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Electronic Supplementary Information

Supramolecular hydrogel with tunable multi-color and white-light fluorescence from sulfato-β-cyclodextrin and aminoclay

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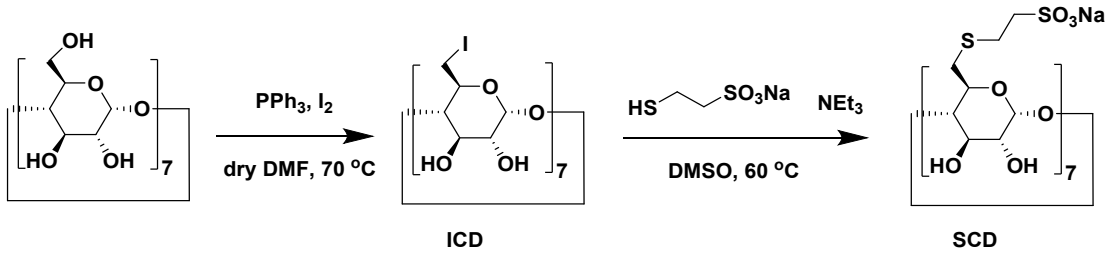
1. Generial information

Materials. All reagents and solvents were obtained from commercial suppliers and used as received unless specified otherwise. All aqueous solutions were prepared with distilled water.

Purification and characterization. ^{1}H NMR spectra were recorded on a Bruker DMX 400 MHz spectrometer. SEM images were obtained with a JSM-7500F scanning electron microscope. Solid-state fluorescence emission spectra were measured on a FLS 920P fluorescence spectrophotometer. Zeta potentials were measured with a Zeta PALS+BI-90 instrument (Brookhaven Co. USA). The rheology test was done on an AR 2000ex (TA Instrument) system, and 40 mm parallel plates were used during the experiment at the gap of 800 μm.

2. Synthesis procedure of target molecules.



Scheme S1 Synthesis route of **SCD**

ICD[S1]: Triphenylphosphine (20.2 g, 77.0 mmol) was dissolved in dry DMF (80 mL) and iodine (20.2 g, 77.2 mmol) was carefully added during 10-15 minutes. Dry β-cyclodextrin (5 g, 4.4 mmol) was then added to the resulting dark-brown solution, which was stirred at 70 ºC under Ar atmosphere for 18 h. The resulting reaction mixture was concentrated under reduced pressure to half volume. The concentrated solution was adjusted to pH 9-10 by addition of 3 M sodium methoxide in methanol under cooling in an ice bath. Once at room temperature, the mixture was stirred for 30 minutes and was then poured over 400 mL of cold methanol under vigorous stirring to form a brownish precipitate. The precipitate was filtered, washed with methanol and air-dried. Soxhlet extraction with methanol of this solid was done until no more discoloration of the solvent could be seen, finally obtaining a white solid (7.70 g, 92 % yield). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ (ppm): 6.21–5.75 (m, 14H), 4.97 (d, J = 3.0 Hz,

7H), 3.79 (d, J = 9.4 Hz, 7H), 3.69–3.52 (m, 14H), 3.45–3.40 (m, 7H), 3.38–3.34 (m, 7H), 3.27 (t, J = 9.0 Hz, 7H).

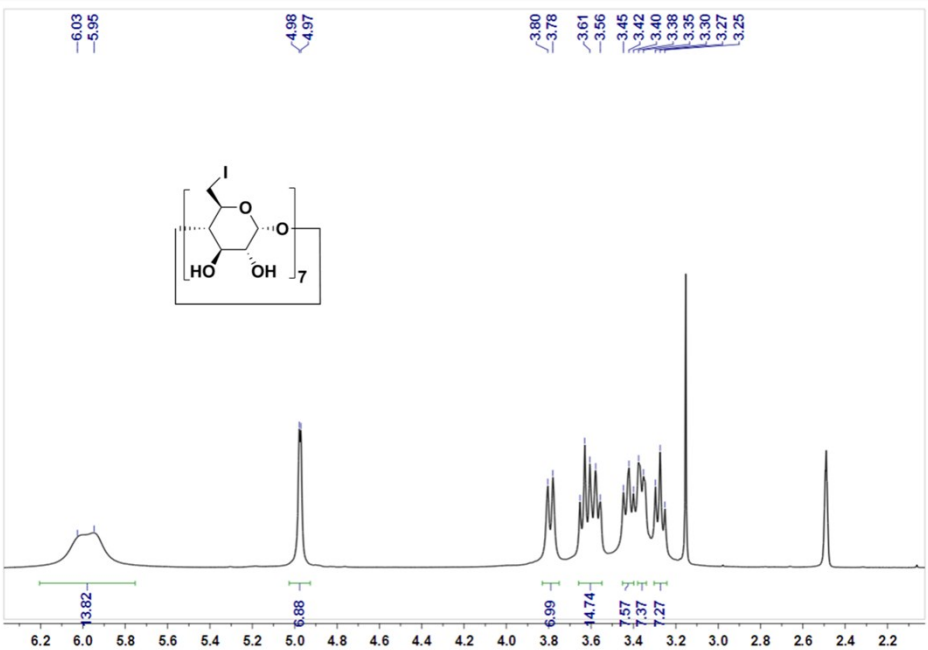


Figure S1 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K,) of **ICD**

SCD[S2]: **ICD** (1.33 g, 0.70 mmol), sodium 2-mercaptoethanesulfonate (2.00 g, 12.20 mmol) and triethylamine (1.70mL, 12.20 mmol) were dissolved in 10 mL DMSO. After heating to 60°C for three days, the product was precipitated in acetone, dissolved in water, nanofiltered and lyophilized; yield: 64%.^{1}H NMR (400 MHz, D_2O, 298 K): δ (ppm): 5.13 (d, J = 4 Hz, 7H), 4.05 (t, J = 7.2 Hz, 7H), 3.93 (t, J = 10 Hz, 7H), 3.68–3.55 (m, 14H), 3.24–3.10 (m, 21H), 3.05–2.88 (m, 21H).

