Supporting Information For

Supramolecular multicolor fluorescent hydrogels with a single fluorescent group based on host-guest Interactions

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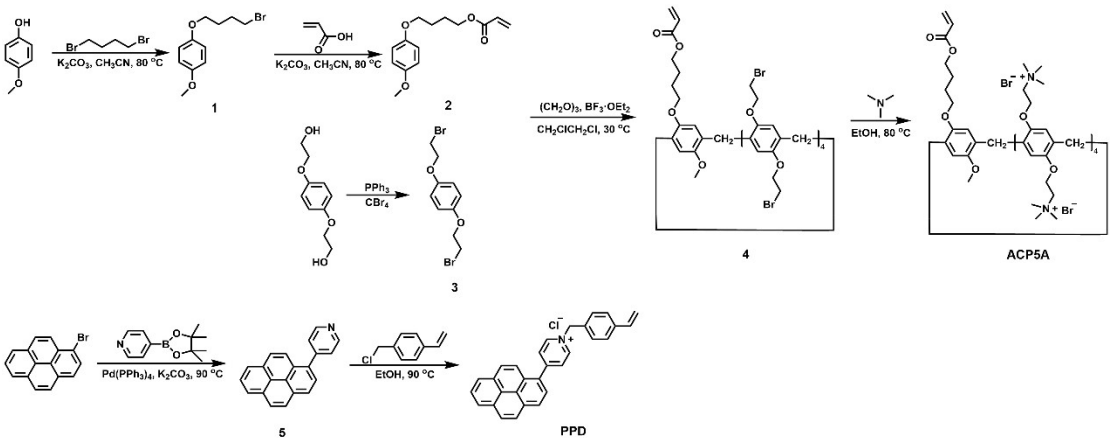
1. Materials and Methods

1,4-Dibromobutane (99%), 4-methoxyphenol, Acrylic acid (99%), paraformaldehyde (99%+), Tetrabromomethane (97%+), Triphenylphosphine (99%), Trimethylamine (27%-30% in ethanol), 1,4-Bis(2-Hydroxyethoxy)Benzene (98%), Aluminum(III) Oxide, Sodium Sulfate (99%+), Potassium Carbonate (99.99%), 1-(Chloromethyl)-4-Vinylbenzene (98%), Boron Trifluoride Etherate (48% BF_3), 2-Hydroxy-4′-(2-Hydroxyethoxy)-2-Methylpropiophenone (98%), 1-Bromopyrene (98%+), Tetrakis(triphenylphosphine)palladium (99%), 4-Pyridineboronic acid pinacol ester (98%+) and 3-Sulfopropyl Acrylate Potassium Salt (98%) were purchased from Shanghai Titan Scientific Co. (Shanghai, China) and used as received. Iron(III) Chloride (97%), Acetonitrile, Ethanol, 1,2-Dichloroethane, Petroleum Ether, Ethyl Acetate, Dichloromethane, Methyl Alcohol and Toluene were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) and used as received. Ethylenediaminetetraacetic acid disodium salt was purchased from Acmec Biochemical Technology Co. (Shanghai, China). Ultrapure water was used in all relevant experiments. All of materials given above were used directly without further purification.

^{1}H NMR (500 MHz) spectra were recorded on a Bruker DPX500 spectrometer using tetramethylsilane as an internal standard in $CDCl_3$ or D_2O. Conductivity of the supramolecular hydrogel was tested by electrochemical impedance spectroscopy (EIS) at room temperature, and it was performed using a CHI 660C electrochemical workstation (Shanghai Chenhua Equipments, China). Using an HY-0580 electronic tensile tester with an extending rate of 10 mm min^{-1}, the tensile test was carried out under Chinese GB/T 528–2009. For each sample, at least five specimens were tested for tensile strength and elongation at break. UV–vis spectra were obtained employing a UV-1800 spectrometer double beam spectrophotometer in 1.0 cm length quartz cell. ATR-IR spectra were observed on Thermo Scientific Fourier Transrorm Infrared spectrometer. Fluorescent luminescence (FL) spectra were recorded on FLS980 or F-7000 FL series of fluorescence spectrometers. The rheological properties of the

hydrogels were tested using the DHR3 multi-function rotational rheometer. The quantum yield was recorded on Fluorolog-QM series of steady-state and transient fluorescence spectrometer.

2. Syntheses and Characterizations



Scheme S1. Syntheses of monomers.

Synthesis of compound 1

Under a nitrogen atmosphere, 4-methoxyphenol (4.96 g, 40 mmol) and 1,4-dibromobutane (25.90 g, 120 mmol) were dissolved in acetonitrile (250 mL), followed by addition of dry potassium carbonate (11. 04 g, 80 mmol). The reaction mixture was stirred at reflux for 48 h. Then the cooled reaction mixture was filtered and washed with dichloromethane. The filtrate was concentrated and purified by column chromatography (eluent: petroleum ether/ethyl acetate = 5:1, v/v) to afford the desired product 1 as a white solid (8.3 g, 80%).

