

Supporting Information

Light-responsive spiropyran derivative with tunable assembly morphology and solid-state photochromism for rewritable optical printing and multi-level anti-counterfeiting

Zhen Wu, Leping Xiao, Kaifeng Liao, Jiani Liu, Qiming Zou, Wenzhao Wang, Min Gong* and Guojie Wang*

Z. Wu, L. Xiao, K. Liao, J. Liu, Q. Zou, W. Wang, G. Wang

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

E-mail: guojie.wang@mater.ustb.edu.cn

M. Gong

School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China

E-mail: gongmin@ustb.edu.cn

Materials. 2,3,3-trimethyl-3H-indole (98%), 2-bromoethan-1-ol (97%), potassium hydroxide (98%), 2-hydroxy-5-nitrobenzaldehyde (98%) were purchased from HEOWNS. 4-(1,2,2-triphenylvinyl)benzoic acid (97%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC, 97%), 4-dimethylaminopyridine (DMAP, 98%) were purchased from Alfa Aesar and used without further purification. Analytical thin layer chromatography was performed on Yantai chemical industry silica gel plates. Column chromatography was performed using silica gel 60 (200-300 mesh).

Methods. ^1H NMR and ^{13}C NMR spectra were performed using a Bruker 400 (USA) (^1H : 400 MHz; ^{13}C : 100 MHz) spectrometer at room temperature. Mass spectrometry (MS) was performed using a XEVO-G2QTOF (ESI) instrument (Waters, USA). The surface morphology

was performed with a SU8010 (Hitachi, Japan) scanning electron microscopy (SEM) at an accelerating voltage of 10 kV. UV-vis spectra were measured on a spectrometer (Shimadzu 2550, Japan). Fluorescence emission spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. Powder X-ray diffraction (PXRD) patterns were produced by a D/max2500 VB2+/PC X-ray diffractometer (Rigaku) using Cu K α radiation in the 2 θ range 5-90°.

Preparation of SEM samples. SPD was dissolved in MeOH to a concentration of 1×10^{-4} M. Then, a syringe was used to pipet the solution onto the surface of silicon wafer at 25 °C, followed by UV irradiation until MeOH was completely evaporated.

Fabrication of the photochromic filter paper. 10 mg SPD was dissolved in 10 mL dichloromethane (DCM) at room temperature. The filter paper was immersed in the solution for 2 min and the solvent was subsequently evaporated to give the photochromic filter paper.

Fabrication of the dynamic anti-counterfeiting materials. The number pattern “886” was drawn on the filter paper by a combination of 9,10-dianthracene derivative (DSA), SPD/DSA (mass ratio 12.5/1), and SPD solutions, respectively. The concentration of the DSA and SPD solution was 0.08 mg/mL and 1mg/mL, respectively. The mixture of SPD/DSA solutions was obtained by adding 5 mL of DSA (0.08 mg/mL) and 5 mL of SPD (1mg/mL).

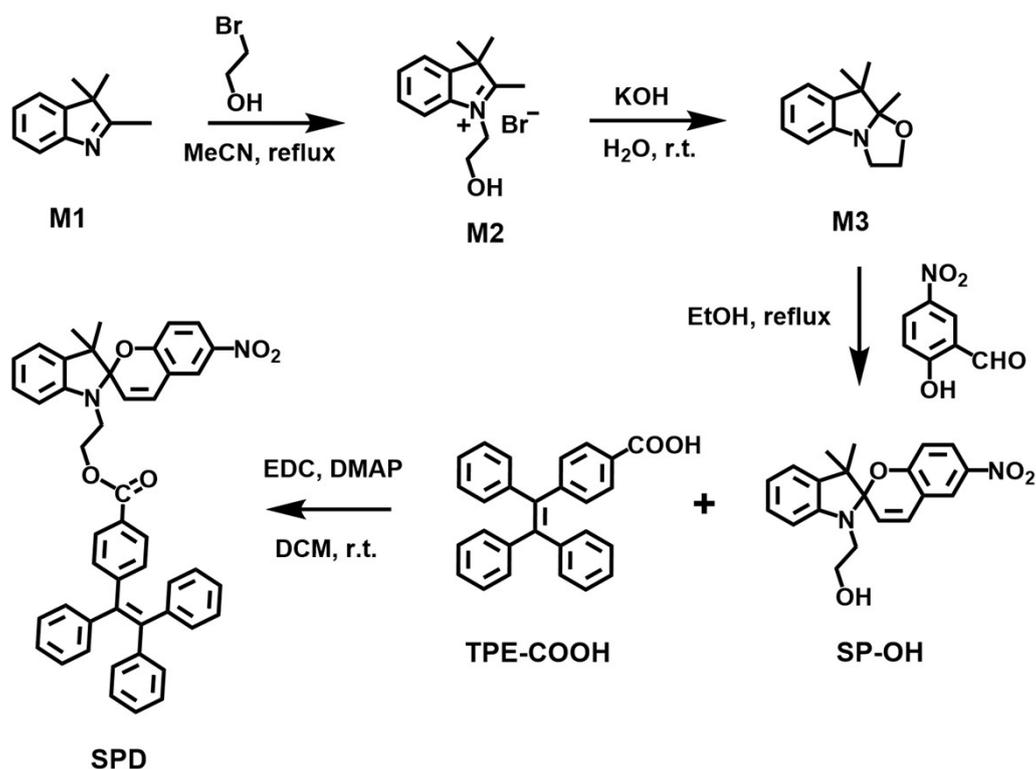
Density functional theory (DFT) calculations. The structures were optimized at the B3LYP/6-311G(d,p) level. The intermolecular interactions were carried out by the wave function analysis program Multiwfn, and the results were visualized by the VMD program.^{1,2} To quantify the intermolecular interactions, the binding energies (E_{bind}) are carried out according to the following equation:

$$E_{bind} = E_{AB} - E_A - E_B + E_{BSSE}\#(1)$$

in which E_{AB} represents the energy of complex AB, E_A represents the energy of individual A, E_B represents the energy of individual B, and E_{BSSE} represents the basis set superposition error (BSSE) corrected energy.^{3,4}

Syntheses and characterizations

The synthesis protocols of SPD are outlined below.



Scheme S1 Synthesis routes for the compound of SPD.

