Electronic Supplementary Material (ESI) for Polymer Chemistry.

Dual Encryption of Digital Information in a Tough Fluorescent Hydrogel

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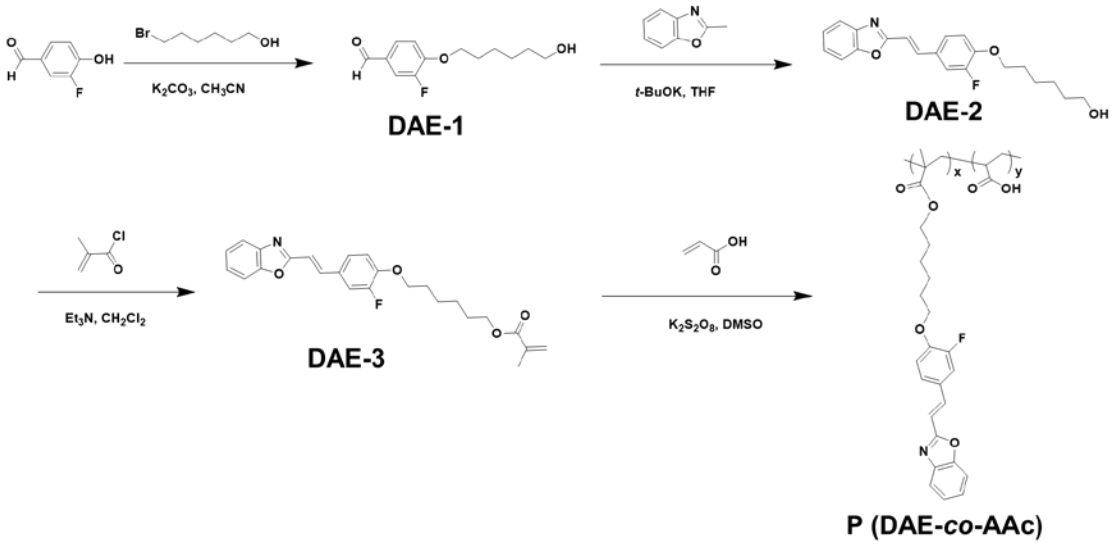
1. *Materials and methods*

All reagents were commercially available and used as supplied without further purification. Water used in this work was deionized water. ^{1}H NMR spectra were collected on a Bruker AVANCE DMX-400, Bruker Avance III 500 spectrometer or DMX-600 spectrometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{13}C NMR spectra were collected on a Bruker AVANCE DMX-400 spectrometer with use of the deuterated solvent as the lock and the residual solvent as the internal reference. Mass analysis was performed on an ion trap-time of flight (IT-TOF) mass spectrometer (Shimadzu, Tokyo, Japan). The mass spectrometer was operated in the full MS scan and automatic multiple-stage fragmentation scan modes over an *m*/*z* range of 50–500 in positive ion mode. In full MS scan mode, the ion accumulation time was 30 msec. The optical powers of UV 365 nm and 254 nm irradiations were 28 and 8 mw/cm^2, respectively. UV-vis spectra were taken on a Perkin-Elmer Lambda 35 UV-vis spectrophotometer. Fluorescence spectra of solid samples were obtained on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). Tensile and compression tests of the hydrogels were performed on a commercial tensile tester (Instron 3343) at room temperature.

*2. Syntheses of compounds **DAE-1**, **DAE-2**, and **DAE-3***



Scheme S1. Syntheses of **DAE-1, DAE-2, DAE-3** and **P(DAE-*co*-AAc).**

*2.1. Preparation of compound **DAE-1***

3-Fluoro-4-hydroxybenzaldehyde (5.00 g, 36.0 mmol) and 6-bromo-1-hexanol (32.3 g, 178 mmol) were dissolved in 300 mL of acetonitrile followed by the addition of K_2CO_3 (24.66 g, 178 mmol). The mixture was stirred for 24 h at 84 °C in an argon atmosphere. After the reaction, dichloromethane was added and the mixture was filtered. The filtrate was concentrated and purified by flash column chromatography on silica gel (dichloromethane/ethyl acetate, *v*/*v* = 15:1) to afford **DAE-1** as a yellow liquid (7.29 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ ppm 9.84 (s, 1 H), 7.63–7.58 (q, *J* = 23.5 Hz, 2 H), 7.07 (t, *J* = 13.5 Hz, 1H), 4.12 (t, *J* = 11 Hz, 3 H), 3.65 (t, *J* = 11 Hz, 3 H), 1.88 (m, *J* = 23.5 Hz, 2 H), 1.61 (m, *J* = 23.5 Hz, 2 H), 1.53 (m, *J* = 24.5 Hz, 2 H), 1.47 (m, *J* = 19.5 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm 190.16, 153.74, 152.65, 151.26, 129.67, 128.35,115.39, 113.54, 69.33, 62.47, 33.91, 28.85, 25.65, 25.43. FTICR MS: *m*/*z calcd for* $[M + H]^+$ $C_{13}H_{18}O_3F^+$, 241.1240; found 241.1261; error 2.1 ppm.

