Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Planar Rigid Steric Groups Modified Spiropyran Derivative with Photochromism and Mechanochromism for Optical Printing Application

Bing Fang[a], Mingyu Fan[b], Han Gao[a], Yu Wang[a], Dahai Gao[a], Jianxiang Yu[a], Meizhen Yin[b]*, Yuhua Dai[a]*

[a]Beijing Key Laboratory of Special Elastomer Composite Materials, College of New Materials and Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617 (China)

[b]State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, PR China

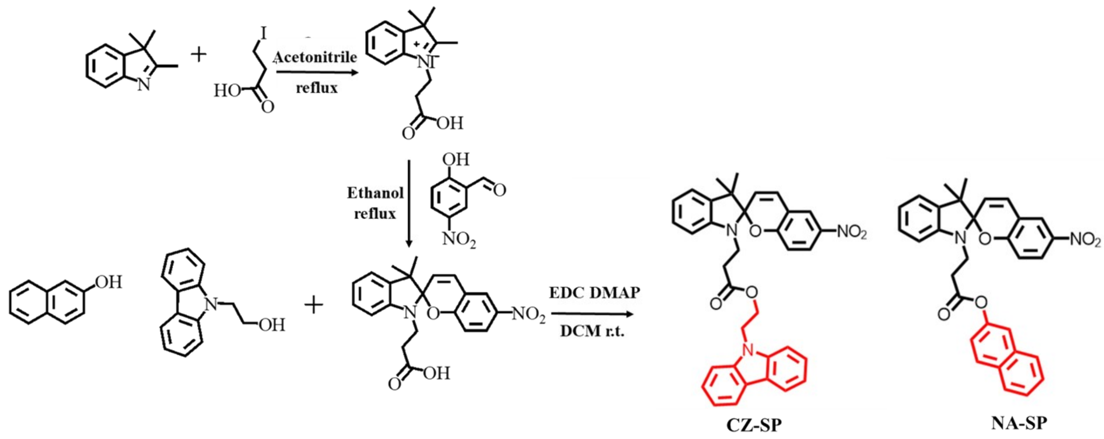
Corresponding Author: yinmz@mail.buct.edu.cn; daiyuhua@bipt.edu.cn

Materials

All starting materials were purchased from Innochem and used without further purification. The solvents for synthesis were common commercial grade and were used as received.

Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 (400 MHz) spectrometer at room temperature. Fluorescence studies were performed on a fluorescence spectrophotometer (FS-5). UV-vis spectra were measured on a spectrometer (Shimadzu 2600, Japan). Powder X-ray diffraction (PXRD) patterns carried by a D/max2500 VB2+/PC X-ray diffractometer (Rigaku) using Cu Kα radiation in the 2θ range 5-60°.



Scheme S1. The synthesis route for CZ-SP and NA-SP.

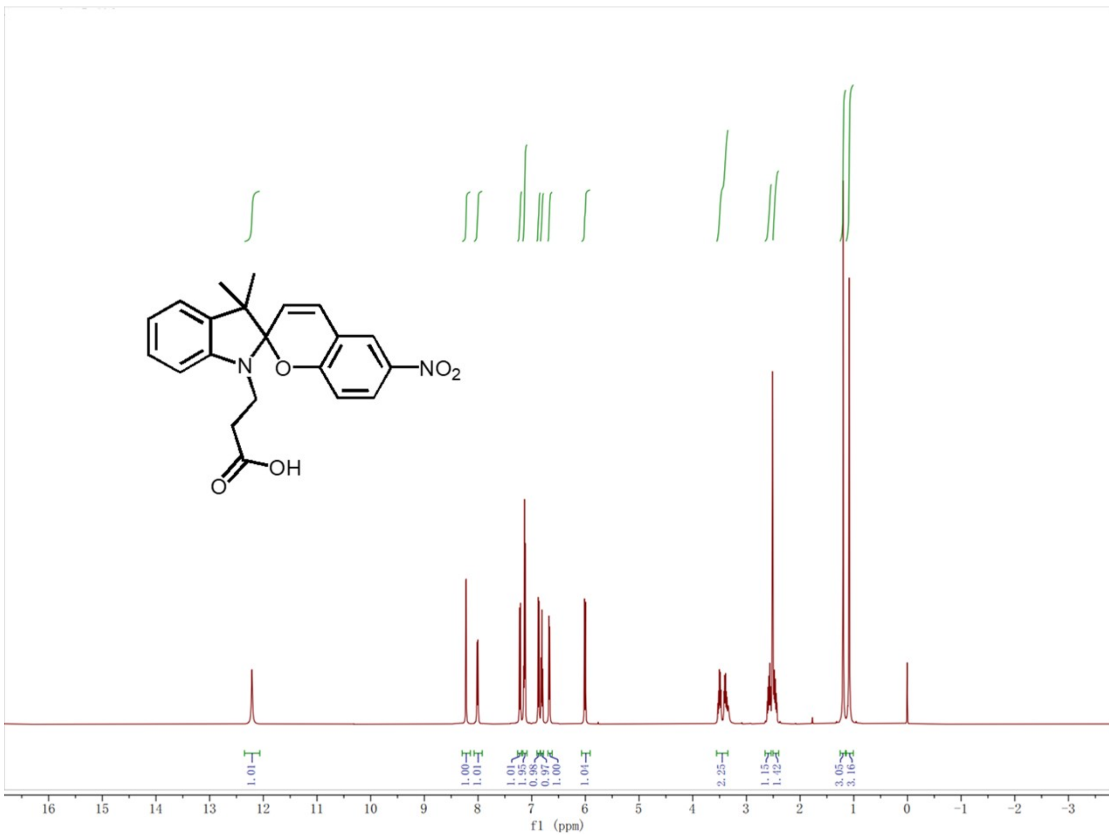


Figure S1. ^{1}H NMR of SP-COOH.