Compound M2: M1 (1.6 g, 10 mmol) and 2-bromoethanol (1.25 g, 10 mmol) were dissolved in acetonitrile (MeCN , 15 mL) and refluxed for 10 h, then allowed to cool to room temperature. The solution was dispersed in diethyl ether and centrifuged to obtain the crude product. The crude was finally washed with diethyl ether and dried under reduced pressure to give M2 as a pink solid (2.13 g, yield 75%). $^1\text{H NMR}$ (500 MHz, MeOD) δ 7.90 (dd, $J = 5.8, 2.8$ Hz, 1H), 7.81 (dd, $J = 5.4, 2.9$ Hz, 1H), 7.72 – 7.61 (m, 2H), 4.74 – 4.65 (m, 2H), 4.12 – 4.01 (m, 2H), 1.65 (s, 6H).

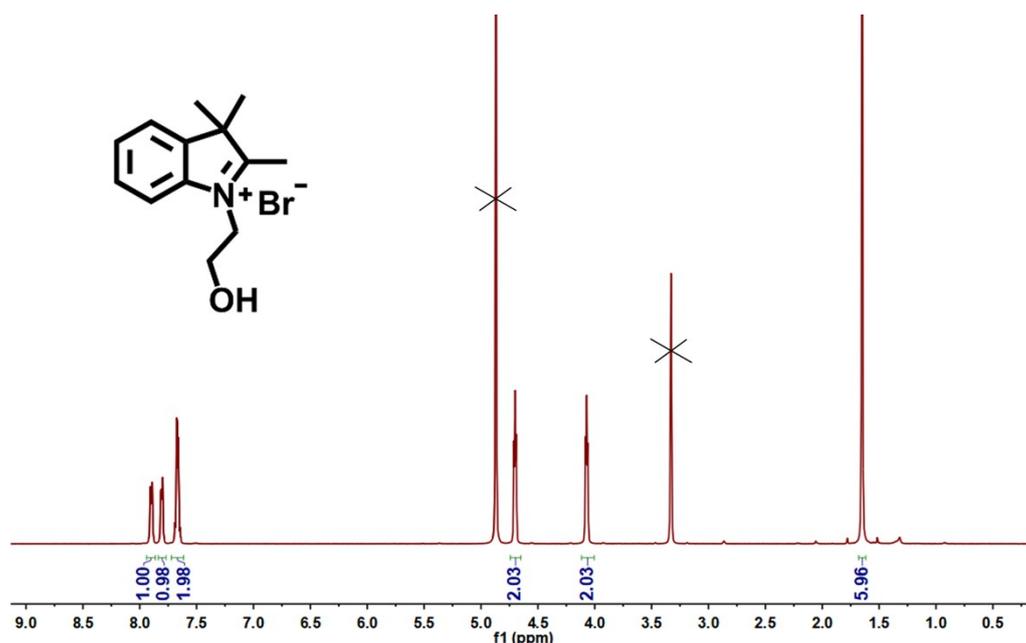


Fig. S1 ^1H NMR of compound M2 in MeOD.

Compound SP-OH: M2 (800 mg, 2.8 mmol), and potassium hydroxide (KOH, 252 mg, 4.5 mmol) were dissolved in 30 mL H_2O under stirring at room temperature. After stirring for 40 min, the solution was extracted with ether to obtain the organic phase. The solvent was then removed under reduced pressure through a rotary evaporator to obtain M3 as a brown oily liquid (400 mg, yield 75%). M3 was not characterized and went straight to the next reaction. M3 (340 mg, 1.68 mmol), 2-hydroxy-5-nitrobenzaldehyde (281 mg, 1.68 mmol), and pyridine (1.0 mL) in ethanol (15 mL) were refluxed under N_2 for 8 hours. After cooling to room temperature, the crude product was filtered and then washed three times with ethanol to obtain SP-OH as a purple solid (414 mg, yield 70%). ^1H NMR (400 MHz, DMSO) δ 8.22 (d, $J = 2.8$ Hz, 1H), 8.00 (dd, $J = 9.0, 2.8$ Hz, 1H), 7.20 (d, $J = 10.4$ Hz, 1H), 7.12 (t, $J = 6.1$ Hz, 2H), 6.89 (dd, $J = 8.1, 5.0$ Hz, 1H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 6.02 (d, $J = 10.4$ Hz, 1H), 4.74 (s, 1H), 3.60 – 3.45 (m, 2H), 3.23 – 3.10 (m, 2H), 1.20 (s, 3H), 1.09 (d, $J = 10.9$ Hz, 3H). ESI-TOF: m/z calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4$, 352.14231; found, 353.14949 ($\text{M}+\text{H}^+$).

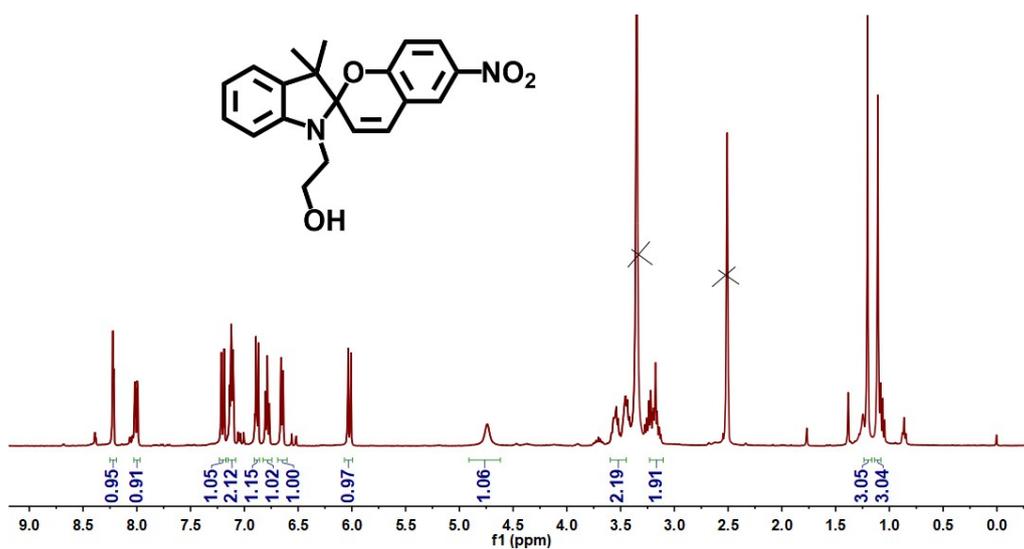


Fig. S2 $^1\text{H NMR}$ of compound SP-OH in DMSO.

