Supporting Information

Water-soluble, neutral 3,5-diformyl-BODIPY with extended fluorescence lifetime in a self-healable chitosan hydrogel

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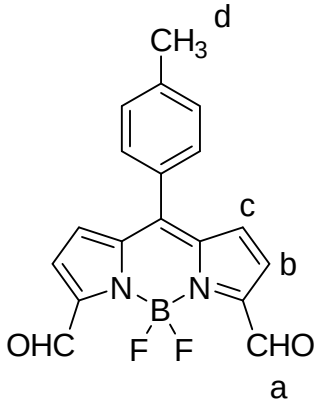
Synthesis of 3,5-diformyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (3,5-diformyl BODIPY)

The 1,9-diformyl dipyrromethane (500 mg, 1.7 mmol) was dissolved in dry dichloromethane (150 mL) and oxidized with DDQ (774 mg, 3.4 mmol) for 30 min at room temperature. The reaction mixture was then treated with triethylamine (864 mg, 1.19 mL, 8.5 mmol) followed by $BF_3.Et_2O$ (1.207 g, 1.05 mL, 8.5 mmol) and the mixture was stirred for an additional 30 min at room temperature. The solvent was removed in a rotary evaporator and the resultant crude compound was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1) and afforded pure 3,5-diformylboron dipyrromethene as a dark solid in 43% yield (248 mg, 0.73 mmol). Mp: 242−243 °C; R_f=0.62 ($C_6H_{14}/C_4H_8O_2$, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=2.52 (s, 3H; -CH_3), 7.11 (d, J=4.42 Hz, 2H; py), 7.19 (d, J=4.46 Hz, 2H; py), 7.42 (d, J=7.61 Hz, 2H; Ar), 7.52 (d, J=7.85 Hz, 2H; Ar), 10.48 (br s, 2H; -CHO). ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=178.9, 143.6, 141.3, 137.6, 135.9, 132.7, 132.6, 131.1, 130.4, 129.8, 129.7, 128.2, 122.1, 119.9, 44.0 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ_B=−3.75 ppm (t, $^1J_{B–F}$=28.9 MHz, 1B); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F=−135.17 (q, $^1J_{F–B}$=28.6 MHz, 2F); UV-Vis ($CHCl_3$): λ_{max} (lg ε)=500 nm (4.9); fluorescence: λ_{em}=520 nm with excitation at 490 nm; HRMS (MALDI): *m/z* calcd. for [$C_{18}H_{13}BF_2N_2O_2$] M^+ 338.1038; found 338.1046 (M^+).



