

Supporting Information:

Supramolecular Polymer Networks Based on Cucurbit[8]uril Host-Guest Interactions as Aqueous Photo-Rheological Fluids

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S.I. Instrumentation

Instrumentation

¹H NMR (500 MHz) spectra was recorded using a Bruker Avance BB 500. Chemical shifts were recorded in ppm (δ) in D₂O with the internal reference set to δ 4.79 ppm. ATR FT-IR

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spectroscopy was conducted using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory.

Rheological characterisation was performed using a Discovery Hybrid Rheometer (DHR)-2 from TA Instruments fitted with a Peltier Plate as the temperature control system. All measurements were performed using a 20- and 40-mm parallel plate geometry with a gap of 500 nm and results were analysed using TA Instruments' TRIOS software. Dynamic oscillatory strain amplitude sweep measurements were conducted at a frequency of 10 rad/s. Dynamic oscillatory frequency sweep measurements were conducted at a 1% strain amplitude, between 0.01 to 100 rad/s, while flow sweep tests were done between 0.01 and 100 s⁻¹. Real-time photorheological measurements were done on DHR-2 Rheometer with a UV accessory that uses a light guide and reflecting mirror assembly to transfer UV radiation from a high-pressure mercury light source. The UV Light Guide accessory is configured using a lower Smart Swap assembly with light source mount, collimator, and 5 mm light guide. A UV light source (Exfo Omnicure S2000), with wavelengths in the range of 320 to 500 nm, and triggering cable are attached.

ITC titration experiments were carried out on a VP-ITC from Microcal Inc. at 25 °C in 10 mM sodium phosphate buffer (pH 7). In a typical experiment, the host was in the sample cell at a concentration of 0.05 - 0.1 mM, and the guest was in the syringe at a 10 - 20 fold higher concentration. In the case of functional polymers, the concentration used is determined from the concentration of functional monomer units in solution and not the concentration of polymer. A titration consisted of 20 consecutive injections of 2-10 μ L with at least 60 s intervals between injections. The first data point was removed from the data set prior to curve fitting. Heats of dilution were checked by titration well beyond saturation or by titration of the guest into a buffer solution and subtracted from the normalised enthalpies, but relatively small in all cases. The data were analysed with Origin 7.0 software, using the one set of sites model.

Gel permeation chromatography (GPC) was carried out in water (H₂O) on a Shodex

glucose column with a Shimadzu SPD-M20A prominence diode array detector, Optilab refractive index detector and dynamic light scattering detector (both Wyatt). Before injection, samples were filtered through 0.2 μm PVDF filters before injection using a 0.5 mL/min flow rate.

UV-Vis spectra were recorded on a Varian Cary 4000 UV-Vis spectrophotometer in aqueous solutions with 1 nm resolution at 25 °C. Photoirradiation was carried out using a LZC-ORG photoreactor from Luzchem Research Inc. equipped with both UV and white T5 type lamps centered at ~ 360 nm and ~ 420 nm, respectively. Visible light was obtained with white T5 type lamps combined with a sharp-cut filter (< 420 nm).

Diffraction data for CB[8]·**Z-3** was collected using a standard method¹ on beamline I19. Beamline I19 is situated on an undulator insertion device with a combination of double crystal monochromator, vertical and horizontal focussing mirrors and a series of beam slits (primary white beam and either side of the focussing mirrors). The experimental hutch (EH1) was equipped with a Crystal Logic 4-circle kappa geometry goniometer with a Rigaku Saturn 724 CCD detector and an Oxford Cryosystems Cryostream plus cryostat (80 - 500 K). For conventional service crystallography, the beamline was operated at a typical energy of 18 keV (Zr K absorption edge) and a Rigaku ACTOR robotic sample changing system was available. Software package CrystalClear-SM Expert 2.0 r5 (Rigaku, 2010) was used for the initial cell determination and data collection, with CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) used for the integration, scaling and absorption correction. The structure was solved using SUPERFLIP² and was refined against F^2 using full matrix least squares refinement in SHELXL-2014.³ ORTEP3 for Windows was used for the production of the crystal graphics in Figure S16.

S.II. Experimental

Synthesis of Cucurbit[8]uril, CB[8].

Cucurbit[8]uril, CB[8] was prepared according to previously reported procedures.⁴

Synthesis of PSTMV, P4.

PSTMV was prepared according to previously reported procedures.⁵

Synthesis of HEC-Np, P5.

HEC 1.3MDa (1.00 g) was dissolved in *N*-methylpyrrolidone (NMP, 120 mL) at 110 °C overnight. The solution was cooled to room temperature and Np-NCO (29.7 mg, 0.18 mmol) and dibutyltin dilaurate (TDL, 3 drops) were added and the mixture stirred at room temperature overnight. The crude product was then purified by precipitation from acetone, filtered, and dried overnight under vacuum at 60 °C (1.01 g, 98%). ¹H NMR Spectroscopy (D₂O, 500 MHz) δ (ppm) = 7.99 - 7.29 (7H, br, Np-H), 4.50 - 2.90 (307H, br, cellulose backbone). Elemental analysis: Found C, 46.76; H, 6.95; N, 0.21. C₂₁₅H₃₆₇O₁₅₁N₁ required C, 47.98; H, 6.83; N, 0.26. FT-IR (ATR) = 3410 (br), 2950 (br), 2910 (br), 1395, 1075 (s) cm⁻¹. GPC (H₂O): M_n (PDI) = 664 KDa (1.14).

Synthesis of 2-Np-PEG-OMe-Np (PEG-Np, 2).

Poly(ethylene glycol) monomethyl ether (5000 g/mol) was dried by azeotropic distillation in toluene. A solution of poly(ethylene glycol) monomethyl ether (1.0 g, 0.2 mmol) in anhydrous DCM (30mL) was added with 2-naphthol isocyanate (101.5 mg, 0.6 mmol). Dibutyltin dilaurate (TDL, 2 drops) was added and the mixture was stirred for 24 h at room temperature. The mixture was diluted with DCM (100 mL) and the slurry was sonicated for 5 min. The remaining solid was filtered off and the solvent was removed under pressure to yield a yellowish solid. The yellowish solid was redissolved in DCM (20 mL), filtered and precipitated in cold diethyl ether (2x). Suction filtration yielded 2-Np-PEG-OMe (1.00 g, 97 %) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm)= 8.03 (s, 1H), 7.79 - 7.77 (m, 3H), 7.45

- 7.38 (m, 4H), 4.39 (t, 2H), 3.85 - 3.45 (m, PEG backbone), 3.39 (s, 3H). GPC (THF): M_n = 5 KDa (1.1).

Synthesis of *p*-(phenylazo)benzyl alcohol.

p-(phenylazo)benzyl alcohol was prepared according to previously reported procedures.⁶

Synthesis of *p*-(phenylazo)benzyl bromide.

p-(phenylazo)benzyl bromide was synthesised following a published procedure.⁷ To a stirring solution of *p*-(phenylazo)benzyl alcohol (1.50 g, 7.10 mmol) in anhydrous THF (50 mL) kept stirring at 0 °C, triphenylphosphine (2.78 g, 10.6 mmol) and *N*-bromosuccinimide (1.89 g, 10.6 mmol) were added in small portions alternately. The reaction mixture was stirred at room temperature overnight. Insoluble material was filtered through a pad of silica and washed with copious amount of THF. The filtrate was evaporated under vacuum and the residue was purified by column chromatography (eluent: hexane/ethyl acetate 8/2 vol.) to afford a pure orange solid (1.31 g, 67 %). ¹H NMR (CDCl₃, 400 MHz) δ (ppm) = 4.56 (s, 2H); 7.48 - 7.56 (m, 5H); 7.88 - 7.94 (m, 4H).

Synthesis of 1-[*p*-(phenylazo)benzyl]imidazolium bromide, **E-3**.

p-(phenylazo)benzyl imidazolium bromide was synthesised following a published procedure.⁷ A mixture of *p*-(phenylazo)benzyl bromide (0.50 g, 1.82 mmol) and 1-methylimidazole (0.18 g, 2.18 mmol) in toluene (3 mL) was stirred at room temperature for 10 h. The reaction mixture was centrifuged, washed with toluene (2 x 20 mL) and dried in vacuo to yield a pure orange solid (0.47 g, 72 %). ¹H NMR (CDCl₃, 400 MHz) δ (ppm) = 10.94 (s, 1H); 7.95 (m, 4H, 7.65 (d, 2H); 7.52 (m, 3H); 7.20 (s, 2H), 5.72 (s, 2H); 4.10 (s, 3H).

S.III. General preparation of supramolecular polymer networks.

Naphthyl-functionalised hydroxyethyl cellulose (**P5**, 5 mg) was dissolved in water (0.5 mL) with mild heating and vortexing. A solution of PSTMV (**P4**) (1.5 mg) and CB[8] (1 mg) was heated gently to dissolve in water (0.5 mL) separately. Both solutions were then mixed, heated and shaken to obtain pinkish, transparent hydrogels. The hydrogels resulted from the formation of ternary complex CB[8]·**P4**·**P5** with molar ratio of 1:1:1 and they were pinkish in color due to the charge transfer between the electron-deficient and electron-rich guests in the CB[8].

S.IV. Supporting Results.