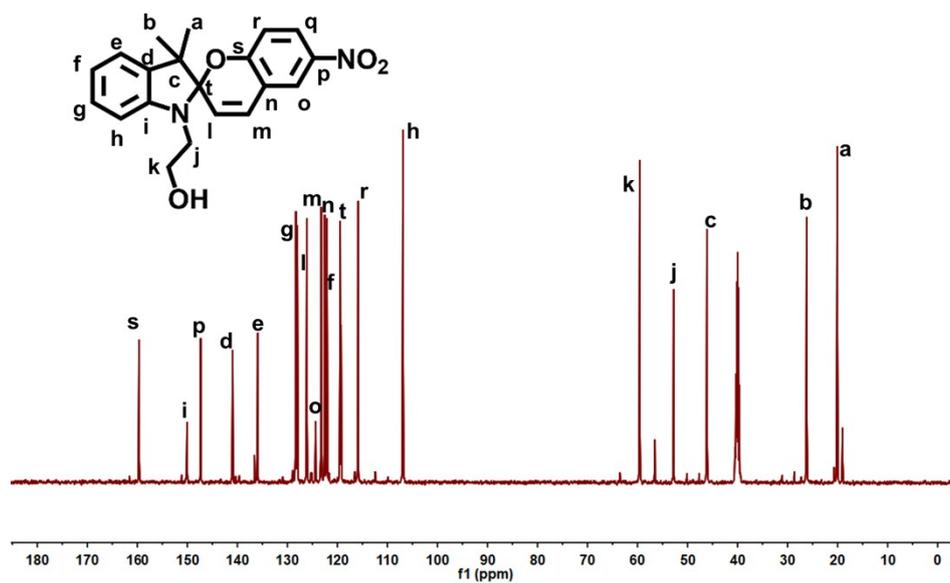


Fig. S3 $^{13}\text{C NMR}$ of compound SP-OH in DMSO.

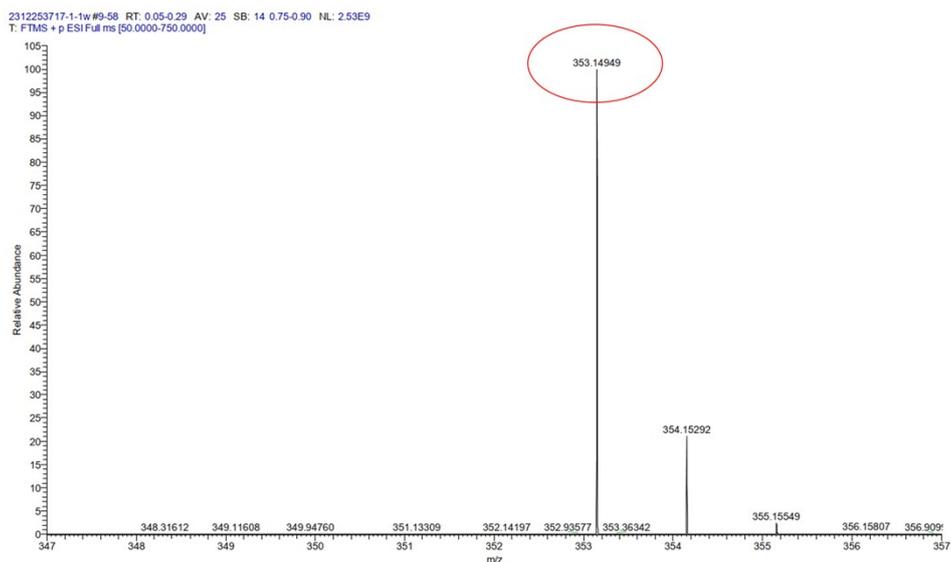


Fig. S4 ESI-MS spectrum of compound SP-OH.

Compound SPD: SP-OH (352 mg, 1 mmol), DMAP (20 mg, 0.16 mmol), and EDC (252 mg, 1.2 mmol) were dissolved in 15 mL DCM under stirring at room temperature, followed by the addition of TPE-COOH (376 mg, 1 mmol). After stirring for 48 h, the solvent was removed under reduced pressure through a rotary evaporator. The residue was purified by chromatography (using DCM) to give SPD as a light yellow solid (350 mg, yield 49%). ^1H NMR (500 MHz, CDCl_3) δ 8.08 – 7.96 (m, 2H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.28 – 6.96 (m, 19H), 6.92 (t, $J = 7.3$ Hz, 1H), 6.85 (d, $J = 10.4$ Hz, 1H), 6.76 (dd, $J = 11.5, 8.6$ Hz, 2H), 5.84 (d, $J = 10.3$ Hz, 1H), 4.44 (t, $J = 5.5$ Hz, 2H), 3.61 (dt, $J = 13.8, 6.7$ Hz, 1H), 3.53 – 3.42 (m, 1H), 1.31 (s, 3H), 1.17 (s, 3H). ESI-TOF: m/z calcd for $\text{C}_{47}\text{H}_{38}\text{N}_2\text{O}_5$, 710.27807; found, 711.28303 ($\text{M}+\text{H}^+$).

