

Supporting Information

Acid-, mechano- and photochromic molecular switches based on a spiropyran derivative for rewritable paper

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Materials

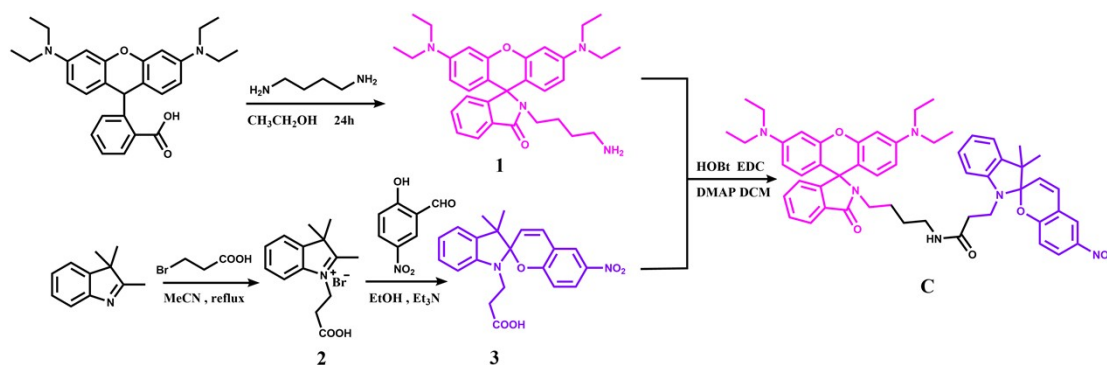
Rhodamine B (RhB), 1,4-butanediamine, 4-dimethylaminopyridine (DMAP), (1-ethyl-3(3-dimethylpropylamine) carbodiimide (EDCI) and 1-Hydroxybenzotriazole were purchased from Aladdin. 2,3,3-trimethyl-3H-indole, 3-iodopropanoic acid, ultra-dry dichloromethane and 2-hydroxy-5-nitrobenzaldehyde were purchased from J&K Scientific. Solvents were purchased from Hangzhougaojing Chemical Co., Ltd. All the chemicals were used as received without further purification.

Instruments and methods

¹H NMR were with a BRUKER AVANCE AV400MHz (¹H: 400 MHz) spectrometer at room temperature. UV-vis spectra were measured on a spectrometer (solid: UH4150, HITACHI, Japan; liquid: UV1901PC, Aucy Instrument, China). Fluorescence spectra were conducted by using a fluorescence spectrophotometer (solid: F-46001, HITACHI, Japan; liquid: FluoroMax-4, HORIBA Scientific, French) Thermogravimetric analyzer was performed with a PYRIS 1(PerkinElmer, USA). The surface morphology was

tested with a Carl Zeiss SMT Pte Ltd ultra55 (Germany) SEM at an accelerating voltage of 3 kV. Mass spectrometry (MS) was performed with a XEVO-G2STOF (ESI) (Waters, USA). Contact angles were measured on a contact angle measurement instrument (JCY, Shanghai FangRui Instrument Co., Ltd, China). The film was prepared by Spin Coater (KW-4B, Beijing Saidecase Electronics Co. Ltd, China). The UV irradiation (365 nm) was offered by the Portable UV lamp (WFH-204B, Shanghai Chitang Industrial Co., Ltd, China).

Synthesis



Scheme 1. Synthesis of compound C.

Synthesis of compound 1 (Rh-NH₂)

To a solution of rhodamine B (1700 mg, 3.13 mmol) in EtOH (30 mL) was added 1,4-Diaminobutane (3.135 mL, 31.3 mmol) over 10 min. The solution was refluxed for 18 h, cooled to room temperature, and the precipitates were filtered and washed with EtOH (3×10 mL). The product was dried in vacuo to give 1.27 g (74.7%).

