

Supporting Information

Preparation and properties of polyurethane film based on novel photochromic spirooxazine chain extension

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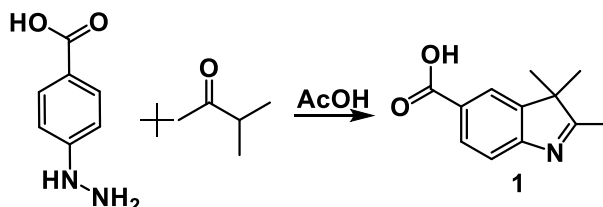
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Experimental Procedures

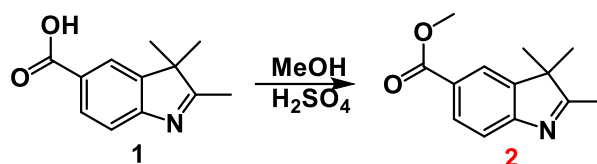
Methods and Materials

1. 5-Carboxy-2,3,3-trimethyl-3H-indole (compound 1) [30]



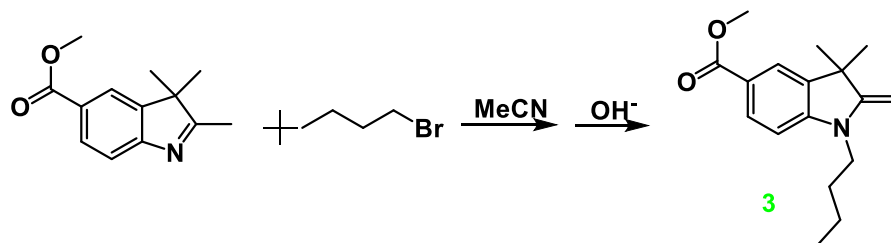
6.2 g (40 mmol) of 4-carboxyphenylhydrazine, 6.0 g (68 mmol) of 3-methyl-2-butanone mixed with 50 mL of glacial acetic acid were added into the flask (100 mL). The mixture was stirred under the nitrogen atmosphere, heated, and refluxed for 16 h. Then it should be distilled under reduced pressure to remove acetic acid. The remained part was adjusted pH to about 4 with saturated Na₂CO₃ solution, extracted with CH₂Cl₂, and dried for 24h with anhydrous MgSO₄. The filtrate was retained by filtration, and CH₂Cl₂ was distilled off under normal pressure to obtain 8.0 g (39 mmol) of a reddish-brown solid with a yield of 98.52%.

2. 5-Carboxymethyl-2,3,3- trimethyl-3H-indole (compound 2) [31]



2.1 g (10 mmol) of 5-carboxy-2,3,3-trimethyl-3H-indole, 1.2 mL 98% H₂SO₄ with 50 mL distilled water were added into the three-necked flask (250 mL). The mixture reacted under reflux at 65°C for 18h. Then it should be distilled under reduced pressure to remove methanol. The remained part was adjusted pH to about 7 with saturated Na₂CO₃ solution, extracted with ethyl acetate, and dried for 24 h with anhydrous MgSO₄. The filtrate was retained by filtration, and ethyl acetate was distilled off to obtain 2.0 g (9 mmol) of compound 2 with a yield of 91.74%.

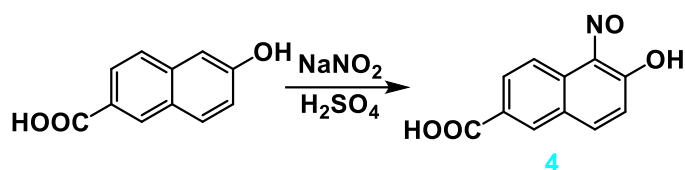
3. 1-N-butyl-3,3-dimethyl-5-carboxylate-2-methyleneindoline (compound 3) [32]



1.5g (10 mmol) compound 2, 1.8 g (13 mmol) CH₃CH₂CH₂CH₂Br mixed with 20 mL CH₃CN were added into the three-necked flask (100 mL). The mixture was stirred under the nitrogen atmosphere, heated, and refluxed for 48 h. CH₃CN was cooled and distilled under reduced pressure to obtain a purple-red viscous substance. Dissolved and washed in distilled water (50mL). The resulting aqueous phase was adjusted pH to 9-10 with NaOH solution, added 15 mL of n-hexane, and stirred at 25°C for 30 min. Then it should be extracted with n-hexane, collected the organic phase, dried with anhydrous MgSO₄, filtered, and concentrated filtrate to obtain 1.4 g (5 mmol) of yellow

