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Supporting Information

Polymerization Boosting Cascade Energy Transfer Based on Opened Glucopyranosyl β-cyclodextrin

Jie Yu,[a] Hui Wang,[a] Xian-Yin Dai,[a] Jie Niu[a] and Yu Liu[ab]*

[a]Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University Tianjin 300071, P. R. China

[b]Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

E-mail: yuliu@nankai.edu.cn

Materials and methods

β-cyclodextrin was purchased from Wako Company, the other chemicals and solvents were commercially available. The reaction was monitored using analytical thin layer chromatography (TLC). 200-300 mesh silica gel was applied in column chromatography. Both ^{1}H NMR and ^{13}C NMR spectrums were collected from Bruker Avance spectrometers, TMS as an internal standard. Varian Cary Eclipse fluorescence spectrometer and HITACHI fluorescence spectrophotometer (F-4600S) were applied to investigate the steady-state fluorescence spectrum. X-ray photoelectron spectroscopy (XPS) were collected on an instrument (Kratos Analytical Ltd.-Axis Ultra DLD) with monochromatized Al Kα X-ray source. The rheological properties of the hydrogel were performed on the AR-G2 rheometer (TA instruments, Etten-Leur, The Netherlands) equipped with 11 steel cone geometry of 20 mm diameter and a solvent trap. TEM pictures were investigated by a high-resolution transmission electron microscope (Philips Tecnai G2 20 S-TWIN microscope).

1. The Synthesis of aldehyde-β-cyclodextrin (ACD)

ACD was synthesized according to Mao and Ostrikov reported method.[1]

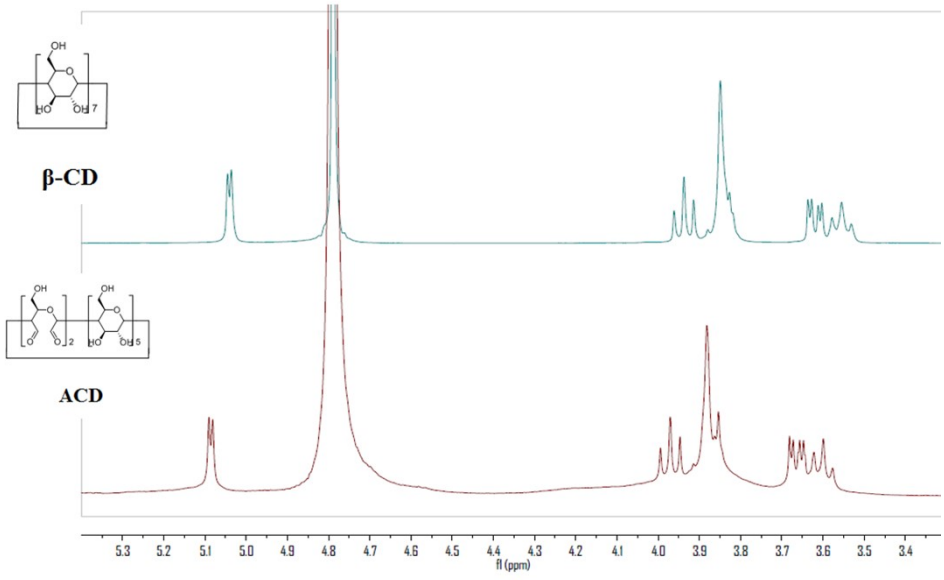


Figure S1. ^{1}H NMR (400 MHz) spectrum of β-CD and ACD in D_2O at room temperature.

2. The preparation of ACD/CS hydrogel:

Chitosan (100 mg, Deacetylation degree≥95%, Viscosity: 100-200 mpa.s) was added in 2% acetic acid solution (5 mL), stirring for 1 hour until it is completely dissolved. ACD was added to the Chitosan solution and stirred for 30 minutes, after that, the solution was heated to 50 ℃ for 1 hour to give hydrogel.

$$\text{ACD} + \text{CS} \xrightarrow{50\,℃} \text{GEL}$$

Sample	CS/mg	ACD/mg	
1	100	0	
2	100	30	
3	100	50	
4	100	70	
5	100	90	
6	100	100	Gel

Table S1. The condition for the formation of ACD/CS hydrogel.

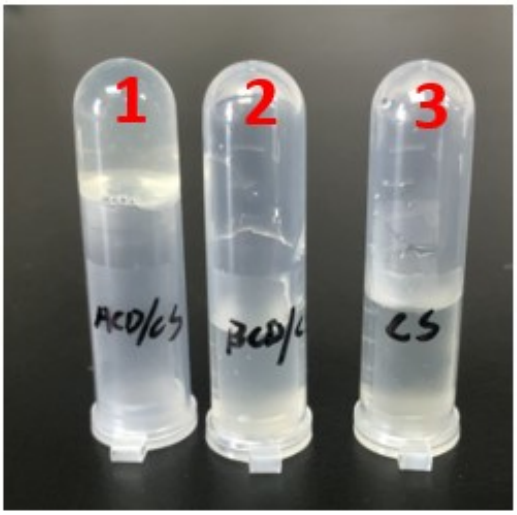


Figure S2. The pictures of 1)ACD/CS, 2)β-CD/CS and 3)CS.

