Electronic Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information

Cross Linked Supramolecular Polymer Networks with Responsive, Elastic Gel Properties via Host-Guest Complexation: Controlled Release of Squaraine Dyes

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Content

1. ^{1}H NMR and ^{13}C NMR spectra of compounds 4 and 5

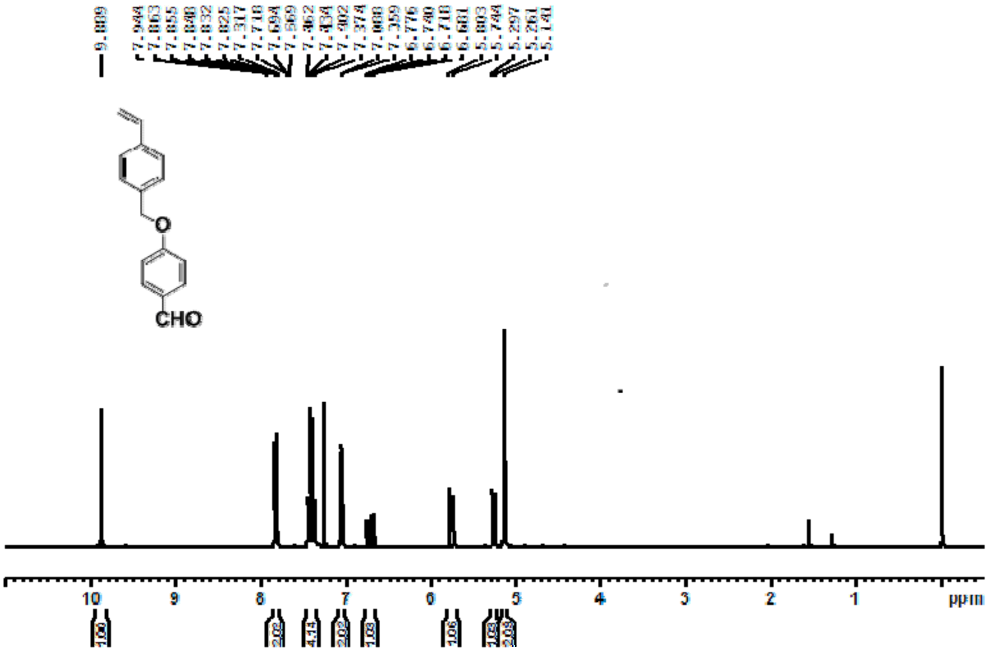


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 295 K) of compound **4**.

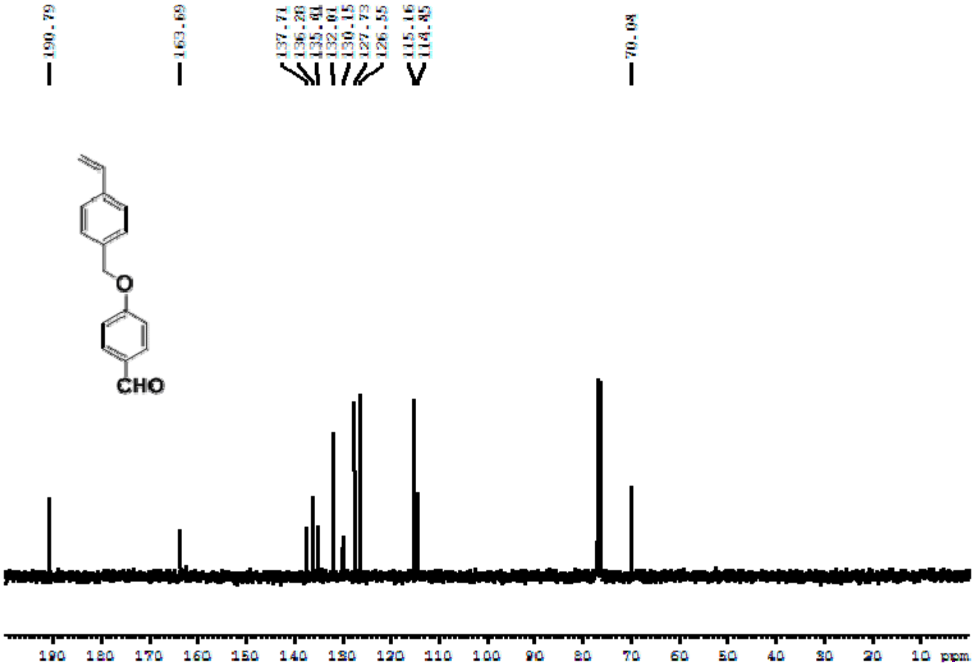


Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 295 K) of compound **4**.