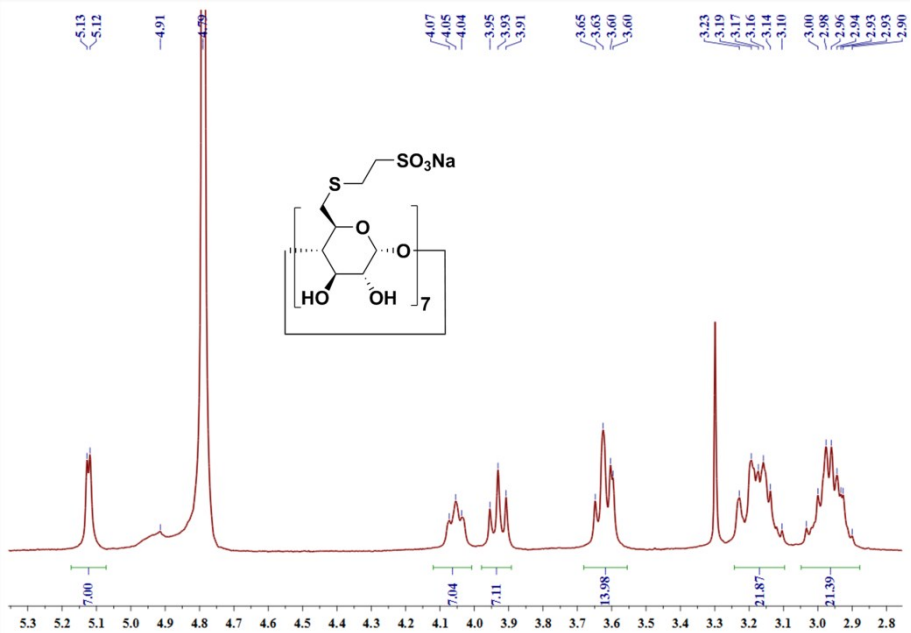
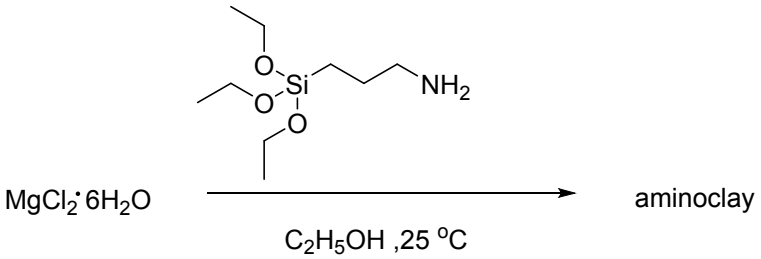


Figure S2 ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of SCD



Scheme S2 Synthesis route of aminoclay.

AC[S3]: 3-Aminopropyltriethoxysilane (2.59 mL, 11.10 mmol) was dissolved in 10 mL absolute ethanol, into which magnesium chloride hexahydrate (1.68 g, 8.30 mmol) solution in 40 mL absolute ethanol was added. After stirred 24 h at room temperature (20-25 °C), the white precipitate was collected by centrifugation, washed with ethanol for three times, and dried over vacuum. Finally, the product was obtained as the light yellow powder.

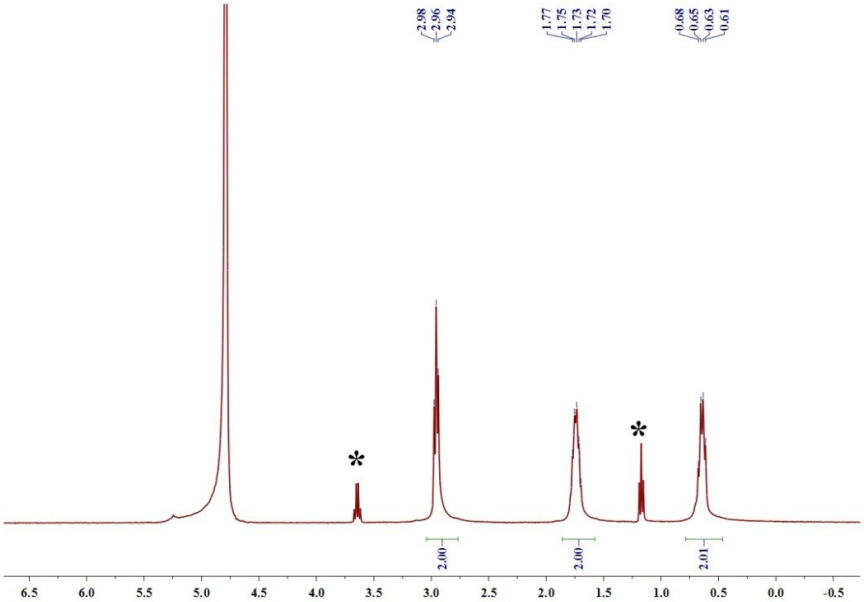
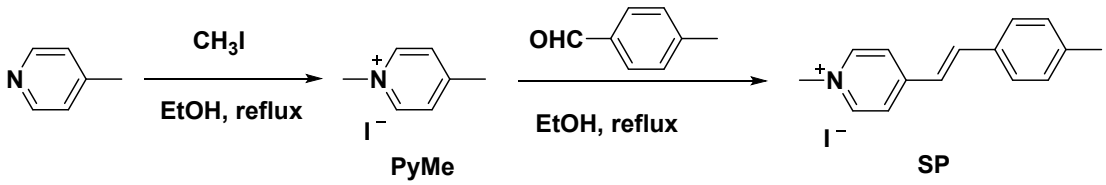


