

Mutual Binding of Polymer End-Groups by Complementary π - π -Stacking: A Molecular "Roman Handshake"

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Analytical Techniques, Instrumentation and Materials

NMR Spectroscopy.

Proton and ^{13}C NMR spectra were recorded at 296 K on either a Bruker AMX 400 MHz, Bruker Nanobay 400 MHz, Bruker Avance III 500 MHz or Bruker Avance III 700 MHz spectrometer. Spectrometers operated at either 400, 500 or 700 MHz for ^1H spectra and 100, 125 or 175 MHz for ^{13}C spectra. Chemical shifts are given in δ (ppm), referenced to either tetramethylsilane (TMS) or residual solvent resonances.

Mass Spectrometry.

Conventional mass spectra were recorded using a ThermoFisher Orbitrap XL (ESI) instrument. Polymer MS data were acquired using a Bruker Ultraflex ToF/ToF instrument, calibrated with PEG 1000 (Sigma-Aldrich) and an in-house peptide calibration standard. Samples were prepared by mixing 1 μL of saturated aqueous 2,5-dihydroxybenzoic acid, 0.5 μL of 1 M aqueous KCl and 0.5 μL of a 10 - 50 mg/mL aqueous polymer solution directly on a stainless steel target, and drying in air. Spectra were obtained by summing the data from 500 - 600 laser shots at various positions on the sample.

FT-IR Spectroscopy.

Infra-red spectra were measured using either a Perkin-Elmer 1720-X, Perkin-Elmer FT-IR Spectrum RX I or Perkin-Elmer Spectrum 100 series spectrometer. Spectra were recorded either as thin films cast from appropriate solvents, or as KBr discs.

UV-visible spectroscopy.

Spectra were acquired on a Cary 300 Bio UV-visible spectrophotometer at 21 $^\circ\text{C}$.

Differential Scanning Calorimetry (DSC).

Melting points and glass transition temperatures were measured by DSC using either a TA Instruments Q2000 or Mettler DSC823^o instrument. Analyses were carried out under a nitrogen atmosphere at a heating rate of either 10 $^\circ\text{C}$ or 20 $^\circ\text{C min}^{-1}$ using 40 μL aluminium sample crucibles.

Single Crystal X-ray Diffraction

Single crystal X-ray data for **3** were collected at the Advanced Light Source, Berkeley, California. Structure solution and refinement were carried out using the SHELXL suite of programmes.

Transmission electron microscopy (TEM)

TEM samples were prepared by direct dissolution of the supramolecular polymer in Nanopure water at 1 mg/mL and then stirring overnight. The samples were diluted to 0.2 mg/mL and dialysed against Nanopure water using 12,000 - 14,000 MW cut-off dialysis tubing. The solutions were then drop-deposited onto GO-TEM grids, dried, and imaged unstained.¹ The images were recorded on a JEOL 2000FX TEM equipped with a Gatan Orius Digital camera operating at 200 kV.

Gel permeation chromatography

GPC data were acquired on either a Polymer Laboratories PL-GPC 220 at 40 °C in DMF, or in chloroform using an Agilent 390MDS system fitted with 1 × PLgel 5 µm guard column and 2 × PLgel 5 µm mixed D columns using a differential refractive index detector. The chloroform solvent was passed through a 0.22 µm hydrophobic filter immediately prior to use. Molecular weights were estimated by comparison with narrow-PDI PEG standards.

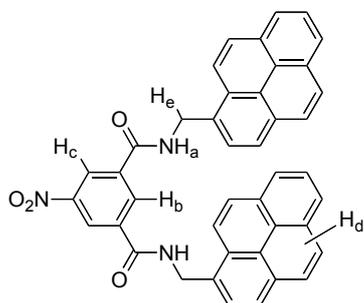
Starting materials.

Reagents and solvents were purchased from either Alfa Aesar, Aldrich or Fisher and were used as received, with the exceptions of triethylamine and dichloromethane which were dried by heating under reflux over calcium hydride for 1 hour prior to distillation under dry nitrogen. Dimethylacetamide (anhydrous grade) was used as received.

¹ J. P. Patterson, A. M. Sanchez, N. Petzetakis, T. P. Smart, T. H. Epps III, I. Portman, N.R. Wilson and R. K. O'Reilly, *Soft Matter* 2012, **8**, 3322.

Synthesis and characterisation of tweezer molecules 2, 3, and 4

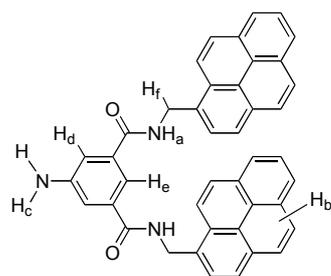
5-Nitro-*N,N'*-bis(1-pyrenemethyl) isophthalamide (A)



In a reactor fitted with a condenser and nitrogen inlet 5-nitroisophthalic acid (4.00 g, 18.95 mmol) and thionyl chloride (25.0 mL, 334.2 mmol) were heated under reflux for 4 hours. The excess thionyl chloride was then removed by evaporation under reduced pressure to give a solid residue. This residue was dissolved in chloroform (100 mL) and pyrenemethylamine hydrochloride (10.34 g, 38.84 mmol) was then added as a slurry in chloroform (50 mL). The resulting suspension was diluted with chloroform (30 mL) and triethylamine (21.1 mL, 151.4 mmol) was subsequently added slowly with stirring over 5 min. After stirring for 24 h the reaction mixture was filtered and the filtrand was washed with chloroform (75 mL) and then with hot water (150 mL). The insoluble fraction was again filtered and the solid was washed with water and dried at 120 °C in a vacuum oven to yield the product, **A**, as an orange solid (10.22 g, 85%).

M.p. = 315 °C; HRMS (ESI): m/z calcd. for $C_{42}H_{26}O_4N_3$, 636.1918; found, 636.1895; 1H NMR (DMSO- d_6), 400 MHz: δ (ppm) = 9.74 (br t, J = 5.5 Hz, 2H_a), 8.93 (t, J = 1.4 Hz, 1H_b), 8.90 (d, J = 1.4 Hz, 2H_c), 8.49 (d, J = 9.3 Hz, 2H_d), 8.32-8.25 (m, 8H_d), 8.17-8.05 (m, 8H_d), 5.28 (d, J = 5.4 Hz, 4H_e), ^{13}C NMR (DMSO- d_6), 100 MHz: δ (ppm) = 164.0, 148.2, 136.2, 133.0, 132.6, 131.1, 130.6, 130.6, 128.6, 128.0, 127.7, 127.5, 127.4, 126.6, 125.7, 125.6, 125.1, 124.8, 124.4, 124.3, 123.6, 41.8. FT-IR (KBr disc): 3307 (amide ν N-H), 3084 (aromatic ν C-H), 3038 (aromatic ν C-H), 1646 (amide ν C=O), 1526 (nitro ν N=O), 1346 (nitro ν N=O), 1274, 1183, 842 cm^{-1} (aromatic δ C-H).

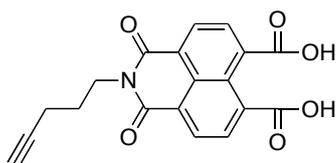
5-Amino-*N,N'*-bis(1-pyrenemethyl) isophthalamide (B)



To a reactor fitted with a magnetic stirrer and septum a suspension of 5-nitro-*N,N'*-bis(pyrenemethyl) isophthalamide (**A**, 8.00 g, 12.55 mmol) and 5% wt palladium on carbon (5.34 g, 1.254 mmol) in ethanol (250 mL) and DMF (600 mL) was stirred vigorously under an atmosphere of hydrogen (1 bar) for 24 hours. The

resulting mixture was filtered through Celite filter-aid and the insoluble material was washed with hot DMF (300 mL). The Celite filter cake was washed in a further portion of hot DMF (200 mL) to extract any remaining product and then the resulting slurry was again filtered through Celite. After combination, the filtrate and washings were concentrated under vacuum to ca. 40 mL. The resulting slurry was added to water to fully precipitate the product, which was again collected by filtration. Water (150 mL) was used to wash the filtrand and after drying at the pump the product was dried in a vacuum oven at 120 °C to give **B** as an off-white solid (7.263 g, 95%). M.p. = 337 °C, HRMS (ESI): m/z found 608.2333 $[M + H^+]$, calculated = 608.2333; 1H NMR (DMSO- d_6), 400 MHz: δ (ppm) = 9.10 (br t, $J = 5.7$ Hz, $2H_a$), 8.62 (d, $J = 7.8$ Hz, $2H_b$), 8.31-8.23 (m, $8H_b$), 8.15-8.04 (m, $8H_b$), 7.56 (t, $J = 1.1$ Hz, $1H_e$), 7.22 (d, $J = 1.1$ Hz, $2H_d$), 5.47 (br s, $2H_c$), 5.19 (d, $J = 5.5$ Hz, $4H_f$), ^{13}C NMR (DMSO- d_6), 100 MHz: δ (ppm) = 167.1, 149.2, 135.9, 133.4, 131.1, 130.7, 130.4, 128.4, 127.9, 127.7, 127.3, 127.0, 126.6, 125.6, 125.5, 125.0, 124.4, 124.3, 123.6, 115.7, 113.8, 41.3. FT-IR (Nujol): 3401 (amine ν_{N-H}), 3335 (amine ν_{N-H}), 3263 (amide ν_{N-H}), 3227 (amide ν_{N-H}), 3069 (aromatic ν_{C-H}), 3035 (aromatic ν_{C-H}), 1638 (amide $\nu_{C=O}$), 1614 (amine δ_{N-H}), 1553 (amine δ_{N-H}), 1376, 1334, 1290, 842 cm^{-1} (aromatic δ_{C-H}).

