Supplementary Information

Dynamic Phosphorescent Gel with Dual Supramolecular Interactions for Visualization of Moisture Monitoring

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Contents

1. Materials and general procedures.

1.1 Materials. All reagents were purchased from Adamas-beta® or TCI Chemicals and used without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using ^{1}H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy.

1.2 General methods. All reagents used for the synthesis or measurements were commercially available without further purification. Water used in tests and to prepare solution was ultrapure. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brüker AV-500 spectrometers. Coupling constants *J* are given in Hz. Chemical shifts were shown in ppm relative to the solvent residual peak was used as the internal standard. Molecular masses were determined by a Waters LCT premier XE spectrometer. ESI high-resolution time-of-flight mass spectra were measured on a Waters XEVO G2 TOF mass spectrometer. Fourier Transform Infrared Transmission Spectra (FT-IR) were measured on an INVENIO R instrument, and the solid powders of the samples were measured in cm-1 after preparation of the samples by KBr flakes. UV-Vis absorption spectra were measured on a Varian-Cary 500 spectrophotometer. Fluorescence emission spectra and excitation spectra were measured using an Edinburgh FLS1000 transient and steady state fluorescence spectrometer. Absolute quantum yields of photoluminescence were measured using an integrating sphere on an Edinburgh FLS1000 transient and steady-state fluorescence spectrometer.

2. Synthesis and characterization of Upy3-BrBP and intermediates.

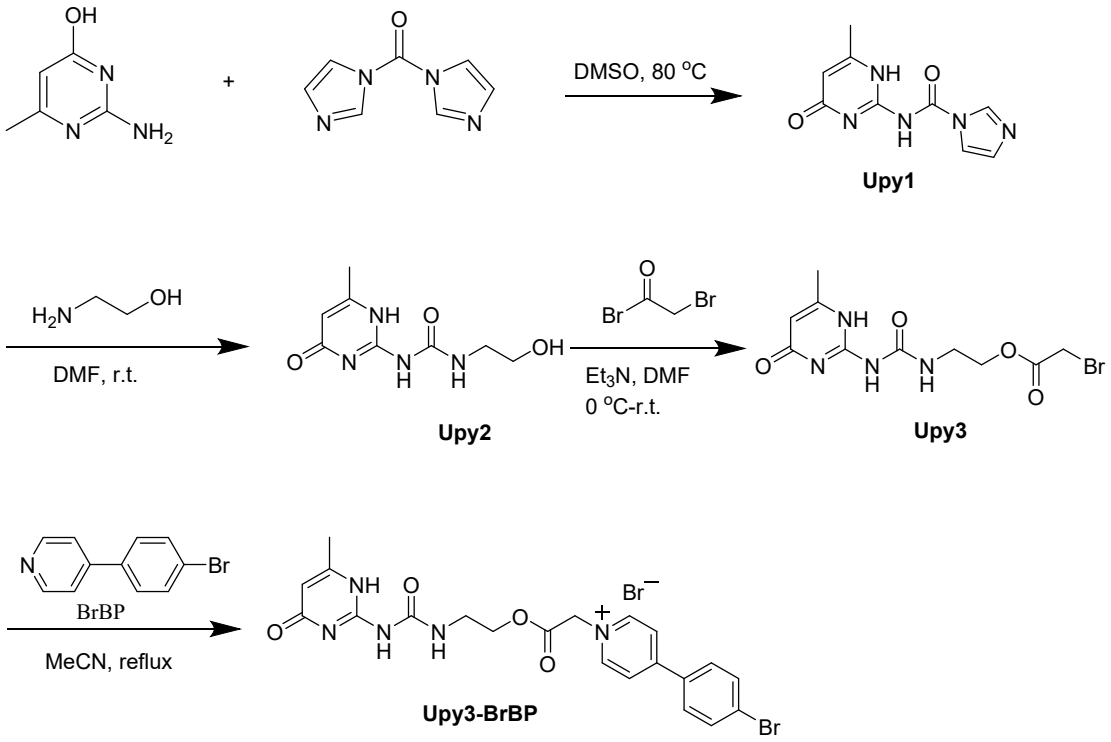

Fig.S1 Synthetic route of **Upy3-BrBP.**

Synthesis of *N*-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)-1*H*-imidazole-1-carboxamide (Upy1). Compound **Upy1** was synthesized according to literature procedure.[1]

Synthesis of 1-(2-hydroxyethyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (Upy2). To **Upy1** (20 mmol, 1.0 eq) and ethanolamine (30 mmol, 1.5 eq) was added DMF (60 mL). The mixture was stirred at room temperature for 3 hours. The mixture was filtered and washed with acetonitrile to afford white solid as product (78% yield, 3.346 g).

Synthesis of 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl 2-bromoacetate (Upy3). Compound **Upy2** (1.0 eq) was mixed with DMF and triethylamine (1.2 eq) at 0 ℃ under an inert gas atmosphere. Bromoacetyl bromide (1.3 eq) was added slowly followed by an overnight reaction at room temperature. The reaction was quenched by addition of water and the partition was extracted with dichloromethane and the organic phases were combined. The organic phase was

washed three times with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate, filtered and concentrated to give a light brown solid. Refining in ethanol gave the product as a white solid.

Synthesis of 4-(4-bromophenyl)-pyridine (BrBP). Compound **BrBP** was synthesized according to literature procedure.[2]

Synthesis of 4-(4-bromophenyl)-1-(2-(2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethoxy)-2-oxoethyl)pyridin-1-ium (Upy3-BrBP). Compound **Upy3** (0.5 mmol, 1.0 eq) and **BrBP** (0.55 mmol, 1.1 eq) were homogeneously dispersed in acetonitrile. The mixture was heated to 90 ℃ for two days. A light brown solid precipitated, cooled and filtered, the filter cake was washed with acetonitrile and subsequently dried under vacuum to give the pure product. (43% yield, 122 mg). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.06 (d, J = 6.5 Hz, 2H), 8.61 (d, J = 6.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 5.78 (s, 1H), 5.66 (s, 2H), 4.27 (t, J = 5.5 Hz, 2H), 3.47 (d, J = 5.5Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.8, 155.1, 146.8, 133.2, 133.0, 130.8, 127.1, 124.7, 65.5, 60.1, 38.5. ESI-HRMS calcd. for $[C_{21}H_{21}Br_2N_5O_4Na]^+$ $(M+Na^+)^+$: 587.9853, Found: 587.9850.

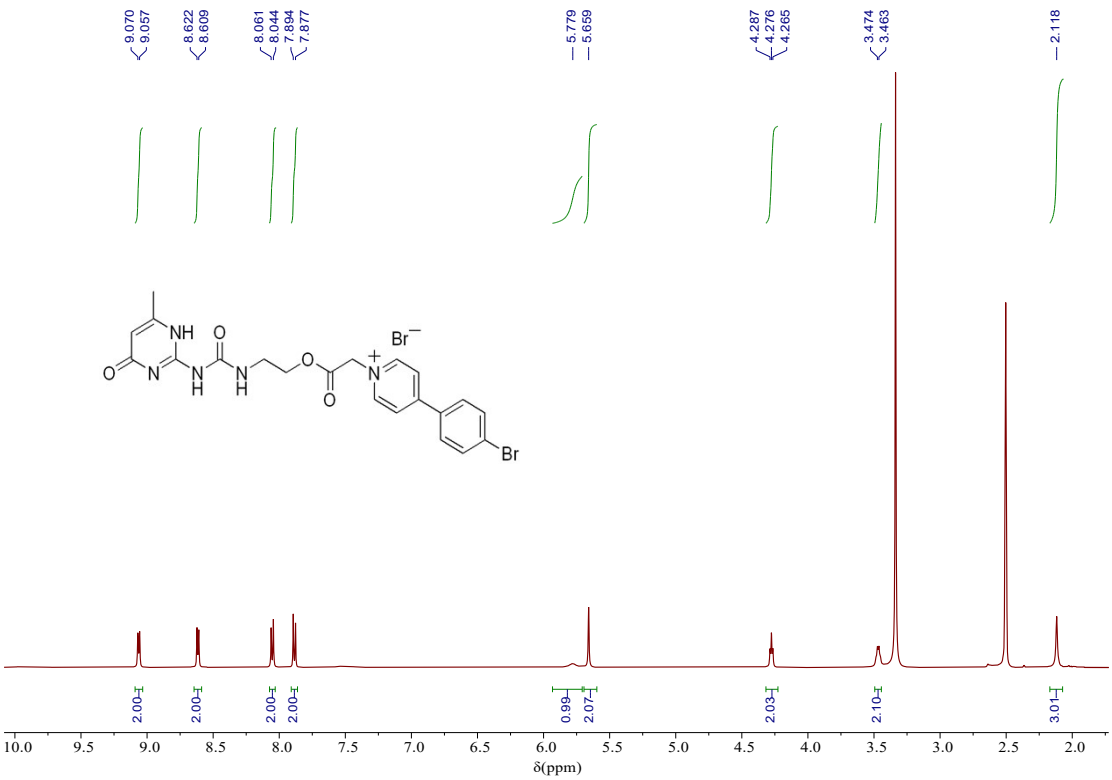

Fig. S2. ^{1}H NMR spectrum (500 MHz) of **Upy3-BrBP** in DMSO-d_6.

