Supplementary information

Dual host-guest interactions-mediated photoswitchable fluorescent supramolecular polymers for anti-counterfeiting and encryption

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Experimental section

Materials

All starting chemicals and solvents were purchased from commercial sources and used without further treatment, unless indicated otherwise. 9-(diethylamino)-5-oxo-5H-benzo[a]phenoxazin-2-yl-methacrylate (NRME) are prepared by our previous work and 2-(3,3-dimethyl-6'-nitrospiro[indoline-2,2'-thiochromen]-1-yl)ethanol (STP-OH) are prepared by previous work [1-2]. The water used throughout this work is the double-distilled water which was further purified with a Milli-Q system.

Characterization

^{1}H NMR spectra was recorded on a 500 MHz NMR spectrometer (Bruker Avance). UV-Vis spectra were recorded on a Shimadzu UV-2501PC spectrophotometer at room temperature. Fluorescence spectra and fluorescence lifetime (τ) measurements were carried out with a time-correlated single photon counting (TCSPC) nanosecond fluorescence spectrometer (Edinburgh FLS920) at ambient temperature (298 K).

Spectral test

Taking **SPS-4** as an example: the as-prepared solution containing NC-DSA-CN (0.35 mg), P(MMA$_{91}$-*co*-BA$_{52}$-*co*-P5A$_7$-*co*-AD$_7$) (0.93 mg), CDSP (7.2 μg), and DMSO (3 mL) was transferred to a cuvette. Subsequently, all samples were exposed to visible light for 2 min. For photo-response experiment, the samples were exposed to UV for different times and then tested. The fluorescence and absorption spectra were obtained using a time-correlated single photon counting (TCSPC) nanosecond fluorescence spectrometer (Edinburgh FLS920), and a Shimadzu UV-2501PC spectrophotometer, respectively. The excitation wavelength is 420 nm (λ_{ex} = 420 nm). For other samples containing NC-DSA-CN or CDSP, detailed sample information can be found in Table 1.

Information encryption

SPS-5 without CDSP and SPS-4 with CDSP were selected as encryption unit to add into the 96-well plates based on the binary codes of the standard 8 bit ASCII characters. Subsequently, all samples were exposed to visible light for 5 min. Finally, the optical photographs of these samples were recorded before and after UV irradiation.

Association constants between P5A and NC-DSA-CN

^{1}H NMR was used to measure the association constants (K_a) between P5A and NC-DSA-CN. P5A and NC-DSA-CN were dissolved in DMSO. The concentration of NC-DSA-CN was kept at 100 mM. The concentrations of P5A were 0, 3.7, 7.5, 11.2, 15.0, 18.1, 22.5 and 30 mM. ^{1}H NMR spectra of P5A/NC-DSA-CN mixtures in DMSO were measured. Due to the host-guest interaction between P5A and NC-DSA-CN, the signals of protons will shift. A modified Benesi-Hildebrand equation (1) was used for the calculation of the association constants between P5A and NC-DSA-CN.

$$\frac{1}{\Delta\delta_{obs}} = \frac{1}{\Delta\delta} \cdot \frac{1}{K_a} \cdot \frac{1}{C_{P5A}} + \frac{1}{\Delta\delta} \quad (1)$$

where $\Delta\delta_{obs}$ is the observed shifts of the peaks; K_a is the association constant; $\Delta\delta$ is a constant correlated to the concentration of the NC-DSA-CN; and C_{P5A} is the concentration of P5A.

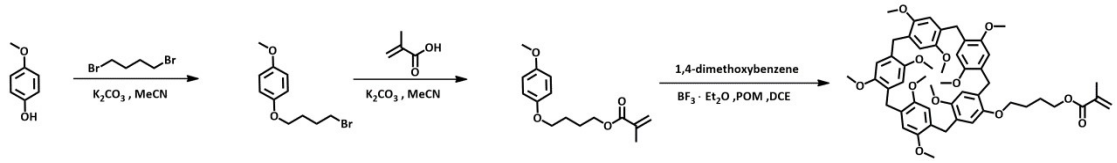

Figure S1. Synthetic route of P5A-Aly.