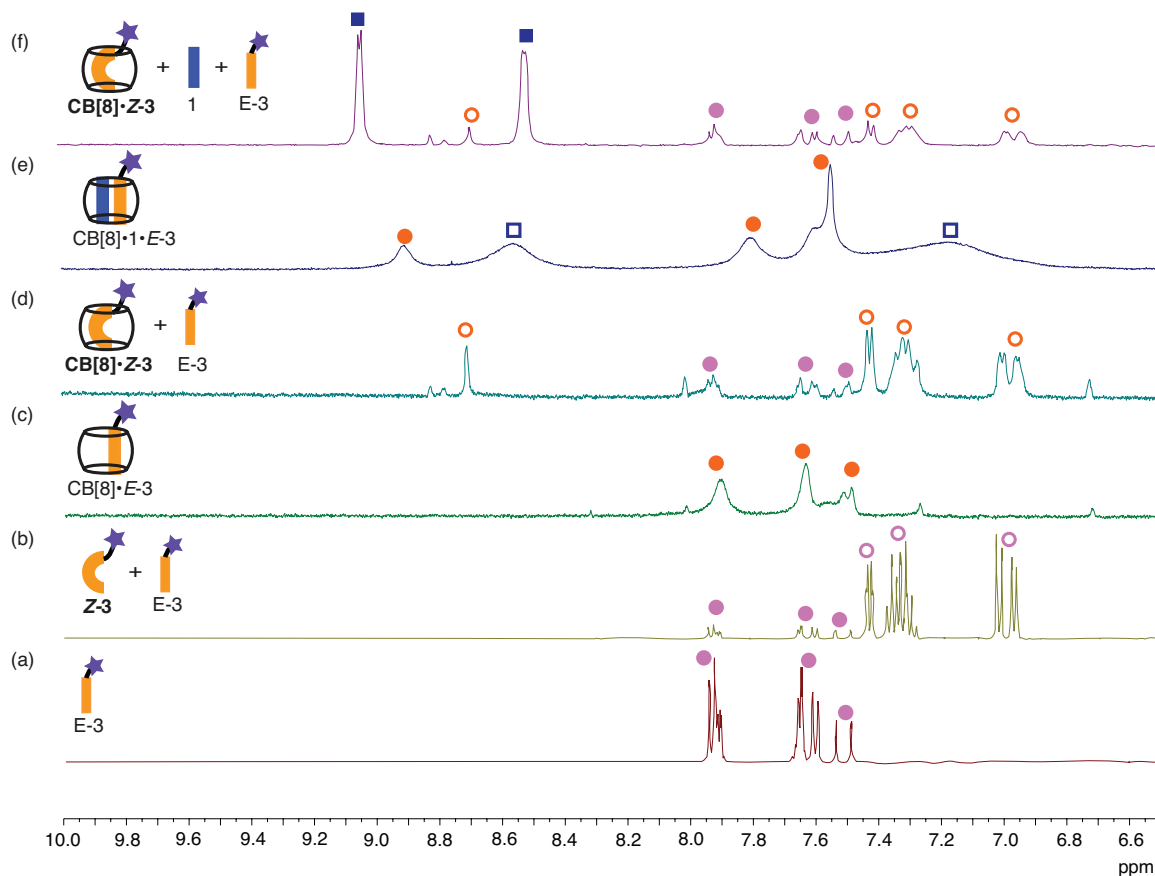


Figure S1: Partial ¹H NMR spectra (500 MHz, D₂O, 298 K) of **E-3** alone before (a); after UV irradiation (b); **CB[8]·E-3** before (c); after UV irradiation (d); **CB[8]·1·E-3** before (e) and after UV irradiation (f). Labels of small molecules used in NMR titration: protons of uncomplexed **1** (filled blue square), complexed **1** (open blue square), uncomplexed **E-3** (filled pink circle), uncomplexed **Z-3** (open pink circle), complexed **E-3** (filled orange circle) and complexed **Z-3** (open orange circle) are highlighted. Predominant species are highlighted in bold.

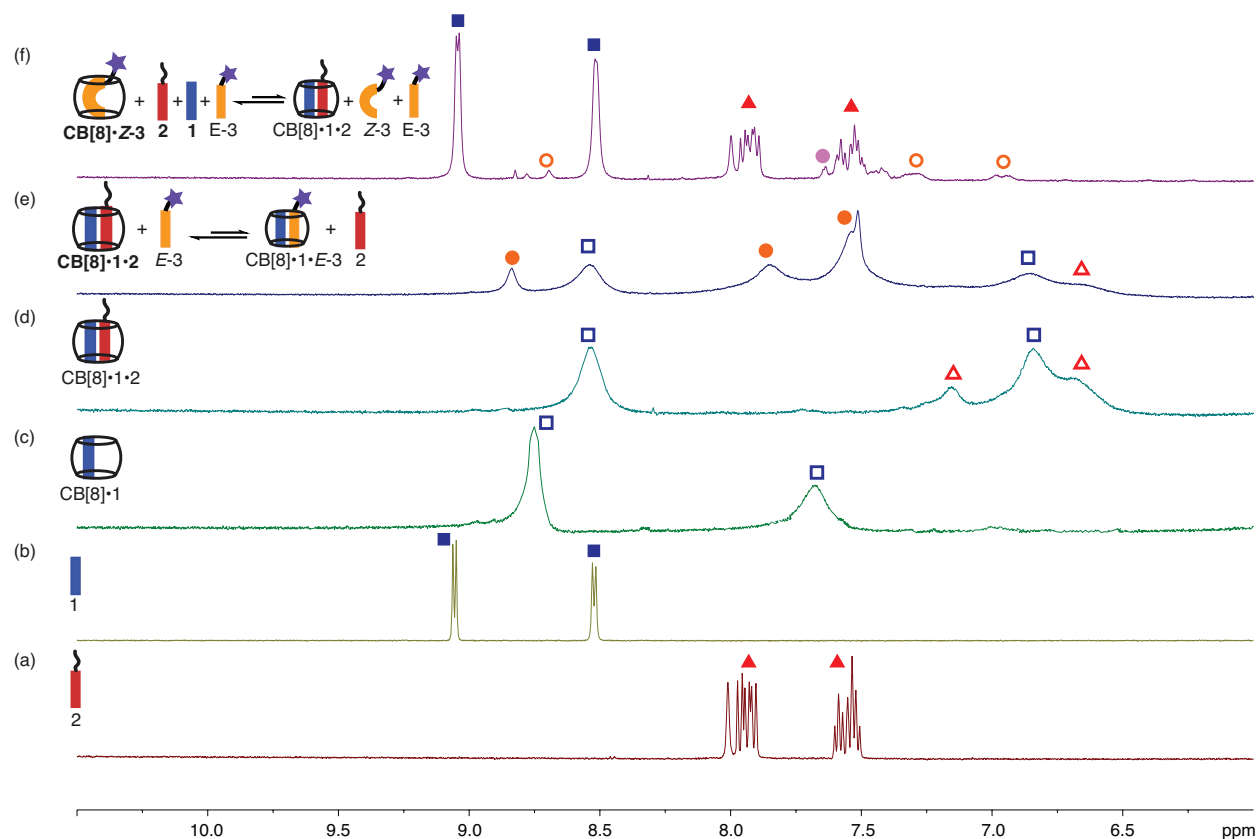


Figure S2: Partial ^1H NMR spectra (500 MHz, D_2O , 298 K) of **2** only (a); **1** only (b); $\text{CB}[\text{8}]\cdot\text{1}$ (c); $\text{CB}[\text{8}]\cdot\text{1}\cdot\text{2}$ (d); mixture of $\text{CB}[\text{8}]\cdot\text{1}\cdot\text{2}$ and $\text{CB}[\text{8}]\cdot\text{1}\cdot E\text{-3}$ complexes at equilibrium before (e) and after UV irradiation (f). Labels of small molecules used in NMR titration: protons of uncomplexed **1** (filled blue square), complexed **1** (open blue square), uncomplexed **2** (filled red triangle), complexed **2** (open red triangle), uncomplexed $E\text{-3}$ (filled pink circle), uncomplexed $Z\text{-3}$ (open pink circle), complexed $E\text{-3}$ (filled orange circle) and complexed $Z\text{-3}$ (open orange circle) are highlighted. Predominant species are highlighted in bold.