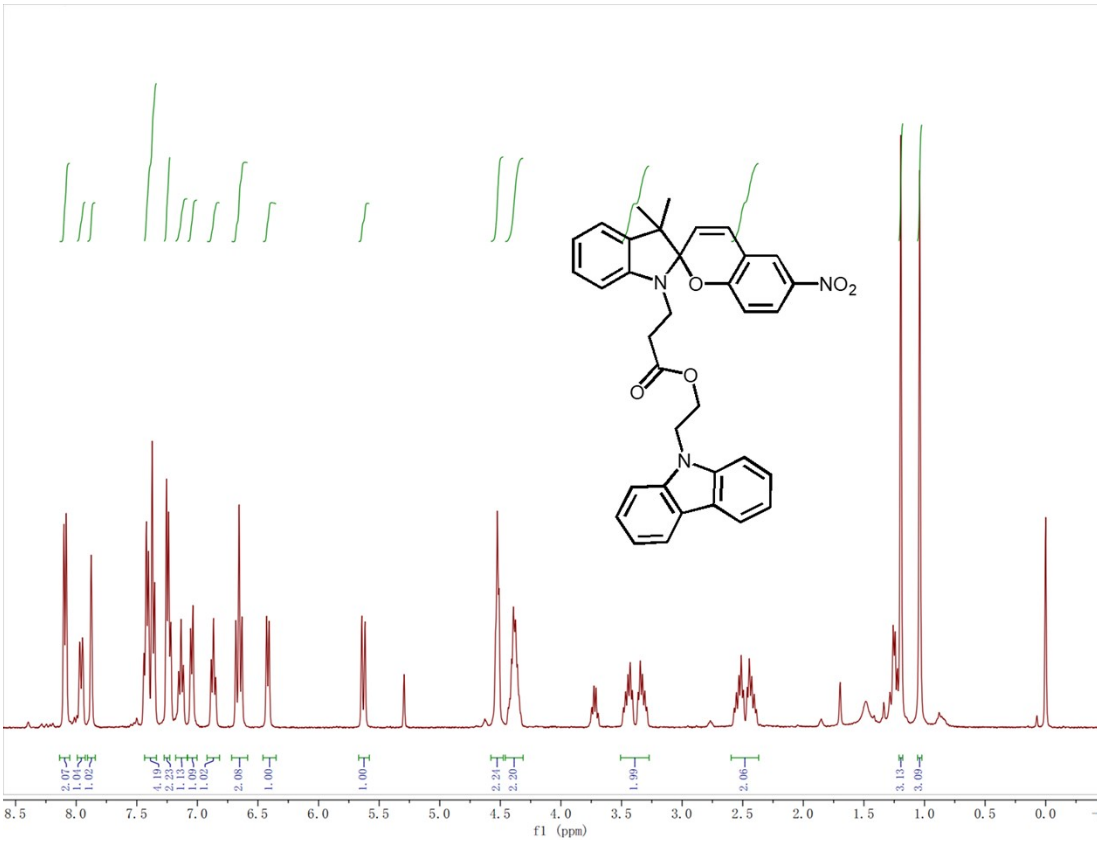


Figure S2. ^{1}H NMR of CZ-SP.

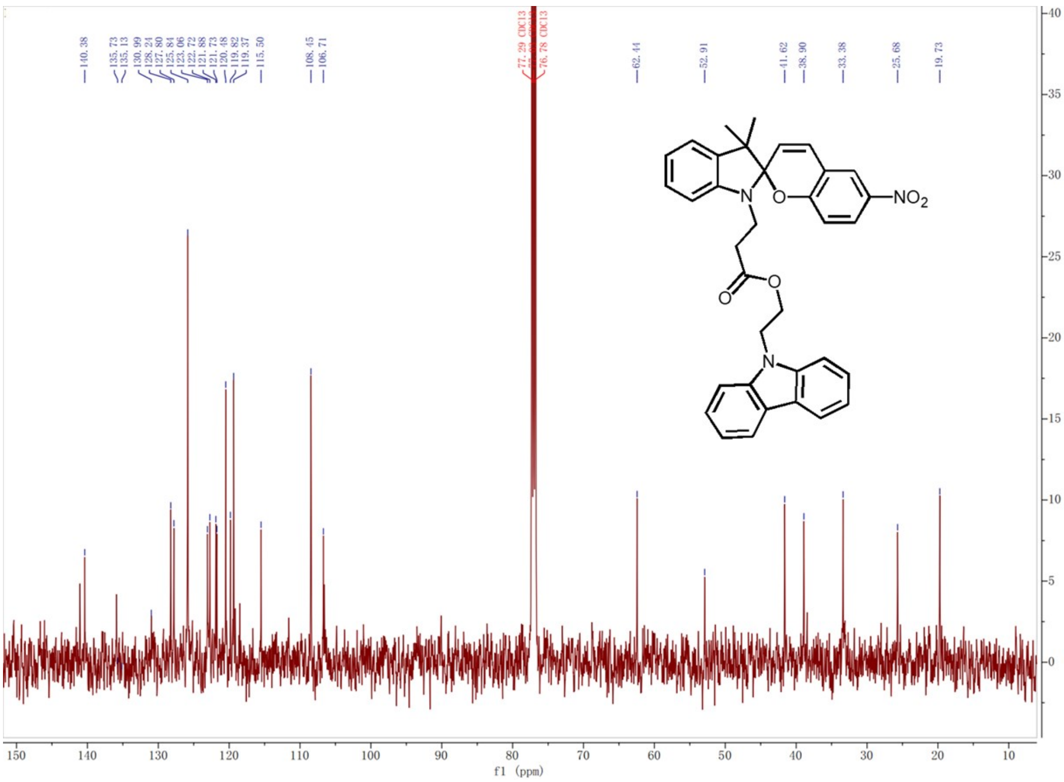


Figure S3. ^{13}C NMR of CZ-SP.

