Supporting Information

Host-Enhanced Phenyl-Perfluorophenyl Polar–π Interactions

Zehuan Huang,[†] Xiaoyi Chen,[†] Guanglu Wu,[†] Pierangelo Metrangolo,[‡] Daniel Whitaker,[†] Jade A. McCune, [†] and Oren A. Scherman[*,†]

† Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

‡ Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Via L. Mancinelli 7, 20131 Milano, Italy

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SI-1 Materials and methods

Materials. Unless otherwise specified, all the materials as following were purchased from commercial suppliers and were used without further purification: acrylamide, N-vinylimidazole, 2,3,4,5,6-perfluorobenzyl bromide, benzyl bromide, 2,3,5,6-tetrafluorobenzyl bromide, 3,4,5-trifluorobenzyl bromide, 3,5-difluorobenzyl bromide, N-methylimidazole, pyridine, trimethylamine, acetonitrile, diethyl ether, deuterium oxide (D_2O, D 99.8%), and 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (I-2959). Cucurbit[8]uril (CB[8]) was prepared and purified using a previously reported method.[1] Water was obtained from a Milli-Q Integral Water Purification System (18.2 MΩ·cm). Unless noted, all the sample solutions for characterization were prepared in D_2O or Milli-Q H_2O.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H and ^{19}F NMR spectra were acquired in deuterium oxide at 298.15 K and recorded on a Bruker AVANCE 400 (400 MHz) apparatus. Chemical shifts were referenced to the residual solvent peak at 4.79 ppm. ^{13}C NMR spectra were acquired in in deuterium oxide at 298.15 K and recorded on a Bruker AVANCE 500 apparatus with TCI Cryoprobe system (500 MHz).

Isothermal Titration Calorimetry (ITC). ITC experiments were carried out with a Malvern MicroCal Auto-ITC200 apparatus at 298.15 K in pure water. In a typical titration experiment for homoternary complexation, the host molecule (CB[8]) was loaded in the sample cell at a concentration of 0.05 mM, and the guest molecule was loaded in the syringe at a 20-fold higher concentration of 1.0 mM. One titration experiment consisted of 1 injection of 0.6 μL and 32 consecutive injections of 1.2 μL with 90 s intervals between injections. The first data point was removed from the data set before analysis. The obtained ITC curves were fitted by MicroCal Analysis Centre software using sequential binding site model. As for the titration experiment for second binding, the binary complex of 5FBVI-CB[8] was loaded in the sample cell at a concentration of 0.5 mM, and the second guest molecule of BVI was loaded in the syringe at 10-fold higher concentration of 5 mM. Same titration method setting was followed as the above one. The first data point was also removed from the data set and the obtained ITC data were fitted by MicroCal Analysis Centre software using one set of sites model. All the data obtained were an average of three repeats.

Electrospray Ionization Mass Spectrometry (ESI-MS). ESI-MS spectra were acquired on a Thermo Fisher Q Exactive Orbitrap mass spectrometer with a nanospraying ion source. Positive mode was chosen for all the experiments with the working temperature of 320 °C and the capillary voltage of 1.5 kV. All the sample solutions were prepared in pure water, and all the data was analyzed in Origin 10.0.

Rheology. Rheological characterization was conducted by a Discovery Hybrid Rheometer (DHR)-2, TA Instruments, with a Peltier Plate for temperature control. All measurements were performed using a 20 mm parallel stain steel plate geometry with a gap of 1500 μm. Dynamic oscillatory amplitude sweep measurements were performed at 10 rad s^{-1} in the strain range from 0.01 to 2000 %. Dynamic oscillatory frequency sweep measurements were conducted at 1 % strain in the frequency range from 0.1 to 100 rad s^{-1}.

Continuous step-strain measurements were carried out at 1 rad s^{-1} in high-amplitude oscillatory (500 %) and low-amplitude oscillatory (5 %), respectively. All of the above data was collected at 293.15 K, analyzed by TRIOS software, TA Instruments, and then plotted by Origin 10.0. Time-temperature superposition (TTS) experiments were performed as the frequency sweep measurements at 1 % strain in the temperature range from 273.15 K to 353.15 K with 10 K intervals, and 303.15 K was used as the reference temperature. The obtained data was analyzed to calculate the activation energy of local chain motion.

SI-2 Molecular design and synthetic protocols

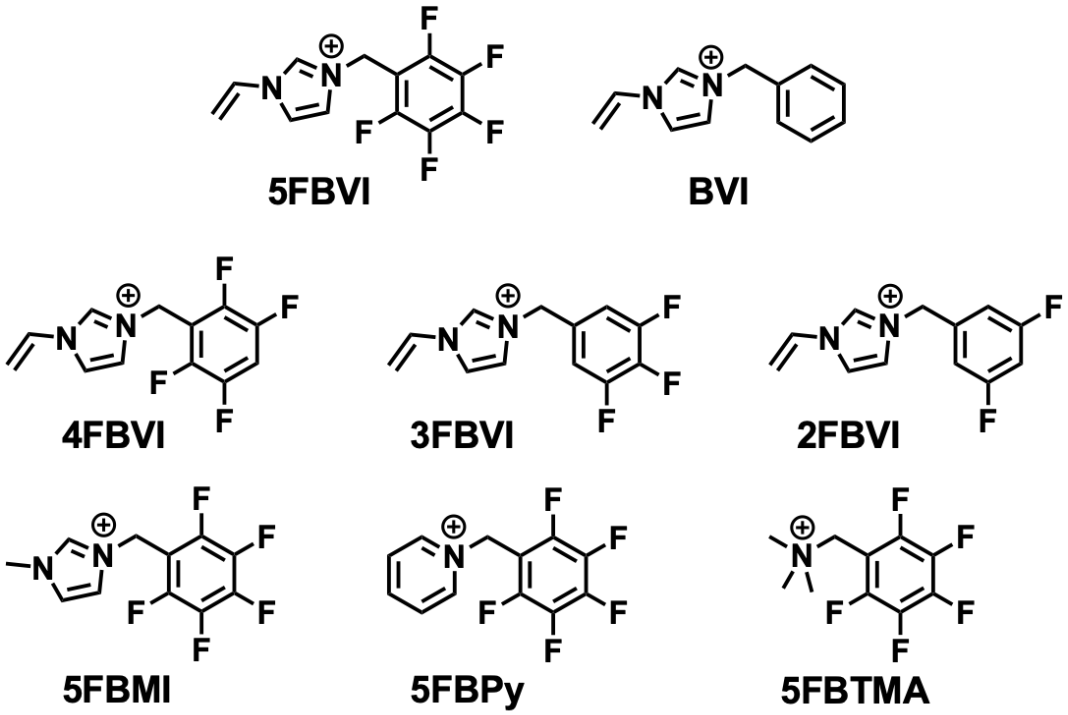

Chart S1 Molecular structures of all the guest molecules with the counter ion of bromide.

As shown in Chart S1, all of the guest molecules were rationally designed and easily prepared by salt formation reaction.[2] The representative synthetic route is shown in Figure S1 using 5FBVI as the example.

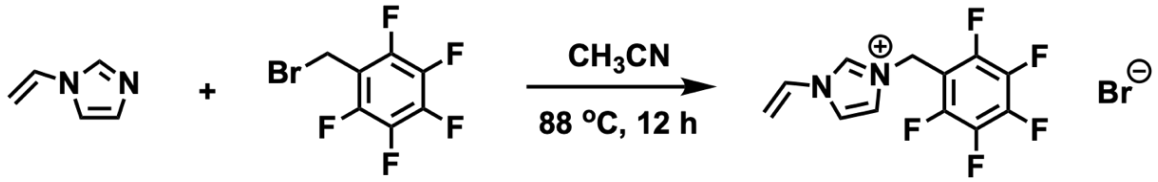

Figure S1 Representative synthetic route for the preparation of guest molecules.

