Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Tunable White-Light Emission by Supramolecular Self-sorting in Highly Swollen Hydrogel

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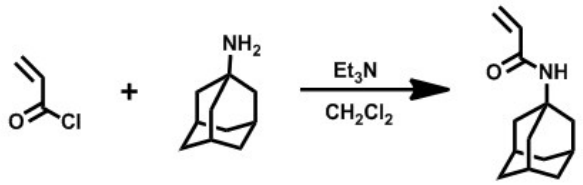
Contents

1. General Infromation.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE AV400 (400 MHz and 100 MHz). Signal positions were reported in part per million (ppm) relative to the residual solvent peaks used as an internal standard with the abbreviations s, d, t, quart and quint, denoting singlet, doublet, triplet, quartlet and quintlet, respectively. The residual ^{1}H peak of deuterated solvent appeared at 7.26 ppm in $CDCl_3$, 4.79 ppm in D_2O and 2.50 ppm in DMSO, while the ^{13}C peak of $CDCl_3$ at 77.0 ppm and 39.5 ppm in DMSO. All coupling constants *J* are quoted in Hz. Scanning electron microscopy (SEM) images were obtained using a JSM-7500F scanning electron microscope. UV/vis spectra were recorded in a quartz cell (light path 5 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Solid-state fluorescence emission spectra and fluorescence decay profiles were measured on a FLS 920P fluorescence spectroscopy. The fluorescent confocal images were performed on a Leica TCS SP8 fluorescence microscope. 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 1000 μm.

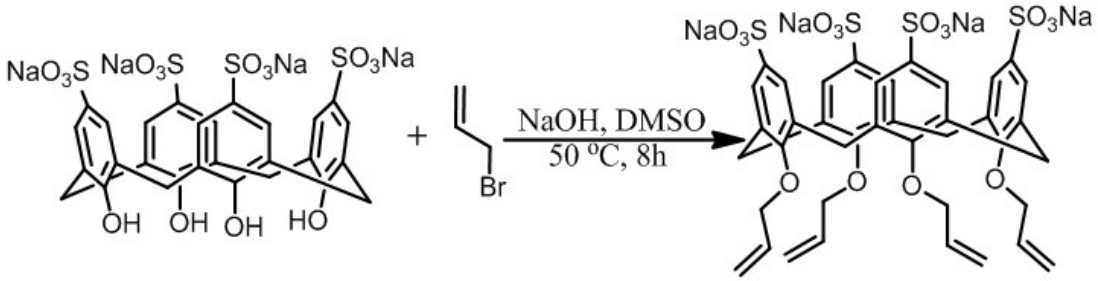
2. Synthesis of the monomers and polymers.

Synthesis of adamantanyl acrylamide (AAmAd)[S1] (Scheme S1): To a 50 ml round-bottomed flask, 1-Adamantylamine (0.76 g, 5 mmol), triethylamine (0.84 ml, 6 mmol) and 4-dimethylaminopyridine(10 mg, 0.082 mmol) was dissolved in 25 ml of dried CH_2Cl_2, and acryloyl chloride(490 μl, 6 mmol) was added to the mixture drop by drop. After the solution was stirred at room temperature for 4 hours, then concentrated under reduced pressure. The obtained crude product was purified by column chromatography with CH_2Cl_2 to get AAmAd with 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.22 (d, J = 16.8 Hz, 1H), 6.02 (dd, J = 16.9, 10.2 Hz, 1H), 5.56 (d, J = 10.2 Hz, 1H), 5.27 (d, J = 28.2 Hz, 1H), 2.07 (d, J = 17.8 Hz, 9H), 1.71 (d, J = 12.6 Hz, 6H).



Scheme S1. Synthetic route of AAmAd.

Synthesis of 4-(allyloxy)sulfonatocalix[4]arene (SC[4]AA) (Scheme S2): To a 50 ml round-bottomed flask, the mixed solution of 5 ml H_2O and 20 ml DMSO, sulfonatocalix[4]arene(SC4A)[S2] (1 g, 1.3 mmol), bromopropyne (2.5 ml, 29 mmol) and NaOH (1 g, 25 mmol) were added, and the mixture was kept at 50 ^{o}C for 24 h. After cooling, the mixture was slowly added to MeOH and white precipitation was gained through filtration. Then the white precipitation was recrystallized with H_2O and MeOH for two times to remove excess NaBr. Finally, the white solid was purified by reverse column chromatography with H_2O and CH_3CN at the ratio of 4:1 to get SC[4]AA with 70% yield. ^{1}H NMR (400 MHz, D_2O) δ: 7.27 (s, 8H), 6.33 (dd, J = 9.7, 6.6 Hz, 4H), 5.21 (dd, J = 33.2, 12.7 Hz, 8H), 4.54 (s, 8H), 4.41 (t, J = 11.6 Hz, 4H), 3.37 (d, J = 13.2 Hz, 4H). ^{13}C NMR (101 MHz, D_2O) δ: 157.80 (s), 137.34 (s), 135.19 (s), 134.91 (s), 125.92 (s), 118.55 (s), 76.11 (s), 31.18 (s).



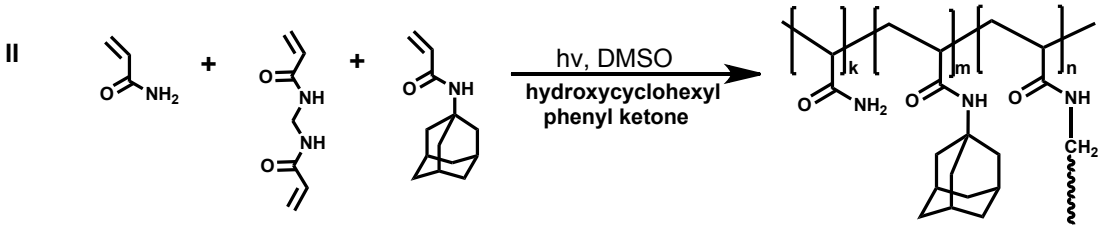
Scheme S2. Synthetic route of SC[4]AA.

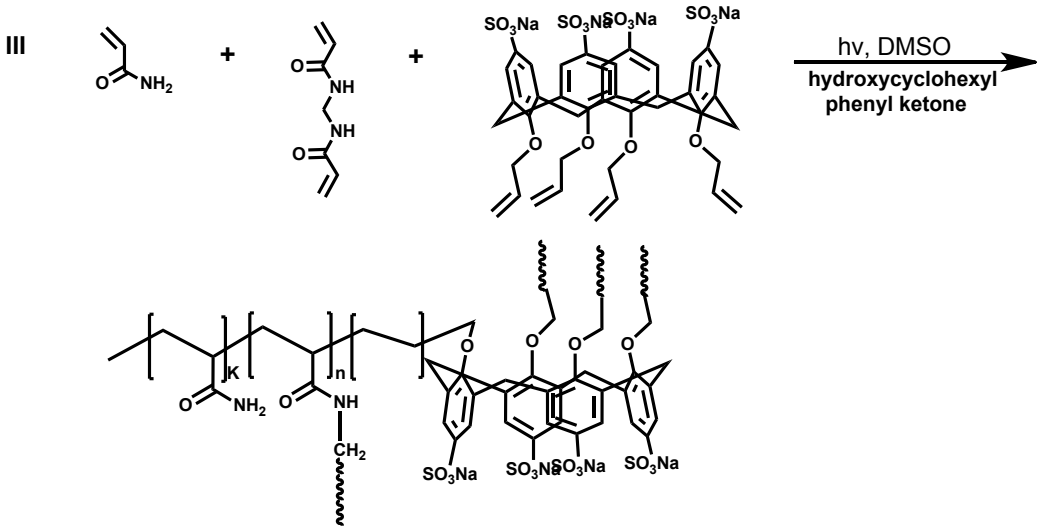
Table S1. Molar ratio of substrates for I ~ VI[a]

	AAm	AAmAd	SC4AA	bisAAm	IAGURE
Hydrogel-1	2.11	0.0974	0.0101	0.0324	0.0245
Hydrogel-II	2.11	0.0974	—	0.0324	0.0245
Hydrogel-III	2.11	—	0.0101	0.0324	0.0245
polymer-IV	2.11	0.0974	0.0101	—	0.0245
polymer-V	2.11	—	0.0101	—	0.0245
polymer-VI	2.11	0.0974	—	—	0.0245

[a] Preparation of hydrogels and polymers with various substrates (μmol) in 1 ml DMSO as list in the Table S1.