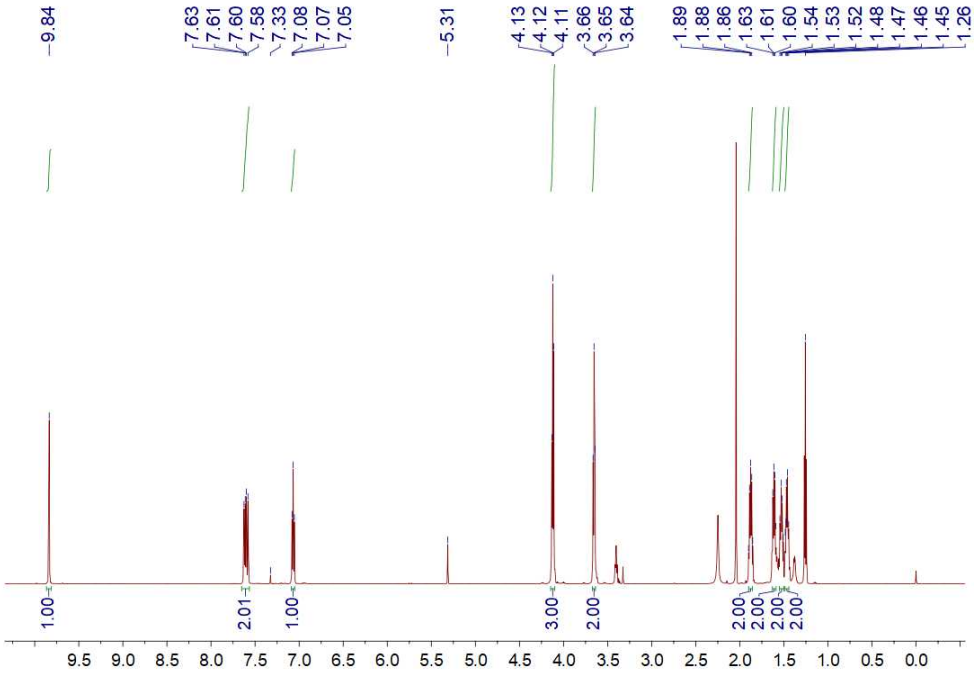


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **DAE-1.**

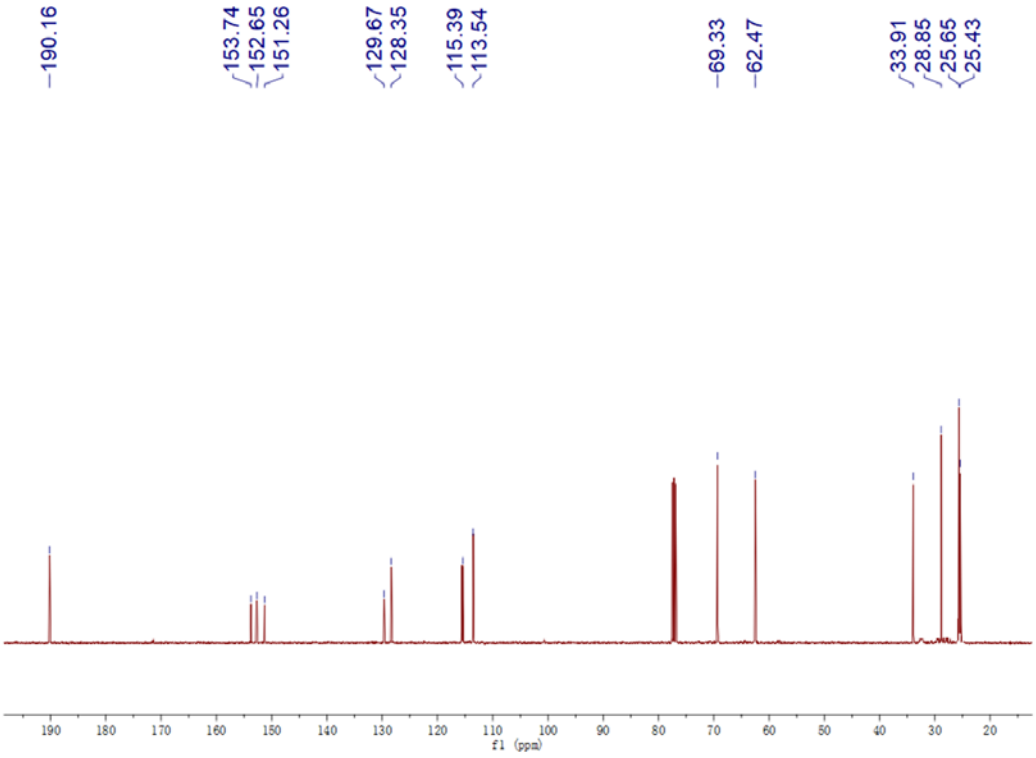


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **DAE-1.**

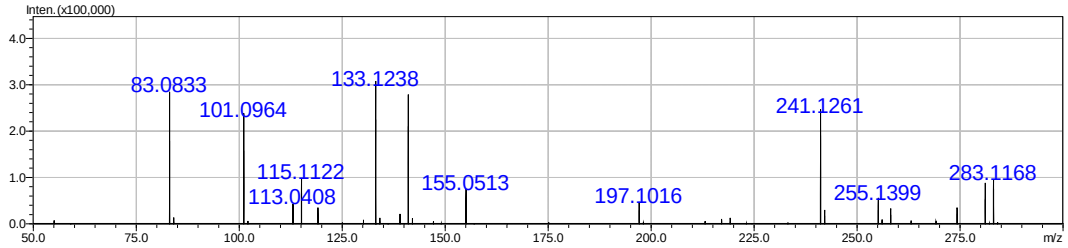


Figure S3. FTICR mass spectrum of **DAE-1**.

*2.2. Preparation of compound **DAE-2***

t-BuOK (6.06 g, 54.0 mmol) was added into dry THF (80.0 mL) and stirred for 10 min at 0 °C. Then, 2-methylbenzoxazole (3.30 mL,24.8 mmol) was added dropwise and the mixture was stirred at 0 °C for another 10 min. After that, a solution of **DAE-1** (6.00 g, 25.0 mmol) in THF was added dropwise into the above mixture at 0 °C. After stirring for 2 h at 0 °C, the mixture was poured into water (500 mL) and a light yellow solid was collected by filtration. The crude product was purified by flash column chromatography on silica gel (dichloromethane/ethyl acetate, *v*/*v* = 15/1) to afford **DAE-2** as a yellow solid (1.50 g, 17%). *m.p.* 82.5-85.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ ppm 7.70 (t, *J* = 19.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.35–7.32 (m, *J* = 15.5 Hz, 3 H), 7.29 (d, *J* = 7 Hz, 1 H), 6.97 (t, *J* = 14.5 Hz, 1 H), 6.93 (d, *J* = 13.5 Hz, 1 H), 4.08 (t, *J* = 11 Hz, 2 H), 3.67 (t, *J* = 11 Hz, 2 H), 1.86 (m, *J* = 23.5 Hz, 2 H), 1.63 (m, 2 H), 1.53 (m, *J* = 24.5 Hz, 2 H), 1.47 (m, *J* = 19.5 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm 160.80, 153.93, 151.47, 150.39, 148.66, 148.55, 142.17, 138.16, 128.35, 125.17, 124.53, 119.79, 114.51, 114.32, 112.78, 110.30, 69.28, 62.84, 32.63, 29.07, 25.76, 25.51. FTICR MS: *m*/*z calcd* for $[M + H]^+$ $C_{21}H_{23}O_3FN^+$, 356.1662; found 356.1667; error 0.5 ppm.