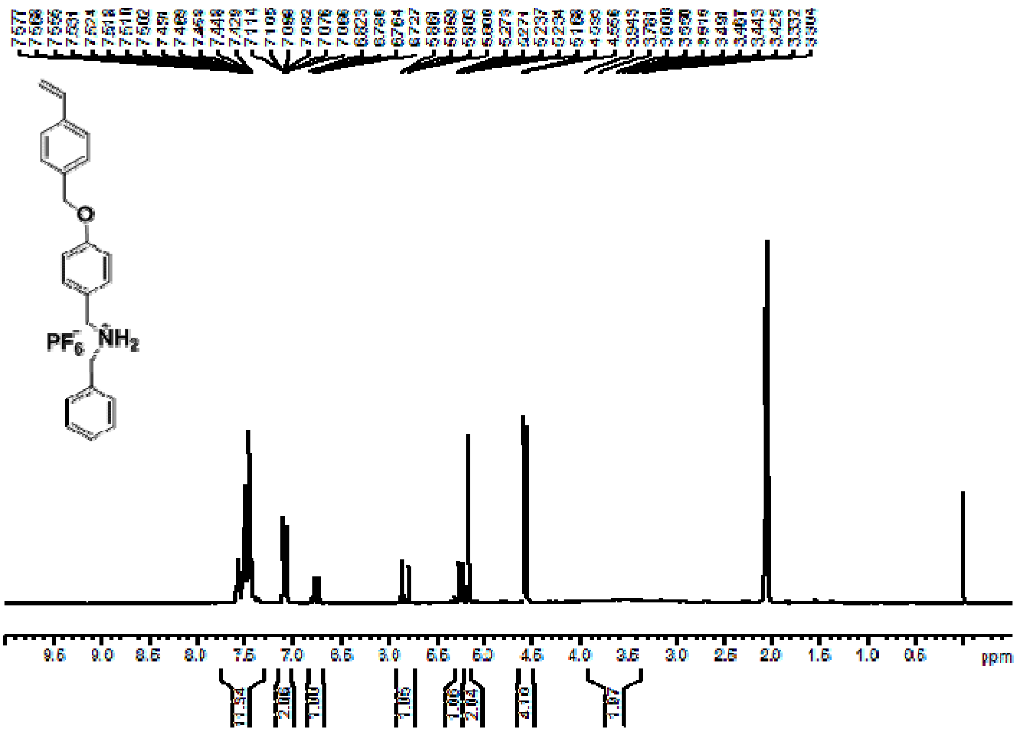


Figure S3. ^{1}H NMR spectrum (300 MHz, CD_3COCD_3, 295 K) of compound **5**.