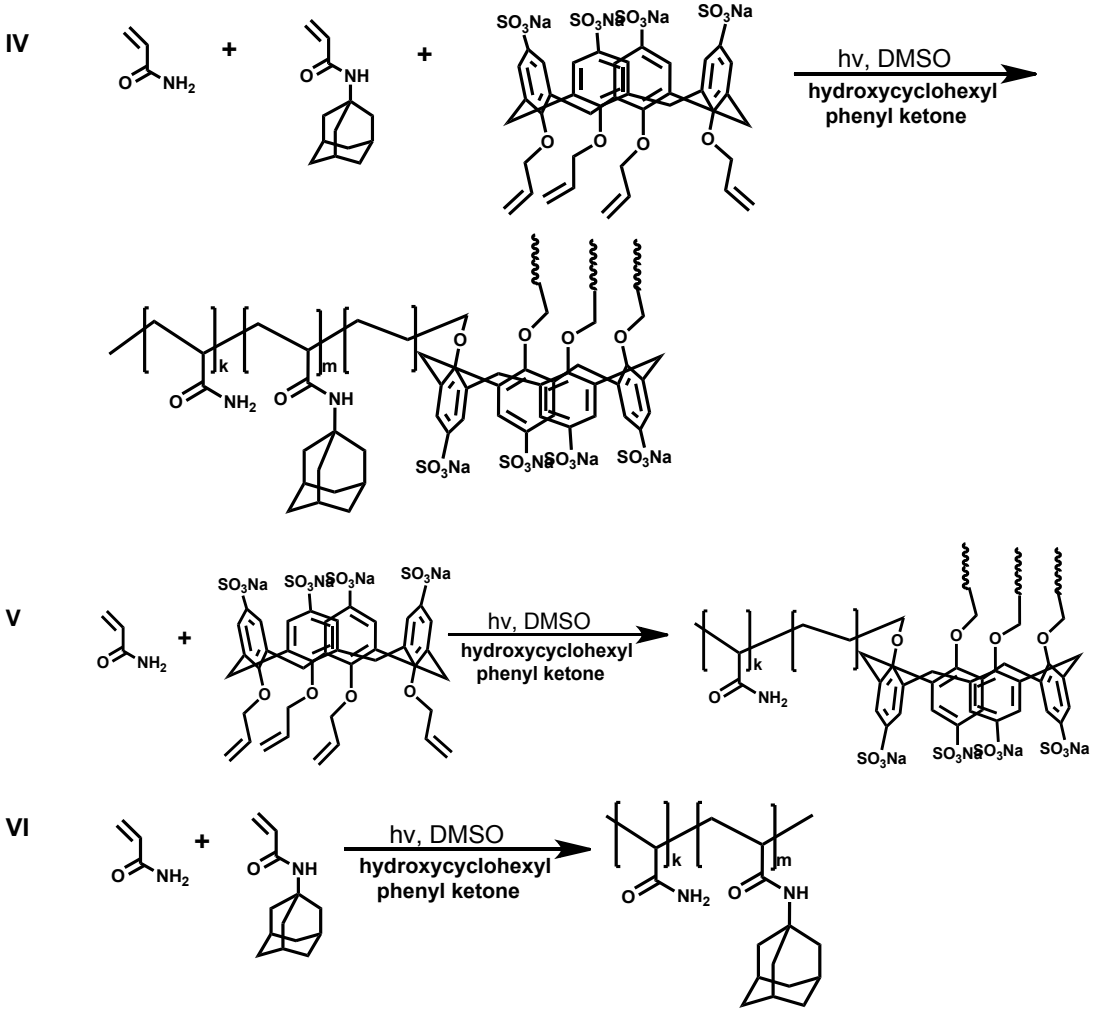
Preparation of hydrogel I/II/III (Scheme S3): Gel I was prepared by copolymerization of acrylamide(AAm) (150 mg), AAmAd (20 mg), SC[4]AA (10 mg) and N,N'-methylenebis-(acrylamide) (5 mg) by radical polymerization using hydroxycyclohexyl phenyl ketone in 1 ml DMSO under 365 nm for 2h. The gel was purified by immersing in DMSO for several hours and then repeated washing with water and finally the well swollen hydrogel was obtained. Gel II/III was prepared in similar way as shown above except for the cut of raw material AAmAd or SC[4]AA.





Scheme S3. Synthetic route of hydrogel II/III.

Preparation of polymer IV, V, VI (Scheme S4): Polymer IV/V/VI was prepared in similar way as shown above except for the cut of raw material N,N'-methylene bis-(acrylamide) or AAmAd or SC[4]AA.



Scheme S4. Synthetic route of copolymer IV/V/VI.

3. NMR and MS spectra of the monomers and polymers

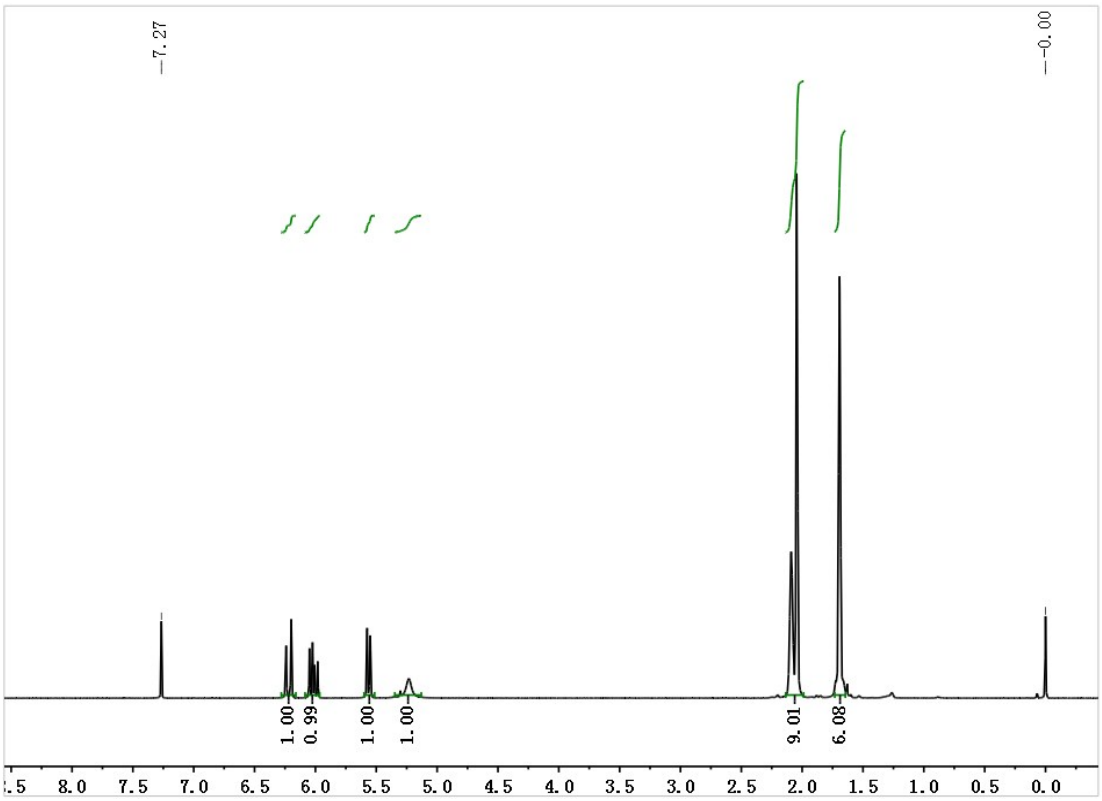


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of AAmAd at 298 K.

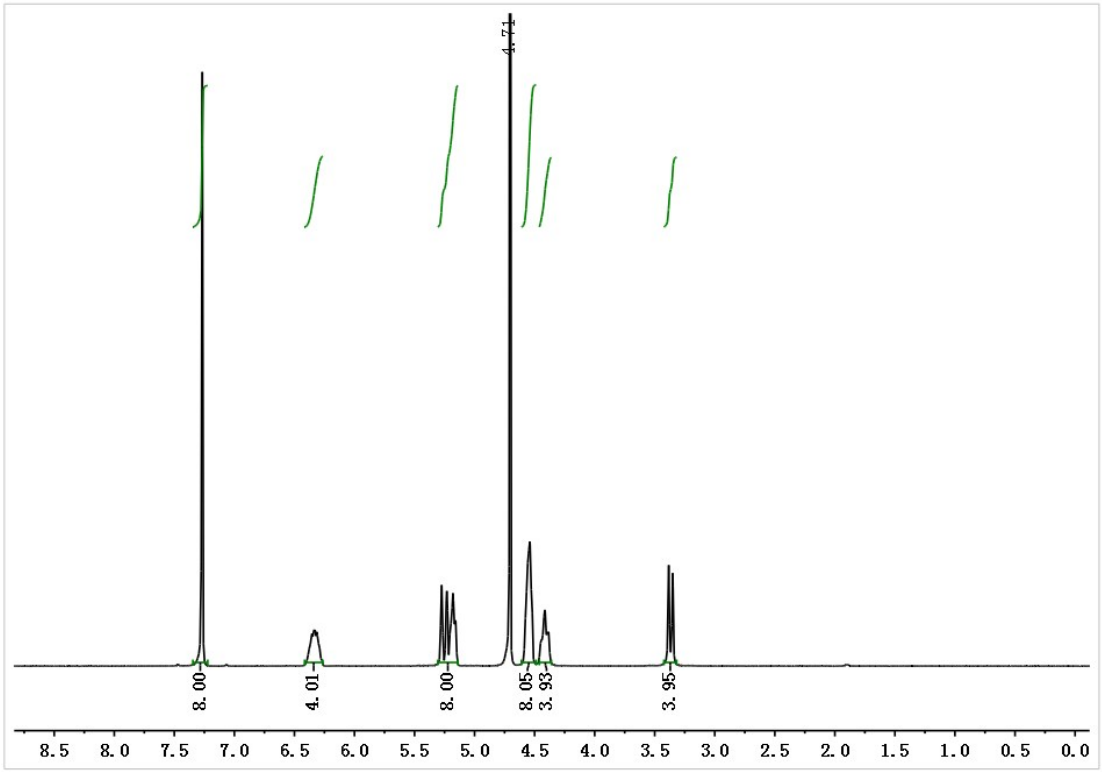


Figure S2. ^{1}H NMR spectrum (400 MHz, D_2O) of SC4AA at 298 K.