Figure S3 ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of aminoclay (**AC**) (* remarked as ethanol)



Scheme S3 Synthesis route of 4-methyl-styrylpyridinium (**SP**)

PyMe[S5]**:** CH_3I (4.26 g, 30 mmol) was added into the ethanol solution containing 4-methylpyridine (1.40 g, 15 mmol), and the mixture was refluxed for 12 h. After the removal of the solvent, a minimum amount of methanol was added to redissolve the residue. Then, the solution was added dropwise into Et_2O (300 mL) to generate a white precipitate. After

filtration the target product was obtain as a white solid (4.61 g, 93%). ^{1}H NMR (400 MHz, D_2O, 298 K): δ (ppm): 8.47 (d, J = 6.0 Hz, 2H), 7.75 (d, J = 6.0 Hz, 2H), 4.20 (s, 3H), 2.54 (s, 3H).

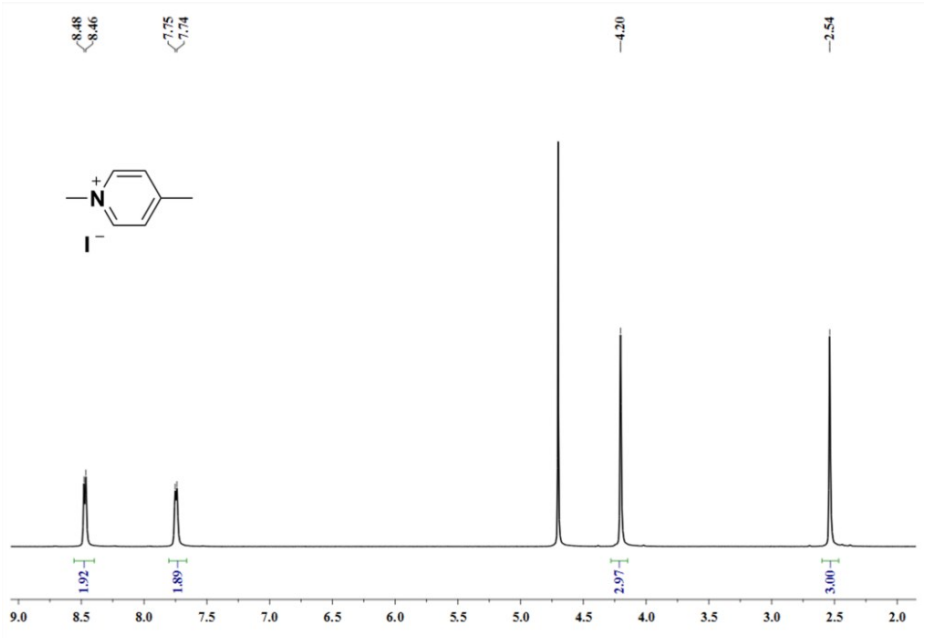


Figure S4 ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of **PyMe**

SP[S6]: PyMe (2.35 g, 10 mmol) and 4-methylbenzaldehyde (1.05 g, 10 mmol) were added into ethanol (30 mL), then three drops of piperidine was added under the refluxed condition. After stirred for 4h, the mixture was cooled to room temperature, and the participate was collected and recrystallized in ethanol. The target product was obtained as a yellow solid (2.19 g, 65% yield). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ (ppm): 8.84 (d, J = 6.8 Hz, 2H), 8.19 (d, J = 6.8 Hz, 2H), 7.97 (d, J = 16.4 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 16.4 Hz, 1H), 7.31 (d, J = 8.01 Hz, 2H), 4.24 (s, 3H), 2.36 (s, 3H).

