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Dual-stimuli response of spiropyran derivative modified by long-chain: high-contrast photochromism and mechanochromism

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Experiments

1. Materials and Measurements

All the solvents and reactants were brought from commercialized companies (J&K Chemicals and Aladdin. Analytical) and no further purified before use except for specifying otherwise. Analytical thin layer chromatography (TLC) was carried on silica gel plates produced by Yantai chemical industry and Column chromatography was using silica gel 60 in 200-300 mesh.

^{1}H NMR and ^{13}C NMR spectra were with a BRUKER AVANCE AV400MHz (^{1}H: 400 MHz; ^{13}C: 100MHz) spectrometer, using $CDCl_3$ as solvent at room temperature. Mass spectrometry (MS) was performed with a XEVO-G2STOF (ESI) (Waters, USA). The UV irradiation (365 nm) was offered by the Portable UV lamp (WFH-204B, Shanghai Chitang Industrial Co., Ltd, China). Fluorescence spectra were conducted by using a fluorescence spectrophotometer (solid: F-46001, HITACHI, Japan; liquid: FluoroMax-4, HORIBA Scientific, French). UV-vis spectra were measured on a spectrometer (solid: UH4150, HITACHI, Japan; liquid: UV1901PC, Aucy Instrument, China). Thermogravimetric analyzer (TGA) was performed with a PYRIS 1 and PYRIS Diamond (PerkinElmer, USA). The surface morphology was tested with a Carl Zeiss SMT Pte Ltd vltra55 (Germany) SEM at an accelerating voltage of 3 kV. The powder X-ray diffraction patterns (PXRD) were recorded by A8 Advance (Bruker AXS, Germany) with Cu Kα radiation at 25℃ (scan range: 5-80°, scan rate: 3°(2θ)/min). The differential scanning calorimetry (DSC) experiments were performed using a DSC Q2000 (TA Instruments, USA) with scan rates of 10°C/min. Fourier transform infrared (FT-IR) spectra were obtained on a Thermo Scientific Nicolet iS50 spectrometer in the range of 400 - 4000 cm^{-1}.

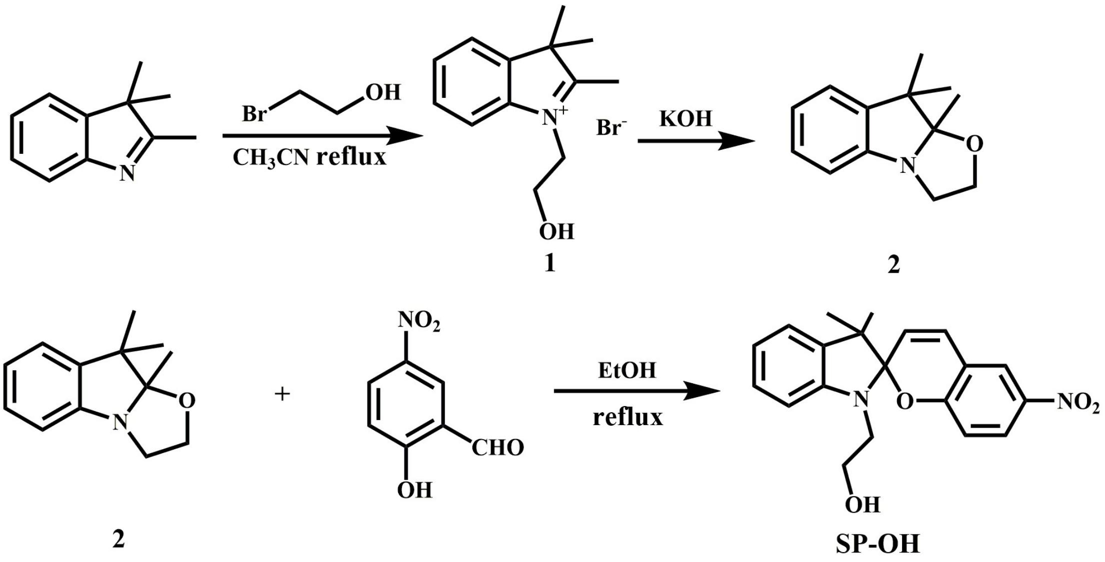
2. Synthesis

2.1 Synthesis of SP-OH

A mixture of 2,3,3-trimethyl-3H-indol (2.72 mL, 16 mmol) and 2-bromoethanol (1.48 mL, 20 mmol) in acetonitrile (20 mL) was reflux at 80 °C under nitrogen for 24 h. The solvent was removed and resuspended in 25 mL hexane. After filtering and drying, compound 1 was obtained.