¹H NMR (400 MHz, CDCl₃) δ 7.89 (dt, *J*=7.5, 3.3 Hz, 1H), 7.48–7.40 (m, 2H), 7.12–7.06 (m, 1H), 6.43 (d, *J*=8.8 Hz, 2H), 6.37 (d, *J*=2.5 Hz, 2H), 6.28 (d, *J*=2.6 Hz, 1H), 6.26 (d, *J*=2.6 Hz, 1H), 3.33 (q, *J*=7.1 Hz, 8H), 3.21 (t, *J*=6.2 Hz, 2H), 2.45 (t, *J*=6.2 Hz, 2H), 1.26–1.22 (m, 2H), 1.18 (s, 4H), 1.16 (t, *J*=7.0 Hz, 12H).

ESI-TOF: *m/z* calcd for C₃₂H₄₀N₄O₂, 513.3224 (M+H); found, 513.3226

Synthesis of compound 2 and 3

They are synthesised according to our previous work.

Synthesis of compound C

Compound **1** (373 mg, 0.479 mmol), **3** (211 mg, 0.479 mmol), DMAP (66.7 mg, 0.547mmol), EDC (275.47 mg, 1.437 mmol) and catalysts HOBt (32.36 mg, 0.24 mmol) were dissolved in CH₂Cl₂(30 mL). The solution was kept stirring for 48 h, and the solvent was evaporated under vacuum. The residue was concentrated and purified by column chromatography (CH₂Cl₂: ethyl acetate =1:4, v/v). The product was dried in vacuo to afford 478 mg of **C** (63.3% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.10 –7.78(m, 3H), 7.56 (s, 2H), 7.20 – 7.02 (m, 3H), 6.93 – 6.79 (m, 2H), 6.71 (m, 2H), 6.48 – 6.16 (m, 7H), 5.89 (d, *J* = 10.4 Hz, 1H), 3.75 – 3.58 (m, 2H), 3.33 (m, 8H), 3.15–3.08 (m,2H), 3.02– 2.86 (m, 2H), 2.45 (m, 2H), 1.66 (m, 4H), 1.25 (s, 6H), 1.11 (m, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 171.06, 168.48, 159.61, 153.33, 148.86, 146.61, 141.01, 135.96, 132.56, 131.16, 128.82, 128.27, 127.87, 125.85, 123.89, 122.78, 122.63, 122.21, 121.70, 119.61, 118.78, 115.53, 108.07, 107.04, 106.99, 105.52, 97.76, 60.45, 52.92, 44.42, 40.23, 39.20, 35.88, 29.75, 26.11, 25.84, 25.30, 22.71, 19.83, 14.25, 14.18, 12.62.

ESI-TOF: *m/z* calcd for C₅₃H₅₈N₆O₆, 875.4491(M+H); found, 875.4474

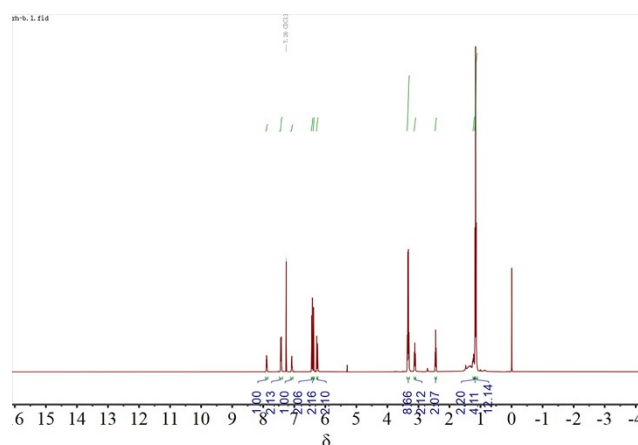


Figure S1 ¹H NMR spectrum of compound **1** in CDCl₃.