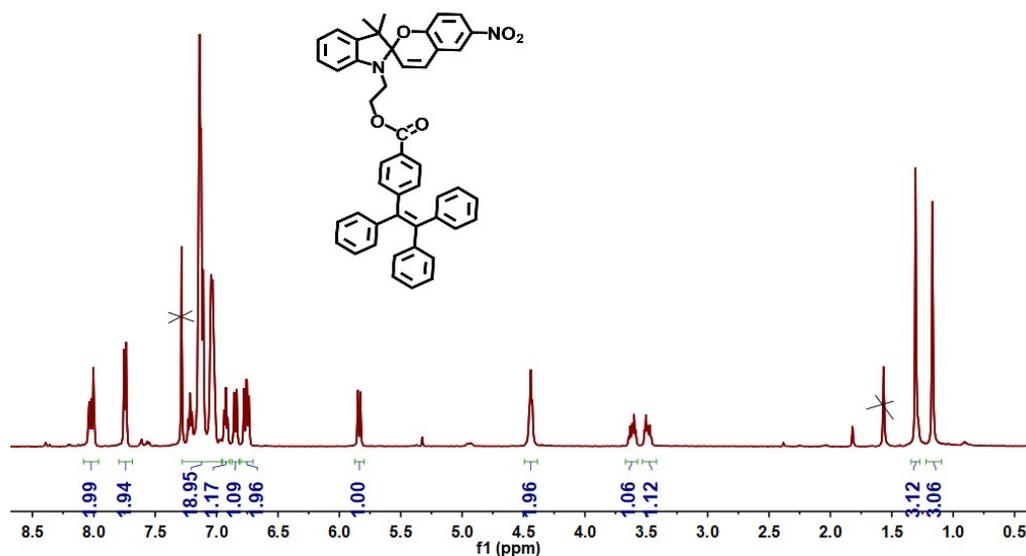


Fig. S5 ^1H NMR of compound SPD in CDCl_3 .

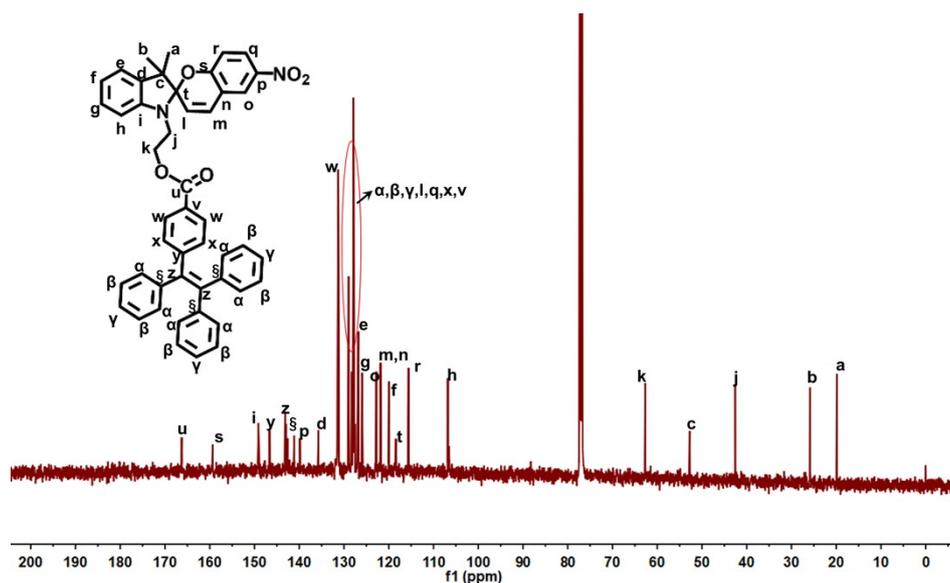


Fig. S6 ^{13}C NMR spectrum of compound SPD in CDCl_3 .

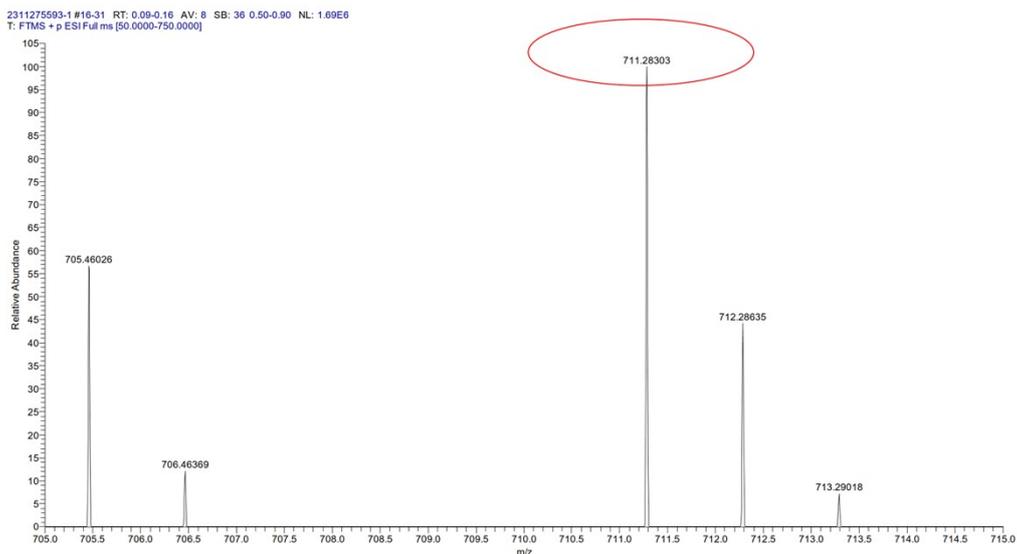
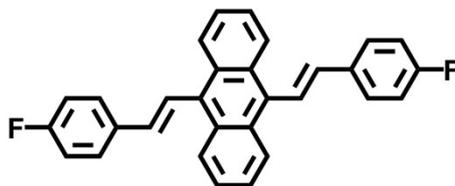


Fig. S7 ESI-MS spectrum of compound SPD.



Scheme S2 Molecular structure of DSA.

Compound SPD: DSA was synthesised according to the previous literature.⁵ ^1H NMR (400 MHz, CDCl_3) δ 8.37 (dd, $J = 6.8, 3.3$ Hz, 1H), 7.84 (d, $J = 16.5$ Hz, 1H), 7.66 (dd, $J = 8.4, 5.5$

Hz, 1H), 7.48 (dd, $J = 6.9, 3.2$ Hz, 1H), 7.15 (t, $J = 8.6$ Hz, 1H), 6.90 (d, $J = 16.5$ Hz, 1H). ESI-TOF: m/z calcd for $C_{30}H_{20}F_2$, 418.1533; found, 419.1562 ($M+H^+$).