Compound 1 was dissolved in aqueous solution mixed with KOH (0.66 g, 12 mmol). The mixture turned from pink to dark yellow within 10 min at room temperature. Then, the mixture was extracted with diethyl ether (3 × 20 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure, thus obtaining yellow oily compound 2.

Compound 2 (0.85 g, 4.2 mmol) and 2-hydroxy-5-nitrobenzaldehyde (1.05 g, 6.3 mmol) were mixed in 10 mL of ethanol and heated under reflux for 3 h. After cooling to room temperature, the remaining solution was filtered and washed with ethanol to get a purple solid SP-OH (0.63 g, 33%): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (dt, J = 8.1, 2.6 Hz, 2H), 7.19 (tt, J = 9.2, 4.6 Hz, 1H), 7.10 (dd, J = 7.2, 0.7 Hz, 1H), 6.90 (dd, J = 8.8, 6.3 Hz, 2H), 6.75 (t, J = 7.1 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 5.89 (d, J = 10.4 Hz, 1H), 3.87-3.68 (m,2H), 3.52-3.29 (m, 2H), 1.29 (s, 3H), 1.19 (s, 3H).

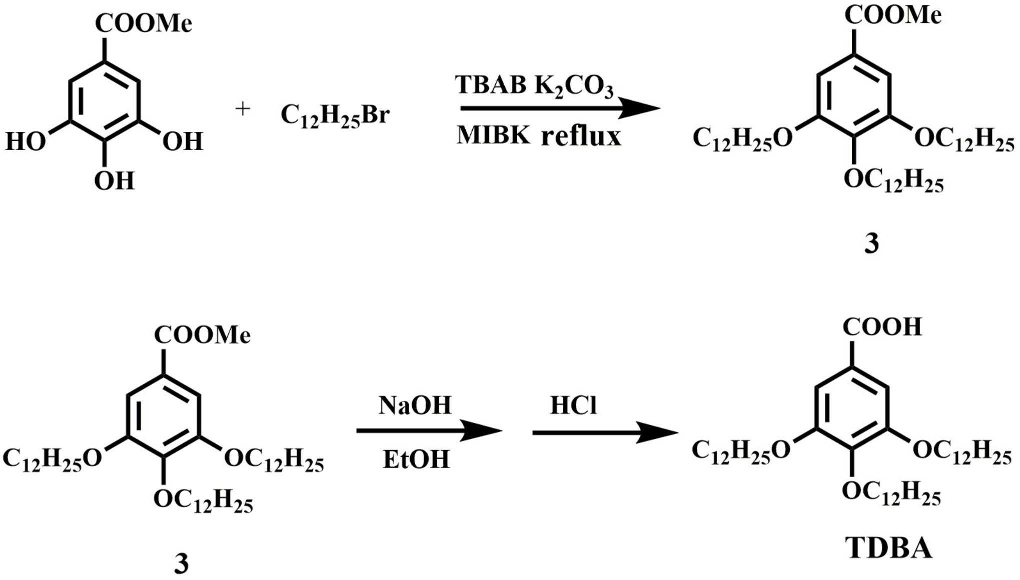


Scheme S1. Synthetic route for SP-OH.

2.2 Synthesis of TDBA

Methyl gallate (2.95 g, 16 mmol), K_2CO_3 (13.27 g, 96 mmol), tetrabutylammonium bromide (TBAB, 0.26 g, 0.8 mmol), methyl isobutyl ketone (MIBK, 40 mL), and 1-bromododecane (12.37 g, 50 mmol) were added to a 100 mL three-necked flask. Subsequently, the reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 12 h. Upon completion, the brown mixture was cooled to below 100 °C, and water (40 mL) was added. The aqueous layer was separated and the organic layer was washed with water (40 mL), diluted HCl solution (40 mL 1.0 M), and water (40 mL) again. Solvent evaporation from the resulting organic layer gave a yellow oil (11.7 g), which crystallized at approximately 40 °C to afford a light brown solid. Purification by column chromatography (hexane/ethyl acetate = 30/1, v/v) yielded white powder (compound 3, 10.2 g).