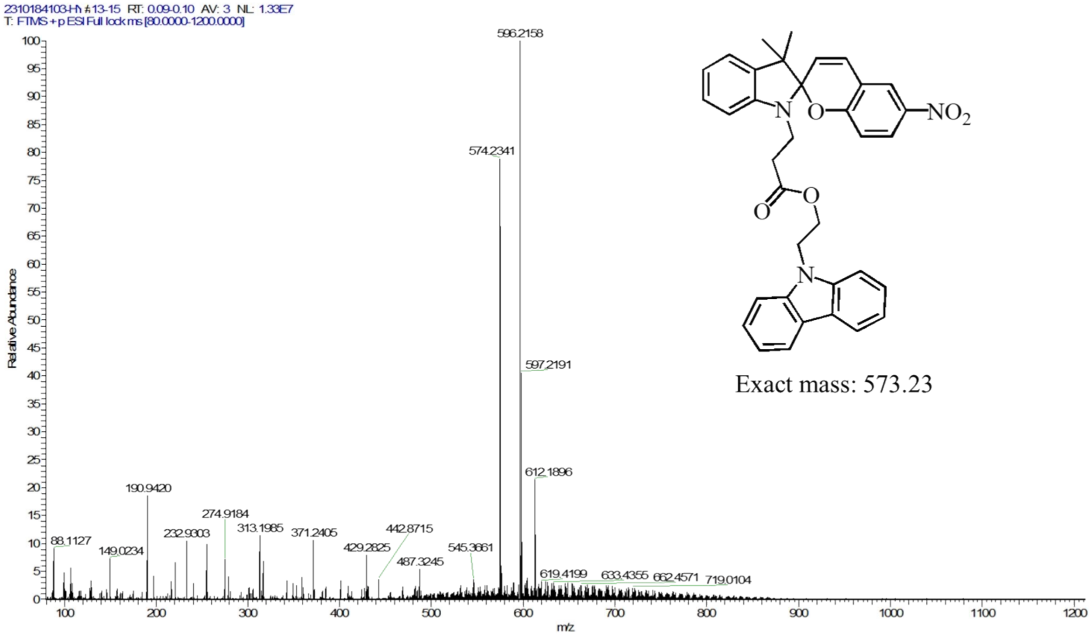


Figure S4. ESI-TOF of CZ-SP.

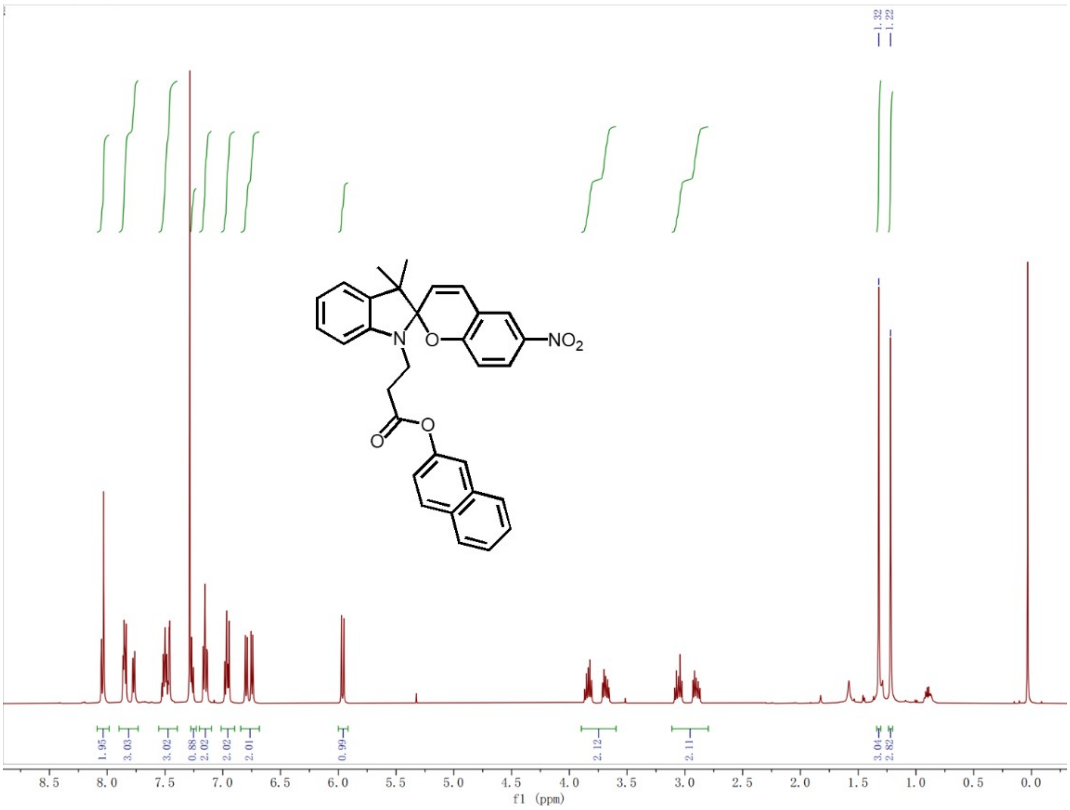


Figure S5. ^{1}H NMR of NA-SP.