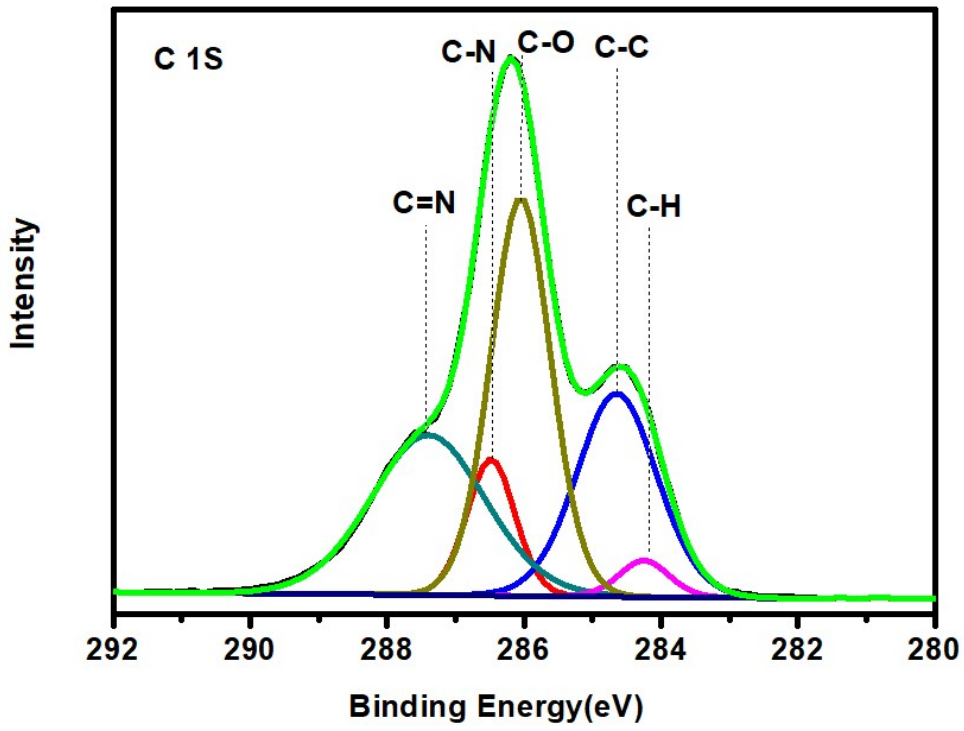


Figure S3. C1s X-ray photoelectron spectrum of ACD/CS

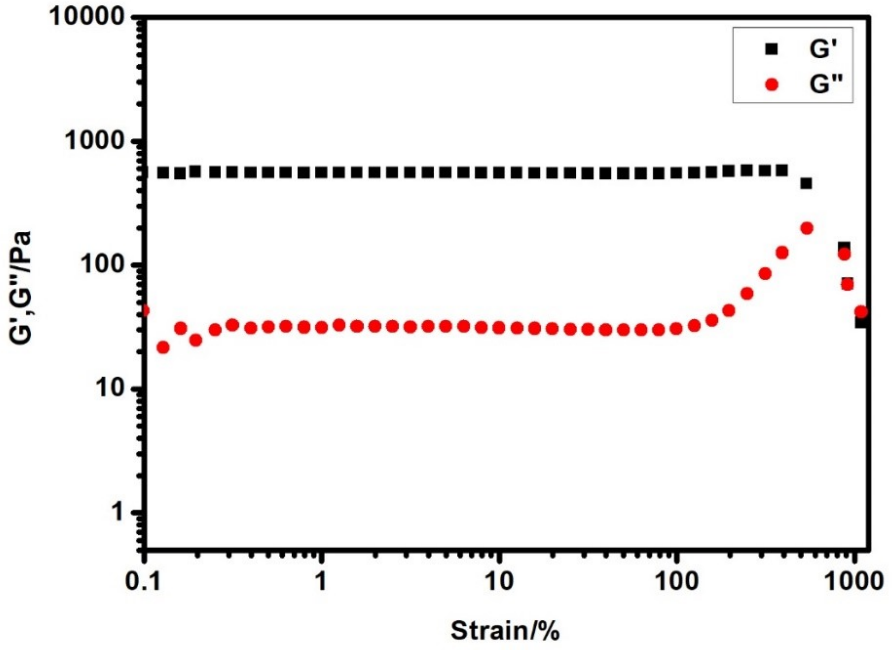


Figure S4. Strain sweep test of ACD/CS hydrogel (ω = 1.00 Hz).

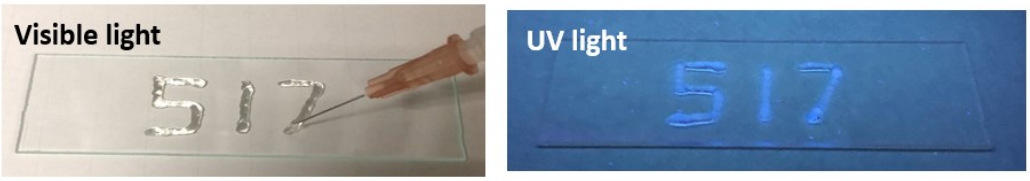


Figure S5. ACD/CS hydrogel was injected on glass plate under visible light and UV light (365 nm).

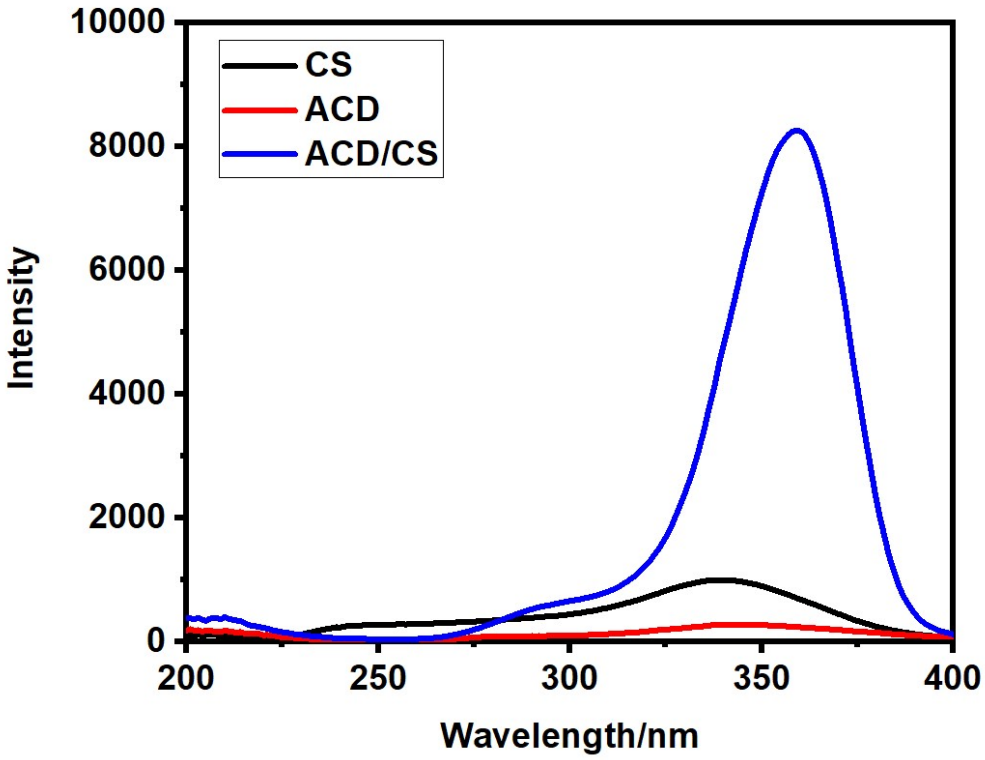


Figure S6. Excitation spectrum of CS, ACD and ACD/CS (λ_{em} = 425 nm).

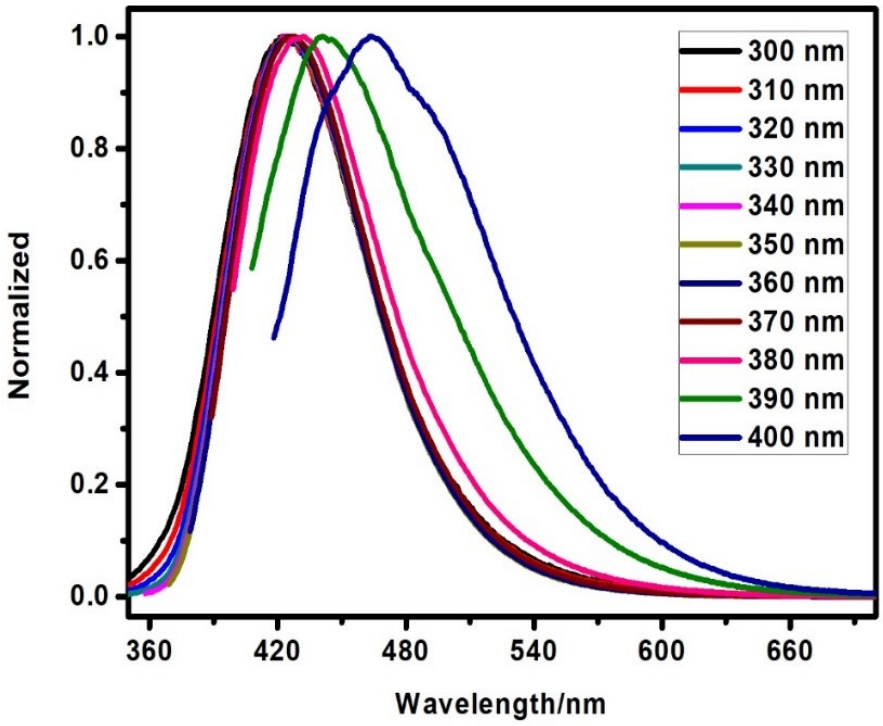


Figure S7. Fluorescence spectrum of ACD/CS under different excitation wavelength.

