Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for

Supramolecular polymer hydrogels induced by host-guest interactions with di-[cyclobis(paraquat-*p*-phenylene)] cross-linkers: from molecular complexation to viscoelastic properties

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Materials

1,1'-Azobis(cyclohexanecarbonitrile) (V-40, 98%), Benzene (99.9%), 1,3,5-Trioxane (≥ 99%), $[(CH_3CN)_4Cu]PF_6$ (97%), tetraethylammonium chloride (≥ 98%) and ammonium hexafluorophosphate (≥ 98%) were purchased from Sigma Aldrich and were used as received. *N,N*-Dimethylacrylamide (DMAc, 99%) was purified by vacuum distillation under reduced pressure at room temperature before use. All polymerizations were conducted under argon atmosphere. 1-[2-(2-Hydroxyethoxy)ethoxy]-5-[2-(2-methoxyethoxy)ethoxy]naphthalene, 1,6-diazidohexane, 2-(((isobutylthio)carbonothioyl)thio)-2-methylpropanoate (Bz-CTA), the tetracationic cyclophane cyclobis(paraquat-p-phenylene)-alkyne (HC≡C-$CBPQT^{4+}$, $4PF_6^-$) and $CBPQT^{4+}$, $4Cl^-$ were synthesized according to literature procedures.

Instrumentation

Nuclear Magnetic Resonance (NMR): The purity of RAFT agents, homoditopic tetracationic macrocycle cyclobis(paraquat-*p*-phenylene) was determined by ^1H and ^{13}C NMR spectroscopy in acetone-d_6, $CDCl_3$ or D_2O at room temperature (Bruker Advance 200 or 500 MHz spectrometer). The conversion of DMAc was determined by ^1H NMR spectroscopy in acetone-d_6 by the relative integration of the internal reference (1,3,5-trioxane) peak at 5.1 ppm and the vinylic proton peaks of DMAc at 6.6, 6.3 and 5.7 ppm.

Isothermal Titration Calorimetry (ITC): The formation of blue box (**B**) complexes was studied at fixed temperature, 20 °C or 60 °C, using a nano-ITC titration calorimeter from TA Instruments following standard procedures. The sample cell (1 mL) was initially filled with naphthalene derivatives (molecule or polymers), or water (for dilution measurements), while the blue box (**B**) solution, was introduced into a 250 μL injection syringe. The titration was carried out by a step-by-step injection of the **B** solution into the sample cell under continuous stirring (400 rpm). A similar procedure was carried out at 25 °C for the titration of **P(DMA-N1)$_{1100}$** with di-blue box (**BB**) using a MicroCal VP-ITC titration calorimeter from Malvern with a sample cell volume of 1.42 mL and a 300 µL injection syringe. The enthalpy of complexation (ΔH) was obtained after subtraction of the dilution curve from the titration one. The binding constant (K_a), as well as other thermodynamic parameters including free energy (ΔG) and entropy (ΔS), were obtained after data fitting using a single set of identical sites.

UV-vis**:** measurements were carried out on a Varian Cary 50 Scan UV/vis spectrophotometer equipped with a single cell Peltier temperature controller.

Size exclusion chromatography (SEC) : The number-average molar masses (M_n), the weight-average molar masses (M_w), and the dispersities ($Đ = M_w/M_n$) were determined by SEC. Measurements were performed in DMF (+ LiBr, 1g L^{-1}) at 60 °C, at a flow rate of 0.8 mL min^{-1} and at a polymer concentration of 5 mg mL^{-1} after filtration through a 0.22 µm pore-size membrane. The chromatography was carried out on two PSS GRAM 1000 Å columns (8 × 300 mm; separation limits: 1 to 1000 kg mol^{-1}) and one PSS GRAM 30 Å (8 × 300 mm; separation limits: 0.1 to 10 kg mol^{-1}) coupled with three detectors (Viscotek, TDA 305): a differential refractive index (RI) detector, a viscosimeter detector and a light scattering (LS) detector (laser λ = 670 nm at 7° and 90°). The number-average molar masses, M_n^{PMMA}, and the dispersities ($Đ = M_w/M_n$), were calculated with a calibration curve based on narrow poly(methyl methacrylate) (PMMA) standards (from Polymer Standard Services), using only the RI detector. The absolute number-average molar masses, M_n^{LS}, were calculated from combined LS and RI signals with the OmniSEC 4.6 software, using an average refractive index increment (*dn/dC*) of 0.0754 mL.g-1 for the **P(DMA-N1)** polymer. The *dn/dC* was measured with the online RI detector by injecting polymer solutions at three different concentrations.

Synthesis of P(DMA-N1)

Synthesis of Napht-Ac

The synthesis of ***Napht-Ac***, described in **Figure S1**, has already been reported in [1].