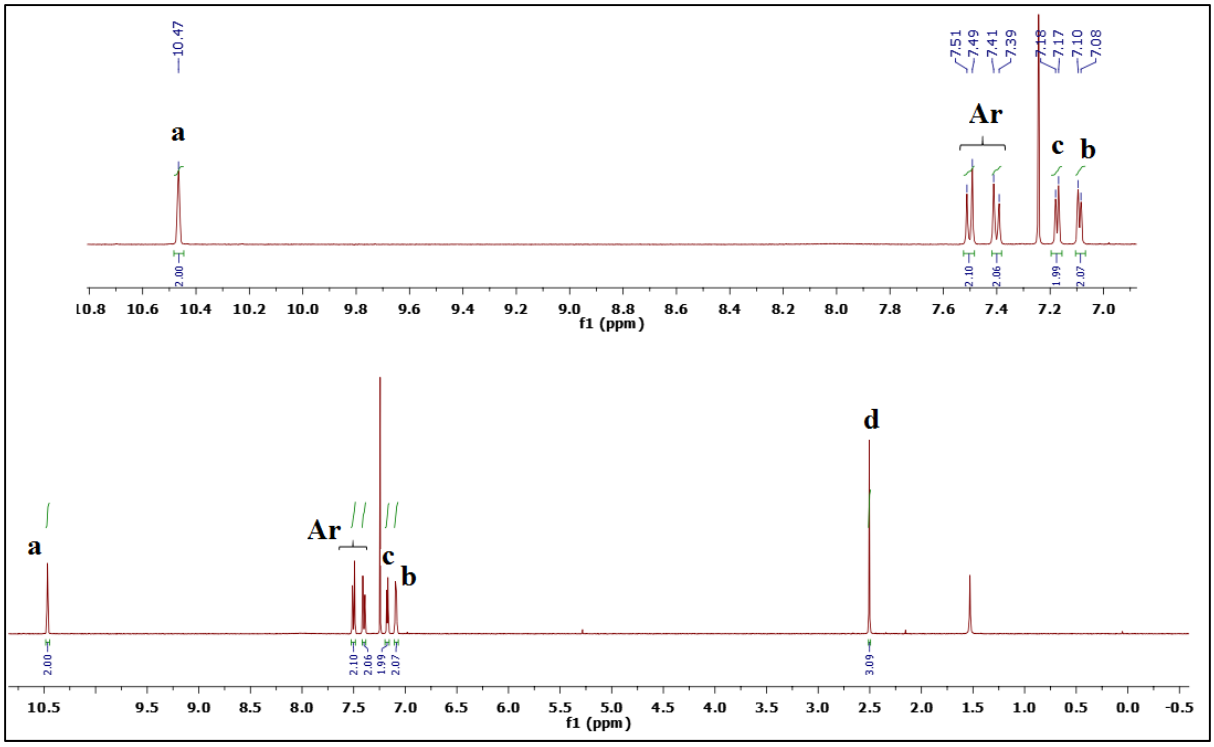


Figure S1. ^{1}H NMR spectrum of 3,5-diformyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene recorded in $CDCl_3$.