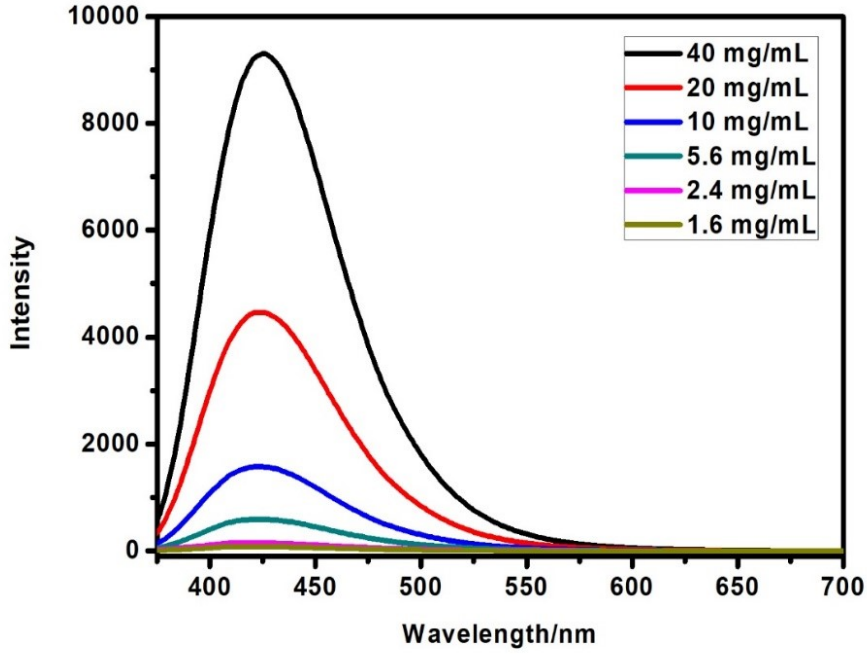


Figure S8. Fluorescence spectrum of ACD/CS in different concentrations.

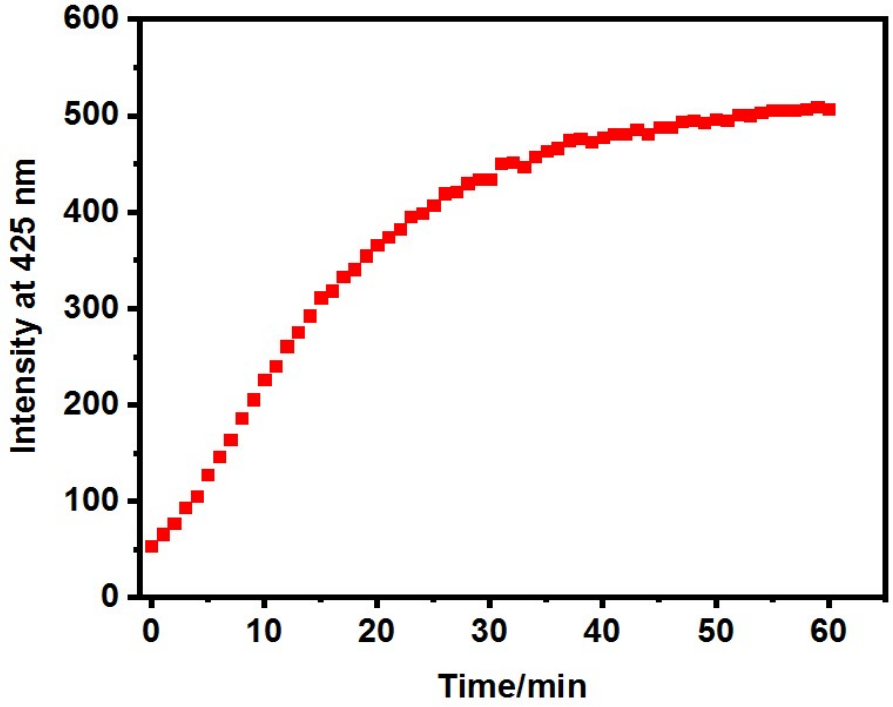


Figure S9. Fluorescence intensity of ACD/CS in different heating time at 50 ℃.

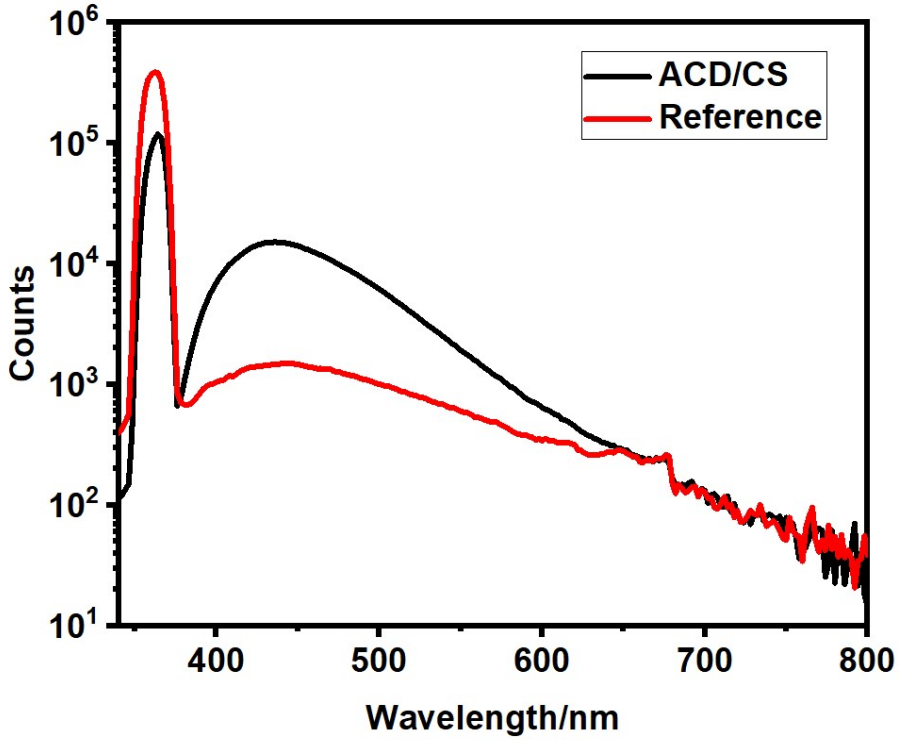


Figure S10. The absolute fluorescence quantum yield of ACD/CS (32.25%).