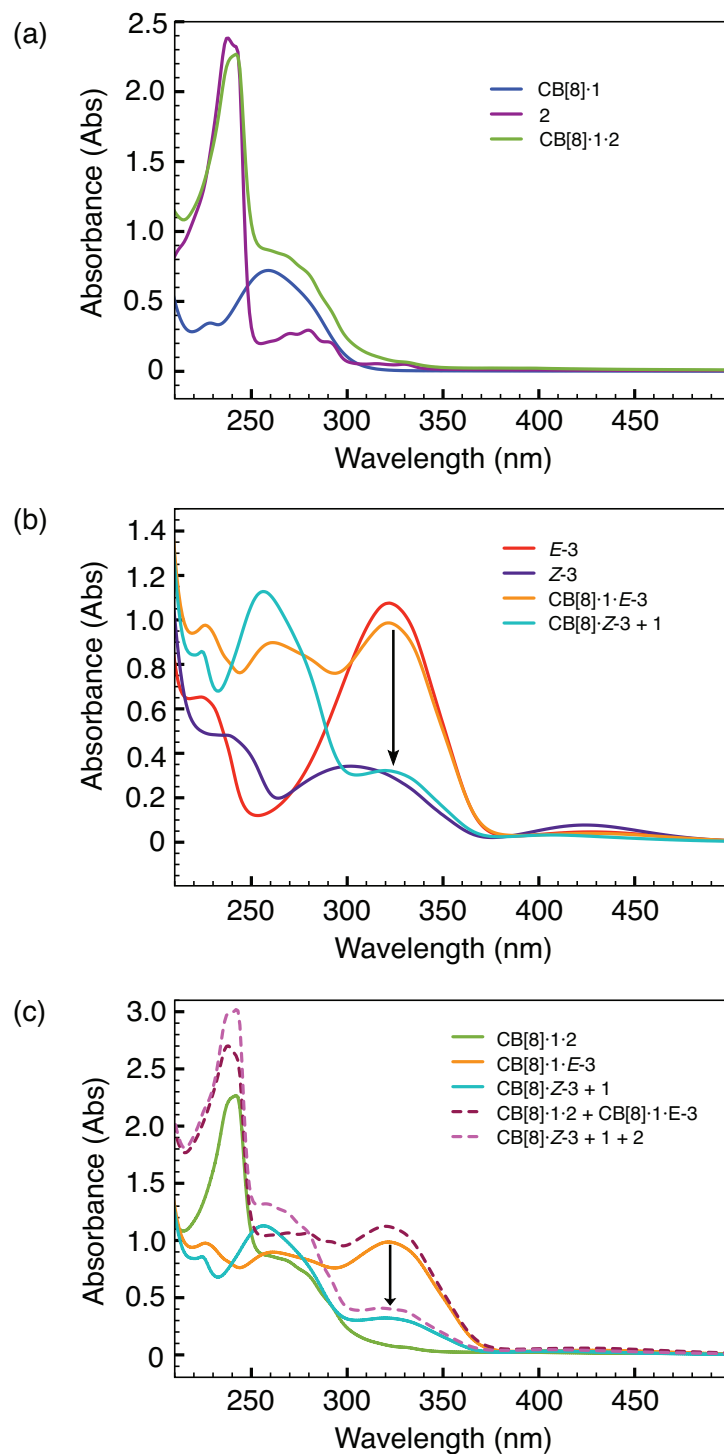


Figure S3: UV-Vis absorption spectra of CB[8]·1 binary complex, **2** and CB[8]·1·**2** (a); *E*-3 and CB[8]·1·*E*-3 ternary complex before and after UV irradiation (b) and CB[8]·1·**2** ternary complex in the presence of *E*-3 before and after UV irradiation (c) in solution (0.05 mM, H₂O, 298 K).

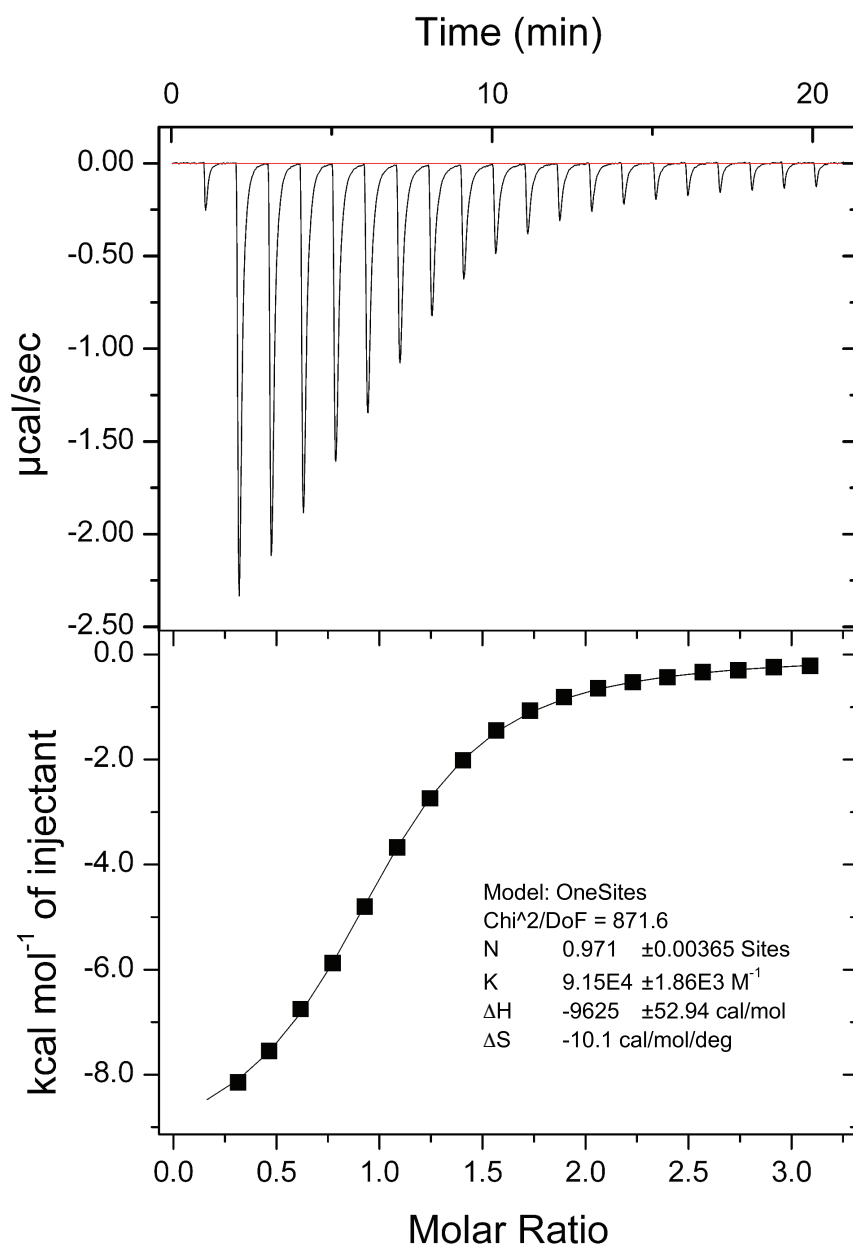


Figure S4: 1 mM PEG-Np was titrated into 0.1 mM CB[8]·1 solution in PBS buffer, pH 7, 298K.

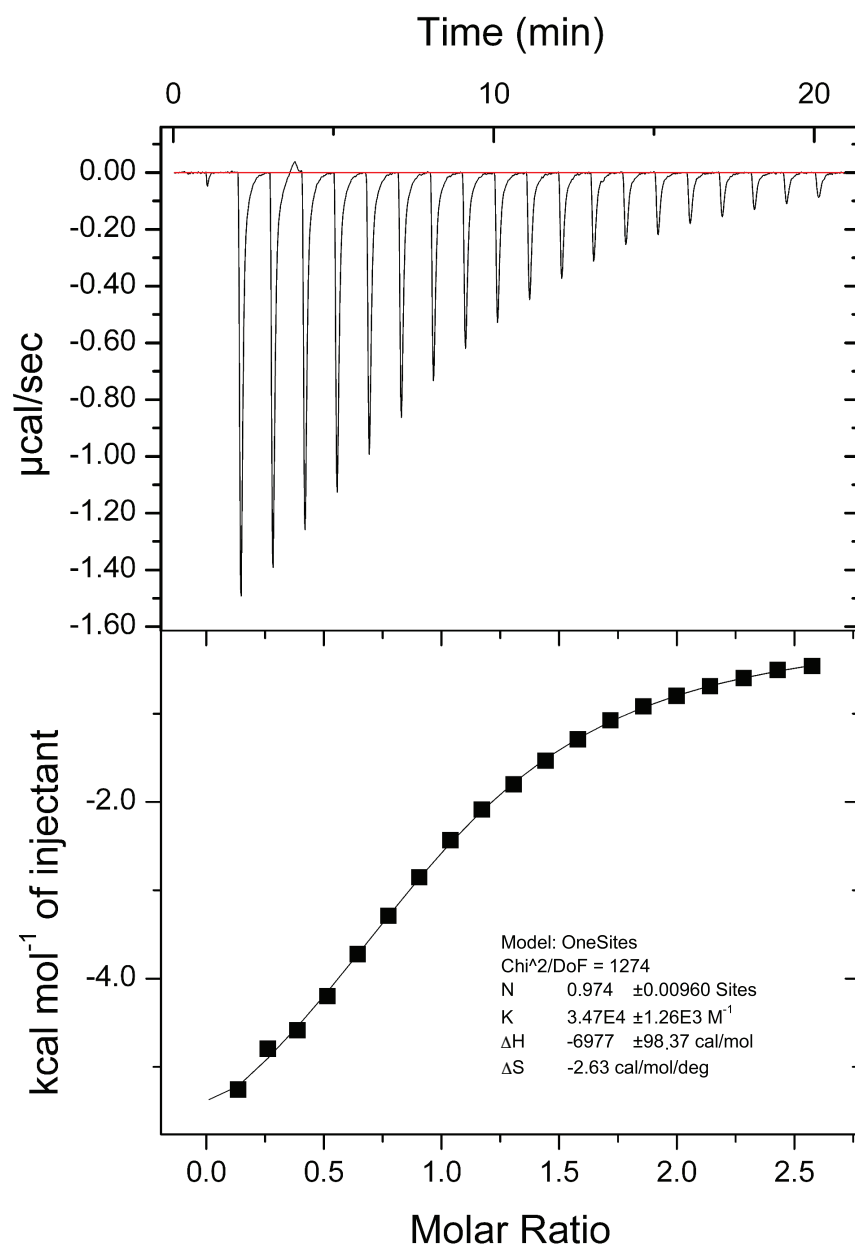


Figure S5: 1 mM *E-3* was titrated into 0.1 mM CB[8]·1 solution in PBS buffer, pH 7, 298K.