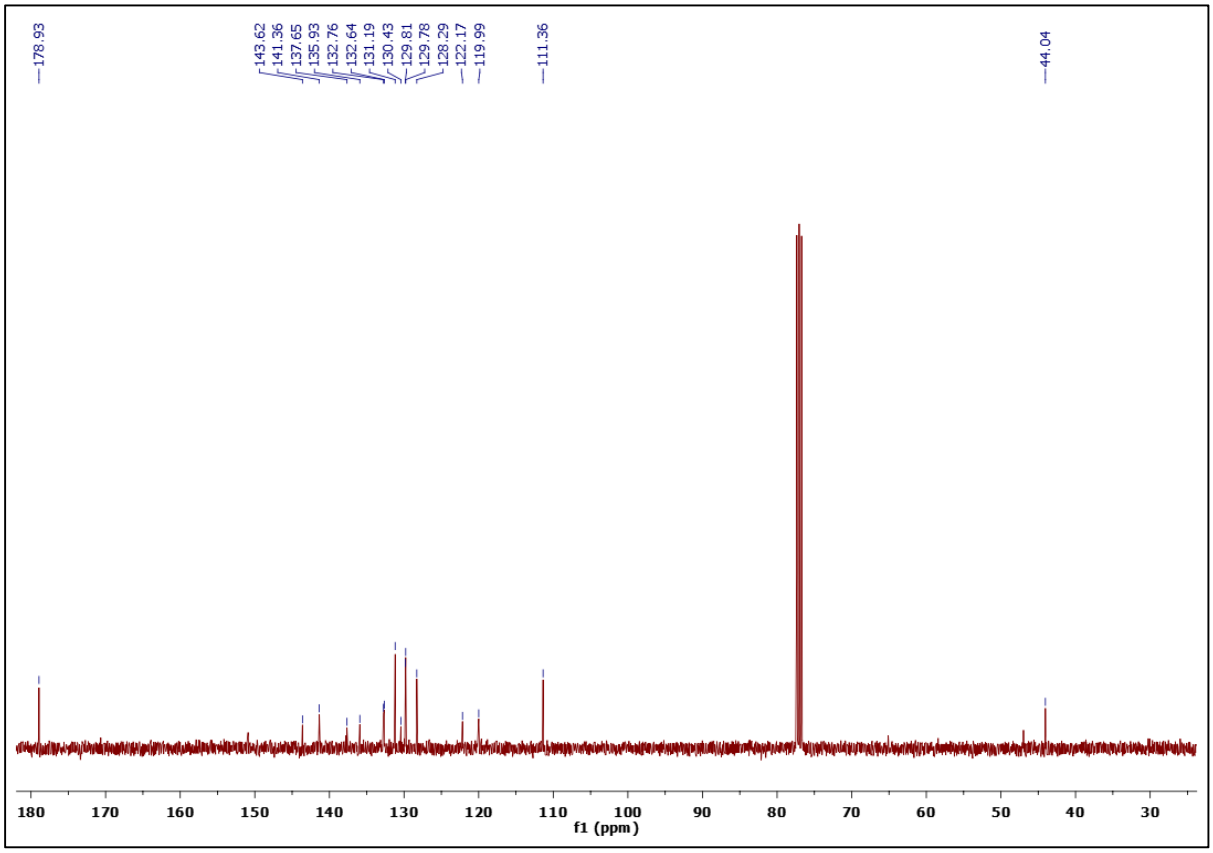


Figure S2. ^{13}C NMR spectrum of 3,5-diformyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene recorded in $CDCl_3$.

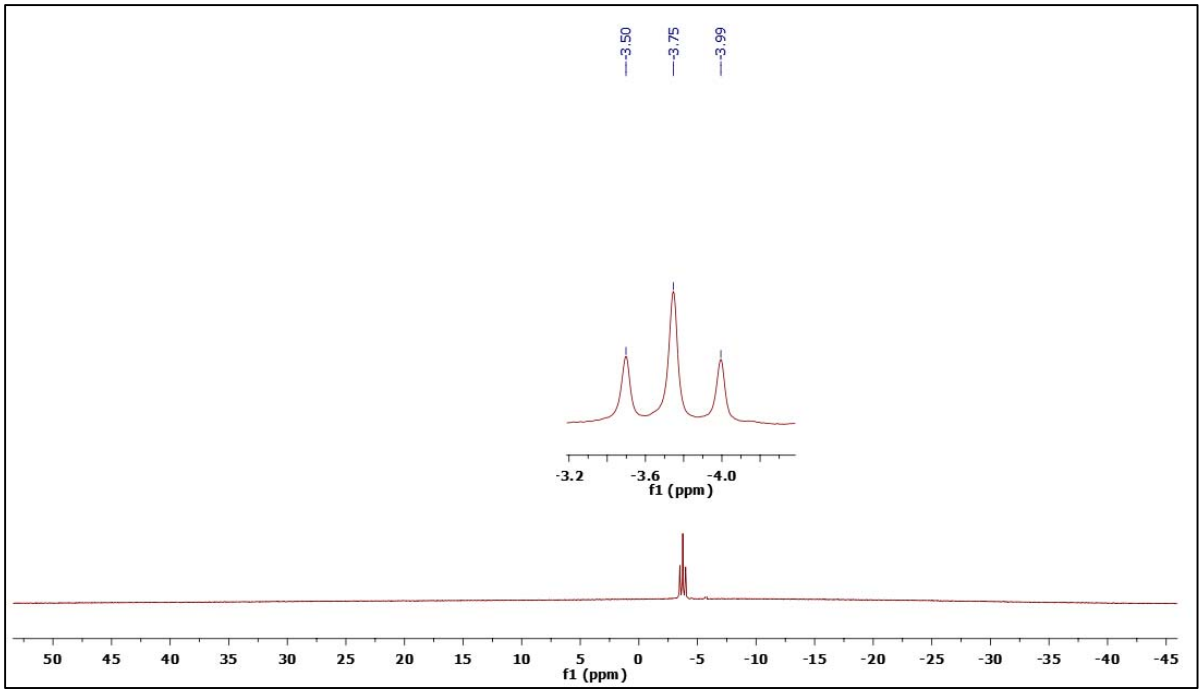


Figure S3. ^{11}B NMR spectrum of 3,5-diformyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene recorded in $CDCl_3$.