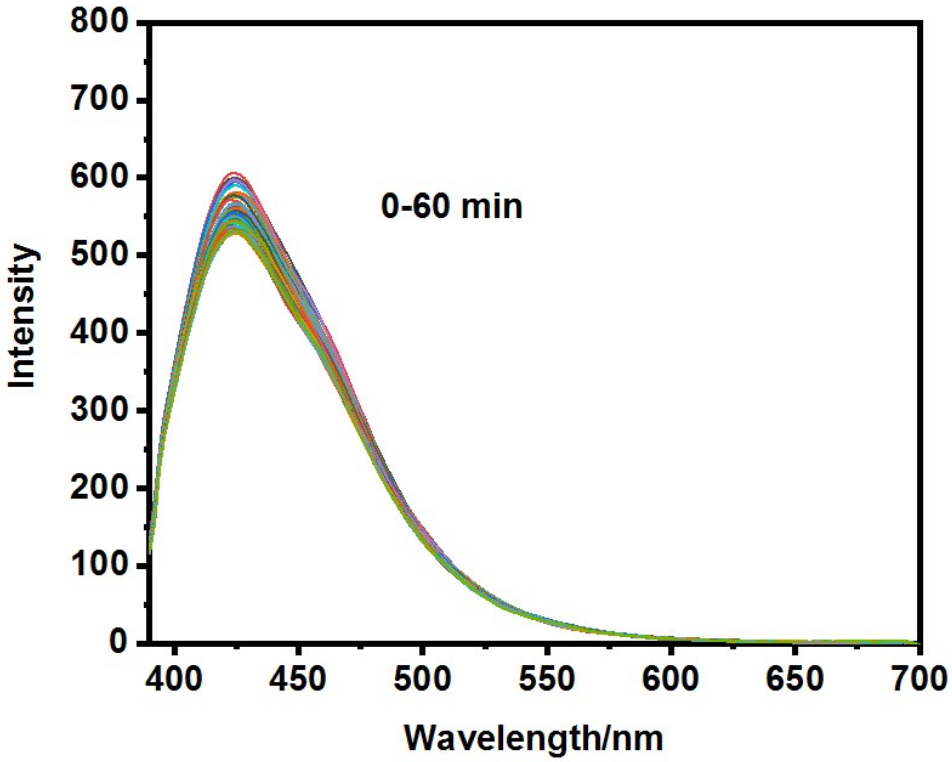


Figure S11 Fluorescence spectrum of ACD/CS hydrogel under different illumination time (λ_{ex} = 360 nm).

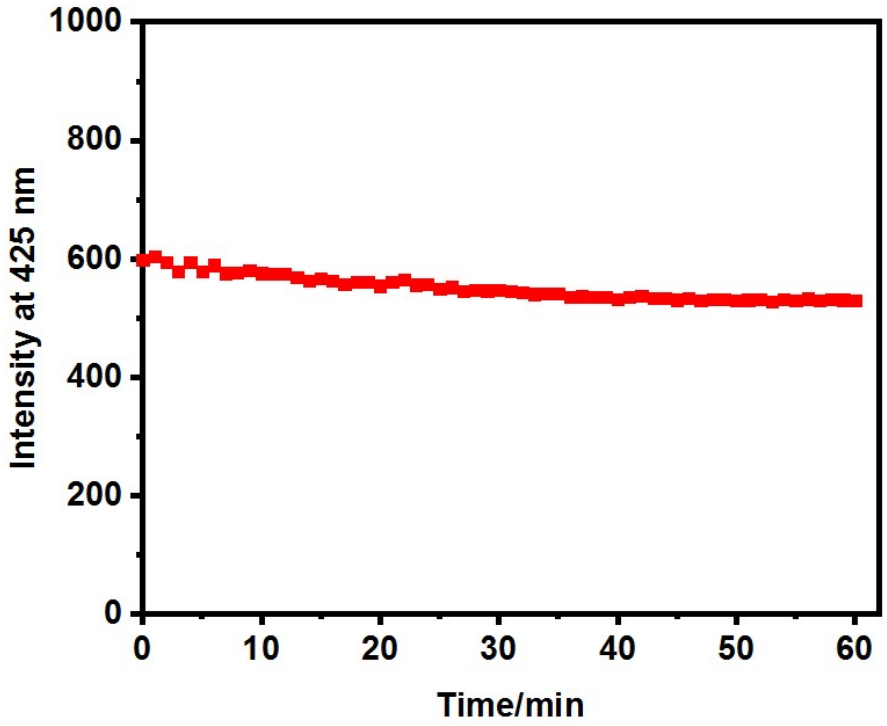
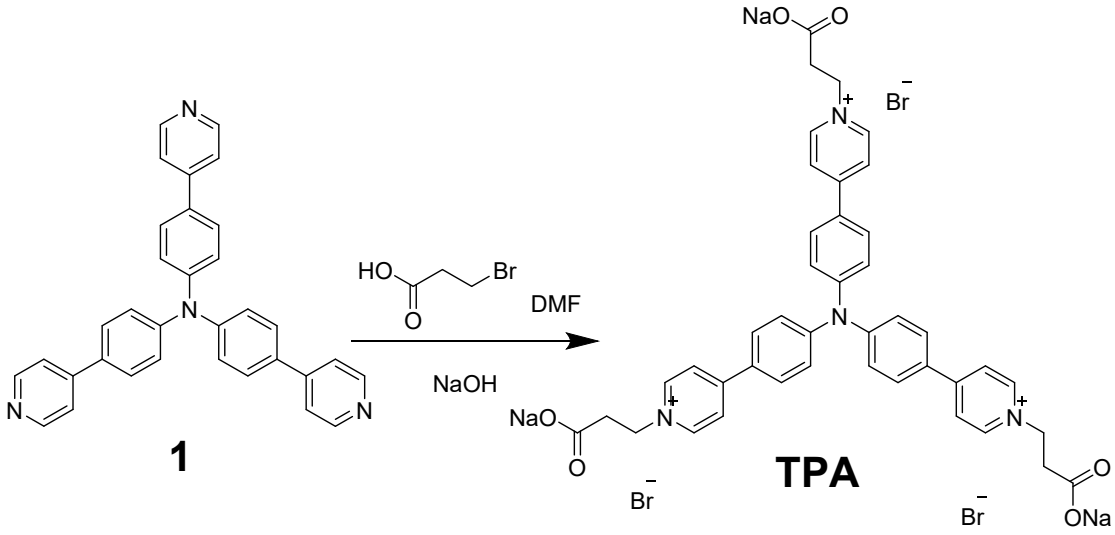


Figure S12. Fluorescence intensity of ACD/CS at 425 nm under different illumination time (λ_{ex} = 360 nm).

3. The Synthesis of TPA:



Compound 1 (200 mg, 0.42 mmol) and 3-Bromopropionic acid (385 mg, 2.52 mmol) were added in dry DMF and refluxed for 2 days. After that the above reaction mixture was poured in diethyl ether to give yellow precipitate, then filtrated. The yellow solid was dissolved in CH3OH, then added to the ethanol solution of NaOH give yellow precipitate, then filtrated and dried to give TPA (0.11 g, yield 26.2 %). ^{1}H NMR (400 MHz, D_2O) δ 8.81 (d, *J* = 6.8 Hz, 6H), 8.27 (d, *J* = 6.8 Hz, 6H), 7.97 (d, *J* = 8.8 Hz, 6H), 7.45 (d, *J* = 8.7 Hz, 6H), 4.83-4.82 (m, 6H), 3.13 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR(100 MHz, D_2O): δ 173.96, 155.25, 149.57, 144.39, 129.57, 128.84, 125.12, 123.80, 55.97, 34.66.