Pentynylimido dicarboxylic acid intermediate (C)

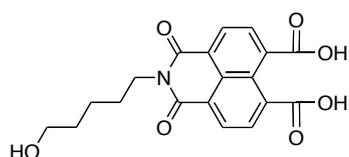


To a stirring solution of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (5.74 g, 21.5 mmol) and KOH (5.62 g, 100 mmol) in water (780 mL) was added dilute phosphoric acid (10% by volume of 85% H_3PO_4 in water) until the pH of the brown solution was 6.3. 5-Aminopent-1-yne² (2.00 g, 21.5 mmol) was added and the solution re-acidified to pH 6.3 by with dilute H_3PO_4 and the solution heated to 110 °C for 20 h. After cooling, a fine precipitate was removed by filtration and the resulting solution acidified to pH 4 with acetic acid whilst being vigorously stirred. After 1 h the cream precipitate was removed by filtration and washed with dilute acetic acid (10% v/v AcOH in water) before being dried at 60 °C overnight to give intermediate **C** as a tan powder (5.5 g, 73%). M.p. = 235 °C; FT-IR KBr disk $\nu = 3411, 2960, 2925, 1706, 1658, 1595, 1581, 1467, 1447, 1393, 1356,$

² T.-B. Yu, J. Z. Bai and Z. Guan, *Angew. Chem. Int. Ed.* 2009, **48**, 1097.

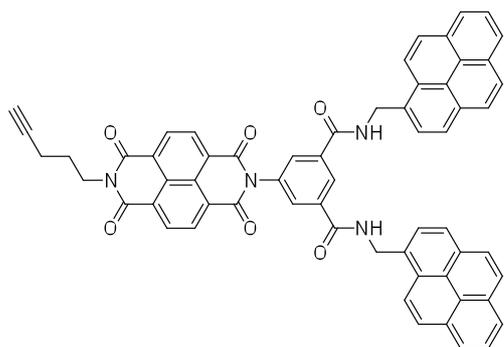
1330, 1268, 1242, 1205, 1162, 1077, 963, 875, 766; ^1H NMR (DMSO- d_6), 400 MHz: δ (ppm) = 8.56 (d, J = 7.5 Hz, 2H), 8.19 (d, J = 7.5 Hz, 2H), 4.14 (t, J = 7.0 Hz, 2H), 2.76 (t, J = 2.6 Hz, 1H), 2.29 (dt, J = 2.6 & 7.1 Hz, 2H), 1.89-1.81 (m, 2H); ^{13}C NMR (DMSO- d_6), 100 MHz: δ = 168.5, 162.9, 136.7, 130.0, 129.1, 128.5, 125.4, 124.5, 83.8, 71.3, 39.3, 26.2, 15.7.

Hydroxypentylimido dicarboxylic acid intermediate (D)



Synthesised using the procedure detailed for **C** above using: 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (4.38 g, 16.4 mmol) and 5-aminopentanol (1.69 g, 16.4 mmol) to give intermediate **D** as a tan solid (4.6 g, 76%). M.p. = 184 °C; FT-IR (KBr disk) ν = 3269, 3070, 3296, 1706, 1660, 1452, 1392, 1359, 1303, 1231, 1054, 887, 767 cm^{-1} ; ^1H NMR (DMSO- d_6), 400 MHz, δ (ppm) = 8.56 (d, J = 8.1 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H), 4.03 (t, J = 7.5 Hz, 2H), 3.40 (t, J = 6.3 Hz, 2H), 1.69-1.61 (m, 2H), 1.51-1.44 (m, 2H), 1.36-1.33 (m, 2H); ^{13}C NMR (DMSO- d_6) 100 MHz, δ = 168.9, 163.0, 137.2, 130.2, 129.2, 128.6, 125.5, 124.4, 60.6, 40.0, 32.3, 27.4, 23.1.

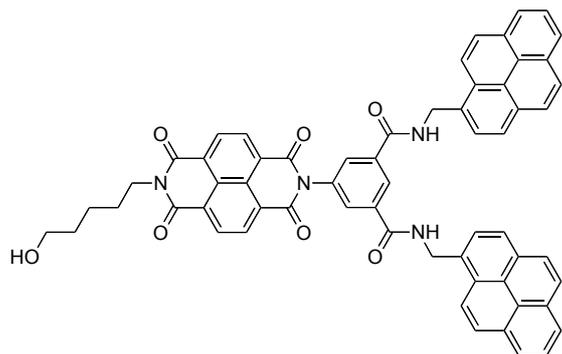
Alkynyl imido-tweezer (3)



A stirred solution of the pentynylimido dicarboxy acid intermediate **C** (100 mg, 0.285 mmol) and dipyrenyl amino tweezer **B** (173 mg, 0.285 mmol) in DMSO (4 mL) was heated to 135 °C in a sealed screw top vial for 20 h. After cooling to room temperature, the resulting brown precipitate was collected by filtration and washed sequentially with DMSO (2 \times 10 mL), MeOH (2 \times 10 mL) and diethyl ether (2 \times 10 mL) before being dried in vacuo at 120 °C overnight to give the title compound as a brown solid (220 mg, 81%). M.p. > 350 °C; FT-IR KBr disk ν = 3399, 1702, 1658, 1580, 1529, 1451, 1347, 1248, 1197, 847, 770 cm^{-1} ; ^1H NMR (DMSO- d_6), 400 MHz: δ (ppm) = 9.40 (t, J = 5.5, 2H), 8.63-8.15 (m, 7H), 8.28-7.99 (m, 18 H), 5.25 (d, J = 5.5, 4H), 4.14 (t, J = 7.1, 2H), 2.77, (t, J = 2.6, 1H), 2.46 (dt, J

= 7.0 & 2.6, 2H), 1.87 (quin, $J = 7.0$, 2H). ^{13}C NMR (DMSO- d_6), 100 MHz: δ (ppm) = 165.5, 163.3, 163.1, 133.0, 131.5, 131.1, 130.69, 130.66, 130.57, 128.6, 128.0, 127.8, 127.5, 127.4, 126.9, 126.73, 126.68, 126.5, 125.7, 125.6, 125.1, 124.4, 124.3, 123.7, 84.3, 71.9, 41.7, 26.8, 16.3. HRMS (MALDI-ToF) calcd. for $\text{C}_{61}\text{H}_{38}\text{N}_4\text{O}_6\text{Na} = 945.2689$, found = 945.2689.

Hydroxypentylyl imido-tweezer (2)

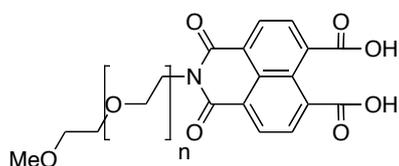


Synthesised using the above procedure with the following quantities:

Hydroxypentylimido dicarboxylic acid intermediate **D** (200 mg, 0.587 mmol) and dipyrrenyl amino tweezer **B** (357 mg, 0.587 mmol) gave **2** as a red/brown solid (420 mg, 75%). M.p. >

350 °C; FT-IR (ATR) $\nu = 2890, 1708, 1660, 1526, 1347, 1257, 849, 769 \text{ cm}^{-1}$; ^1H NMR (DMSO- d_6), 400 MHz: δ (ppm) = 9.45 (t, $J = 5.3$, 2H), 8.70-4.40 (m, 7H), 8.35-8.00 (m, 18H), 5.26 (t, $J = 5.3$, 4H), 4.40 (br, 1H), 4.08 (t, $J = 7.5 \text{ Hz}$, 2H), 3.43 (t, $J = 6.3 \text{ Hz}$, 2H), 1.68 (quin, $J=7.1$, 2H), 1.55-1.49 (m, 2H), 1.47-1.36 (m, 2H). ^{13}C NMR (DMSO- d_6), 100 MHz: δ (ppm) = 165.6, 163.3, 163.0, 136.4, 136.0, 133.0, 131.5, 131.2, 130.1, 30.7, 130.6 128.6, 128.1, 127.8, 127.5, 127.4, 127.0, 126.9, 126.7 126.6, 125.7, 125.6, 125.2, 124.5, 124.3, 123.7, 61.0, 41.7, 40.9, 32.6, 27.9, 23.6; HRMS (MALDI-ToF): calcd. for $\text{C}_{61}\text{H}_{42}\text{N}_4\text{O}_7\text{Na} = 965.2951$, found = 965.2913.