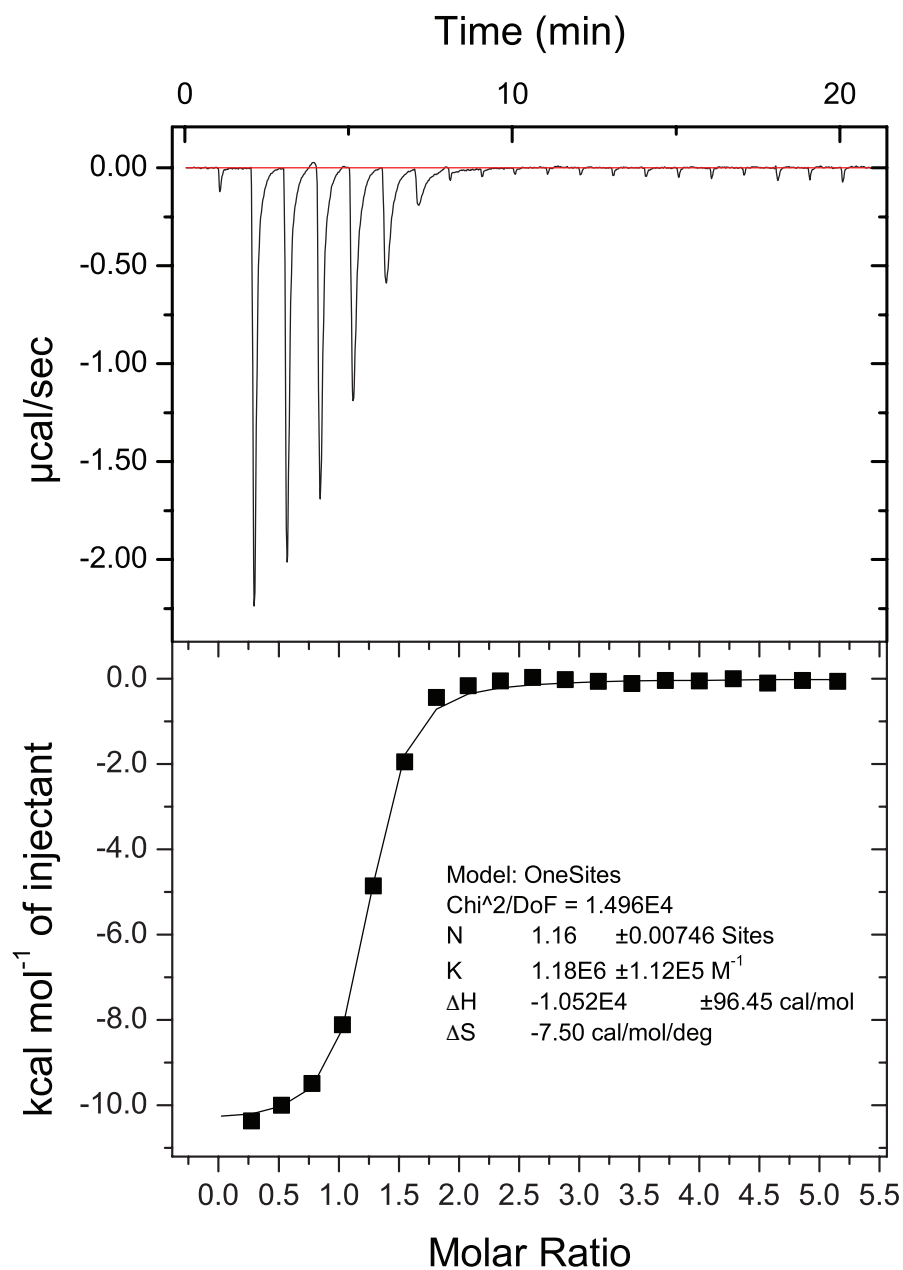


Figure S6: 1 mM **Z-3** was titrated into 0.05 mM CB[8] solution in PBS buffer, pH 7, 298K.

Since photoisomerisation of *trans*-azobenzene to its *cis* conformation is known to be incomplete, this binding constant of **Z-3** into CB[8] was reported for **Z-3** solution at an *E:Z* ratio of 20:80.

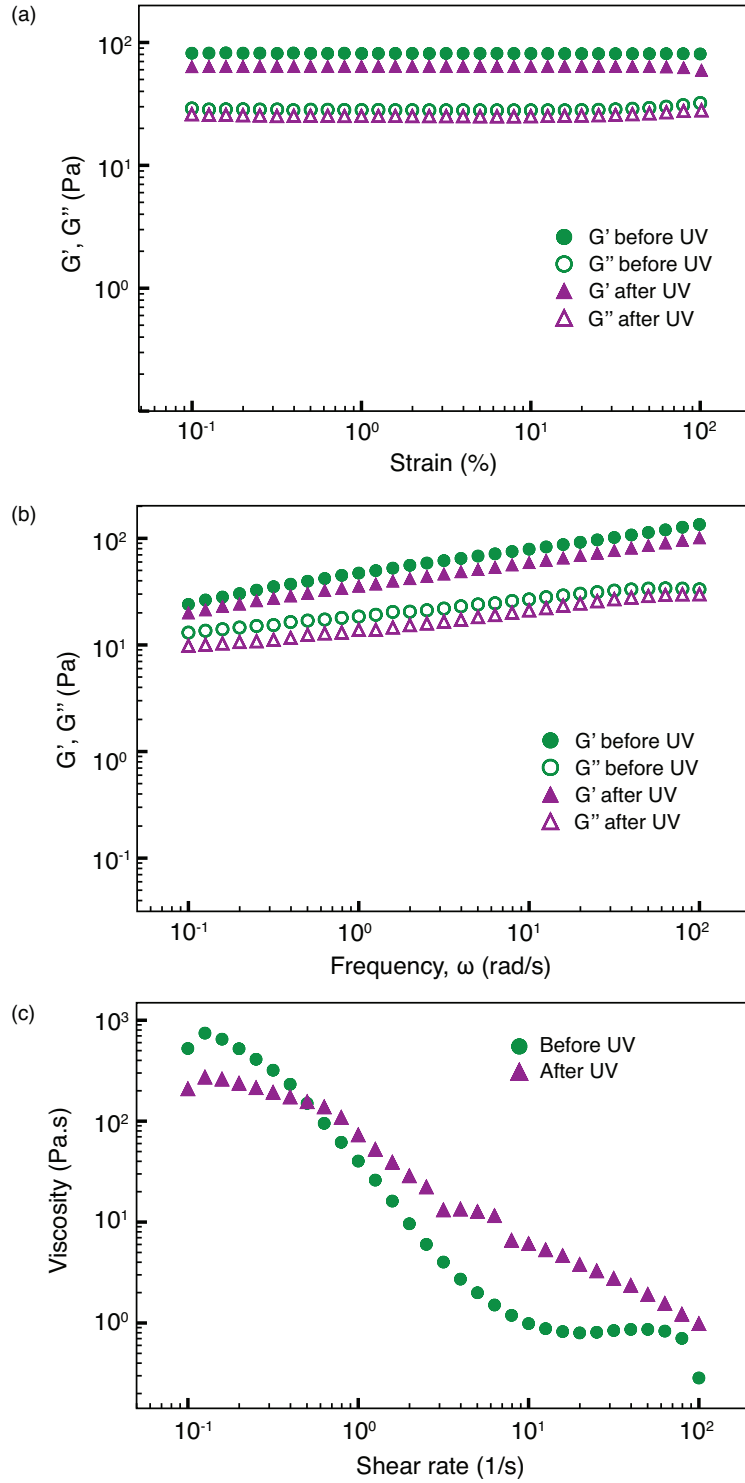


Figure S7: Storage (G') and loss (G'') moduli from strain-amplitude sweep at 10 rad/s (a), frequency sweep at 1% strain (b) and steady-shear rheology (c) of 0.75 *wt.*% HEC control samples before and after UV irradiation (360 nm, 4.8 mW/cm², 5 min, 20 °C). Note: Small changes in the zero-shear viscosity in the fluids after the UV irradiation might be attributed to the rearrangement of polymer chain in the mixture.