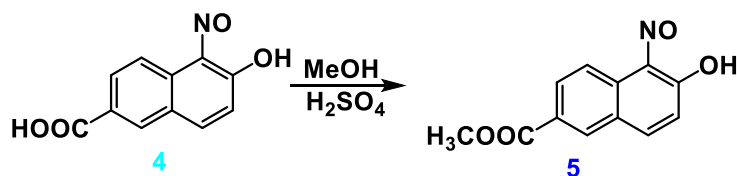
oil with a yield of 51.21%.

4. Methyl 6-hydroxy-2-naphthoate (compound 4)



10.0 g (53 mmol) 6-hydroxy-2-naphthoic acid was added to 40 mL methanol in a three-necked flask (250 mL). After the dissolution was complete, 4 mL concentrated sulfuric acid was added dropwise as a catalyst, and the reaction was stirred for 18 h under reflux conditions. The solid was gradually precipitated out. Then the product was transferred to a beaker with adding NaHCO_3 saturated solution dropwise until no bubbles were generated, filtered, and dried to obtain a white powder with a yield of 88.70%.

5. Methyl 6-carboxylate-1-nitroso-2-naphthol (compound 5) [33]



4.0 g (20 mmol) of methyl 6-hydroxy-2-naphthoate was added into a three-necked flask (250 mL) containing 0.8 g (20 mmol) of NaOH and 50 mL of hot water. 0 °C, an aqueous solution containing 1.6 g (20 mmol) of NaNO_2 was added dropwise. Under the nitrogen atmosphere, 2.2 g (22 mmol) of H_2SO_4 (V%=9%) solution was slowly added. During the dripping of sulfuric acid, yellow solid particles had gradually formed in the flask, and the system gradually became turbid yellow. Then the temperature was raised to room temperature and the reaction was continued for 2 h. A small amount of $(\text{NH}_4)_2\text{SO}_4$ saturated solution was added to remove the unreacted NaNO_2 . Finally, it was transferred to a beaker, neutralized with NaHCO_3 solution until no bubbles are formed, filtered with suction, and dried naturally to obtain 4.4 g (19 mmol) yellow solid,

the yield is 95.15%.

Structure and performance characterization of SO-OH

The photochromic compound SO-OH was characterized and tested by using $^1\text{H-NMR}$, MS, Fourier transform infrared spectroscopy and ultraviolet-visible spectrophotometer. The results are shown in Fig.1. The chemical shifts corresponding to the hydrogen atoms at different positions in the $^1\text{H-NMR}$ spectrum have been indicated in Fig.S1(a). Fig.S1(b) is the mass spectrum of SO-OH, and the related molecular ion peaks of SO-OH can be seen. The infrared spectrum (FTIR) of SO-OH is shown in Fig.S1(c). It can be observed that the absorption peak of 3364 cm^{-1} is attributed to the two reactive groups $-\text{OH}$ of spirooxazine. Two peaks at 2961 cm^{-1} and 2870 cm^{-1} are characteristic absorption peaks of C-H . 1613 cm^{-1} and 1494 cm^{-1} are the stretching vibration peak of the aromatic ring. The peak at 1187 cm^{-1} belongs to the C-O-C stretching vibration peak [35].