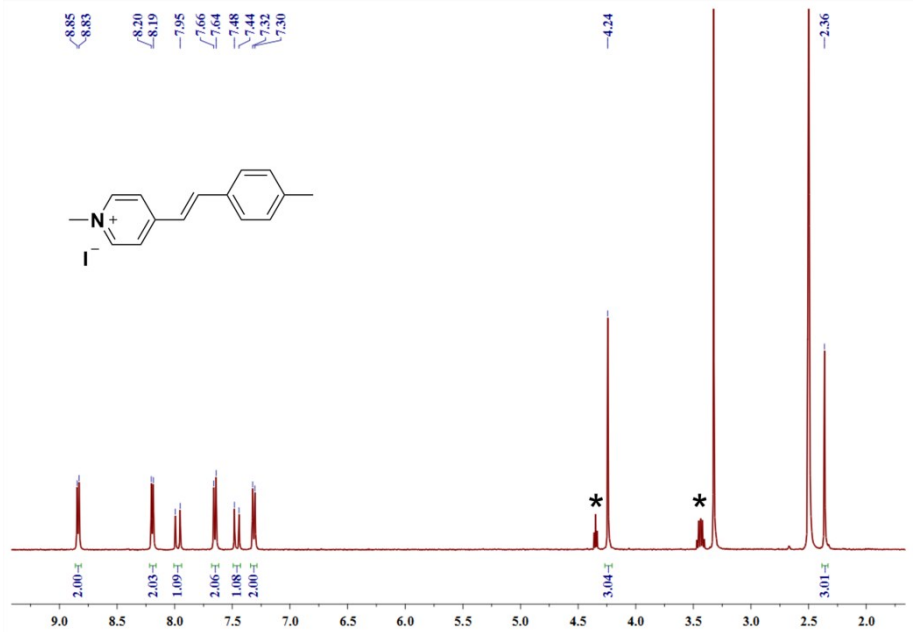


Figure S5 ^{1}H NMR spectrum (400 MHz, 298 K, D_2O) of **SP**

3. Partial 2D ROESY spectrum of SCD⊃SP complex

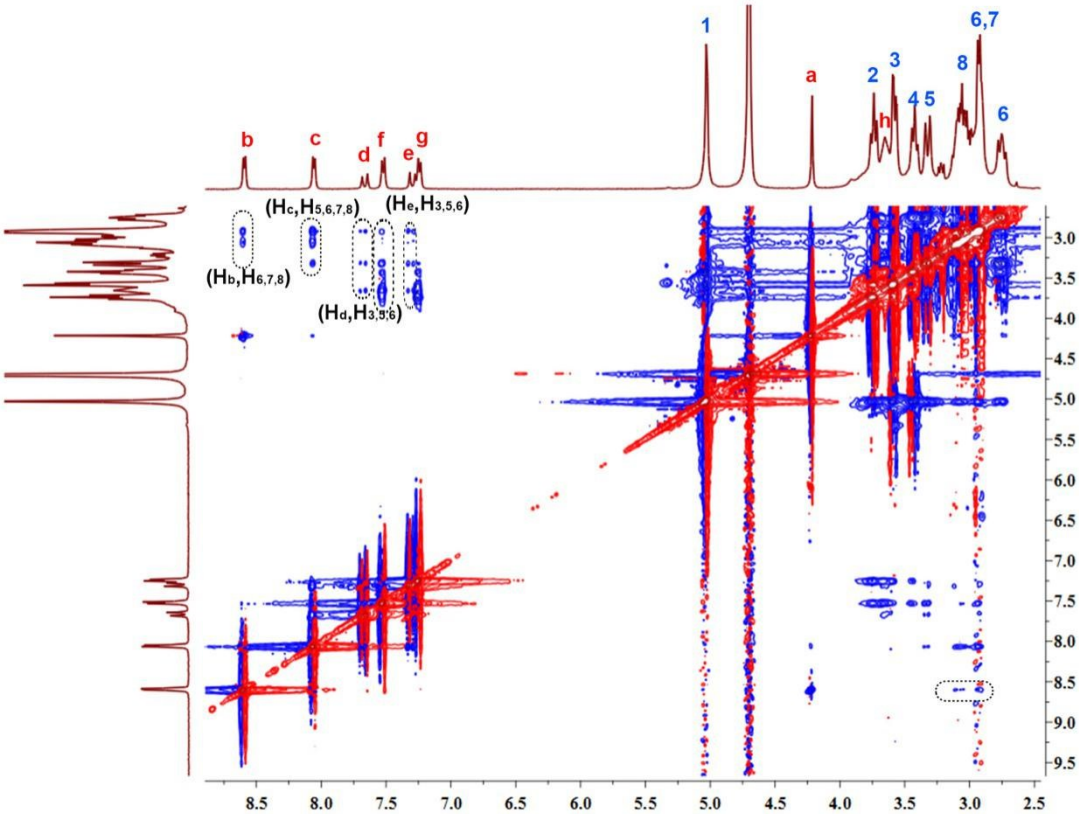


Figure S6. Partial 2D ROESY spectrum (400 MHz, 298 K, D2O) of **SCD⊃SP** ([**SCD**] = 32 mM, [**SP**] = 20 mM).

4. Job's plot for SCD⊃SP

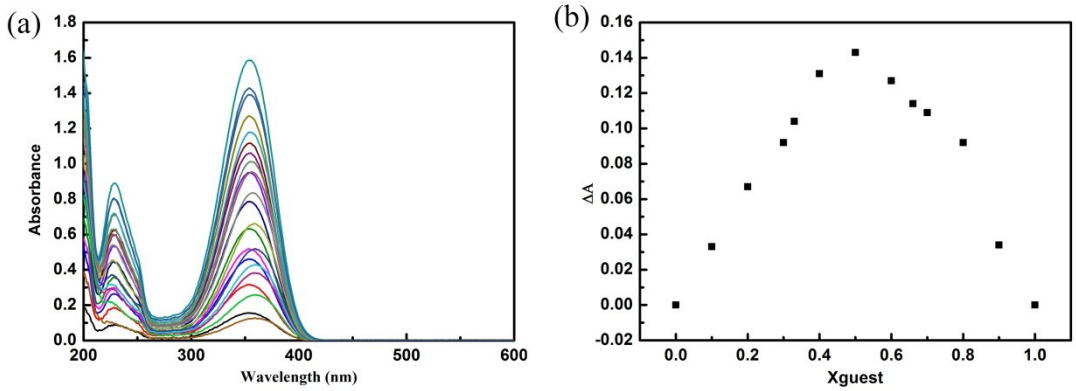


Figure S7 (a) UV-vis spectra of **SP** in presence and abesence of **SCD**, (b) Job's plot showing 1:1 stoichiometry of the complex between **SCD** and **SP** at 354nm. ([**SCD**] + [**SP**] = 0.1 mM)