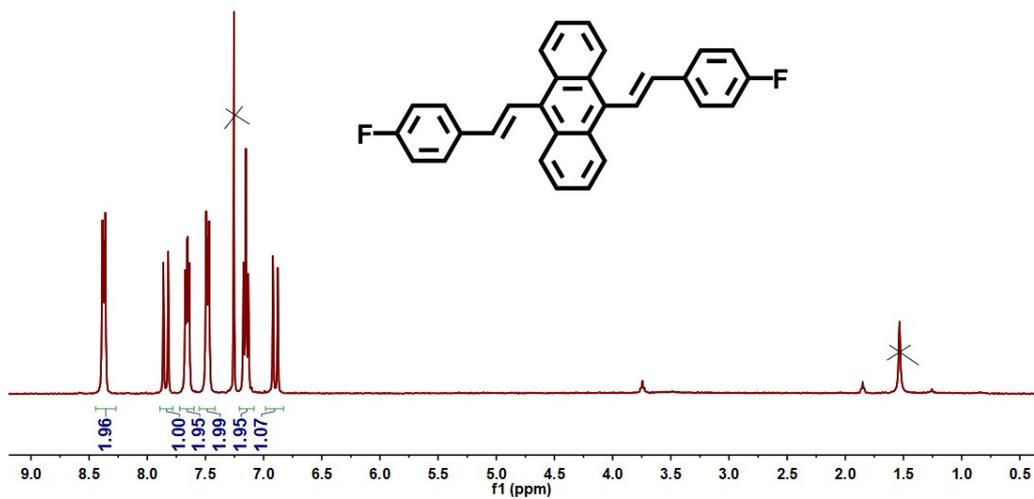


Fig. S8 1H NMR of compound DSA in $CDCl_3$.

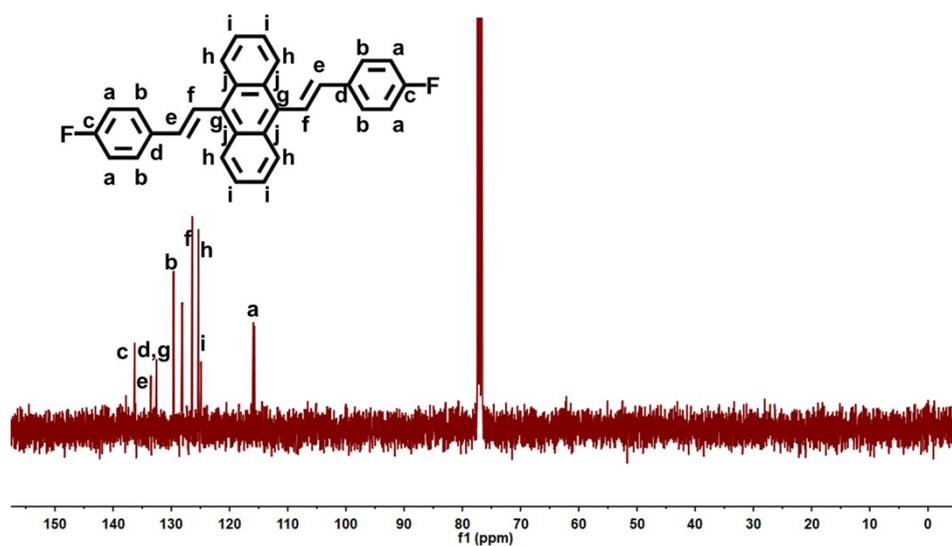


Fig. S9 ^{13}C NMR spectrum of compound DSA in $CDCl_3$.

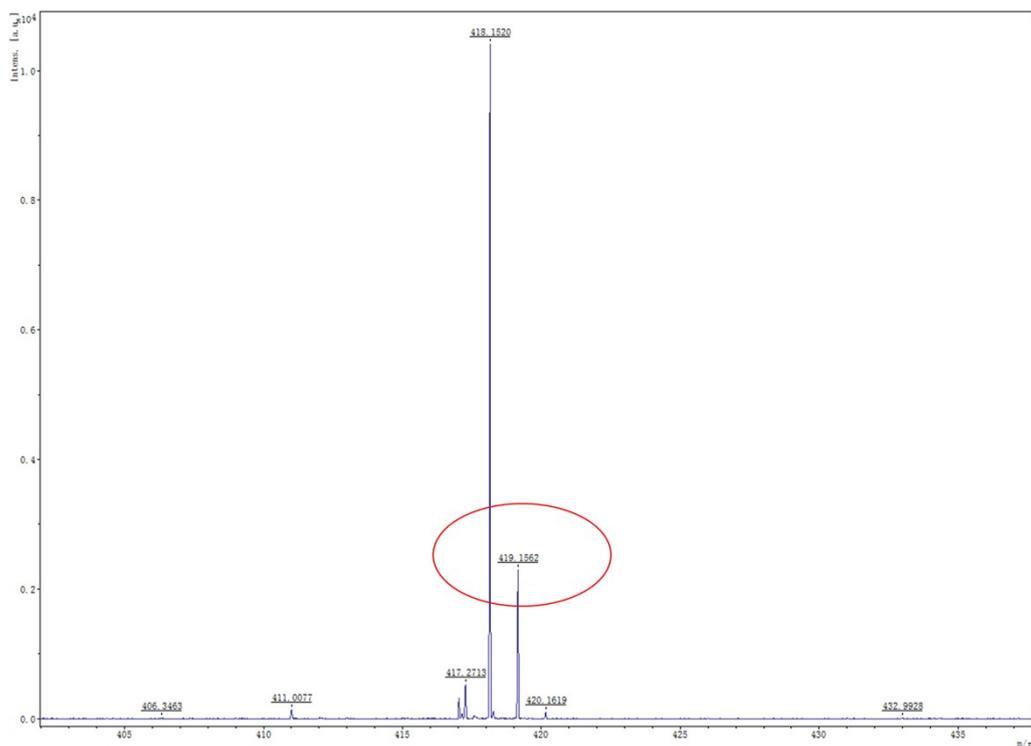


Fig. S10 ESI-MS spectrum of compound DSA.