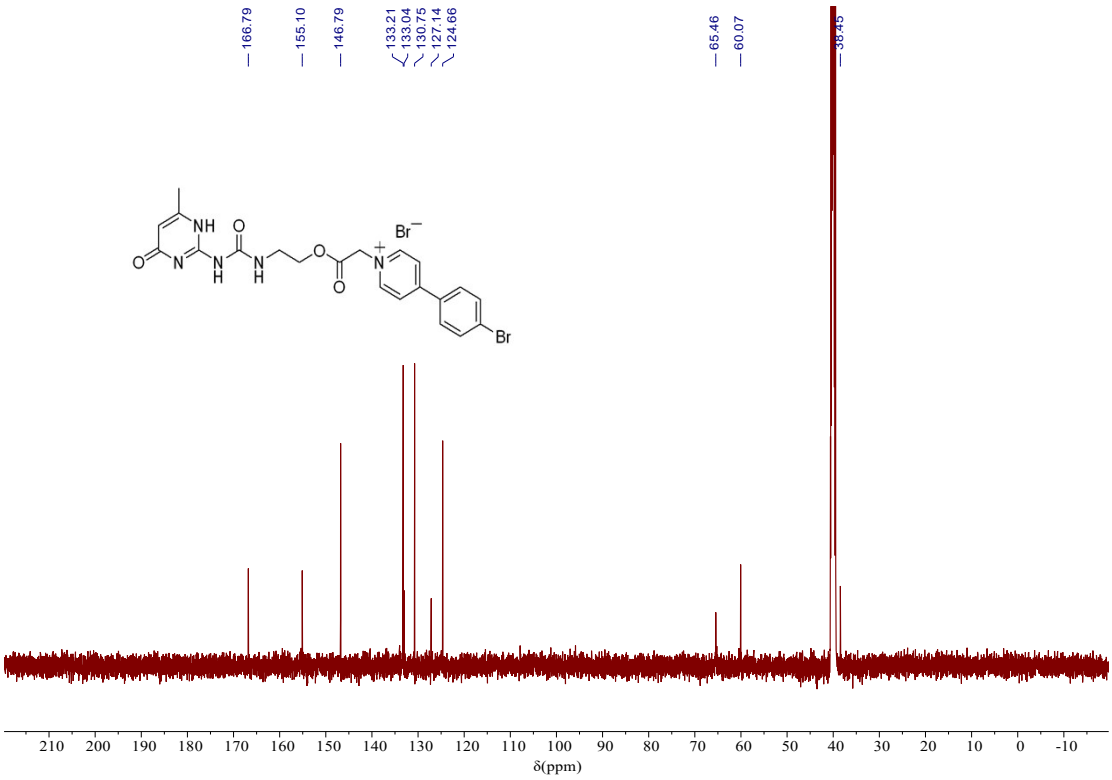

Fig. S3. ^{13}C NMR spectrum (125 MHz) of **Upy3-BrBP** in DMSO-d_6.

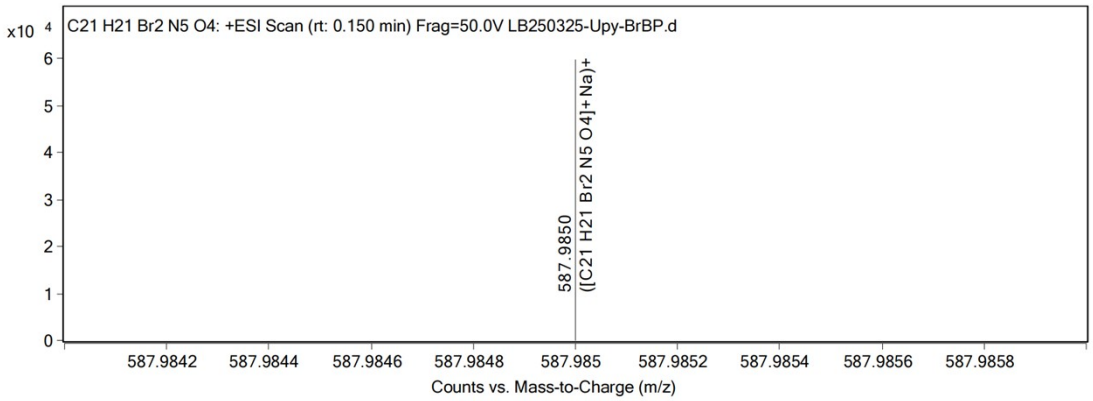

Fig. S4. ESI-HRMS spectrum of solid **Upy3-BrBP**.

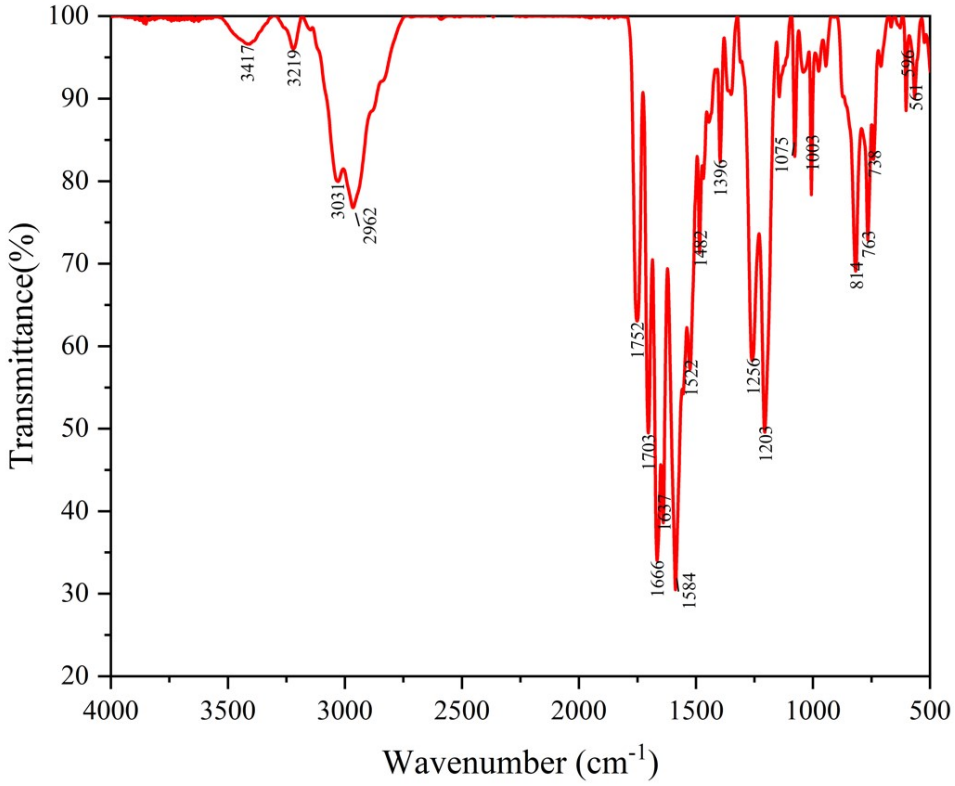

Fig. S5. FT-IR transmission spectrum of solid **Upy3-BrBP**, 298 K.

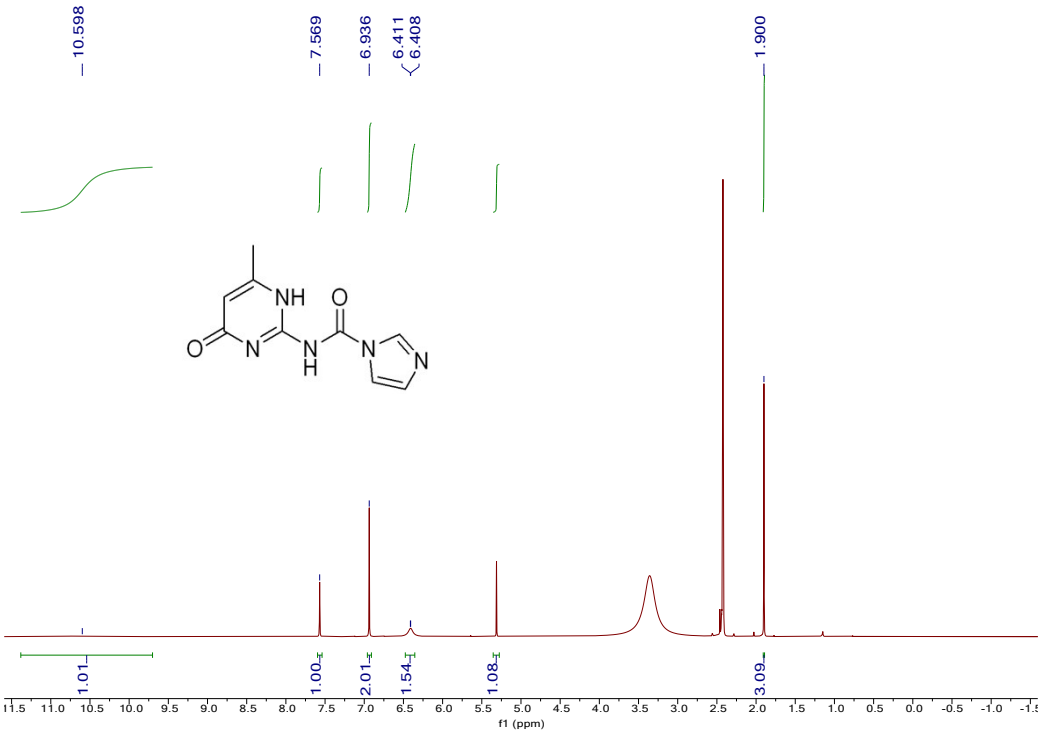

Fig. S6. ^{1}H NMR spectrum (500 MHz) of **Upy1** in DMSO-d_6.