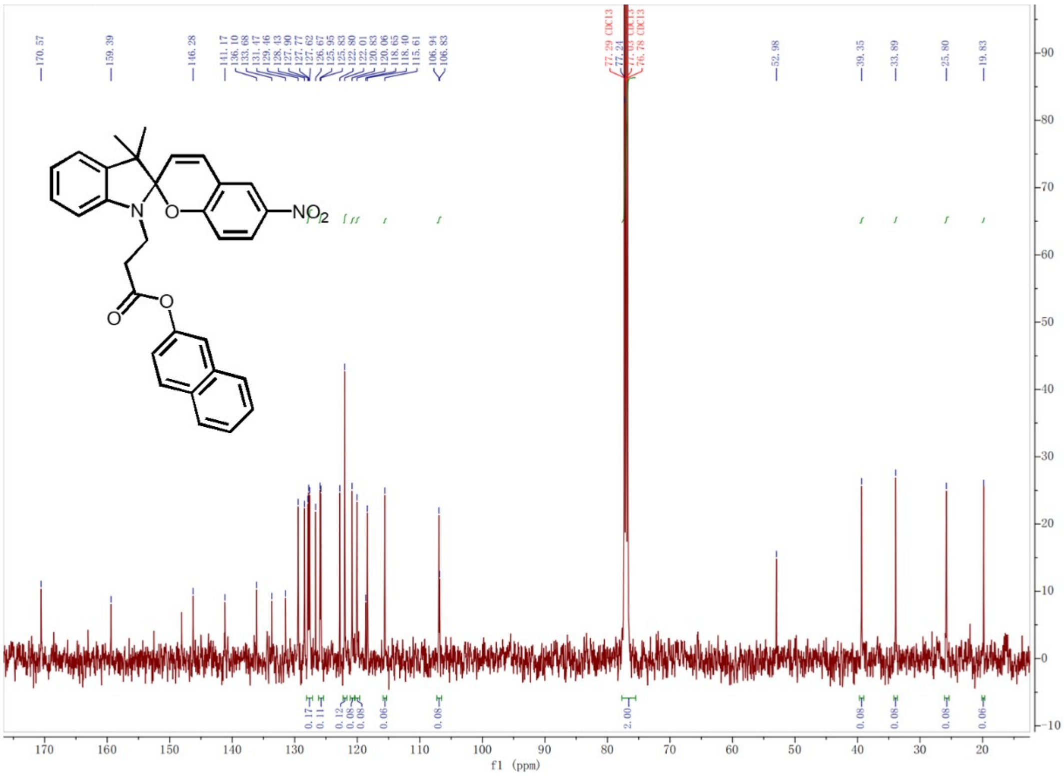


Figure S6. ^{13}C NMR of NA-SP.

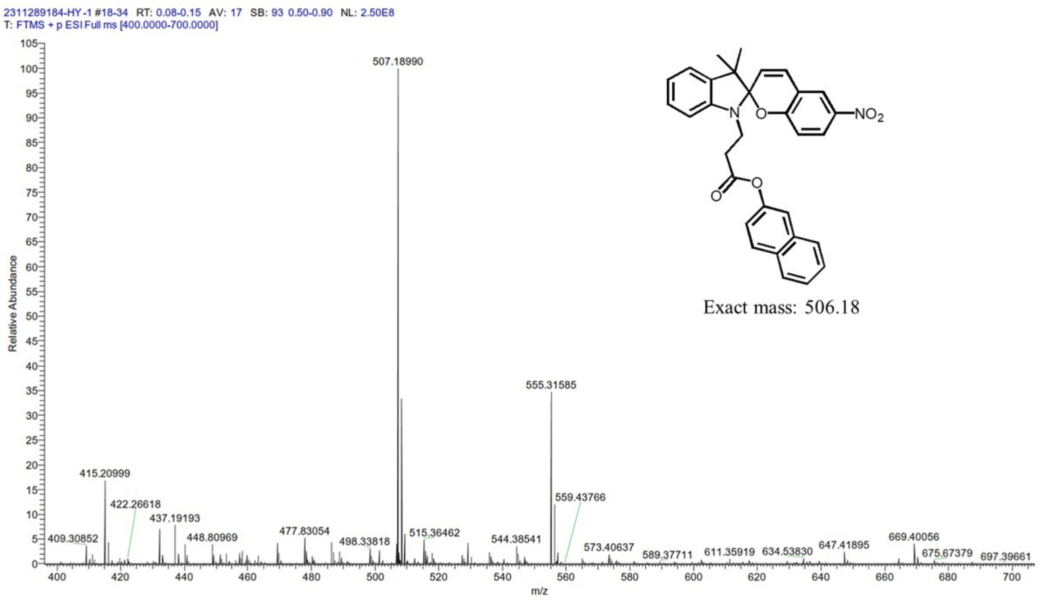


Figure S7. ESI-TOF of NA-SP.