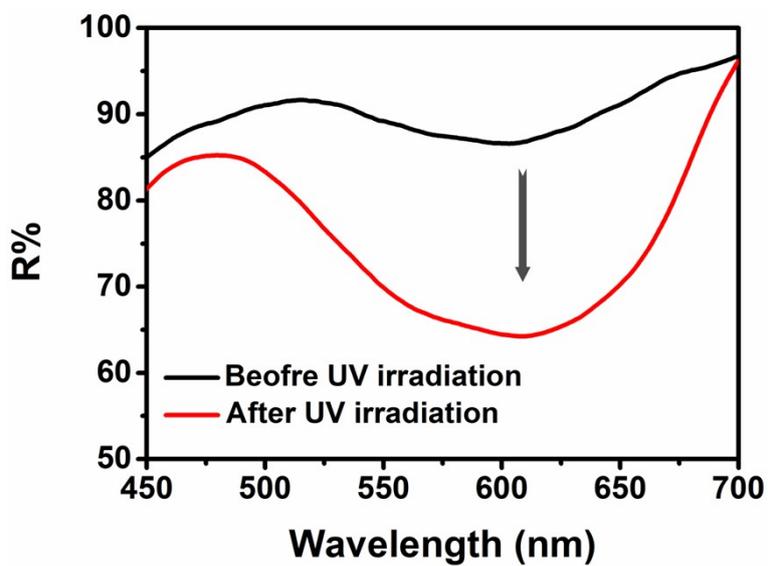


Fig. S11 Diffuse reflectance spectra of SPD in the solid state before and after UV light irradiation.

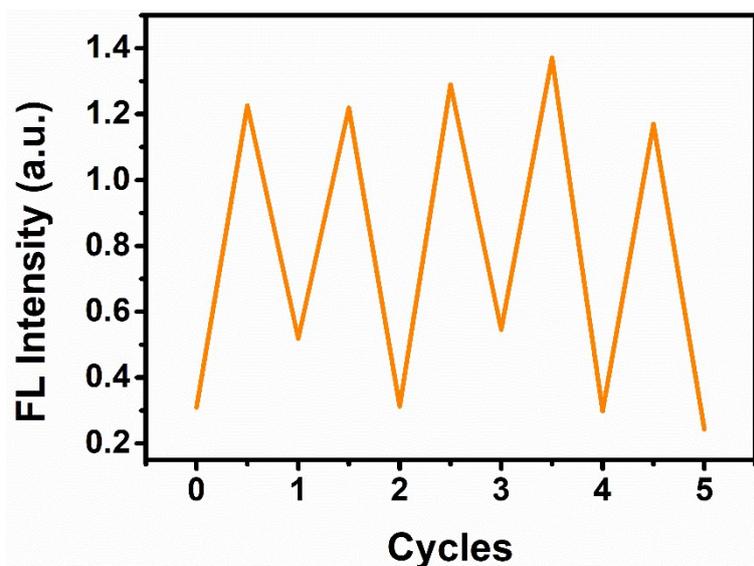


Fig. S12 Reversible switch of the fluorescence intensity of SPD at 685 nm upon alternate UV and visible light/heat treatment.

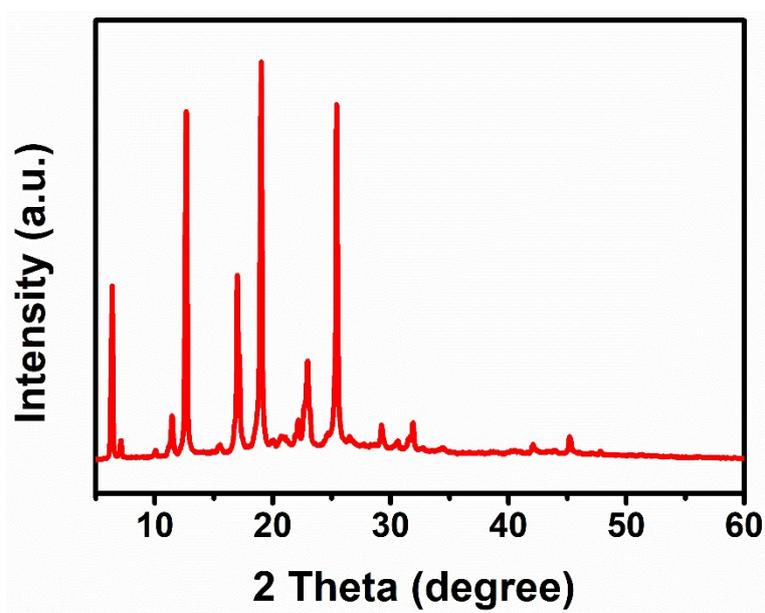


Fig. S13 XRD patterns of SP-OH powders.

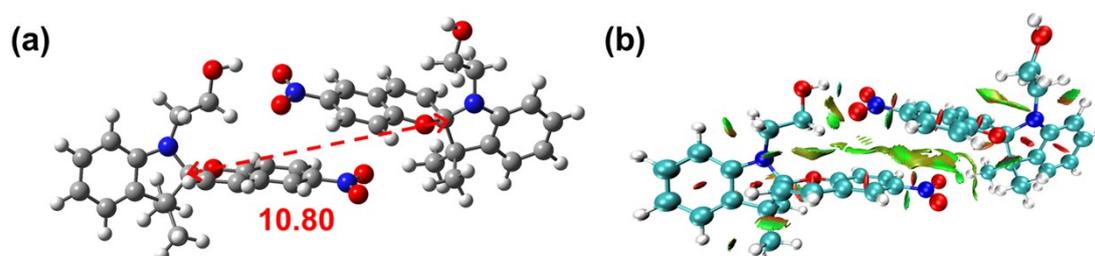


Fig. S14 (a) Optimized molecular structure of SP-OH molecules. (b) Strength and distribution of intermolecular interactions of SP-OH molecules.

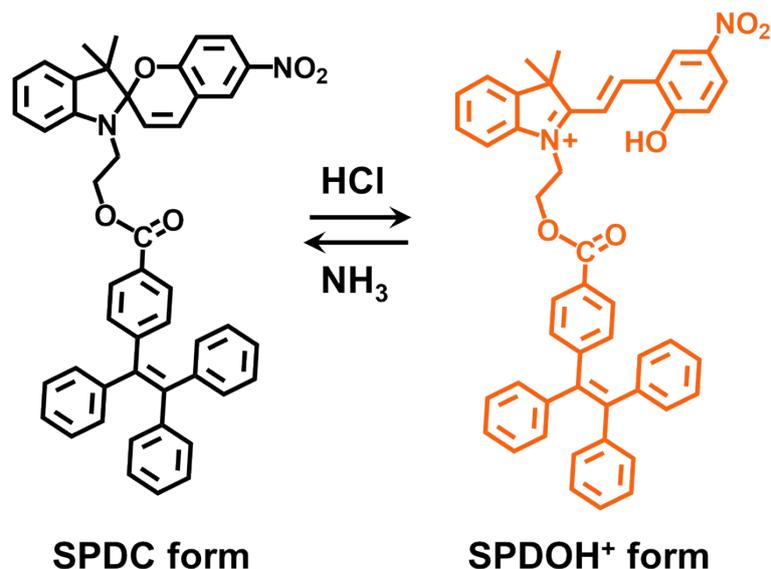


Fig. S15 Reversible structural transformation between SPDC form and SPDOH⁺ form upon alternate HCl and NH₃ gas treatment.