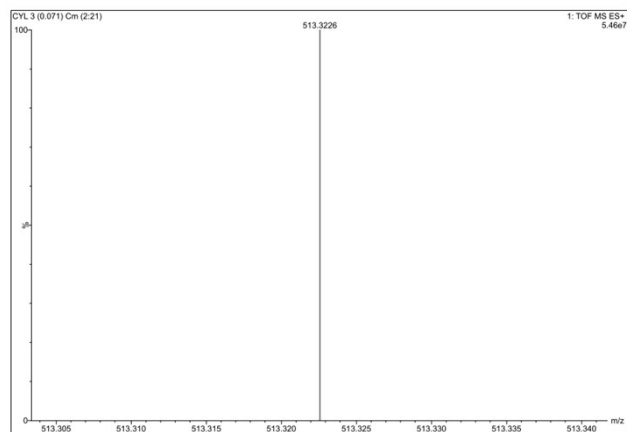


Figure S2 HRMS (ESI) of compound **1**.

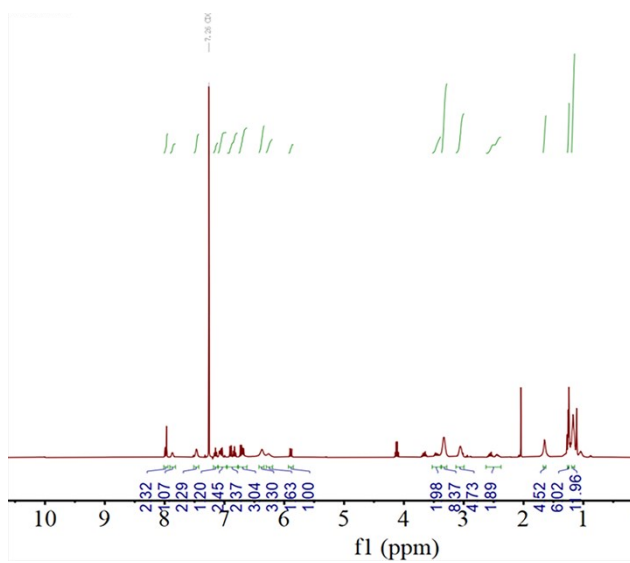


Figure S3 ¹H NMR spectrum of compound **C** in CDCl₃.

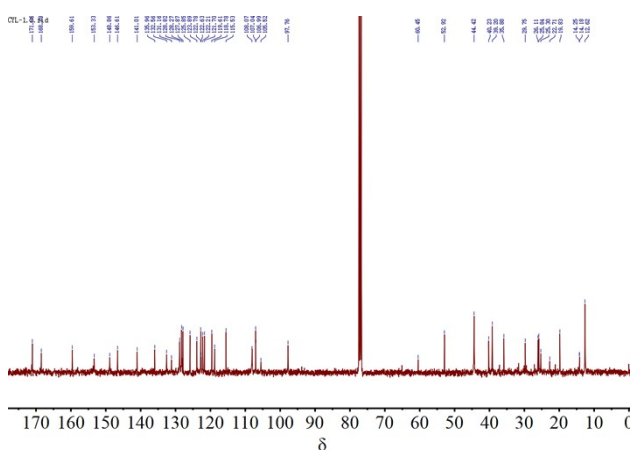


Figure S4 ¹³C NMR spectrum of compound **C** in CDCl₃.

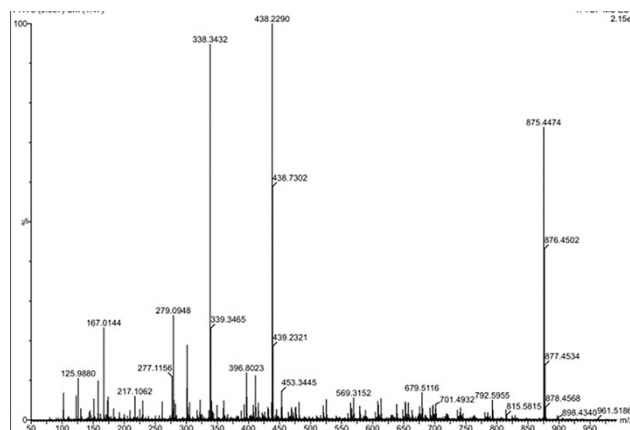


Figure S5 HRMS (ESI) of compound C.