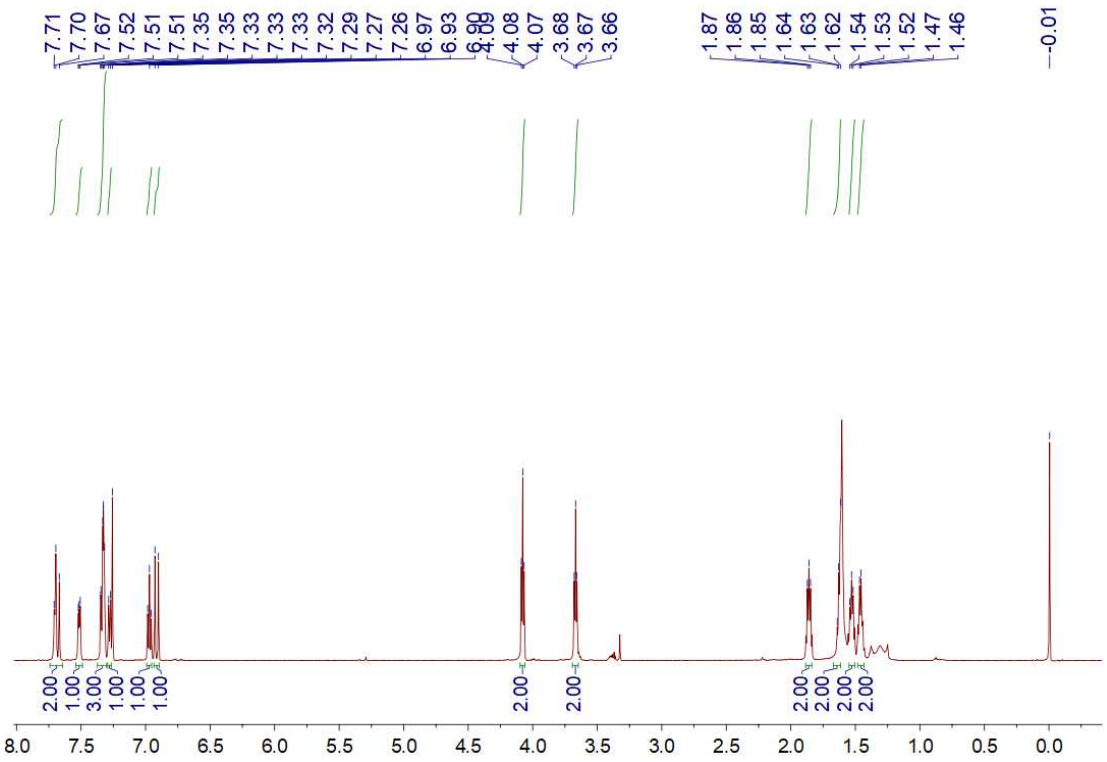


Figure S4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **DAE-2.**

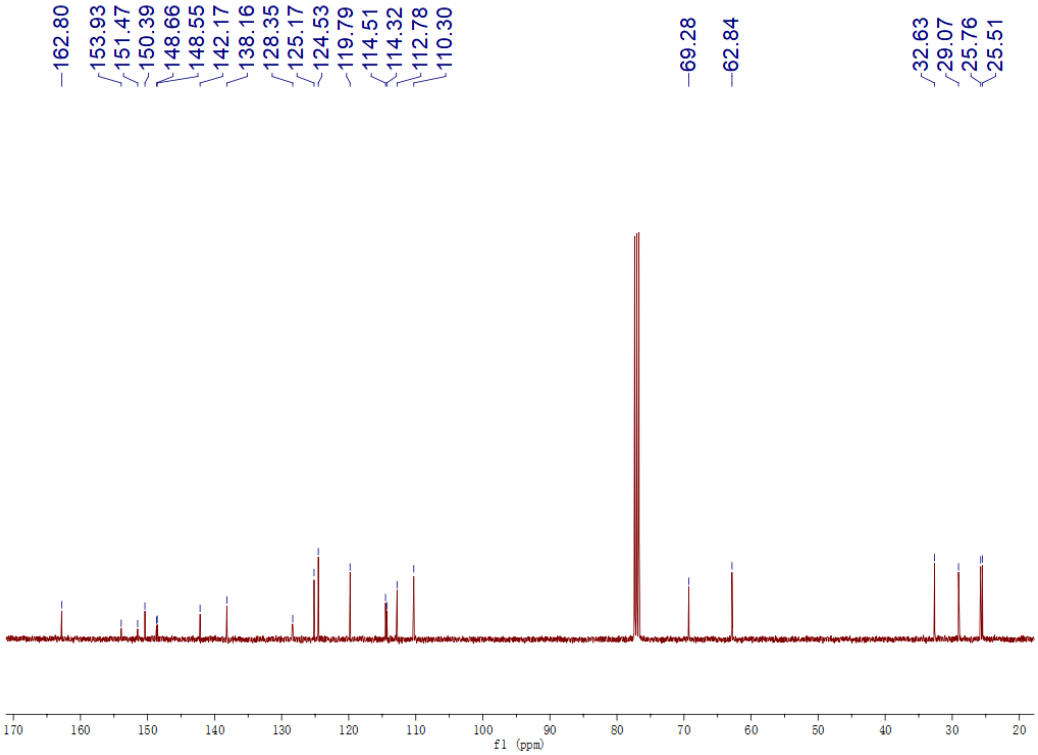


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **DAE-2.**

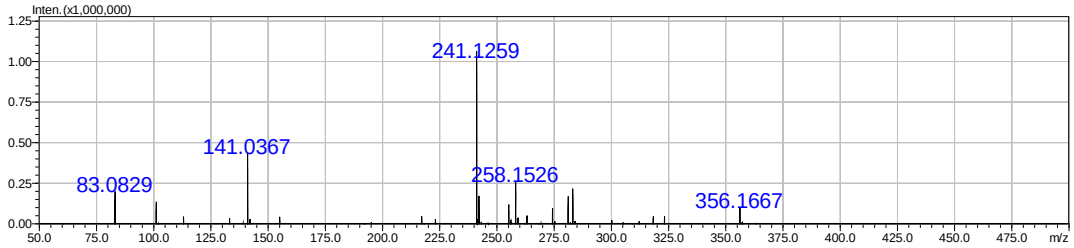


Figure S6. FTICR mass spectrum of **DAE-2**.

*2.3. Preparation of compound **DAE-3***

To a mixture of compound **DAE-2** (1.15 g, 3.23 mmol) and triethylamine (393 mg, 3.88 mmol) in dichloromethane (20.0 mL), acryloyl chloride (406 mg, 3.88 mmol) was added dropwise over 10 min at room temperature and the mixture was stirred overnight. The reaction mixture was poured into a saturated aqueous solution of $NaHCO_3$ and then extracted with $CHCl_3$. The organic layer was collected and purified by flash column chromatography on silica gel (dichloromethane/ethyl acetate, *v*/*v* = 30:1) to afford compound **DAE-3** as a yellow solid (1.20 g, 88%). *m.p.* 59.3-62.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm 7.71 (m, *J* = 12.8 Hz, 2 H), 7.52 (m, *J* = 9.2 Hz, 1 H), 7.34 (m, *J* = 16.4 Hz, 3 H), 7.30 (d, *J* = 8.8 Hz, 1 H), 6.94 (m, *J* = 37.6 Hz, 2 H), 6.10 (s, 1 H), 5.55 (q, *J* = 3.2 Hz, 1 H), 4.17 (t, *J* =13.2 Hz, 2 H), 4.08 (t, *J* =13.2 Hz, 2 H), 1.95 (s, 3 H), 1.87 (t, *J* = 27.6 Hz, 2 H), 1.73 (t, *J* = 28 Hz, 2 H), 1.51 (t, *J* = 30 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ ppm 167.55, 162.78, 153.92, 151.47, 150.39, 148.63, 148.52, 142.18, 138.12, 138.10, 136.49, 128.44, 125.27, 125.16, 124.52, 119.80, 114.50, 114.32, 112.80, 110.29, 69.22, 64.62, 29.01, 28.54, 25.77, 25.63, 18.34. FTICR MS: *m/z calcd for* $[M + H]^+$ $C_{25}H_{27}O_4FN^+$, 424.1924; found 424.1925; error 0.1 ppm.