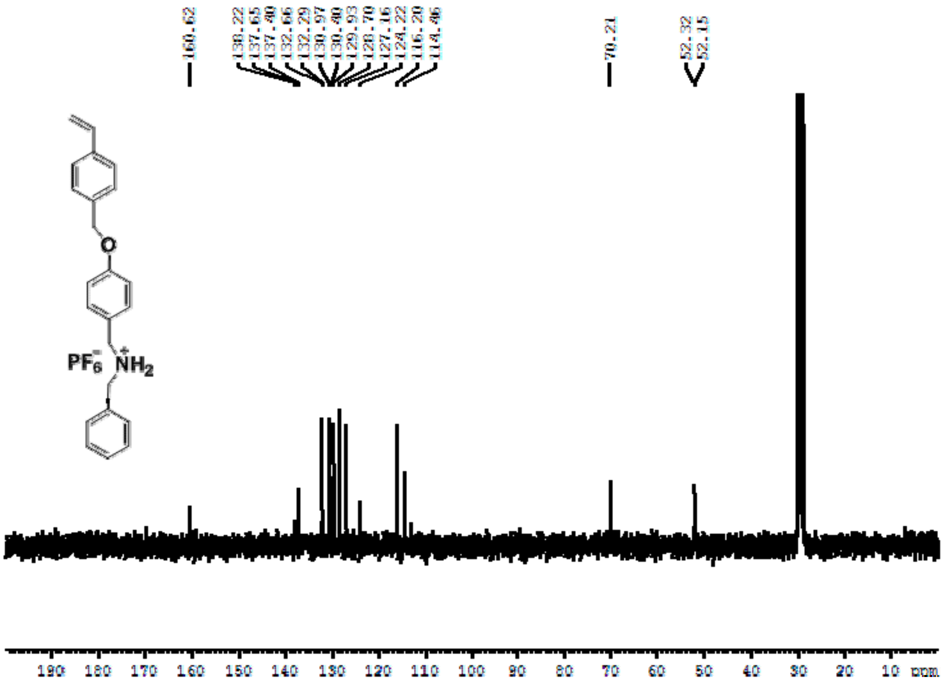


Figure S4. ^{13}C NMR spectrum (75 MHz, CD_3COCD_3, 295 K) of compound **5**.

2. ^{1}H NMR spectrum of copolymer 3

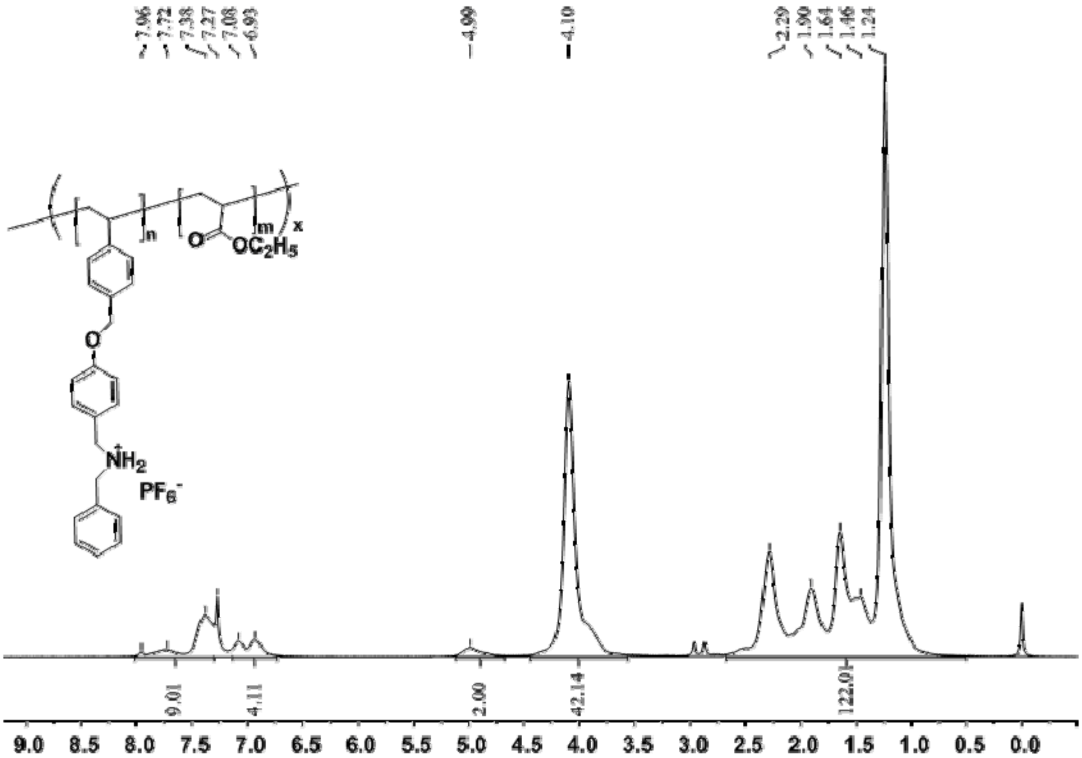
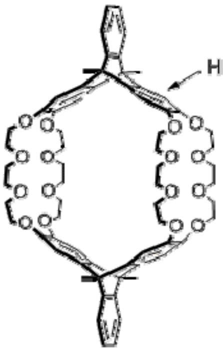
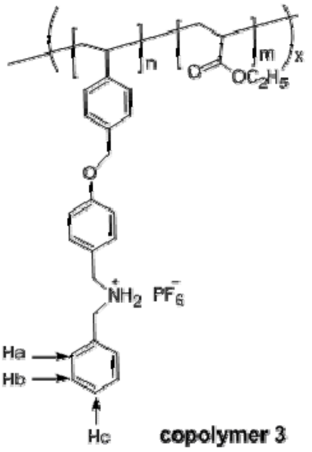


Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 295 K) of copolymer **3**.

3. Complexation between host 1 and copolymer 3



host 1



copolymer 3

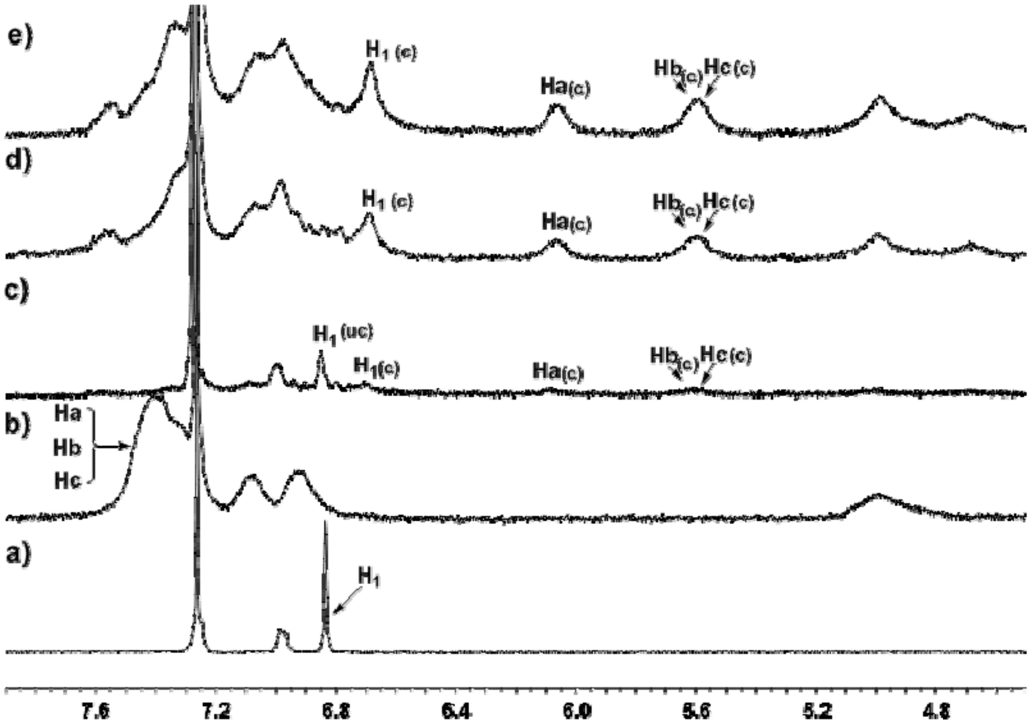


Figure S6. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 295 K) of a) free host **1**, b) free copolymer **3**, c) host **1** and copolymer **3** (molar ratio=1:1 host **1**/DBA), d) host **1** and copolymer **3** (molar ratio=1:2 host **1**/DBA) , e) host **1** and copolymer **3** (molar ratio=1:3 host **1**/DBA), $[\mathbf{1}]_0$ = 2.1 mM (c and uc denote complexed and uncomplexed moieties, respectively).