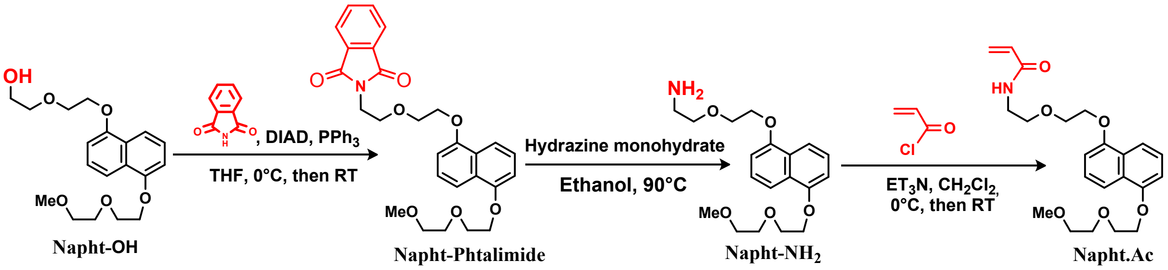

Figure S1. Preparation of Naphthalene acrylamide monomer

Synthesis of P(DMA-N1)

The synthesis of the P(DMA-N1) copolymer, summarized in **Figure S2**, has been carried out as follows.

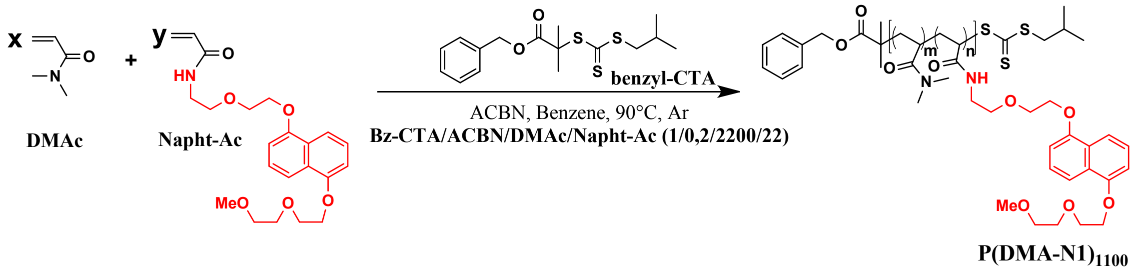

Figure S2 : Synthesis of P(DMA-N1)

A round-bottomed flask (50 mL) was loaded with *N,N*-dimethylacrylamide (16 g, 160 mmol), Bz-CTA (25 mg, 0.073 mmol)), 1,1'-azobis(cyclohexanecarbonitrile) (3.5 mg, 0.014 mmol), 1,3,5-trioxane (144 mg, 1.6 mmol) and benzene (32 mL). The reaction mixture was purged with argon for 45 min in iced water and was then immersed in an oil bath thermostated at 90 °C. Samples were periodically withdrawn via purged syringes to measure the conversion by ^{1}H NMR. After complete drying, the raw polymer from each sample was dissolved in DMF

(/LiBr) for size exclusion chromatography analysis (see **Figure S3**). After 250 min at 90°C, the reaction was stopped and the polymer was isolated by precipitation into diethylether, dissolved in water, dialyzed (Spectra/Por® 7, molecular weight cut off : 8 kDa) and lyophilized. The chromatogram and ^{1}H NMR spectrum of the purified copolymer are given in **Figures S4** and **S5**.

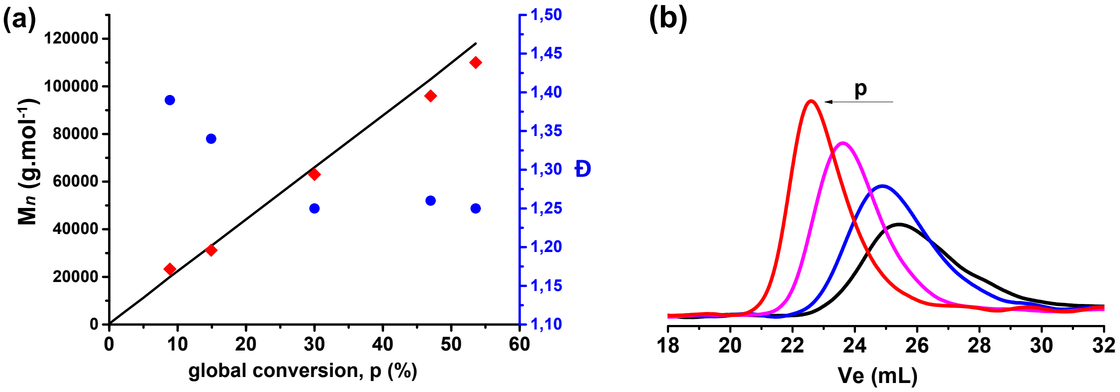

Figure S3. (a) Evolution of the number-average molar mass, M_n (♦) and dispersity, *Đ* (●) determined by SEC in DMF (+ LiBr) using PMMA standards versus monomers conversion for the RAFT polymerization of (DMAc + Napht.Ac) at 90°C. **(b)** Size exclusion chromatograms vs. monomers conversion.