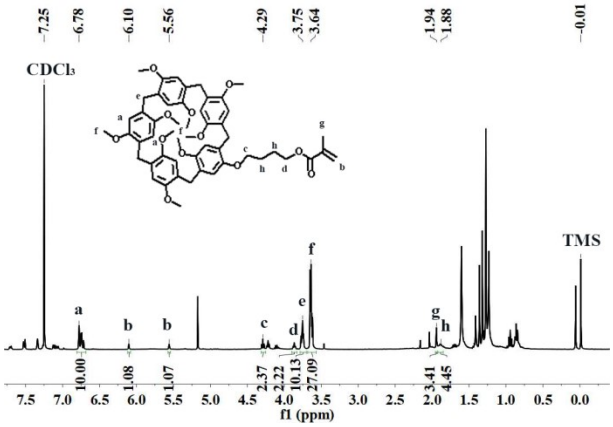

Figure S2. ^{1}H-NMR spectrum (in $CDCl_3$) of P5A-Aly.

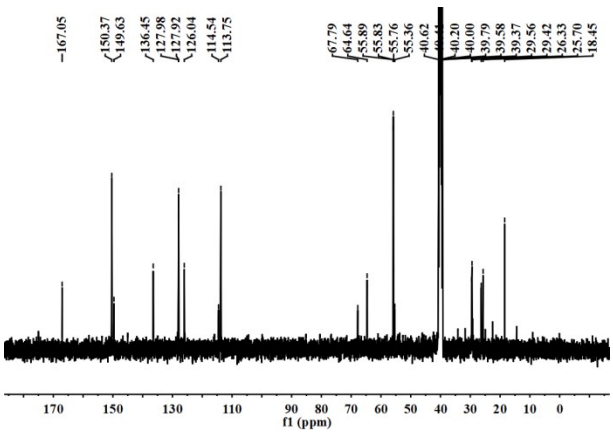

Figure S3. ^{13}C-NMR spectrum (in $CDCl_3$) of P5A-Aly.

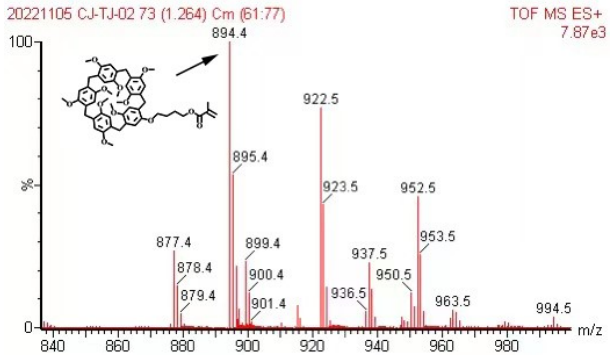

Figure S4. TOF MS spectrum of P5A-Aly.