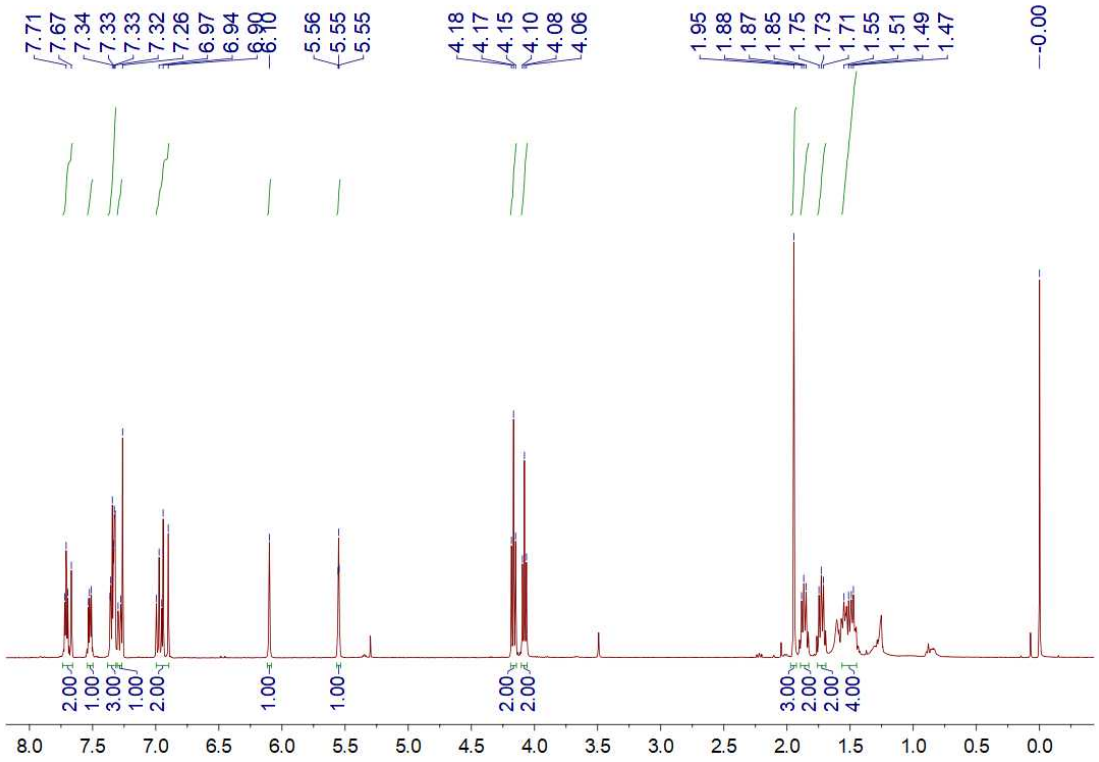


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **DAE-3.**

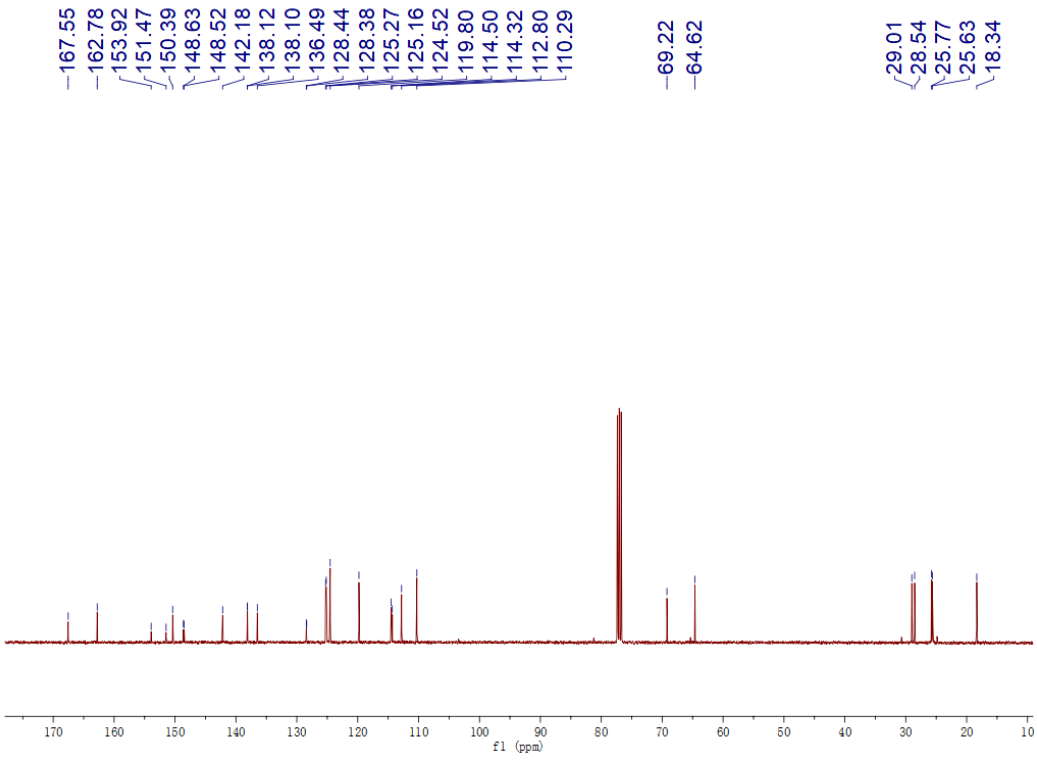


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **DAE-3.**

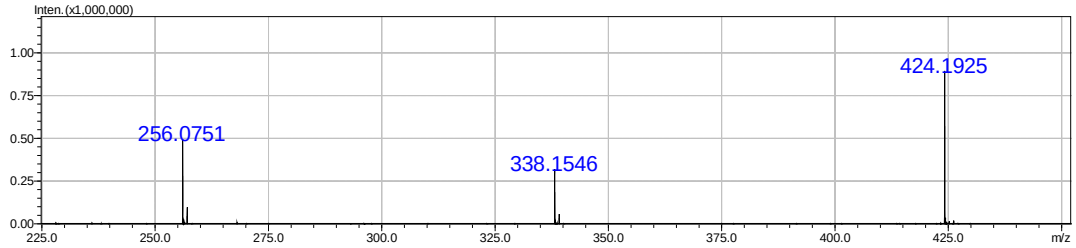


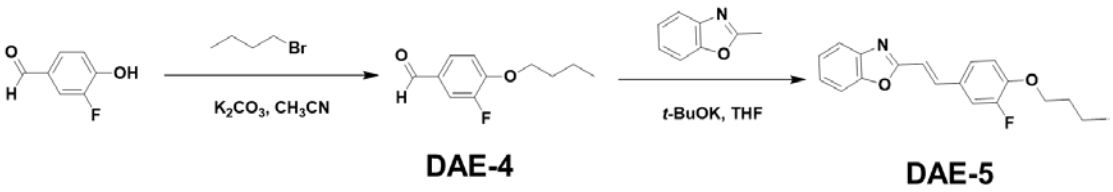
Figure S9. FTICR mass spectrum of **DAE-3**.

*3. Synthsis of polymer **P(DAE-co-AAc)***

The polymer was prepared through a modified procedure from a previous paper.[S1] Compound **DAE-3** (254 mg, 0.60 mmol, 3.00 mol%), $K_2S_2O_8$ (27.0 mg, 0.10 mmol) and 2-methyl-2-propenoic acid (1.44 g, 20.0 mmol) were mixed in DMSO (5.00 mL). The mixture was stirred and purged with nitrogen at room temperature for 0.5 h to obtain a precursor solution. This precursor solution was injected into a reaction cell consisting of a pair of glass substrates separated with 0.5-mm-thick silicone rubber spacer, which was kept in an oven at 60 °C for 6 h to complete the polymerization. The resulting organogel was immersed in a gradient ratio of 10:1 to 1:10 of DMSO and water as solvent exchange to remove impurities. The water was exchanged every day, and the equilibrated hydrogel ***P(DAE-co-AAc)*** was obtained after one week.

Preparations of other polymers containing different contents of **DAE-3** employed the same procedure.

*4. Syntheses of compounds **DAE-4** and **DAE-5***



Scheme S2. Synthesis of compounds **DAE-4** and **DAE-5.**

*4.1. Preparation of compound **DAE-4***

3-Fluoro-4-hydroxybenzaldehyde (5.00 g, 35.7 mmol) and butyl bromide (24.5g, 178 mmol) were mixed in 300 mL of acetonitrile followed by the addition of K_2CO_3 (24.7 g, 178 mmol), the mixture was stirred for 24 h at 84 °C in an argon atmosphere. As a result, pure compound **DAE-4** was obtained by flash column chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* = 1:1) to afford **DAE-4** as a colorless transparent liquid (6.02 g) in a yield of 86%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K) *δ* ppm 9.85 (s, 1 H), 7.61 (q, *J* = 19 Hz, 2 H), 7.06 (t, *J* = 16 Hz, 1H), 4.12 (t, *J* = 13.5 Hz, 2 H), 1.85 (m, *J* = 28 Hz, 2 H), 1.54 (m, *J* = 37.5 Hz, 2 H), 1.00 (t, *J* = 24.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) *δ* ppm 189.92, 153.81, 152.79, 151.33, 19.69, 128.22, 115.56, 113.48, 69.15, 30.92, 19.05, 13.71. FTICR MS: *m*/*z calcd* for $[M + H]^+$ $C_{11}H_{14}O_2F^+$, 197.0978; found 197.1004; error 2.6 ppm.