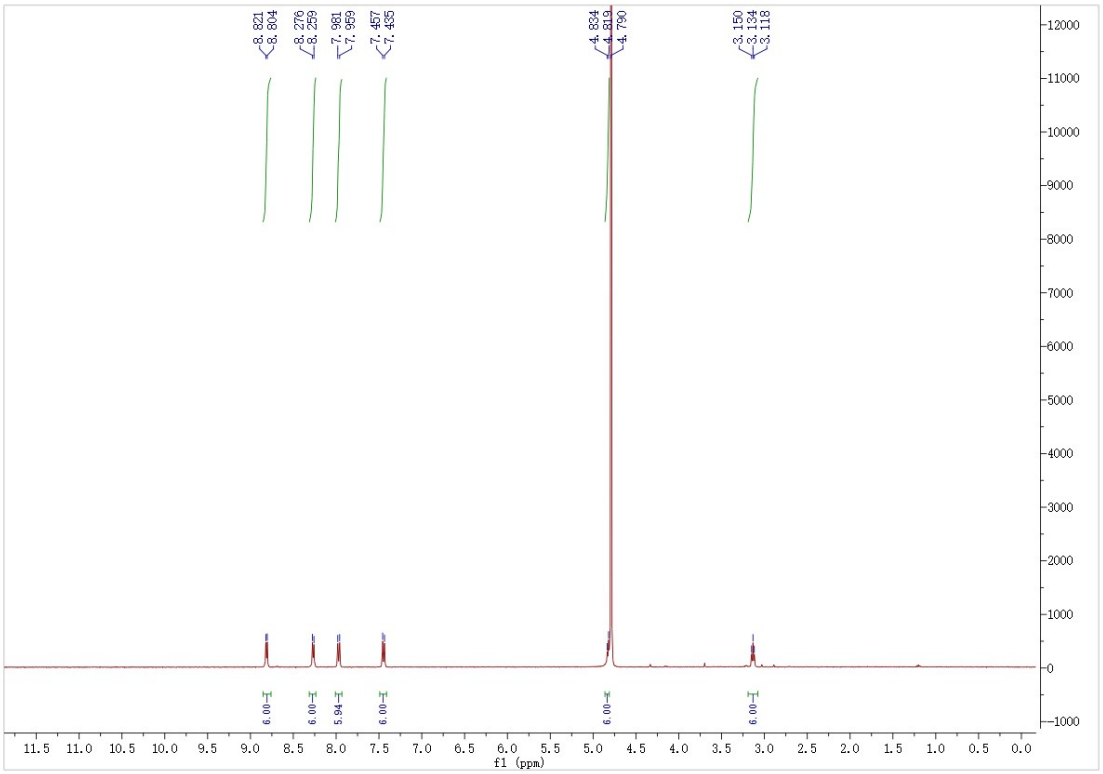


Figure S13. ^{1}H NMR (400 MHz) spectrum of TPA in D_2O at room temperature.

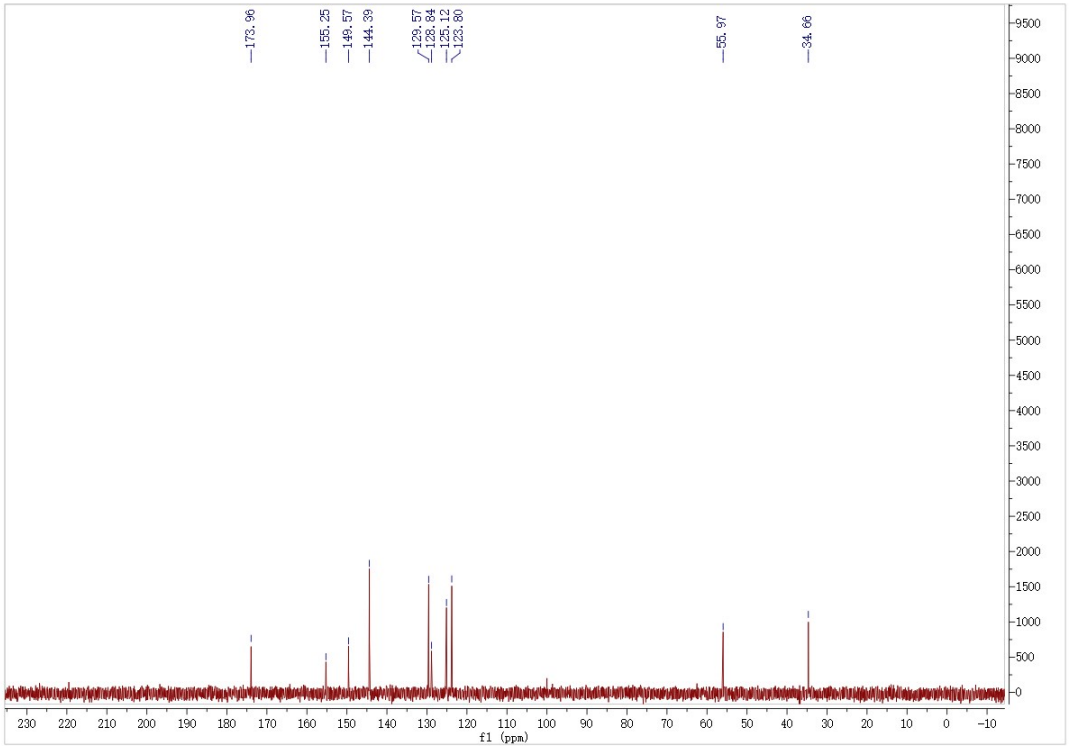


Figure S14. ^{13}C NMR (100 MHz) spectrum of TPA in D_2O at room temperature.

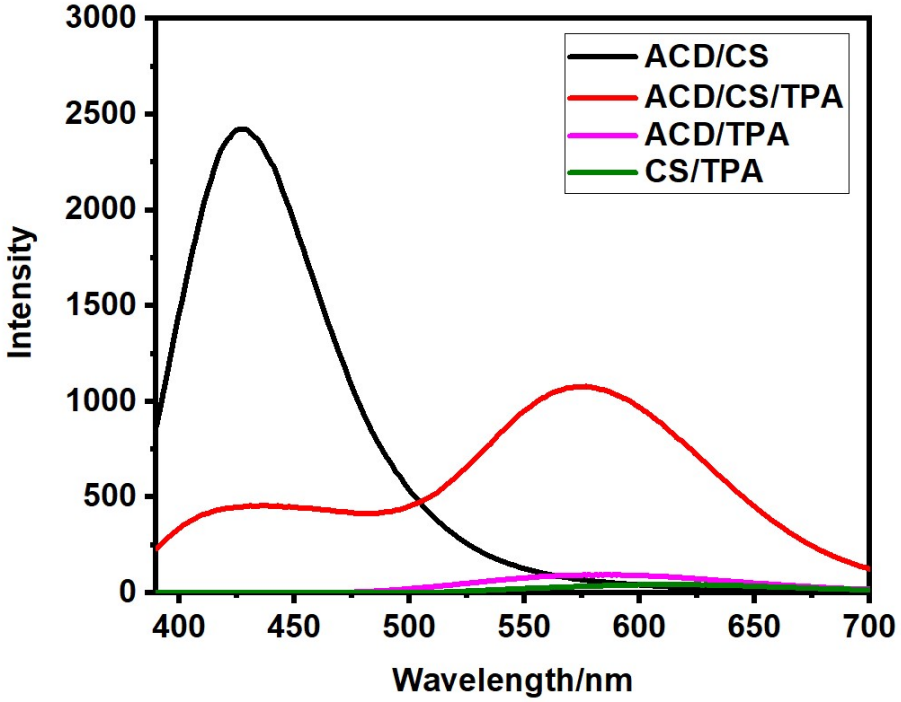


Figure S15. Fluorescence spectrum of ACD/CS, ACD/CS/TPA, ACD/TPA and CS/TPA (λ_{ex}= 360 nm).