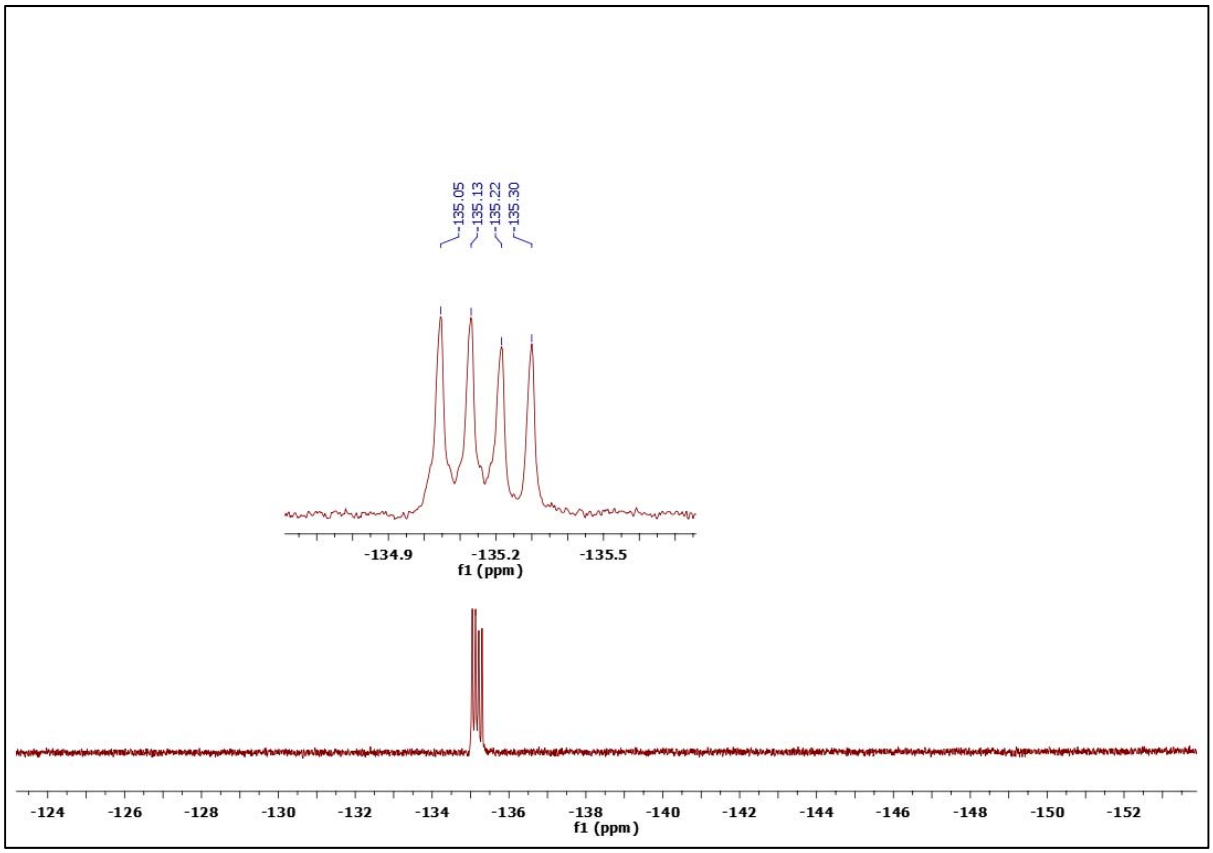


Figure S4. ^{19}F NMR spectrum of 3,5-diformyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene recorded in $CDCl_3$.