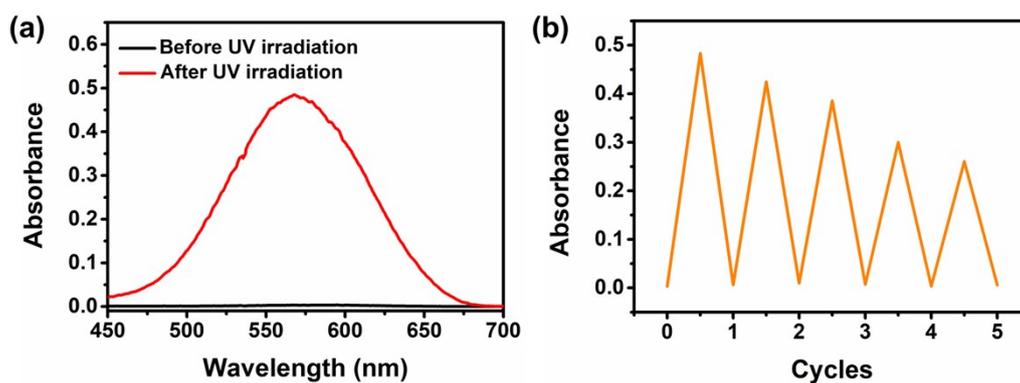


Fig. S16 (a) UV-vis absorption of SPD on the filter paper before and after UV irradiation. Reversible switch of the absorption intensity at 567 nm of SPD upon alternate UV and visible light/heat treatment.

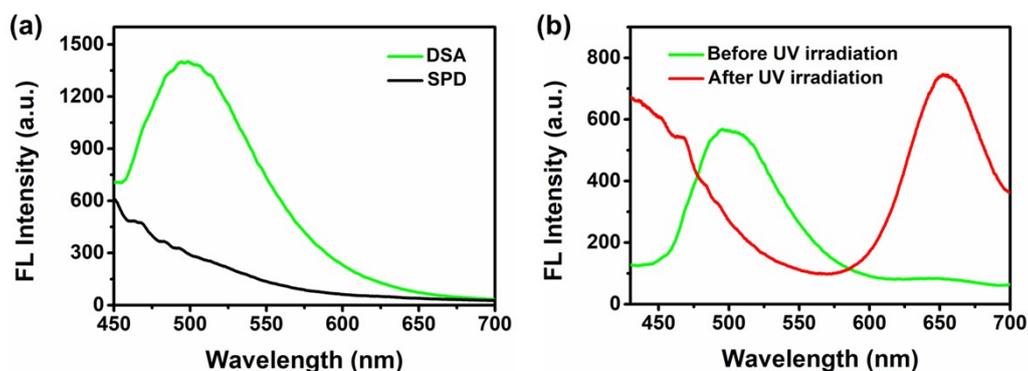


Fig. S17 (a) Fluorescence spectra of DSA and SPD on filter paper excited by 420 nm. (b) Fluorescence spectra of SPD/DSA on filter paper excited by 365 nm.

Previous work (J. Phys. Chem. Lett. 2021, 12, 1290–1294)

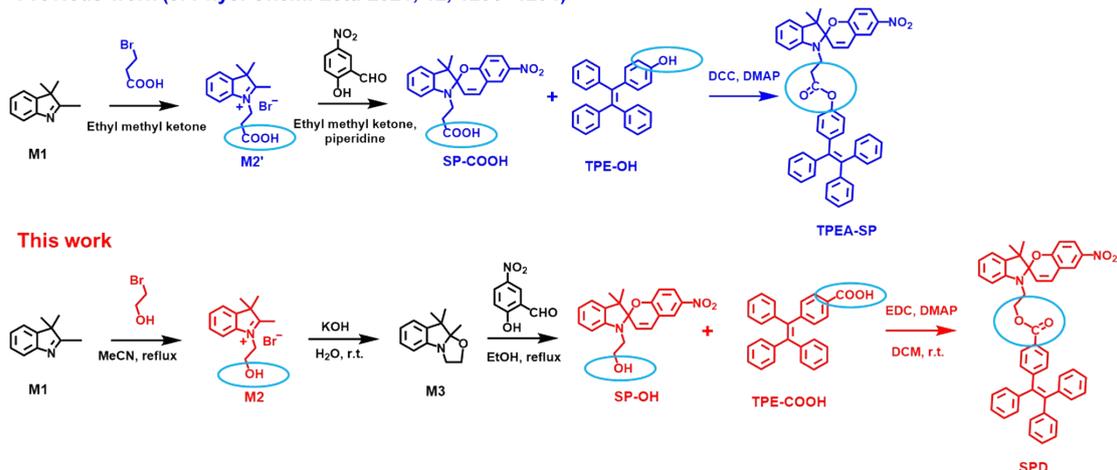


Fig. S18 Synthesis routes of TPEA-SP (previous work) and SPD (this work).

Compound M2': The synthesis method is according to the previous reference.⁶ ¹H NMR (400 MHz, MeOD) δ 7.95 – 7.88 (m, 1H), 7.83 – 7.76 (m, 1H), 7.71 – 7.63 (m, 2H), 4.80 (t, J = 6.5 Hz, 2H), 3.12 (t, J = 6.5 Hz, 2H), 1.63 (s, 6H).