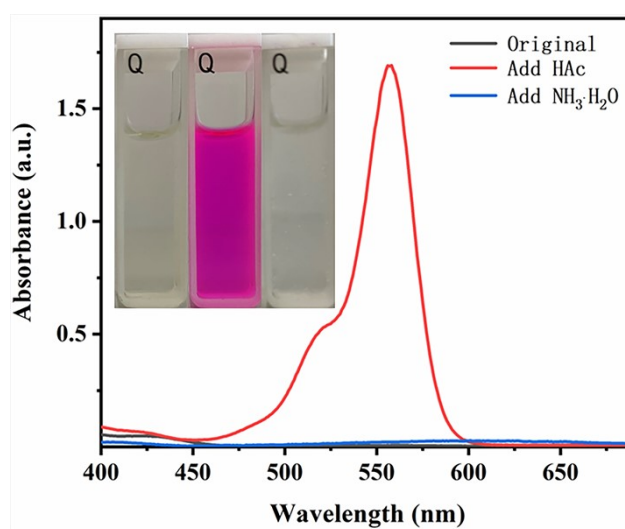


Figure S6 The acidochromism reversibility of compound C.

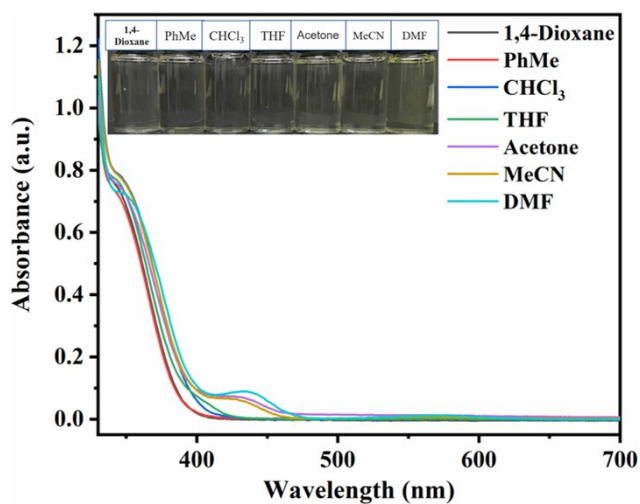


Figure S7 Influence of different polar solvents on compound C.

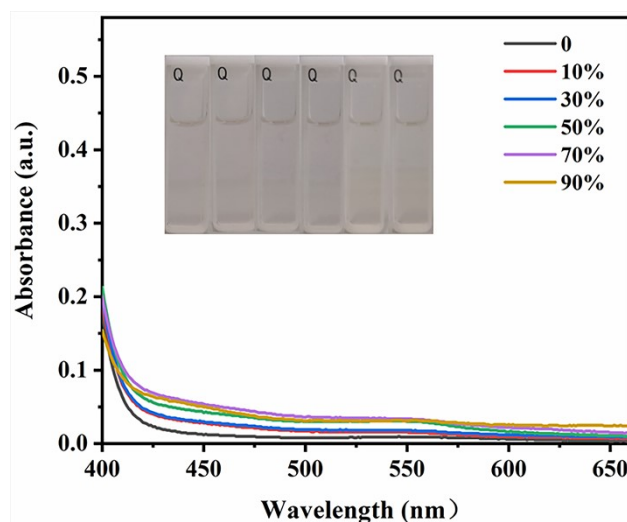


Figure S8 UV-vis absorption spectra of SP-COOH solution (1×10^{-4} M) with increasing HAc content (0 to 90%, by volume) (The illustrations are the colors under different volumes).