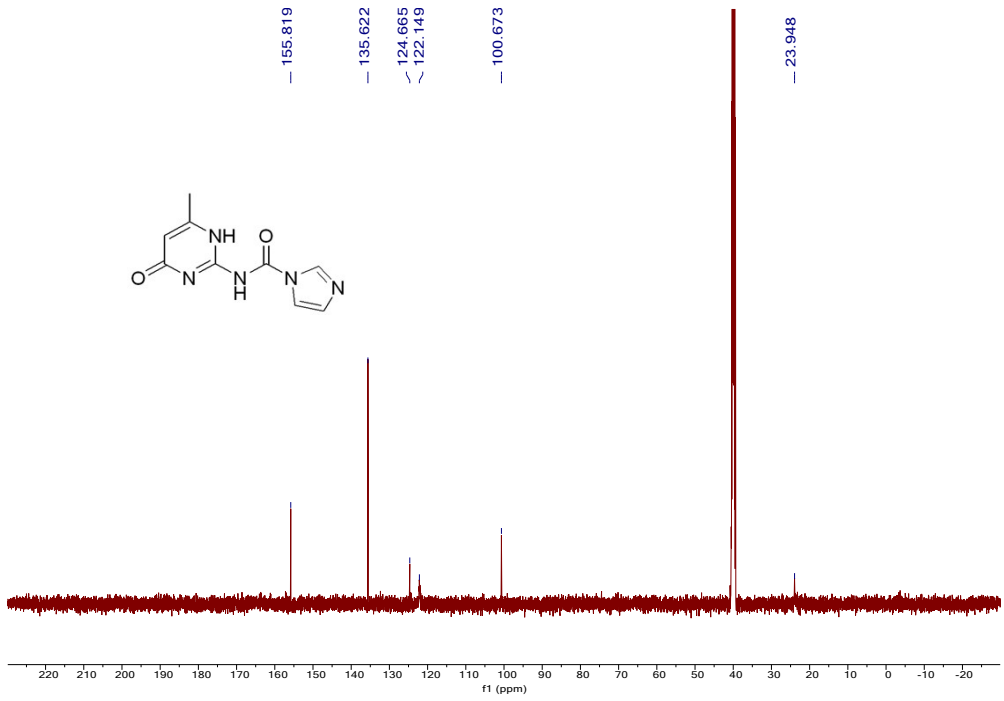

Fig. S7. ^{1}C NMR spectrum (125 MHz) of **Upy1** in DMSO-d_6.

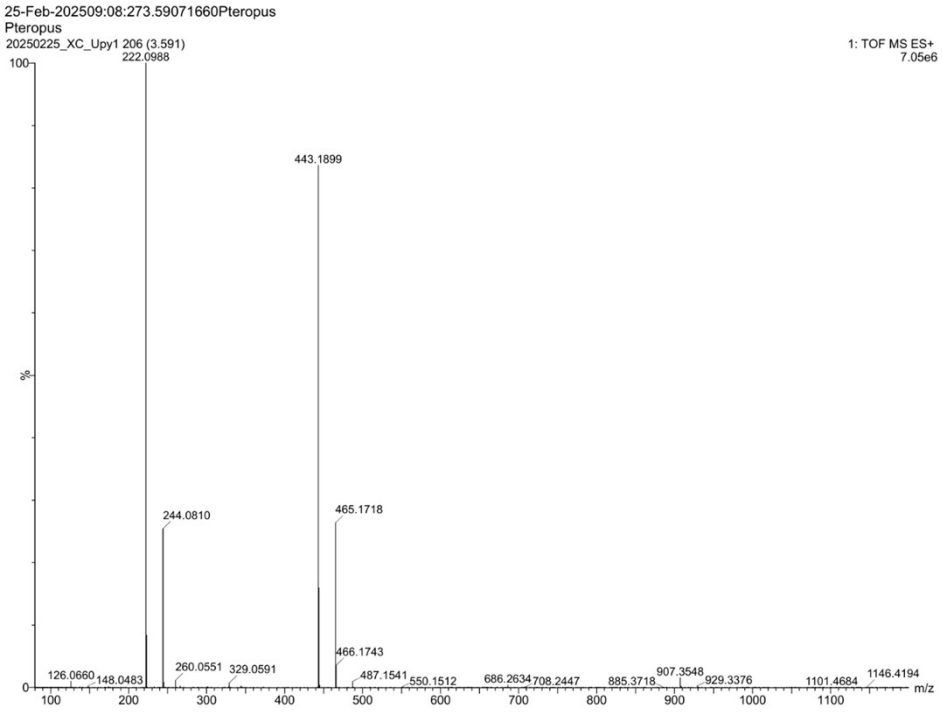

Fig. S8. ESI-HRMS spectrum of solid **Upy1.**

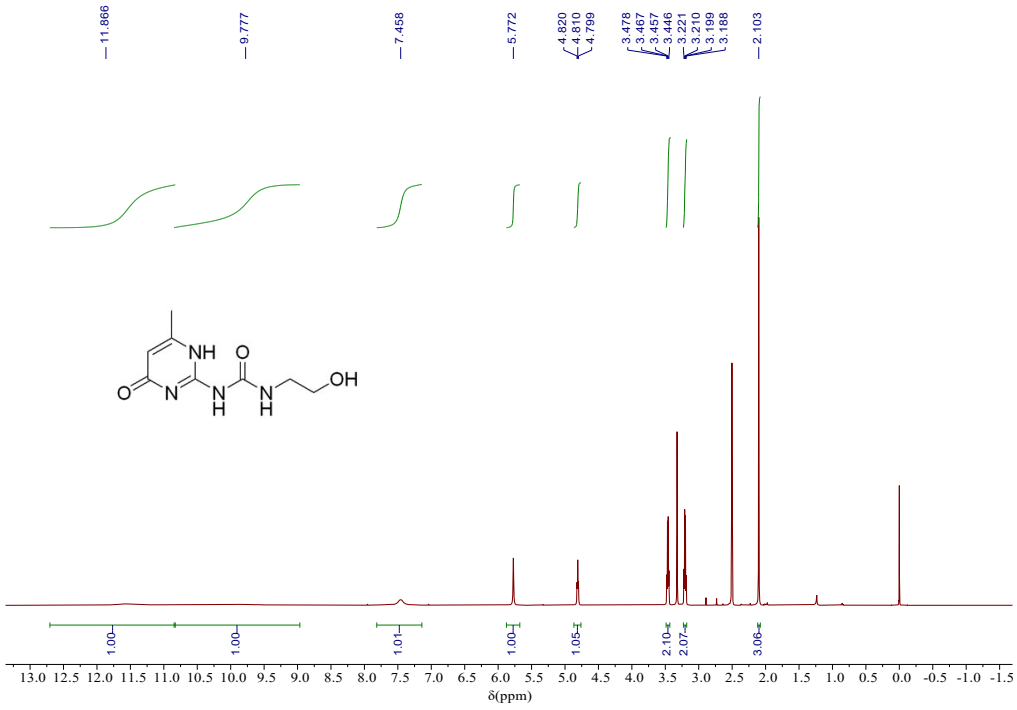

Fig. S9. ^{1}H NMR spectrum (500 MHz) of **Upy2** in DMSO-d_6.

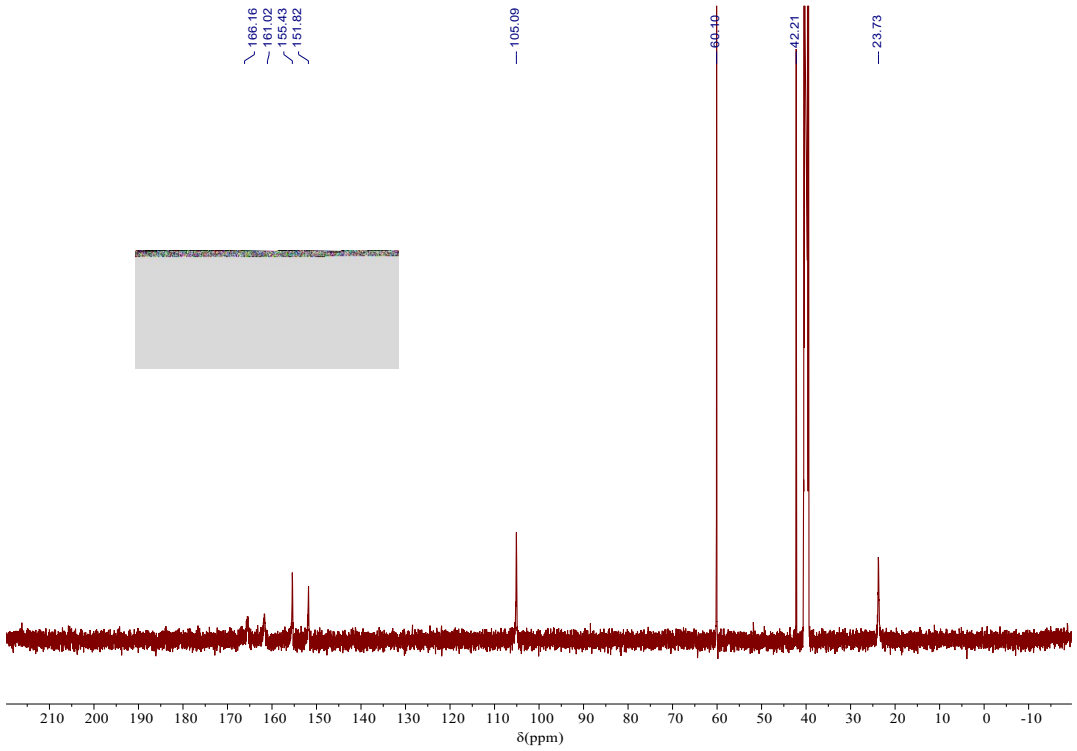

Fig. S10. [1]C NMR spectrum (125 MHz) of **Upy2** in DMSO-d_6.