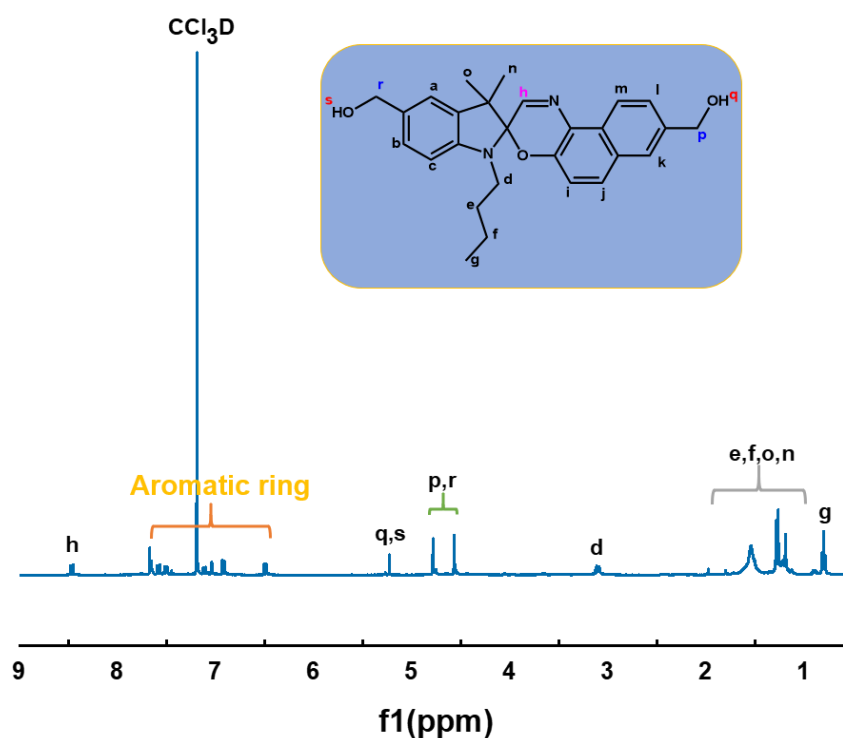


Fig.S1(a) $^1\text{H-NMR}$ spectra of the SO-OH

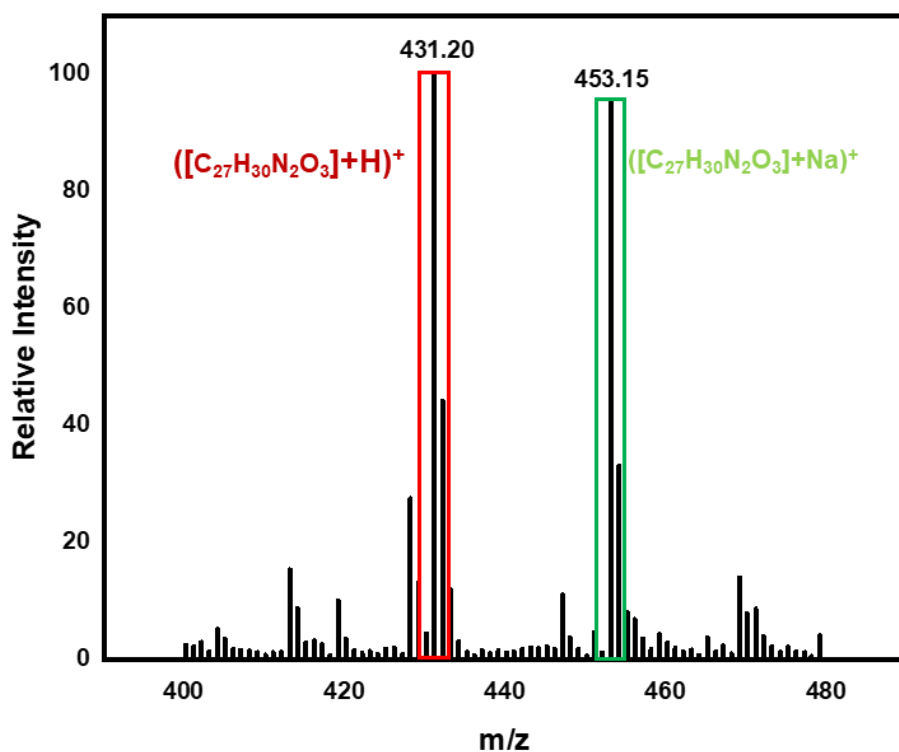


Fig.S1(b) MS spectra of the SO-OH

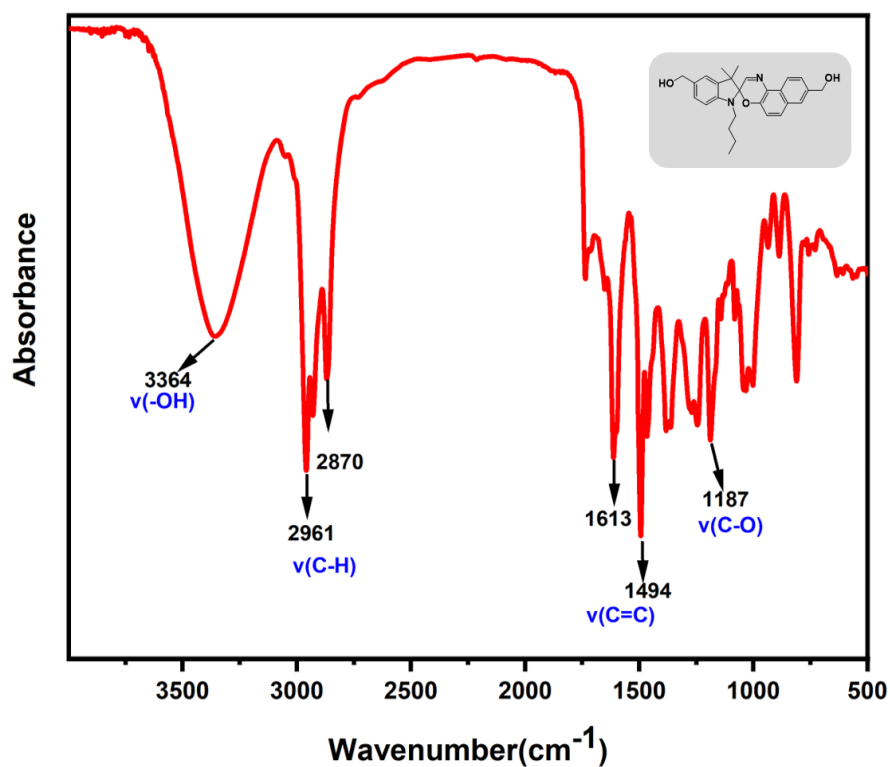


Fig.S1(c) FTIR spectrum of the target photochromic compound SO-OH

The ultraviolet-visible spectrum of the photochromic compound SO-OH is shown in Fig.S1(d). Before UV irradiation, the target compound has almost no absorption at

500 ~ 700 nm, and its color is almost colorless. After being irradiated with 365 nm light for 30 s, the color of the solution quickly