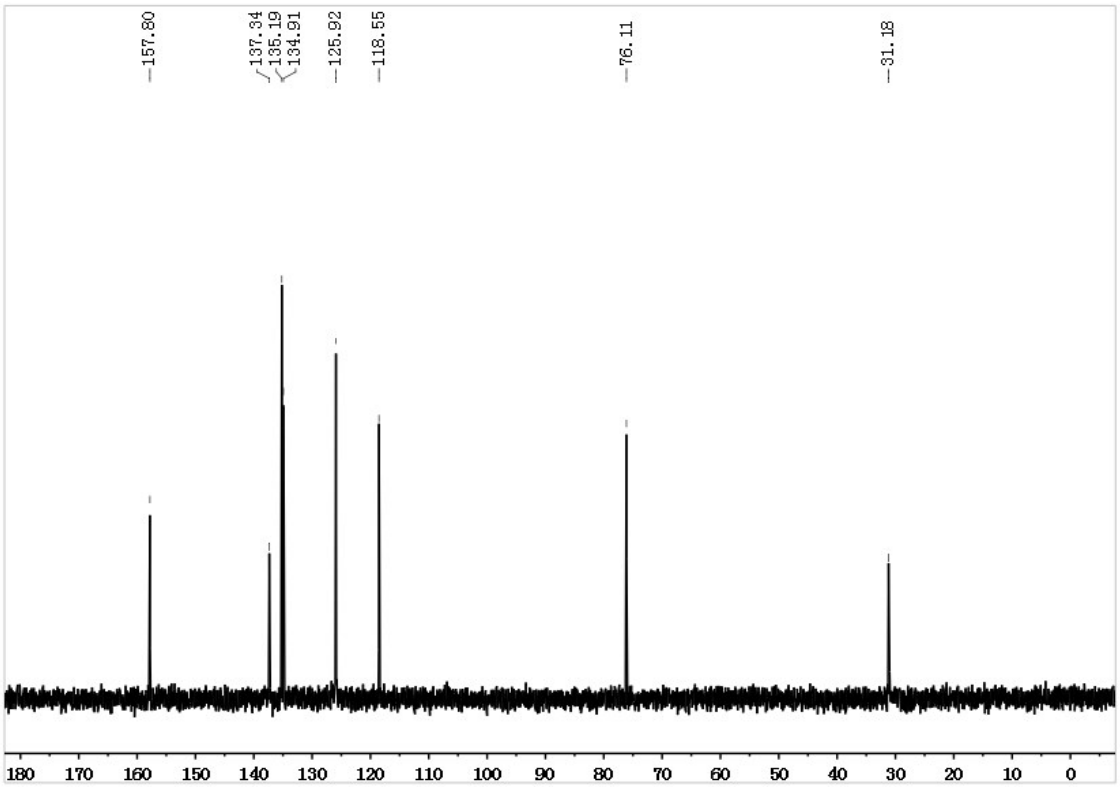


Figure S3. ^{13}C NMR spectrum (100 MHz, D_2O) of SC4AA at 298 K.

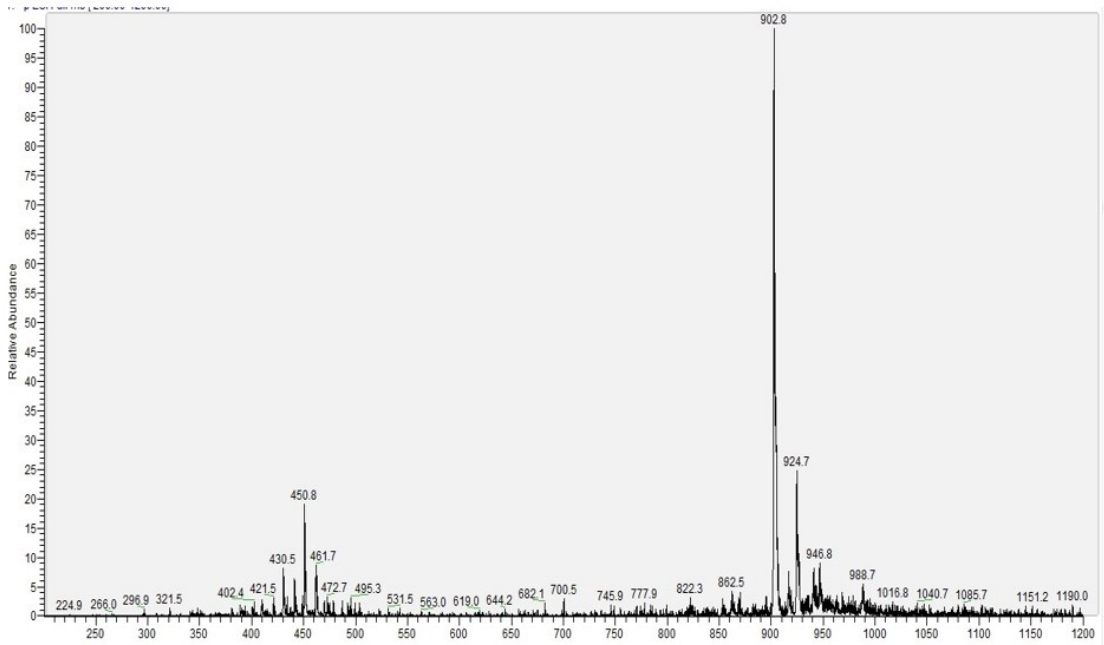


Figure S4. MS spectrum of SC4AA.

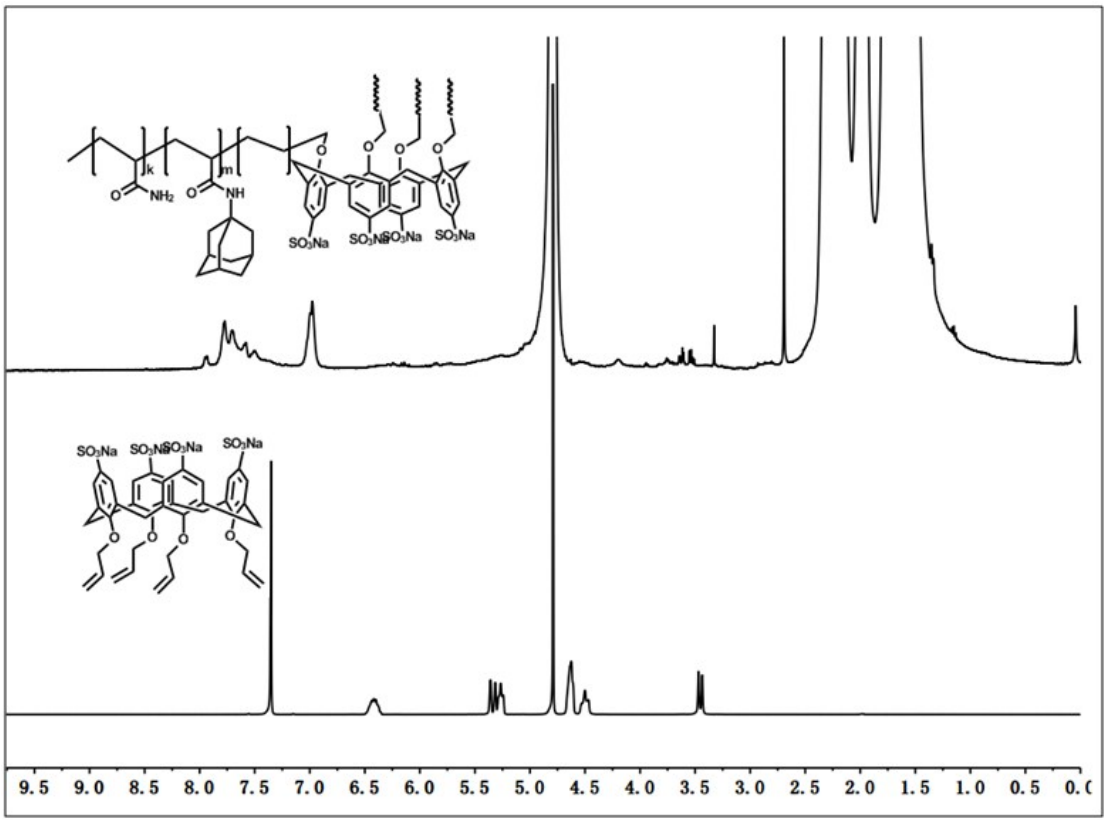


Figure S5. ^{1}H NMR spectrum (400 MHz, D_2O) of Polymer IV at 298 K.

4. Characterizations of the Hydrogels.

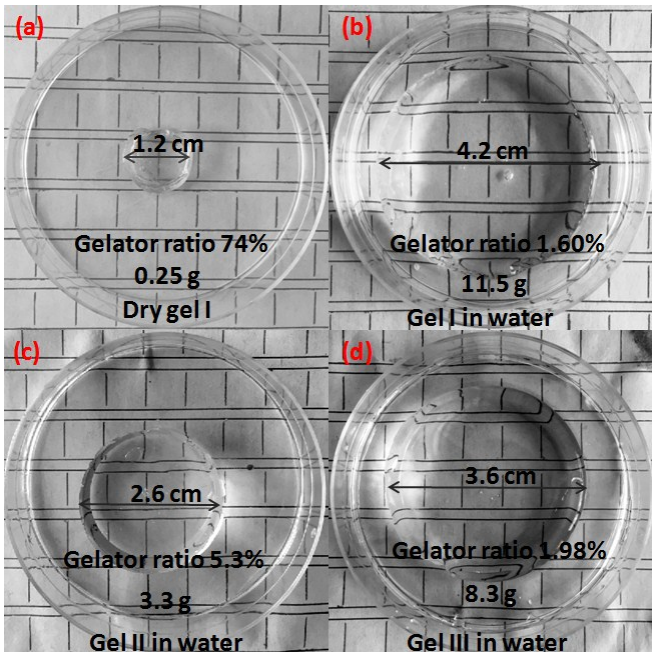


Figure S6. Photos, diameters and weights of a) dry hydrogel I, b) fully swollen hydrogel I, c) fully swollen hydrogel II and d) fully swollen hydrogel III.

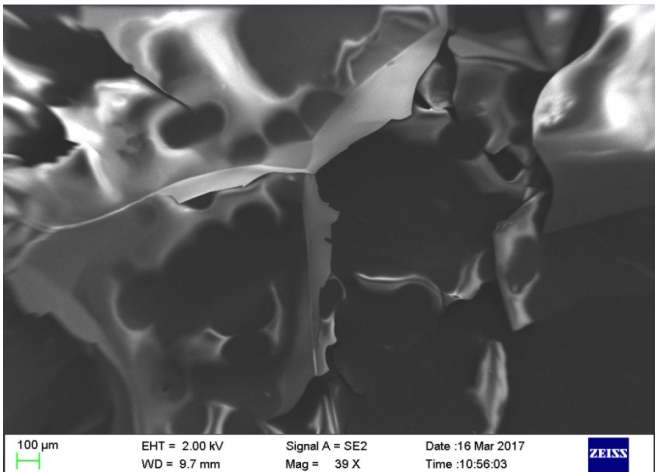


Figure S7. SEM images of lyophilized fully swollen hydroge-I.