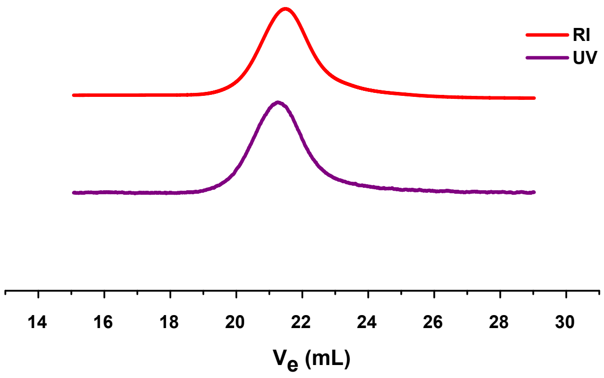

Figure S4

Size exclusion chromatograms of P(DMA-N1) polymer after purification (precipitation and dialysis). obtained with a UV detector at 254 nm and a refractive index detector

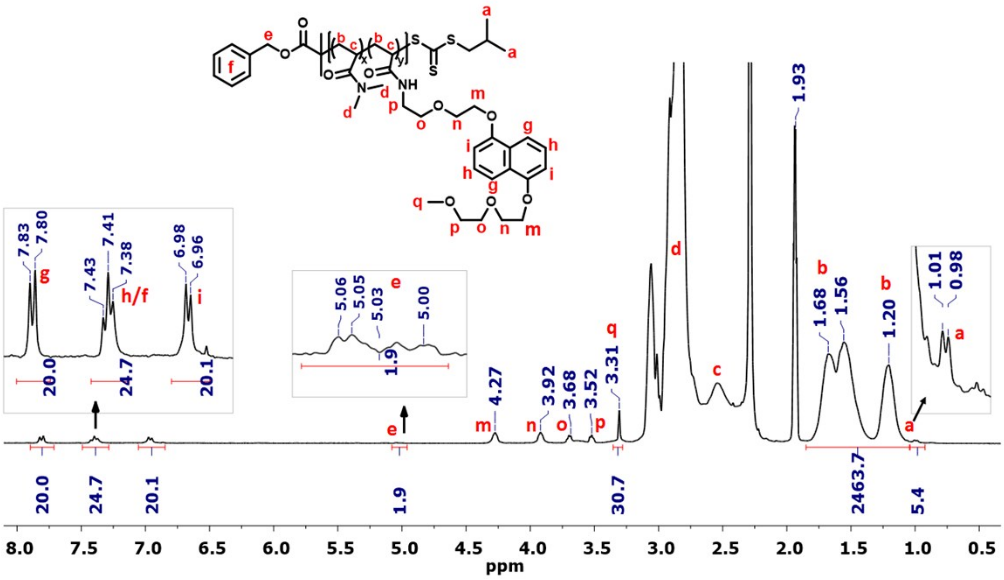

Figure S5 ^{1}H NMR spectrum of the P(DMA-N1) recorded in CD_3CN at 25°C (300 MHz).

Mono-blue box complexes

UV-Vis spectroscopy

The capability of **B** units to bind pendant naphthalene groups of **P(DMA-N1)** was investigated tby UV-Vis spectroscopy. For that purpose, a spectroscopic titration of a **P(DMA-N1)** solution (1mM in N groups) was carried out by adding increasing amounts of an aqueous solution of **B**. As shown in **Figure S6**, the resulting complex gives rise to an optical absorption band centered around λ_{max} = 525 nm which is characteristic of B/N type complexes. The intensity of the charge-transfer band decreases with temperature, demonstrating qualitatively that the strength of the complex decreases during heating.