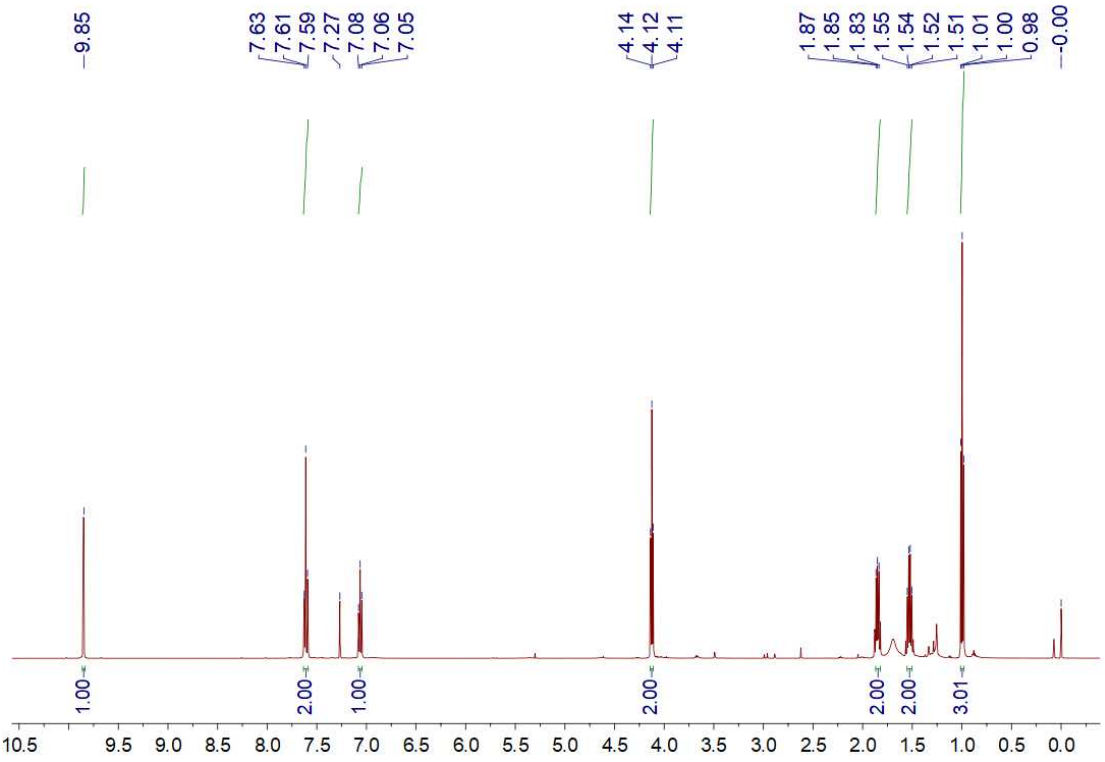


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **DAE-4.**

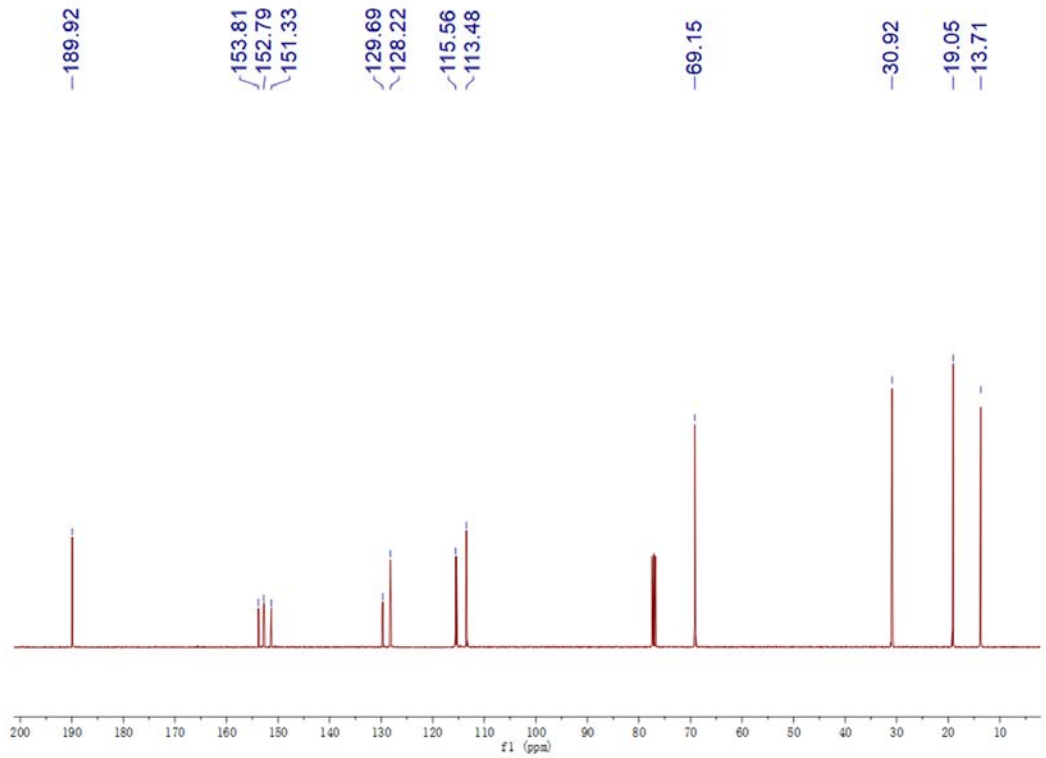


Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **DAE-4.**

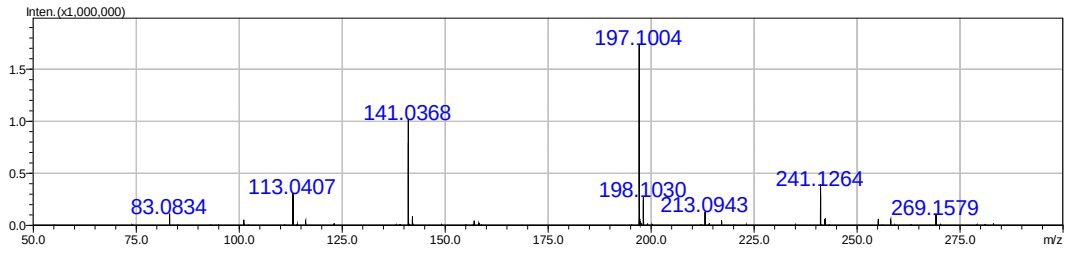


Figure S12. FTICR mass spectrum of **DAE-4**.

*4.2. Preparation of compound **DAE-5***

t-BuOK (3.37 g, 30.00 mmol) was added into dry THF (38 mL) and stirred for 10 min at 0 °C. Then, 2-methylbenzoxazole (1.45 mL,12.23 mmol) was added dropwise and the mixture was stirred at 0 °C for another 10 min. After that, the solution of **DAE-4** (2.00 g, 10.19 mmol) in THF was added dropwise into the above mixture at 0 °C. After stirring for 2 h at 0 °C, the mixture was poured into water (300 mL) and a light yellow solid was collected by filtration. The crude product was purified by flash column chromatography on silica gel (petroleum ether/dichloromethane, *v*/*v* = 1:5) to afford **DAE-5** as a yellowish solid

(1.27 g) in a yield of 40%, *m.p.* 96.4-99.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ ppm 7.71 (m, *J* = 20.8 Hz, 2 H), 7.52 (m, *J* = 13.6 Hz, 2 H), 7.36–7.32 (m, *J* = 21.2 Hz, 3H), 7.30 (d, *J* = 8.8 Hz, 1 H), 6.98 (t, *J* = 16.8 Hz, 1 H), 6.94 (d, *J* = 16.4 Hz, 1 H), 4.08 (t, *J* = 13.2 Hz, 2 H), 1.83 (m, *J* = 28 Hz, 2 H), 1.53 (m, *J* = 37.6 Hz, 2 H), 0.99 (t, *J* = 14.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm 162.81, 153.94, 151.48, 150.40, 148.73, 148.62, 142.20, 138.17, 128.28, 125.14, 124.51, 119.80, 114.48, 114.44, 114.29, 112.75, 110.29, 69.12, 31.13, 19.14, 13.81. FTICR MS: *m/z calcd* for [M + H]+ $C_{19}H_{19}O_2FN^+$, 312.1400; found 312.1418; error 1.8 ppm.