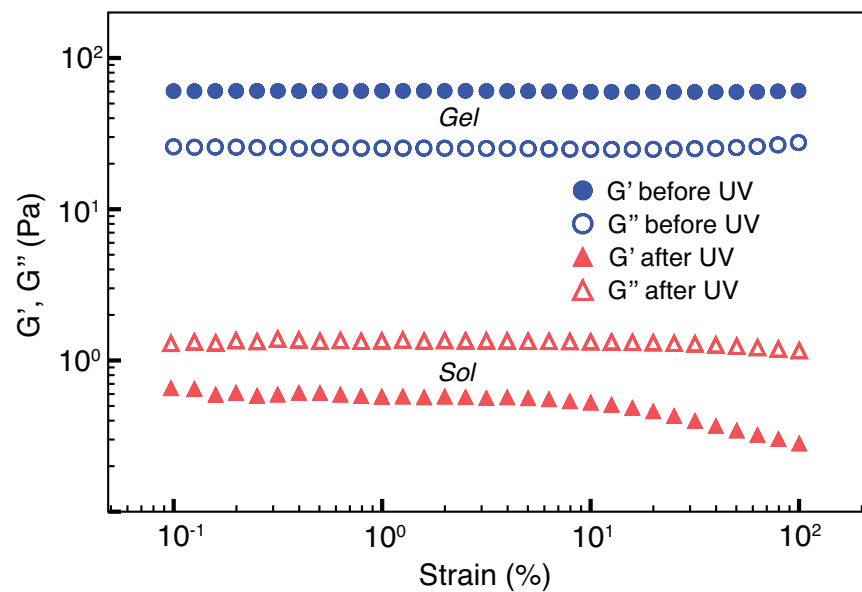


Figure S8: Strain-amplitude sweep performed at 10 rad/s for 0.75 *wt.*% HEC samples containing 0.5 mol eq *E-3* before and after UV irradiation (360 nm, 4.8 mW/cm², 5 min, 20 °C).

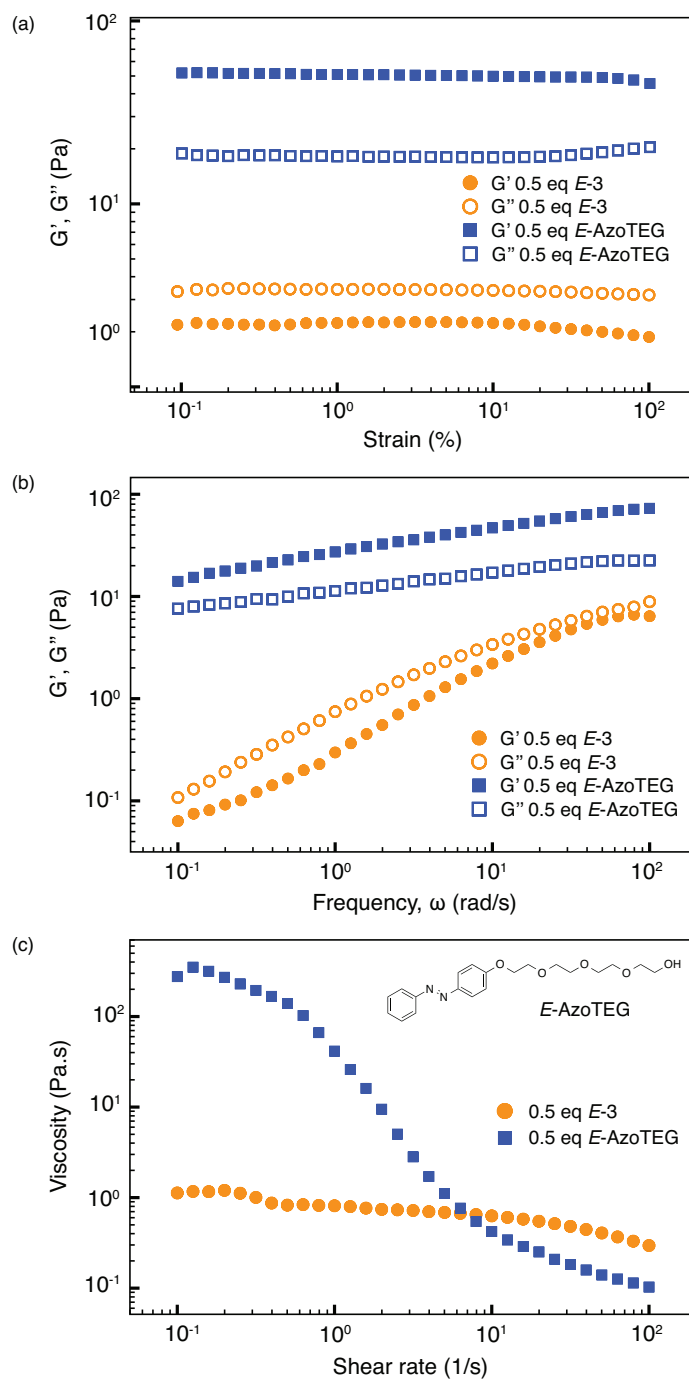


Figure S9: Storage (G') and loss (G'') moduli from strain-amplitude sweep at 10 rad/s (a), frequency sweep at 1% strain (b) and steady-shear rheology (c) of 0.75 wt.% HEC containing 0.5 mol eq *E-AzoTEG* and *E-3* after UV irradiation (360 nm, 4.8 mW/cm², 5 min, 20 °C). Inset (c): Chemical structure of neutral AzoTEG molecule.

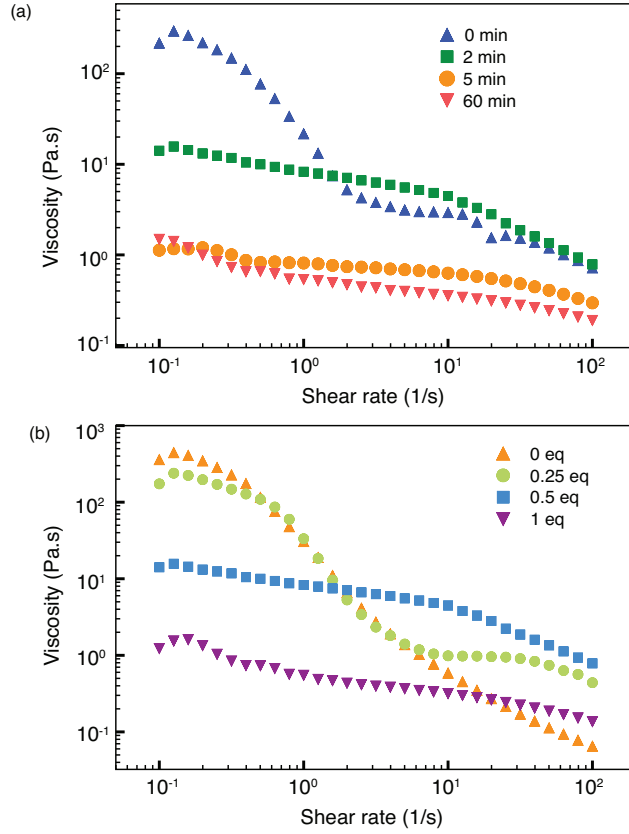


Figure S10: Viscosity vs shear rate plots for 0.75 *wt.*% HEC mixture containing 0.5 mol eq *E-3* at different UV irradiation times (a) and for 0.75 *wt.*% HEC samples with different concentration of *E-3* after UV irradiation for 5 min (b).

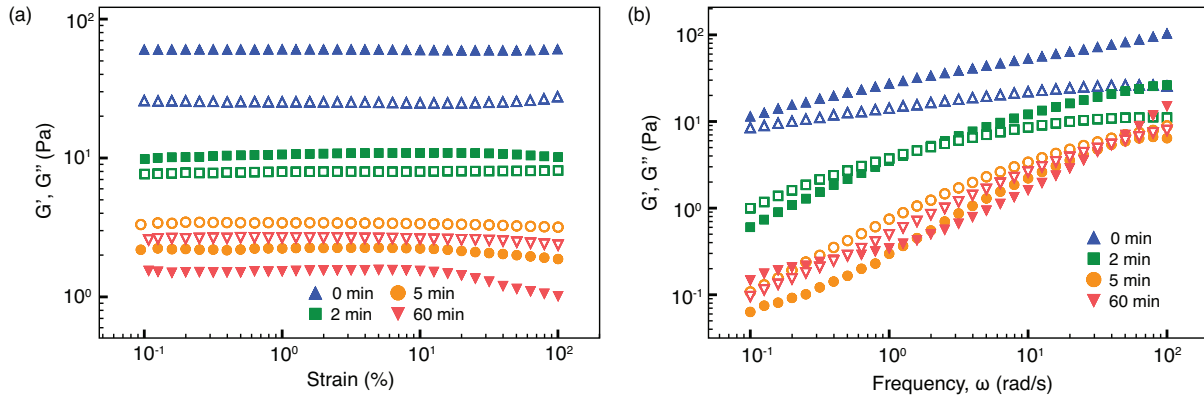


Figure S11: Dynamic rheology of 0.75 *wt.*% HEC samples containing 0.5 mol eq *E-3* at different UV irradiation times: storage and loss moduli obtained from a strain-amplitude sweep performed at 10 rad/s (a) and storage and loss moduli obtained from a frequency sweep performed at 1% strain (b). Notes: filled symbols represent G' and open symbols represent G'' .