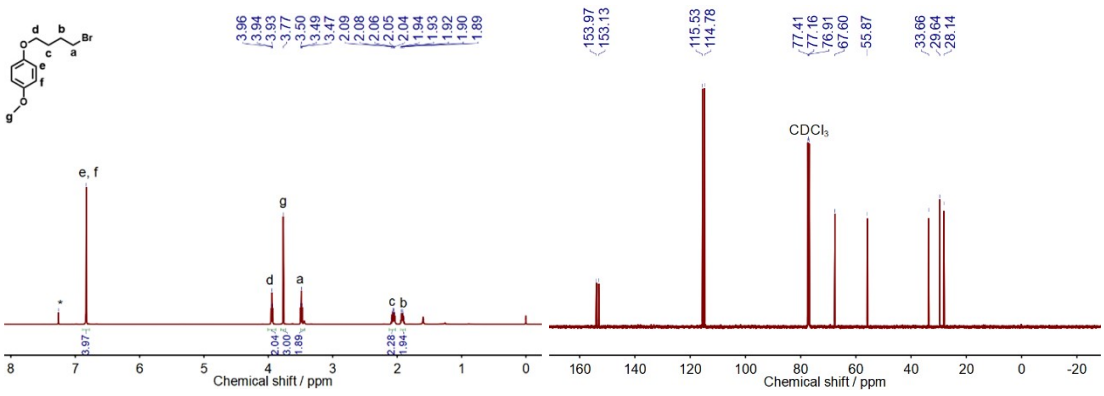


Figure S1. ^{1}H and ^{13}C NMR of compound **1** in $CDCl_3$.

The ^{1}H and ^{13}C NMR spectra of the compound **1** were shown in **Figure S1**. ^{1}H NMR

($CDCl_3$, 500 MHz, 298K) δ (ppm): 6.83 (s, 4H), 3.95 (t, J = 6.1 Hz, 2H), 3.77 (s, 3H), 3.49 (t, J = 6.7 Hz, 2H), 2.11–2.02 (m, 2H), 1.92 (dq, J = 9.6, 6.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 153.97 (s), 153.13 (s), 115.53 (s), 114.78 (s), 77.41 (s), 77.16 (s), 76.91 (s), 67.60 (s), 55.87 (s), 33.66 (s), 29.64 (s), 28.14 (s).

Synthesis of compound 2

Under a nitrogen atmosphere, compound **1** (5.2 g, 20 mmol) and acrylic acid (4.3 g, 60 mmol) were dissolved in acetonitrile (200 mL), followed by addition of dry potassium carbonate (13.8 g, 100 mmol). The reaction mixture was stirred at reflux for 48 h. Then the cooled reaction mixture was filtered and washed with sodium bicarbonate saturated solution and sodium chloride saturated solution. The filtrate was concentrated and purified by column chromatography (eluent: petroleum ether/ethyl acetate =5:1, v/v) to afford light yellow liquid (4.1 g, 81%). The ^1H and ^{13}C NMR spectra of the compound **2** were shown in **Figure S2**. ^1H NMR ($CDCl_3$, 500 MHz, 298K) δ (ppm): 6.83 (s, 4H), 6.40 (dd, J = 17.3, 1.5 Hz, 1H), 6.12 (dd, J = 17.4, 10.4 Hz, 1H), 5.82 (dd, J = 10.4, 1.4 Hz, 1H), 4.26–4.21 (m, 2H), 4.01–3.91 (m, 2H), 3.77 (s, 3H), 1.93–1.81 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 166.35 (s), 153.91 (s), 153.17 (s), 130.73 (s), 128.62 (s), 115.53 (s), 114.75 (s), 77.41 (s), 77.16 (s), 76.91 (s), 68.02 (s), 64.34 (s), 55.84 (s), 26.10 (s), 25.55 (s).

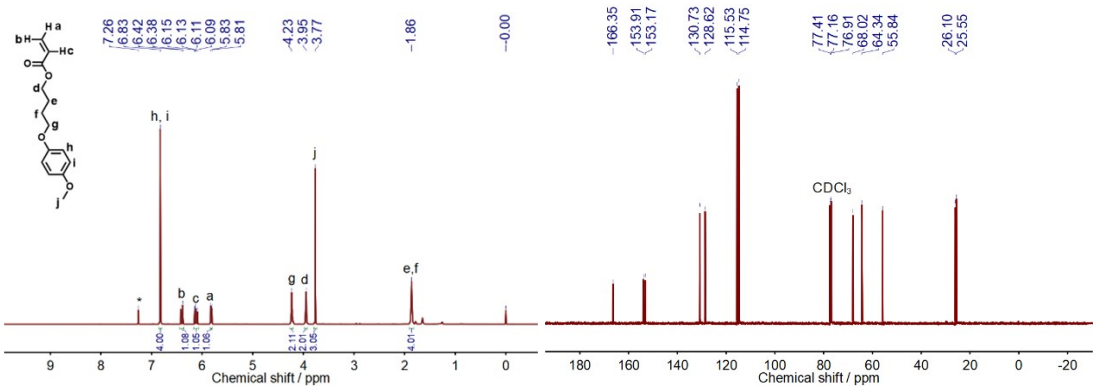


Figure S2. ^1H and ^{13}C NMR of compound **2** in $CDCl_3$.