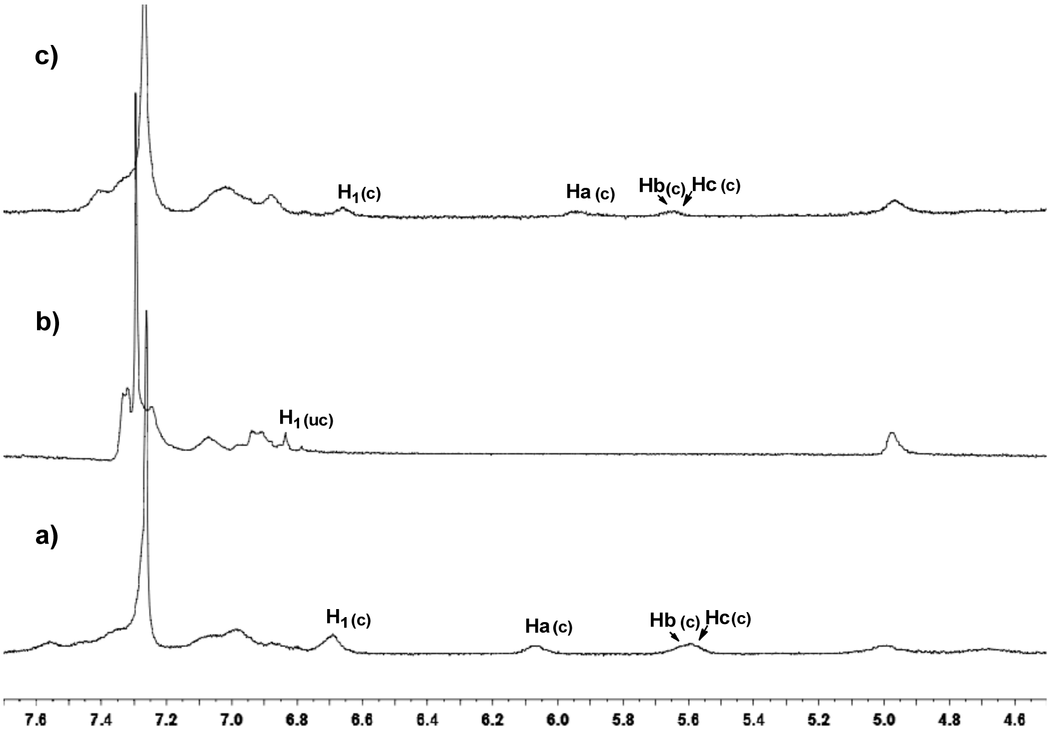


Figure S7. Partial ^{1}H NMR spectra (300 MHz, CDCl$_3$, 295 K) of a) host **1** and copolymer **3** (molar ratio=1:2 host **1**/DBA), b) after added 2.2eq TEA to a, c) after added 2.4eq TFA to b, [**1**]$_0$ = 2.1 mM (c and uc denote complexed and uncomplexed moieties, respectively).

4. The preparation and morphology of different cross-link density supramolecular gels

General preparation of supramolecular polymer gel. To a solution of copolymer **3** (50 mg, 0.021 mmol DBA) in $CHCl_3$ (1.3 mL) was added host **1** (12.08 mg, 0.0105 mmol, 5% cross-link density). The mixture was shaken smoothly for a few seconds, and a yellow organogel was then formed.