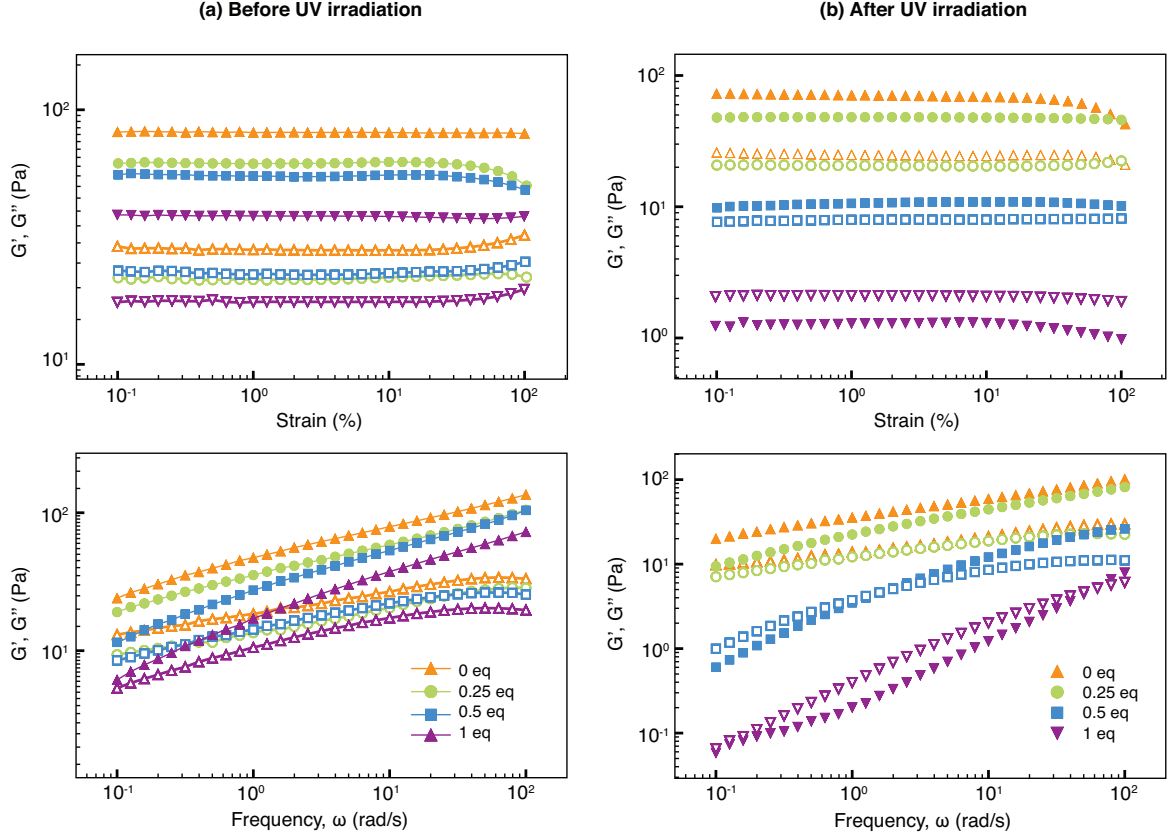


Figure S12: Storage and loss moduli from strain-amplitude sweep at 10 rad/s and frequency sweep at 1% strain of 0.75 *wt.*% HEC samples with different concentration of *E-3* before (a) and after (b) UV irradiation for 5 min. Notes: filled symbols represent G' and open symbols represent G'' .

Their flow properties were altered as a function of concentration and photoirradiation. Figure S8a shows that the sample was very viscous and strongly thixotropic before UV irradiation. After 5 min of irradiation at 360 nm, the zero-shear viscosity decreased one order of magnitude and the degree of shear-thinning also gradually reduced. No further changes in zero-shear viscosity occur with longer irradiation time (> 5 min) because all *E-3* had been converted into *Z-3* within 5 min and complexed with CB[8], by removing other guests.

Steady-shear rheological data for four samples of HEC mixtures, each containing 0, 0.25, 0.5 and 1 mol eq *E-3*, respectively, were compared. All mixtures containing some *E-3* shear-thin under the shear rate tested. Significant reduction in their zero-shear viscosities (Figure

S8b) and G' (Figure S9) was seen after UV irradiation. The viscosity of the sample with 0.25 eq *E-3* was similar to that of the HEC mixture without *E-3*, however at higher shear rate, its viscosity dropped drastically to 1 Pa·s. Further increase in the *E-3* content decrease initial viscosities of the samples by more than one order or magnitude with a slight dependence on the shear rate (Figure S8b).

Increasing duration of photoirradiation also lowered G' as a function of strain and frequency, measured at ambient temperature . The crossover point of G' and G'' of the sample shifted to higher frequencies after 5 min of UV irradiation. Prolonged exposure to UV caused the breakdown of the entire network ($G'' > G'$) throughout the frequency range measured (Figure S9).The length of UV irradiation is also dependent on the concentration of *E-3*. Higher *E-3* concentration added to the gel matrix requires longer irradiation time to isomerise *E-3* completely (Figure S10).

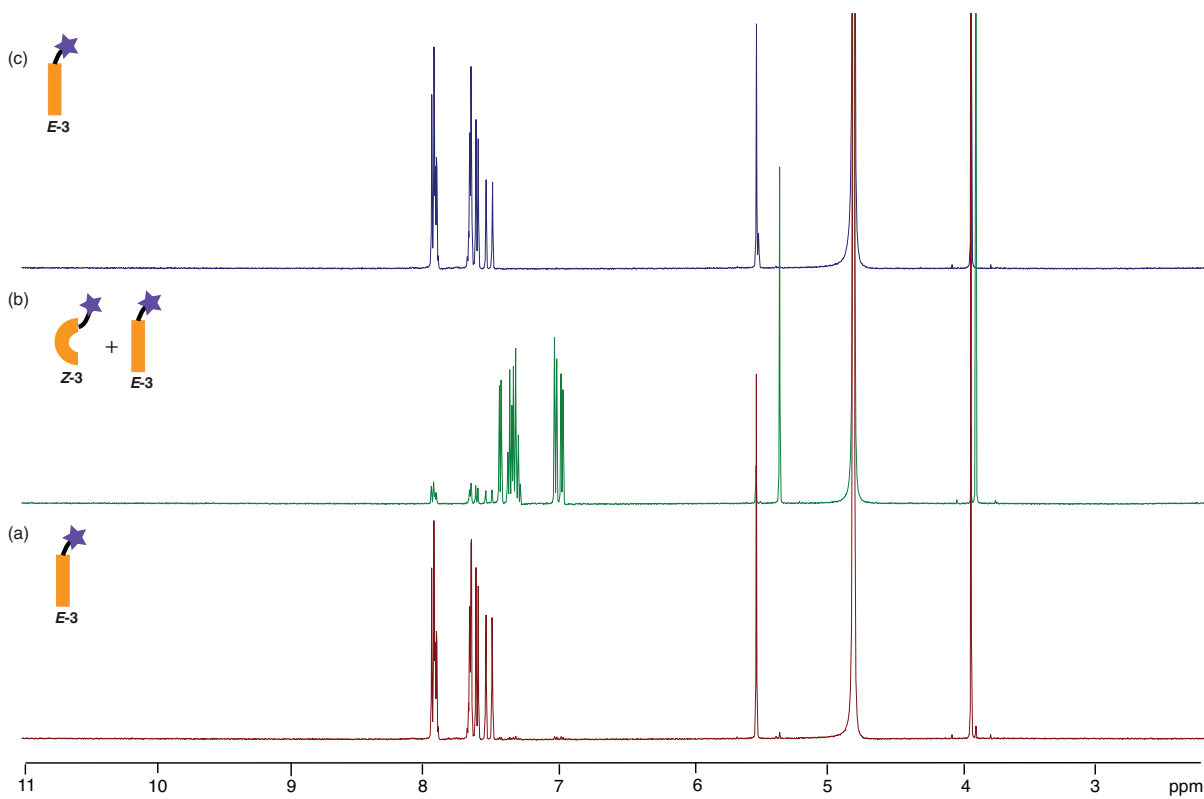


Figure S14: ^1H NMR spectra (500 MHz, D_2O) of *E*-**3** before UV irradiation (a), after (b) UV irradiation and after heating at 343K, 24 h (c).