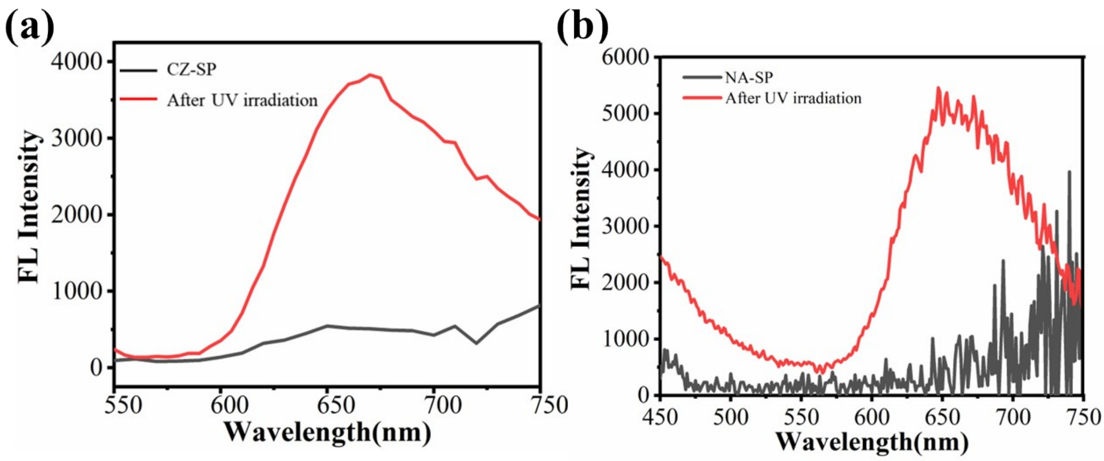


Figure S8. FL spectra of CZ-SP (a) and NA-SP (b) in DCM solution before and after UV irradiation for 30 s (λ_{exc} = 365 nm).

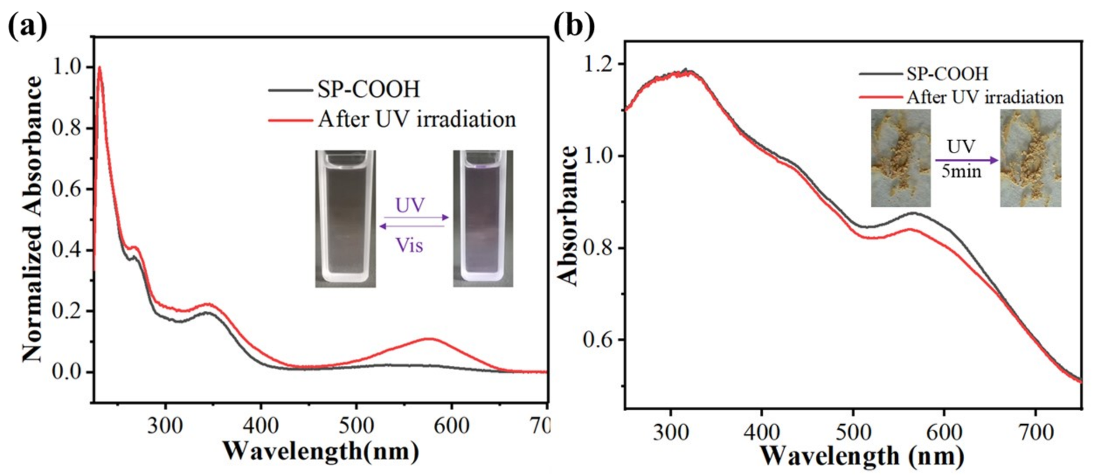


Figure S9. UV-vis absorption spectra of SP-COOH solution (a) and powders (b) before and after UV light irradiation (Inset: Images of SP-COOH solution and powder before and after UV irradiation under visible light.

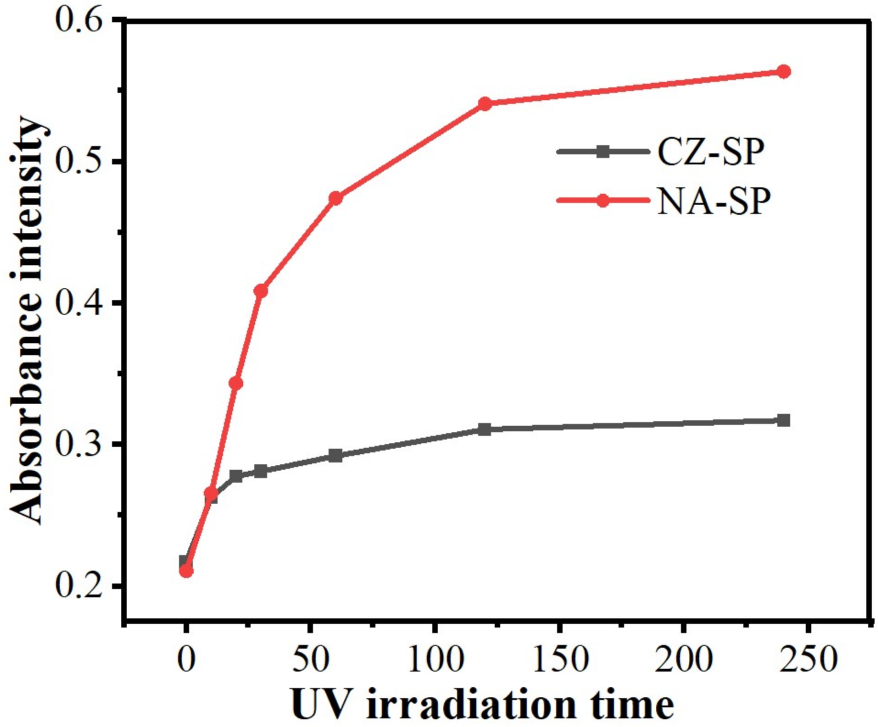


Figure S10. Absorbance intensity of NA-SP and CZ-SP under increased UV irradiation time.