changes from colorless to dark blue, and an absorption peak centered at 629 nm is formed at 500-700 nm of the absorption spectrum. Under ultraviolet light, the two ring structures in the system change from an orthogonal state to a large conjugated plane, which increases the conjugated surface of the system, and redshifts the ultraviolet absorption wavelength [29].

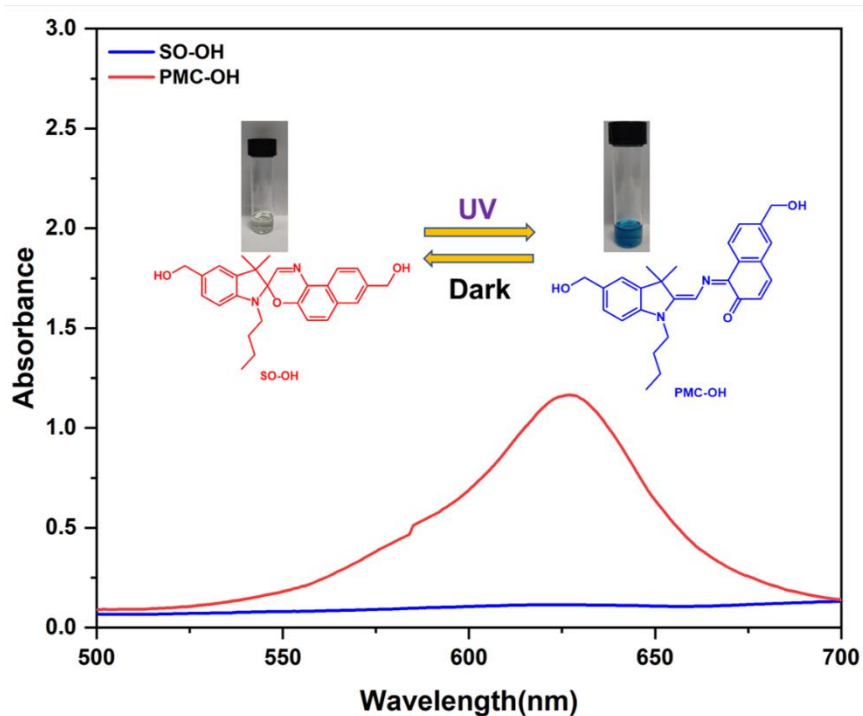


Fig.S1(d) UV-Vis spectra of SO-OH in ethanol (5×10^{-4} M)

Characterization data

1. $^1\text{H-NMR}$ of compound 7



Fig.S2. $^1\text{H-NMR}$ of compound 7.