Synthesis of 1-(2,3,4,5,6-perfluoro)-benzyl-3-vinylimidazolium bromide (5FBVI)

2,3,4,5,6-perfluorobenzyl bromide (20 mmol) and N-vinylimidazole (21 mmol) were dissolved together in acetonitrile (20 mL) and heated at 88 °C for 12 h. Next the reaction mixture was divided into four portions and precipitated separately by 35 mL diethyl ether for each in 50 mL Falcon tubes, and then centrifuged at 10000 rpm for 10 min. The supernatants were removed, and the crude product was resuspended by 40 mL diethyl ether for each and centrifuged again. Finally, the white solid of 5FBVI was collected, combined and dried under vacuum till a constant weight, yielding ca. 91 %. ^{1}H NMR (400 MHz, D_2O, ppm): δ = 9.28 - 9.24 (d, 1H), 7.84 - 7.82 (d, 1H), 7.66 - 7.65 (d, 1H), 7.20 - 7.11 (q, 1H), 5.88 - 5.80 (q, 1H), 5.68 - 5.64 (s, 2H), 5.50 - 5.45 (q, 1H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -142.58, -151.41, -161.29; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 146.48, 144.50, 142.28, 141.26, 138.64, 136.65, 134.85, 128.00, 122.85, 119.92, 110.09, 106.97, 40.39; ESI MS for $[5FBVI\text{-}Br]^+$: calc. m/z = 275.0602, found m/z = 275.0598.

Synthesis of 1-benzyl-3-vinylimidazolium bromide (BVI)

The same synthetic procedure used to prepare 5FBVI was followed using benzyl bromide as the starting material. The white solid of BVI was obtained, yielding ca. 94 %. ^{1}H NMR (400 MHz, D_2O, ppm): δ = 7.82 - 7.76 (d, 1H), 7.59 - 7.55 (d, 1H), 7.54 - 7.42 (m, 5H), 7.16 - 7.08 (q, 1H), 5.83 - 5.76 (q, 1H), 5.47 - 5.40 (m, 3H); ^{13}C NMR (125 MHz, D_2O, ppm): δ = 134.25, 133.05, 129.39, 129.34, 128.70, 128.11, 122.79, 119.62, 109.50, 53.12; ESI MS for $[BVI\text{-}Br]^+$: calc. m/z = 185.1073, found m/z = 185.1078.

Synthesis of 1-(2,3,5,6-perfluoro)-benzyl-3-vinylimidazolium bromide (4FBVI)

The same synthetic procedure used to prepare 5FBVI was followed using 2,3,5,6-tetrafluorobenzyl bromide as the starting material. The white solid of 4FBVI was obtained, yielding ca. 90 %. ^{1}H NMR (400 MHz, D_2O, ppm): δ = 7.87 - 7.79 (d, 1H), 7.66 - 7.58 (d, 1H), 7.37 - 7.26 (m, 1H), 7.21 - 7.10 (q, 1H), 5.88 - 5.78 (q, 1H), 5.58 - 5.52 (s, 2H), 5.50 - 5.43 (q, 1H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -138.67, -142.31, -153.70, -155.01; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 148.01, 147.20, 146.03, 145.21, 142.12, 141.66, 140.13, 139.65, 134.70, 128.02, 122.79, 119.85, 116.83, 112.39, 109.95, 46.30; ESI MS for $[4FBVI\text{-}Br]^+$: calc. m/z = 257.0696, found m/z = 257.0705.

Synthesis of 1-(3,4,5-perfluoro)-benzyl-3-vinylimidazolium bromide (3FBVI)

The same synthetic procedure used to prepare 5FBVI was followed using 3,4,5-trifluorobenzyl bromide as the starting material. The white solid of 3FBVI was obtained, yielding ca. 89 %. ^{1}H NMR (400 MHz, D_2O, ppm): δ = 7.86 - 7.82 (d, 1H), 7.61 - 7.58 (d, 1H), 7.24 - 7.12 (m, 3H), 5.88 - 5.80 (q, 1H), 5.68 - 5.64 (s, 2H), 5.50 - 5.42 (m, 3H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -133.78, -160.04; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 152.06, 150.08, 140.88, 138.88, 138.64, 134.56, 129.44, 128.06, 122.82, 119.89, 113.16, 109.85, 51.76; ESI MS for $[3FBVI\text{-}Br]^+$: calc. m/z = 239.0791, found m/z = 239.0786.

Synthesis of 1-(3,5-perfluoro)-benzyl-3-vinylimidazolium bromide (2FBVI)

The same synthetic procedure used to prepare 5FBVI was followed using 3,5-difluorobenzyl bromide as the starting material. The white solid of 2FBVI was obtained, yielding ca. 92 %. ^{1}H NMR (400 MHz,

D_2O, ppm): δ = 7.85 - 7.82 (d, 1H), 7.62 - 7.59 (d, 1H), 7.20 - 7.12 (q, 1H), 7.07 - 7.00 (m, 3H), 5.86 - 5.80 (q, 1H), 5.50 - 5.43 (m, 3H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -109.06; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 164.02, 162.05, 136.64, 134.61, 128.08, 122.90, 119.84, 111.51, 109.80, 104.56, 52.03; ESI MS for $[2FBVI-Br]^+$: calc. m/z = 221.0885, found m/z = 221.0882.

Synthesis of 1-(2,3,4,5,6-perfluoro)-benzyl-3-methylimidazolium bromide (5FBMI)

The same synthetic procedure used to prepare 5FBVI was followed using N-methylimidazole as the starting material. The white solid of 5FBMI was obtained, yielding ca. 87 %. ^1H NMR (400 MHz, D_2O, ppm): δ = 8.95 - 8.91 (s, 1H), 7.57 - 7.51 (s, 1H), 7.50 - 7.45 (s, 1H), 5.65 - 5.55 (s, 2H), 4.00 - 3.80 (s, 3H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -142.58, -151.75, -161.42; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 146.43, 144.44, 143.17, 141.12, 138.62, 136.62, 136.36, 123.96, 122.23, 107.33, 40.02, 35.81; ESI MS for $[5FBMI-Br]^+$: calc. m/z = 263.0602, found m/z = 263.0609.

Synthesis of 1-(2,3,4,5,6-perfluoro)-benzylpyridinium bromide (5FBPy)

The same synthetic procedure used to prepare 5FBVI was followed using pyridine as the starting material. The white solid of 5FBPy was obtained, yielding ca. 92 %. ^1H NMR (400 MHz, D_2O, ppm): δ = 9.00 - 8.94 (d, 2H), 8.66 - 8.59 (t, 1H), 8.17 - 8.10 (t, 2H), 6.06 - 6.02 (s, 2H), 4.00 - 3.80 (s, 3H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -141.35, -150.19, -160.89; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 146.76, 146.70, 144.73, 144.63, 143.66, 141.63, 138.74, 136.74, 128.64, 106.52, 51.93; ESI MS for $[5FBPy-Br]^+$: calc. m/z = 260.0493, found m/z = 260.0501.

Synthesis of 1-(2,3,4,5,6-perfluoro)-benzyl-N,N,N-trimethylammonium bromide (5FBTMA)

The same synthetic procedure used to prepare 5FBVI was followed using trimethylamine as the starting material. The white solid of 5FBTMA was obtained, yielding ca. 90 %. ^1H NMR (400 MHz, D_2O, ppm): δ = 4.77 - 4.74 (s, 2H), 3.30 - 3.17 (s, 3H); ^{19}F NMR (375 MHz, D_2O, ppm): δ = -137.23, -148.31, -160.36; ^{13}C NMR (125 MHz, D_2O, ppm): δ = 147.56, 145.60, 144.26, 142.21, 138.93, 136.93, 102.32, 56.53, 52.83; ESI MS for $[5FBPy-Br]^+$: calc. m/z = 240.0806, found m/z = 240.0801.