Synthesis of compound 3

Hydroquinone bis(2-hydroxyethyl) ether (10 g, 50.4 mmol) and triphenylphosphine (31.5 g, 120 mmol) were added into acetonitrile (250 mL). The reaction mixture was cooled with an ice bath under vigorous stirring, followed by slow

addition of carbon tetrabromide (39.8 g, 120 mmol). Then the reaction mixture was stirred at room temperature for 4 hours. Cold water (200 mL) was then added to the reaction mixture to give white precipitation. The precipitate was collected, washed with methanol/water (3:2, v/v, 3 × 100 mL), recrystallized from methanol and dried under vacuum to afford the compound as white crystals (9.9 g, 61%). The ^{1}H and ^{13}C NMR spectra of the compound **3** were shown in **Figure S3**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298K) δ (ppm): 6.86 (s, 4H), 4.24 (t, J = 6.3 Hz, 4H), 3.61 (t, J = 6.3 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 152.94 (s), 116.21 (s), 77.41 (s), 77.16 (s), 76.91 (s), 68.83 (s), 29.40 (s).

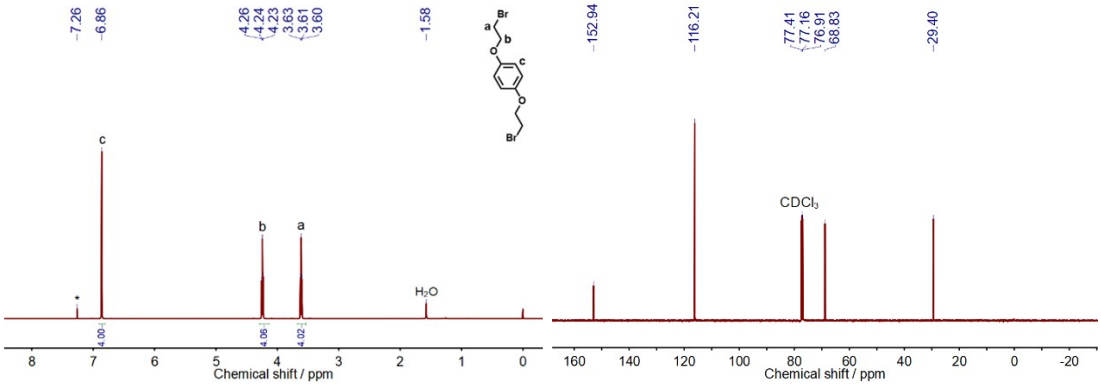


Figure S3. ^{1}H and ^{13}C NMR of compound **3** in $CDCl_3$.

Synthesis of compound 4

Compound **2** (0.25 g, 1 mmol), compound **3** (1.30 g, 4 mmol) and paraformaldehyde (0.45 g, 5 mmol) were dissolved in $CHCl_2CHCl_2$ (50 mL), followed by the addition of Boron trifluoride etherate [($BF_3 \cdot OEt_2$), 1.44 g, 1.3 mL, 10 mmol]. The reaction mixture was stirred at room temperature for 10 min. After the color of solution changed from white to light yellow to olivine to dark green, water (100 mL) was poured into the solution to quench the reaction. After the reaction mixture has been washed with water three times, the solvent was removed under vacuum and the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane= 1:2, v/v) to afford the compound as a white solid (350 mg, 22%). The ^{1}H and ^{13}C NMR spectra of compound **4** were shown in **Figure S4**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ (ppm): 6.91 – 6.88 (m, 8H), 6.82 (d, J = 2.0 Hz, 2H), 6.40 (ddd, J = 17.3, 10.4, 1.4

Hz, 2H), 6.12 (ddd, J = 17.3, 10.4, 5.6 Hz, 1H), 5.82 (ddd, J = 18.9, 10.4, 1.4 Hz, 2H), 4.29 – 4.12 (m, 20H), 3.86 – 3.75 (m, 14H), 3.64 – 3.58 (m, 17H), 1.91 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 166.36 (s), 150.83 (s), 149.86 (d, J = 13.0 Hz), 130.93 (s), 129.56 (s), 129.21 (s), 128.93 (d, J = 8.2 Hz), 128.56 (s), 128.18 (s), 116.25 (s), 115.81 (s), 115.41 (s), 114.16 (s), 77.41 (s), 77.16 (s), 76.91 (s), 69.13 (s), 64.45 (s), 56.20 (s), 53.51 (s), 30.77 (s), 30.75 – 30.32 (m), 29.56 (s), 26.67 (s), 25.88 (s).