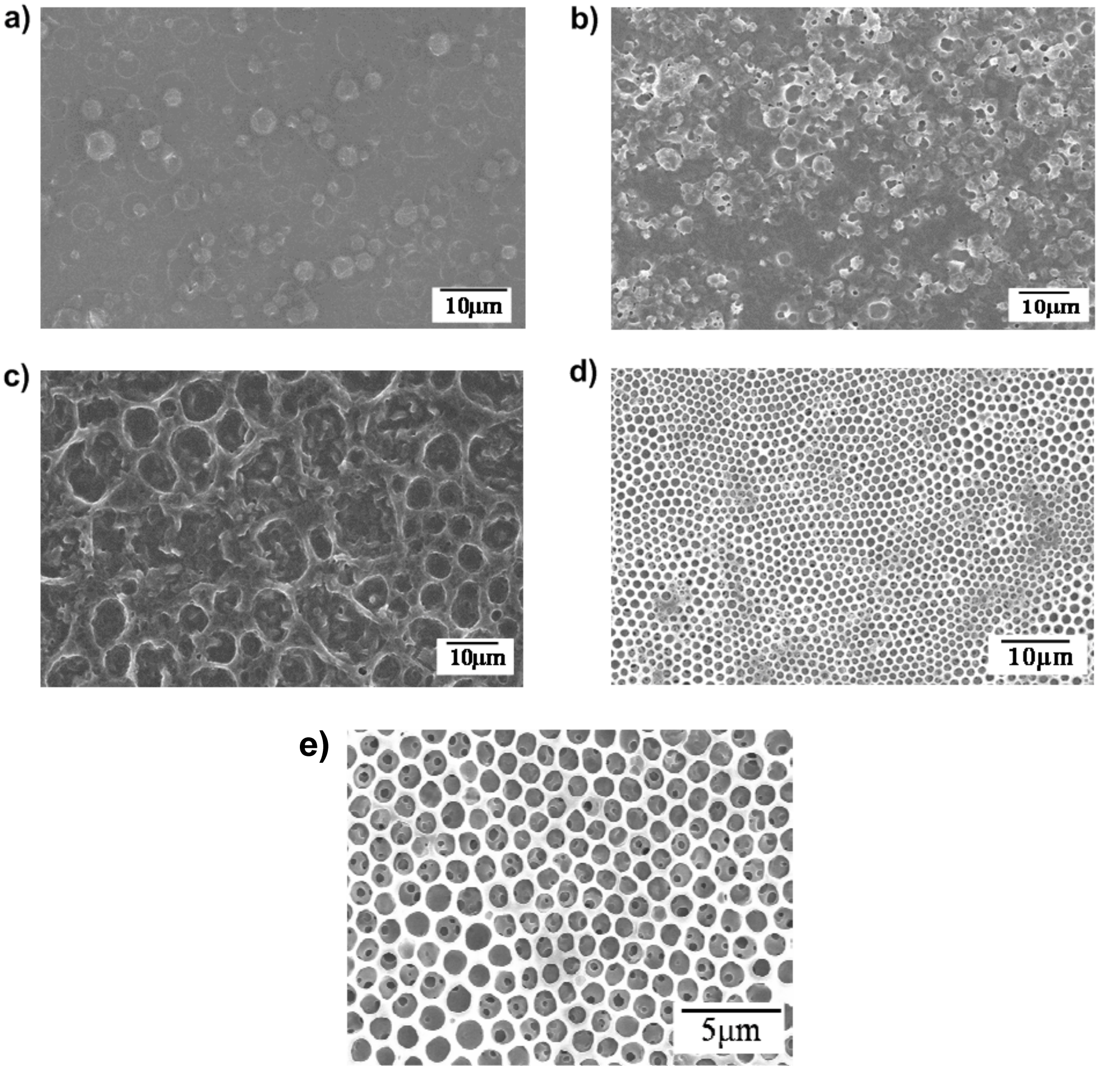


Figure S8. Scanning electron micrography of the supramolecular polymer gels with different cross-link densities. a) 1.25%, b) 2.50%, c) 3.75%, and d) and e) 5.00%.

5. Encapsulation and controlled release of squaraine dyes

*Preparation of the supramolecular polymer gel carrying squaraine dyes **6a-b***: To a solution of squaraine dye **6a** or **6b** (0.1 mg) and copolymer **3** (12.5 mg) in $CHCl_3$ (0.2 mL) was added host **1** (3.02 mg). The mixture was shaken smoothly for a few seconds, and a organogel carrying squaraine dye **6a** or **6b** was formed. Then, 2.00 mL of $CHCl_3$ was added onto the supramolecular polymer gel.