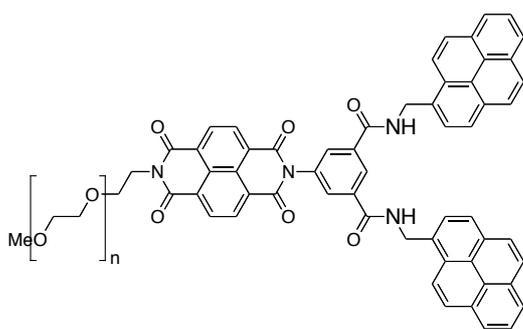
PEG₅₀₀₀ imido dicarboxylic acid intermediate (E)



To a stirring solution of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (0.050 g, 0.19 mmol) and KOH (0.052 g, 0.94 mmol) in water (50 mL) was added dilute phosphoric acid (10% by volume of 85% H_3PO_4 in water) until the pH was 6.3. Methoxy amino PEG₅₀₀₀ (0.95 g, 0.19 mmol) was added and the solution re-acidified to pH 6.3 with dilute H_3PO_4 and heated to 110 °C for 20 h. After cooling, the stirred solution was acidified to pH 4 with acetic acid and extracted with dichloromethane (5 × 50 mL). The combined

extracts were dried over MgSO_4 , filtered, and the solvent removed under reduced pressure. The resulting tan solid was dissolved in the minimum amount of chloroform, precipitated from cold diethylether, collected by filtration and dried at 40 °C overnight to give the PEG-based intermediate diacid **E** as a tan solid (0.78 g, 78%). DSC: $T_m = 61$ °C. FT-IR (ATR) $\nu = 3503, 2883, 1710, 1666, 1470, 1341, 1281, 1243, 1108, 1057, 946, 842$ cm^{-1} ; $^1\text{H NMR}$ (D_2O), 400 MHz, δ (ppm) = 8.52 (d, $J = 7.4$ Hz, 2H), 8.52 (d, $J = 7.4$ Hz, 2H), 8.10 8.52 (d, $J = 7.4$ Hz, 2H), 4.31 (m, 2H), 3.80-3.40 (m, CH_2 in PEG), 3.32 ppm (s, 3H); GPC (DMAc, PEG standards) $M_n = 5000$, PDI = 1.24; MALDI-ToF, calc. for potassium salt of 110mer = 4960.00, found 4959.97.

Imido-tweezer molecule with PEG₅₀₀₀ chain (**4**)



A stirred solution of PEG diacid **E** (525 mg, 0.100 mmol) and dipyrrenyl amino tweezer **B** (72 mg, 0.120 mmol) in DMSO (10 mL) was heated to 135 °C in a sealed screw top vial for 5 days. After cooling to room temperature, the brown solution was added dropwise to stirring chloroform (25 mL) and the resulting fine brown suspension (excess starting material **B**) was removed by filtration. The solvent was removed under vacuum and the resulting brown solid was precipitated into diethyl ether from chloroform, collected by filtration and passed through a silica plug with chloroform as eluent. The solvent was removed under reduced pressure to leave **4** as a red solid. (380 mg, 65%). DSC: $T_m = 58$ °C. FT-IR (ATR) $\nu = 2883, 1708, 1669, 1653, 1465, 1341, 1281, 1243, 1145, 1106, 1058, 961, 842$ cm^{-1} . $^1\text{H NMR}$ ($\text{DMSO-}d_6$), 400 MHz: δ (ppm) = 9.46 (t, $J = 5.2$ Hz, 2H), 8.64 (d, $J = 7.7$ Hz, 2H), 8.81 (d, $J = 7.7$ Hz, 2H), 8.48 (d, $J = 9.2$ Hz, 2H), 8.28-8.02 (m, 44H), 5.25 (d, $J = 5.2$ Hz, 4H), 4.28 (m, 2H), 3.72 – 3.30 (m, CH_2 in PEG), 3.25 (s, 3H); MALDI-ToF, calc. for potassium salt of 110mer = 5799.85, found 5799.99; GPC (DMAc, PEG standards) $M_n = 4200$, PDI = 1.31; GPC (chloroform, PEG standards) bimodal distribution with signal maxima at ca. 11,500 and 4,900 Da.

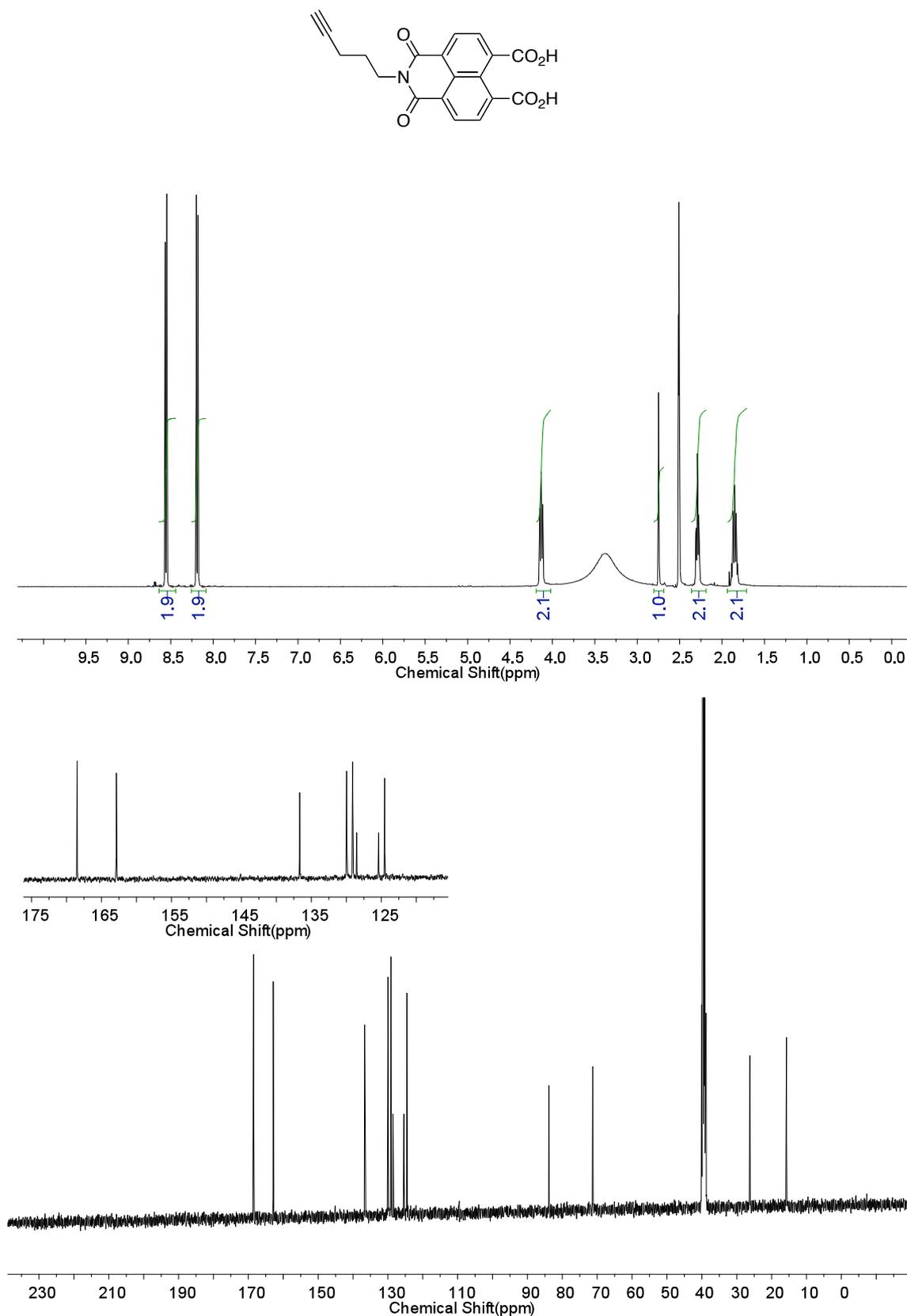


Fig. S1. ¹H and ¹³C NMR spectra of pentynylimido dicarboxylic acid **C** (*d*₆-DMSO, 400 & 100 MHz respectively).

