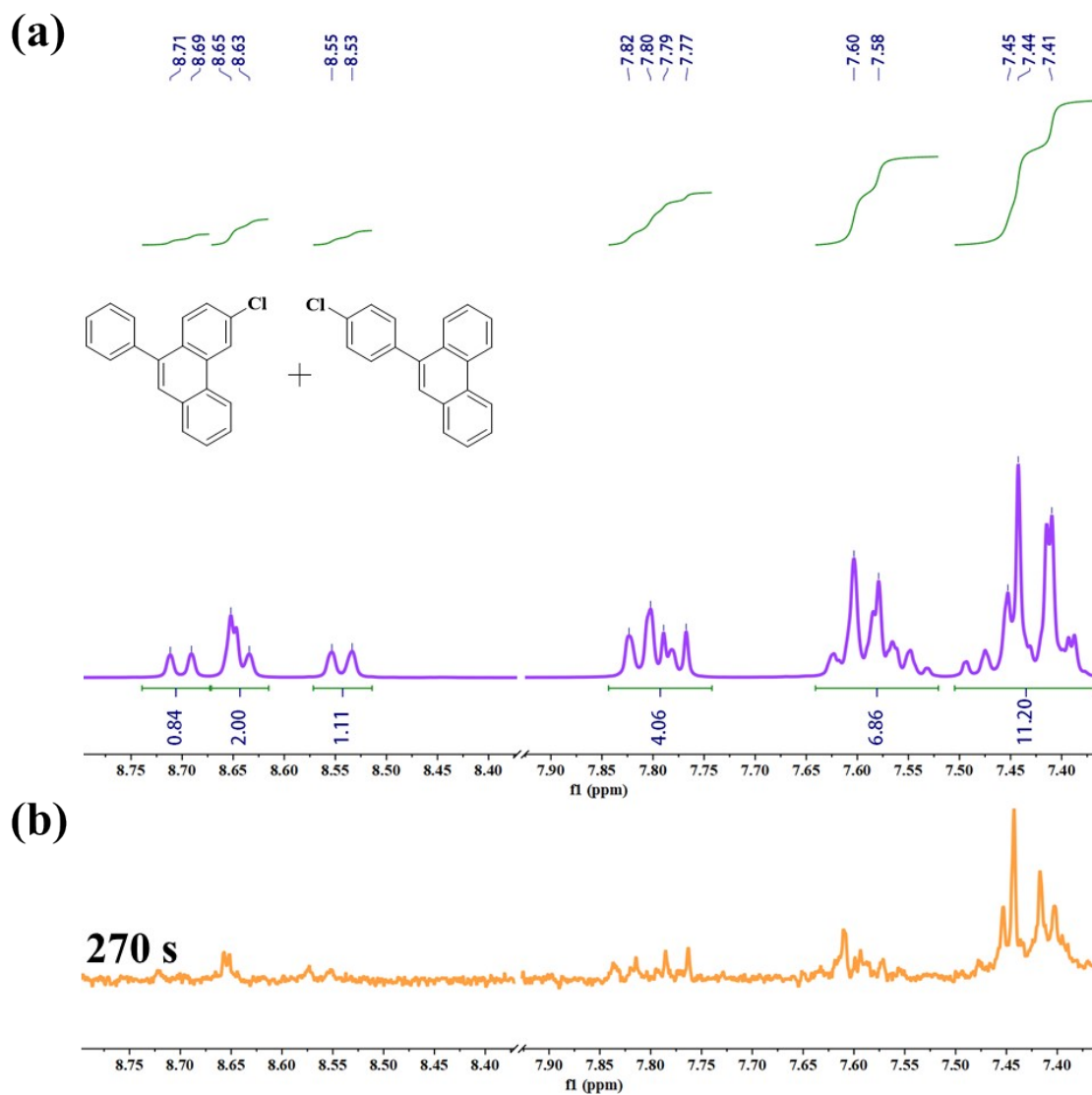
Table S1 Crystal data and structure refinement of TP, TP-F, TP-Cl and TP-Br.

| Compound | TP | TP-F | TP-Cl | TP-Br |
|--|---------------------------------|-----------------------------------|------------------------------------|------------------------------------|
| Formula | C ₂₀ H ₁₆ | C ₂₀ H ₁₅ F | C ₂₀ H ₁₅ Cl | C ₂₀ H ₁₅ Br |
| Formula weight | 256.13 | 274.12 | 290.09 | 334.04 |
| Temperature/K | 296 (2) | 296 (2) | 296 (2) | 296 (2) |
| Crystal system | monoclinic | orthorhombic | triclinic | triclinic |
| Space group | P21/c | Pbca | P-1 | P-1 |
| a/Å | 8.4084 (18) | 18.104 (9) | 9.406 (3) | 9.380 (2) |
| b/Å | 16.183 (3) | 8.521 (4) | 12.232 (3) | 12.428 (4) |
| c/Å | 10.936(2) | 19.345(9) | 15.420 (4) | 15.481 (4) |
| α /° | 90 | 90 | 72.748(4) | 72.298(5) |
| β /° | 92.264 (3) | 90 | 73.634 (4) | 72.889 (4) |
| γ /° | 90 | 90 | 69.980 (4) | 70.044 (3) |
| Volume/Å ³ | 1486.8 (5) | 2984 (2) | 1559.6 (7) | 1579.2 (8) |
| Z | 4 | 8 | 4 | 2 |
| Calculated density /Mg m ⁻³ | 1.145 | 1.217 | 1.238 | 1.410 |
| μ /mm ⁻¹ | 0.065 | 0.078 | 0.235 | 2.594 |
| F (000) | 544.0 | 1144.0 | 608.0 | 680.0 |
| CCDC reference number | 2080256 | 2087955 | 2080255 | 2285411 |