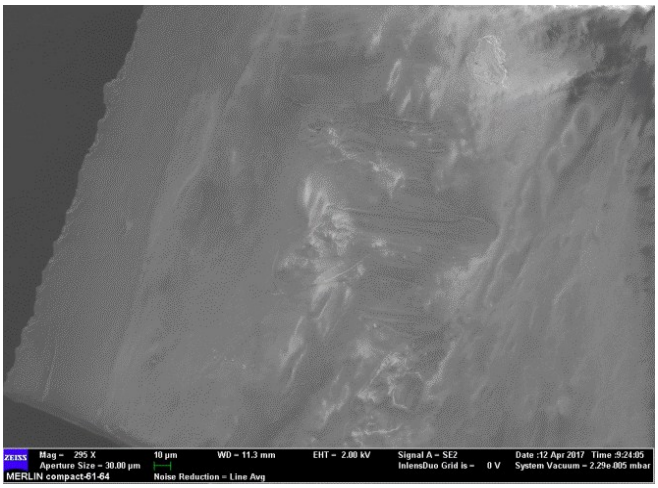
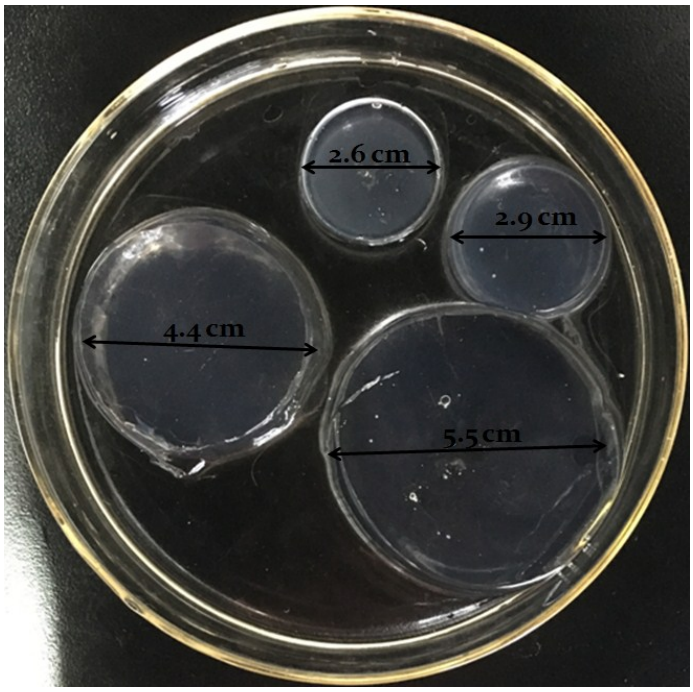


Figure S8. SEM images of naturally dried hydrogel-I.



SC4A (mg)	0	5	10	15
Diameter (cm)	2.6	2.9	4.4	5.5
Weight (g)	3.3	4.9	10.7	24.2
Gelator ratio	5.3 %	3.7 %	1.7 %	0.79 %

Figure S9. Photos, diameters, weights and gelator ratios of fully swollen hydrogels with different content of SC4AA.

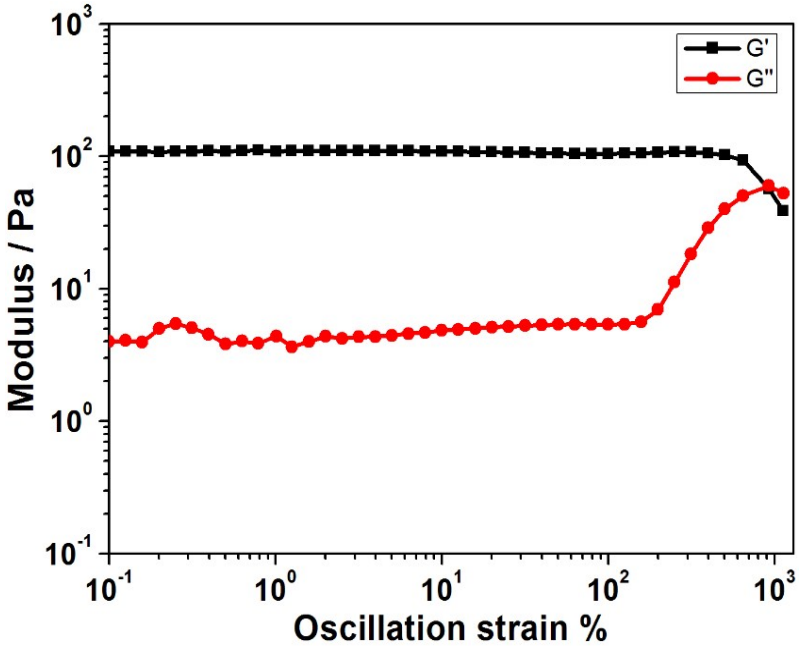


Figure S10. Rheological characterization of hydrogel (dynamic strain sweep curves at fixed angular frequency of 1 rad/s).

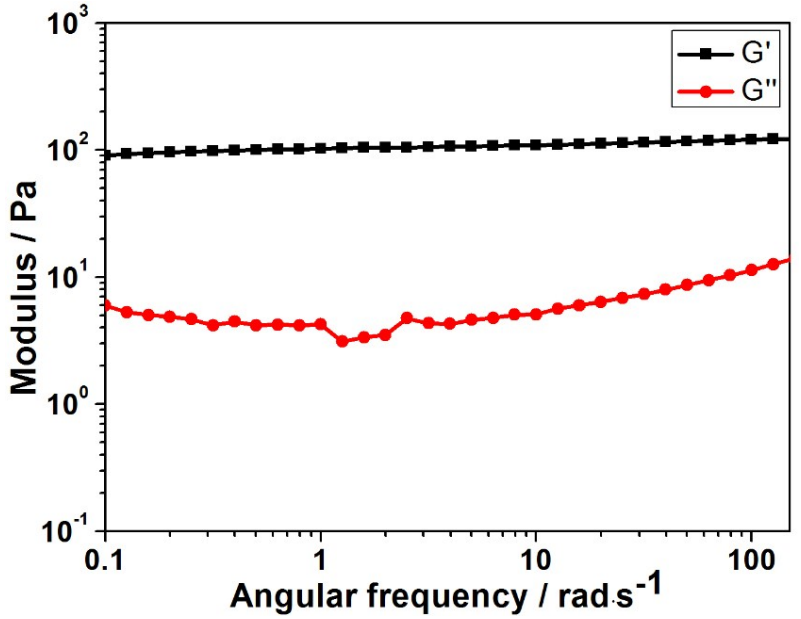
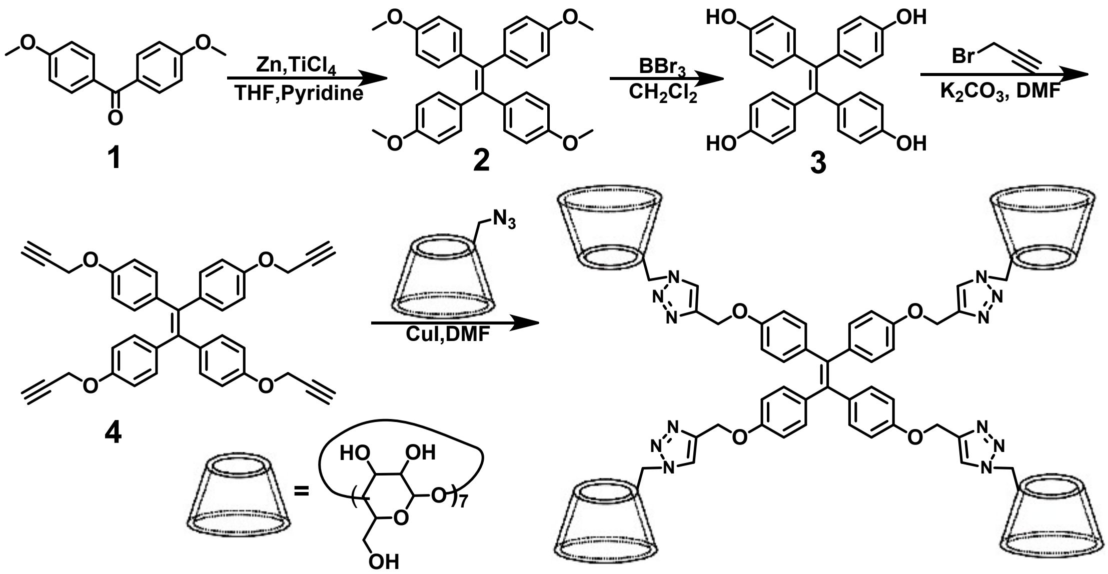


Figure S11. Rheological characterization of hydrogel (dynamic frequency sweep curves at fixed strain of 1%).

5. Synthesis and NMR&HRMS spectra of Dyes.

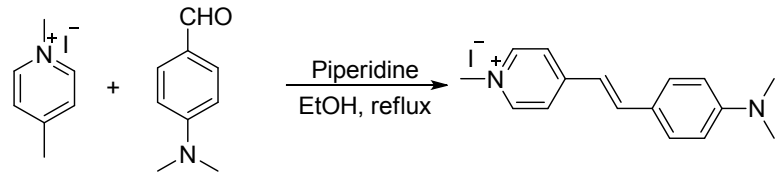
Synthesis of TPECD (Scheme S5): TPECD was synthesized according to a reported method.[S3] To the solution of 2[S4] (60 mg, 0.11 mmol) and β-CD azide[S5] (1 g, 0.86 mmol) in DMF, CuI (1 g, 5.25 mmol) was added as a catalyst. The mixture was

stirred at 60 oC for 48 h, then concentrated and purified by column chromatography on silica gel (EtOH:NH_3·H_2O:H_2O = 6:3:1) to remove the excess amount of CuI. The resulting solution was dialyzed against an excess amount of water for 5 days. After being freeze-dried, TPECD was obtained as a slightly yellow solid in 70% yield. ^{1}H NMR (400MHz, DMSO-d6): δ 8.15 (s, 4H), 6.87 (dd, J = 31.9, 8.0 Hz, 16H), 5.95 - 5.57 (m, 64H), 5.23 - 4.27 (m, 84H), 4.06 -3.48 (m, 111H). ^{13}C NMR (100 MHz, DMSO): δ 156.90, 142.92, 138.46, 136.92, 132.63, 126.26, 114.22, 102.40, 83.73, 82.00, 73.47, 72.72, 72.51, 61.24, 60.45, 59.50, 50.75. HRMS (MALDI-TOF): calculated for $C_{206}H_{304}N_{12}O_{140}Na$, 5210.70; found, 5210.70.