SI-3 Procedures for preparation of supramolecular polyacrylamide networks

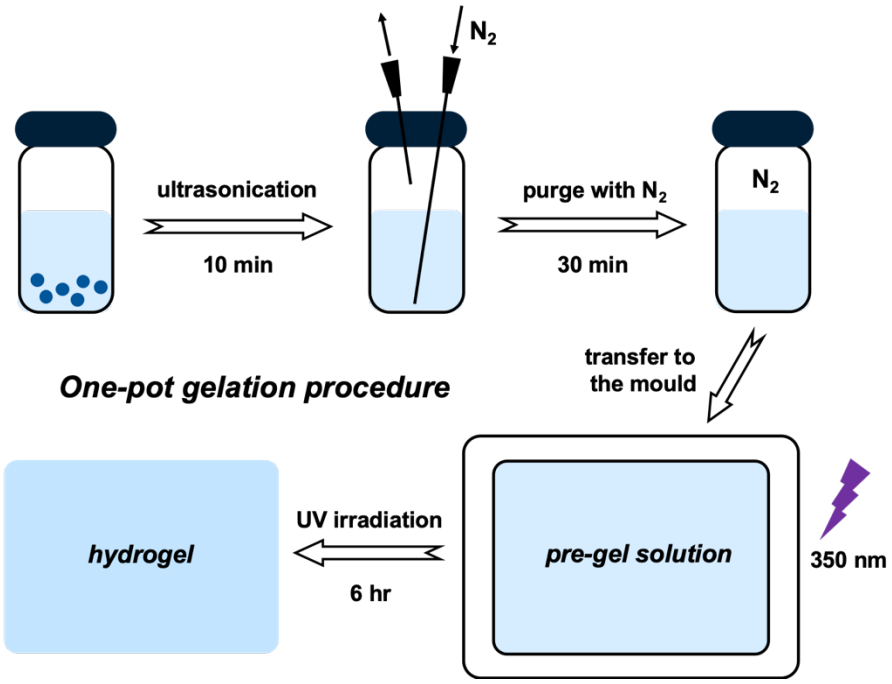

Figure S2 Schematic representation of one-pot gelation procedure in a glass mould.

In a typical procedure, the amounts of acrylamide, supramolecular cross-linker of 5FBVI-BVI-CB[8] and photoinitiator I-2959 were predetermined and weighed out precisely in a glass vial. Then, the solid mixture was dissolved together in Milli-Q H_2O with the precalculated volume under ultrasonication for 10 min. The obtained pre-gel solution was sealed and purged with nitrogen for 30 min. Next it was transferred into a laboratory-made glass mould with a certain thickness (1 or 2 mm), before being exposed to UV irradiation of 350 nm light with 4.8 mW/cm^2 for 6 hr. Finally, the hydrogel was removed from the glass mould and then cut into the required shape. Similarly, hydrogels could be directly prepared in a cell culture bottle or a small glass vial. The obtained hydrogels were cut using a dumbbell-shaped cutter or a razor blade into different sizes and shapes required for certain characterization.

SI-4 Study on CB[8]-mediated polar–π interaction by ^{1}H and ^{19}F NMR

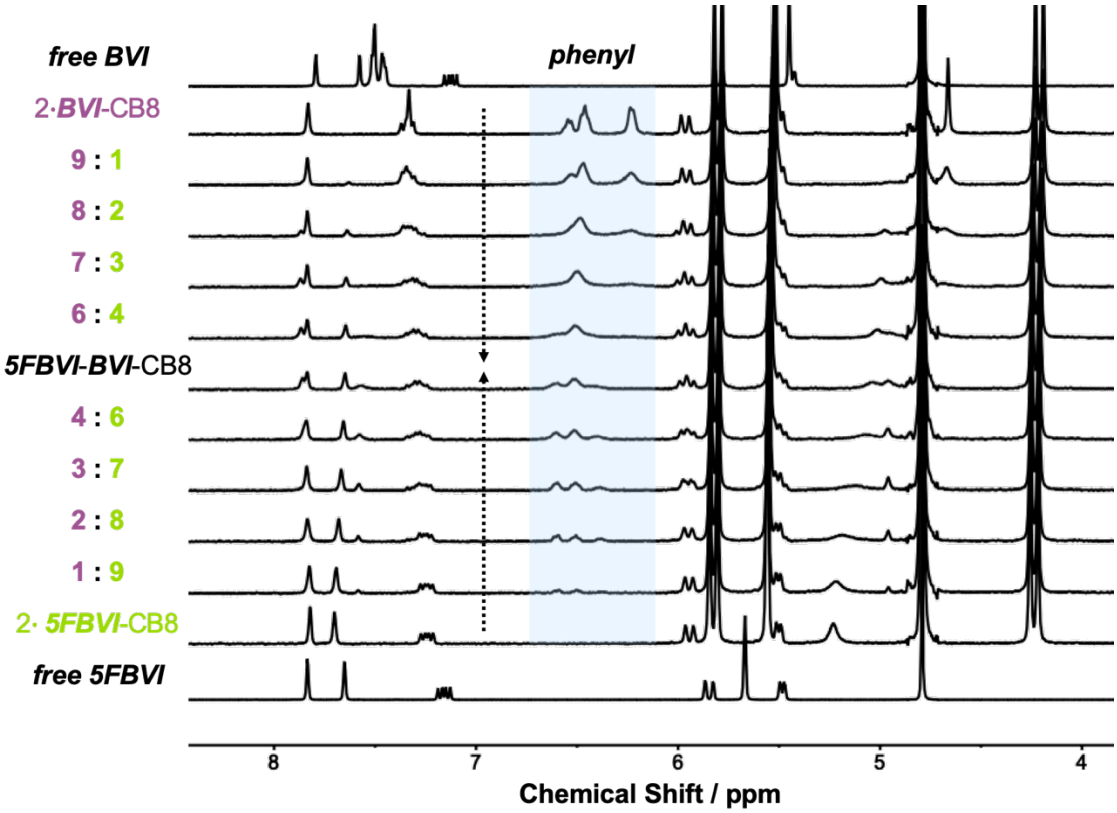

Figure S3 ^{1}H NMR titrations by mixing 2·BVI-CB[8] and 2·5FBVI-CB[8] at the molar ratio of 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 together with four controls of pure 2·BVI-CB[8], pure 2·5FBVI-CB[8], free BVI and 5FBVI.

As shown in Figure S3, by adding 2·BVI-CB[8] into 2·5FBVI-CB[8], three proton peaks of the phenyl moiety on 2·BVI-CB[8] at 6.23, 6.49, 6.59 ppm gradually disappeared with the appearance of three new peaks at 6.39, 6.49, 6.59 ppm. This data is consistent with the ^{1}H NMR titrations in Figure 1a, which again indicates the formation of a new heteroternary complex of 5FBVI-BVI-CB[8]. This series of titrations also suggests the self-sorting phenomenon in the equimolar mixture of BVI, 5FBVI, and CB[8].