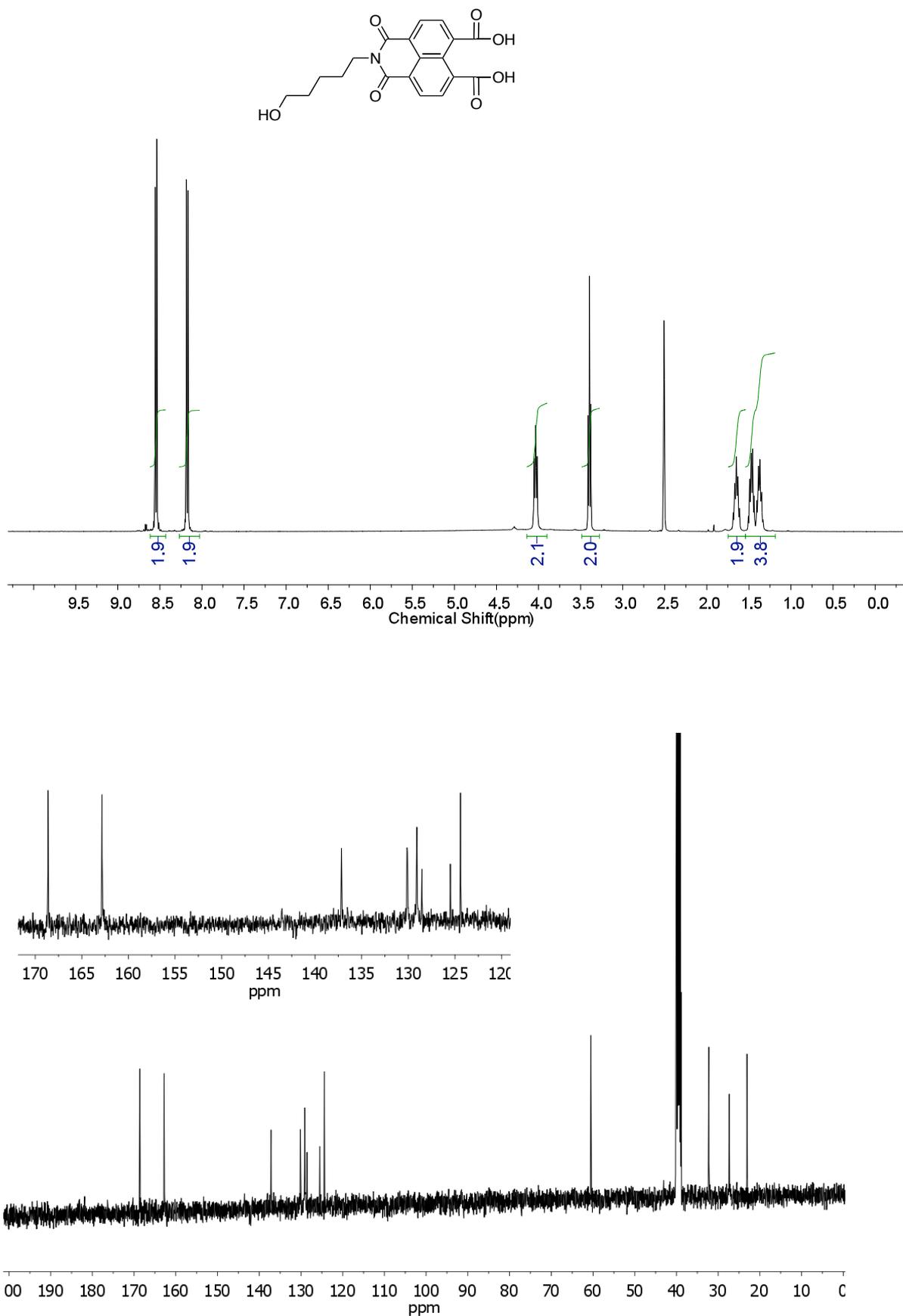


Fig. S2. ¹H and ¹³C NMR spectra of hydroxypentylimido dicarboxylic acid **D** (*d*₆-DMSO, 400 & 100 MHz respectively)

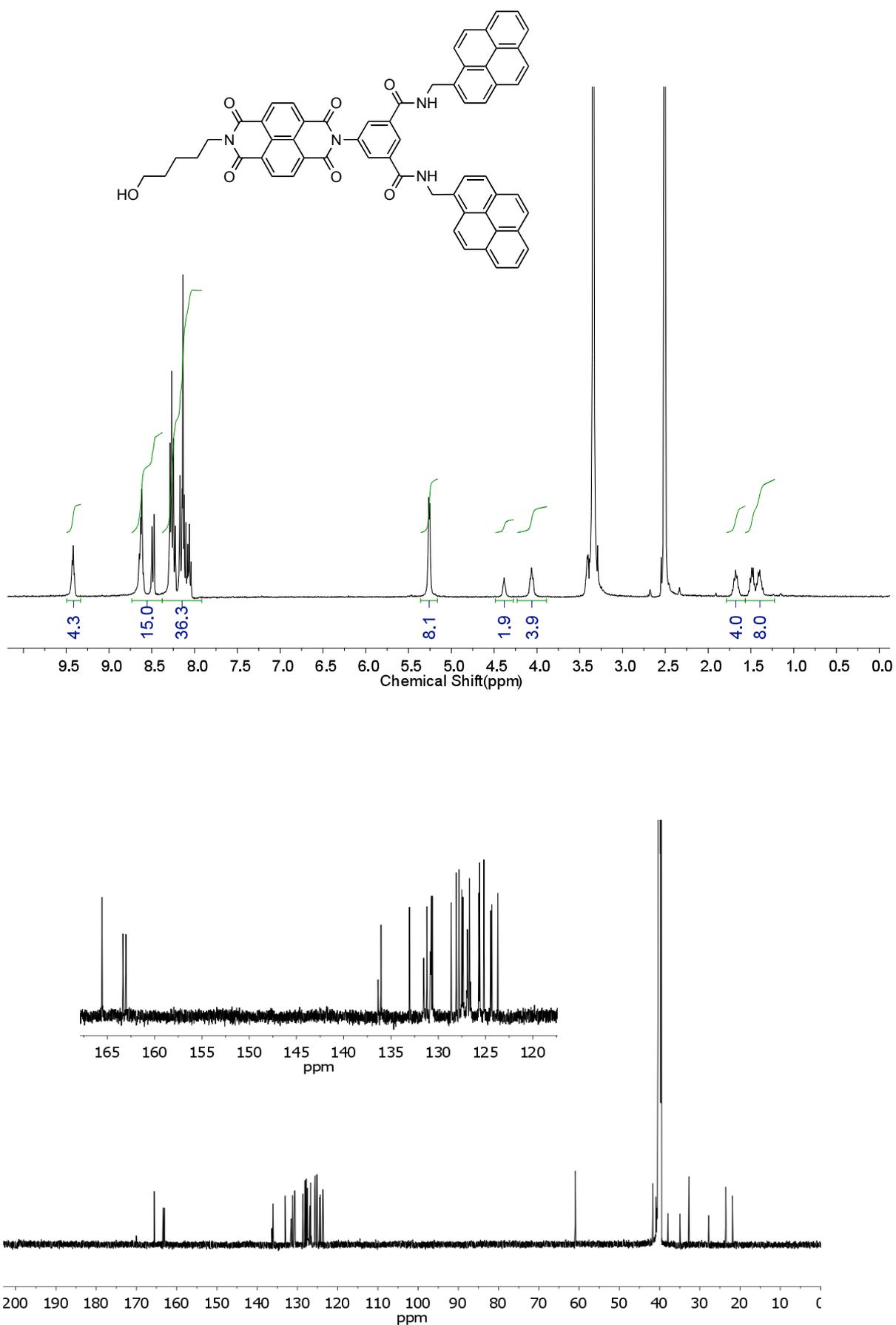


Fig. S3. ^1H and ^{13}C NMR spectra of imido-tweezer **2** (d_6 -DMSO, 400 & 100 MHz respectively)