Compound 3 (5 g, 7mmol) was dissolved in ethanol (20 mL) at 45 °C. Sodium hydroxide pellets (0.39 g, 10 mmol) were added, and the mixture was heated to reflux. After 2 h of reflux, the reaction mixture was cooled and acidified with 12 M HCl solution (1.7 mL, 20.4 mmol). At 45°C, an off-white lump product precipitated out of the solution. The precipitate was filtered and washed twice with water (20 mL) to obtain a product (4.2 g). Crude product was absorbed into CH_2Cl_2, and the insoluble inorganic salts were removed by filtration. Evaporating the filtrate to obtain the pure white solid TDBA (4.05 g, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (s, 2H), 4.02 (m, 6H), 1.80 (m, 6H), 1.50 - 1.20 (m, 54H), 0.88 (t, J = 6.8 Hz, 9H).

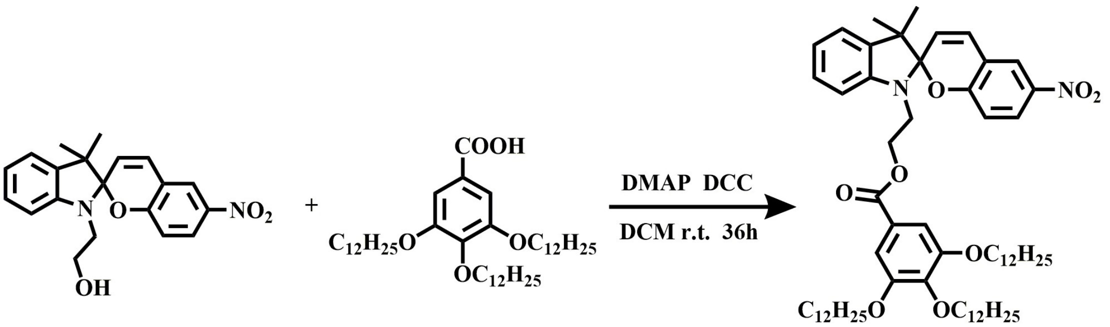


Scheme S2. Synthetic route for TDBA.

2.3 Synthesis of TDBA-SP

To a degassed mixture of SP-OH (0.86 g, 2.44 mmol), TDBA (2.0 g, 2.9 mmol) and a catalytic amount of DMAP (0.03 g ,0.24 mmol) in dry dichloromethane (100 mL) was added DCC (0.61 g ,2.96 mmol). The resulting solution was allowed to stir at room temperature for 36 h under nitrogen atmosphere. After filtering out the resulting 1,3-dicyclohexylurea (DCU), the solvent was removed under reduced pressure to obtain the residue, which was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (10/1, v/v) as the eluent. Then recrystallized from dichloromethane-methanol to obtain the pure product in solid form, which was light yellow solid TDBA-SP (1.25 g, 51

%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.96 (m, 2H), 7.23-7.16 (m, 3H), 7.09 (d, J = 7.2 Hz, 1H), 6.93-6.84 (m, 2H), 6.79-6.72 (m, 2H), 5.87 (d, J = 10.3 Hz, 1H), 4.43 (t, J = 6.1 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.98-3.90 (m, 4H), 3.67-3.45 (m, 2H), 1.83-1.69 (m, 6H), 1.52-1.40 (m, 6H), 1.40-1.22 (m, 51H), 1.16 (s, 3H), 0.88 (t, J = 6.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.28, 159.35, 152.83, 146.77, 142.51, 141.07, 135.70, 128.33, 127.88, 125.98, 124.30, 122.76, 121.83, 121.71, 119.91, 118.36, 115.56, 107.93, 106.73, 106.49, 73.51, 69.14, 62.94, 52.80, 42.50, 31.93, 30.34, 29.75, 29.71, 29.67, 29.65, 29.58, 29.41, 29.37, 29.30, 26.10, 26.06, 25.90, 22.70, 19.82, 14.13. ESI-TOF: m/z calcd for $C_{63}H_{96}N_2O_8$, 1008.7167; found, 1009.7242 [M+H$^+$].



SP-OH **TDBA** **TDBA-SP**

Scheme S3. Synthetic route for TDBA-SP.