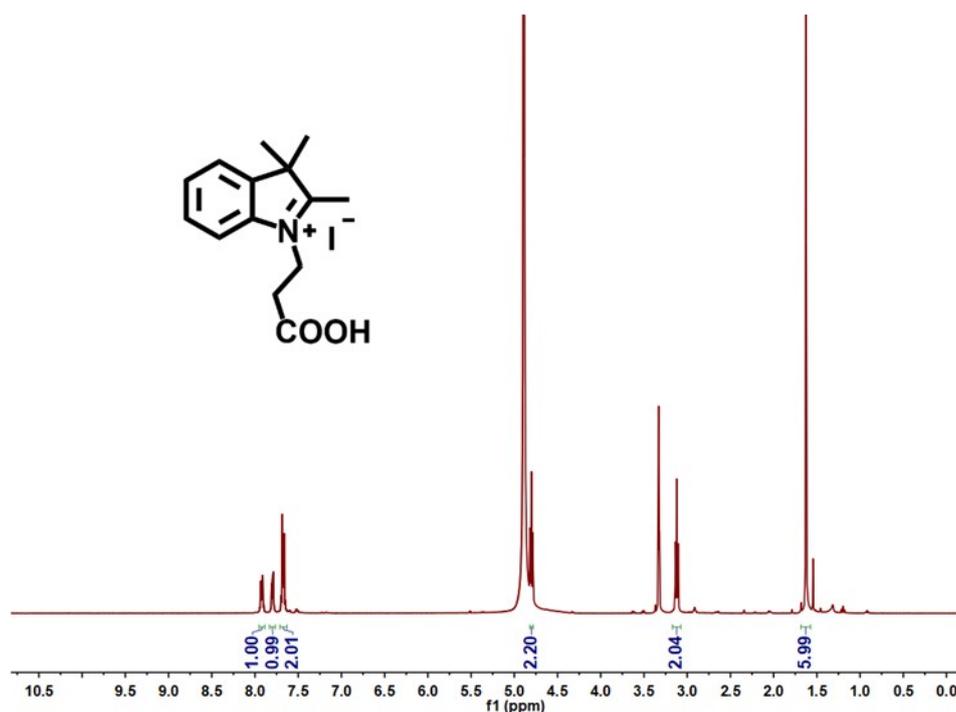


Fig. S19 ¹H NMR spectrum of compound M2' in MeOD.

Compound SP-COOH: ¹H NMR (400 MHz, DMSO) δ 12.17 (s, 1H), 8.22 (d, J = 2.8 Hz, 1H), 8.01 (dd, J = 9.0, 2.8 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 6.86 (t, J = 8.4 Hz, 1H), 6.81 (t, J = 7.1 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 6.01 (d, J = 10.4 Hz, 1H), 3.45 (ddd, J = 14.5, 11.3, 4.3 Hz, 2H), 2.68 – 2.58 (m, 1H), 2.47 – 2.33 (m, 1H), 1.17 (d, J = 15.1 Hz, 3H), 1.07 (d, J = 7.9 Hz, 3H).

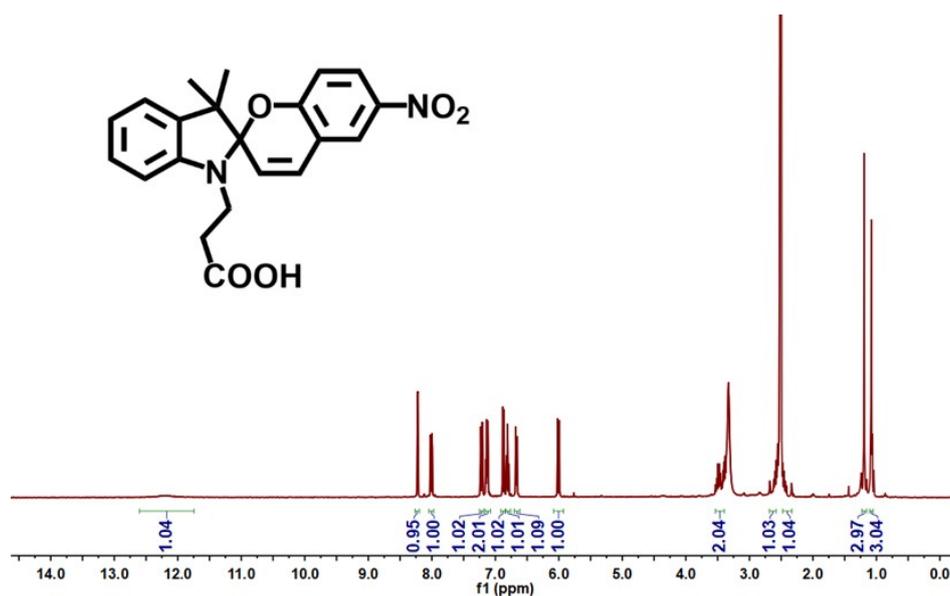


Fig. S20 ^1H NMR spectrum of compound SP-COOH in DMSO.

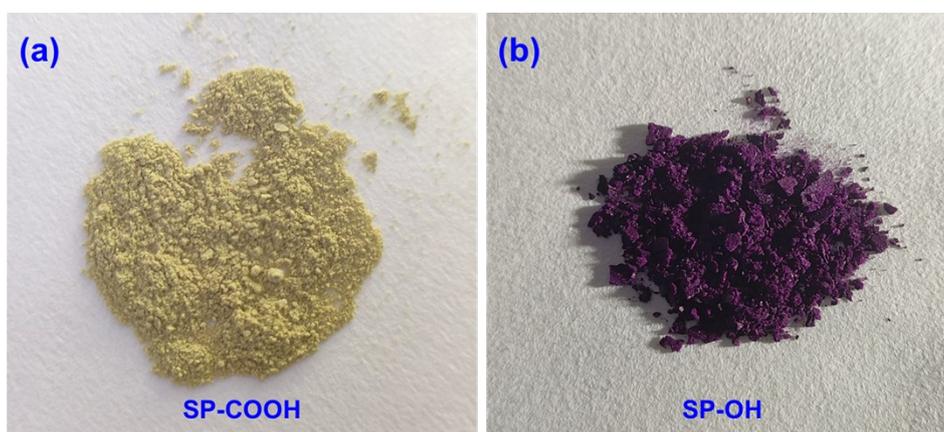


Fig. S21 Apparent color of (a) SP-COOH and (b) SP-OH in the solid state.

References

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