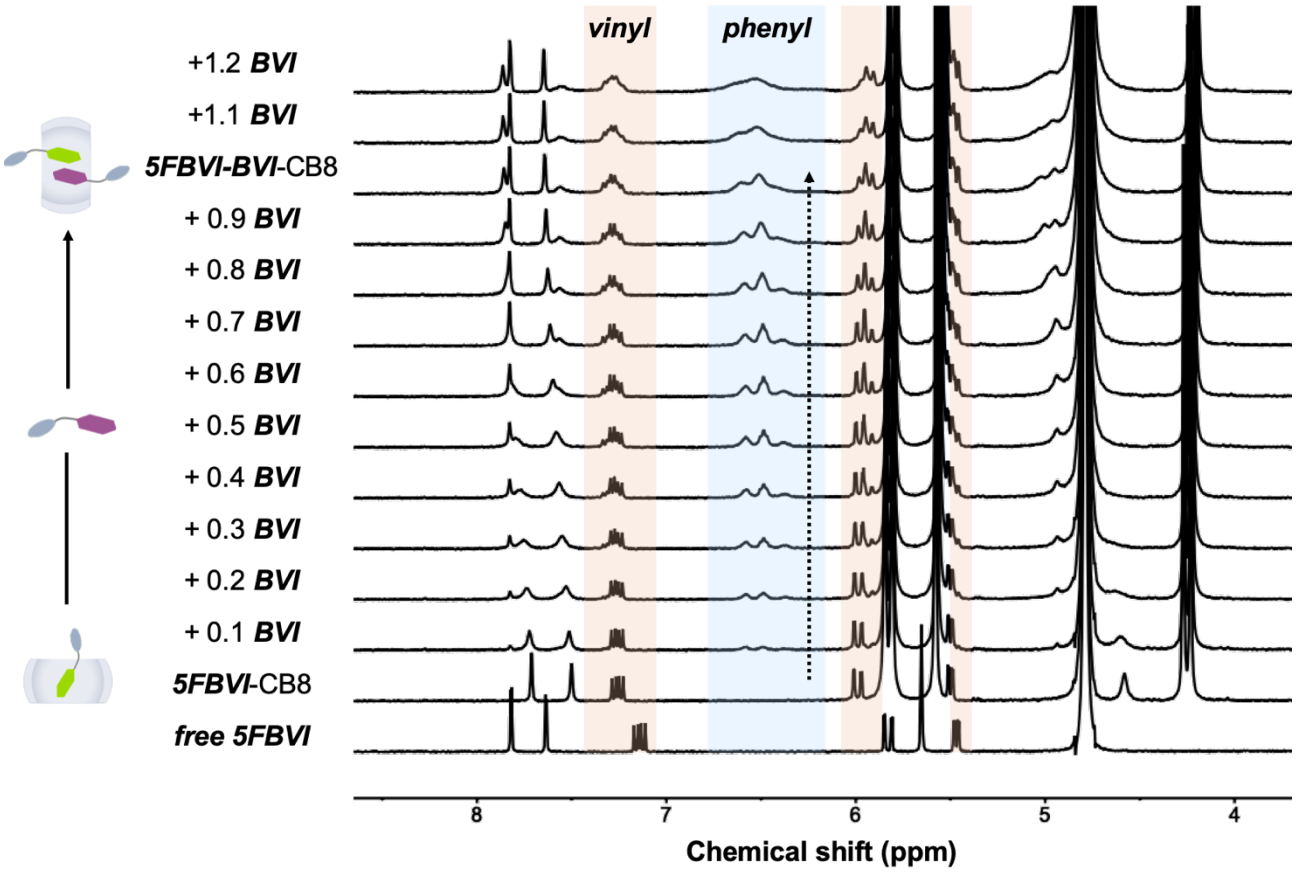

Figure S4 ^{1}H NMR titrations by adding BVI into 5FBVI-CB[8] with the molar ratio from 0.1 to 1.2 together with two controls of pure 5FBVI-CB[8] and free 5FBVI.

This is the extended version of Figure 2a (left). As shown in Figure S4, a new series of proton peaks attributed to the phenyl moiety of BVI gradually appears, which suggests the formation of a new heteroternary complex of 5FBVI-BVI-CB[8]. It is also observed that there are two series of vinyl groups that can be attributed to the vinyl groups of BVI and 5FBVI. This suggests the self-sorting phenomenon during the titration process.

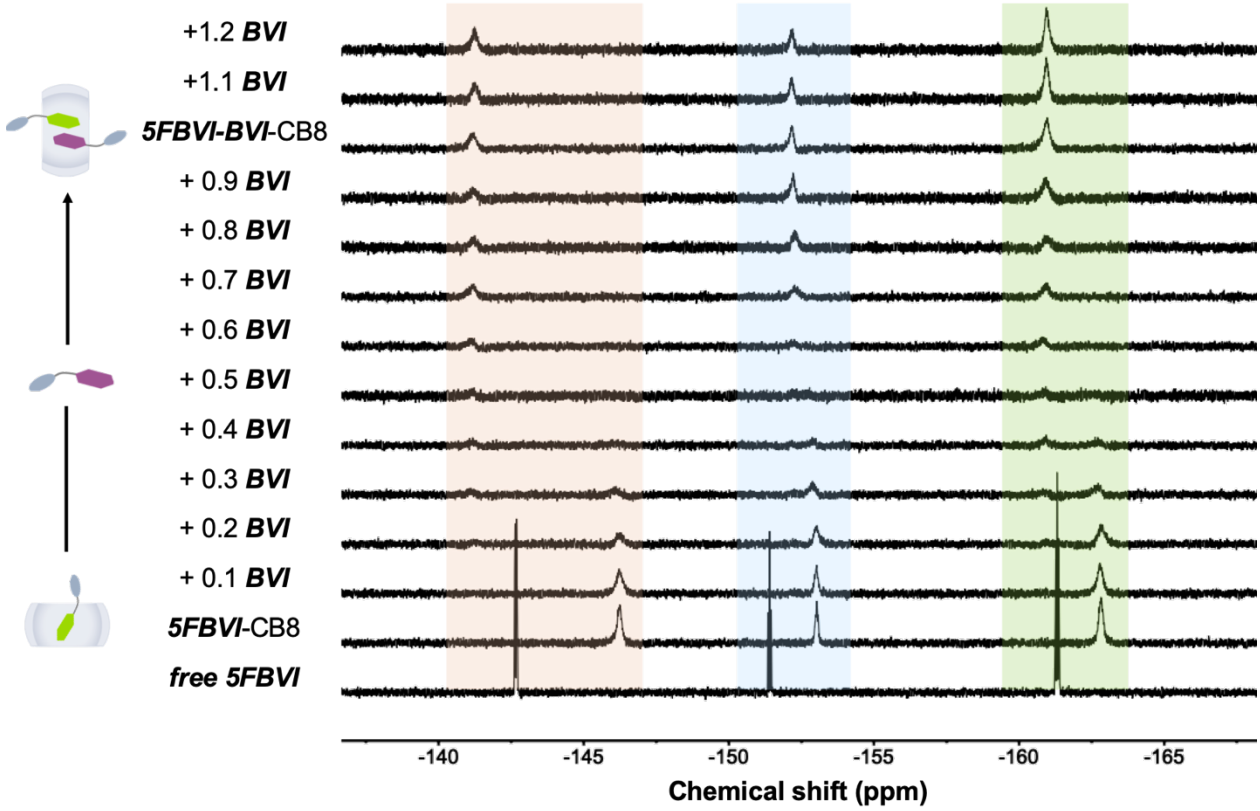

Figure S5 ^{19}F NMR titrations by adding BVI into 5FBVI-CB[8] with the molar ratio from 0.1 to 1.2 together with two controls of pure 5FBVI-CB[8] and free 5FBVI.

This is the extended version of Figure 2a (right). As shown in Figure S5, three new fluorine peaks gradually appears with the addition of BVI into 5FBVI-CB[8], strongly suggesting the formation of a new heteroternary complex of 5FBVI-BVI-CB[8]. It should be mentioned that for clarity the intensity of 5FBVI in Figure 2a is one fourth of its original intensity in Figure S5, which is also labelled with 'x 0.25'.

