## **Supporting Information**

## Multivalency in Healable Supramolecular Polymers: The Effect of

Supramolecular Cross-Link Density on the Mechanical Properties and

## Healing of Non-Covalent Polymer Networks

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SI Figure 1. <sup>1</sup>H NMR spectrum of divalent pyrenyl-terminated polymer 1.



SI Figure 2. <sup>13</sup>C NMR spectrum of divalent pyrenyl-terminated polymer 1.



**SI Figure 3.** MALDI-TOF MS of divalent pyrenyl-terminated polymer 1, showing peak intervals of 44 Da, corresponding to the ethylenoxy repeat unit.



**SI Figure 4.** DSC thermogram (second heating scan) of divalent pyrenyl-terminated polymer 1, showing the glass transition  $T_{\rm g}$ , cold crystallisation  $T_{\rm cc}$ , and melting point  $T_{\rm m}$ .



SI Figure 5. <sup>1</sup>H NMR spectrum of trivalent pyrenyl-terminated polymer 2.



SI Figure 6. <sup>13</sup>C NMR spectrum of trivalent pyrenyl-terminated polymer 2.



**SI Figure 7.** MALDI-TOF MS of trivalent pyrenyl-terminated polymer **2** showing peak intervals of 44 Da, corresponding to the ethyleneoxy repeat unit.



SI Figure 8. DSC thermogram of trivalent pyrenyl-terminated polymer 2 showing only a  $T_g$  for this material.



To a suspension of 1,4,5,8-naphthalenetetracarboxylic anhydride 7 (1.5 g, 5.6 mmol) in dry DMAc (10 ml) and toluene (2 ml) was added dropwise a solution of Jeffamine D-400 **8** (1.20 g, 2.7 mmol), 2,2'-(ethylenedioxy)bis(ethylamine) **9** (0.48 g, 2.7 mmol) and 2-ethyl hexylamine **10** (0.07 g, 0.6 mmol) in dry DMAc (40 mL). The solution was heated to 135 °C for 18 hours before cooling to room temperature. The solution was then precipitated into diethyl ether (400 mL) and filtered. The crude product was then subjected to Soxhlet extraction with diethyl ether for 5 hours and dried to yield a tan powder **6** (1.90 g, 59 %); IR (ATR)  $\nu/\text{cm}^{-1}$  3317, 2928, 2169, 1706, 1661, 1452, 1333, 1243; <sup>1</sup>H NMR (400 MHz/CDCl<sub>3</sub>)  $\delta$  ppm: 8.79 (8H, s), 5.52 (1.5H, m), 4.49 (7H, s), 4,20-3.30(28H, br), 1.92 (0.2H, br) 1.57 (4H, d, *J* = 6.0 Hz), 1.45-1.05 (16H, br), 0.94 (0.8H, t, *J* = 7.5 Hz), 0.87 (0.6H, t, *J* = 6.5 Hz); <sup>13</sup>C NMR (100 MHz/CDCl<sub>3</sub>)  $\delta$  ppm: 164.0, 131.9, 126.0, 74.7, 72.5, 71.7, 69.6, 68.0, 49.9, 39.6, 30.7, 28.6, 23.2, 14.4, 10.1; GPC (DMF/LiBr, 0.1M)  $M_n$  = 2242 Da,  $M_w$  = 4192 Da, PDI = 1.87.

SI Figure 9. Preparation of chain-folding polydiimide 6



SI Figure 10. <sup>1</sup>H NMR spectrum of chain-folding polydiimide 6.



SI Figure 11. <sup>13</sup>C NMR spectrum of chain-folding polydiimide 6.



**SI Figure 12.** DSC thermogram of chain-folding polydiimide **6** showing the  $T_{\rm g}$  of the soft block (Jeffamine D-400) at 70.2 °C and of the hard block (chain-folding diimide tweezer) at 175.6 °C.



SI Figure 13. UV-Vis spectra of the divalent polymer blend [1+6], and of its separate components, at room temperature and a concentration of  $3 \times 10^{-3}$  mol dm<sup>-3</sup>. Note the charge transfer band at 535 nm in the spectrum of the blend.



SI Figure 14. UV-Vis spectra of the trivalent polymer blend [2+6] at room temperature and a concentration of  $3 \times 10^{-3}$  mol dm<sup>-3</sup>, showing charge transfer band at 535 nm.



**SI Figure 15.** Solutions of pyrene terminated divalent polyer 1, chain-folding polydiimide 6, and an equimolar solution (in terms of interacting sub-units) of [1+6] in chloroform, at 0 °C, 25 °C and 55 °C. Development of a deep red colour on blending is evident, and the temperature dependant nature of this charge-transfer absorption is exemplified by UV-vis spectroscopy over range 0 to 50 °C.



SI Figure 16. Pyrene terminated trivalent polyer (2), chain-folding polydiimide (6) and an equimolar solution blend of [2 + 6] in chloroform at 0 °C, 25 °C and 55 °C showing the temperature dependent nature of the interaction.



**SI Figure 17.** Fluorescence spectra in chloroform of divalent pyrenyl polymer **1**, which exhibits both monomer and excimer emissions, and of the chain-folding diimide **6**, which shows no fluorescence. Supramolecular blends of complementary polymers **1** and **6** show fluorescence quenching. Solutions were  $1 \times 10^{-3}$  M with respect to binding residues.