5. Investigation of the binding constant between SCD and SP

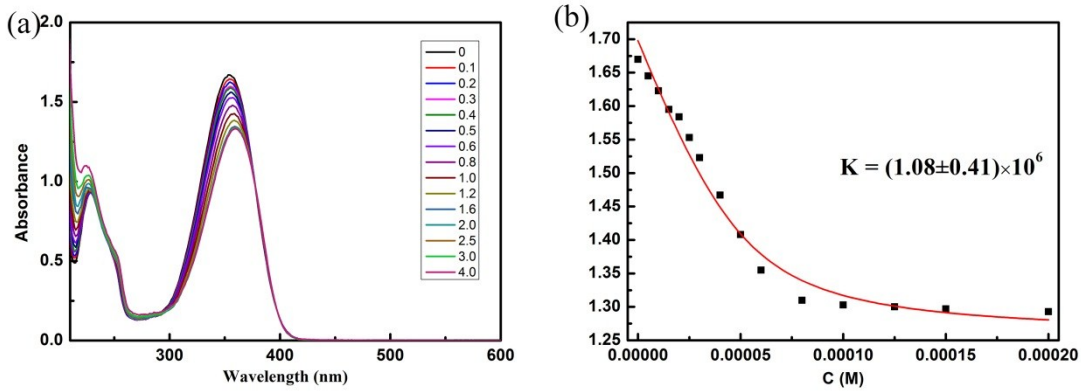


Figure S8 (a) Alterations of the UV/vis absorbance spectra of **SP** (50.0 μM) upon addition of **SCD** (0−200 μM), in aqueous solution at 298K, (b) The nonlinear curve fitting of the variation of UV/vis absorbance intensity with the concentration of **SCD** to calculate the association constant. $R^2 = 0.98$.

6. Zeta-potential of SCD⊃SP

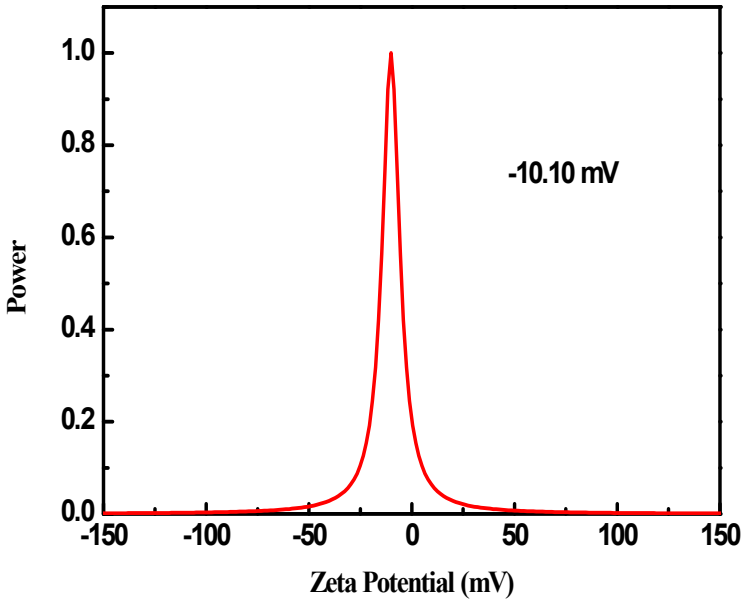


Figure S9 Zeta-potential of **SCD⊃SP**

7. Concentration-depended fluorescence emission behavior of SP

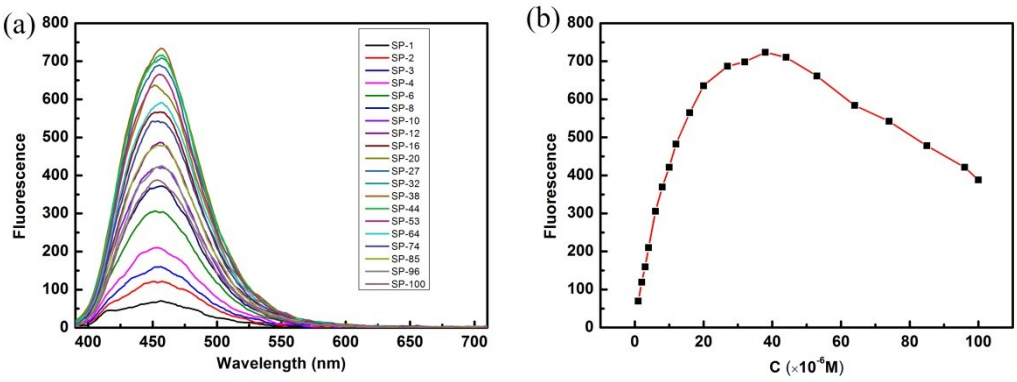


Figure S10. (a) Fluorescence emission spectra of **SP** (1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, 12.0, 16.0, 20.0, 27.0, 32.0, 38.0, 44.0, 53.0, 64.0, 74.0, 85.0, 96.0, 100.0 μM) in water at 298 K under 365 nm light, (b) The Concentration dependent relative emission intensities of **SP** at 455 nm.

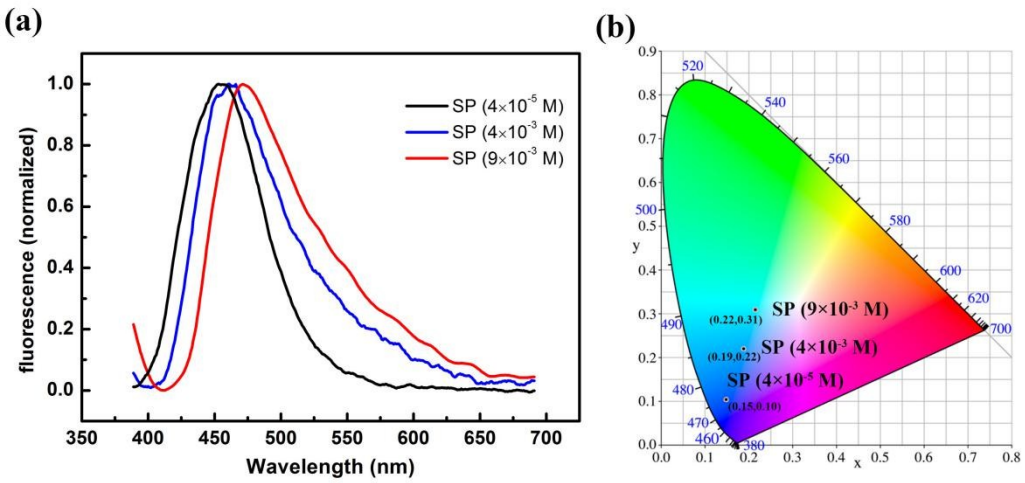


Figure S11. (a) Fluorescence emission spectra, and (b) the 1931 CIE chromaticity coordinate of **SP** in water at 298 K under 365 nm light.