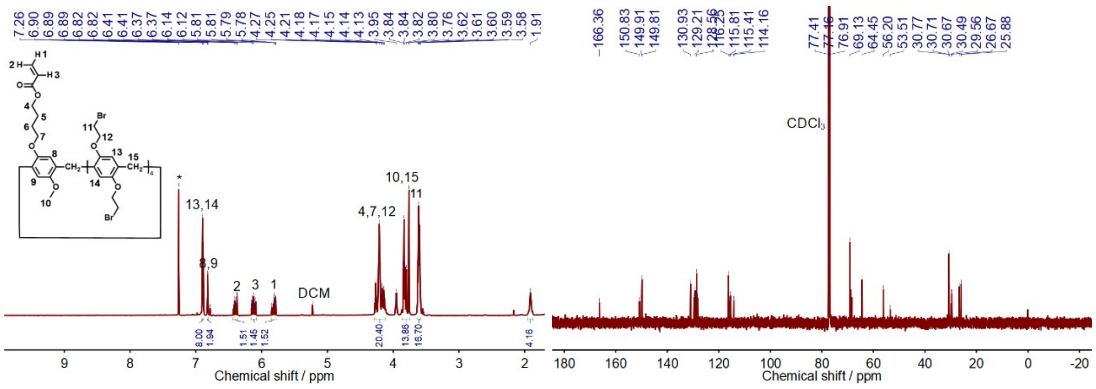


Figure S4. ^{1}H NMR and ^{13}C NMR of compound **4** in $CDCl_3$.

Synthesis of monomer ACP5A

Compound **4** (3.5 g, 2.2 mmol) and trimethylamine (27%-30% in ethanol, 22 mL, 88 mmol) were dissolved in ethanol (150 mL). The reaction mixture was stirred at reflux for 36 h. The solvent was removed under vacuum, and water (20 mL) was then added to the reaction mixture. The clarified solution was obtained by filtration, and then the water was removed under vacuum to afford the compound as white solid (4.1 g, 90%). The ^{1}H and ^{13}C NMR spectra of **ACP5A** were shown in **Figure S5**. ^{1}H NMR (D_2O, 500 MHz, 298 K) δ (ppm): 6.99 (d, J = 34.3 Hz, 10H), 6.44 (d, J = 15.0 Hz, 1H), 6.13 (d, J = 17.4 Hz, 1H), 5.83 (d, J = 18.0 Hz, 1H), 4.55 (s, 20H), 3.90 (t, J = 48.7 Hz, 29H), 3.27 (dt, J = 17.8, 16.9 Hz, 72H), 1.86 (d, J = 71.4 Hz, 4H). ^{13}C NMR (151 MHz, DMSO) δ (ppm): 149.99 (s), 148.79 (s), 128.17 (d, J = 25.8 Hz), 128.02 – 127.55 (m), 127.46 (s), 116.33 – 115.79 (m), 115.24 (d, J = 100.4 Hz), 64.43 (t, J = 21.4 Hz), 62.82 (s), 62.45 (d, J = 35.1 Hz), 54.32 (s), 53.10 (s), 50.80 (s), 29.15 (s), 29.00 (s), 28.85 (s), 28.63 (d, J = 12.8 Hz).

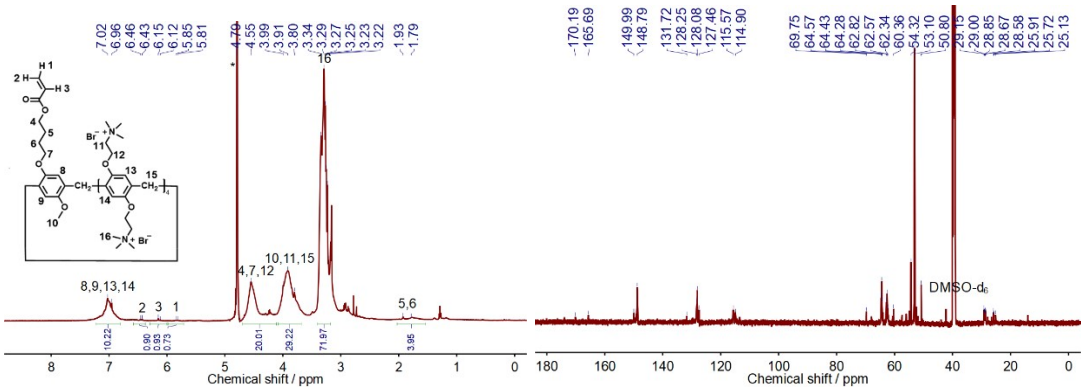


Figure S5. ^{1}H NMR of **ACP5A** in D_2O and ^{13}C NMR of **ACP5A** in DMSO-d_6.

Synthesis of compound 5

Under a nitrogen atmosphere, 1-bromopyrene (2.81 g, 10 mmol), 4-pyridineboronic acid pinacol ester (2.66 g, 13 mmol), tetrakis (triphenylphosphine) palladium (0.23 g, 0.2 mmol), potassium carbonate (1.38 g, 10 mmol) and tetrabutylammonium bromide (0.32 g, 1 mmol) were added into mixed solvent (toluene/water = 10:1, v/v, 30 mL/3 mL). The reaction mixture was stirred at reflux for 36 h. Then the cooled reaction mixture was dried with sodium sulfate, washed with dichloromethane and filtered to obtain yellow liquid. Furthermore, the yellow liquid was recrystallized from ethanol and dried under vacuum to afford the compound as white solid (1.8 g, 65%). The ^{1}H and ^{13}C NMR spectra of compound **5** were shown in **Figure S6**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ (ppm): 8.80 (dd, J = 4.4, 1.6 Hz, 2H), 8.26 – 8.18 (m, 3H), 8.12 (dd, J = 9.4, 6.6 Hz, 2H), 8.10 – 8.02 (m, 3H), 7.94 (d, J = 7.8 Hz, 1H), 7.57 (dd, J = 4.3, 1.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 149.96 (s), 149.24 (s), 134.52 (s), 131.48 (s), 130.90 (s), 128.42 – 128.08 (m), 127.38 (s), 127.08 (s), 126.36 (s), 125.66 (d, J = 12.5 Hz), 125.38 (s), 124.89 (t, J = 11.4 Hz), 124.32 (s), 77.41 (s), 77.16 (s), 76.91 (s).