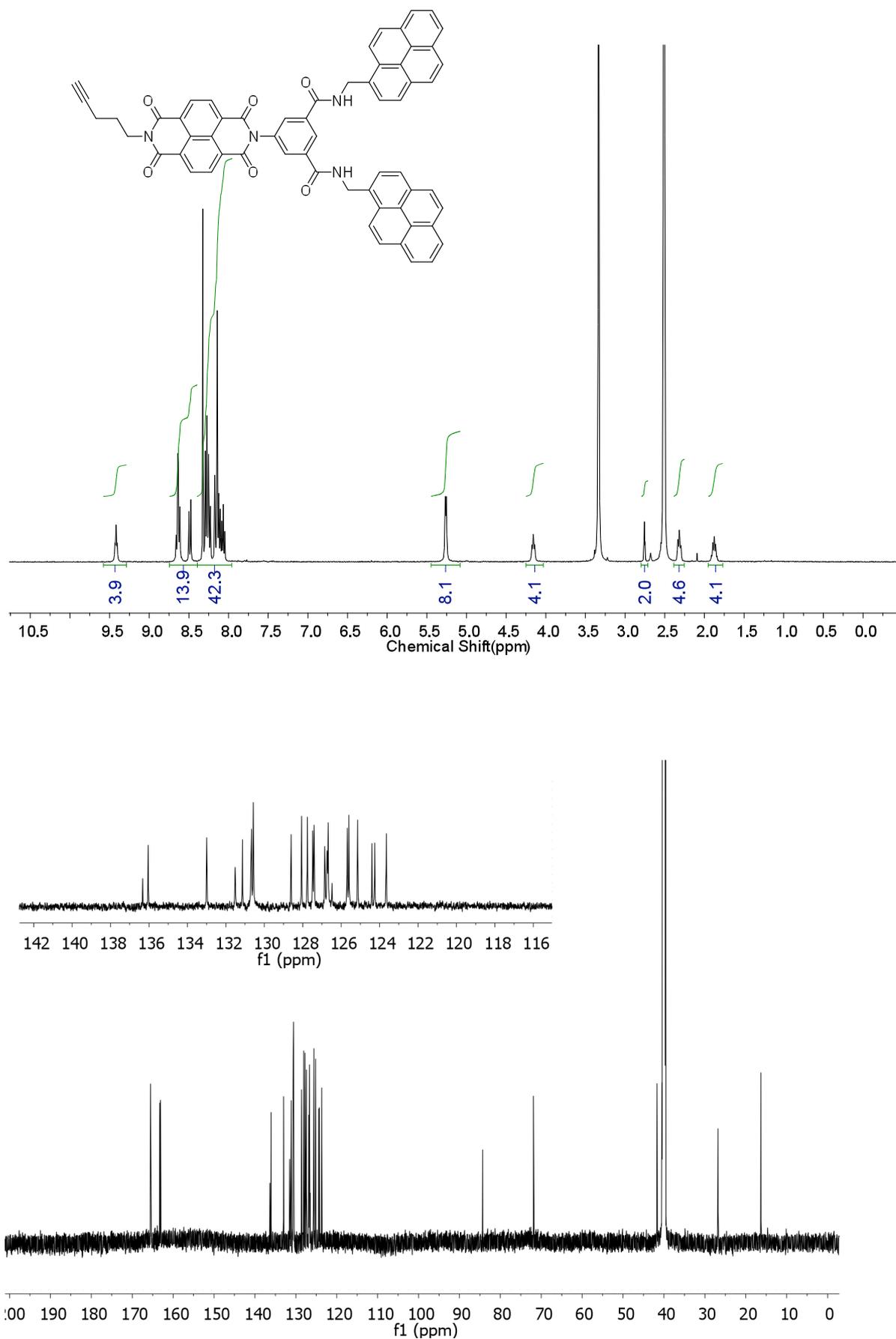


Fig. S4. ¹H and ¹³C NMR spectra of the pentynyl imido-tweezer molecule 3 (*d*₆-DMSO, 400 & 175 MHz respectively)

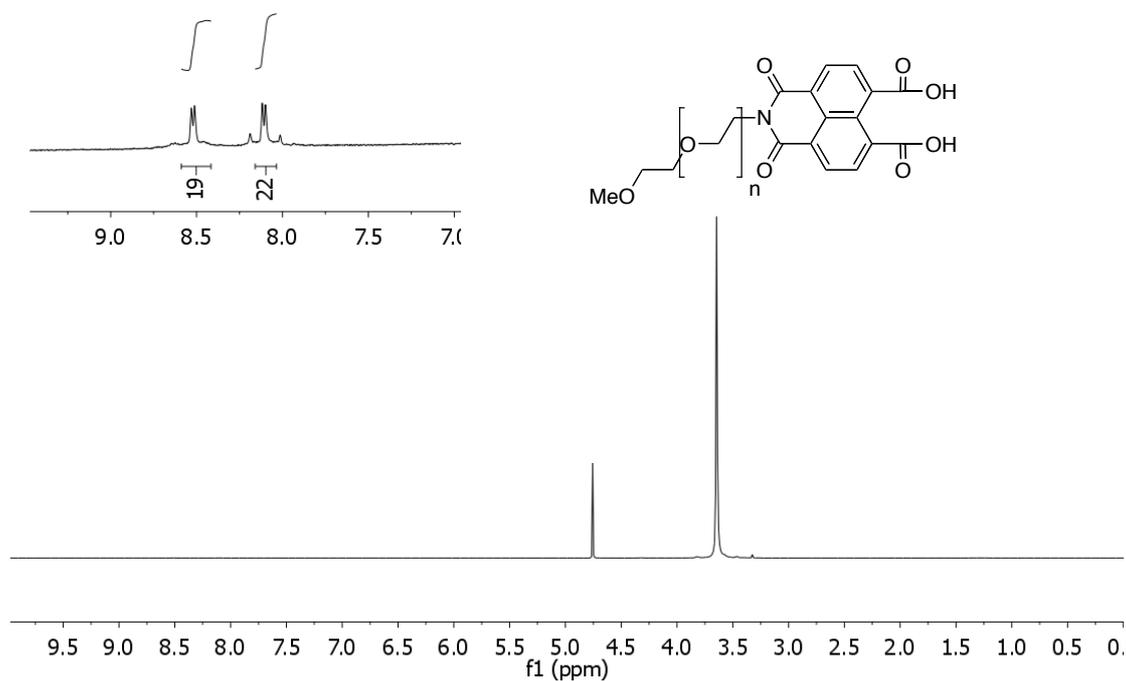


Fig. S5. ¹H NMR spectrum (D₂O, 400 MHz) of PEG₅₀₀₀ diacid **E**. Inset shows diimide resonances.

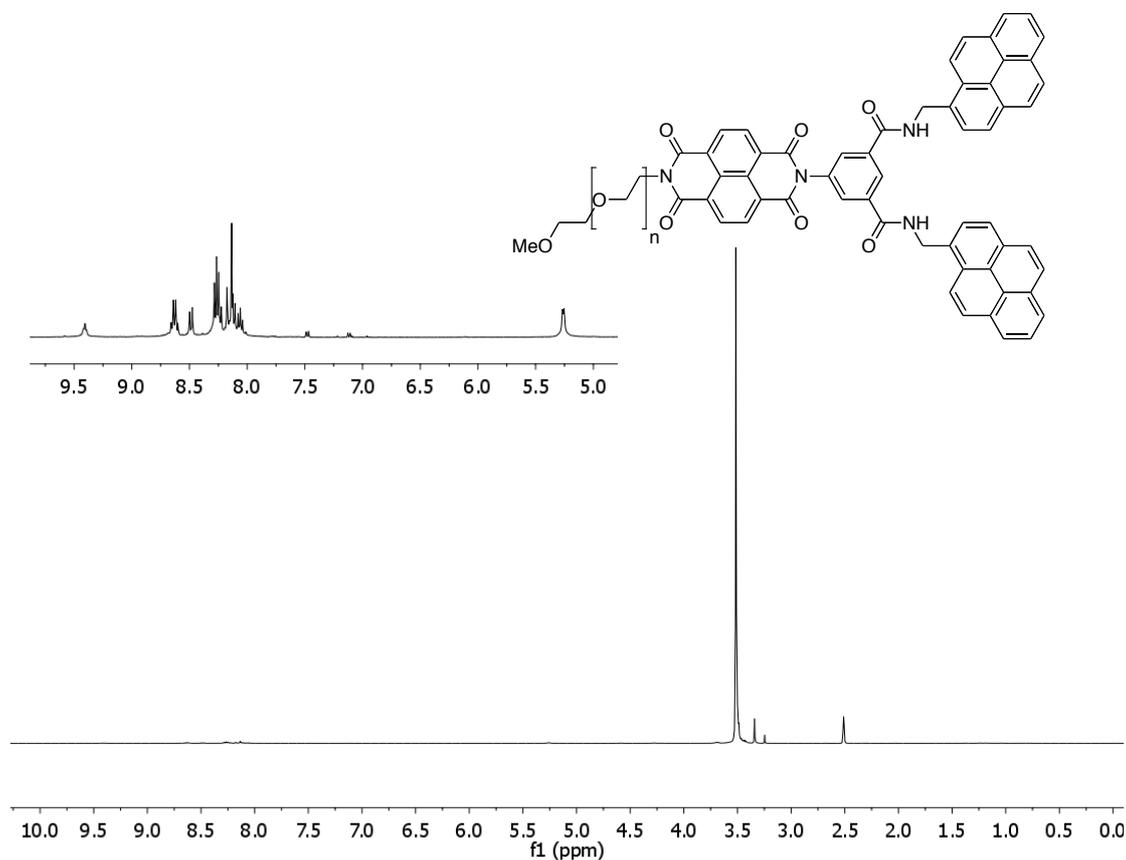


Fig. S6. ¹H NMR (d₆-DMSO 400 MHz) spectrum of PEG₅₀₀₀ imido-tweezer polymer **4**