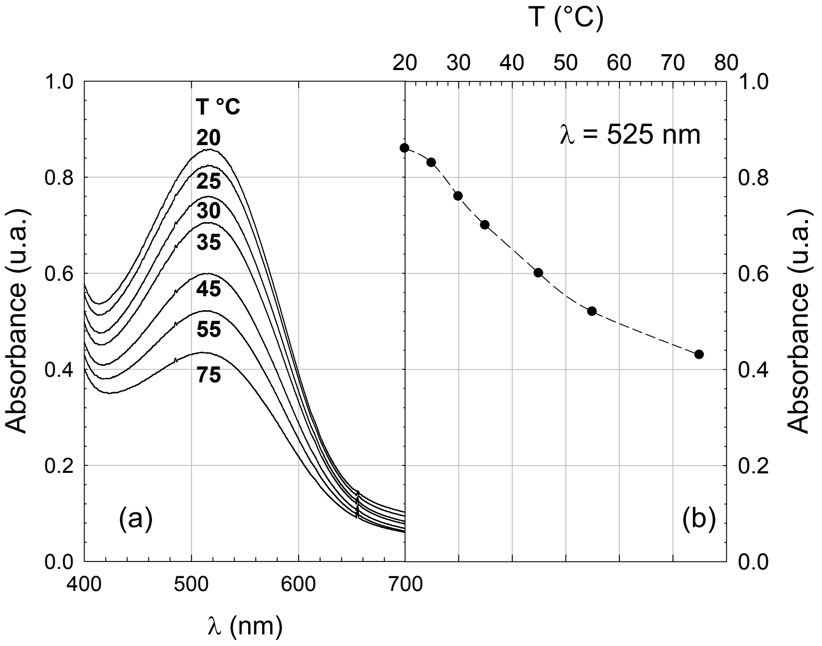

Figure S6. UV-Vis spectroscopy of a stoichiometric aqueous formulation **P(DMA-N1)/B** (B/N=1). Temperature dependence of **(a)** the absorption spectra of the charge-transfer complex, and **(b)** its absorption band centered at λ_{max} = 525 nm.

Isothermal Titration Calorimetry

More quantitative information can be retrieved from ITC experiments that allow simultaneous access to the average stoichiometry of the complex (B/N), as well as thermodynamic parameters like the binding constant (K_a), ΔG, ΔH and ΔS related to the following equations:

$$\mathrm{N} + \mathrm{B} \rightleftharpoons \mathrm{NB} \text{ with } K_a = \frac{[NB]_{eq}}{[N]_{eq}[B]_{eq}} \quad \{\mathrm{S1}\} \qquad \text{and} \quad \Delta G = \Delta H - T\Delta S = -RTLnK_a \quad \{\mathrm{S2}\}$$

$$\text{with} \qquad LnK_a = LnK_{T_{ref}} + \frac{\Delta H}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \quad \{\mathrm{S3}\}$$

where $[N]_{eq}$, $[B]_{eq}$ and $[NB]_{eq}$ are the equilibrium concentrations of naphtalene groups, uncomplexed and complexed blue box molecules, respectively.

A typical ITC experiment is given in **Figure S7** with the titration in water of a **P(DMA-N1)** solution with a concentrated solution of mono-blue box **B**. The enthalpogram obtained at

T=60 °C displays a sharp exothermic titration profile with ΔH ≅ -55 kJ/mol and a stoichiometric ratio of 9.6 $CBPQT^{4+}$ molecules per **P(DMA-N1)** chain, which matches well with the host/guest stoichiometric ratio B/N of 1 previously estimated by UV-Vis spectroscopy.

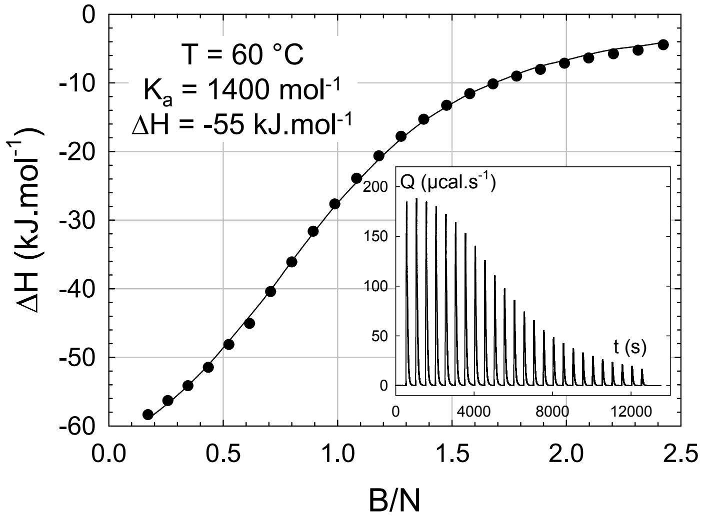

Figure S7. Isothermal calorimetric titration (T= 60 °C) of a **P(DMA-N1)** aqueous solution ([N]=0.4 mM) with **B** ([B]=30 mM).