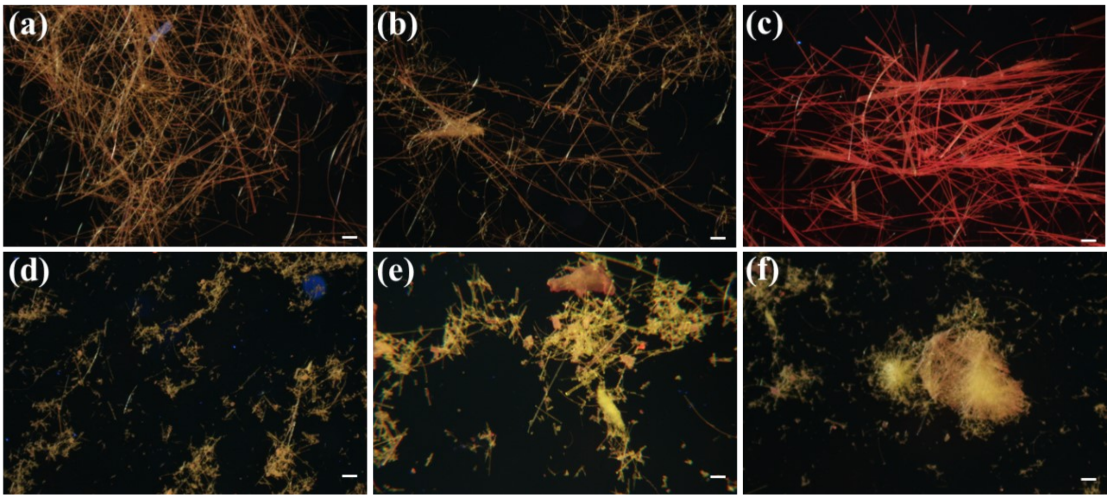


Figure S11. The fluorescence images of the as-prepared CZ-SP (a, b, c) and NA-SP microcrystals (d, e, f) under DCM : MeOH=1:2 (a, d), DCM : Hex=1:2 (b, e); DCM:PE=1:2 (c, f), volume ratio, respectively. Scale bar: 20 μm. DCM is dichloromethane, MeOH is methanol, Hex is hexane, and PE is petroleum ether.

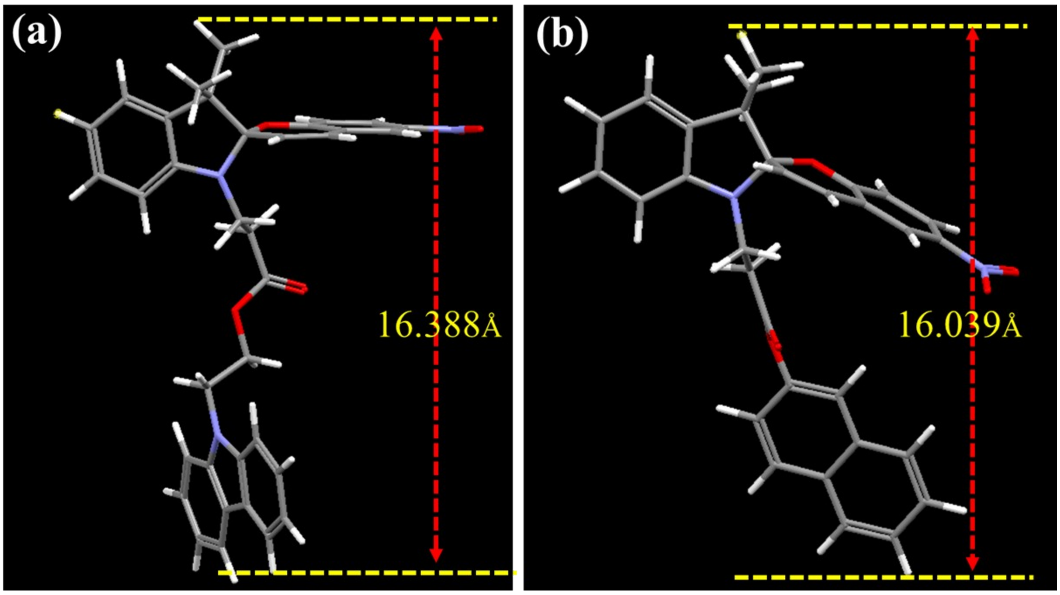


Figure S12. Geometric conformations of CZ-SP and NA-SP.