3. Figures and Tables

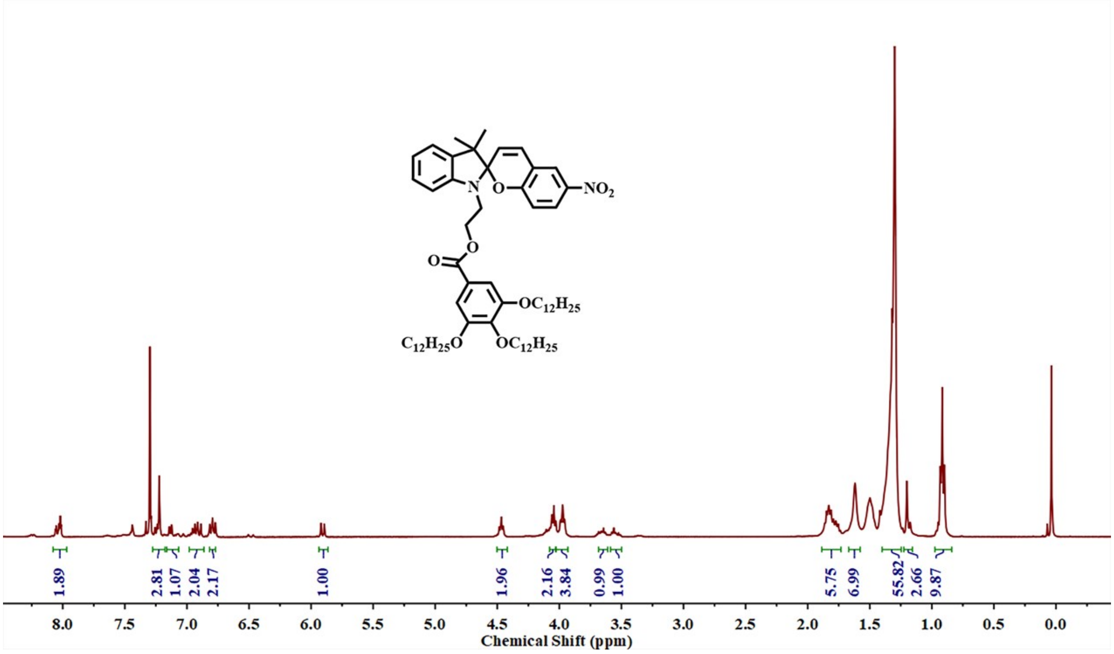


Fig. S1. ^{1}H NMR spectrum of TDBA-SP.