8. Fluorescence decay cueves of AC/SCD⊃SP hydrogel

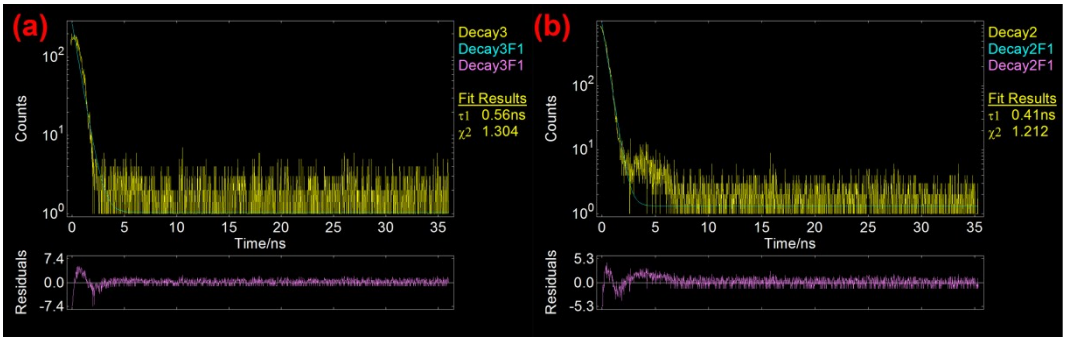


Figure S12. (a) Fluorescence decay curves of **AC/SCD⊃SP** hydrogel at 438 nm, and (b) fluorescence decay curves of **AC/SCD⊃SP** hydrogel at 560 nm.

9. Flourescence emission spectrum of AC/SA-SP hydrogel

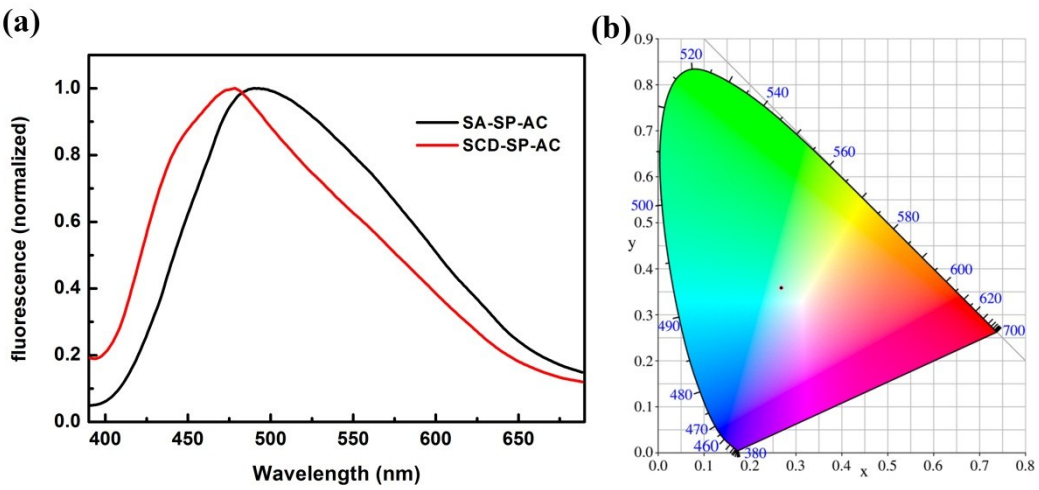


Figure S13. (a) Florescence emission of **AC/SCD⊃SP** and **AC/SA-SP** with same SP concentration and (b) The 1931 CIE chromaticity coordinate of **AC/SA⊃SP** under 365 nm light

10. Flourescence images of PVA/SCD⊃SP hydeogel

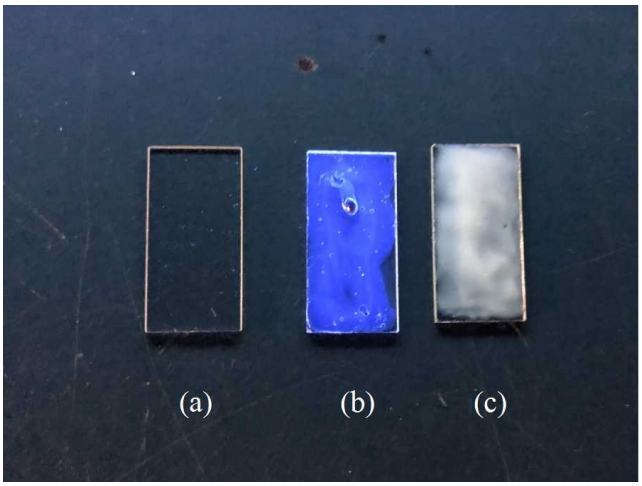


Figure S14. Images of luminescent films on quartz substratequartz plate (a) blank (b) **PVA/SCD⊃SP** (c) **AC/SCD⊃SP** under 365 nm light.