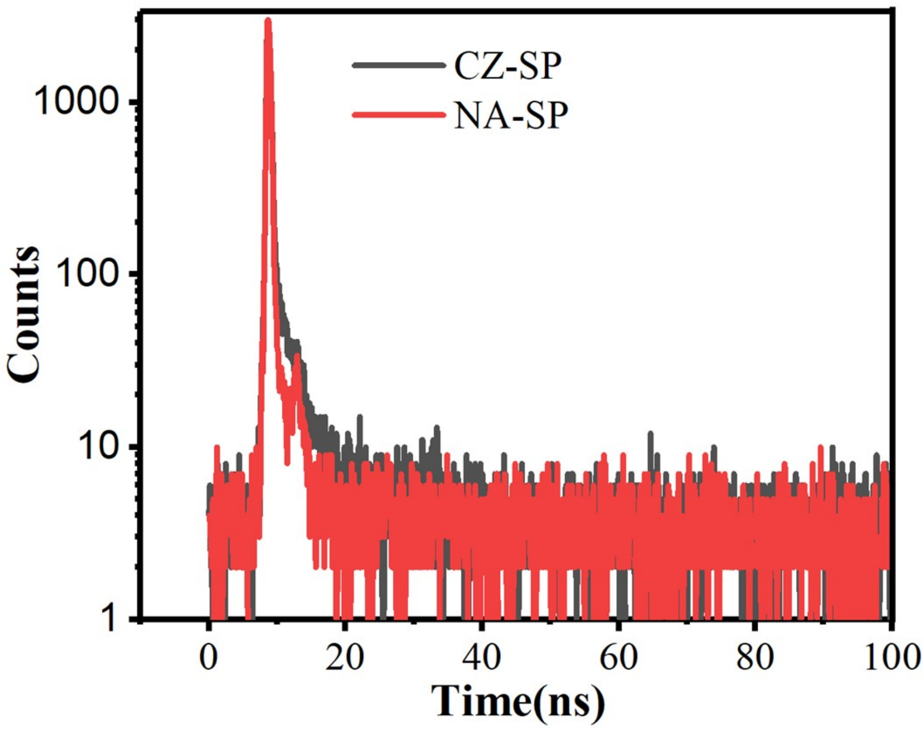


Figure S13. Transient decay spectra of CZ-SP and NA-SP powders under UV irradiation for 60 s.

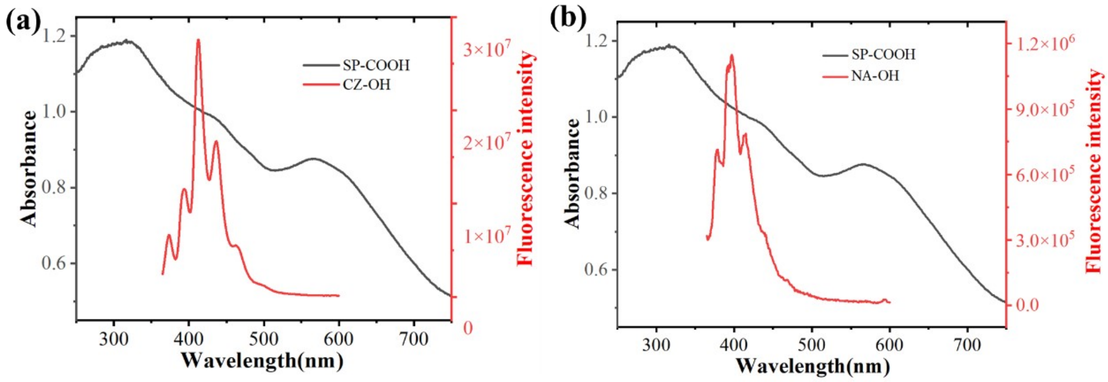


Figure S14. Overlap of SP-COOH absorption spectra and CZ-OH (a), NA-OH (b) fluorescence emission spectra in solid state (λ_{exc} = 365 nm).

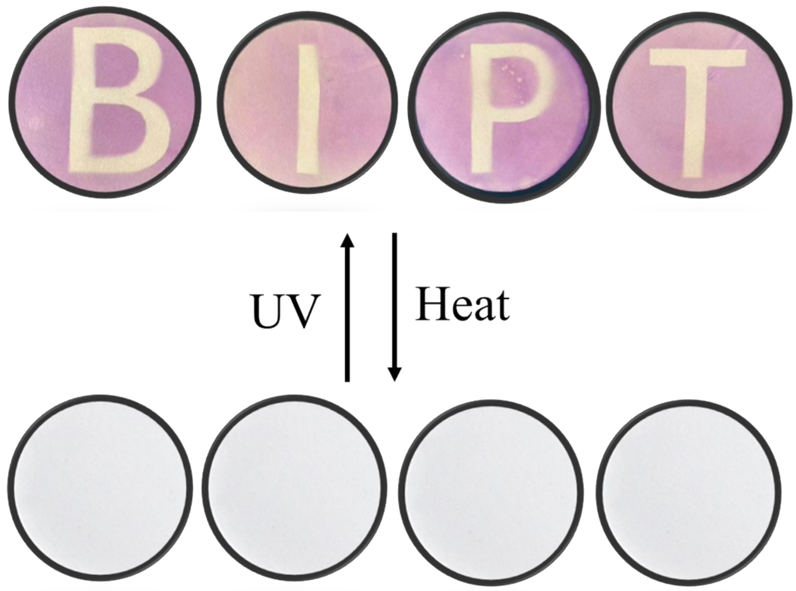


Figure S15. Reversible optical printing under alternating UV and heat treatment.

Figure S16. Fluorescent images of CZ-SP and NA-SP as an anti-counterfeiting ink on letters filter paper under UV irradiation for 60 s.

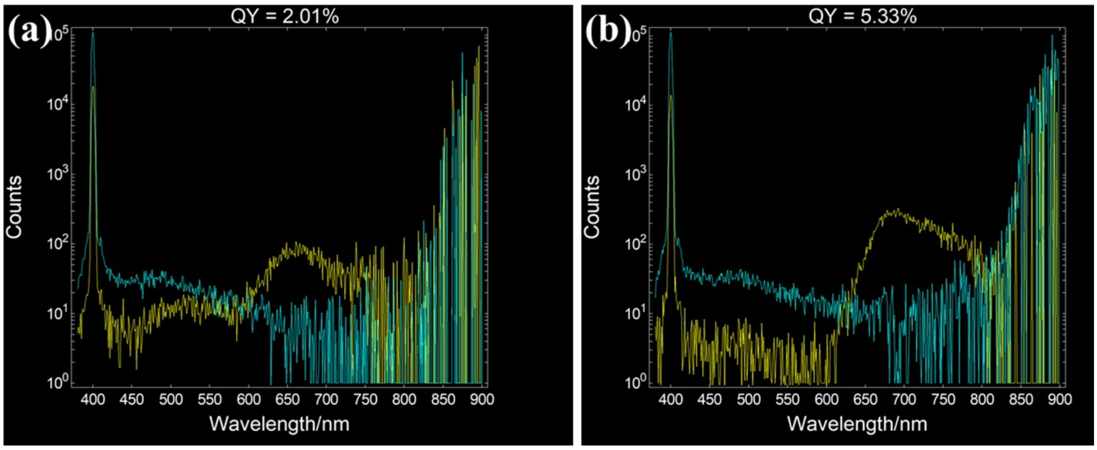


Figure S17. Fluorescence quantum yields of (a) CZ-SP and (b) NA-SP powder after UV irradiation for 60s. The emission range is from 600-750 nm.