SI-5 Study on CB[8]-mediated polar–π interaction by ESI-MS

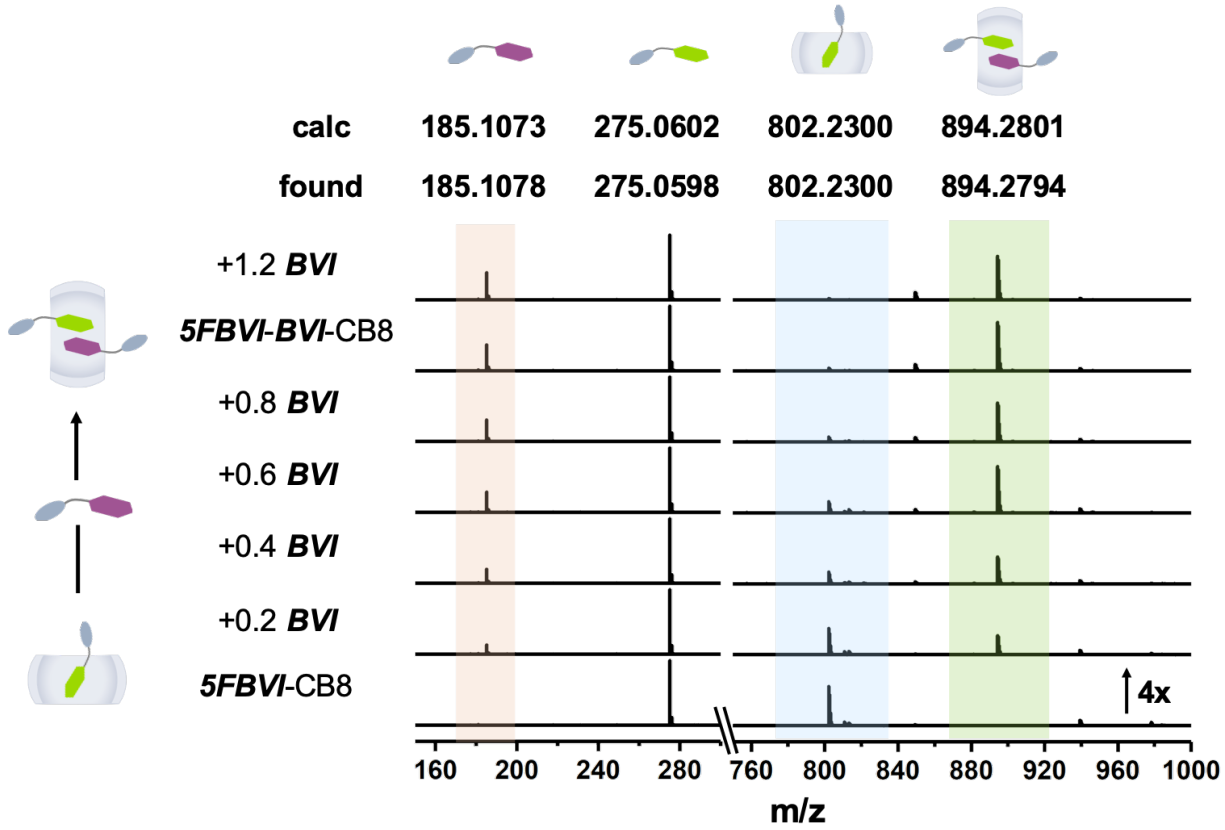

Figure S6 HR ESI-MS titrations by adding BVI into 5FBVI-CB[8] observed in two different m/z ranges of 150-300 (left) and 750-1000 (right) with 4 times higher intensity.

This is the extended version of Figure 2b. As shown in Figure S6, by adding BVI into 5FBVI-CB[8], the residual ion peak of BVI gradually appears at m/z of 185.1078 compared with the ion peak of 5FBVI at 275.0598 as the reference. Although electrospray is a soft ionization method, some of the host-guest complexes will disassociate, thus releasing plenty of free BVI and 5FBVI. The disassociated CB[8] will mostly be trapped in the MS apparatus. Thus, it is suggested to use the free guest solution or sodium chloride solution to wash out CB[8] in the MS apparatus after several experiments.

SI-6 Thermodynamic investigations by ITC

Table S1. Overview of thermodynamic data for homoternary complexations of different guest molecules with CB[8] determined by ITC in pure H_2O at 298 K.

	K_1 (10^4 M^{-1})	ΔH_1 (kJ mol^{-1})	$-T\Delta S_1$ (kJ mol^{-1})	K_2 (10^4 M^{-1})	ΔH_2 (kJ mol^{-1})	$-T\Delta S_2$ (kJ mol^{-1})	α
5FBVI	683 ± 187	-43.2 ± 0.6	4.2 ± 1.1	0.07 ± 0.01	-44.1 ± 2.0	27.9 ± 2.2	0.0004 ± 0.0001
4FBVI	230 ± 36	-37.3 ± 0.2	1.0 ± 0.5	33 ± 6	-31.5 ± 0.5	0.1 ± 0.9	0.57 ± 0.14
3FBVI	95 ± 28	-31.8 ± 0.6	-2.2 ± 0.4	102 ± 54	-41.0 ± 1.3	6.9 ± 2.5	4.27 ± 2.61
2FBVI	61 ± 25	-27.6 ± 0.7	-5.3 ± 0.4	69 ± 43	-48.1 ± 1.7	15.1 ± 2.9	4.52 ± 3.35
BVI	44 ± 5	-27.5 ± 0.9	-4.7 ± 1.0	14 ± 1	-50.8 ± 3.3	21.4 ± 3.2	1.29 ± 0.16
5FBMI	700 ± 212	-40.0 ± 0.5	1.0 ± 0.3	0.58 ± 0.11	-18.4 ± 0.5	-3.0 ± 0.7	0.0033 ± 0.0012
5FBPy	472 ± 130	-36.2 ± 0.3	-1.8 ± 0.9	0.32 ± 0.03	-18.0 ± 0.4	-1.9 ± 0.2	0.0027 ± 0.0008
5FBTMA	556 ± 72	-25.0 ± 0.7	-13.5 ± 0.4	0.40 ± 0.09	-32.4 ± 0.1	11.2 ± 0.5	0.0029 ± 0.0007

Table S1 summarizes all the thermodynamic parameters for homoternary complexations of all guest molecules with CB[8] in H_2O. It should be pointed out that as the second associations of 5FBVI, 5FBBMI, 5FBPy and 5FTMA with CB[8] are very weak as shown in Figure S7, their enthalpy changes and entropy changes obtained from model fitting may not be precise for in-depth analysis. As the macroscopic binding constants (K_1, K_2) were obtained, the interaction parameter (α) is therefore calculated by $\alpha = 4K_2 / K_1$ based on consideration of statistical factors.[2,3]

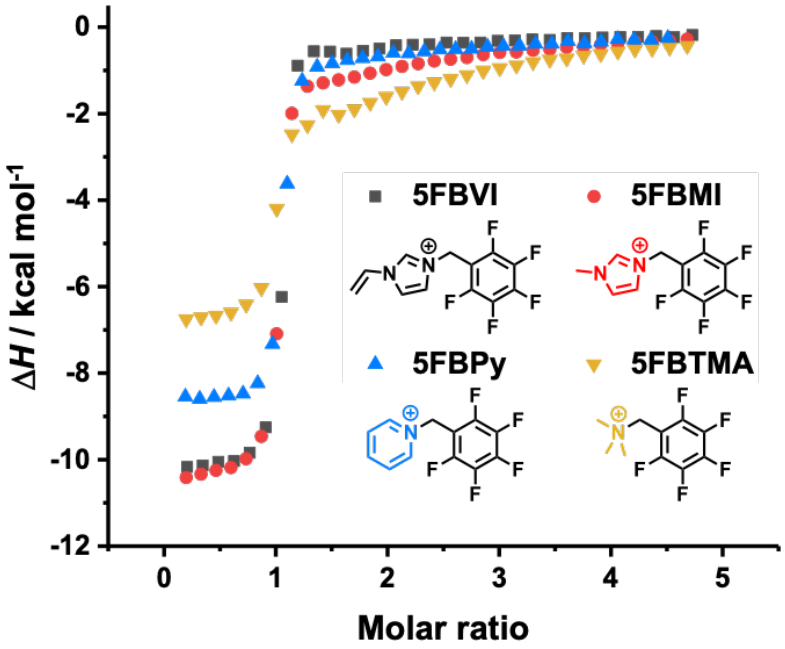

Figure S7 ITC titration plots of CB[8] homoternary complexations with 5FBVI (black), 5FBMI (red), 5FBPy (blue), and 5FBTMA (yellow).