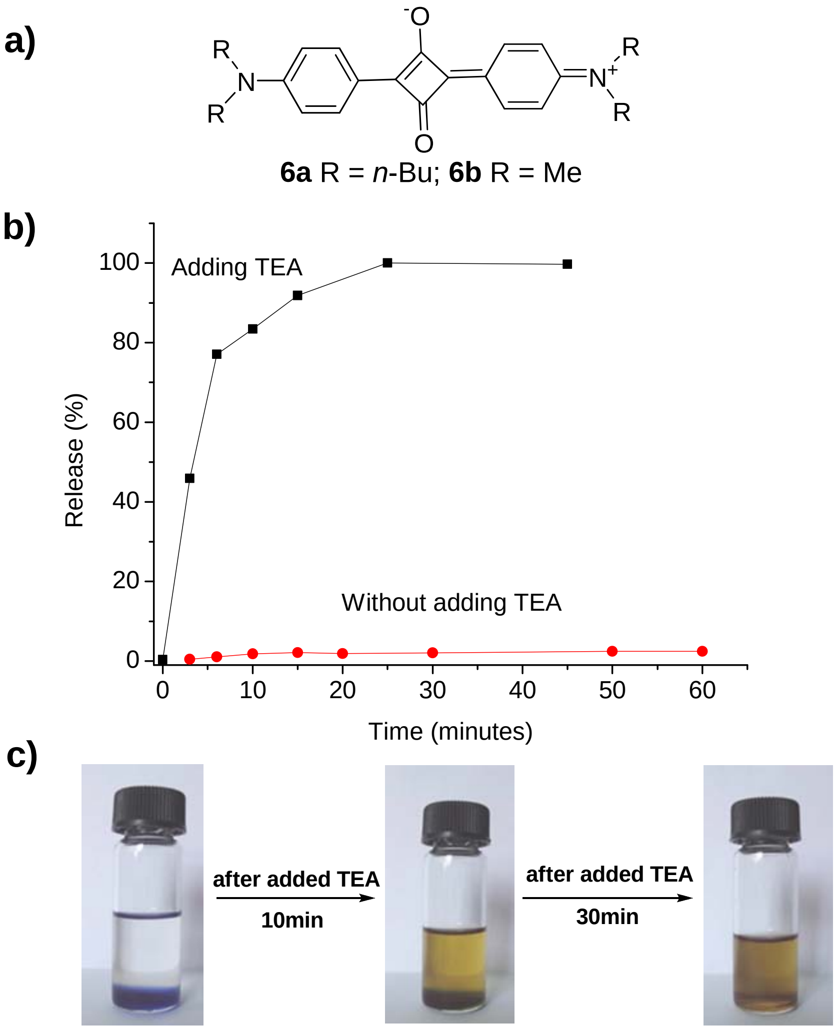


Figure S9. Release of squaraine dyes from the supramolecular polymer gel after the addition of Et_3N at 20 ºC. a) Structures of squaraine dyes **6a-b**, b) the release percentage of squaraine dye **6b** as a function of time with and without addition of Et_3N, c) the color change of the layer of $CHCl_3$ after addition of Et_3N to squaraine dyes carrying gels **6a**.

6. G_0 values of different cross-link density supramolecular gels

Table S1. G_0 value of different cross-link density supramolecular gels

Cross-link density %	G_0 (Pa)
1.25	894
2.50	1512
3.75	2722
5.00	4295

7. Theoretical studies of the supramolecular polymer gels

To future characterize formation of the polymer networks in the supramolecular gels, we considered the extent of cross-linking between the polymer chains. For the reversible cross-linkers in supramolecular polymer networks, a phantom network model[S1,2] is more appropriate, and the number density of elastically active chains of (v_{phantom})[S3] is given by

$$v_{\mathrm{phantom}} = \frac{G_0}{k_B T(1-2/f)} \qquad (1)$$

G_0 is the plateau modulus obtained from the constant value of G' at high frequency, k_B is Boltzmann's constant, and T is the temperature, f is the functionality of the cross-linker. As our host can form a 1:2 complex with two DBA, so the supramolecular gels have four polymer strands joining at one cross-linker and a functionality of four ($f = 4$) is used here. As described by Flory,[S3] the conditions for network formation (gel point) correspond to one interstrand cross-link per polymer chain. At the gel point, therefore, there is on average one elastically active subchain per polymer chain. The mean number of elastically active subchains per polymer chain (f_{eas})[S4] can be found from the eq 2.