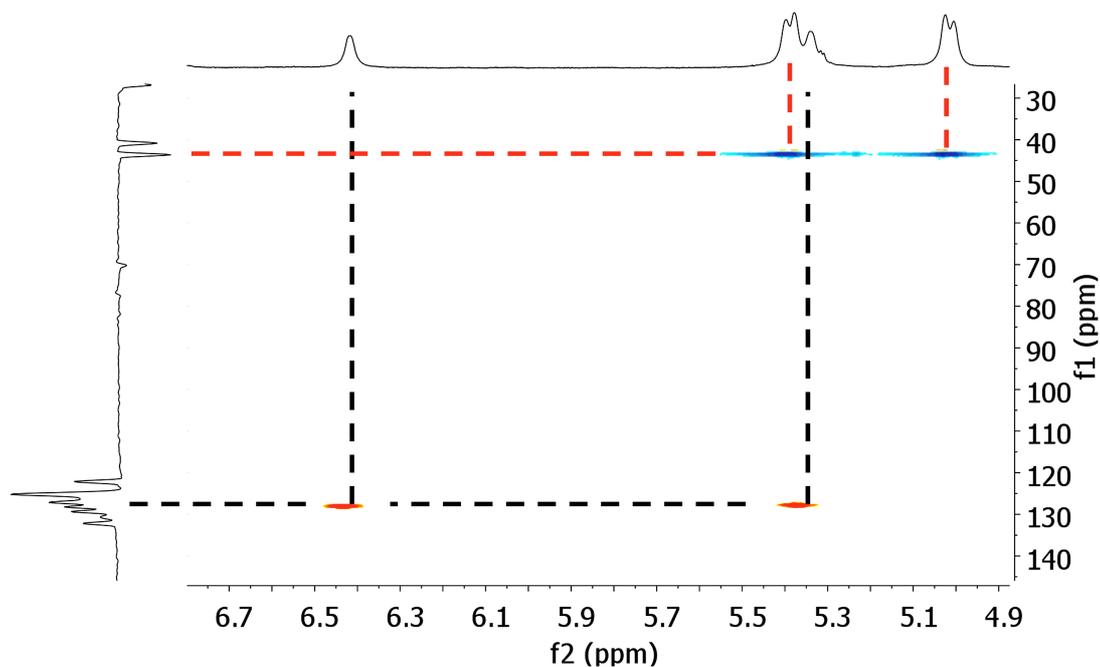


Fig. S7. ^1H , ^{13}C -COSY NMR spectrum of the pentynyl tweezer-imide **3** in CDCl_3/TFA (9:1, v/v) (25 °C, 700 MHz), confirming that the resonance observed at 5.31 ppm in this solvent represents an aromatic (diimide) proton, shifted upfield by ca. 3.1 ppm from its position in $\text{DMSO}-d_6$.

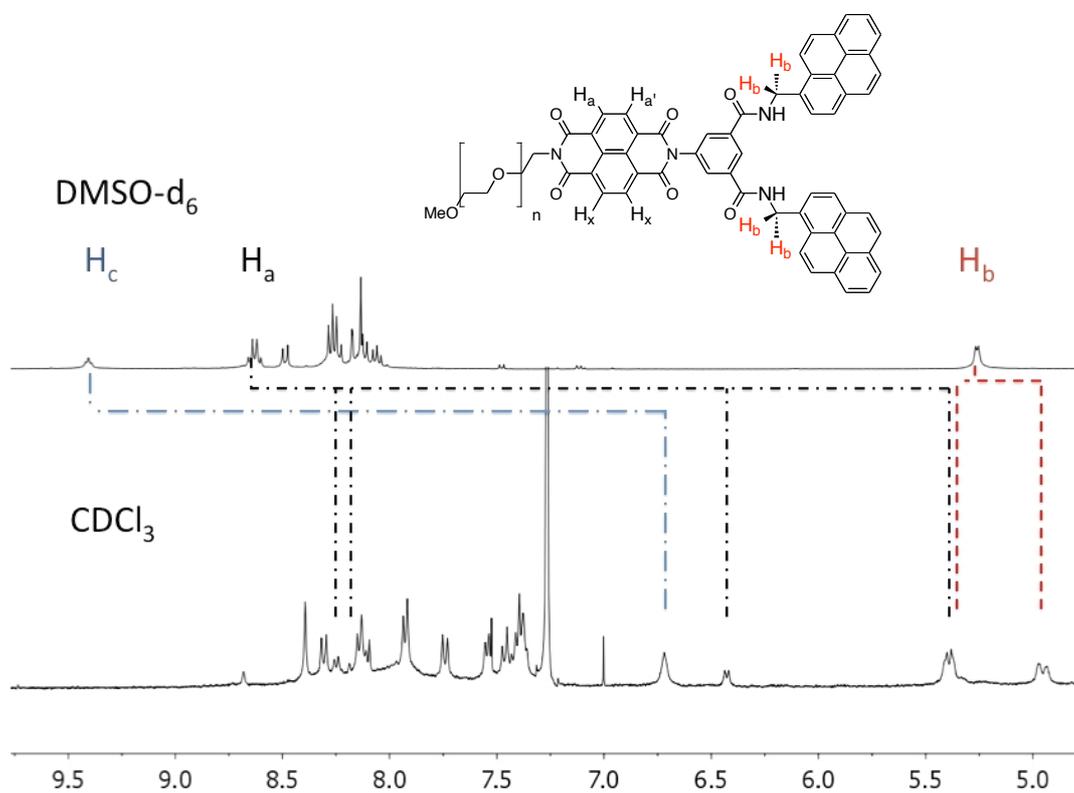


Fig. S8. Comparative ^1H NMR spectra of **4** (R = PEG 5000) in d_6 -DMSO (above) and in CDCl_3 (below). Note again the very large self-complexation-induced resonance shifts and multiple magnetic inequivalencies for protons H_a and H_b in the CDCl_3 spectrum.

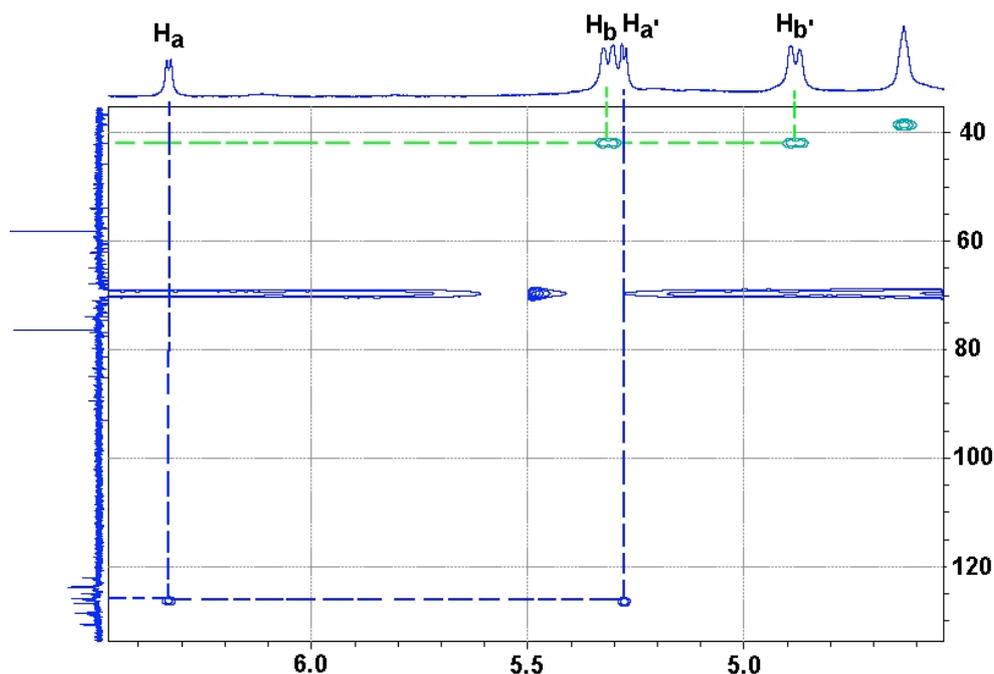


Figure S9. ^1H , ^{13}C -HSQC NMR spectrum of supramolecular polymer **4** in CDCl_3 , (5°C , 700 MHz)

In $\text{DMSO-}d_6$, the methylene protons H_a and H_b of **2**, **3** and **4** appear at ca. 5.2 ppm and are magnetically equivalent (see Figures S3, S4 and S8). However, in solvents where self-complexation occurs (for example in CDCl_3) these two protons resonate separately at 5.3 and 4.9 ppm, and show a *gem* coupling constant of 14 Hz (and couple to the same carbon – see cross-peaks in the HSQC spectrum of **4**, Figure S9). This shows that supramolecular dimerisation restricts rotation around the NH-CH_2 -pyrenyl bonds, so that the two methylene protons (H_b) are magnetically inequivalent.