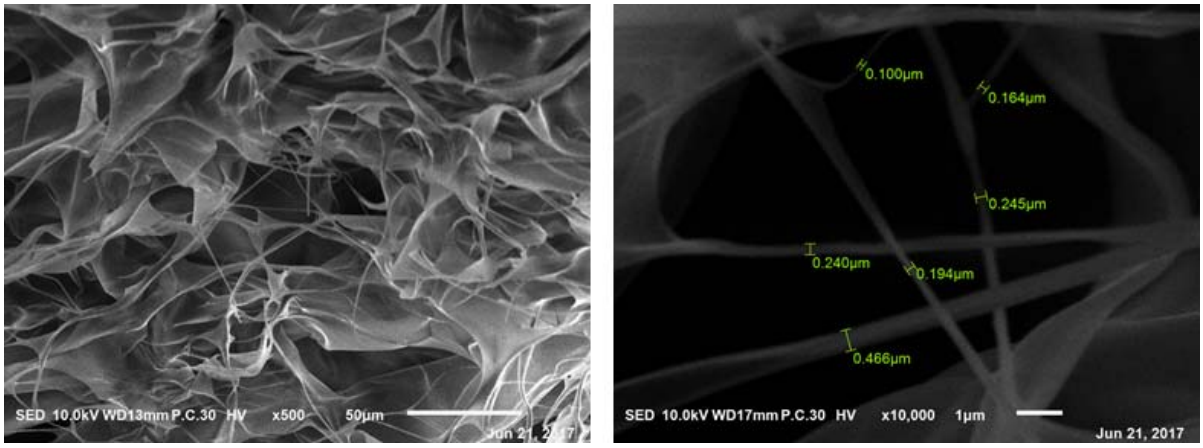


Figure S5. FE-SEM images of nanofiber BDP-CS hydrogels structure.

Pore-size of hydrogels with different wt-% 3, 5-diformyl BODIPY

As shown in Figure SI6, the 3, 5-diformyl BODIPY concentrations as cross-linker show strong regulate on the pore size distribution of the hydrogels.

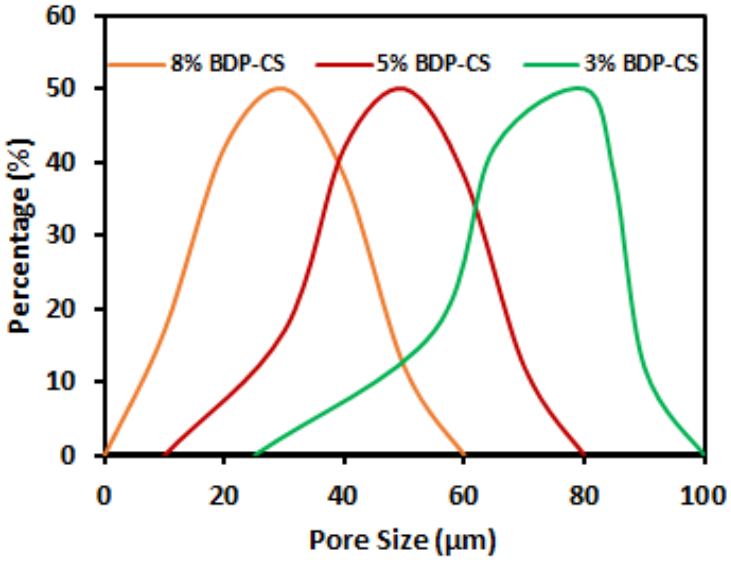


Figure S6. Pore size distributions of the hydrogels with different wt% 3, 5-diformyl BODIPY