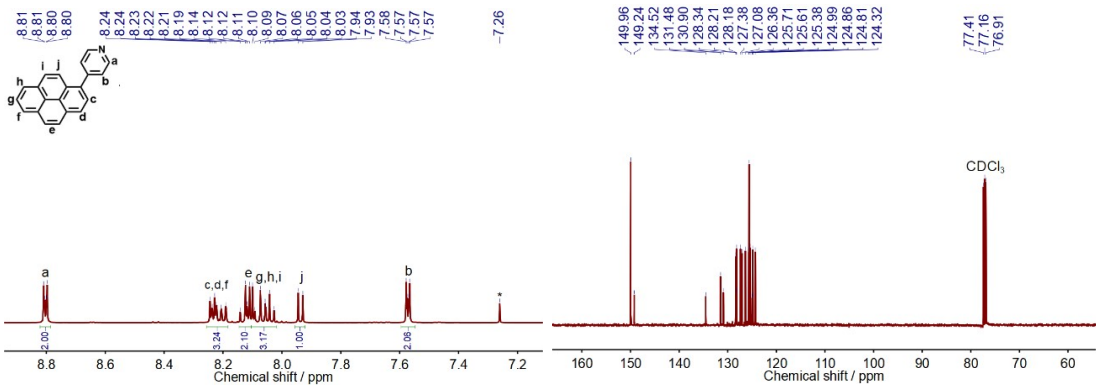


Figure S6. ^{1}H and ^{13}C NMR of compound **5** in $CDCl_3$.

Synthesis of monomer PPD

Compound **5** (0.27 g, 0.97 mmol) and 1-(chloromethyl)-4-vinylbenzene (0.74 g, 4.88 mmol) were dissolved in ethanol (20 mL). The reaction mixture was stirred at reflux for 36 h. Then the cooled reaction mixture was filtered and washed with dichloromethane. The filtrate was concentrated and purified by Al_2O_3 column chromatography (eluent: dichloromethane/methanol = 20:1, v/v) to afford the desired product PPD as orange solid (70 mg, 17%). The ^{1}H and ^{13}C NMR spectra of **PPD** were shown in **Figure S7**. ^{1}H NMR (500 MHz, DMSO) δ (ppm): 9.50 (d, J = 6.4 Hz, 2H), 8.51 (d, J = 6.4 Hz, 2H), 8.47 (d, J = 8.0 Hz, 1H), 8.41 (t, J = 8.3 Hz, 2H), 8.36 – 8.27 (m, 3H), 8.17 (dt, J = 11.4, 7.4 Hz, 3H), 7.73 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 6.78 (dd, J = 17.6, 11.0 Hz, 1H), 6.06 (s, 2H), 5.93 (d, J = 17.7 Hz, 1H), 5.33 (t, J = 14.3 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ (ppm): 156.72 (s), 144.57 (s), 138.15 (s), 135.88 (s), 133.89 (s), 132.33 (s), 130.75 (s), 130.51 (s), 130.16 (s), 129.46 (d, J = 11.6 Hz), 129.20 (s), 127.81 (s), 127.62 (s), 127.19 (s), 126.91 (d, J = 6.6 Hz), 126.51 (s), 126.04 (s), 125.17 (s), 123.88 (s), 123.53 (s), 123.17 (s), 115.69 (s), 62.27 (s), 40.02 (s), 39.85 (s), 39.69 (s), 39.52 (s), 39.35 (s), 39.19 (s), 39.02 (s).

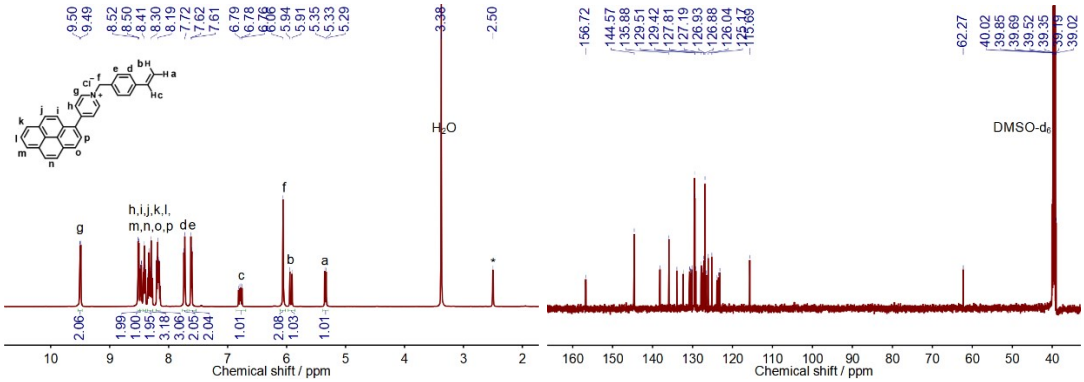


Figure S7. ^{1}H and ^{13}C NMR of **PPD** in DMSO-d_6.