**SI Figure 18.** Fluorescence spectrum of the trivalent pyrenyl polymer **2** which exhibit both monomer and excimer emissions, whilst the chain-folding diimide **6** does not fluoresce. Supramolecular blends between complementary polymers [2 + 6] show fluorescence quenching. All solutions in chloroform, at  $1 \times 10^{-3}$  mol dm<sup>-3</sup> with respect to binding residues.



**SI Figure 19.** Partial <sup>1</sup>H NMR spectra of: (top) polydiimide **6**; (centre) 1:1 blend of **1** and **6**; (bottom) divalent pyrenyl PEG (**1**) showing the effect of  $\pi$ - $\pi$  stacking interactions in terms of an upfield shift in the naphthalenyl protons, giving three distinct populations defined by the binding sequence within the polydiimide **6**. Pyrenyl resonances also shift upfield, and broaden as a result of the approach to slow exchange on the NMR timescale.



**SI Figure 20.** <sup>1</sup>H NMR spectra of: (top) polydiimide 6; (centre) 1:1 blend of 2 and 6, (bottom) trivalent pyrenyl PEG 2. Evidence for  $\pi$ - $\pi$  stacking is given by an upfield shift in the naphthalenyl resonances, which also split into three distinct populations defined by the binding sequence within the polydiimide 6. Pyrenyl resonances are also seen to shift upfield, and to broaden as a result of the approach to slow exchange on the NMR timescale.



SI Figure 21. Variable temperature <sup>1</sup>H NMR spectra of the divalent polymer blend [1+6], providing evidence for disengagement of the  $\pi$ - $\pi$  stacking interactions with increasing temperature.



SI Figure 22. Variable temperature <sup>1</sup>H NMR spectra of trivalent polymer blend [2+6], the downfield shifts providing evidence for disengagement of  $\pi$ - $\pi$  stacking interactions with increasing temperature.



SI Figure 23. Images of films cast from blends between the chain-folding polydiimide (6) and the unfunctionalised PEG pre-polymers 4 (a) and 5 (b) as a control experiment. The unfunctionalised divalent blend (4+6) formed a pealable film which was brittle, whilst the unfunctionalised trivalent polymer blend (5+6) formed an extremely fragile film which was unable to be removed from the casting plate.



**SI Figure 24**. Small angle X-ray scattering as a function of the temperature for the divalent blend [1+6]. The strong scattering signal at 1/d = 0.005-0.020 Å<sup>-1</sup> is indicative of a nanophase-separated morphology. Upon heating, the population of smaller domains increases.



SI Figure 25. Small angle X-ray scattering from the trivalent polymer blend [2+6] as a function of temperature. The intense scattering signal at 1/d = 0.005-0.020 Å is indicative of a nanophase separated morphology in which the degree of phase separation increases with increasing temperature.



**SI Figure 26.** Original ESEM images of the healable polymer blend [2+6] at (a) 25 °C, (b) 100 °C, and (c) 200 °C, showing a homogenous blend and the healability of the polymer at elevated temperatures. Scale bar represents 300  $\mu$ m. Contrast-enhanced, false colour versions of these micrographs are shown as Figure 6 in the main text.



**SI Figure 27a.** Original ESEM images of the healable polymer blend [1+6] at (a) 25 °C, (b) 100 °C, and (c) 200 °C showing a homogenous blend and the healability of the polymer at elevated temperatures. Scale bar represents 500  $\mu$ m.



**SI Figure 27b.** Contrast-enhanced, false-colour images corresponding to those shown in SI Figure 27a.



SI Figure 28. ESEM images of the control polymer blend [4+6] at (a) 25 °C, and upon heating to (b) 100 °C, and (c) 200 °C demonstrating the non-healing nature of the material. Scale bar represents 500  $\mu$ m.

$$E = \frac{3\rho RT}{M_c}$$
 Equation 1

**SI Figure 29.** Relationship between Average molecular weight between cross-links ( $M_c$ ), tensile modulus (E) and the density of the polymer blend ( $\rho$ ). The density of the divalent polymer blend [1+6] was 1.23 g cm<sup>-3</sup>, whilst the density of the trivalent polymer blend [2+6] was 1.37 g cm<sup>-3</sup>.



**SI Figure 30.** Modulus of toughness over 3 break/heal cycles for the divalent polymer blend [1+6], showing a progressive decrease to 11% healing efficiency on the third heal cycle.



**SI Figure 31.** Modulus of toughness over 3 break/heal cycles for the trivalent polymer blend [2+6] showing a progressive decrease to 15% healing efficiency on the third heal cycle.



SI Figure 32. TGA thermogram of the divalent polymer blend [1+6].



SI Figure 33. TGA thermogram of the trivalent polymer blend [2+6].



SI Figure 34. DSC thermogram of divalent polymer blend [1+6] showing a  $T_g$  at 86.96 °C, allowing healing above this temperature.



**SI Figure 35.** DSC thermogram of trivalent polymer blend [2+6] showing the  $T_g$  at 105.1 °C. This transition provided guidance for establishing an appropriate healing temperature.