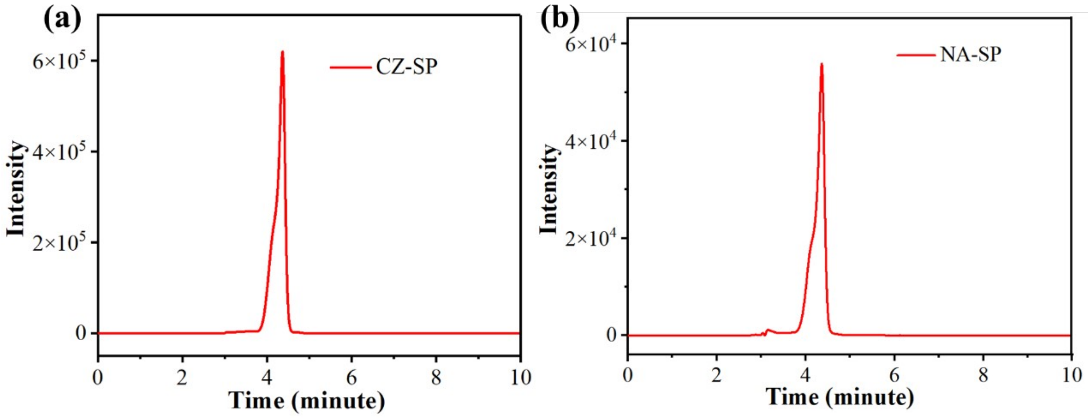


Figure S18. High performance liquid chromatography diagrams of (a) CZ-SP and (b) NA-SP.

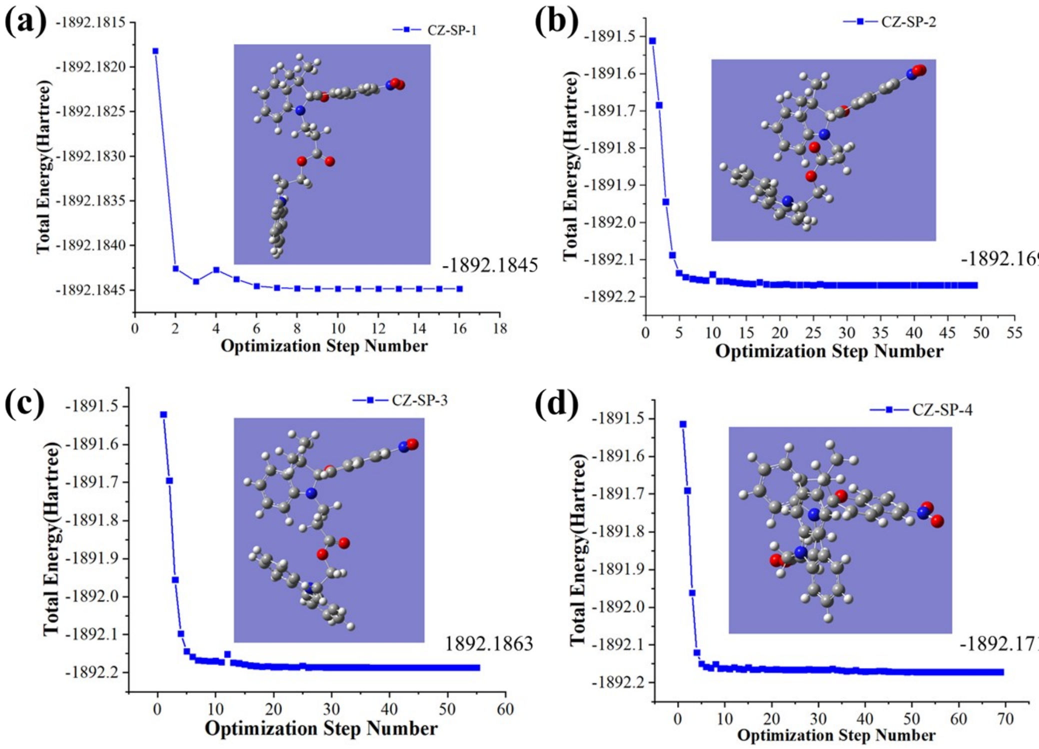


Figure S19. Four different geometries by adjusting flexible linkers in CZ-SP molecule from Materials Studio software (version 7.0). The four different geometries CZ-SP molecules are optimized by Materials Studio and total energies are calculated by density functional theory. Four different geometries CZ-SP molecules share very similar total energies.

Table S1. Fluorescence quantum efficiency and the lifetimes of CZ-SP and NA-SP powders after UV irradiation 60 s (365 nm).

Sample	Φ_f (%)	τ_{FL} (ns)	k_r
CZ-SP	2.0	1.14	1.7×10^7
NA-SP	5.3	0.60	8.0×10^7

Radiative rates (k_r) = Φ_f/τ_{FL}.