3. Constant Determination for the Complexation between H and G

For the ^{1}H NMR titration experiment, a solution of 4 mM G was prepared first and mixed with ACP5A with a concentration of (a) 0.0 mM, (b) 0.8 mM, (c) 2 mM, (d) 3.2 mM, (e) 10 mM, (f) 20 mM, and (g) 40 mM. By fixing the concentration of guest molecule solution and changing the concentration of host molecule solution, a series of solutions with different molar ratios of host and guest could be obtained.

(h): Dissolve 8.3 mg ACP5A (4×10^{-3} mmol) in the D_2O solution (0.5 mL).

(g): Dissolve 41.6 mg ACP5A (20 mmol) in the D_2O solution of 4 mM G (0.5 mL).

(f): Add 0.5 mL solution of G (4 mM) to sample (g) and take out 0.5 mL.

(e): Dissolve 10.4 mg ACP5A (5×10^{-3} mmol) in the D_2O solution of 4 mM G (0.5 mL).

(d): Add 1.06 mL solution of G (4 mM) to sample (e) and take out 0.5 mL.

(c): Add 0.30 mL solution of G (4 mM) to sample (d) and take out 0.5 mL.

(b): Add 0.75 mL solution of G (4 mM) to sample (c) and take out 0.5 mL.

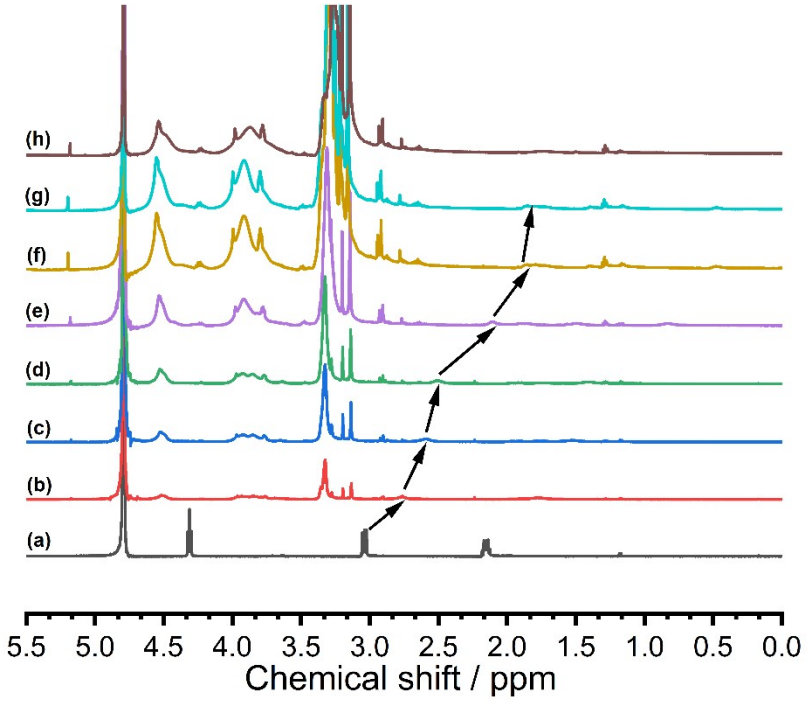


Figure S8. Partial ^{1}H NMR spectra (D_2O, 500 MHz, 298K) of **G** at a concentration of 4 mM upon addition of **ACP5A**: 0.0 mM (a), 0.8 mM (b), 2 mM (c), 3.2 mM (d), 10 mM (e), 20 mM (f), 40 mM (g) and **ACP5A** (h) at 8 mM.

The association constant K_a between free ACP5A and G was calculated as (788 ± 215) M-1 as shown in Figure S9. The binding constant was obtained by the non-linear curve-fitting method, using the equation:

$\Delta\delta = (\delta_\infty / [G]_0) * (0.5 * [H]_0 + 0.5 * ([G]_0 + 1 / K_a) - (0.5 * ([H]_0 \text{ ^ } 2 + (2*[H]_0 (1 / K_a - [G]_0)) + (1/ K_a + [G]_0) \text{ ^ } 2) \text{ ^ } 0.5))$

Where $\Delta\delta$ is the chemical shift change of proton (H_f) from sulfonate anion of G, δ_∞ is the chemical shift change of these protons when the host is completely complexed, $[G]_0$ is the initial concentration of G, and $[H]_0$ is the varying concentrations of ACP5A.