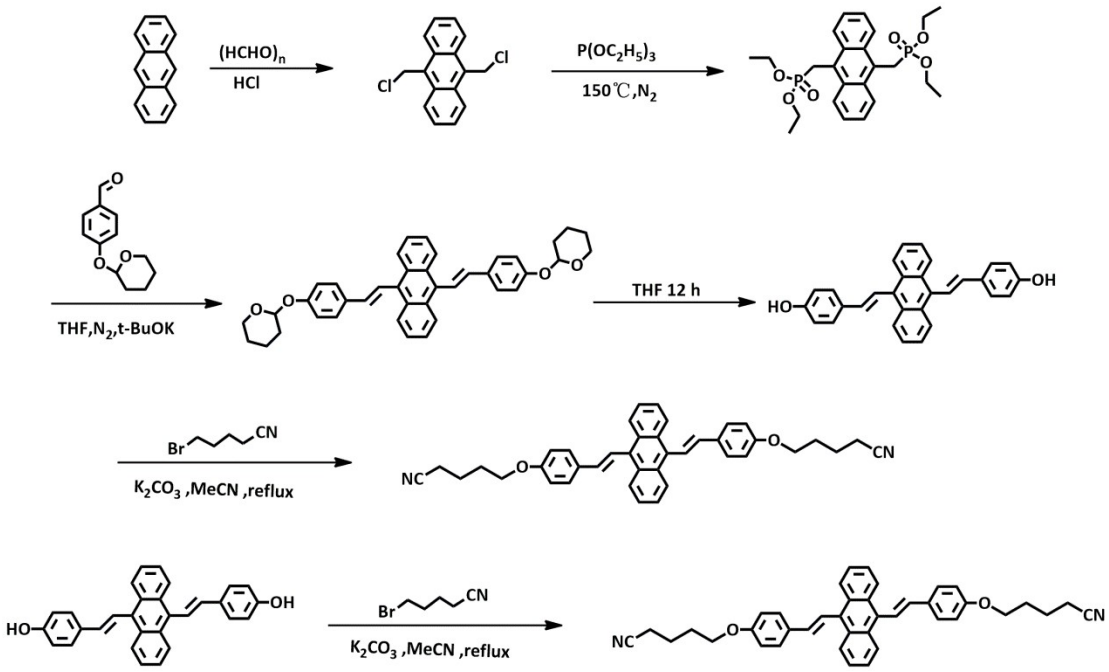

Figure S5. Synthetic route of NC-DSA-CN.

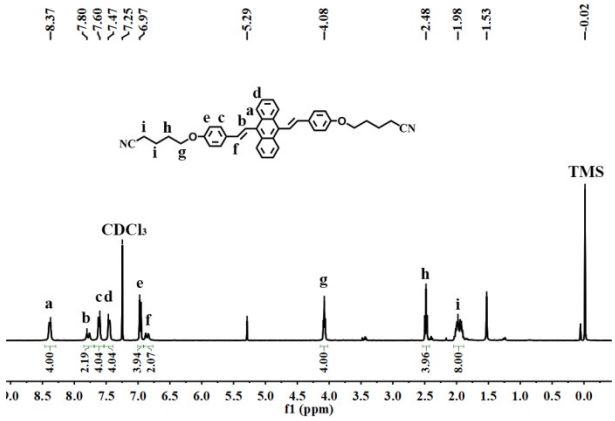

Figure S6. ^{1}H-NMR spectrum (in $CDCl_3$) of P5A-Aly.