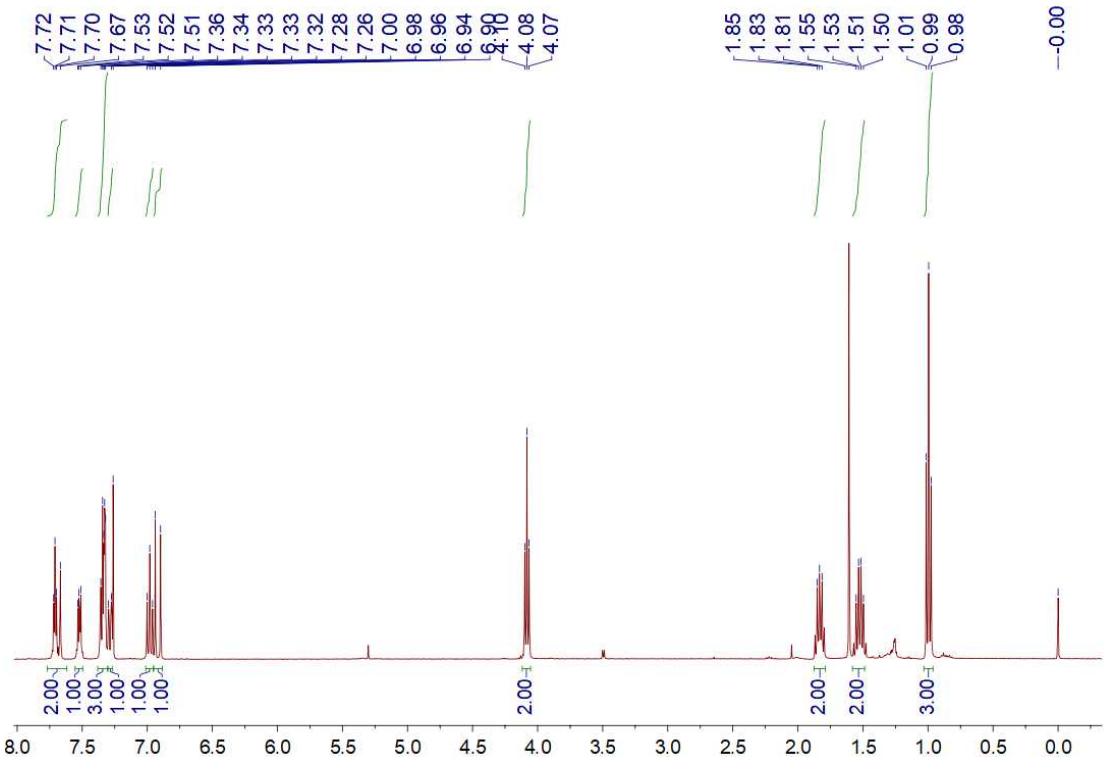


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **DAE-5.**

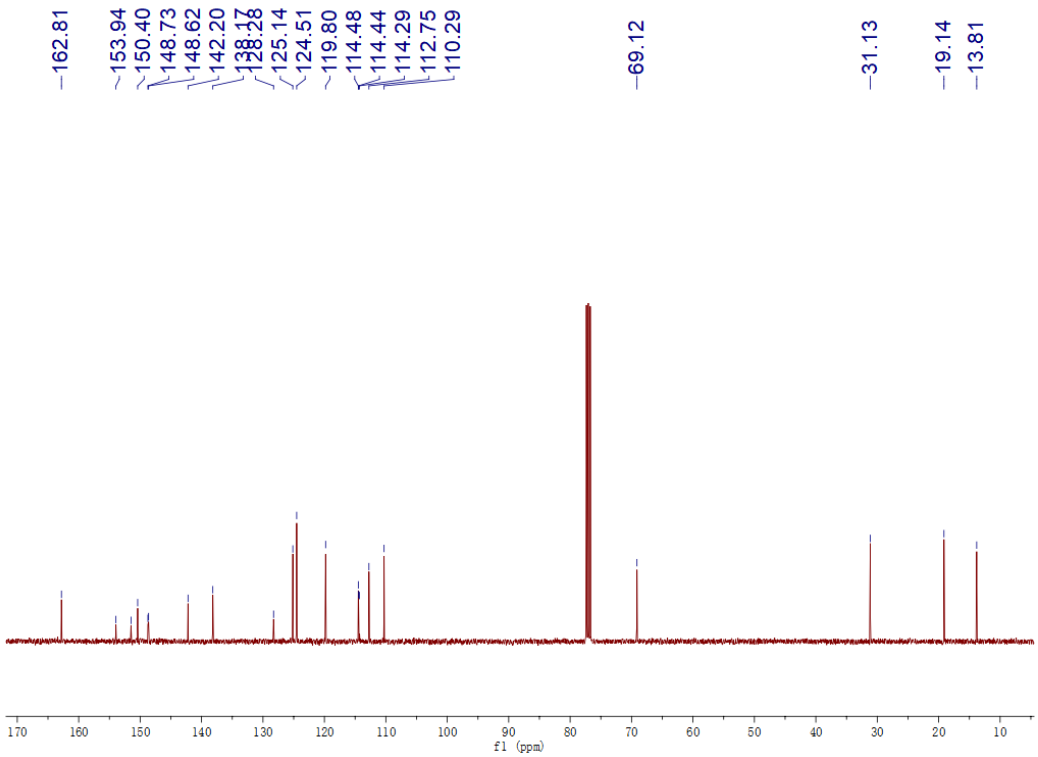


Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **DAE-5.**

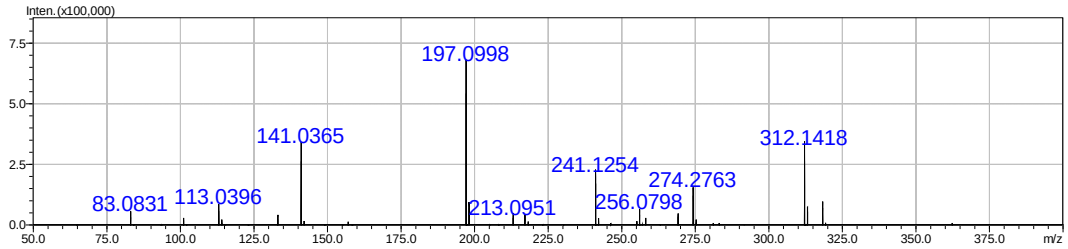


Figure S15. FTICR mass spectrum of **DAE-5**.

*4.3. Irradiation of 365 nm UV light on **DAE-5***

A solution of **DAE-5** (0.12 mol/L, 1.00 mL) was put into a quartz cuvette then irradiated by 365 nm UV for 2 h. The afforded solution was analyzed by ^1H NMR to monitor the dimerization process. ^1H NMR (400 MHz, $CDCl_3$, 298K) δ ppm 7.91 (m, J = 15.2 Hz, 0.75 H), 7.74 (m, J = 40.0 Hz, 1.25 H), 7.51 (m, J = 33.2 Hz, 2 H), 7.35–7.33 (m, J = 11.6 Hz, 2H), 7.30 (d, J = 8.8 Hz, 0.25 H), 6.92 (m, J = 48.4 Hz, 2 H), 6.48 (d, J = 13.2 Hz, 0.75 H), 4.09 (t, J = 17.2 Hz, 2 H), 1.84 (m, J = 28 Hz, 2 H), 1.54 (q, J = 22.4 Hz, 2 H), 1.00 (t, J = 14.8 Hz, 2 H). Q-TOF MS: *m/z calcd* for $[M + Na]^+$ $C_{38}H_{36}O_4F_2N_2Na^+$, 645.2541; found 645.2532; error –0.9 ppm.

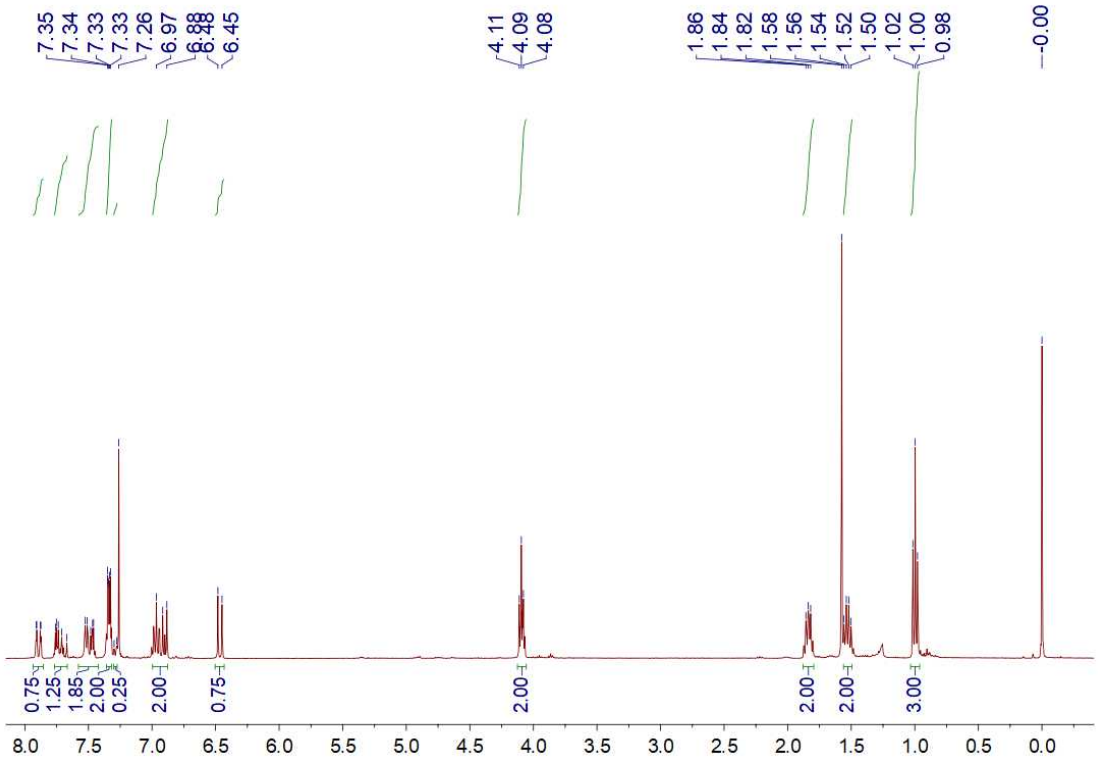


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **DAE-5** after 365 nm UV irradiation**.**

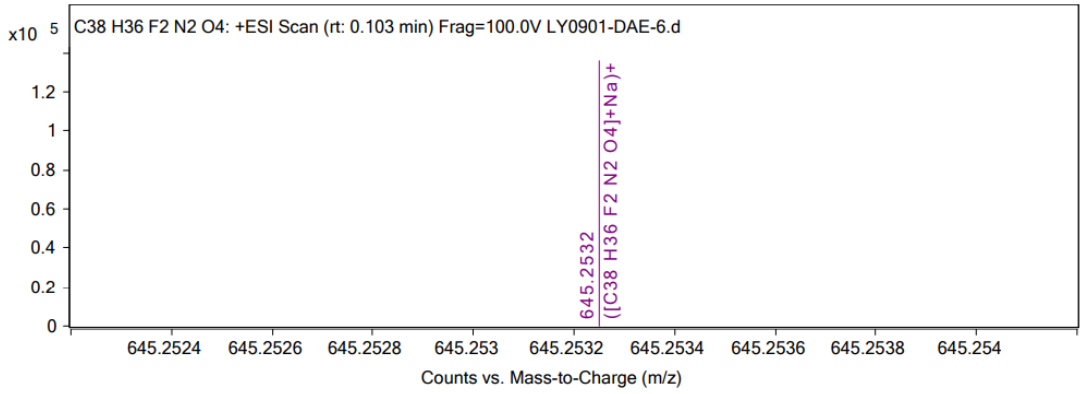


Figure S17. Q-TOF mass spectrum of of **DAE-5** after 365 nm UV irradiation.