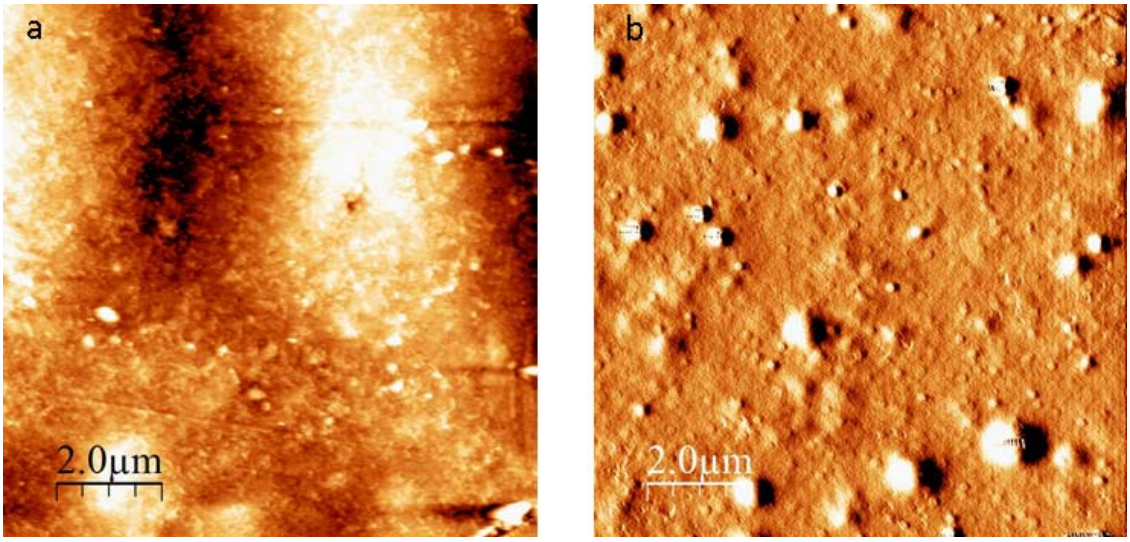


Figure S7. AFM amplitude images of the (a) chitosan film, (b) BDP-CS hydrogel.

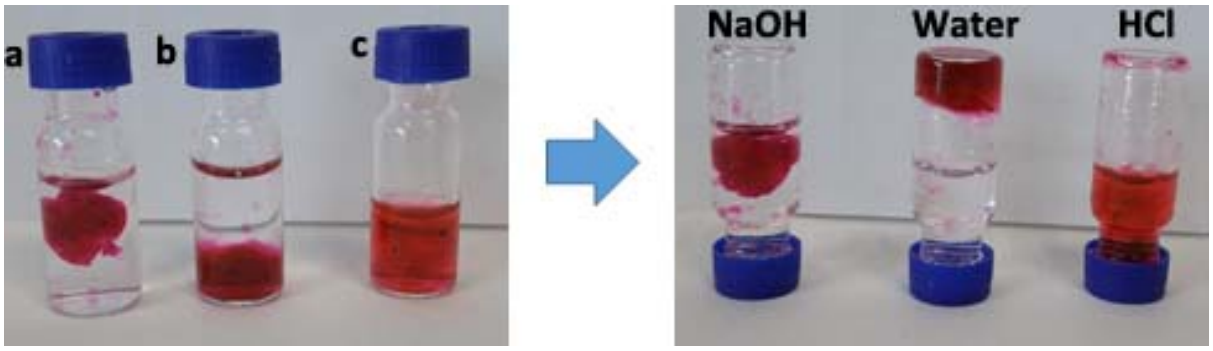


Figure S8. pH sensitivity and stability in aqueous environment of the BDP-CS hydrogel (a) BDP-CS hydrogel in basic (aq. NaOH, 6M), (b) neutral (water pH =7) and (c) acidic (aq. HCl, 6M) incubated at room temperature for 1 hour.