11. Rheology and SEM of AC/SCD⊃SP hydrogels with different SP/SCD molar ratio

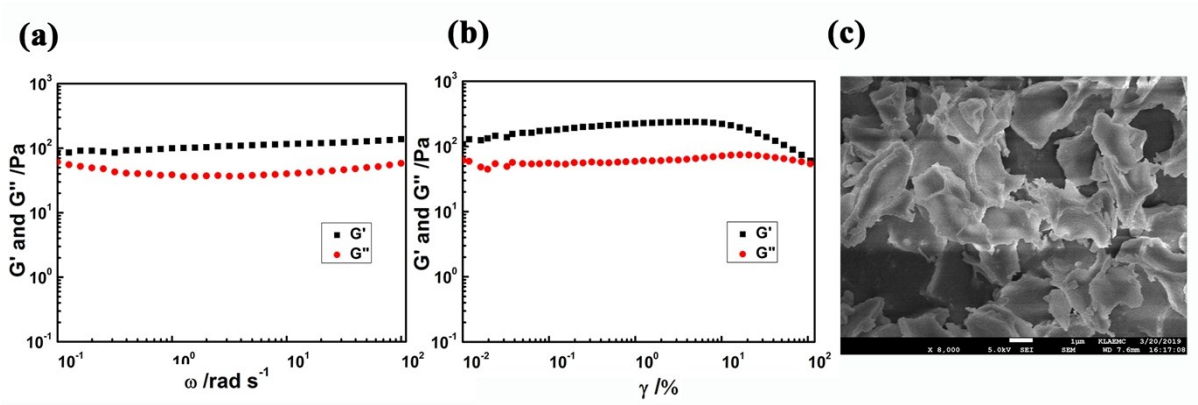


Figure S15. (a) Oscillation frequency sweep of **AC/SCD⊃SP**(SP/SCD = 0.94) hydrogel at a constant strain of 1%, (b) Strain sweep of hydrogel at a constant frequency of 1 Hz. (storage modulus G' (black, ■), loss modulus G'' (red, ●, all the experiments were carried out at 20 °C), (c) SEM image of the **AC/SCD⊃SP** hydrogel.

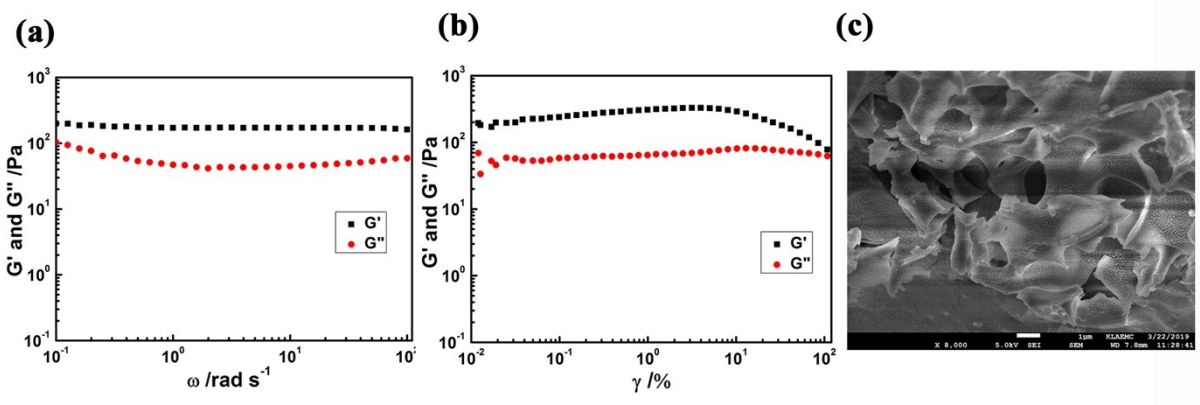


Figure S16. (a) Oscillation frequency sweep of **AC/SCD⊃SP**(SP/SCD = 0.63) hydrogel at a constant strain of 1%, (b) Strain sweep of hydrogel at a constant frequency of 1 Hz. (storage modulus G' (black, ■), loss modulus G'' (red, ●, all the experiments were carried out at 20 °C), (c) SEM image of the **AC/SCD⊃SP** hydrogel.

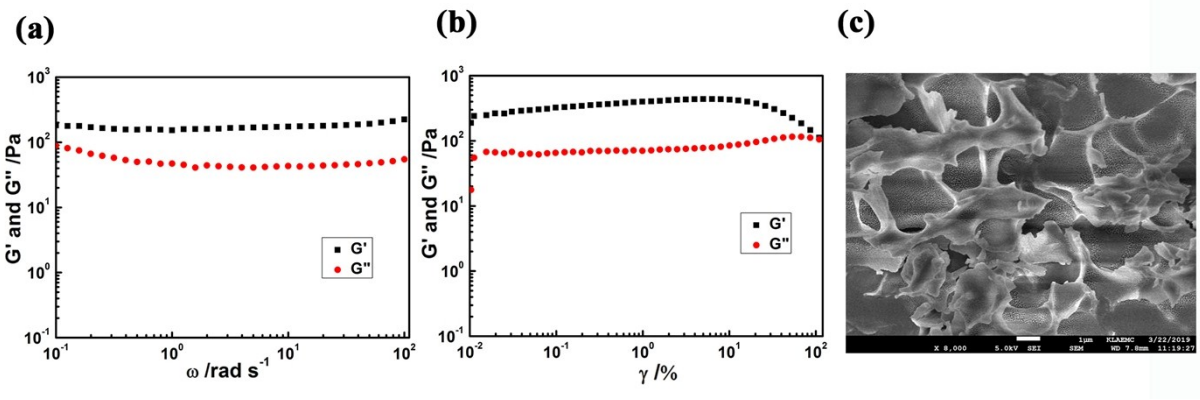


Figure S17. (a) Oscillation frequency sweep of **AC/SCD⊃SP**(SP/SCD = 0.47) hydrogel at a constant strain of 1%, (b) Strain sweep of hydrogel at a constant frequency of 1 Hz. (storage modulus G' (black, ■), loss modulus G'' (red, ●, all the experiments were carried out at 20 °C), (c) SEM image of the **AC/SCD⊃SP** hydrogel.