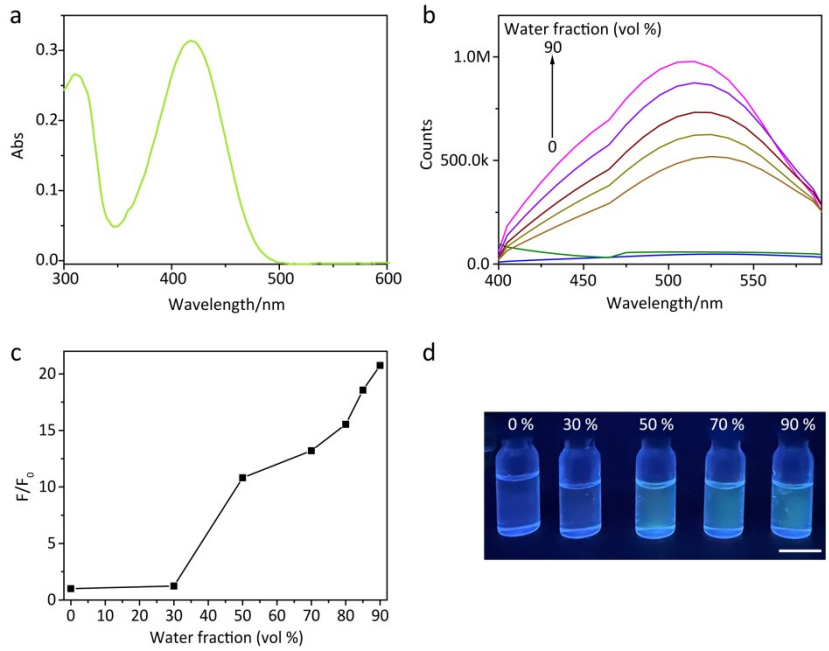

Figure S7. (a) The absorption spectra of NC-DSA-CN in DMSO. (b) Fluorescence emission spectra of NC-DSA-CN (10 μM) in water/DMSO mixtures, f_w= 0-90 vol%. (c) Plot of peak intensity of NC-DSA-CN versus f_w in the mixtures. (d) The photographs of NC-DSA-CN (10 μM) in water/DMSO mixtures, f_w= 0-90 vol%. The scale bars is 0.5 cm.

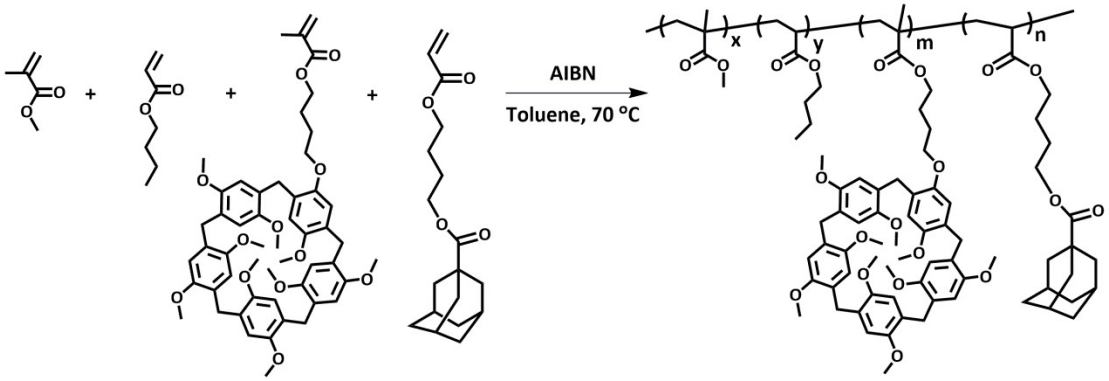

Figure S8. Synthetic route of P(MMA-*co*-BA-*co*-P5A-*co*-AD) (**P0**).

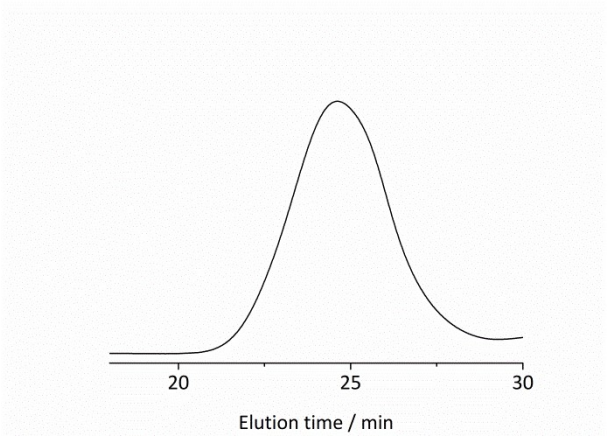

Figure S9. GPC trace of P(MMA-*co*-BA-*co*-P5A-*co*-AD).

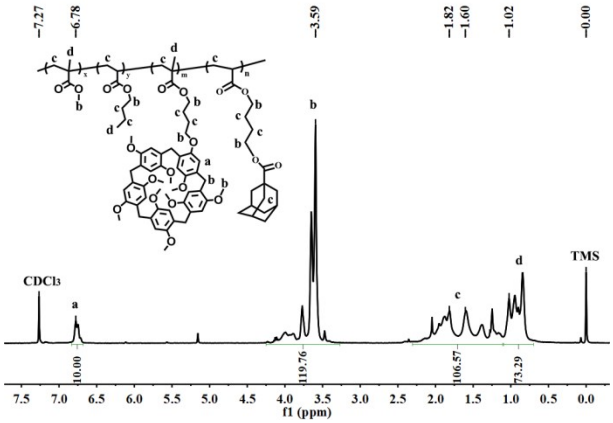

Figure S10. ^{1}H-NMR spectrum (in $CDCl_3$) of P(MMA-*co*-BA-*co*-P5A-*co*-AD).