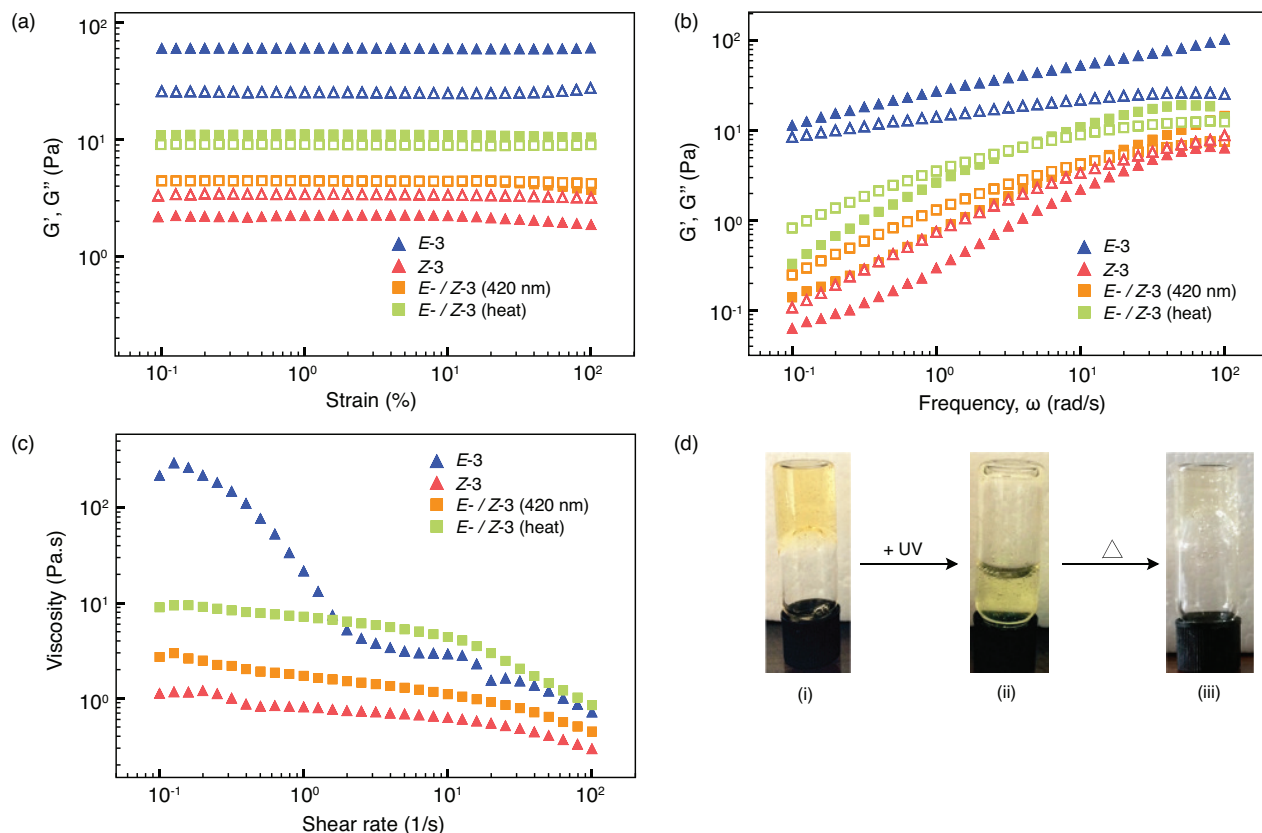


Figure S15: Dynamic and steady-shear rheological measurements of 0.75 *wt.%* HEC mixture containing 0.5 mol eq *E-3* under ambient temperature before and after UV irradiation (a - c). After UV irradiation, the samples were irradiated under visible light at 420 nm and heated at 70 °C for 24 h. Note for plots (a, b): filled symbols refer to G' and open symbols refer to G'' . Inverted vial test for UV-irradiated HEC samples which were then heated to 70 °C for 24 h (d).

The effect of heat on the CB[8]·*Z-3* binary complex under the same condition can only transform a small fraction of the *Z-3* to the *E* isomer, resulting in a runny gel-like matrix with G' slightly above G'' at 10 Pa. Shear-rate dependent viscosity of the matrix after heating resembles that of the sol after UV irradiation, with slightly increased viscosity (10 Pa·s) that shear thins at higher shear rate. In this case, some CB[8] were available to reassemble the MV- and Np-functionalised polymers into networks, resulting in a mechanically weaker hydrogel (Figure S15).

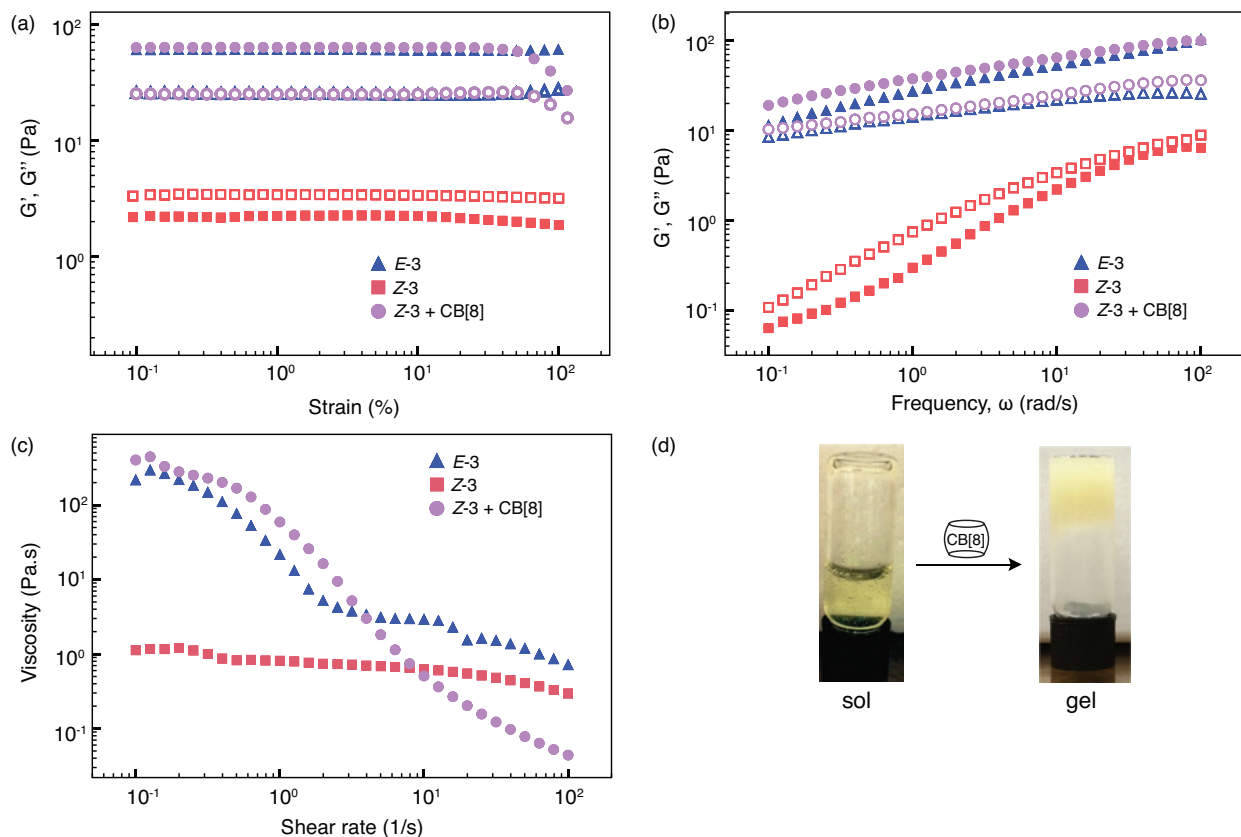


Figure S16: Effects of excess CB[8] addition on the rheology of 0.75 *wt.*% HEC samples and 0.5 mol eq *E-3* after UV irradiation at 20 °C: storage and loss moduli from strain-amplitude sweep at 10 rad/s (a), storage and loss moduli from frequency sweep at 1% strain (b), viscosity vs shear rate plots (c) and photographs of UV-irradiated HEC solution with excess CB[8], which regained its initial gel state (d). Notes for (a, b): filled symbols represent G' and open symbols represent G'' . Blue triangles refer to hydrogel with *E-3*, red squares refer to hydrogel with *Z-3* and purple circles refer to samples added with 2 mg CB[8] after UV treatment.

The sol can be converted back to an elastic state by adding excess CB[8] to the matrix (Figure S14). Unbound polymeric guests in the viscous solution crosslinked with easily accessible CB[8] to reform the supramolecular network. This is illustrated by the recovery of the viscoelastic moduli ($G' > G''$) of the hydrogel being dependent on frequency (Figure S14b). The HEC matrix regained its initial zero-shear viscosity (300 - 400 Pa·s) with shear-thinning flow (Figure S14c). The HEC matrix regained its initial zero-shear viscosity (300 - 400 Pa·s) with a shear-thinning behaviour. The cloudiness of the hydrogel was attributed to the

insoluble CB[8] present in excess (Figure S14d). With time, the presence of excess CB[8] caused the soft material to undergo syneresis; a phenomenon caused by expulsion of water from the gel, therefore altering the overall rheological properties of the thixotropic hydrogel. Phototriggered displacement of polymer bound guests led to the network disassembly highlighted the significance of CB[8] in the ternary complex formation. The non-reversible viscosity change by light irradiation at different wavelengths is also reported in the simple micellar PR fluids and the reversibility of such systems can be achieved by altering their mixture composition and pH.^{8,9}