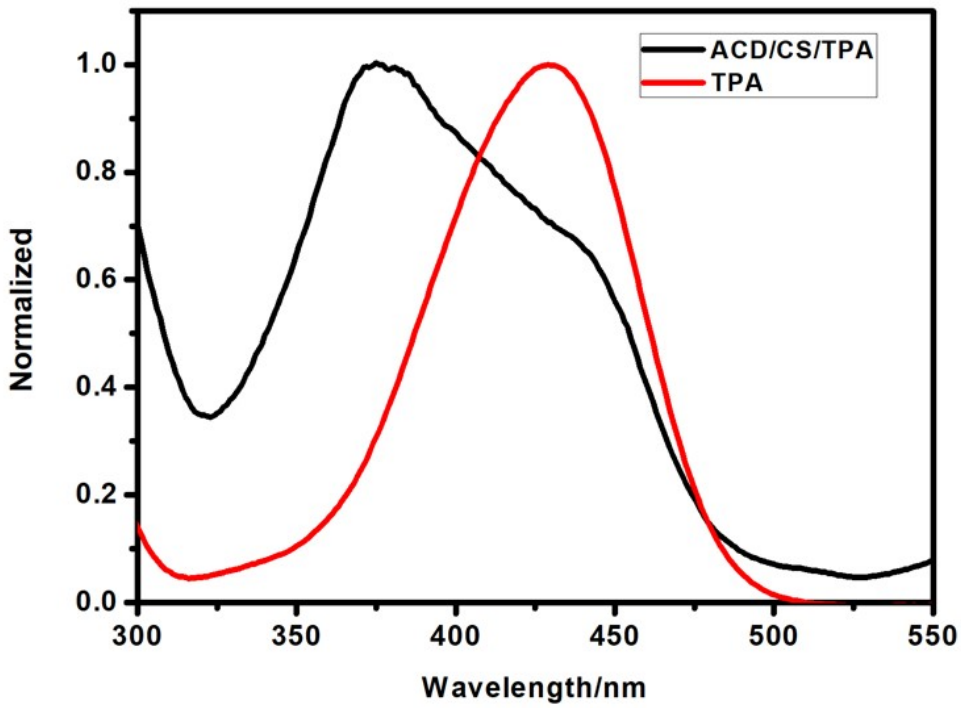


Figure S16 Normalized excitation spectrum of ACD/CS/TPA (λ_{em}= 577 nm) and UV-vis spectra of TPA.

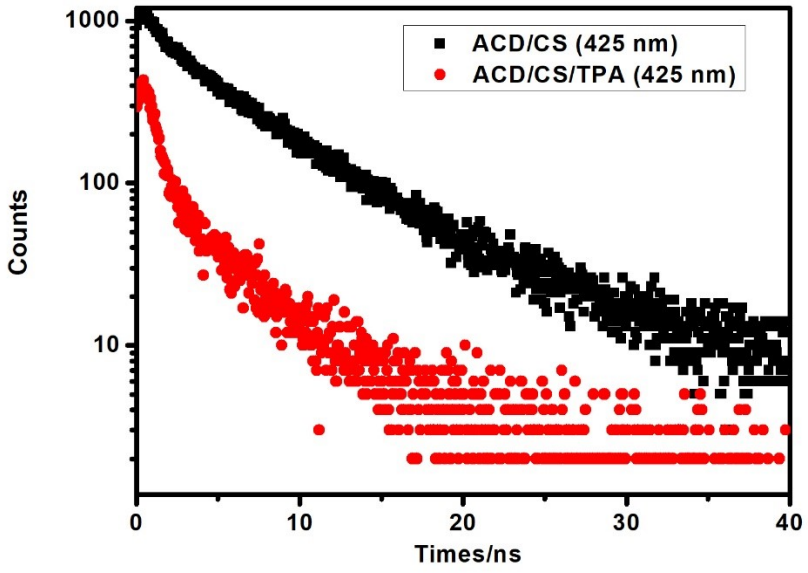


Figure S17. Time-resolved fluorescence decay spectra of ACD/CS (τ = 6.04 ns) and ACD/CS/TPA (τ = 3.36 ns).

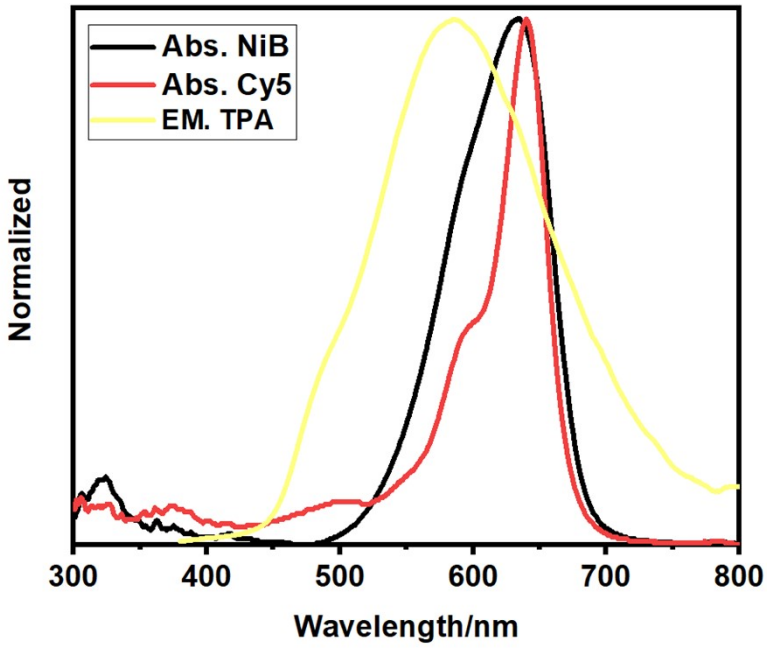


Figure S18. Normalized fluorescence spectrum of TPA and absorption band of NiB or Cy5.

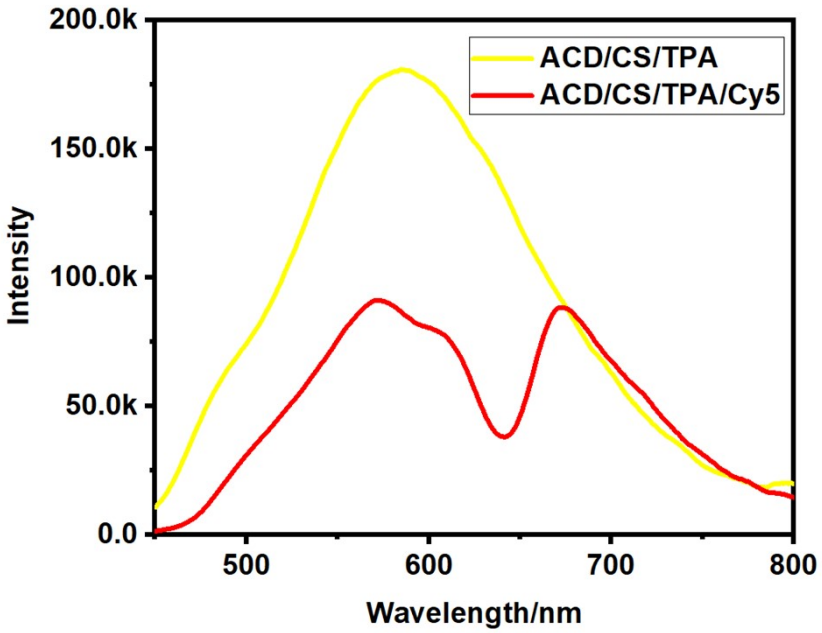


Figure S19. Fluorescence spectrum of ACD/CS/TPA and ACD/CS/TPA/Cy5.