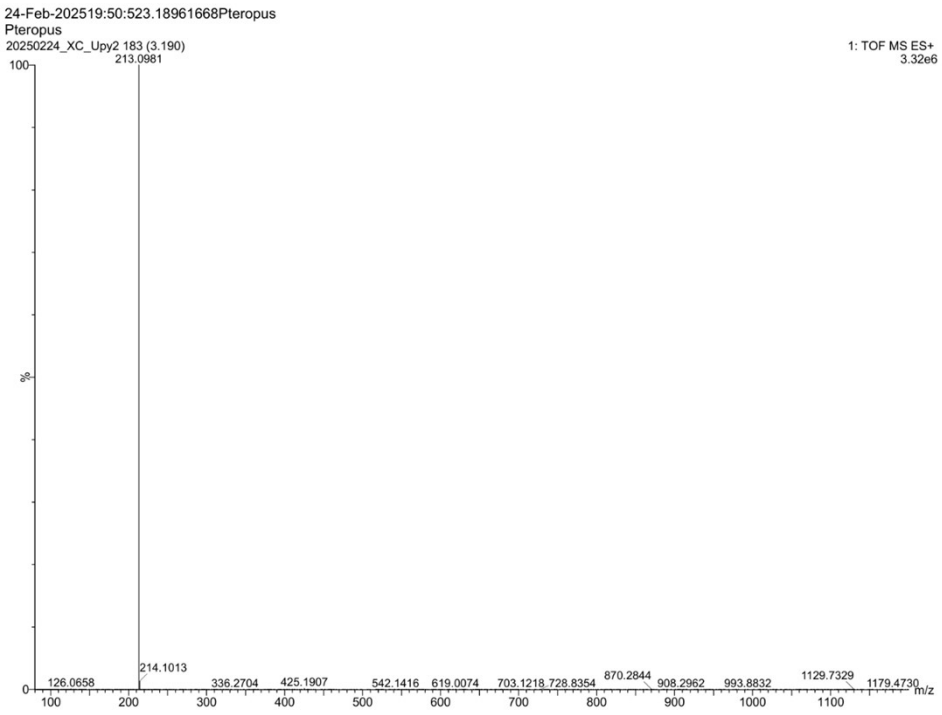

Fig. S11. ESI-HRMS spectrum of solid **Upy2.**

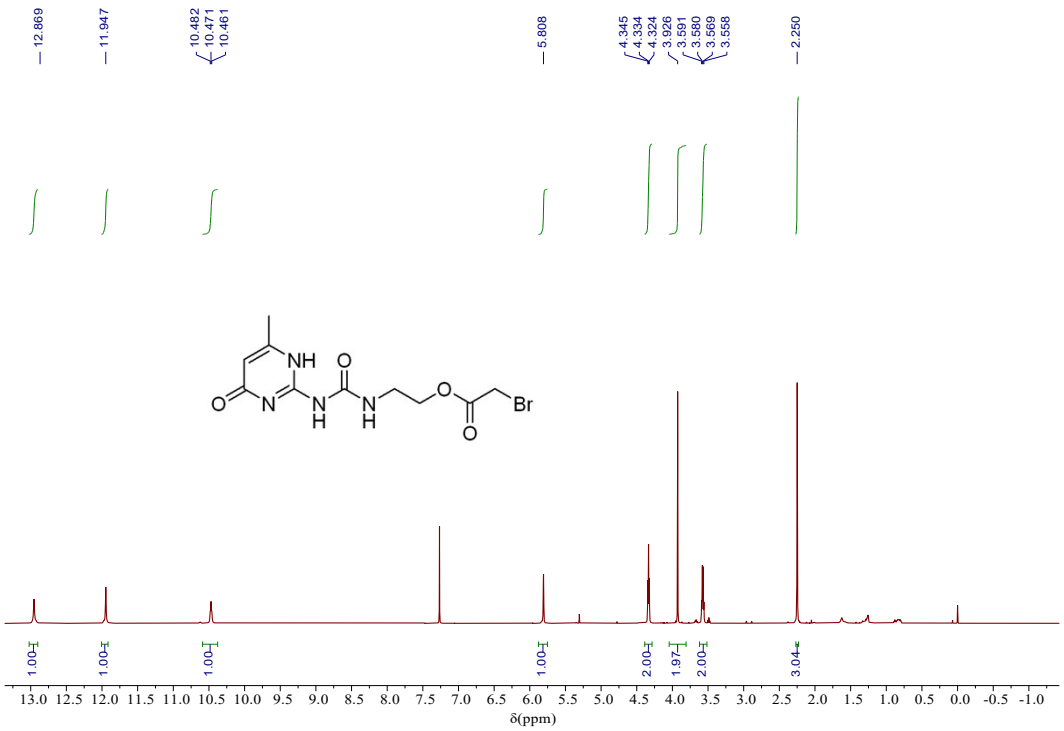

Fig. S12. ^{1}H NMR spectrum (500 MHz) of **Upy3** in $CDCl_3$.

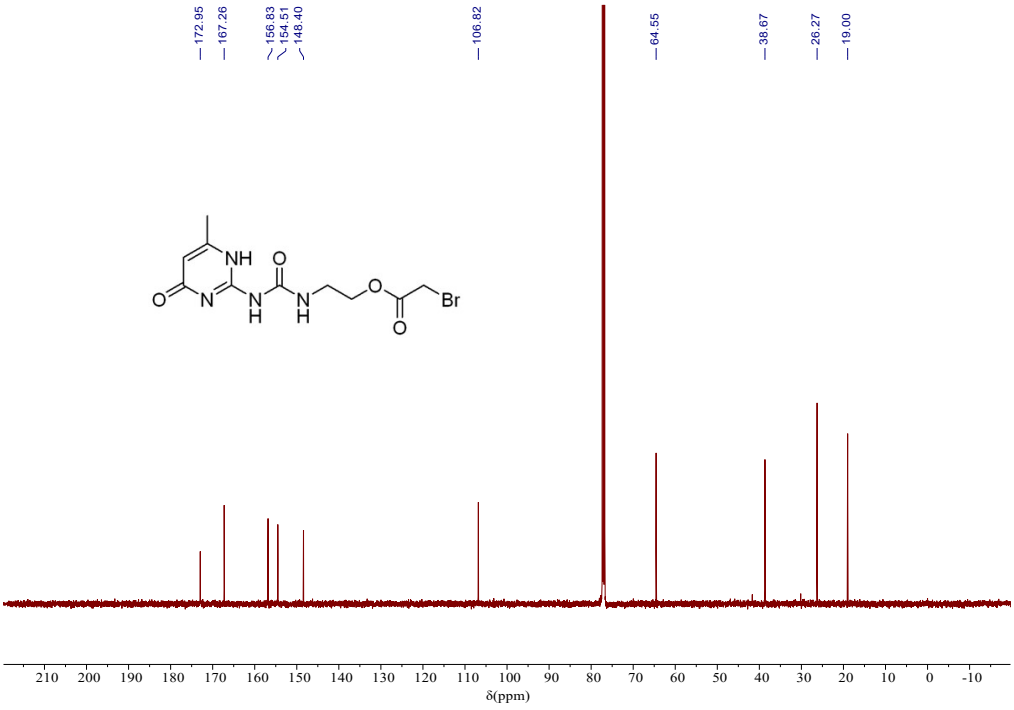

Fig. S13. ^{1}C NMR spectrum (125 MHz) of **Upy3** in $CDCl_3$.

