Supporting Information

Syntheses

[p-(6-Methyl-1,2,4,5-tetrazine-3-yl)phenyl]acetic acid (Tz-COOH)

Tz-COOH was synthesised according to a modified literature precedent.¹ 4-Cyanophenylacetic acid (0.90 g, 5.58 mmol), zinc triflate (1.02 g, 2.79 mmol), acetonitrile (2.91 mL, 55.8 mmol) and hydrazine monohydrate (13.6 mL, 279 mmol) were mixed in a sealed ampoule and placed in an oil bath at 60 °C for 24 h behind a blast shield, after which it was allowed to cool to room temperature and opened carefully due to the pressure build-up during the reaction. The resulting orange mixture was added to sodium nitrite (7.71 g, 112 mmol) in 25 mL water, after which conc. HCl was added extremely slowly, diluting with water as necessary (final volume ca. 500 mL) to control the resulting effervescence and being careful of the evolved nitrous gases, until pH 3 was reached. The aqueous phase was extracted with EtOAc (3 x 200 mL), then the organic phase washed with H_2O and brine and dried over MgSO₄. The product was isolated by flash column chromatography (15:1 CH₂Cl₂/MeOH, R_f 0.20) as a pink solid (234 mg, 1.01 mmol, 18% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.49 (2H, d, J = 8.3 Hz), 7.48 (2H, d, J = 8.3 Hz), 3.74 (2H, s), 3.07 (3H, s). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 176.0 (u), 167.4 (u), 164.0 (u), 138.1 (u), 131.1 (u), 130.5 (dn), 128.4 (dn), 41.0 (u), 21.3 (dn).



Scheme S1. Synthesis of TzCOOEt

Ethyl [p-(6-methyl-1,2,4,5-tetrazin-3-yl)phenyl] acetate (Tz-COOEt)

Tz-COOH (120 mg, 0.521 mmol), EDCI-HCl (99.9 mg, 0.521 mmol) and DMAP (8.49 mg, 0.0695 mmol) were dissolved in EtOH (20 mL) under a N₂ atmosphere, and the mixture stirred at room temperature for 24 h. The residual EtOH was removed *in vacuo*, the crude residue dissolved in CH₂Cl₂ (20 mL), and washed with water (2 x 20 mL), brine (20 mL) and saturated NaHCO₃ (20 mL), and dried over MgSO₄. The solvent was removed *in vacuo* and the product isolated by flash column chromatography (CH₂Cl₂, R_f 0.3) as a bright pink solid (112 mg, 0.434 mmol, 83% yield). HRMS (ESI, [M+Na]⁺) *m/z*: predicted 281.1014, found 281.1009. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.55 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 2H), 3.09 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 171.0 (u), 167.4 (u), 164.1 (u), 139.1 (u), 130.8 (u), 130.4 (dn), 128.3 (dn), 61.3 (u), 41.5 (u), 21.3 (dn), 14.3 (dn). IR *v* (cm⁻¹): 2927, 1723, 1616, 1472, 1402, 1368, 1339, 1223, 1167, 1090, 1017, 889, 800, 755, 689. Elemental analysis: expected C 60.45, H 5.46, N 21.69, O 12.39, found C 60.79, H 5.57, N 20.21.

¹ J. Yang, M. R. Karver, W. Li, S. Sahu and N. K. Devaraj, Angew. Chem., Int. Ed., 2012, 51, 5222-5225.

Control polymer P0 synthesis

Linear PS(Nb) P1 was dissolved in DMF at a concentration of 0.01 M of Nb groups, and **TzCOOEt** (1 eq. relative to Nb groups on the polymer) added. The solution was heated to 80 °C and stirred for 24 h. The polymer was isolated by precipitation from cold MeOH as a powdery orange solid.



Scheme S2. Synthesis of functionalised, uncrosslinked, control polymer P0



Figure S1. ¹H (top) and ¹³C (bottom) NMR spectra (CDCl₃) of Tz–Tz crosslinker



Figure S2. ¹H (top) and ¹³C (bottom) NMR spectra (CDCl₃) of dummy crosslinker Tz-COOEt



Figure S3. SEC traces (dw/dlogM vs. M) for linear P1, control polymer P0 and the result of heating P1 for 24 h in DMF



Figure S4. AFM height (left) and phase (right) images of SCPN P1



Figure S5. AFM control experiments (Z-height in both cases)



Figure S6. TEM images on GO of SCPNs P1



Figure S7. Example measurement of SCPN P1 diameter using greyscale change in the TEM images



Figure S8. Histogram of SCPN P1 diameters measured by TEM



Figure S9. SANS data for linear P1, SCPN P1 and control P0



Figure S10. Kratky plot (left) and logarithmic plot of the Porod region of the SANS data (right)



Figure S11. SANS Guinier plots to calculate *R*_g for the linear and SCPN P1 and control polymer P0



Figure S12. DLS number-average diameters at varying temperature in CHCl₃ (1 mg/mL)