Scheme S5. Synthetic route of TPECD.

Synthesis of DASPI (Scheme S6): DASPI was synthesized according to a reported method.[2] 1,4-dimethylpyridin-1-ium iodide(3 g, 12.8 mmol), *p*-dimethyl-aminobenzaldehyde (2.09 g, 14.0 mmol) and piperidine(3 drops) in 50 ml EtOH were refluxed for 5 hours. Red precipitation was gained through filtration, then it was recrystallized with EtOH for two times gain DASPI in 80% yield. ^{1}H NMR (400 MHz, D_2O) δ: 8.30 (d, J = 6.3 Hz, 2H), 7.78 (d, J = 6.2 Hz, 2H), 7.62 (d, J = 16.2 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 16.1 Hz, 1H), 6.82 (d, J = 8.5 Hz, 2H), 4.07 (s, 3H), 2.88 (s, 6H).



Scheme S6. Synthetic route of DASPI.

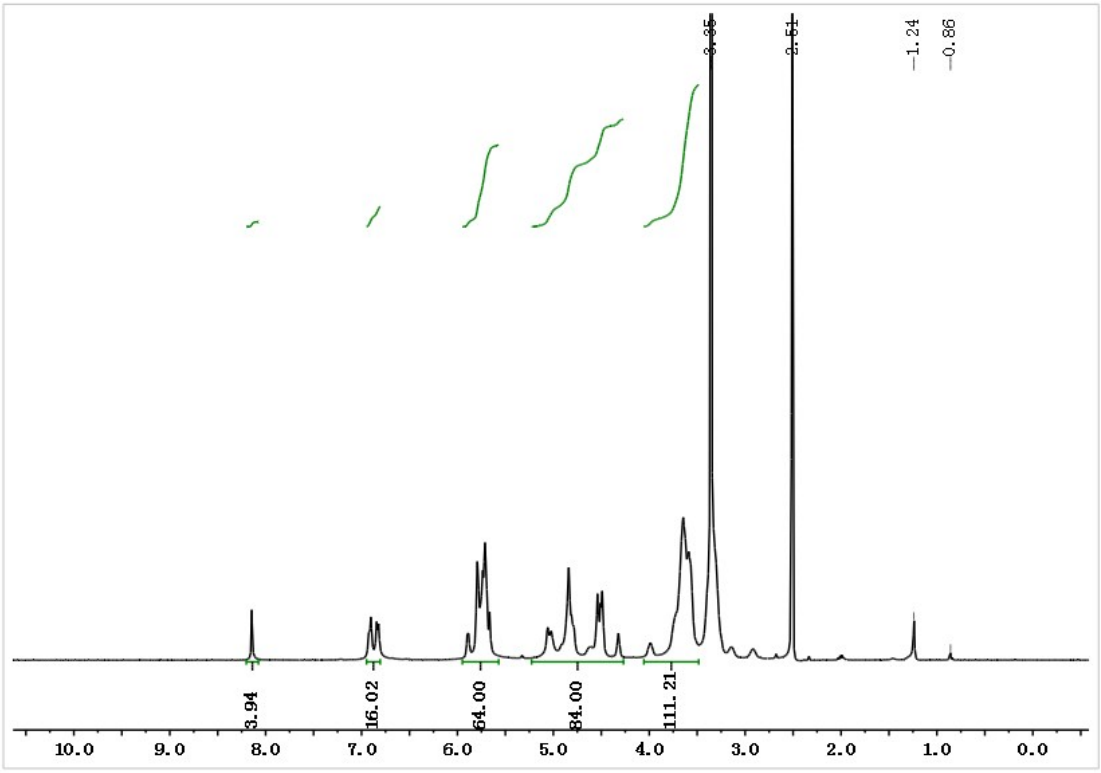


Figure S12. ^{1}H NMR spectrum (400 MHz, DMSO-d6) of TPECD at 298 K.

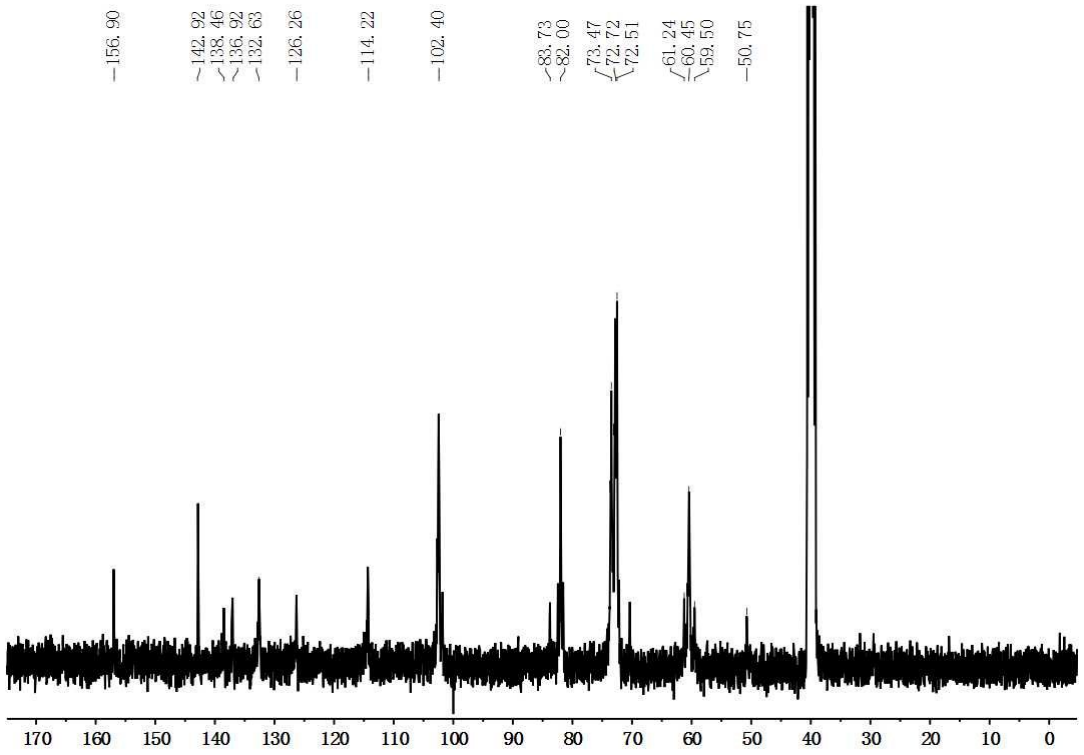


Figure S13. ^{13}C NMR spectrum (400 MHz, DMSO-d6) of TPECD at 298 K.

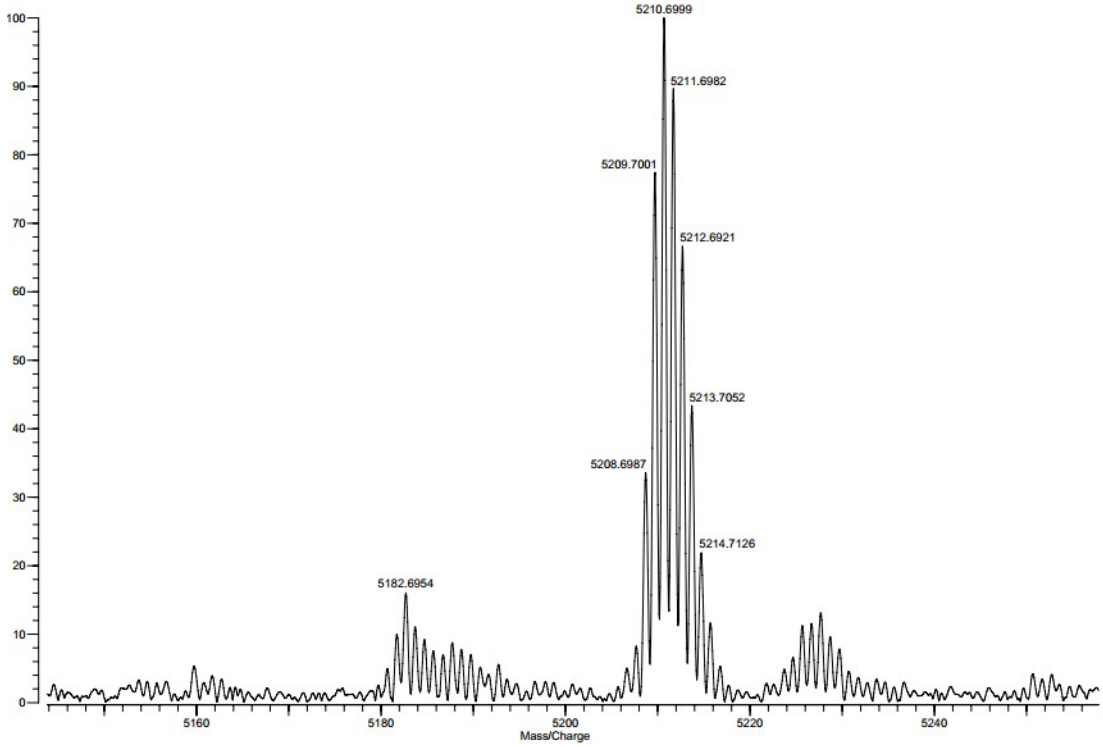


Figure S14. HRMS spectrum of TPECD.