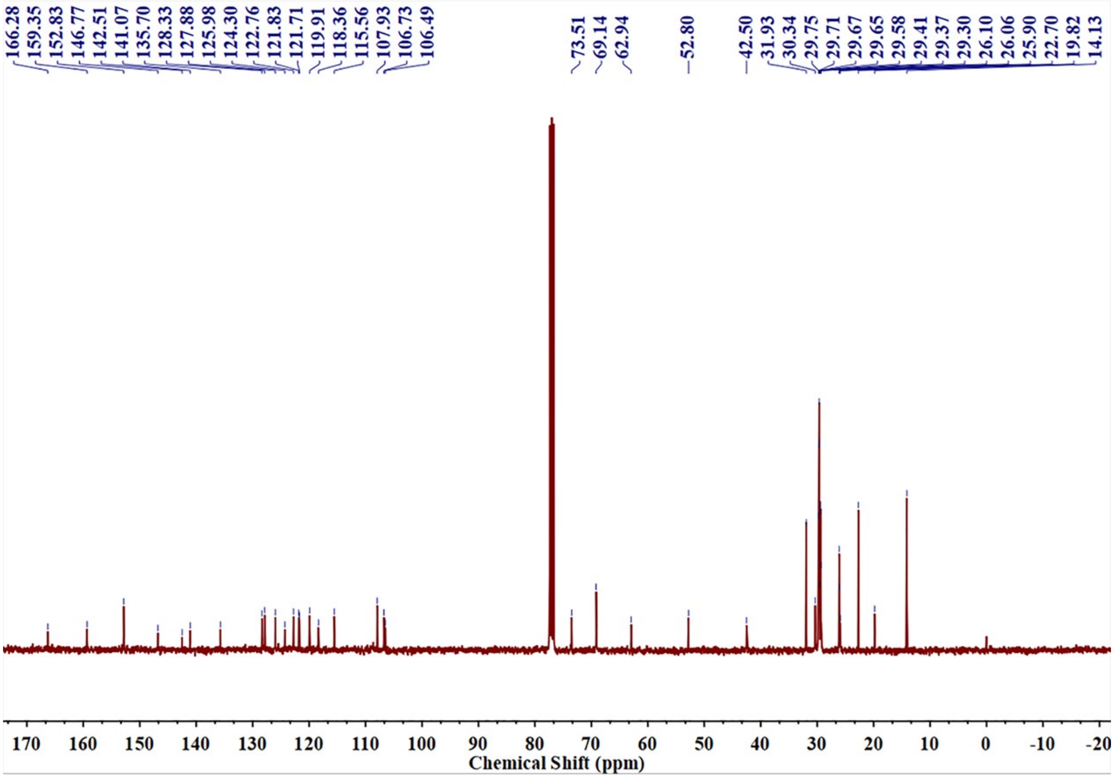


Fig. S2. ^{13}C NMR spectrum of TDBA-SP.

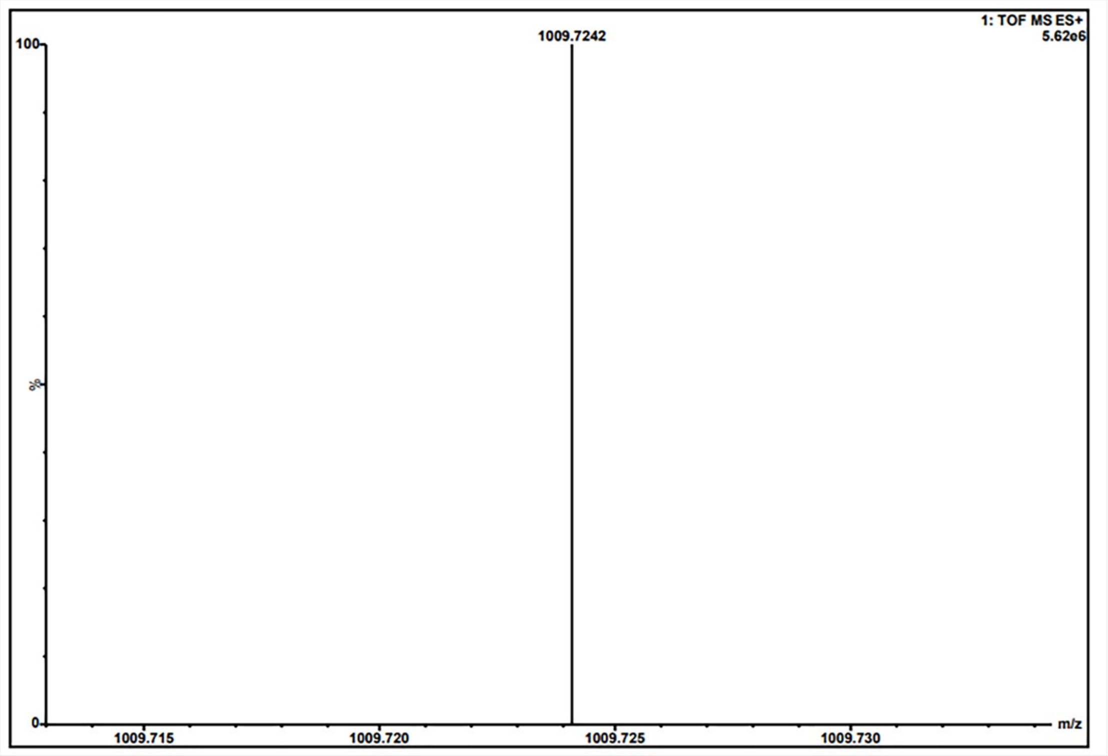


Fig. S3. HRMS (ESI) spectrum of TDBA-SP.

Table S1. The maximum absorption and emission wavelength TDBA-SP in the solid state before and after UV light irradiation.

irradiation time	0 s	10 s	30 s	1 min	3 min	5 min	10 min	15 min
λ_{abs} (nm)	568	590	588	586	582	578	574	572
λ_{em} (nm)	-	670	674	677	681	684	685	685