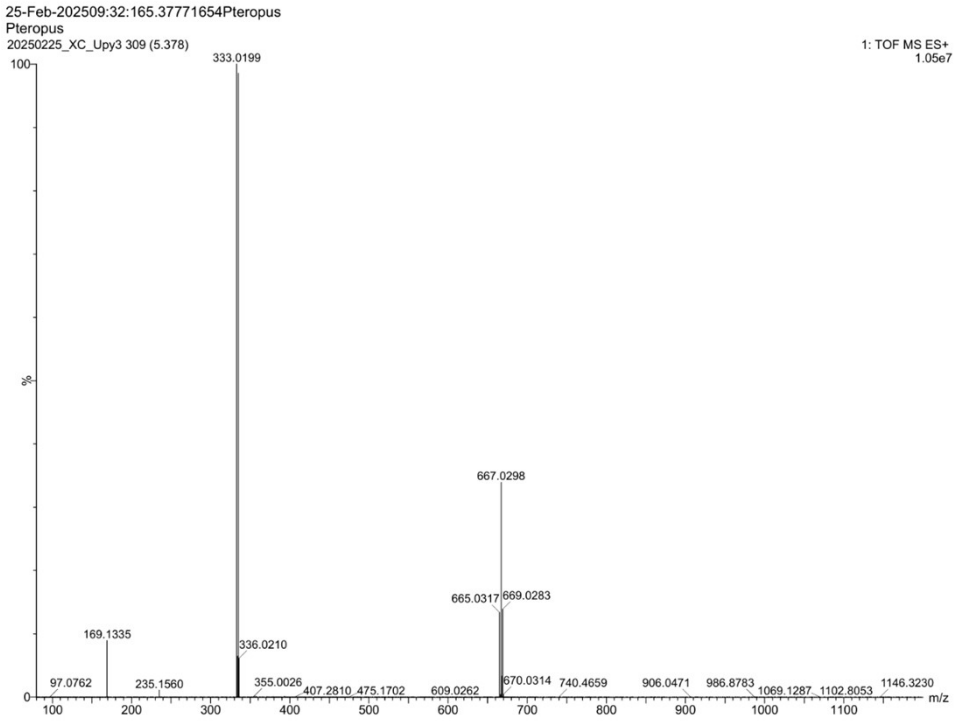

Fig. S14. ESI-HRMS spectrum of solid **Upy3.**

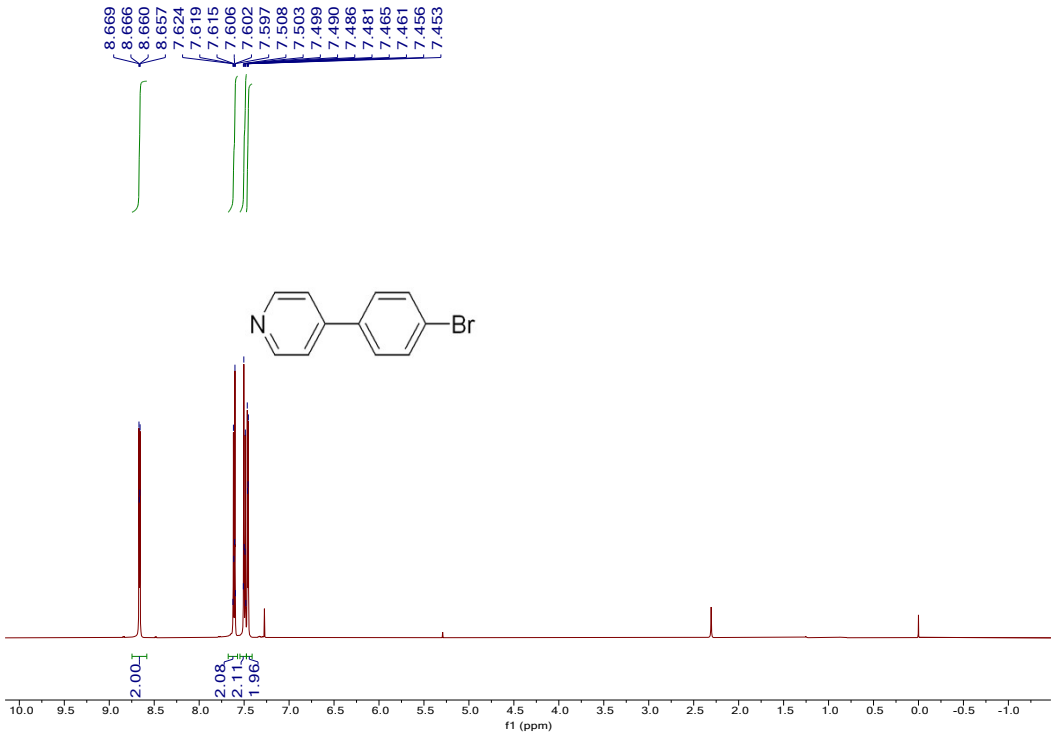

Fig. S15. ^{1}H NMR spectrum (500 MHz) of **BrBP** in DMSO-d_6.

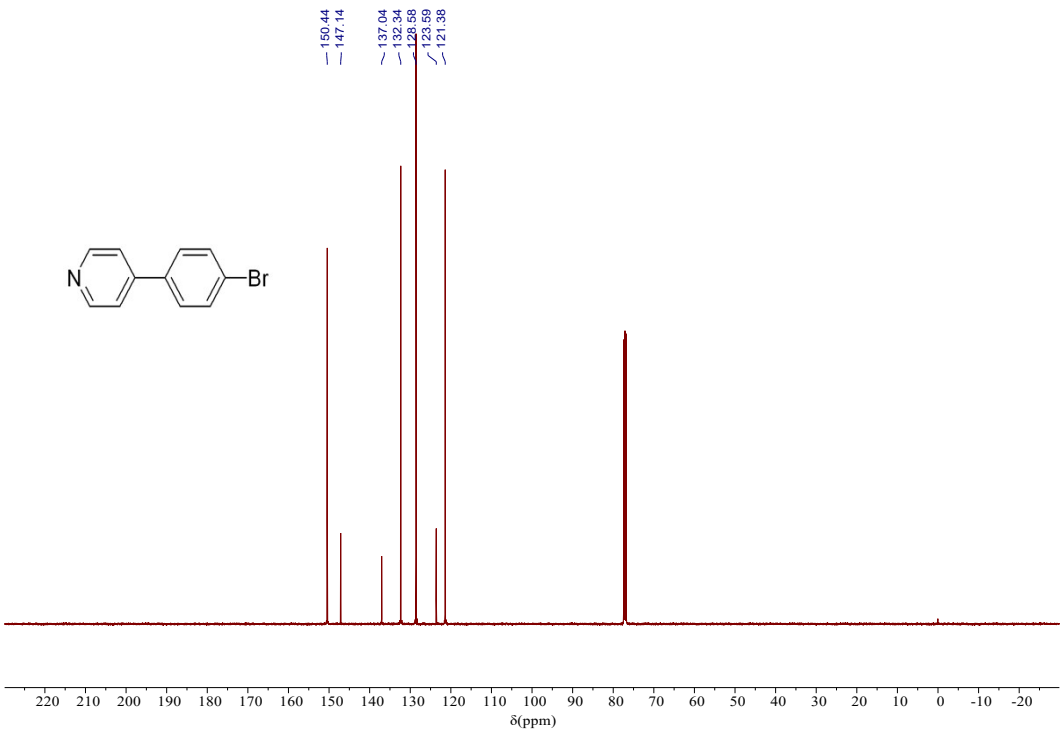

Fig. S16. [1]C NMR spectrum (125 MHz) of **BrBP** in DMSO-d_6.

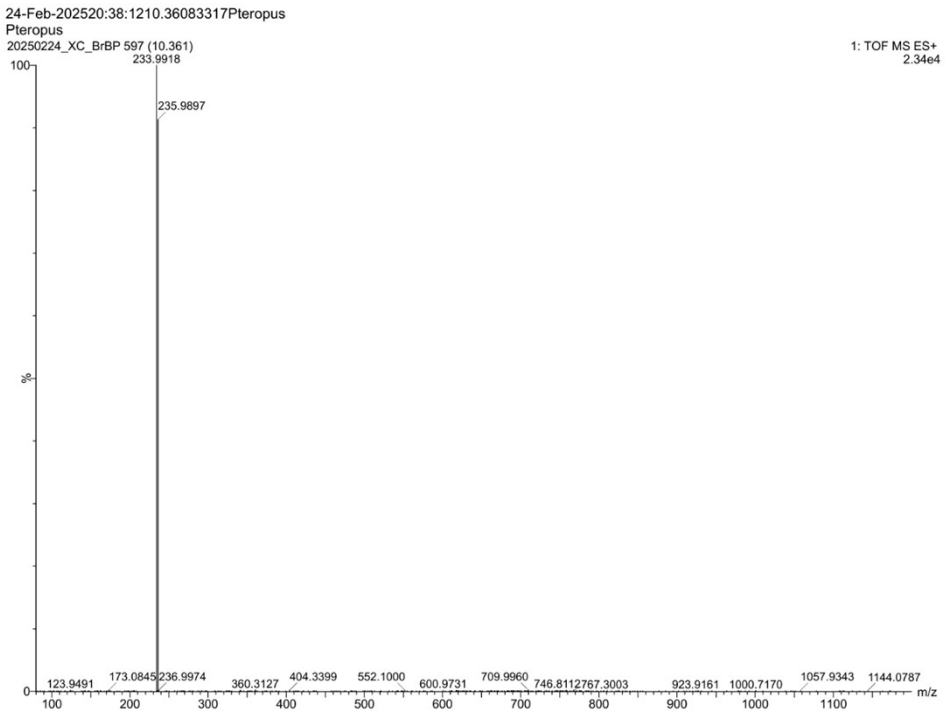

Fig. S17. ESI-HRMS spectrum of solid **BrBP.**

3. Preparation of the supramolecular gel.

The preparation method of the Upy3-BrBP-CB[8]-PVA gel is described as follows: First, PVA (1.0 g) was dissolved in ultrapure water (10 mL) to obtain a PVA solution. CB[8] (5.4 mg, 0.004 mmol) was then added to the PVA solution and stirred at 60°C until dissolved. The temperature was subsequently lowered to room temperature, and Upy3-BrBP (4.6 mg, 0.008 mmol) was added to the solution, which was stirred until it became clear. Finally, the solution was poured into a mold and frozen at -20°C for 8 hours, then thawed at room temperature for 1 hour. This freeze-thaw process was repeated four times, followed by lyophilization to obtain the supramolecular gel.