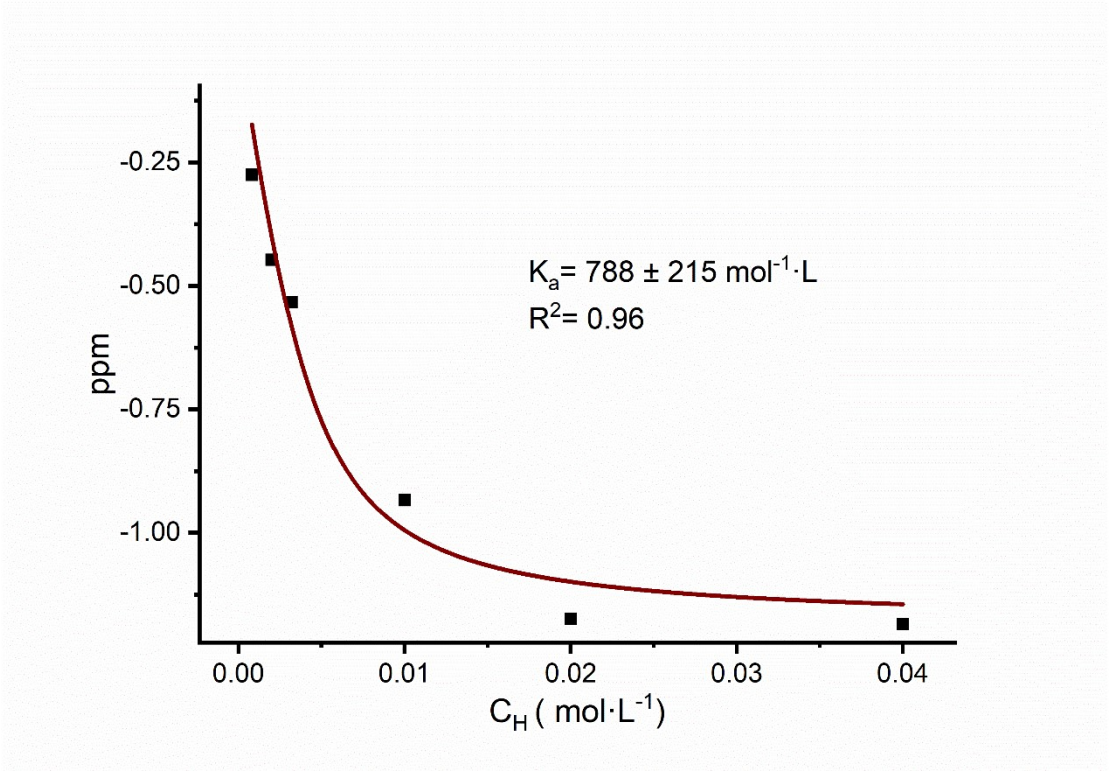


Figure S9. Fitting plot for the chemical shift changes of pyridinium aromatic proton (H_f) from **G** upon addition of **ACP5A**.

4. Preparation of Supramolecular Fluorescent Hydrogel

Table S1. **Components of different hydrogels**

Run	(PPD:ACP5A:G:AM:AA) Molar ratio	PPD (M)	Crosslinker (M)	AM (M)	AA (M)	H_2O (μL)
G0	1:0:200:2800:1400	5×10^{-3}	/	14	7	200
G1	1:100:200:2800:1400	5×10^{-3}	0.5	14	7	200
G2	1:60:120:2800:1400	5×10^{-3}	0.25	14	7	200
G3	1:28:56:2800:1400	5×10^{-3}	0.125	14	7	200
G4	1:100[a]: 1400:700	5×10^{-3}	0.5	14	7	200

[a] refers to the molar ratio of covalent crosslinker (N, N-methylenebisacrylamide, MBA)

* Weight percentage of I-2959 was 2%

Preparation of Supramolecular Fluorescent Hydrogel: The host molecule ACP5A and the guest molecule G were firstly mixed in DI water at a molar ratio of 1:2. The mixture was shaken to dissolve them completely. The supramolecular crosslinker was

successfully constructed by the electrostatic interaction between the pillar[5]arene ACP5A and the anionic guest G, as well as the hydrophobic interaction driven by the aqueous solvent. PPD, AM, AA and photo-initiator I-2959 were then dissolved in it. After ultrasonication for 10 min, it was transferred into a white PTFE mold of 1 cm × 3 cm, and sealed with a transparent glass, before being exposed into UV irradiation of 365 nm light with 40 mW/cm^2 for 30 min. The obtained hydrogel was removed from the PTFE mold and then cut into the required shape.

Figure S10. Photograph of the sample G0 after polymerization reaction for 30 min.