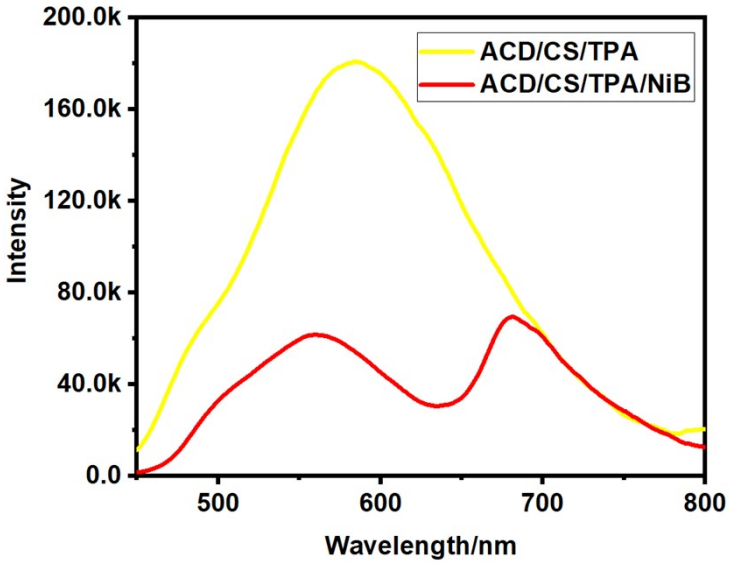


Figure S20. Fluorescence spectrum of ACD/CS/TPA and ACD/CS/TPA/NiB.

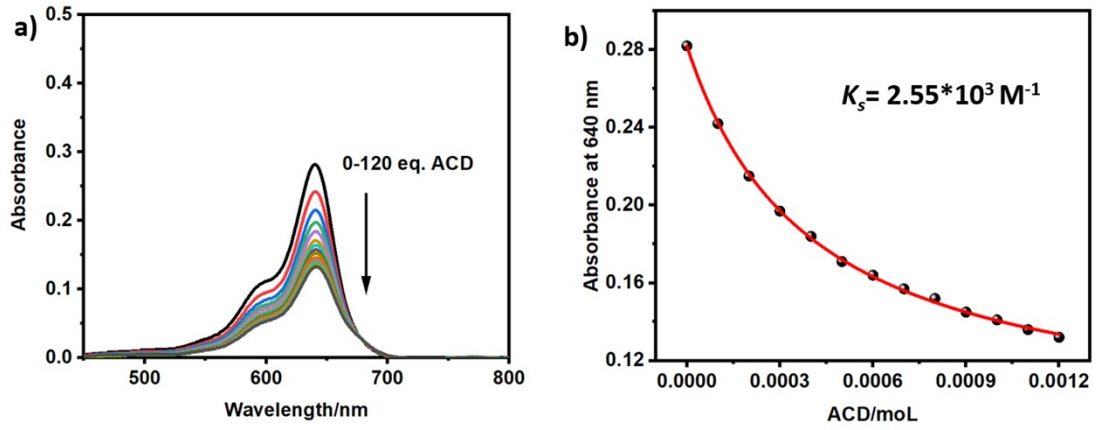


Figure S21. (a)Absorption band of Cy5 in the present of different mount of ACD ([Cy5]=1×10^{-5} M). (b) The binding constant value (*Ks*) was calculated based on the nonlinear least-squares analysis of the absorbance intensity changes of Cy5 upon addition of ACD at 640 nm.

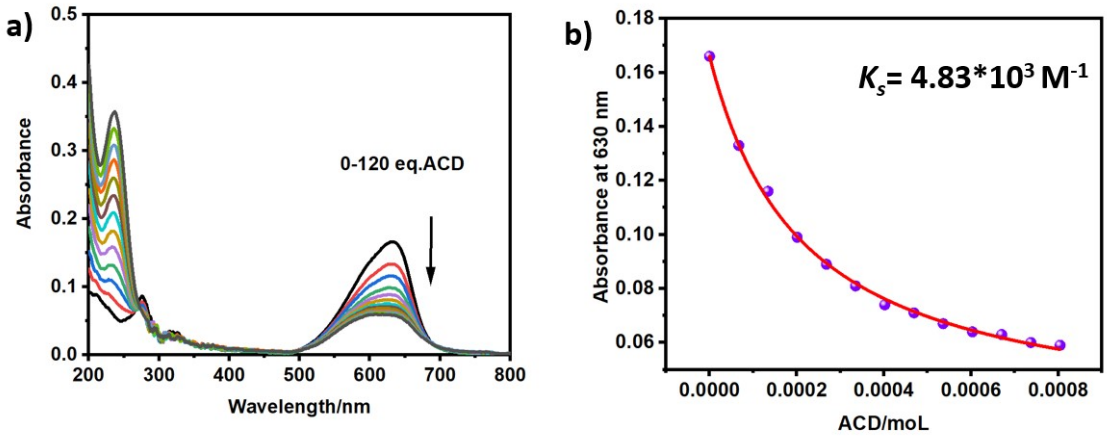


Figure S22. (a)Absorption band of NiB in the present of different mount of ACD ([NiB]=1×10^{-5} M). (b) The binding constant value (*Ks*) was calculated based on the nonlinear least-squares analysis of the absorbance intensity changes of NiB upon addition of ACD at 630 nm.

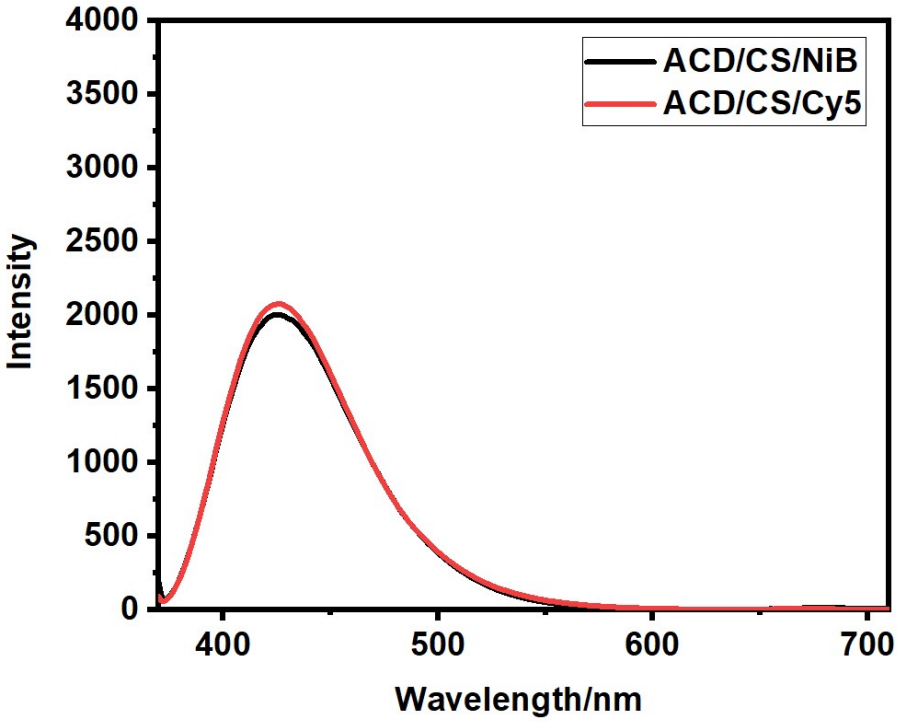


Figure S23. Fluorescence spectrum of ACD/CS/Cy5 and ACD/CS/ NiB.