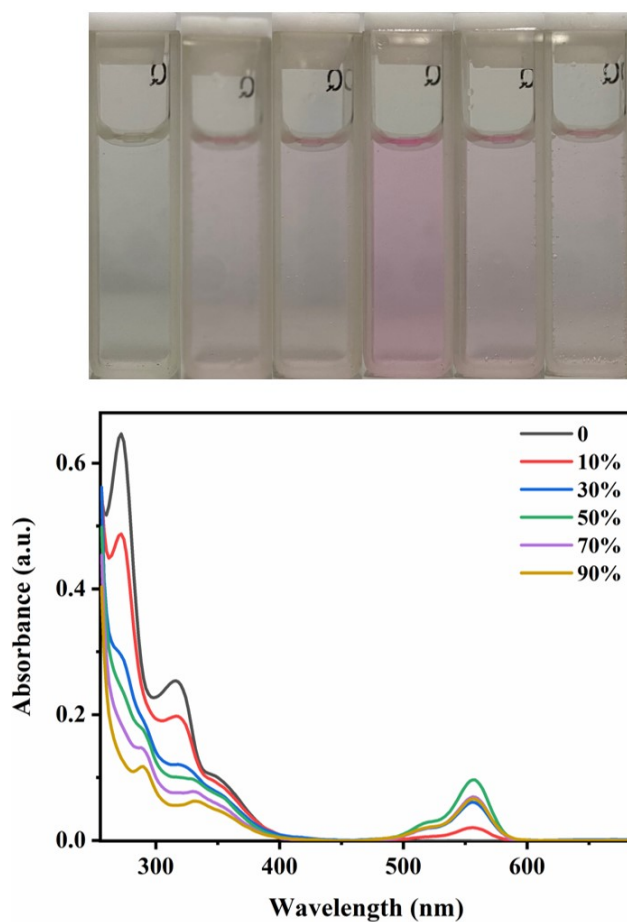


Figure S9 Colour and UV-vis absorption spectra of physical mixing of **1** and **3** (n: n=1:1) in MeCN solution (1×10^{-4} M) with increasing HAc content (0 to 90%, by

volume) at 3 min.

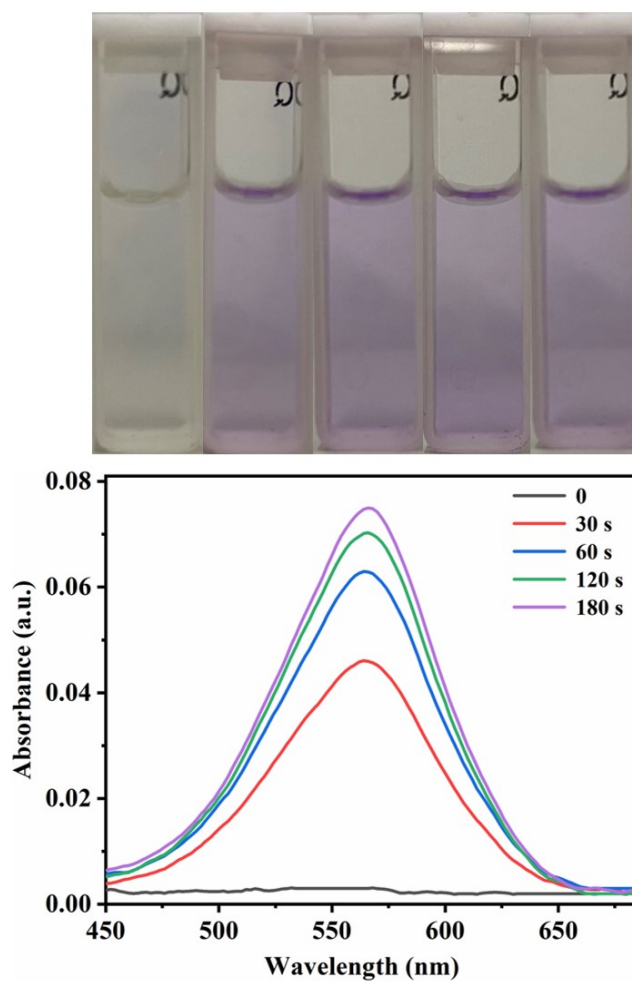


Figure S10 The colour of physical mixing of **1** and **3** ($n: n=1:1$) in MeCN solution (1×10^{-4} M) and corresponding UV-vis absorption spectra with different UV irradiation times (0-180s).