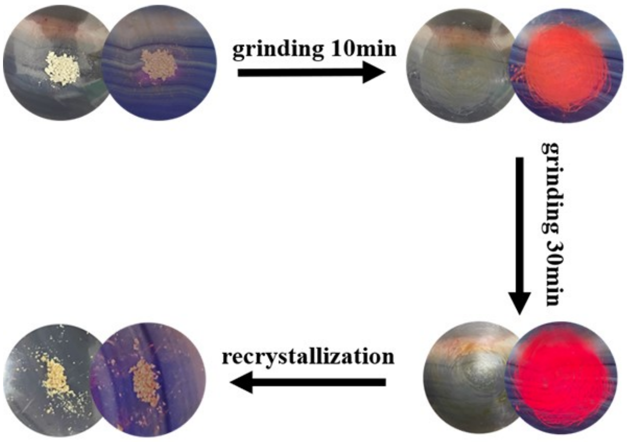


Fig. S4. Photographs of mechanochromism and recovery of TDBA-SP in solid state.

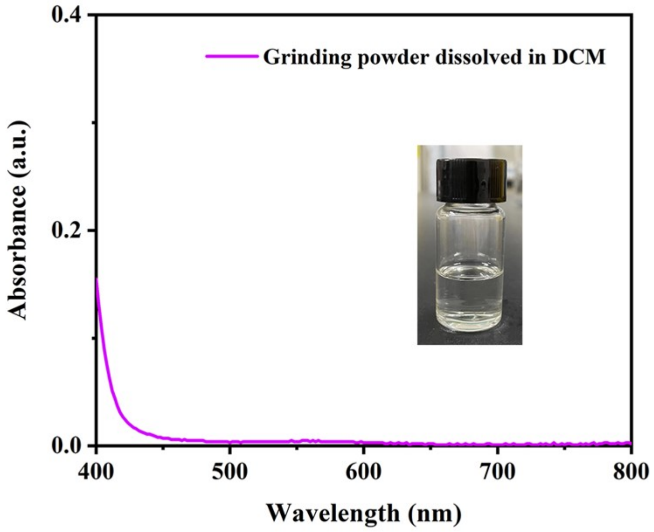


Fig. S5. UV-vis absorption spectra of grinding powder dissolved in DCM (1×10^{-4} M).

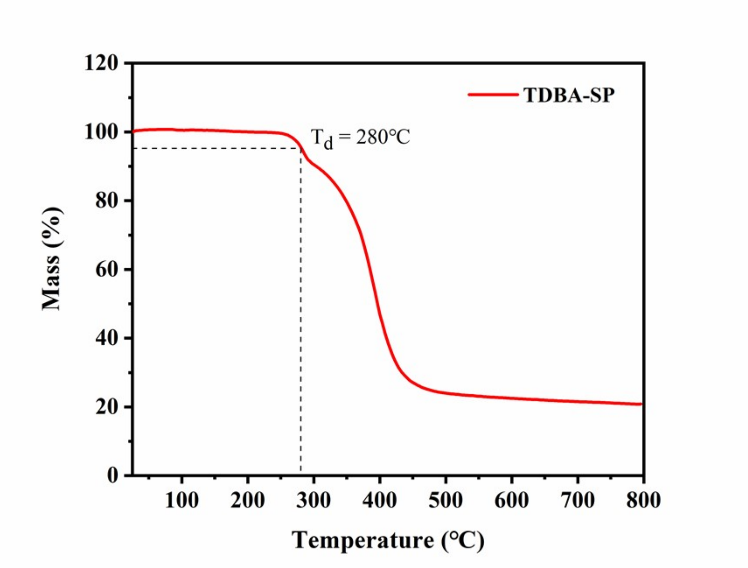


Fig. S6. TGA curves of TDBA-SP.

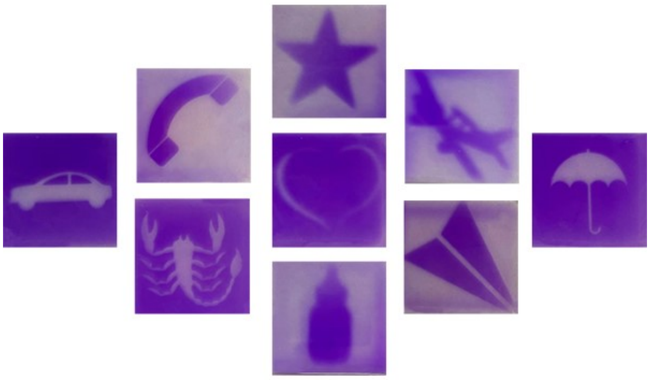


Fig. S7. Nine images continuously produced by the film under UV light irradiation (365 nm) with different masks.