4. Characterization of Upy3-BrBP-CB[n] complex.

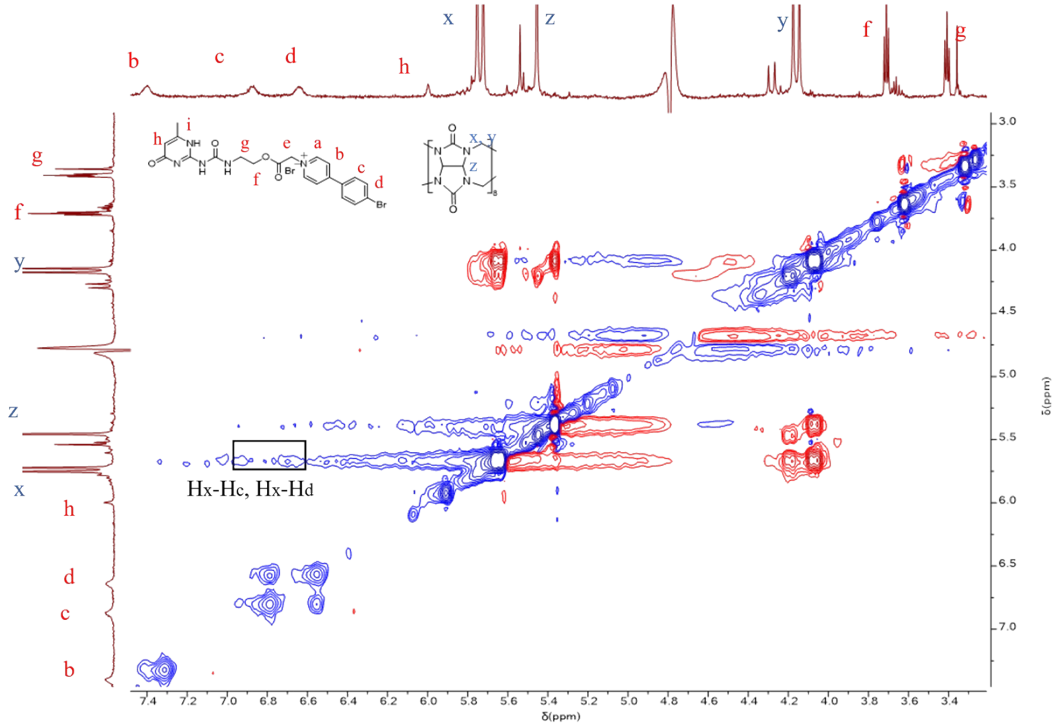

Fig. S18 2D ROESY NMR spectra of assembly in D_2O with presaturation water suppression (500 MHz, 0.4 mM)

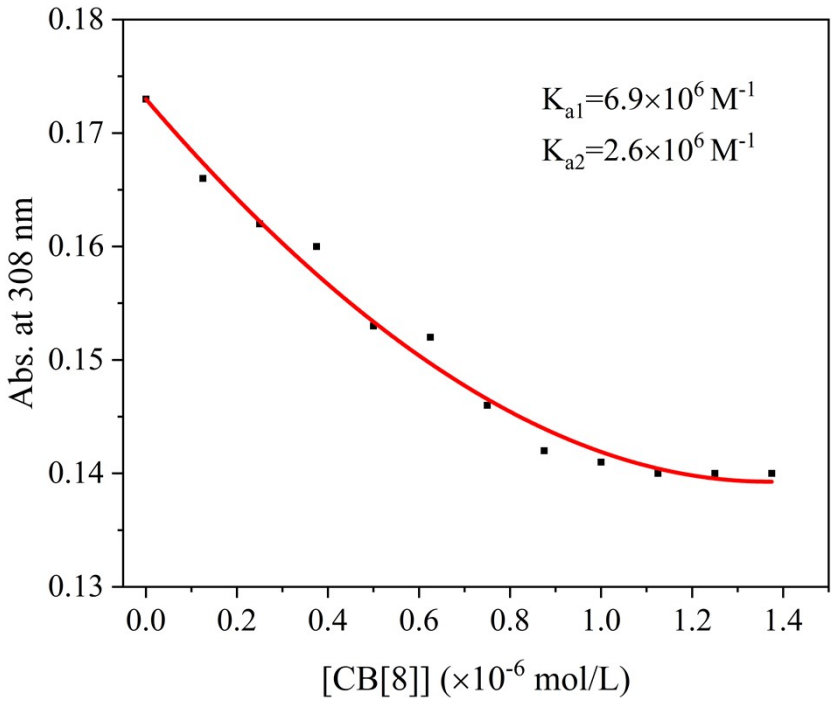

Fig.S19 Binding isotherm obtained from UV–vis titration at 308 nm upon addition of CB[8] to the guest solution

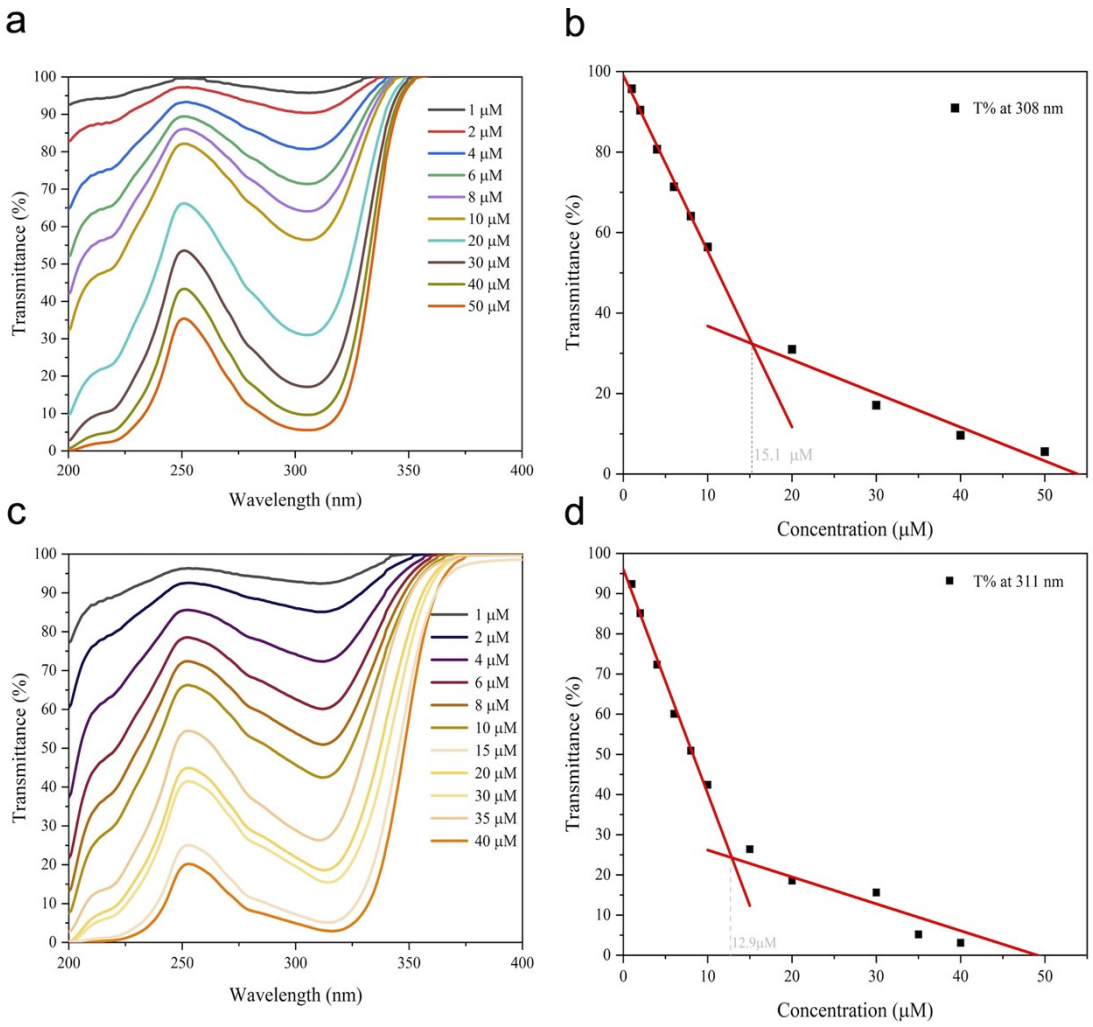

Fig. S20 a) Spectra of transmittance percentage of **Upy3-BrBP** aqueous solution with different concentrations; b) Transmittance percentage versus concentration curve of **Upy3-BrBP** aqueous solution at 308 nm (critical micelle concentration was 15.1 μM); c) Spectra of transmittance percentage of **Upy3-BrBP-CB[8]** aqueous solution with different concentrations; d) Transmittance percentage versus concentration curve of **Upy3-BrBP-CB[8]** aqueous solution at 311 nm (critical micelle concentration was 152.9 μM).