12. Flourescence emission spectra of AC/SCD⊃SP hydrogels

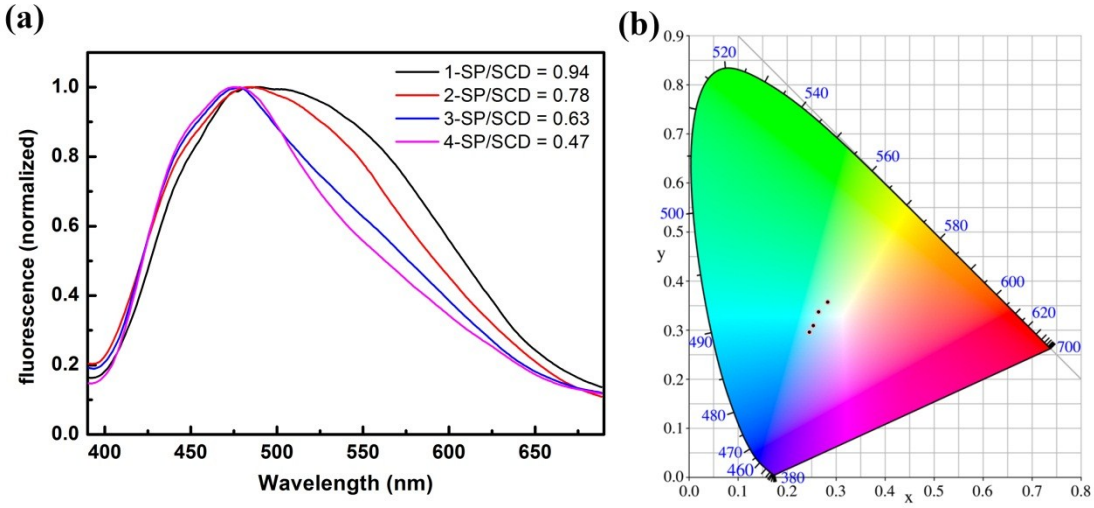


Figure S18. (a) Florescence emission spectra of **AC/SCD⊃SP** hydrogel, and (b) The 1931 CIE chromaticity coordinate of **AC/SCD⊃SP** hydrogels under 365 nm light, which **AC**'s content was 50 mg, with different **SP**/**SCD** molar ratio of 0.94, 0.78, 0.63, 0.47.

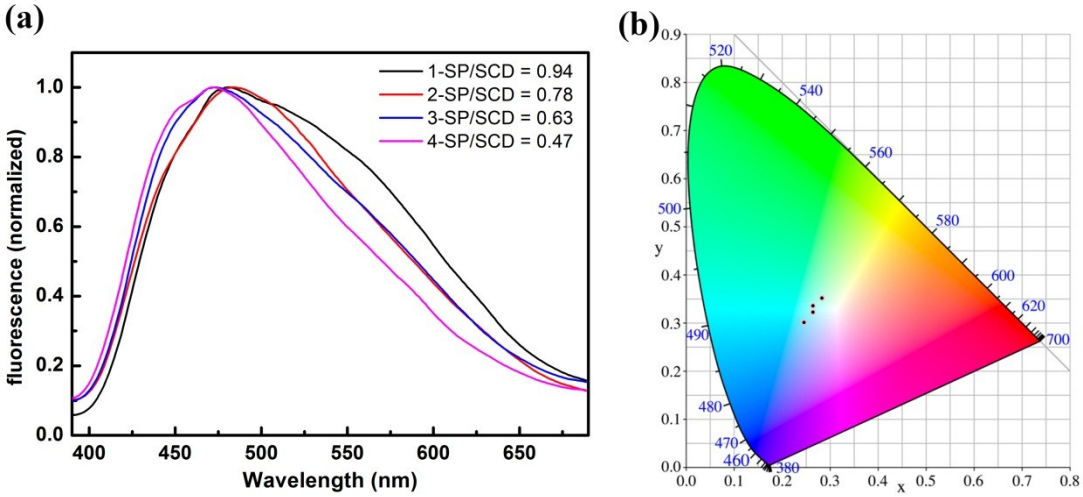


Figure S19. (a) Florescence emission spectra of **AC/SCD⊃SP** hydrogel and (b) The 1931 CIE chromaticity coordinate of **AC/SCD⊃SP** hydrogels under 365 nm light, which AC's content was 40 mg, with different **SP**/**SCD** molar ratio of 0.94, 0.78, 0.63, 0.47

13. Reference

[S1] M. Padilla, F. Peccati, J. L. Bourdelande, X. Solans-Monfort, G. Guirado, M. Sodupe and J. Hernando, *Chem. Commun.*, 2017, **53**, 2126.

[S2] A. Steffen, C. Thiele, S. Tietze, C. Strassnig, A. Kämper, T. Lengauer, G. Wenz and J. Apostolakis, *Chem. Eur. J.*, 2007, **13**, 6801.

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[S5] L.-Y. Wang, X.-G. Zhang, Y.-P. Shi and Z.-X. Zhang, *Dyes and Pigments*, 2004, **62**, 21.