In $\text{DMSO-}d_6$, the protons on the diimide residue typically appear at 8.60 ppm (Figures S3, S4 and S8). However, in the complexed state, these aromatic protons (note the cross-peaks for H_a and $\text{H}_{a'}$ in the HSQC spectrum of **4** shown in Figure S9) resonate at 5.25 and 6.30 ppm respectively as a consequence of extreme ring-current shielding effects by the complexing pyrenyl moieties. These NMR data demonstrate that the supramolecular structures of the dimeric, self-complementary imido-tweezer molecules **2**, **3** and **4** in solution are essentially identical to that observed crystallographically for **3** in the solid state.

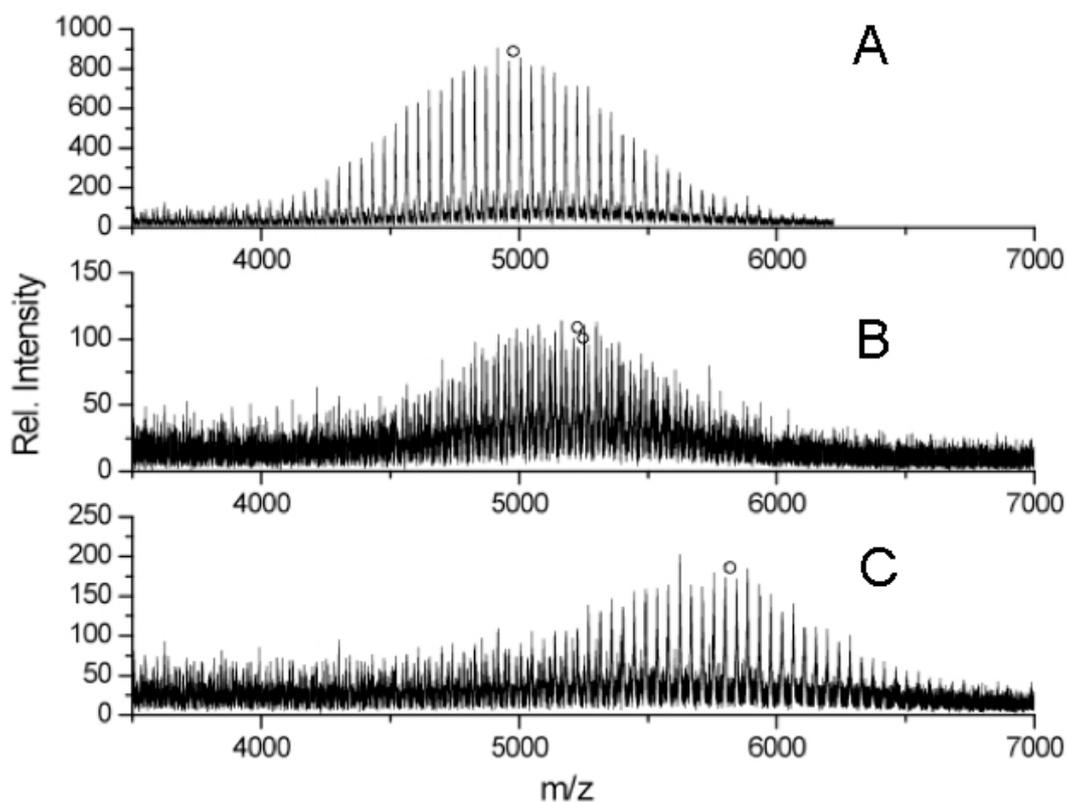


Fig. S10. MALDI-ToF spectra (KCl as cationising agent) of: (a) commercial MeO-PEG₅₀₀₀-NH₂; (b) diacid-functionalised PEG₅₀₀₀ (**E**), appearing as both potassium and sodium adducts; (c) imido-tweezer functionalised PEG₅₀₀₀ (**4**) In each case, the circle marks the 110mer. The calculated molar masses are 4960.00 Da for the potassiated 110mer of **E** and 5799.85 Da for the potassiated 110mer of **4**. The corresponding molar masses determined from the above spectra for [M+K]⁺ are 4959.97 Da and 5799.99 Da, for 110mers of **E** and **4** respectively.

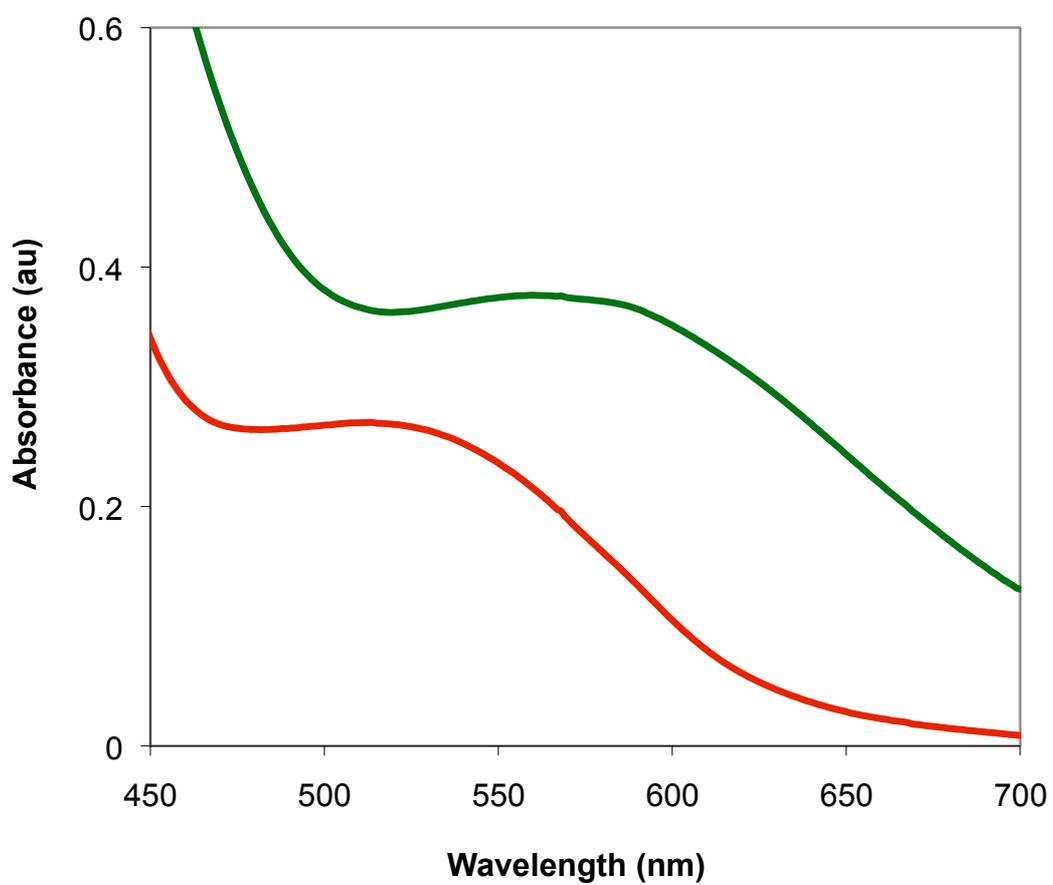


Fig. S11. UV/vis spectra of supramolecular polymer **4** (3 mg/mL, 25 °C) in toluene (red line) and in water (green line). Values for λ_{max} are 520 and 570 nm respectively.