Thermodynamic equilibrium of mono-blue box complexes

Starting from the previous equation {S1}, and defining $[N]_T$ and $[B]_T$ as the initial concentrations of naphthalene units and blue box molecules, it comes in stoichiometric conditions:

$$[N]_T = [B]_T \text{ and } [N]_{eq} = [B]_{eq}\text{, then } K_a = [NB]_{eq} \big/ [N]_{eq}^2$$

As the total concentration of $[N]_T = [NB]_{eq} + [N]_{eq}$ then $K_a[N]_{eq}^2 + [N]_{eq} - [N]_T = 0$

$$\frac{[NB]_{eq}}{[N]_T} = 1 - \frac{\sqrt{1+4K_a[N]_T} - 1}{2K_a[N]_T} \qquad \{S4\}$$

From equations {S3-S4}, the temperature dependence of the equilibrium constant (K_a) and the relative fraction of complexed naphthalene calculated in stoichiometric conditions for various initial naphthalene concentrations ($[N]_T=[B]_T$) has been plotted in **Figure S8**.

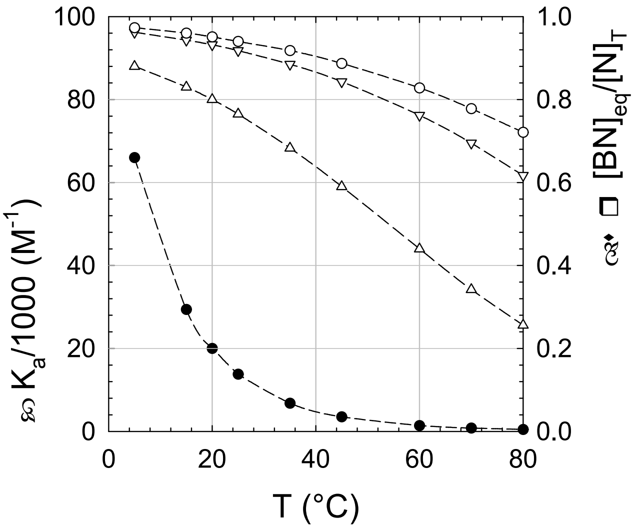

Figure S8

Temperature dependence of the equilibrium constant (K_a ☙) and relative fraction of complexed naphthalene ($[BN]_{eq}/[N]_T$) calculated in stoichiometric conditions for various initial naphthalene concentrations ($[N]_T=[B]_T$):
1mM (❒; $C_p\cong1$ wt%),
10 mM (♦; $C_p\cong10$ wt%) and
20 mM (❧; $C_p\cong20$ wt%).

Di-blue box complexes

Isothermal Titration Calorimetry

A similar titration, performed at 25 °C with di-blue box (**BB**) is given in **Figure S9**.

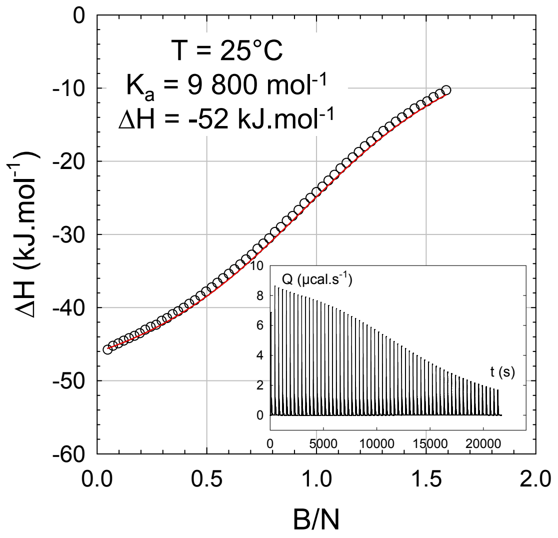

Figure S9

Isothermal calorimetric titration (T=25 °C) of a P(DMA-N1) aqueous solution ([N]=0.63 mM) with di-CBPQT^{4+} ([B]=4.3 mM).

It shows similar enthalpy (ΔH ≅ -52 kJ/mol) and stoichiometry (B/N≅1) as well as an equilibrium constant K_a=9800 mol^{-1} which quantitatively in good agreement with the value that can be extrapolated at the same temperature with the mono-blue box (K_a=13800 mol^{-1}; see **Figure S8**).

Thermodynamic equilibrium of di-blue box complexes

As the complex formation between di-blue box (**BB**) and naphthalene groups (**N**) is labile in nature, there is a distribution between different states that can be described according to the following equilibria and equations:

$$N + BB \rightleftharpoons NBB \qquad \text{with } K_1 = \frac{[NBB]_{eq}}{[N]_{eq}[BB]_{eq}} \qquad \{S5\}$$

$$NBB + N \rightleftharpoons NBBN \qquad K_2 = \frac{[NBBN]_{eq}}{[N]_{eq}[NBB]_{eq}} \qquad \{S6\}$$

where $[N]_{eq}$, $[BB]_{eq}$, $[NBB]_{eq}$ and $[NBBN]_{eq}$ are the equilibrium concentrations of naphthalene groups, uncomplexed di-blue box molecules, mono- and di-coordinated blue box, respectively.