^1H NMR (400 MHz, CDCl_3) δ : 8.71 (d, $J = 8.0$ Hz, 1H), 8.65 (d, $J = 8.0$ Hz, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.31 (d, $J = 2.0$ Hz, 1H), 8.28 (d, $J = 2.0$ Hz, 1H), 7.85~7.76 (m, 5H), 7.64~7.54 (m, 7H), 7.50~7.39 (m, 9H).

Fig.S15 ^1H NMR spectra of the oxidation products of TP-F obtained by iodine dehydrogenation under UV irradiation.



^1H NMR spectra of the oxidation products of TP-Cl obtained by iodine dehydrogenation is shown in Fig.S14a. The analysis results are as follows:

^1H NMR (400 MHz, CDCl_3) δ : 8.70 (d, $J = 8.0$ Hz, 1H), 8.67~8.62 (m, 2H), 8.54 (d, $J = 4.0$ Hz, 1H), 7.84~7.74 (m, 4H), 7.72~7.64 (m, 7H), 7.50~7.36 (m, 11H).

Fig. S16 (a) ^1H NMR spectra of the oxidation products of TP-Cl obtained by iodine dehydrogenation under UV irradiation. (b) ^1H NMR spectra of the oxidation products of TP-Cl obtained by UV irradiation for 270 s in CDCl_3 .

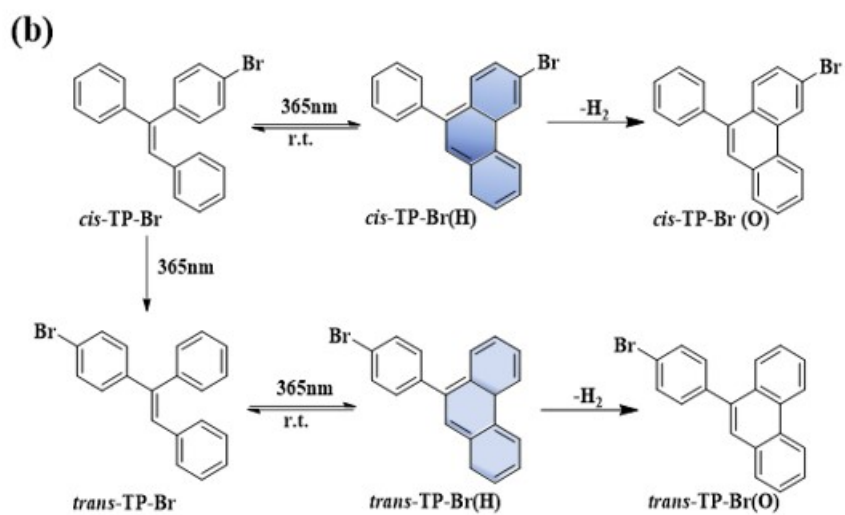
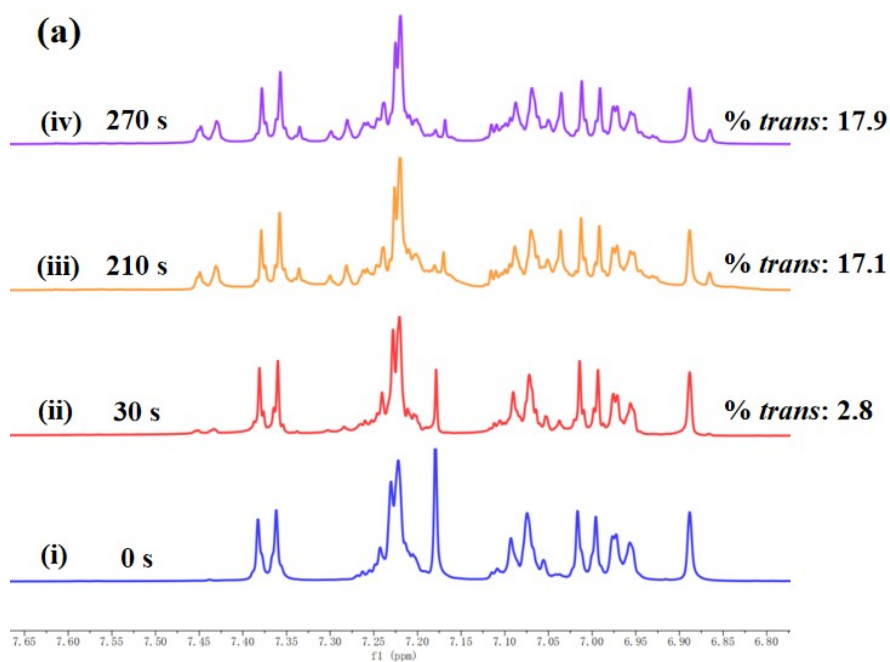


Fig. S17 (a) Changes of ^1H NMR spectra of TP-Br after UV irradiation at 365 nm for 0, 30, 210 and 270 s in CDCl_3 (1.0×10^{-2} M); (b) Proposed mechanism of the photochromism of TP-Br.