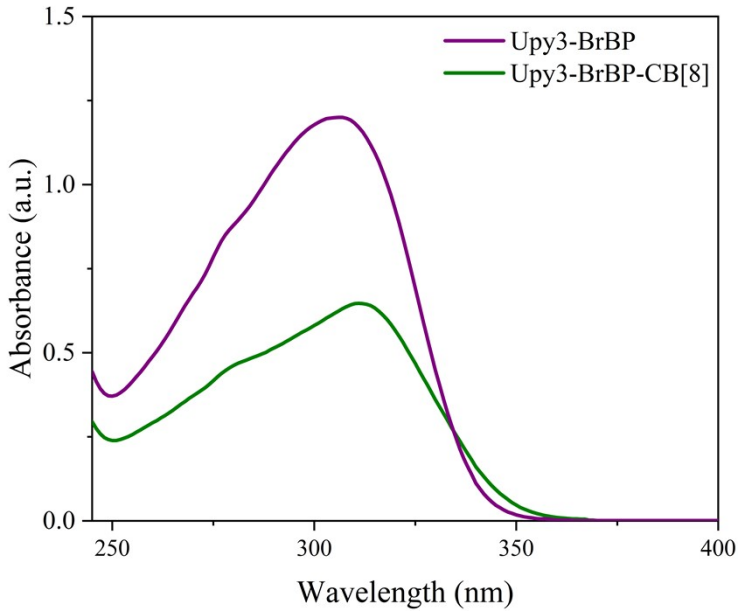

Fig. S21 UV-vis absorption spectra of **Upy3-BrBP** and **Upy3-BrBP-CB[8]**.

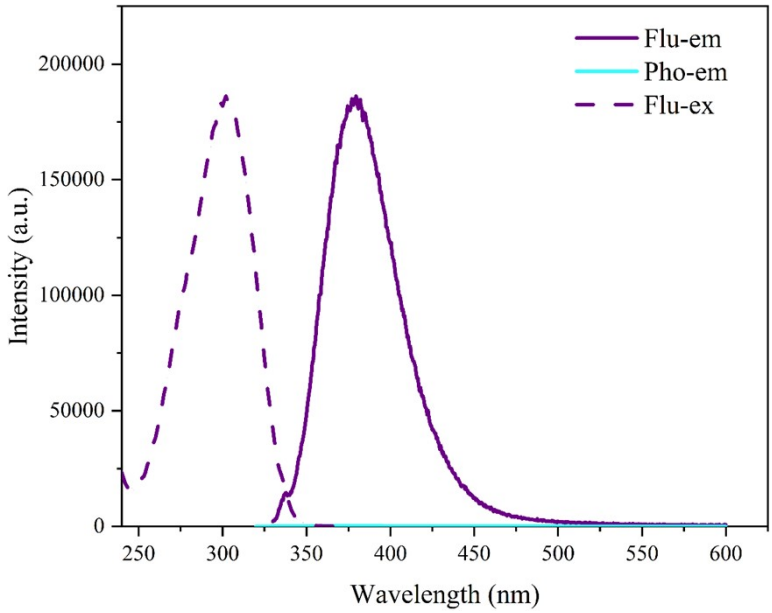

Fig. S22 Fluorescence excitation (deep purple dashed line) and emission (deep purple solid line) spectra of aqueous **Upy3-BrBP** solution ($5x10^{-6}$ M, excitation slit = 1.8 nm emission slit = 1 nm); phosphorescence spectrum (cyan solid line) of aqueous **Upy3-BrBP** solution ($5x10^{-6}$ M, λ_{ex} = 310 nm, excitation slit = emission slit = 5 nm, delay time = 0.1 ms)

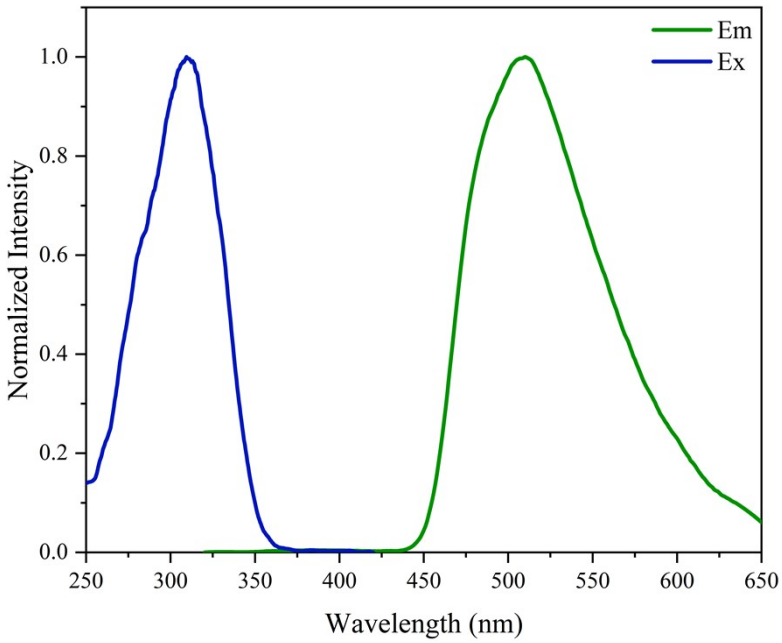

Fig. S23 Normalized phosphorescence exciation (blue solid line) and phosphorescence emission (green solid line) of **Upy3-BrBP-CB[8]** ($5x10^{-6}$ M, excitation slit = emission slit = 5 nm, delay time = 01 ms).

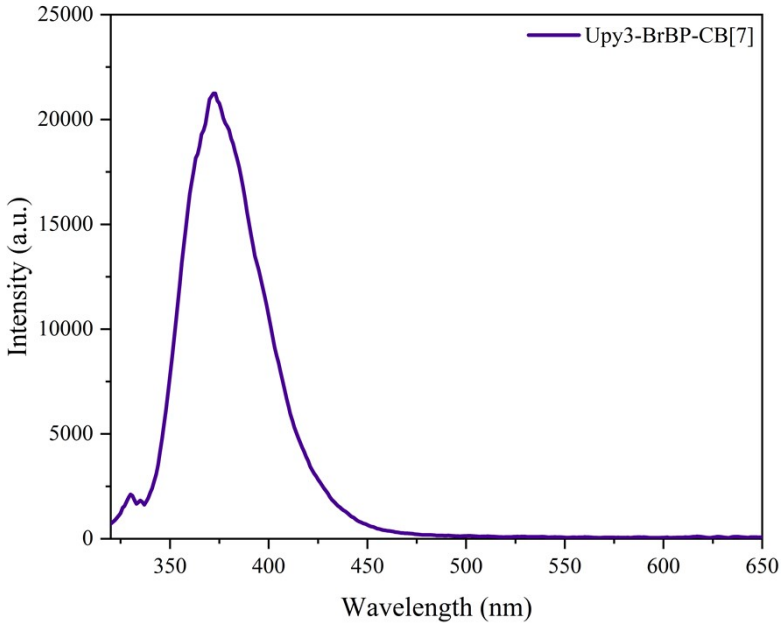

Fig. S24 Photoluminescence spectrum of **Upy3-BrBP-CB[7].**

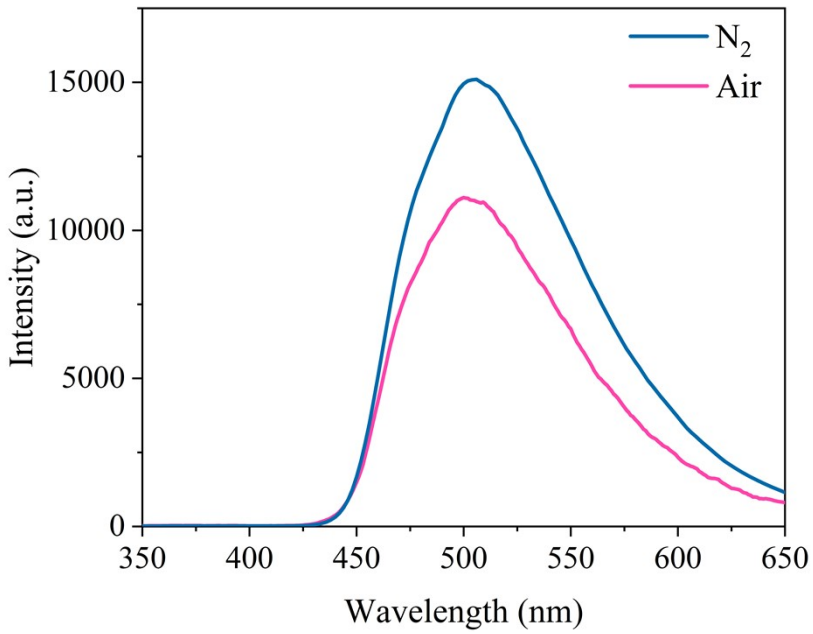

Fig. S25 Phosphorescence emission spectra of the supramolecular gel under N_2 and Air (excitation slim = emission slim = 5 nm, delay time = 0.1 ms)