If $[N]_T$ and $[BB]_T$ are the initial concentrations of naphthalene units and di-blue box molecules, it comes :

$$[BB]_T = [BB]_{eq} + [NBB]_{eq} + [NBBN]_{eq} \qquad \{S7\}$$

$$[BB]_T = [BB]_{eq}\left(1 + K_1[N]_{eq} + K_1K_2[N]_{eq}^2\right) = [BB]_{eq}\Sigma \qquad \{S8\}$$

$$\text{with } \Sigma = \left(1 + K_1[N]_{eq} + K_1K_2[N]_{eq}^2\right) \cong \left(1 + K_1[N]_{eq} + K_1^2[N]_{eq}^2\right) \qquad \{S9\}$$

assuming that K_1=K_2, i.e. the equilibrium association constants are the same for the mono- and di- complexes. From the previous equations, the equilibrium concentrations of BB species can be calculated as follows:

$$[BB]_{eq} = [BB]_T/\Sigma \qquad \{S10\}$$

$$[NBB]_{eq} = K_1 [BB]_T [N]_{eq} / \Sigma \qquad \{S11\}$$

$$[NBBN]_{eq} = [BB]_T K_1 K_2 [N]_{eq}^2 / \Sigma = [BB]_T K_1^2 [N]_{eq}^2 / \Sigma \qquad \{S12\}$$

with $[N]_{eq} = [N]_T - [NBB]_{eq} - 2[NBBN]_{eq}$ {S13}

The corresponding equilibrium concentrations can be calculated graphically as shown in **Figure S10** for a given concentration $[BB]_T$, the concentration of naphthalene units being the variable or plotted versus the complex stoichiometry by working at a fixed concentration of Naphthalene units $[N]_T$.

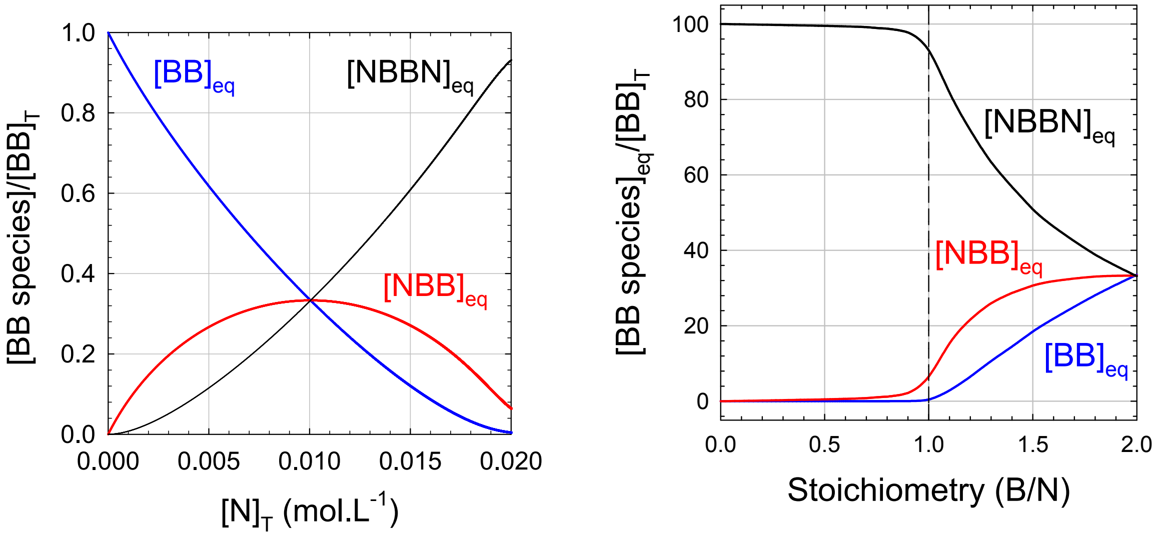

Figure S10. Equilibrium concentrations of **BB** species calculated with an equilibrium constant $K_1=2.10^4$ M^{-1} at T=20 °C: **(left)** $[B]_T=0.01$ mol/L, **(right)** $[N]_T=0.02$ mol/L.

^{1}H NMR characterization of host-guest complexes in aqueous solution.

The formation of host-guest complexes between naphthalene pendant groups of P(DMA-N1) (Cp=10 wt%) and BB molecules has been monitored by ^{1}H NMR (**Figure S11).** Qualitatively, we can notice that while the characteristic resonance of the uncomplexed $H_{3/7}$ protons ($\delta \cong 7.0$ ppm) of **P(DMA-N1)** is observable for B/N=0.5, it totally disappears in stoichiometric conditions (B/N=1). Conversely, the signals corresponding to H_β ($\delta \cong 8.3$ ppm) protons of free host molecules becomes observable only above the stoichiometry; here for B/N=1.5.