2. MS of compound 7

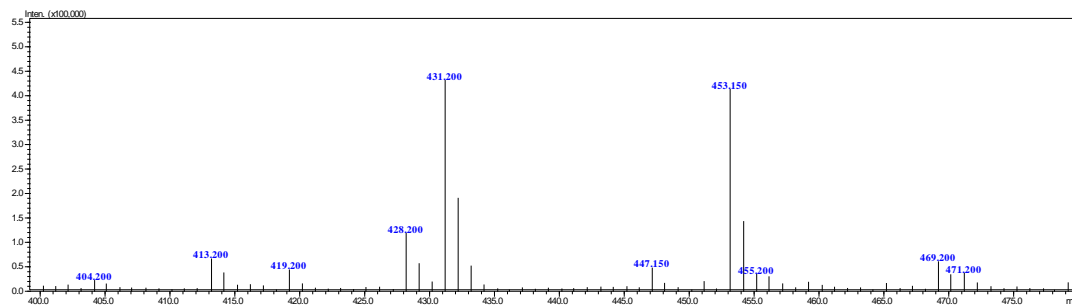


Fig.S3. MS of compound 7.

3. IR of compound 7

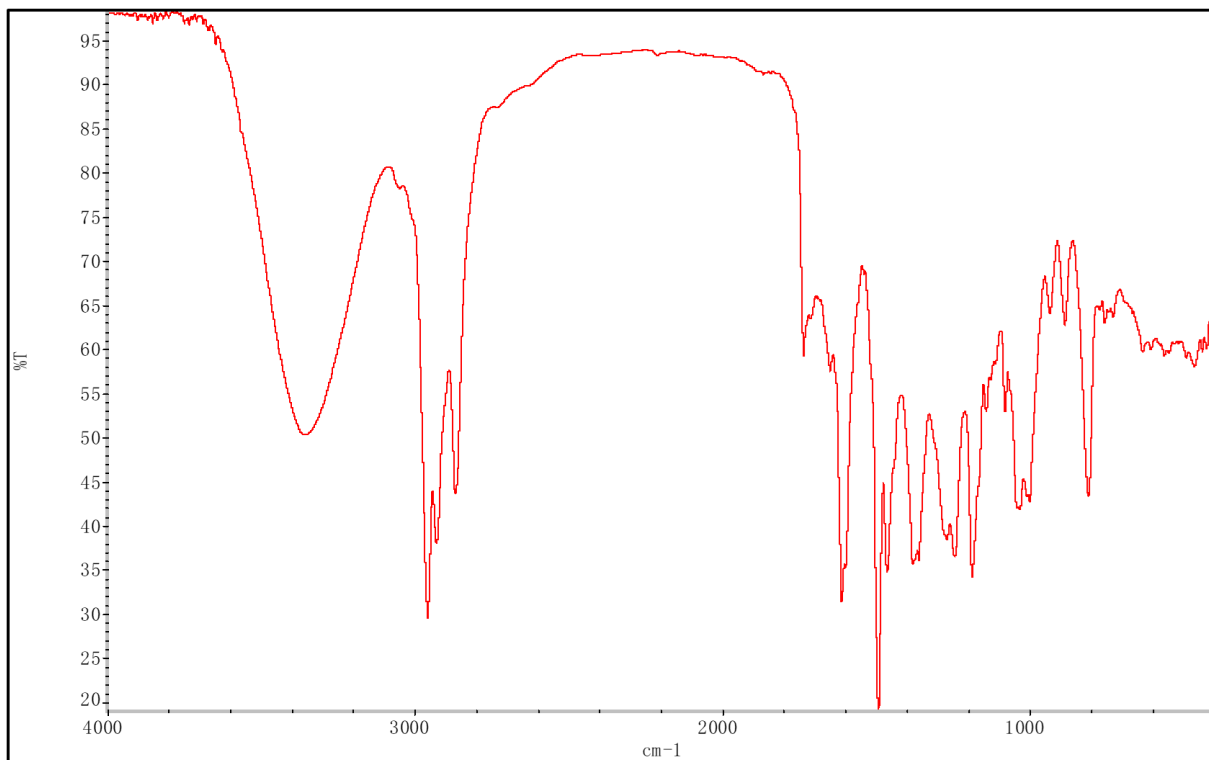


Fig.S4. IR of compound 7.