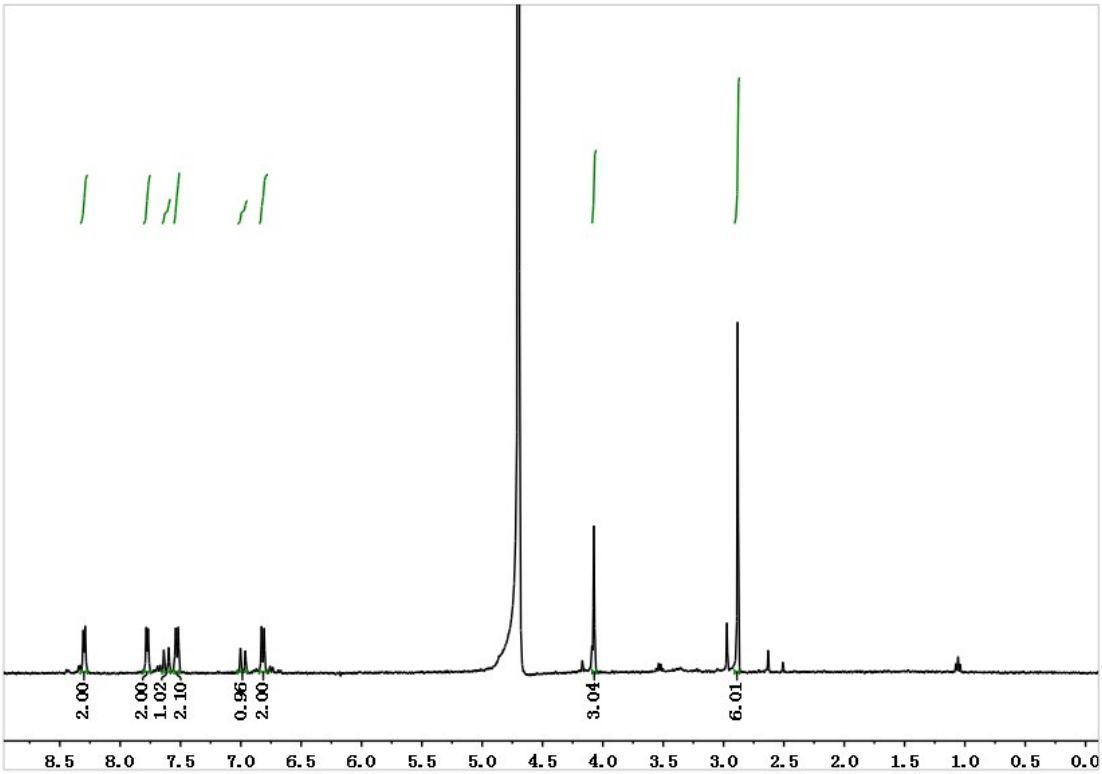


Figure S15. ^{1}H NMR spectrum (400 MHz, D_2O) of DASPI at 298 K.

6. Fluorescent Properties.

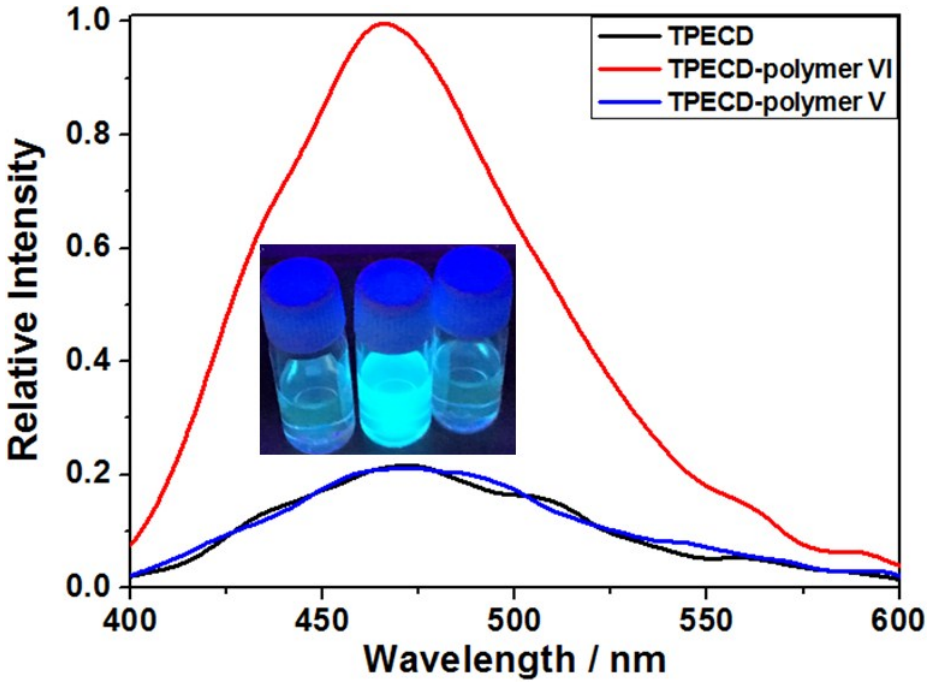


Figure S16. Relative fluorescence spectra and digital photos under 365 nm light of TPECD ($1x10^{-5}$ mol L^{-1}), with polymer VI (0.14 g L^{-1}, molar ratio Ad: CD = 2: 1) and polymer V (0.14 g L^{-1}) (insert photos from left to right).

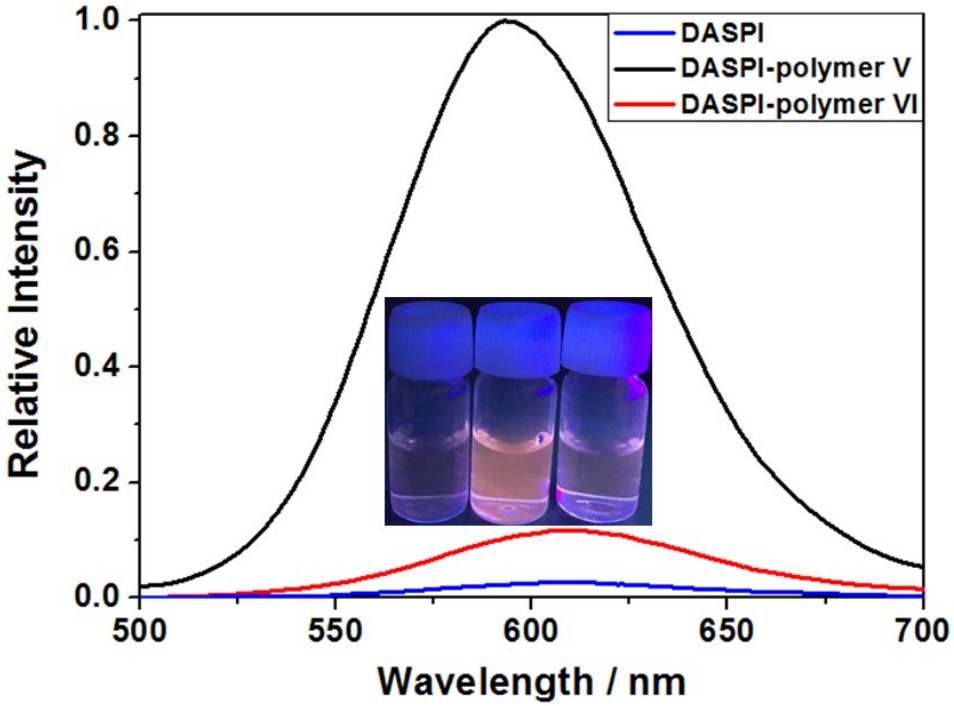


Figure S17. Relative fluorescence spectra and digital photos of DASPI ($1x10^{-5}$ mol L^{-1}), with polymer V (0.32 g L^{-1}, molar ratio SC4A: DASPI = 2: 1) and polymer VI (0.32 g L^{-1}) (insert photos from left to right).

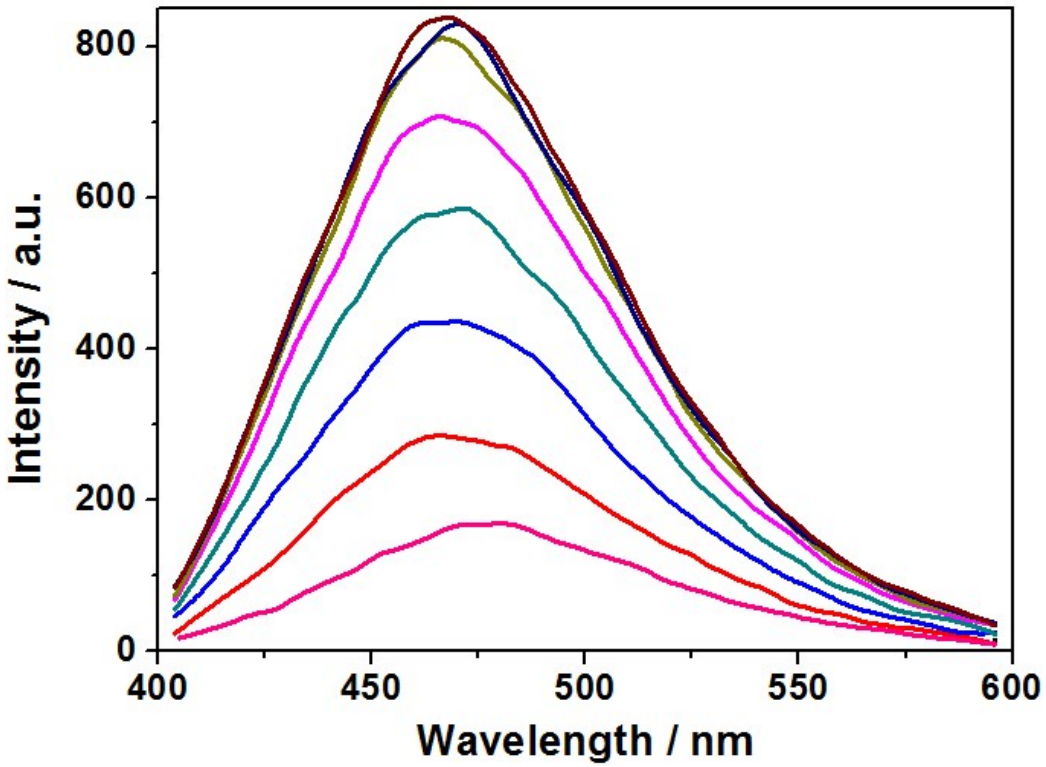


Figure S18. Fluorescence spectra of TPECD (1x10^{-5} mol L^{-1}) with the addition of polymer VI (0, 0.014, 0.028, 0.042, 0.056, 0.07, 0.084, 0.098, 0.112, 0.126, 0.14 g L^{-1}; molar ratio Ad: CD = 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2).