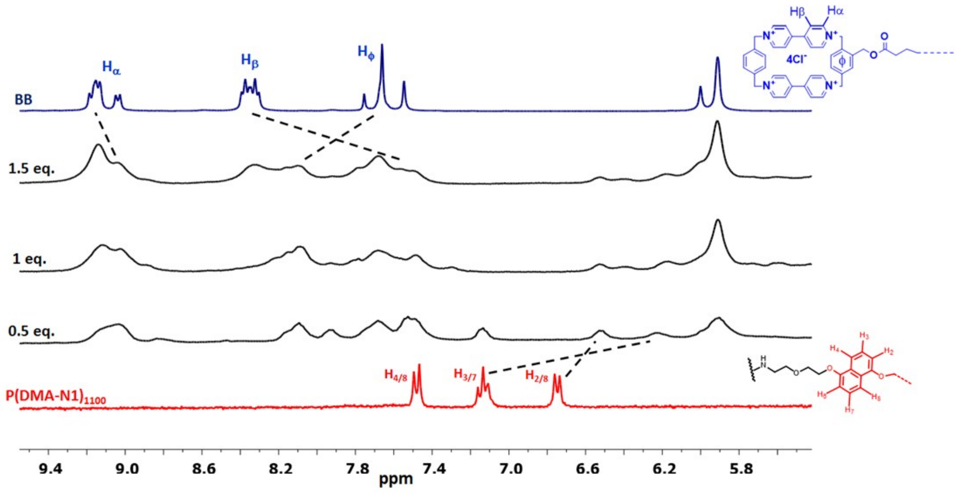

Figure S11. Partial ^{1}H NMR spectra of **P(DMA-N1)** (Cp=10 wt%) with added BB (T=20 °C): B/N=0.5 (a), 1 (b) and 1.5 (c).

Rheological behavior

Well above the gel point, the viscoelastic behavior of supramolecular polymer hydrogels can be well described using a Maxwell model characterized by a plateau modulus G_0 and a single relaxation time (**Figure S12**).

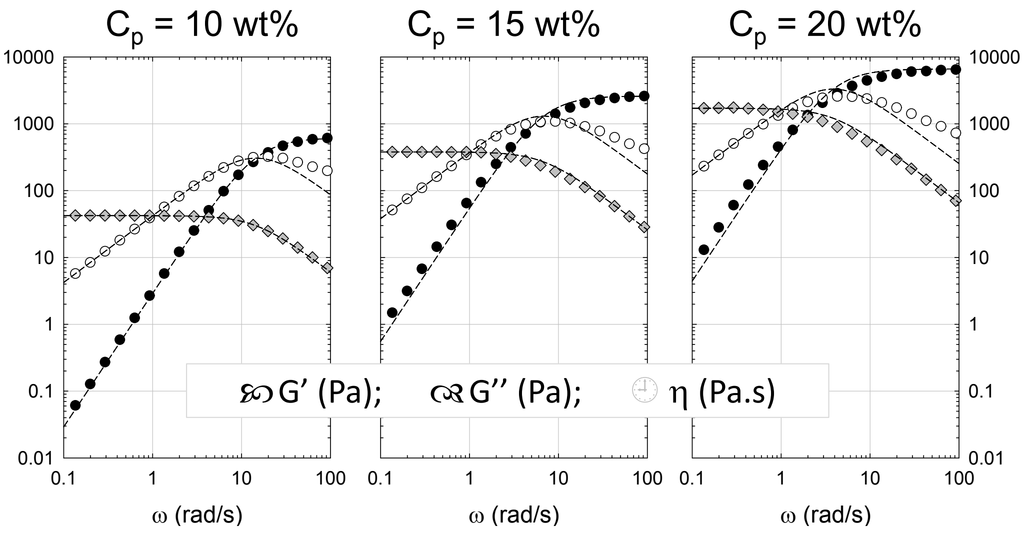

Figure S12 : Viscoelastic properties of **P(DMA-N1)** formulations studied in stoichiometric conditions (B/N=1) at T=5 °C. Experimental data are fitted using single Maxwell model.

Network formation

In the gel regime, which correspond to the situation where all the chains are involved in the network (x>1), the sticky Rouse model predicts $G_0 \approx xRTC_p/M_{n,p}$.

x, the mean number of elastically active chains per copolymer chain, is obtained by dividing the molar concentration of elastically active chains (ν) by the molar concentration of polymer chains (n_p):

$$\nu = \frac{G_0}{RT(1-2/f)} \qquad \{S14\} \qquad x = \frac{\nu}{n_P} = \frac{\nu}{C_p/M_{n,p}} \qquad \{S15\}$$

with R is the gas constant, T the temperature, f the functionality of the crosslinks (f=4 in the present system), Cp the polymer concentration and $M_{n,p}$≅110 kg/mol the number average molar mass of the copolymer.