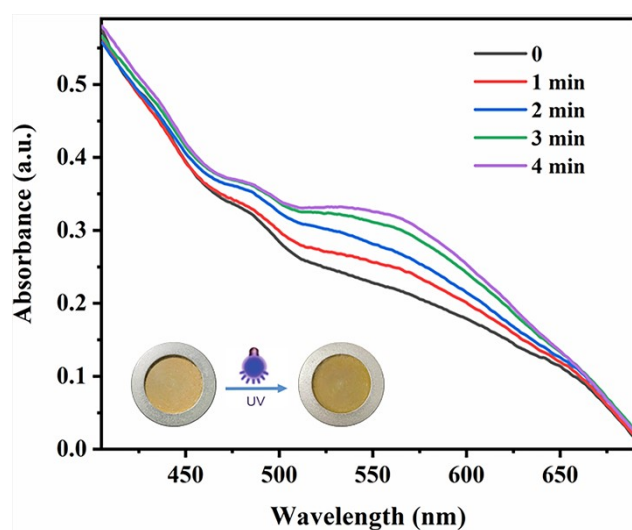


Figure S11 UV-vis absorption spectra of compound **1** and **3** physical blending in the solid state (before and after UV light irradiation).

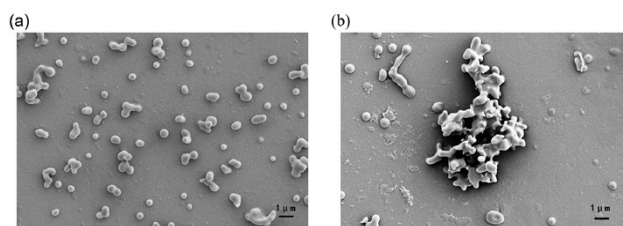


Figure S12 SEM images of the compound C: (a) Before grinding (b) After grinding.

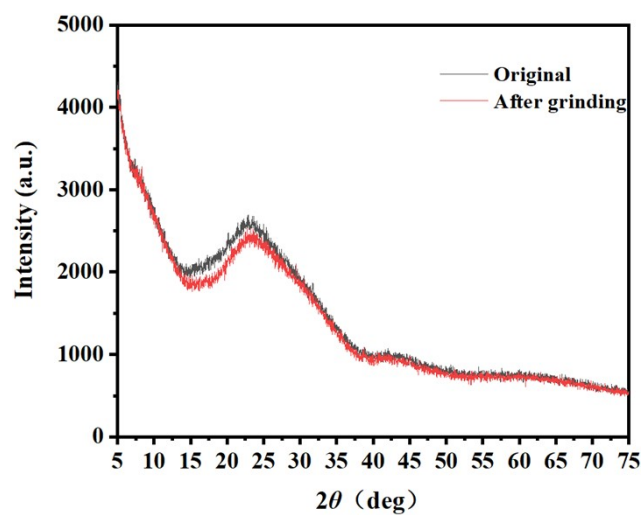


Figure S13 PXRD pattern of the compound C powder before and after grinding.

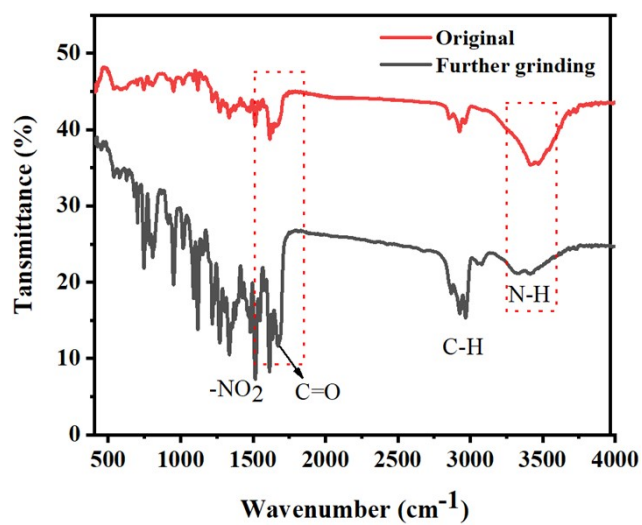


Figure S14 FTIR comparison of compound C (Before and After grinding).