As shown in Figure S7, CB[8]-mediated homoternary complexations with 5FBVI, 5FBMI, 5FBPy, and 5FBTMA all exhibit very strong negative cooperativity with $\alpha < 0.001$ (Table S1). This data indicates that the perfluorophenyl group of the guest molecule plays the key role in its negatively cooperative binding with CB[8]. As for 5FBMTA (yellow data set), its second binding with CB[8] slightly increases. Compared with an imidazolium or pyridium group, the trimethyl group is more hydrophobic which could partially enter into the cavity and interfere with the inner electrostatic repulsion.[3]

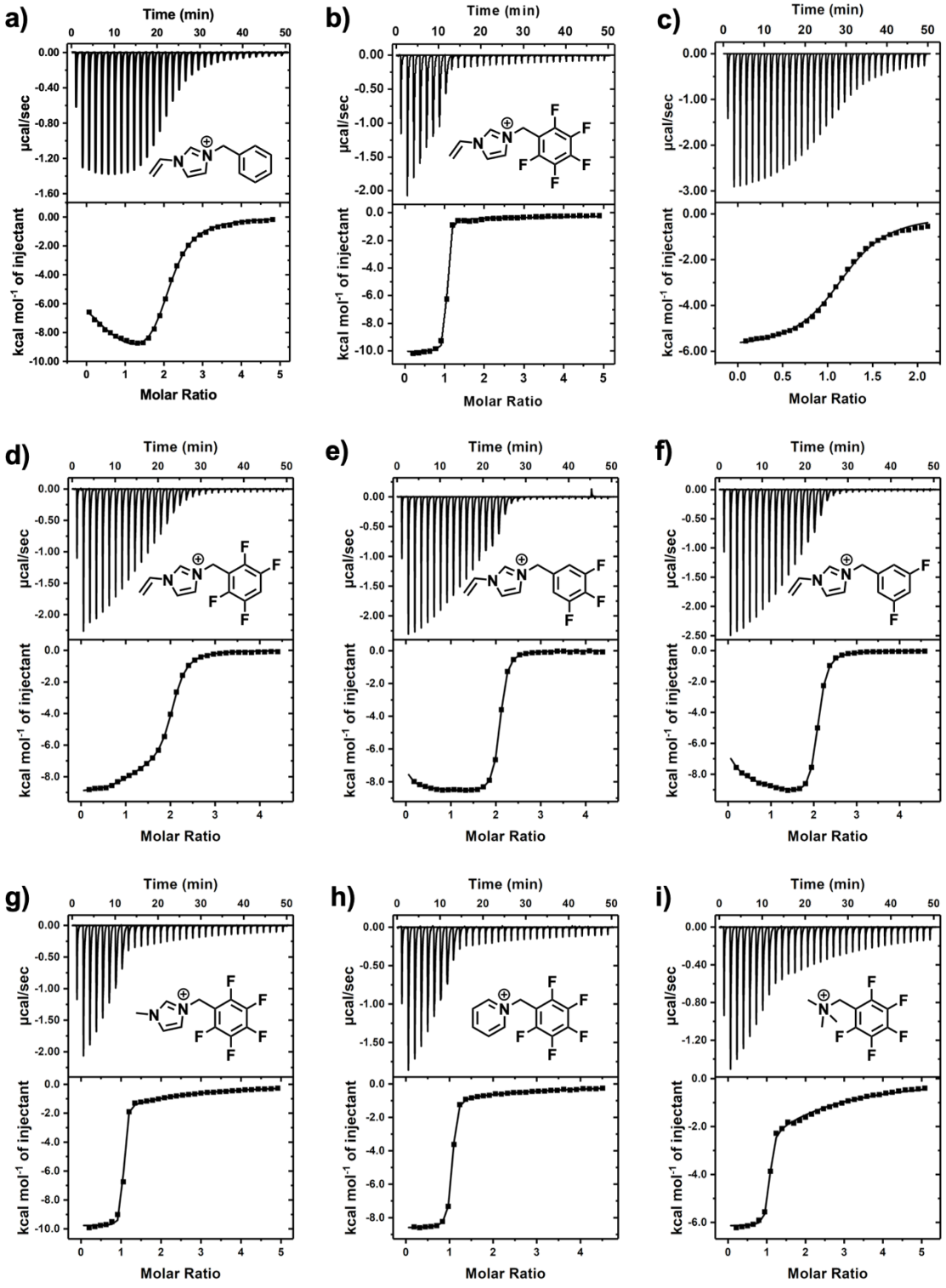

Figure S8 Representative ITC titration curves obtained by titrating a) BVI; b) 5FBVI; d) 4FBVI; e) 3FBVI; f) 2FBVI; g) 5FBMI; h) 5FBPy; and i) 5FBTMA into CB[8], respectively; and that by titrating of BVI into 5FBVI-CB[8] as a second guest. (All ITC experiments were repeated 3 times and the average value plotted)

SI-7 Rheological characterization of supramolecular polyacrylamide networks

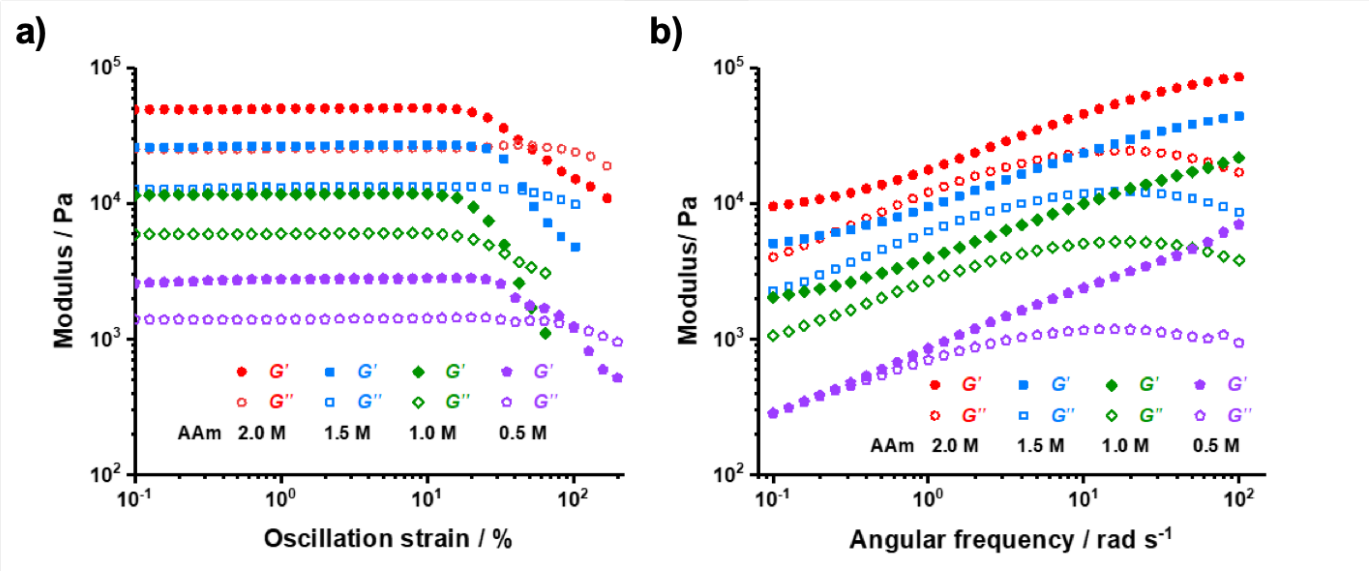

Figure S9 a) Strain-sweep and b) frequency-sweep measurements of supramolecular polyacrylamide networks containing increasing concentrations of AAm and the same amount of 2.5 mol% supramolecular cross-linker (5FBVI-BVI-CB[8]).