*5. Comparison of ^{1}H NMR spectra of **DAE-5** before and after UV irradiation*

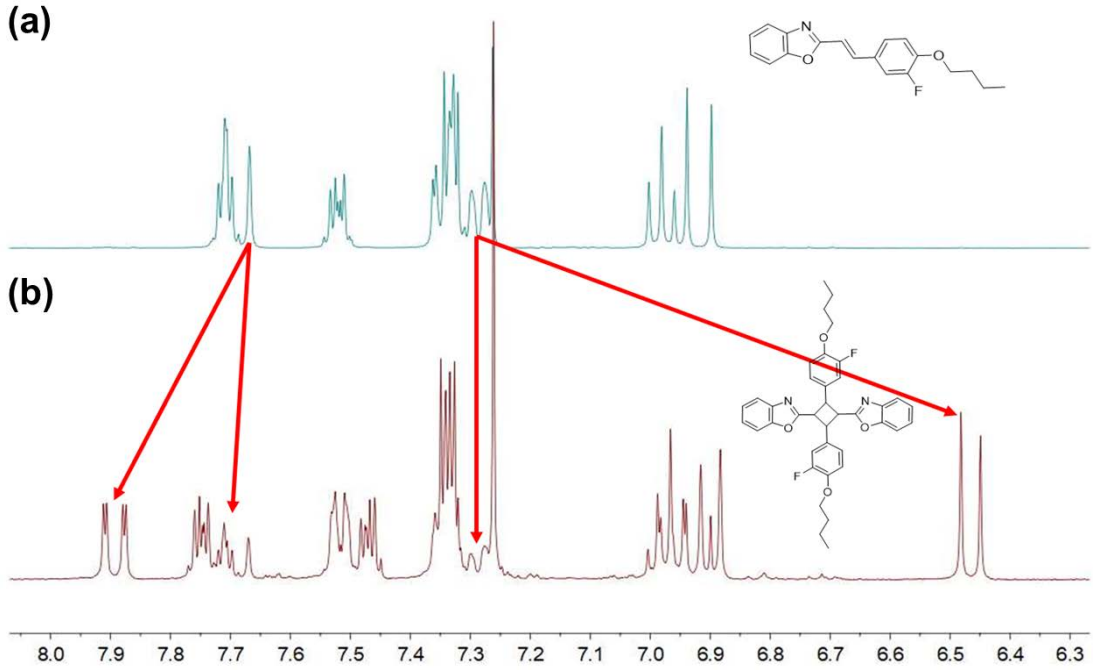


Figure S18. Partial ^{1}H NMR spectra of **DAE-5** (a) before and (b) after 365 nm UV irradiation.

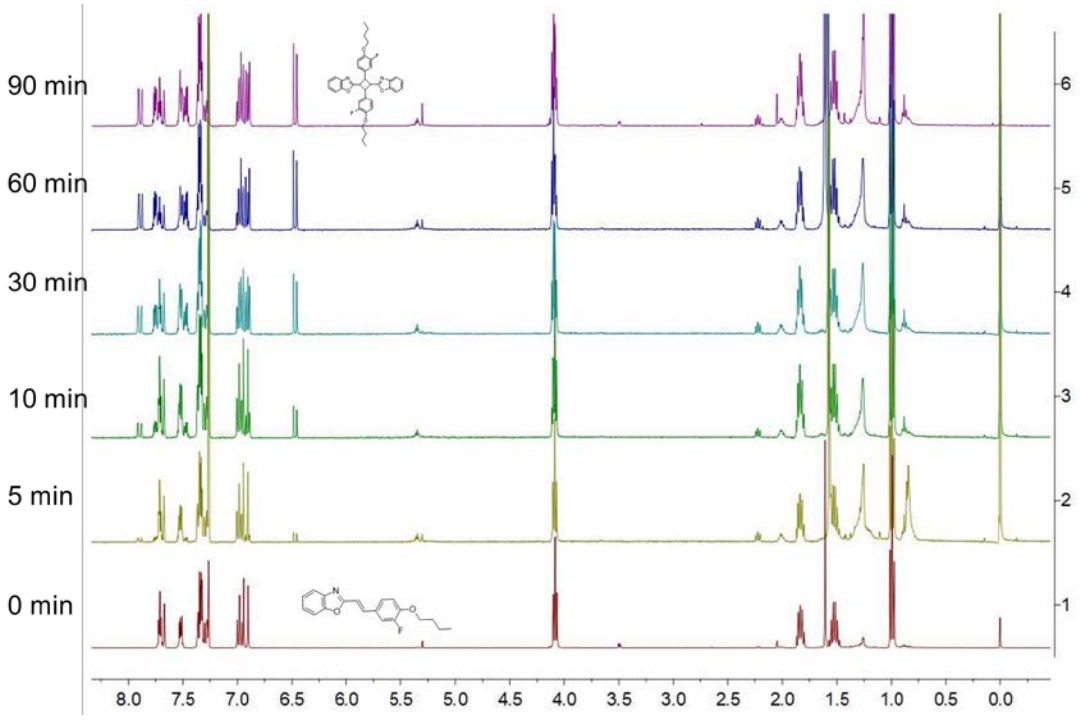


Figure S19. ^{1}H NMR spectra of **DAE-5** with different irradiation times by 365 nm UV light.

*6. UV-vis spectra of **DAE-5** before and after irradiation*

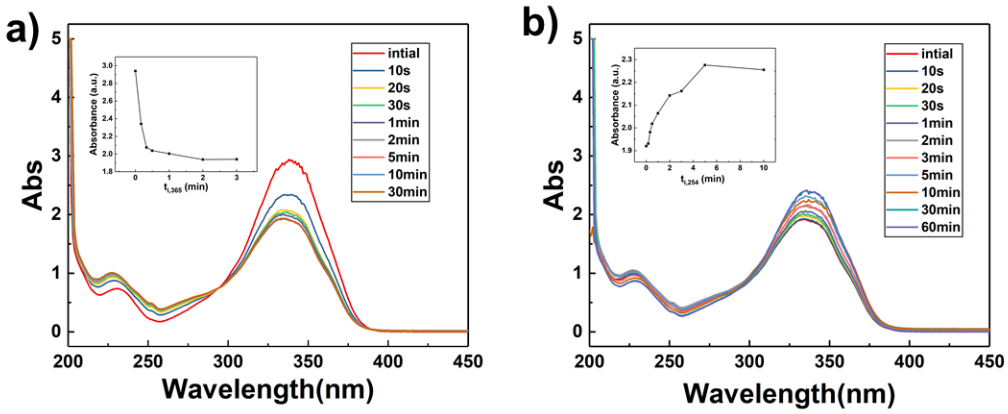


Figure S20. UV absorption changes with different irradiation times by (a) 365 UV light and (b) 254nm UV light.

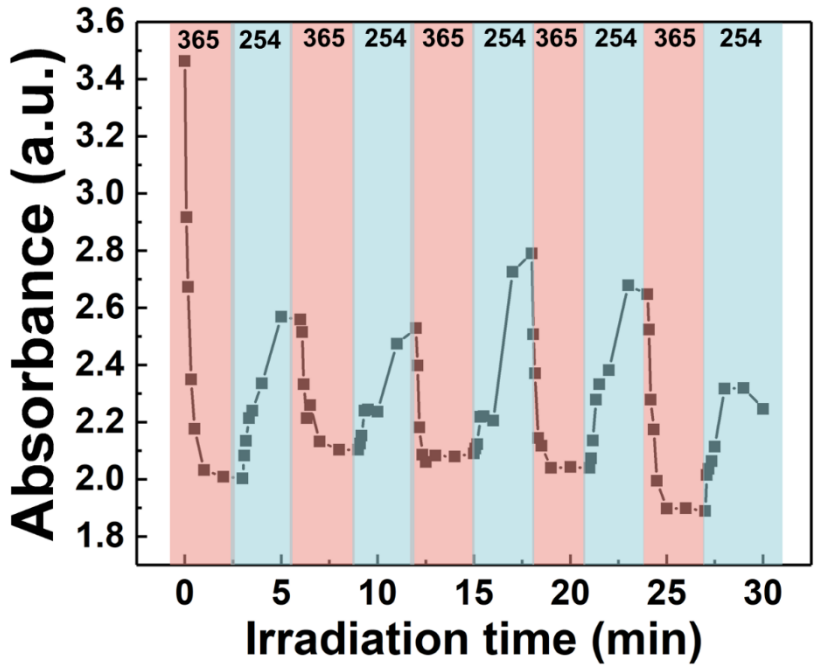


Figure S21. UV absorbance at 338 nm of **DAE-5** upon alternative irradiation under 365 and 254 nm UV light.

7. FT-IR spectra of ***P(DAE-co-AAc)***

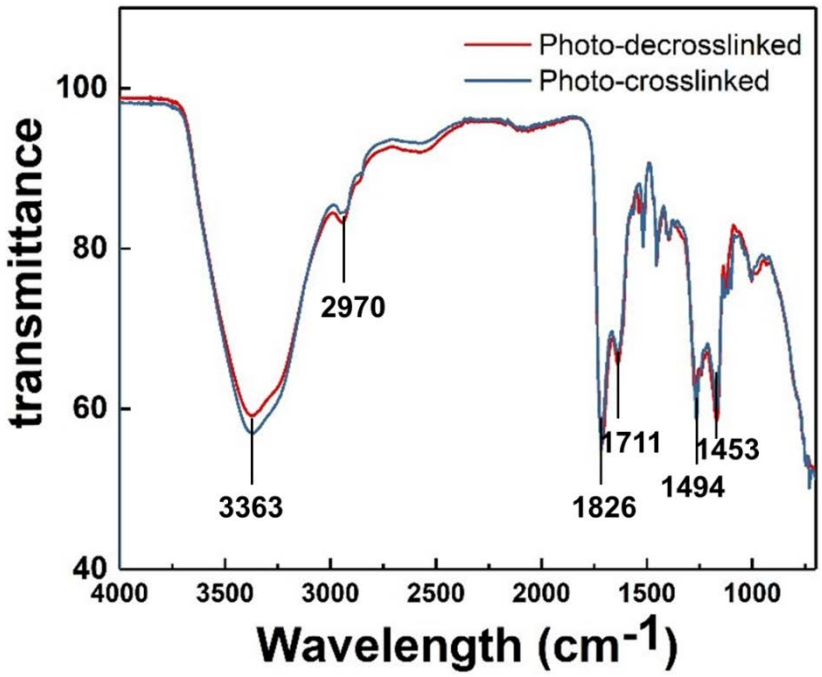


Figure S22. FTIR spectra of ***P(DAE-co-AAc)*** before (red line) and after (blue line) photo-crosslinking.