The variation of x is highlighted in **Figure S13** where x is plotted versus the polymer concentration normalized by the molar fraction of di-coordinated N-BB-N $\left([NBBN]_{eq}/[N]_T = p_{NBBN} = p_{intra} + p_{inter}\right)$ in order to take into account the real content of potential BB cross-linkers independently of the stoichiometry.

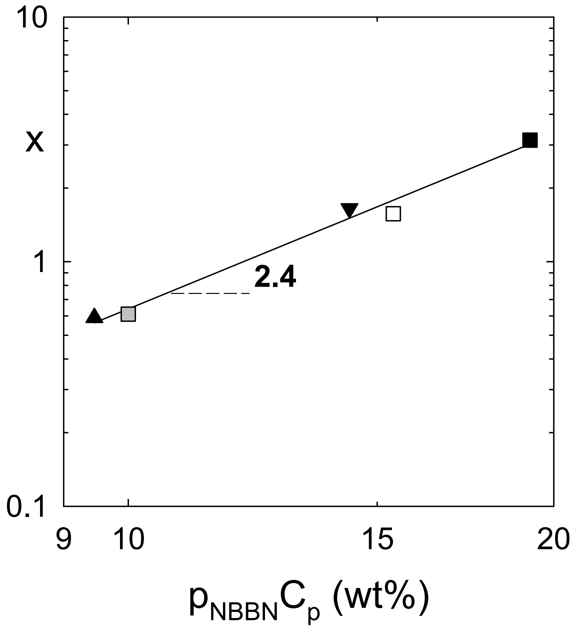

Figure S13

Variation of the mean number of elastically active chains per copolymer chain (x) of **P(DMA-N1)/BB** formulations as a function of the fraction of di-coordinated N-BB-N complexes (p_{NBBN}) times the polymer concentration (C_p).
Black symbols hold for stoichiometric conditions (B/N=1), grey for B/N=1.5 and white for B/N=0.5:
Cp= 10 wt% (□), 15 wt% (❑)
and 20 wt%(○○○).

A common behaviour is obtained for all the formulations, regardless of the stoichiometry, with a strong concentration dependence of x ($x \approx (p_{NBBN}C_p)^{2.4}$). Similarly the logarithmic representation of the fraction of inter-chain bounds with respect to the normalized concentration (**Figure S14**) demonstrates clearly the transformation from intramolecular bond into intermolecular ones: $p_{\mathrm{int}er} \approx (p_{NBBN}C_p)^{1.3}$.

$p_{\mathrm{int}er} = N_x / N_n$, the fraction of interchain bonds, is the ratio between the mean number of cross-links per copolymer chain ($N_x = x + 1$) and the total number of naphthalene groups per polymer chain (N_n).

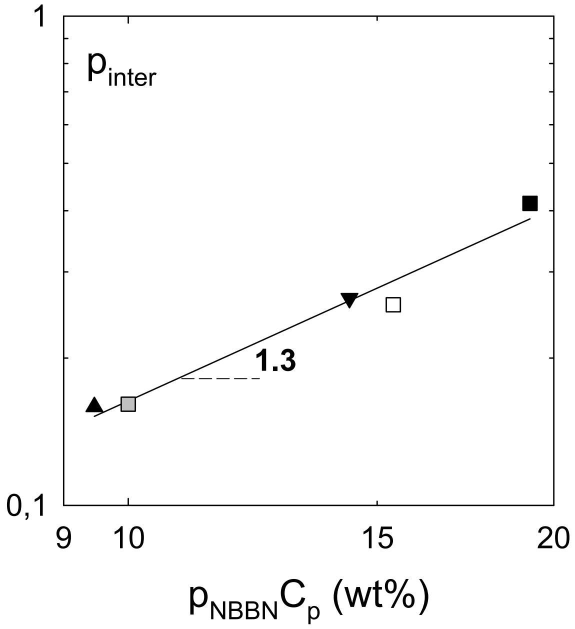

Figure S14

Variation of the fraction of inter-chain bounds (p_{inter}) of **P(DMA-N1)/BB** formulations as a function of the fraction of di-coordinated N-BB-N complexes (p_{NBBN}) times the polymer concentration (C_p). Black symbols hold for stoichiometric conditions (B/N=1), grey for B/N=1.5 and white for B/N=0.5:
Cp= 10 wt% (□), 15 wt% (❑)
and 20 wt%(○○◉).

References

[1]. L. Sambe, V. R. de La Rosa, K. Belal, F. Stoffelbach, J. Lyskawa, F. Delattre, M. Bria, G. Cooke, R. Hoogenboom, P. Woisel, Angew. Chem. Int. Ed. 2014, 53, 5044-5048.