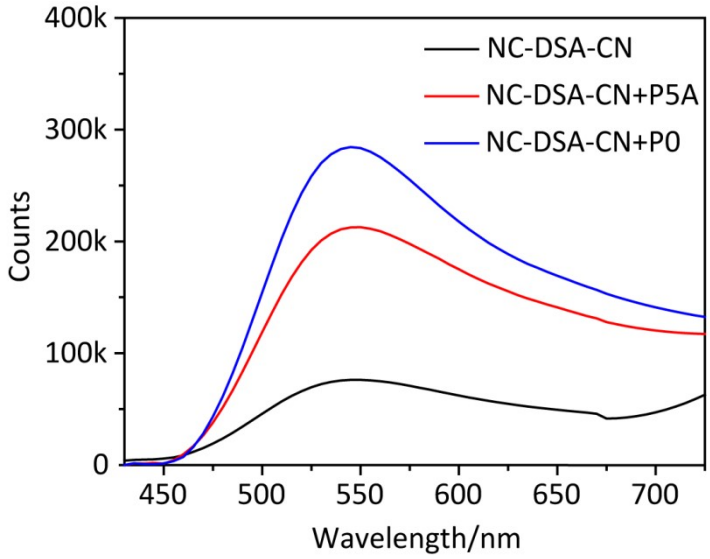

Figure S11. Fluorescence emission spectra of NC-DSA-CN in DMSO, the mixture of NC-DSA-CN and P5A, the mixture of NC-DSA-CN and P0 in DMSO.

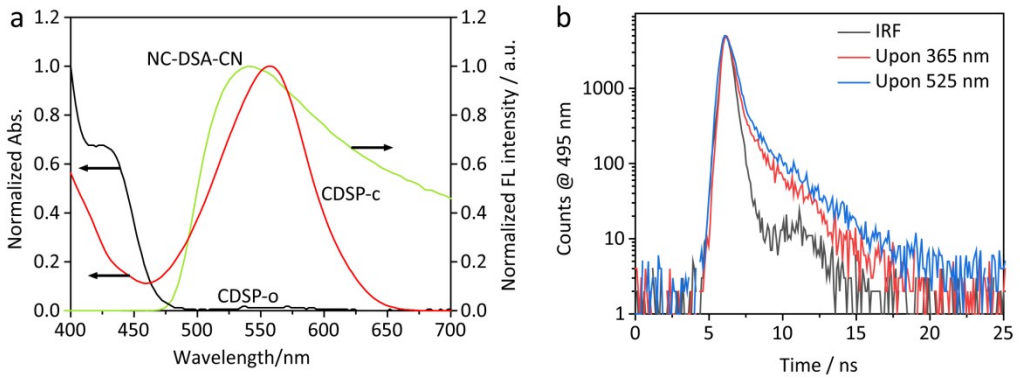

Figure S12. The normalized emission spectrum of NC-DSA-CN and the absorption spectrum of CDSP (before and after 365 nm UV irradiation) in DMSO. (b) Fluorescence lifetime changes of SPS-4 under alternating 365 nm UV and 525 nm Visible light.

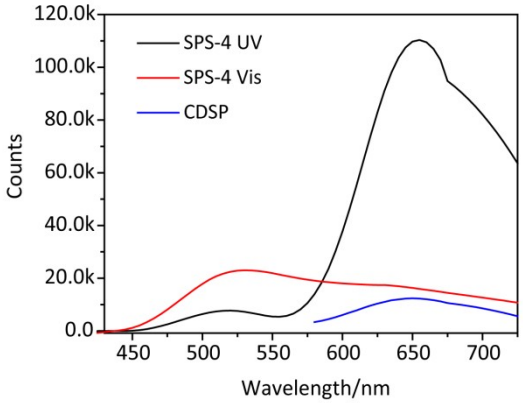

Figure S13. Fluorescence spectra of SPS-4 under alternating 365 nm UV and 525 nm Visible light (red trace: λ_{ex} = 365 nm, black trace: λ_{ex} = 365 nm, blue trace, λ_{ex} = 560 nm). The blue trace represents the fluorescence spectrum (λ_{ex}=560 nm) of CDSP in DMSO (1.8 μg/mL).