8. Water conten of the hydrogel upon alternative photo-crosslinking and photo-decrosslinking

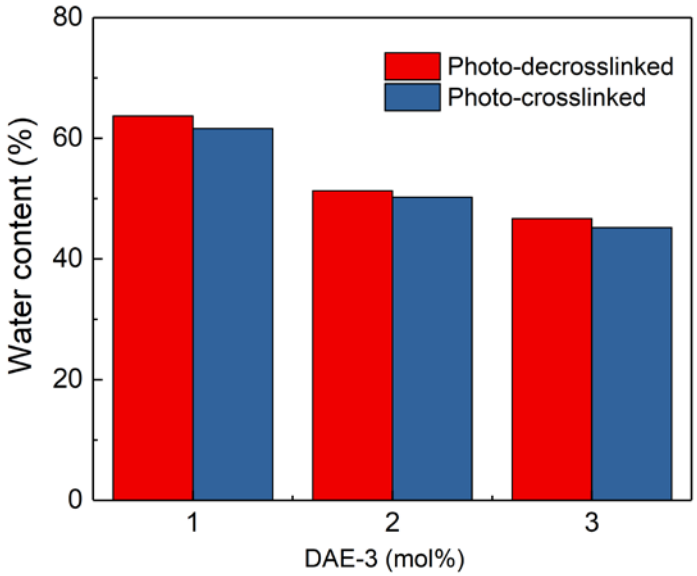


Figure S23. Water content of the hydrogel upon alternative photo-crosslinking and photo-decrosslinking.

9. Photographs of a hydrogel sheet before and after photo-crosslinking

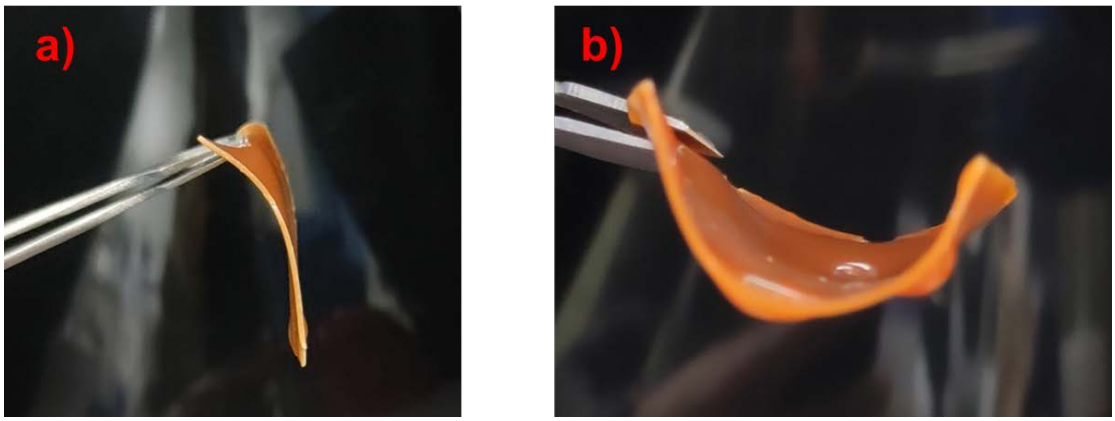


Figure S24. A hydrogel sheet (thickness 1.00 mm) (a) before and (b) after photo-crosslinking.

10. Young's modulus changes of the hydrogel

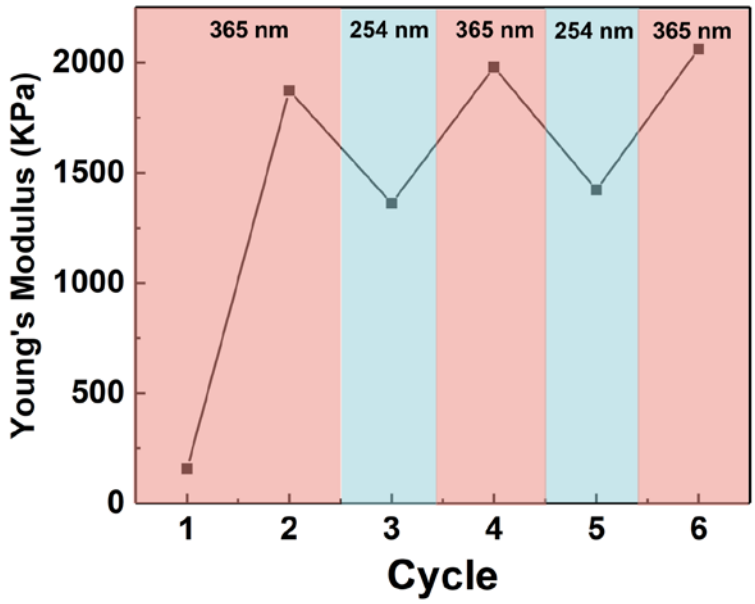


Figure S25. Young's modulus of the hydrogel upon alternative photo-crosslinking and photo-decrosslinking.

11. Thermal stability of the cyclobutane ring

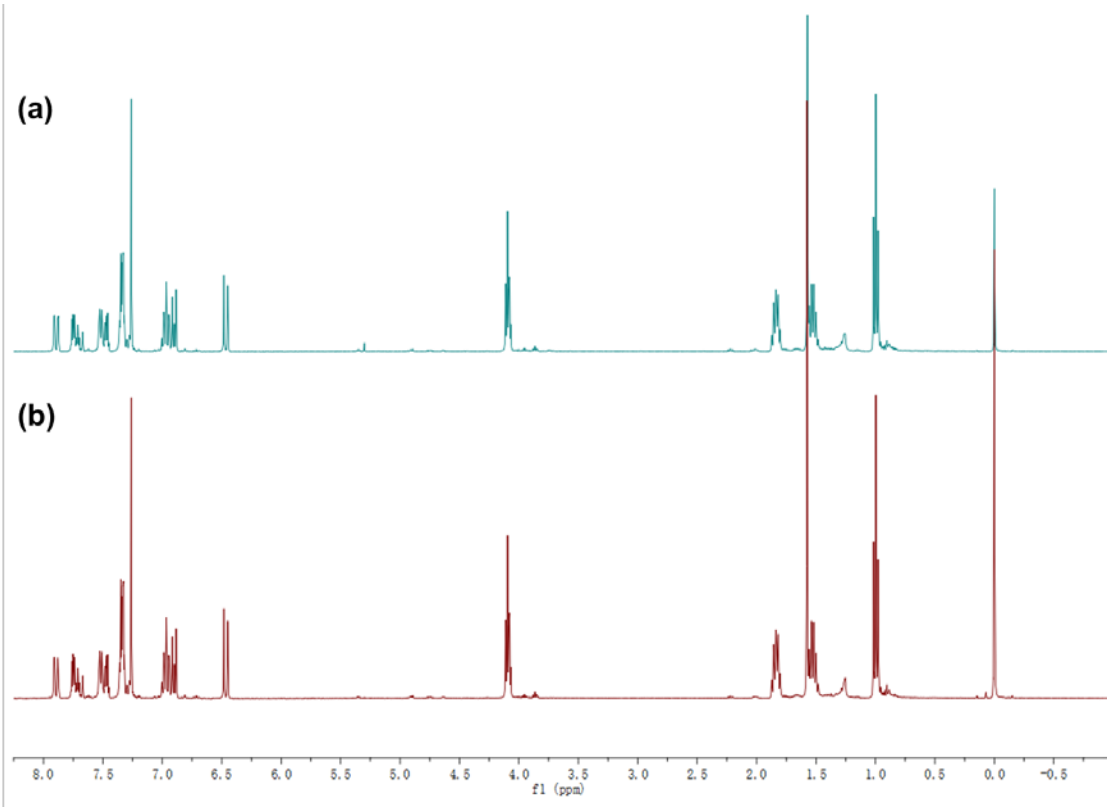


Figure S26. ^{1}H NMR spectra of the cyclobutane ring (a) before and (b) after heating.

12. References

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