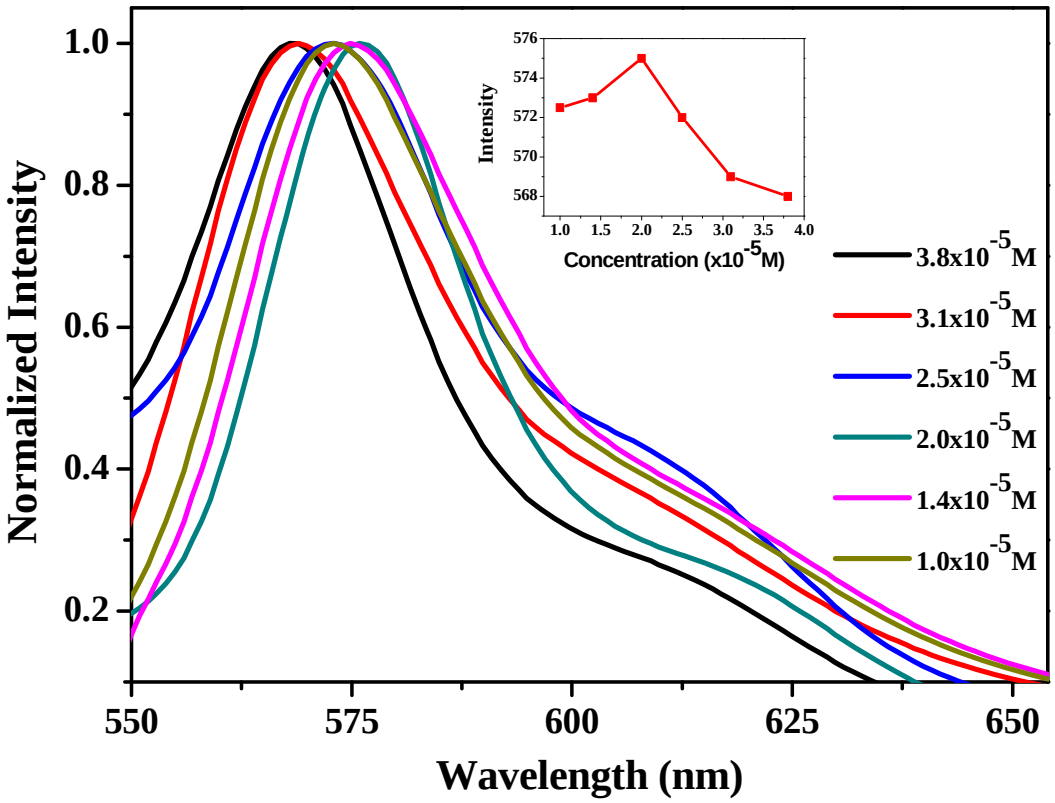


Figure S9. Comparison of normalized emission spectra of BDP-CS hydrogel at different concentrations in water. Inset shows the plot between concentration versus intensity.

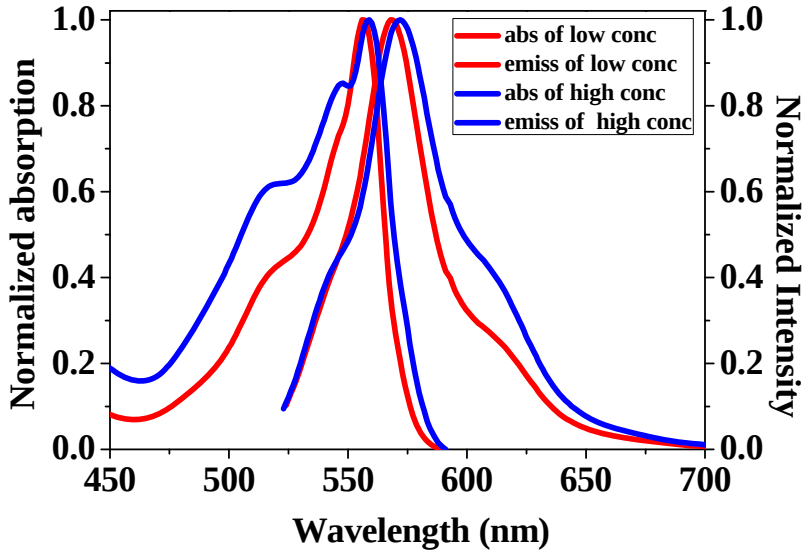


Figure S10. Comparison of normalized absorption and emission spectra of BDP-CS hydrogel at low (red line) and high (blue line) concentrations.

Estimation of the percentage of covalently bound BODIPY content

To estimate the percentage of covalently bonded BODIPY content, we used UV-vis spectroscopy. We used 0.75 mg of BODIPY monomer and dissolved it in 5 mL of DMF (concentration = 4.4×10^{-5}). The same weight of dry hydrogel was dissolved in 5 mL water. The UV-vis absorbance of both monomer and hydrogel were recorded. Then we calculated the relative amount of BODIPY in hydrogel structure based on their corresponding absorbance.

Hydrogel 5%: $4.4 \times 10^{-5} \times 0.38 / 1.15 = 1.4 \times 10^{-5}$ M

Hydrogel 8%: $4.4 \times 10^{-5} \times 0.66 / 1.15 = 2.5 \times 10^{-5}$ M

Relative percent of BODIPY in hydrogel structure based on monomer concentration:

Hydrogel 5% = $\frac{1.4\ x\ 10^{-5}}{4.4\ x\ 10^{-5}}\ x\ 100$ = 31%

Hydrogel 8% = $\frac{2.5\ x\ 10^{-5}}{4.4\ x\ 10^{-5}}\ x\ 100$ = 56%