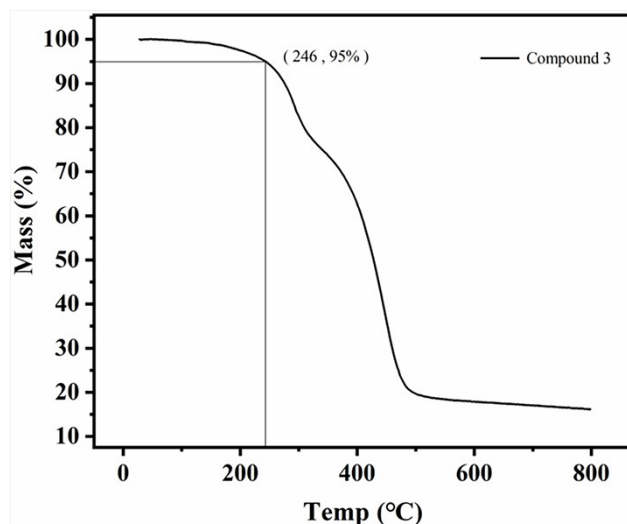


Figure S15 Thermogravimetric analysis of compound C.



Figure S16 Images obtained after UV light on PMMA film (f1, f2, f3).

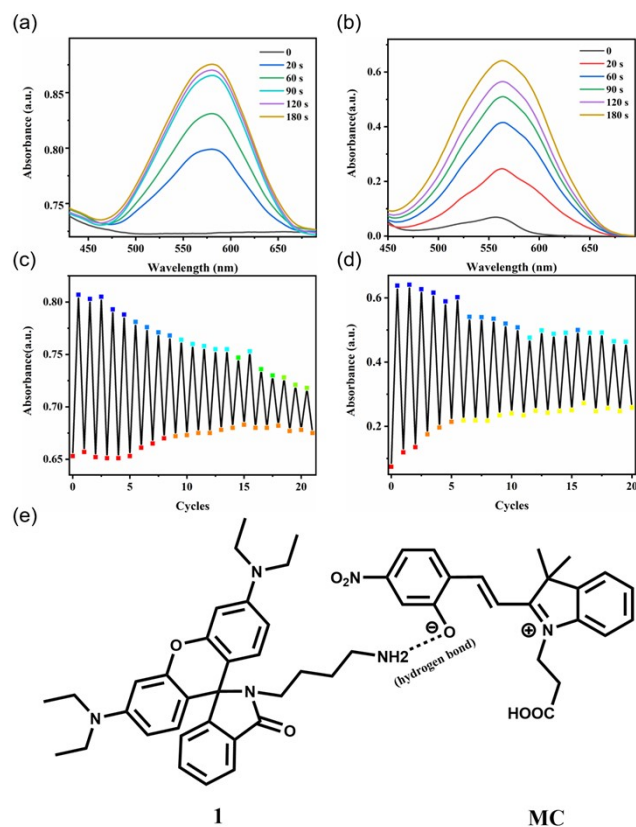


Figure S17 (a) UV-vis absorption results before and after UV light irradiation of f1 (0-

180 s) and (c) photo-fatigue-resistant properties of f1 upon UV irradiation 120s and heating for 5 min. (b) UV-vis absorption results before and after UV light irradiation of f2 (0-180s) and (d) photo-fatigue-resistant properties of f2 upon UV irradiation 120s and heating for 10 min. (e) Schematic diagram of hydrogen bonding between MC form (compound 3 after UV light) and -NH_2 in compound 1.

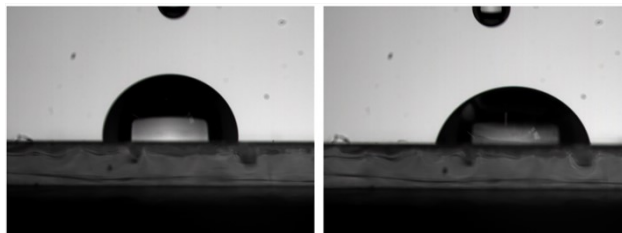


Figure S18 The Change of the contact angle of the film containing only compound C before and after UV light irradiation (decreased from 101.51° to 83.345°).