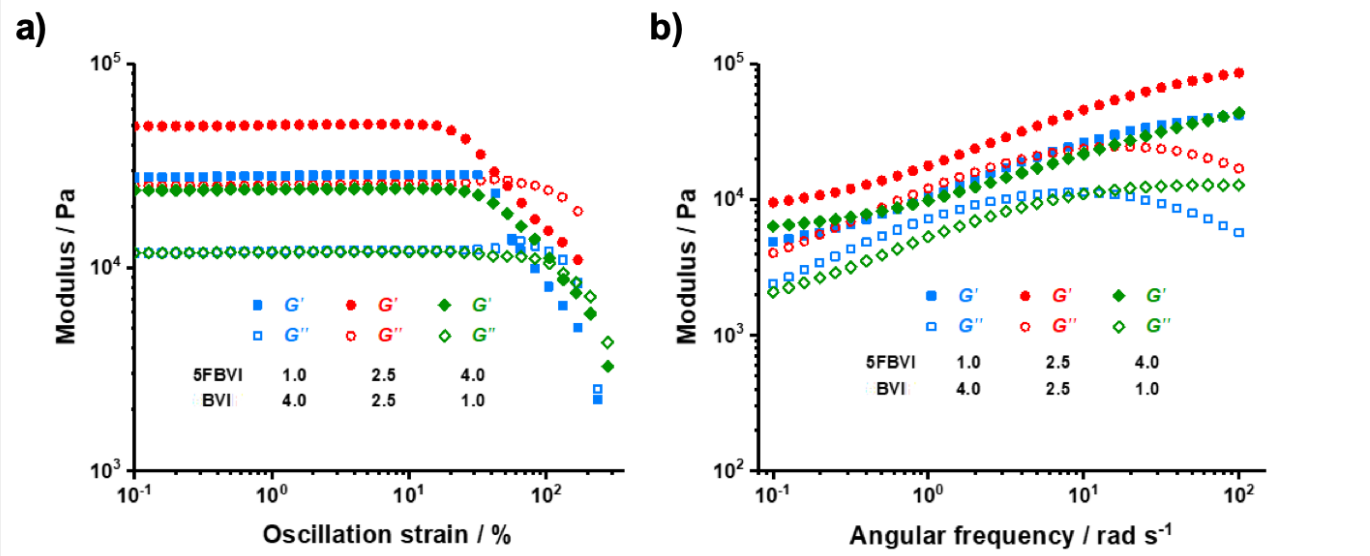

Figure S10 a) Strain-sweep and b) frequency-sweep measurements of supramolecular polyacrylamide networks containing same amounts of AAm and CB[8] (2.5 mol%) and different amounts of 5FBVI and BVI at total monomer concentration of 2.0 M.

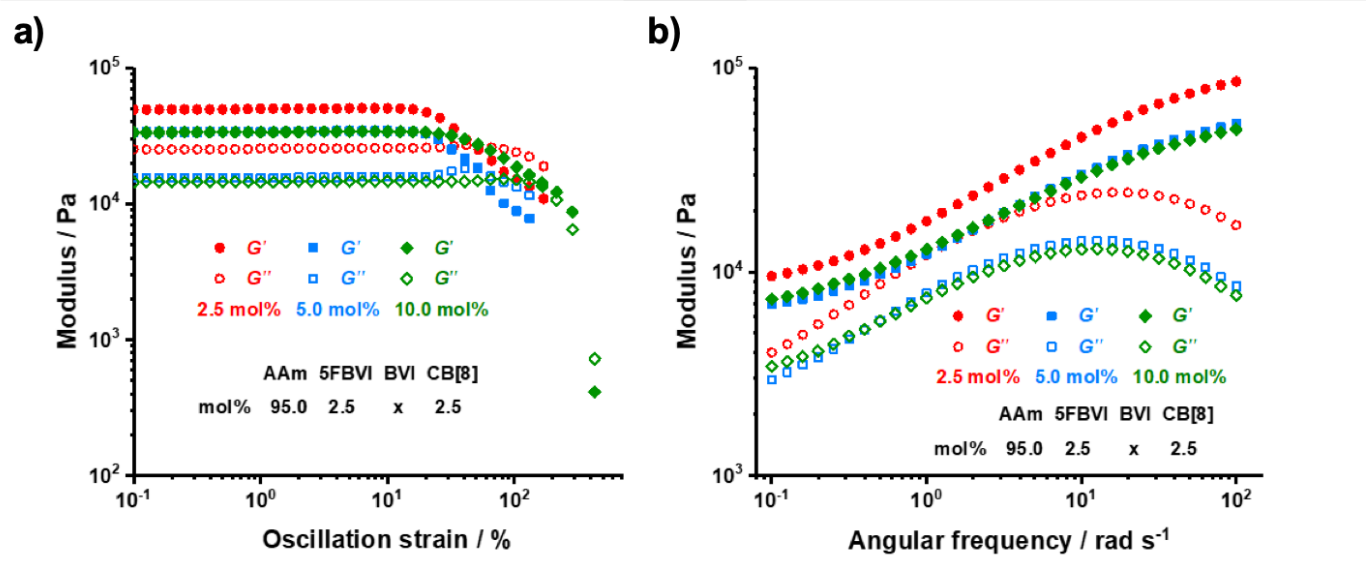

Figure S11 a) Strain-sweep and b) frequency-sweep measurements of supramolecular polyacrylamide networks containing same amounts of AAm, 5FBVI and CB[8] and increasing amount of BVI at total monomer concentration of 2.0 M.

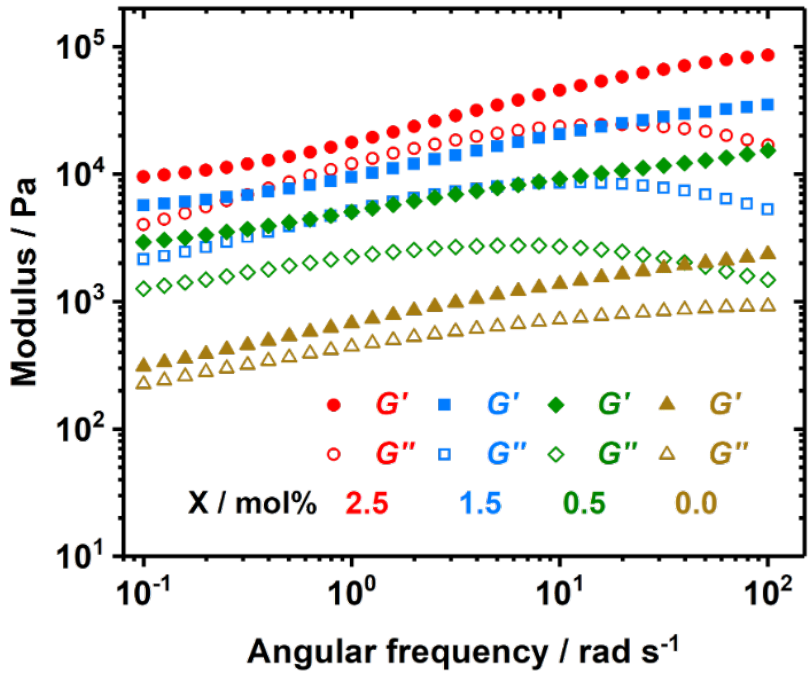

Figure S12 Frequency-sweep measurements of supramolecular polyacrylamide networks containing different ratio of 5FBVI-BVI-CB[8] cross-linker (X / mol%) at total monomer concentration of 2.0 M.