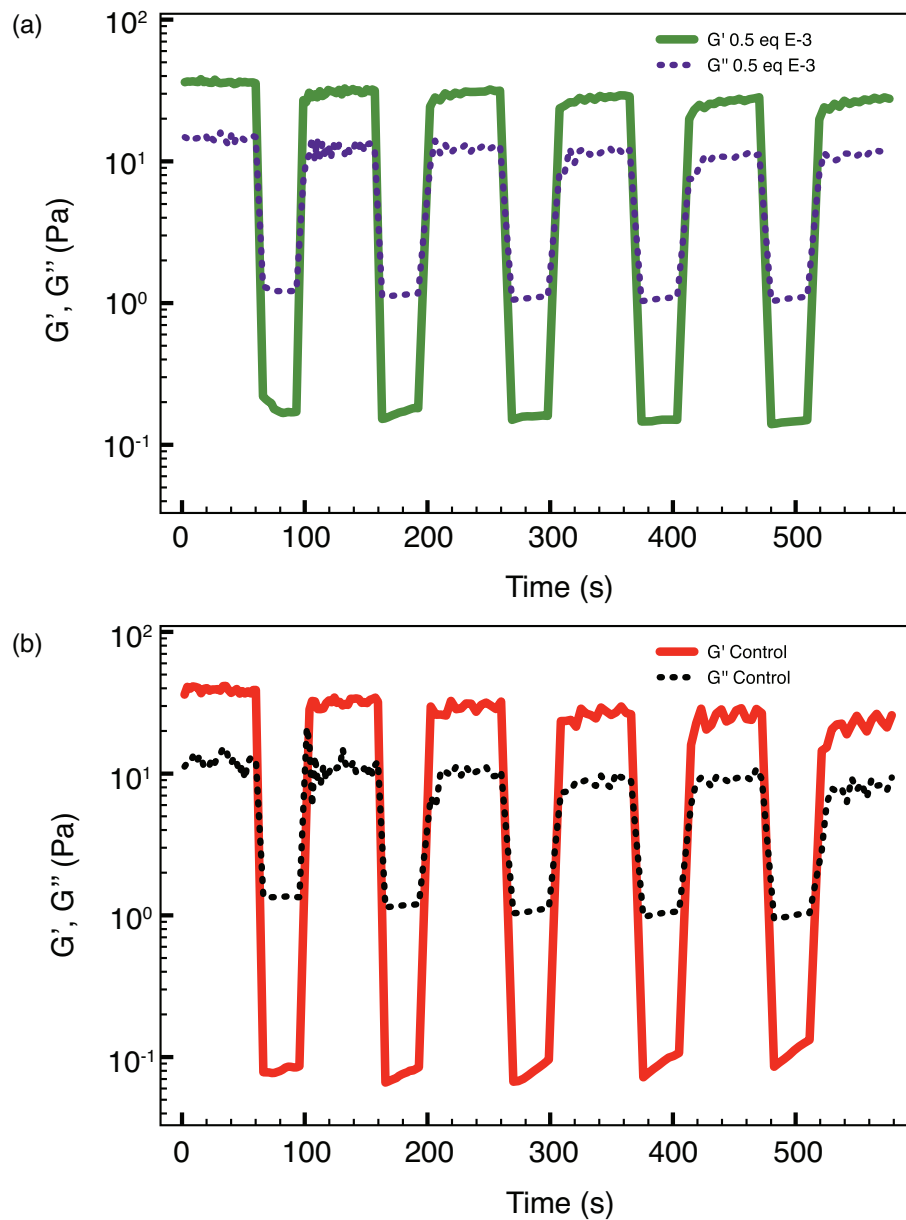


Figure S17: Step-strain time-sweep measurements displaying recovery of 0.75 *wt.*% HEC samples (a) with and (b) without 0.5 mol eq *E-3* structure following successive high-magnitude deformation at 1000 % strain and low-magnitude recovery at 0.05 % strain.

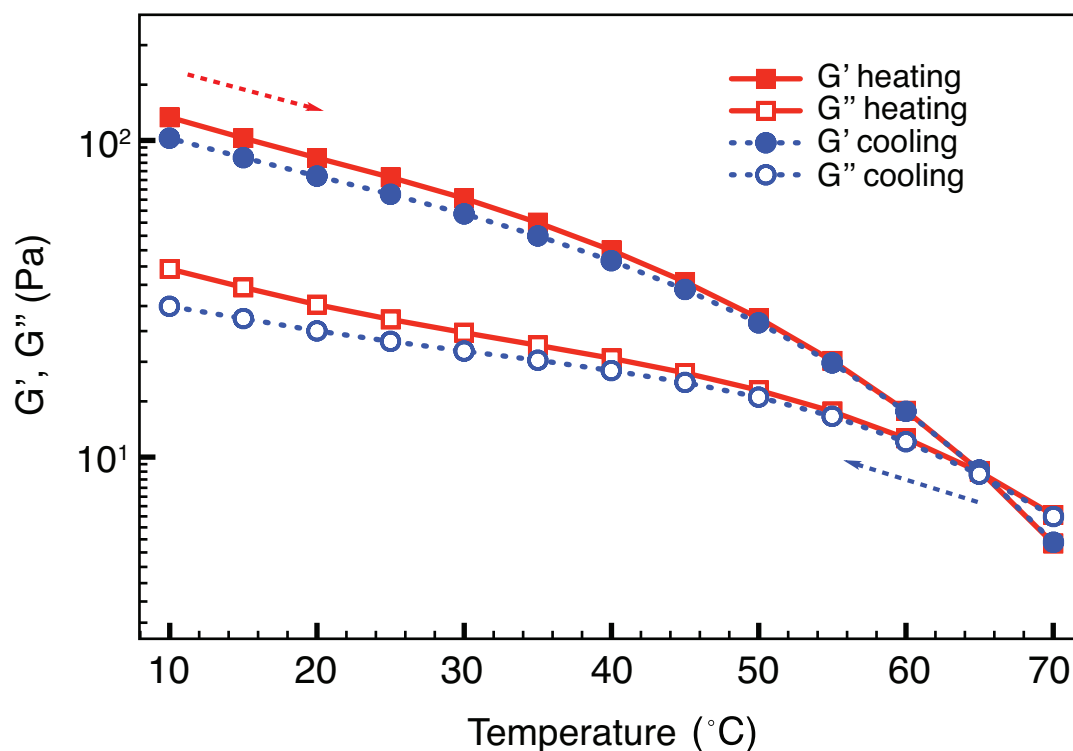


Figure S18: Thermoreversibility of HEC supramolecular networks without *E-3* when heated and then cooled between 10 and 70 °C.

Oscillatory temperature sweep measurements were performed on the HEC samples without *E-3* chromophore between 10 and 70 °C at 1% strain and 10 rad/s (Figure S18). The samples were heated to 70 °C and cooled down to 10 °C. The range of temperature was selected to avoid evaporation of water from the samples on the parallel-plate geometry. In the temperature sweep, viscoelastic components decreased with heat and gradually rose back to their initial moduli without significant changes after the cooling process. This observation indicates the thermoreversible stability of the rapid transient linkages in the supramolecular hydrogels is reproducible at a given temperature.

X-ray Crystal Structure of CB[8]·*Z-3*.

The guest *Z-3* is disordered over 2 positions inside the CB[8] cavity. As such various geometrical (SAME) and displacement (SIMU, RIGU, EADP) restraints have been employed.

There are large voids between the CB[8] guest molecules containing solvent water and the chloride counter anions. However, they were too disordered to accurately determine their location, thus the SMTBX solvent mask routine has been employed as implemented in Olex2.

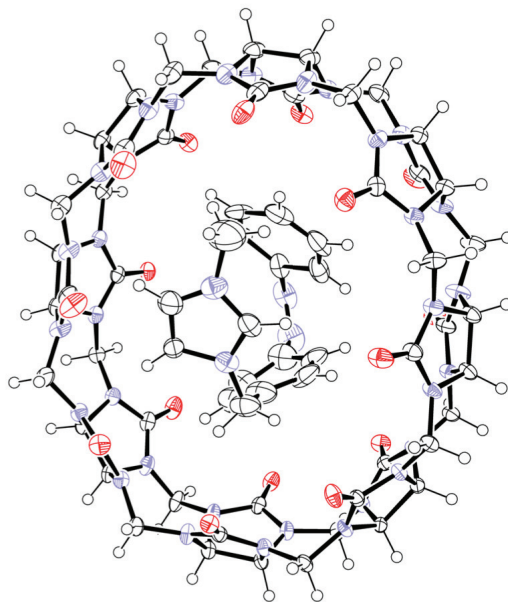


Figure S19: ORTEP (ellipsoids at 50% occupancy) showing the CB[8]·**Z-3** complex.

Table 1. Crystal data and structure refinement details.

Identification code	2013ncs0827	
Empirical formula	C ₆₅ H ₆₅ N ₃₆ O ₁₆	
Formula weight	1606.53	
Temperature	35 K	
Wavelength	0.6889 Å	
Crystal system	Trigonal	
Space group	<i>R</i> −3	
Unit cell dimensions	<i>a</i> = 39.1610(4) Å	$\alpha = 90^\circ$
	<i>b</i> = 39.1610(4) Å	$\beta = 90^\circ$
	<i>c</i> = 26.8389(3) Å	$\gamma = 120^\circ$
Volume	35645.2(8) Å ³	
Z	18	
Density (calculated)	1.347 Mg / m ³	
Absorption coefficient	0.095 mm ^{−1}	
<i>F</i> (000)	15030	
Crystal	Needle; yellow	
Crystal size	0.2 × 0.04 × 0.04 mm ³	
θ range for data collection	1.582 – 27.741°	
Index ranges	−52 ≤ <i>h</i> ≤ 52, −52 ≤ <i>k</i> ≤ 52, −36 ≤ <i>l</i> ≤ 28	
Reflections collected	130475	
Independent reflections	20436 [<i>R</i> _{int} = 0.0508]	
Completeness to $\theta = 26.600^\circ$	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.94581	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	20436 / 983 / 1238	
Goodness-of-fit on <i>F</i> ²	1.077	
Final <i>R</i> indices [<i>F</i> ² > 2 σ (<i>F</i> ²)]	<i>R</i> 1 = 0.0729, <i>wR</i> 2 = 0.2093	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0881, <i>wR</i> 2 = 0.2207	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.543 and −0.499 e Å ^{−3}	

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