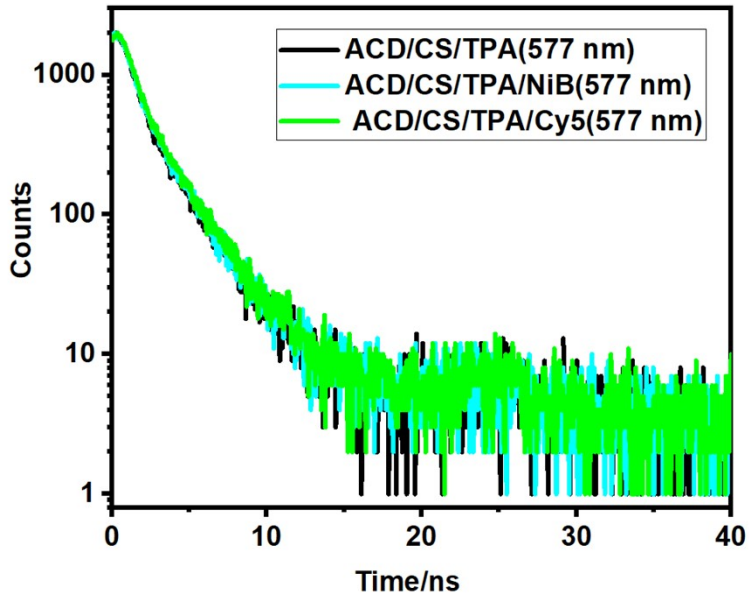


Figure S24. Time-resolved fluorescence decay spectra of of ACD/CS/TPA (τ = 2.37 ns), ACD/CS/TPA/NiB (τ = 2.29 ns) and ACD/CS/TPA/Cy5 (τ = 2.32 ns).

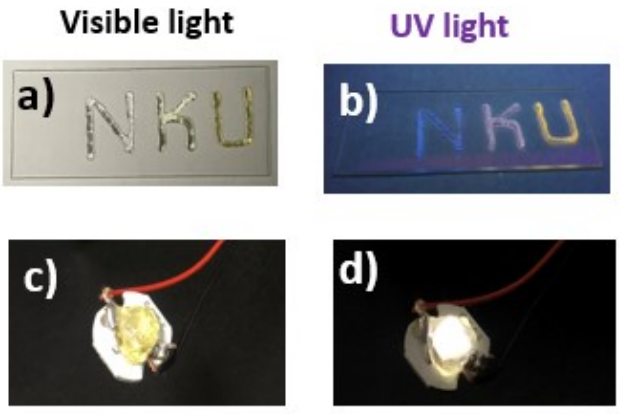


Figure S25. ACD/CS hydrogel doped with different ratios of TPA (1000:0, 1000:5 and 100:1, respectively) on glass plate under visible light a) and 365 nm light b). ACD/CS/TPA hydrogel (1000:5) coated on the surface of the diode (365 nm UV light) switch-off c) and switch-on d).

4. Cell imaging experiments.

A549 cells were purchased from Cell Resource Center, China Academy of Medical Science Beijing, China, and then pre-cultured for 24 h. After incubated with ACD/CS/TPA/Cy5 or ACD/CS/TPA/NiB hydrogels for 12 h, respectively. After that, the sample was washed three times with PBS, then observed by confocal laser scanning microscopy.

5. Cytotoxicity Experiments.

NIH 3T3 cells were purchased from Cell Resource Center, China Academy of Medical Science Beijing, China, and then pre-cultured for 24 h. After that the NIH 3T3 cells were further incubated with ACD/CS for 24 h.

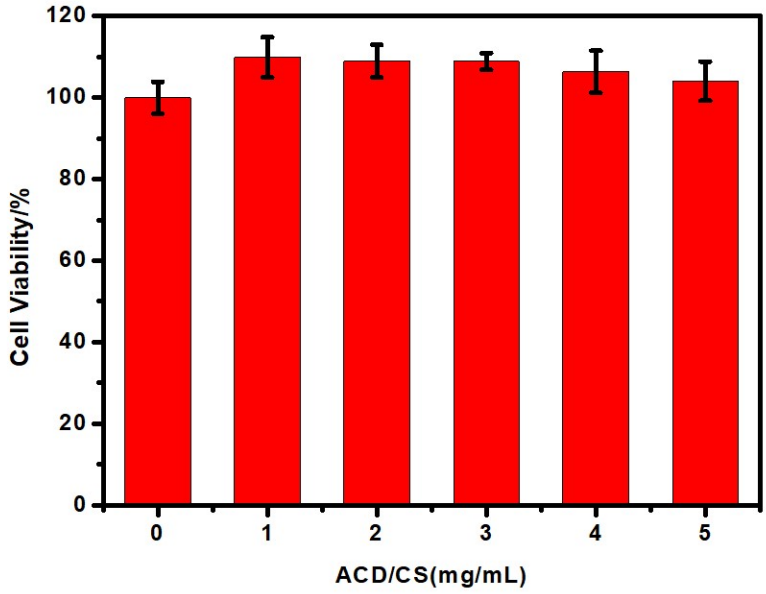


Figure S26. The survival rate of NIH 3T3 cells after incubated with ACD/CS for 24 hours.

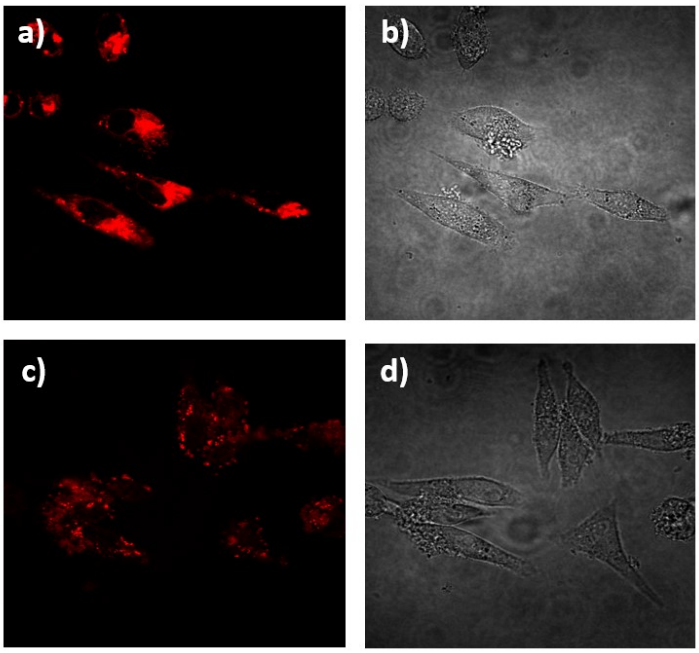


Figure S27. Laser scanning confocal microscopy image of A549 cells treated with supramolecular hydrogel. a) ACD/CS/TPA/Cy5. b) Bright field of ACD/CS/TPA/Cy5. c) ACD/CS/TPA/NiB. d) Bright field of ACD/CS/TPA/NiB.

Reference

[1] Q.J. Li, D.D. Wang, X. Fang, B.Y. Zong, Y. Liu, Z. Li, S. Mao, K. K. Ostrikov, *Chem. Commun.* **2021**, *57*, 1161-1164.