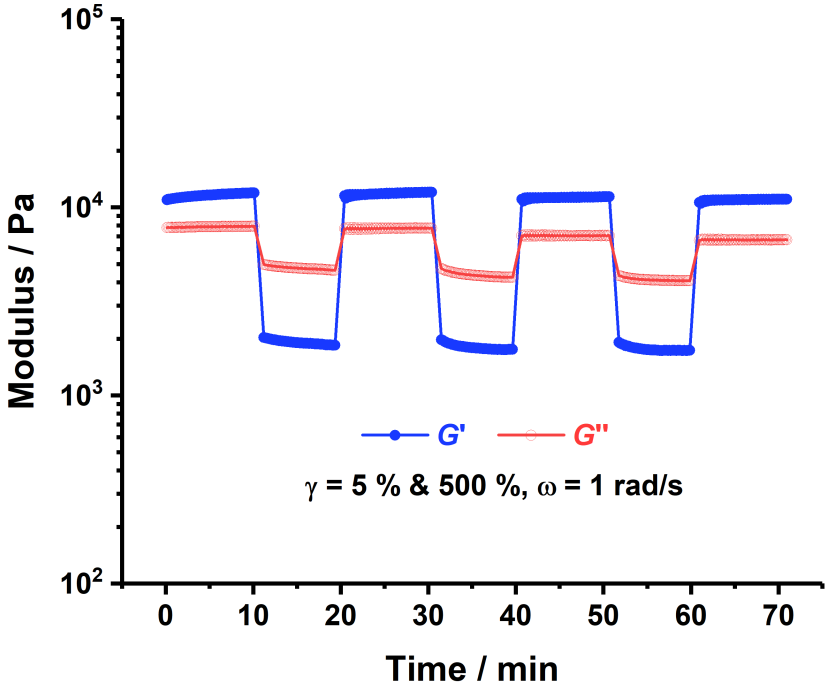

Figure S13 Continuous step-strain measurements of supramolecular polyacrylamide network with 2.5 mol% supramolecular cross-linker of 5FBVI-BVI-CB[8] and total monomer concentration of 2.0 M over a 70 min period of time.

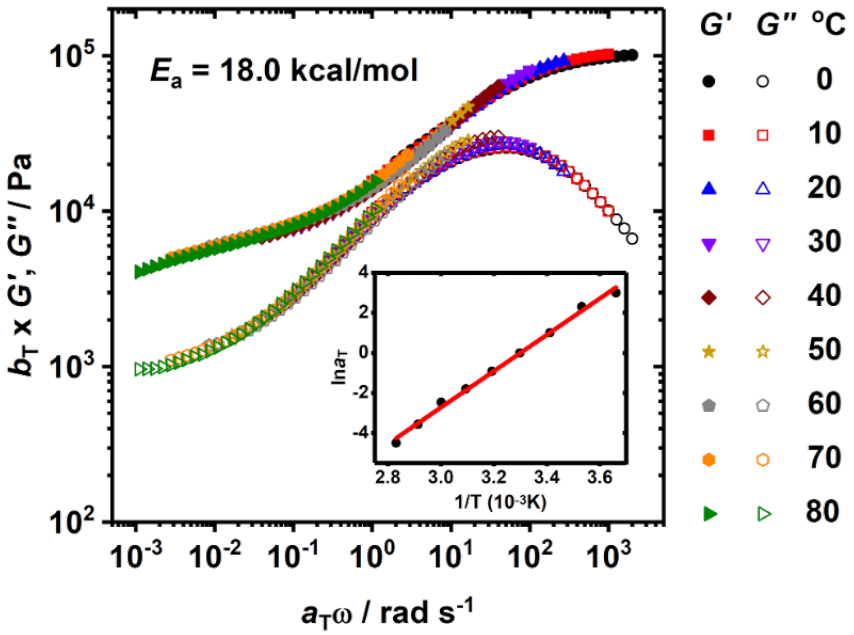

Figure S14 Master curve of the supramolecular polyacrylamide network with 2.5 mol% 5FBVI-BVI-CB[8] cross-linker at 1 % strain and its fitting curve to obtain the activation energy of local chain motion (E_a).

SI-8 Photographs showing ionic conductivity of the 5FBVI-BVI-CB[8] gel

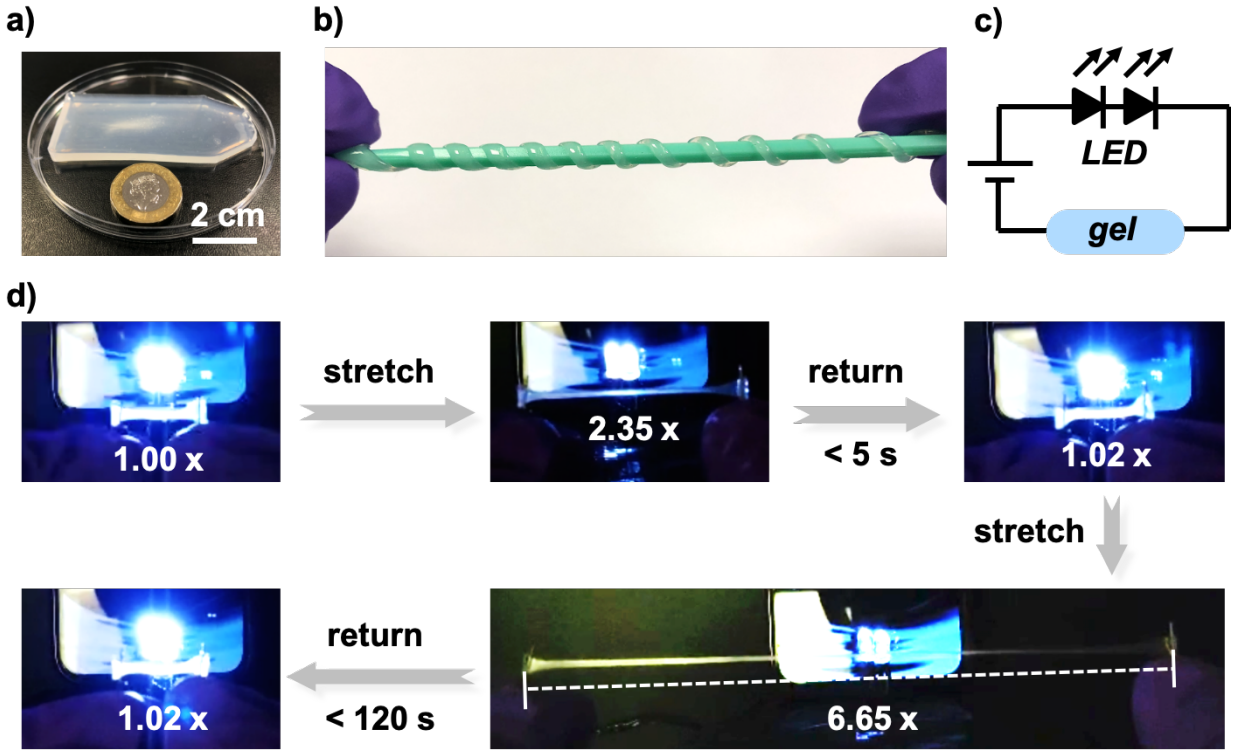

Figure S15 Photographs of a) an example of the obtained gel and b) a piece of gel twined around a plastic rod; c) the circuit diagram and d) photographs for demonstrating the ionic conductivity of the resultant gel in a series circuit with two LED lamps and 9 V battery.

References

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