5. Rheological properties of the hydrogels

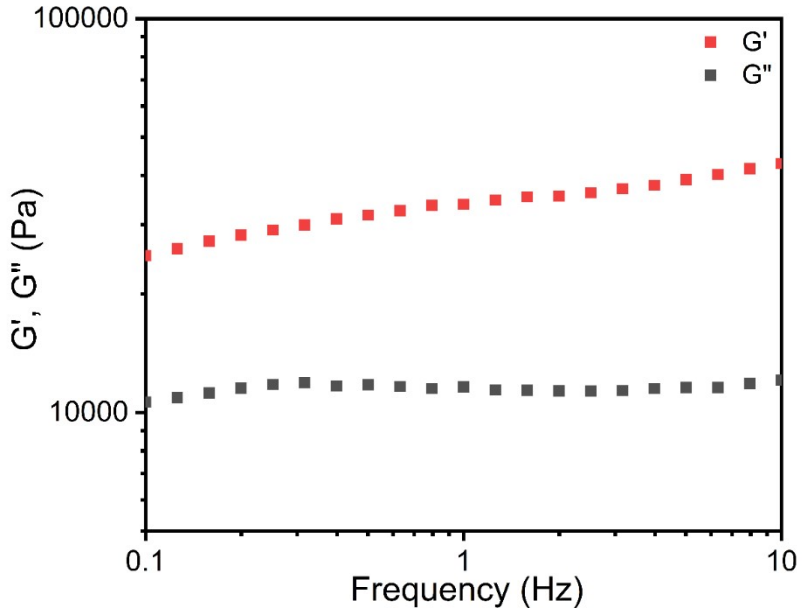


Figure S11. Rheology results of the hydrogel G1.

6. Quantum yield before and after gelation

Table S2. The quantum yield before and after gelation

Run	Solution	Hydrogel
G1	17.57%	36.80%
G2	14.48%	31.14%
G3	13.04%	27.12%

7. Fluorescence lifetimes of the hydrogels

Table S3. Summary of simulated fluorescence lifetimes of hydrogels

Hydrogel	τ_1 (μs)	A_1	φ_1 (%)	τ_2 (μs)	A_2	φ_2 (%)	τ_{ave} (μs)	X^2
G1	3.29	1.04	41.41	13.83	0.35	58.59	9.46	0.994
G2	1.87	1.08	60.06	14.92	0.09	39.93	7.08	0.987
G3	1.52	1.09	66.45	13.94	0.06	33.55	5.69	0.987

The average lifetime (τ_{ave}) of each form was calculated by eq 1 and the experiential fraction (φ_i) of each form was calculated by eq 2.

$$\tau_{ave} = \left(A_1{\tau_1}^2 + A_2\tau_2^2\right)/(A_1\tau_1 + A_2\tau_2) \quad \textbf{(1)}$$

$$\varphi_i = {A_i\tau_i}/{\sum A_i\tau_i} \times 100\% \quad \textbf{(2)}$$

8. Mechanical properties of hydrogels

Table S4. Summary of mechanical properties

Hydrogel	Cross-linker content (%)	Tensile strength (MPa)	Strain at break (%)	Toughness ($MJ \cdot m^{-3}$)
G1	2.3	1.42	523	5.45
G2	1.4	0.43	570	1.56
G3	0.7	0.11	719	0.54
G4	2.3	0.01	94	0.0069

9. Conductivities of hydrogels

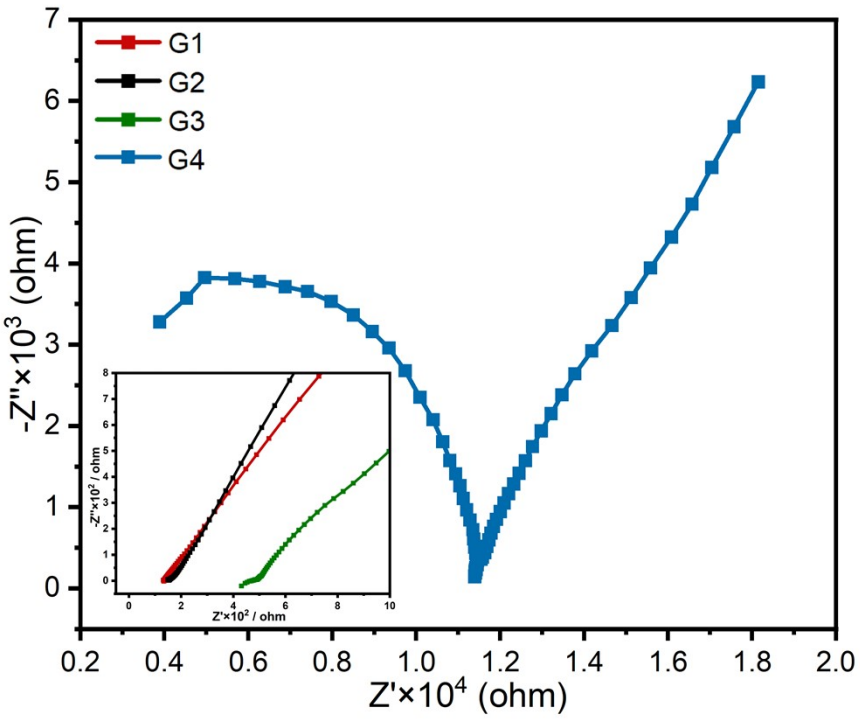


Figure S12. Nyquist polts of hydrogels with different components.

Table S5. **Conductivities of hydrogels**

Hydrogel	Cross-linker content (%)	R^a (Ω)	Conductivity ($S \cdot cm^{-1}$)
G1	2.3	1.3×10^{2}	1.95×10^{-3}
G2	1.4	1.5×10^{2}	1.44×10^{-3}
G3	0.7	4.9×10^{2}	5.85×10^{-4}
G4	2.3	1.1×10^{4}	2.24×10^{-5}