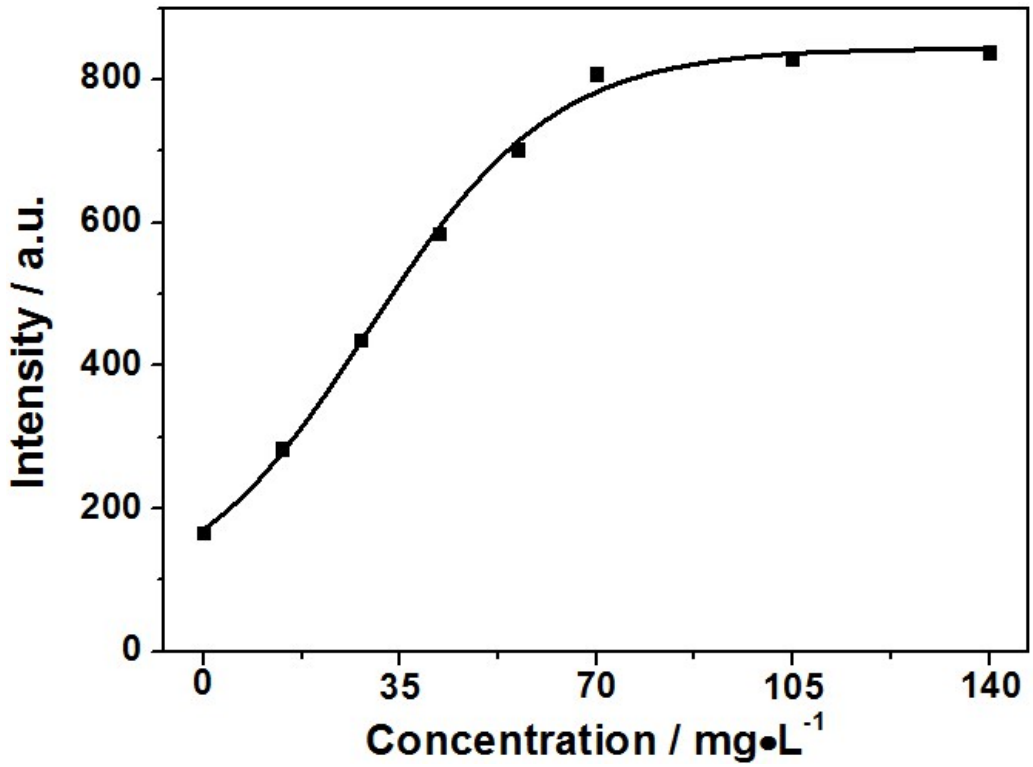


Figure S19. Fluorescence intensity of TPECD (1x10^{-5} mol L^{-1}) at 470 nm with the addition of polymer VI (0, 0.014, 0.028, 0.042, 0.056, 0.07, 0.084, 0.098, 0.112, 0.126, 0.14 g L^{-1}; molar ratio Ad: CD = 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2).

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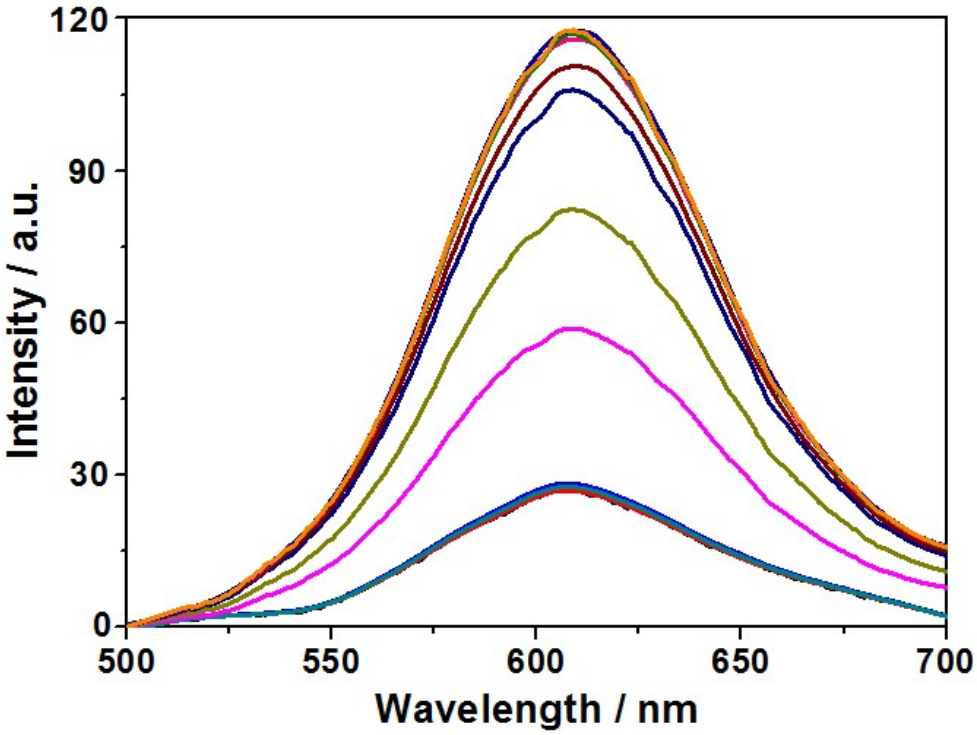

Figure S20. Fluorescence spectra of DASPI (1x10^{-5} mol L^{-1}) with the addition of polymer VI (0, 0.016, 0.032, 0.048, 0.064, 0.08, 0.096, 0.112, 0.128, 0.144, 0.16， 0.32 g L^{-1}).

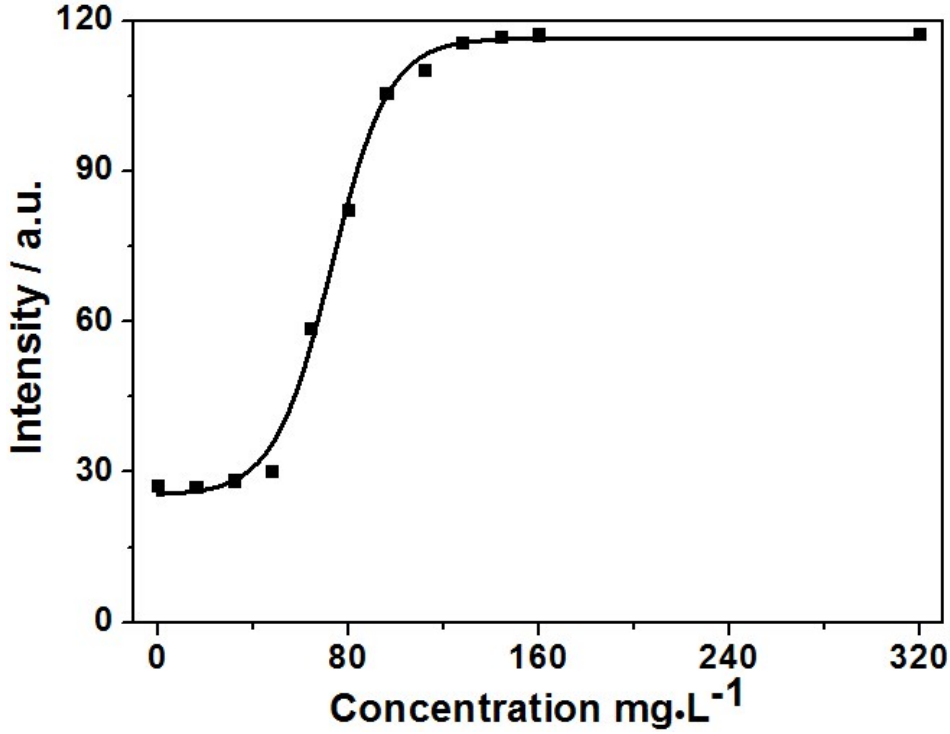

Figure S21. Fluorescence intensity of DASPI (1x10^{-5} mol L^{-1}) at 607 nm with the addition of polymer VI (0, 0.016, 0.032, 0.048, 0.064, 0.08, 0.096, 0.112, 0.128, 0.144, 0.16, 0.32 g L^{-1}).

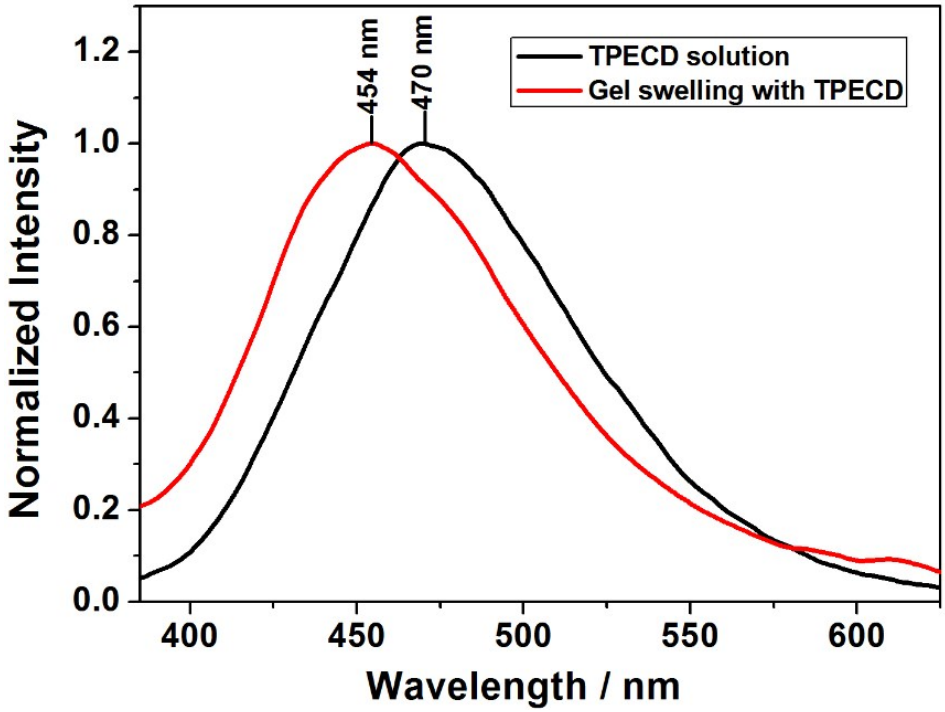

Figure S22. Normalized Fluorescence emission spectra of TPECD solution ($1x10^{-4}$ mol L^{-1}) and hydrogel I swelling with TPECD solution ($1x10^{-4}$ mol L^{-1}).