Antenna effect

The antenna effect under certain concentrations of donor and acceptor equals the ratio of the emission intensity at 655 nm of the acceptor upon excitation of the donor.[1]

$$Antenna\ effect = \frac{I^{655nm}_{SPS-3+UV(\lambda_{ex}\,=\,365\,nm)} - I^{655nm}_{SPS-3(\lambda_{ex}\,=\,365\,nm)}}{I^{655nm}_{SPS-5-UV(\lambda_{ex}\,=\,560\,nm)}}$$

where $I^{655nm}_{SPS-3+UV(\lambda_{ex}\,=\,365\,nm)}$ and $I^{655nm}_{SPS-3(\lambda_{ex}\,=\,365\,nm)}$ are the fluorescence intensities of SPS-4 under alternating 365 nm UV and 525 nm Visible light, $I^{655nm}_{SPS-5-UV(\lambda_{ex}\,=\,560\,nm)}$ the fluorescence

intensities of CDSP in DMSO (SPS-5) under the irradiation of UV, respectively. The antenna effect value was calculated as 7.99.

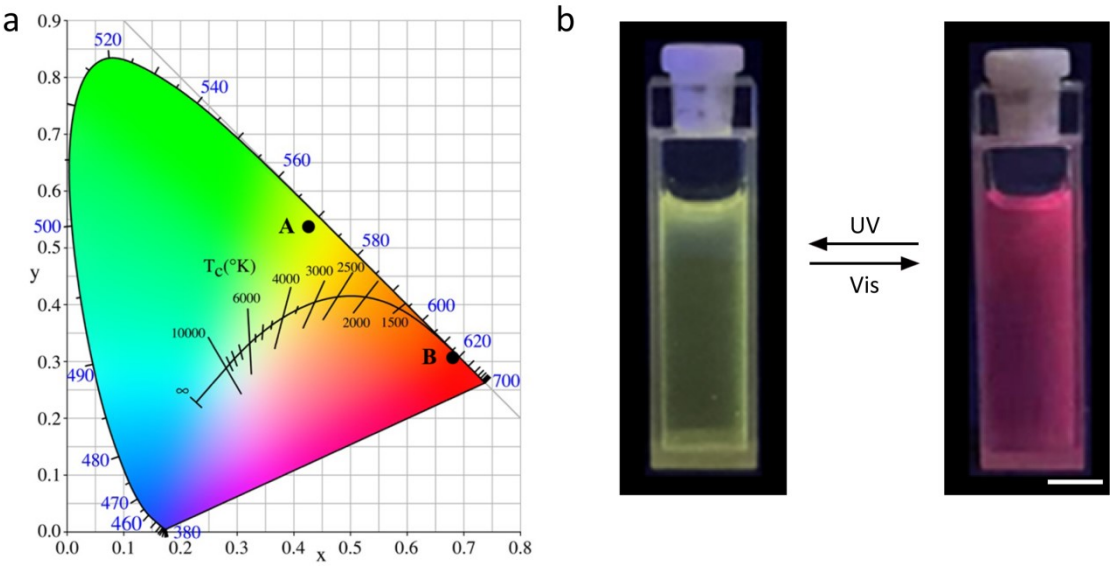

Figure S14. (a) CIE coordinates of supramolecular polymer solution SPS-4: A (initial state), B (after 365 nm UV irradiation). (b) Fluorescence transition of SPS-4. All scale bars are 0.5 cm.

Figure S15. Optical photographs of packaging box.

Reference

1. J.-J. Li, Y. Chen, J. Yu, N. Cheng and Y. Liu, *Adv. Mater.*, 2017, **29**, 1701905.