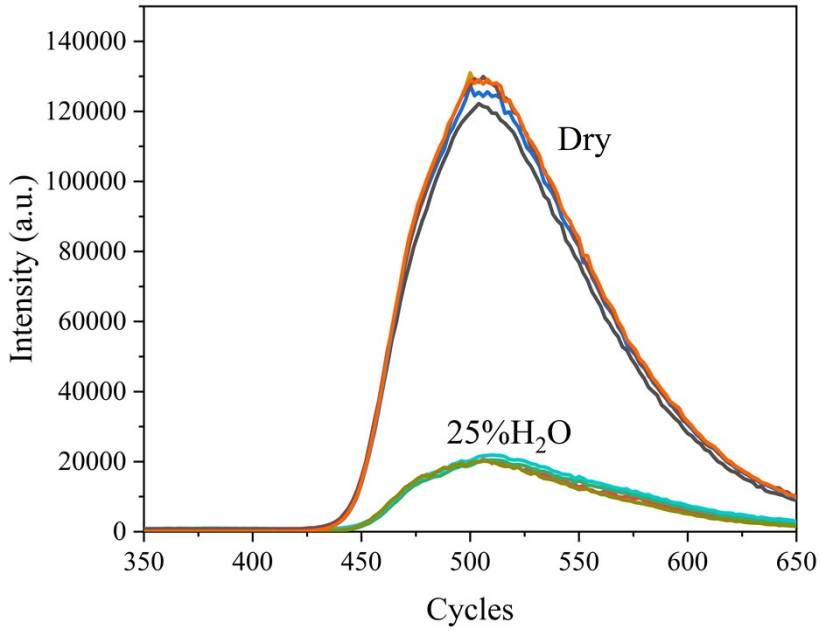

Fig. S26 Phosphorescent emission of supramolecular gels under different drying-hydration cycles

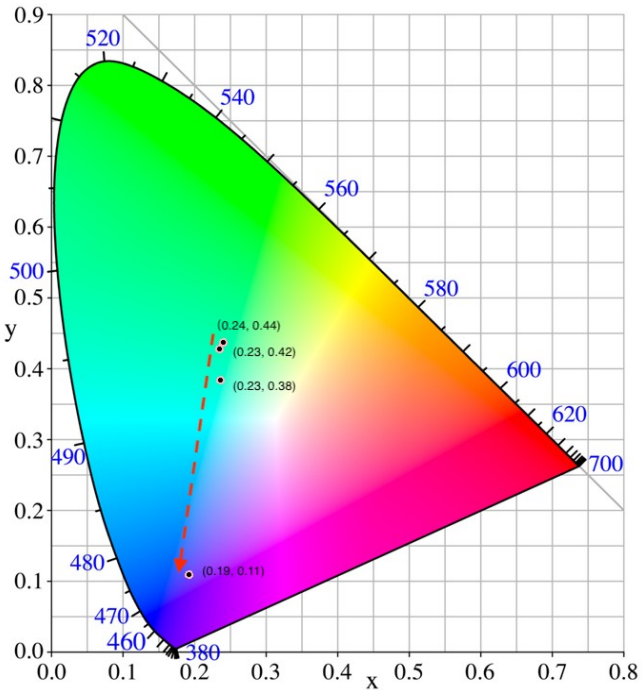

Fig. S27 The CIE coordinated diagram of supramolecular gels with different water content (from top right to bottom left: 5%, 10%, 20%, 50%).

Table S1 Luminescent properties of supramolecular gels with different host-guest ratios

Host-guest content (%)	Life time (ms)	Pl. QY (%)	Phos. QY (%)
0.5	3.92	14.49	13.89
1.0	4.98	19.21	18.84
1.5	4.84	10.93	10.86

5. SEM images of assembly in solution and supramolecular gels.

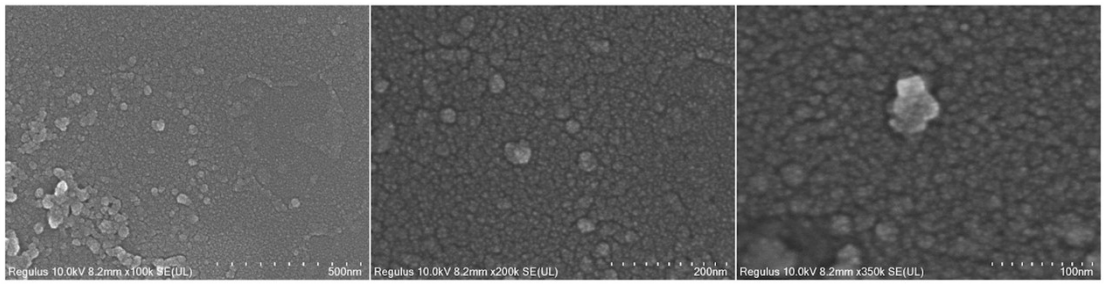

Fig. S28. SEM images of **Upy3-BrBP-CB[8]** prepared from aqueous concentration of 10 μM.

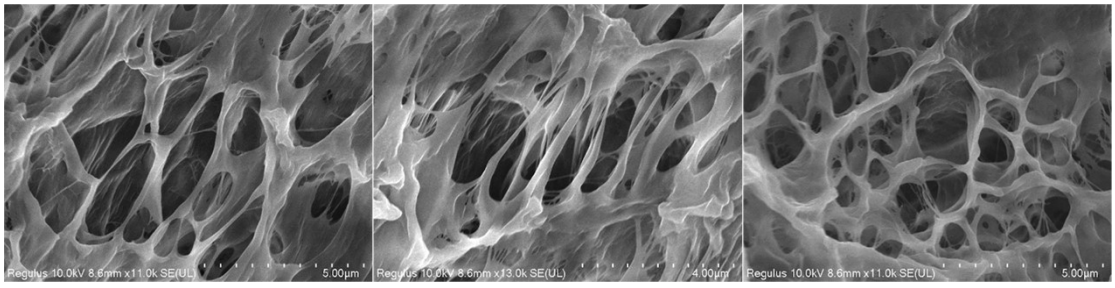

Fig. S29. SEM images of RTP gel with a supramolecular assembly content of 0.5%.

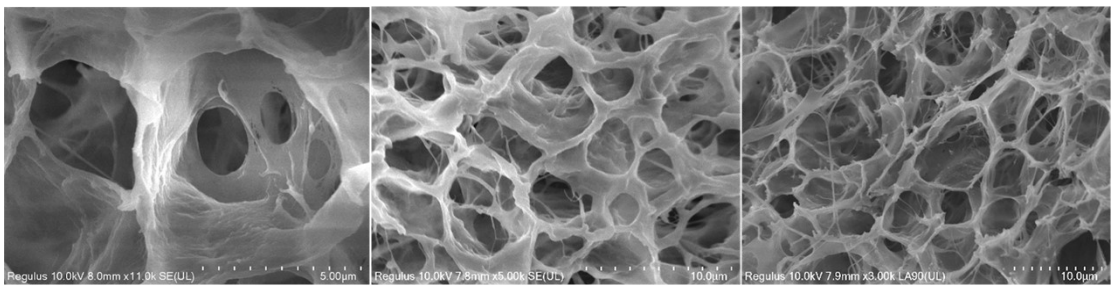

Fig. S30. SEM images of RTP gel with a supramolecular assembly content of 1.0%.

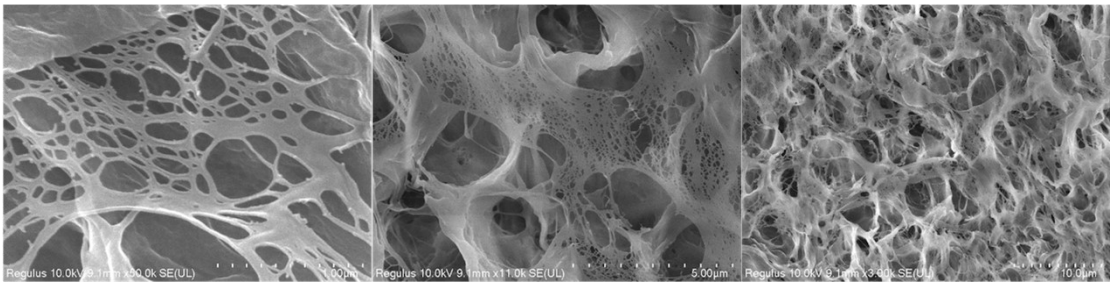

Fig. S31. SEM images of RTP gel with a supramolecular assembly content of 1.5%.

6. References.

[1] P. Y. W. Dankers, P. J. H. M. Adams, D. W. P. M. Löwik, J. C. M. van Hest, E. W. Meijer, *Eur. J. Org. Chem*. **2007**, 3622–3632.

[2] H. L. Ozores, M. Amorín, J. R. Granja, *J. Am. Chem. Soc.* **2017**, *139*, 776.