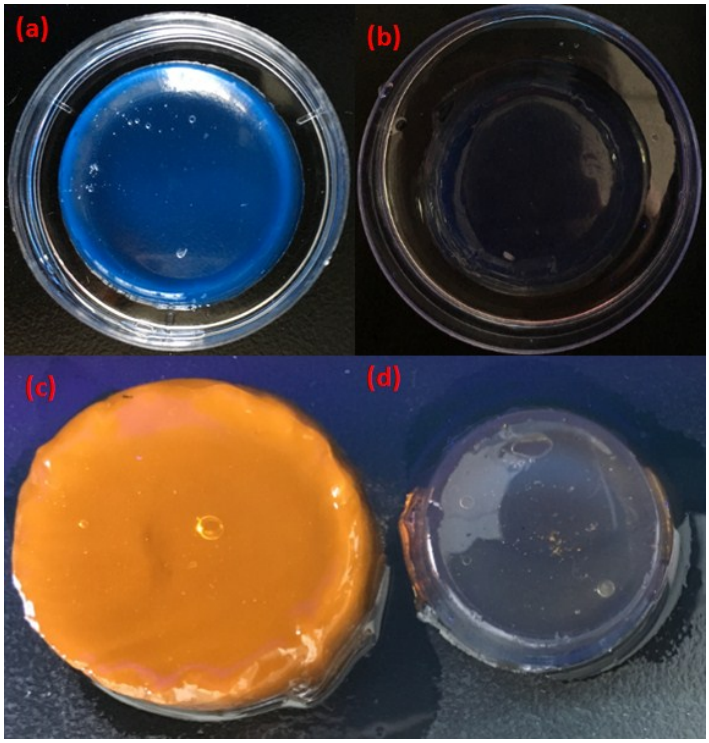

Figure S23. Photos of hydrogel I and hydrogel III extension at TPECD solution($1x10^{-4}$ mol L^{-1})(a & b); hydrogel I and hydrogel II extension at DASPI solution ($1.25x10^{-5}$ mol L^{-1}) (c & d).

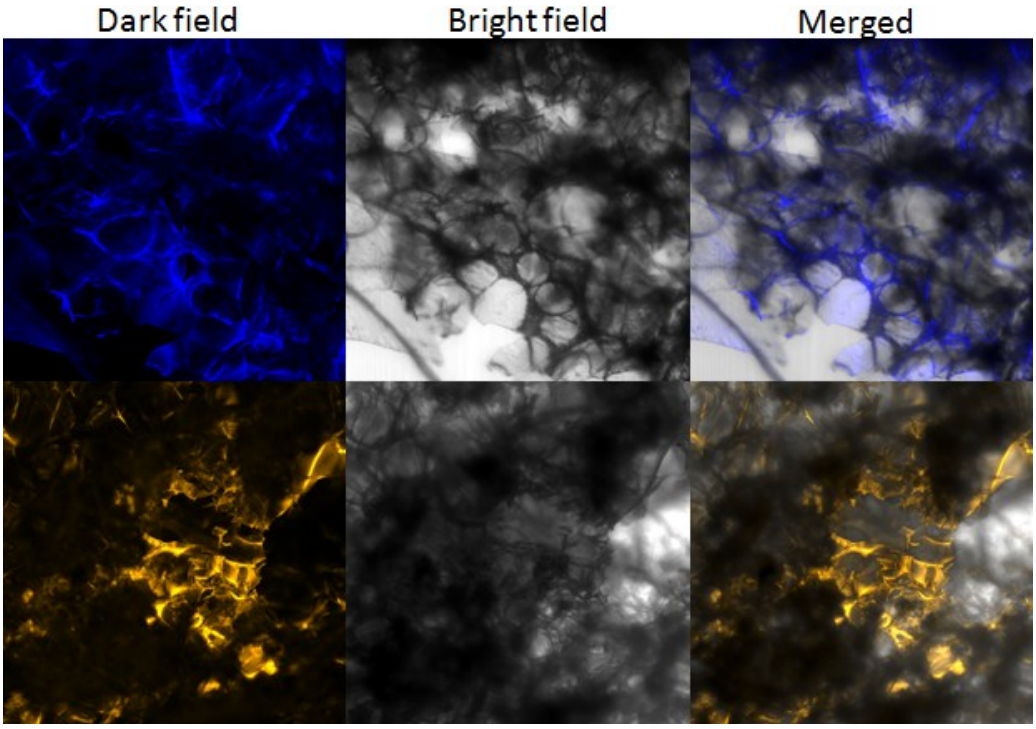

Figure S24. Laser scanning confocal microscope images of the deep blue and yellow hydrogel at dark field, bright field and merged.

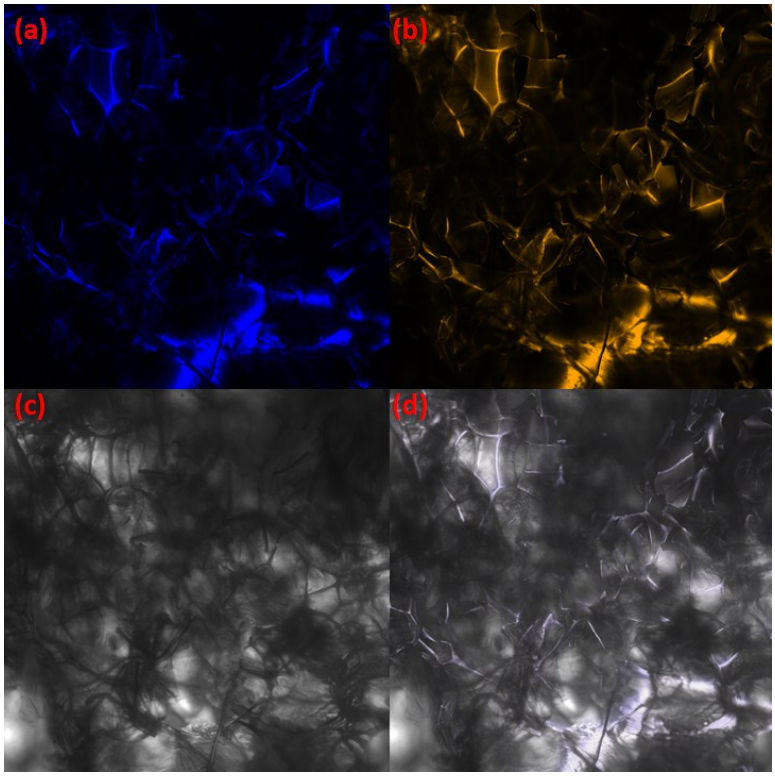

Figure S25. laser scanning confocal microscope images of the white hydrogel at a) dark field receive channel 435-475 nm, b) dark field receive channel 570-610 nm; c) bright field and d) merged .

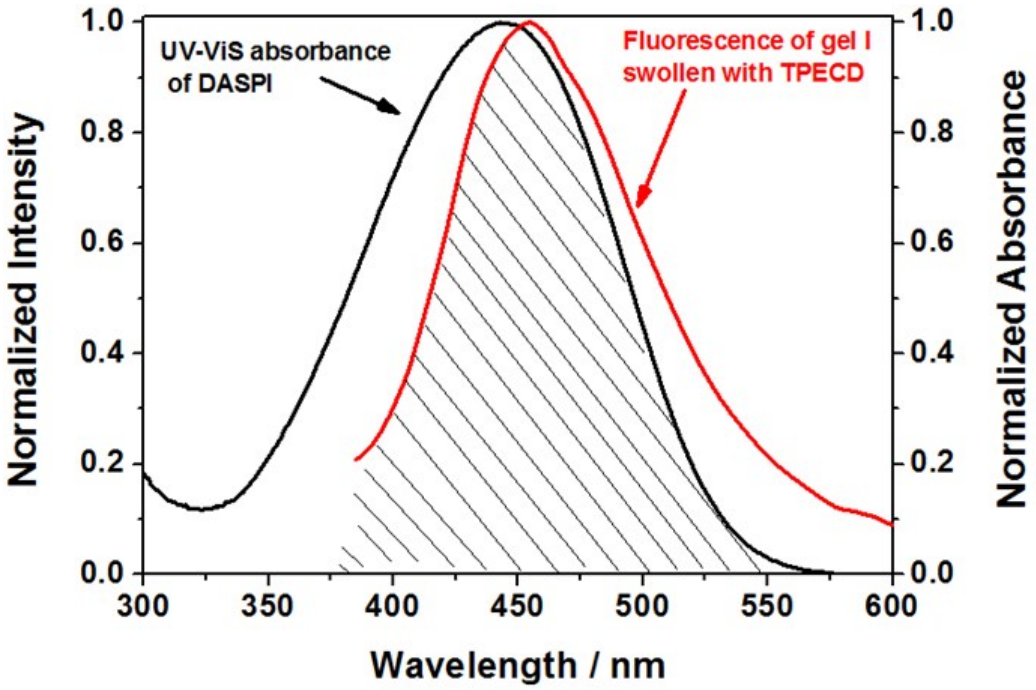

Figure S26. Normalized fluorescence spectrum of hydrogel I swollen with TPECD (red) and UV-Vis absorption of DASPI (black), overlap between them was marked out as shaded area.

Reference

S1. Harada, A.; Takashima, Y.; Nakahata, M. Acc. Chem. Res. 2014, 47, 2128.

S2. Fernández-Abad, S.; Pessêgo, M.; Basílio, N.; García-Río, L. Chem. Eur. J. 2016, 22, 6466.

S3. Zhao, Q.; Chen, Y.; Sun, M.; Wu, X.-J.; Liu, Y. RSC Adv. 2016, 6, 50673.

S4. Song, N.; Chen, D.-X.; Qiu, Y.-C.; Yang, X.-Y.; Xu, B.; Tian, W.; Yang, Y.-W. Chem. Commun. 2014, 50, 8231.

S5. Sun, M.; Zhang, H.-Y.; Zhao, Q.; Hu, X.-Y.; Wang, L.-H.; Liu, B.-W.; Liu, Y. J. Mater. Chem. B 2015, 3, 8170.