$$f_{\mathrm{eas}} = v_{\mathrm{phantom}}/n_{\mathrm{p}} = v_{\mathrm{phantom}} \mathrm{M_n}/(\mathrm{C_p N_A}) \qquad (2)$$

where v_{phantom} is taken from eq 1, n_{p} is the number of polymer chains per 1 mL volume, C_P is the concentration of polymer (g/mL), N_A is Avogadro's number, and M_n is the number-average molecular weight of polymer. The value of f_{eas} can serve as a criterion for the formation of a network structure, and the criterion for network formation is $f_{eas}>2$.[S3] From the date of G_0 in Table S1, the value of f_{eas} from 1.25% to 5% cross-linked supramolecular gels are 1.04 to 5.01. For the supramolecular gels with 1.25% and 2.5% cross-link density, it seems that the empirical rheological criteria are contrary to the Flory criteria to form a network. This difference can be explained by the heterogeneous network structure in gels, as the heterogeneity can induce an apparent low value of f_{eas}. It was noted that the networks are necessarily heterogeneous (SAXS experiments showed no obvious peaks of supramolecular gels, which meant no regular nanostructures), and in all cases, there should be some steady-state fraction of small, discrete polymers and polymer aggregates that are dissociated from the network. The presence of such “non-networked” fragments should not affect the main features of the analyse because (1) they do not contribute substantially to the bulk viscoelastic properties of the samples, and (2) the cross-link density is inferred directly from bulk measurements that reflect the supramolecular polymer networked structure. Additionally, we also pointed out that the heterogeneity means that the value of f_{eas} as calculated above underestimates the true average number of active subchins perpolymer chain within the active network structure because it is the ration of the number of active segments (all of which are in the active network) to the total number of polymer chains (some of which are in the active network and some of which are not).

8. Relationship between the addition of TDMPE 1 and relaxation rate *β* of the network after oscillatory perturbation

A simple representation of viscoelasticity in a material is the single mode Maxwell model that is typically used to describe viscous materials with some elastic response and can be described by a single relaxation rate β.

$$G' = G_0(\omega/\beta)^2/(1+(\omega/\beta)^2) \qquad (3)$$

$$G'' = G_0(\omega/\beta)/(1 + (\omega/\beta)^2) \qquad (4)$$

According to our molecular picture, the reversibly cross-linked 3D networks respond to an applied stress (oscillatory perturbations) by relaxing back to equilibrium at a rate β (exchange rate of host among the crosslink sites). For slow oscillations, $\omega << \beta$ (the reversible cross-links dissociate faster than the experimental scale), and the viscous component G" dominates. Conversely, at very fast oscillations, $\omega >> \beta$ (the reversible cross-links dissociate slower than the experimental scale), and the elastic component G' dominates. As shown in Figures 4b and 4c, the G' value is larger than the G" under frequency sweep range, which demonstrated that $\omega >> \beta$ and supramolecular polymer gel was dominated by its elastic property.

9. Recyclable process of supramolecular polymer gel

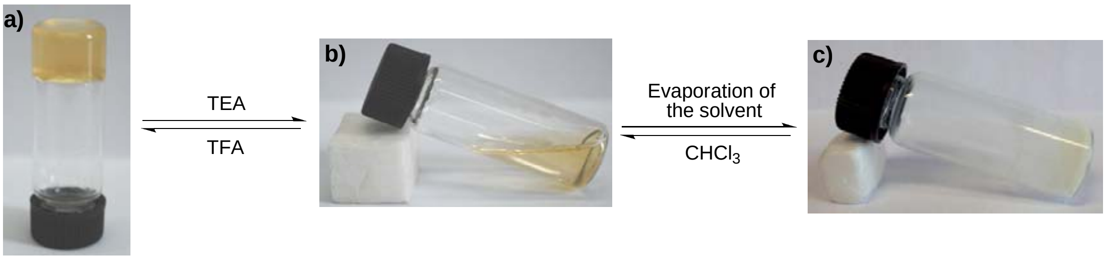


Figure S10. Recyclable process of supramolecular polymer gel. a) Supramolecular polymer gel, b) addition of 2.2 equiv (per host **1**) of triethylamine (TEA) to the supramolecular polymer gel led to the transition of gel to solution, c) evaporation of the solvent can recycle the copolymer and host **1**.

10. References

S1. L. G. Baxandall, *Macromolecules* 1989, **22**, 1982–1988.

S2. M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, New York, 2003.

S3. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.

S4. D. Xu, S. L. Craig, *Macromolecules* 2011, **44**, 5465–5472.