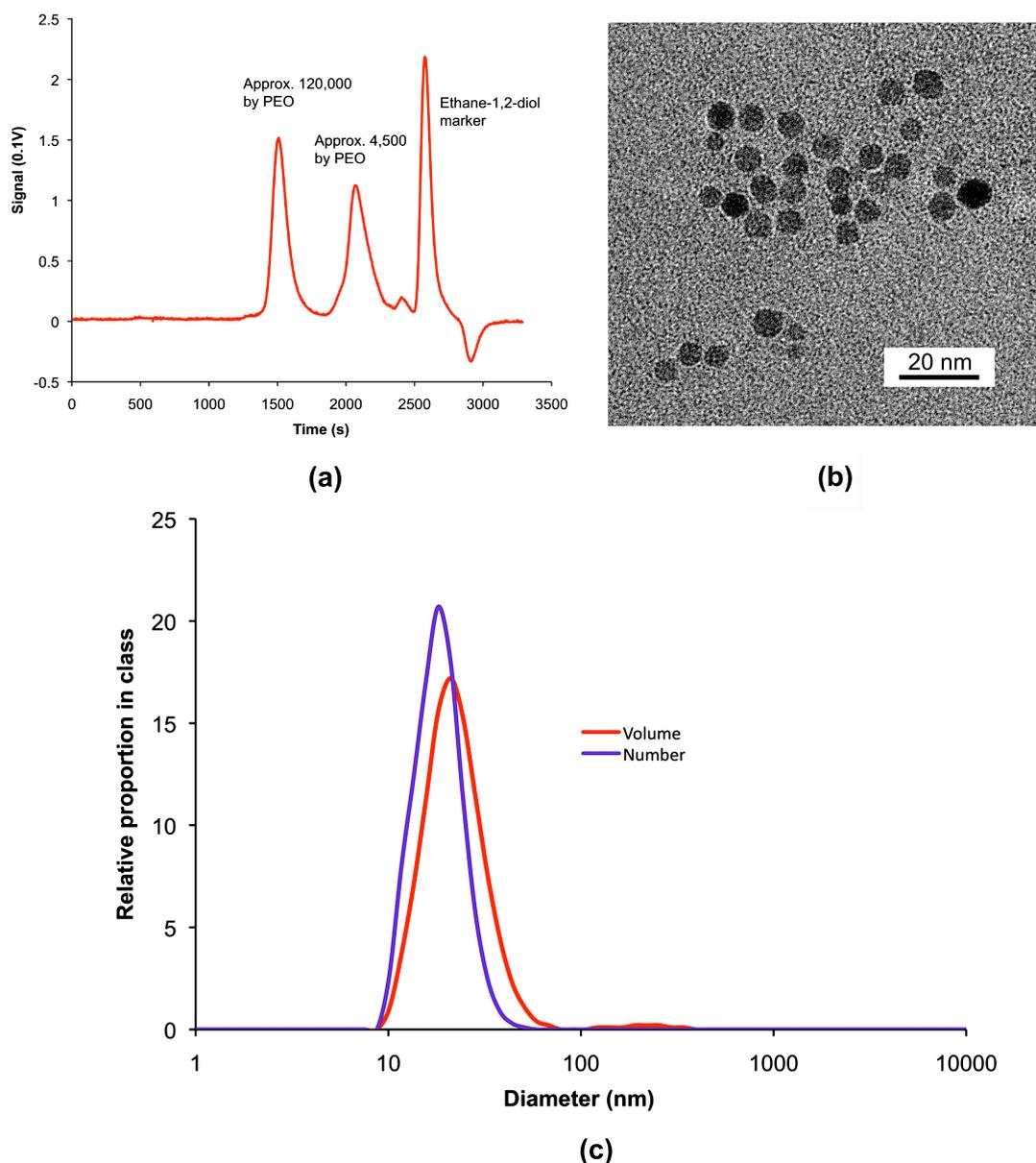


Fig. S12. (a) Aqueous size-exclusion chromatogram (RI detection) of polymer **4** showing the presence of both unimers ($M_p \approx 4,500$) and micellar nanoparticles ($M_p \approx 120,000$); (b) Transmission electron micrograph showing micellar nanoparticles of polymer **4** (an aqueous solution of **4** was dialysed to remove any trace low-MW impurities and then evaporated on a graphene oxide support-film) and (c) Dynamic light-scattering profiles for polymer **4** in aqueous solution, showing size-distribution peaks at ≈ 20 nm and ≈ 200 nm (more evident in volume-distribution).

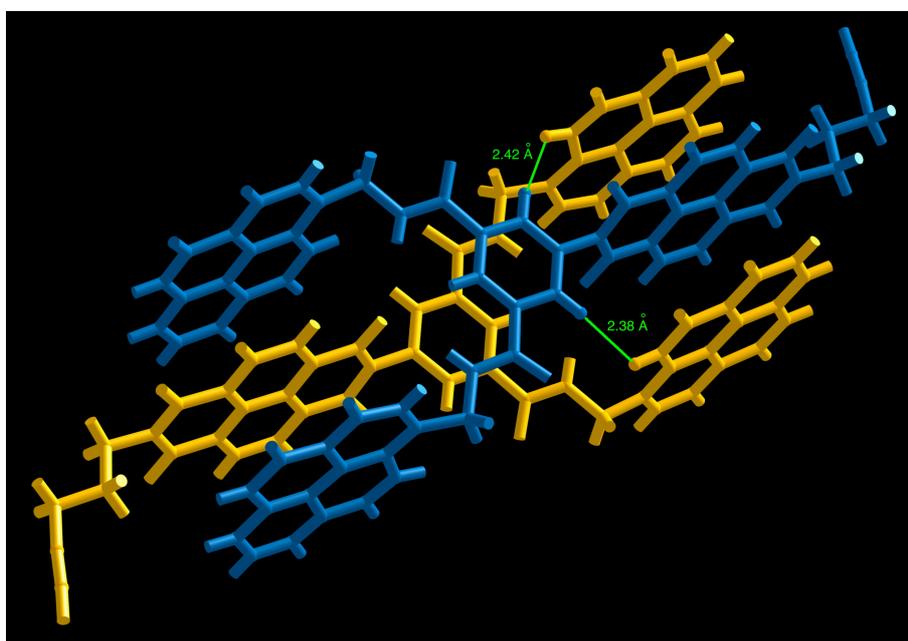
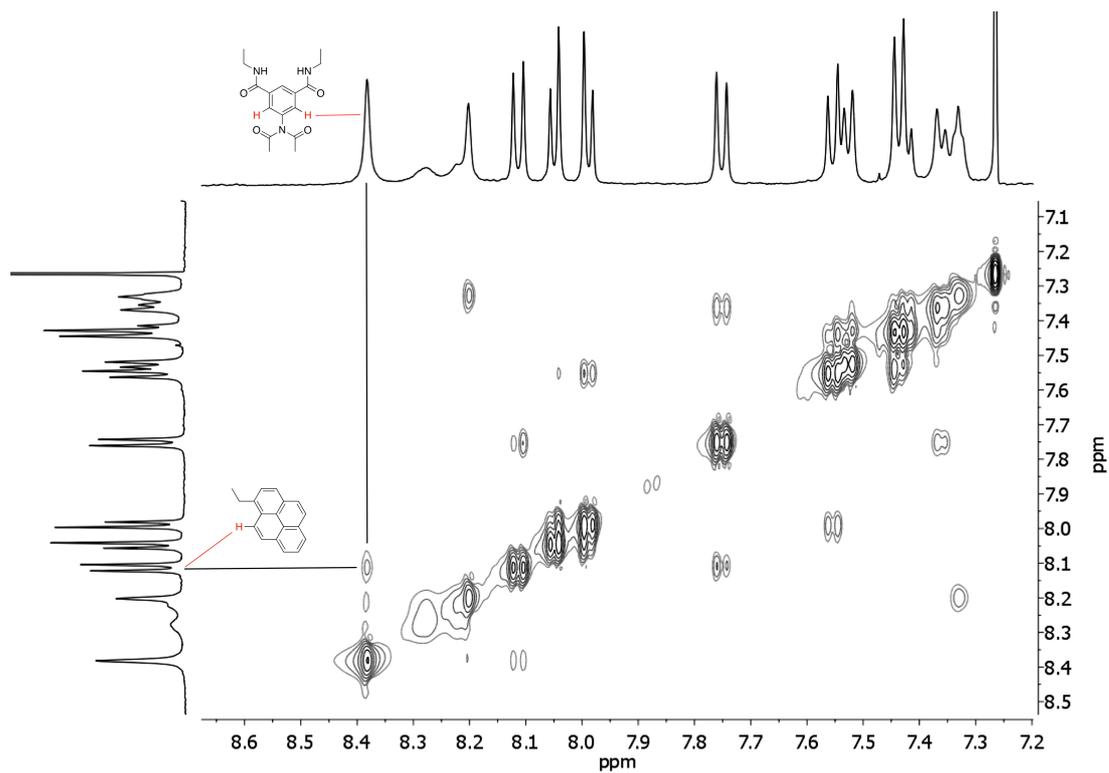


Fig. S13. ^1H - ^1H ROESY NMR spectrum (upper image) of the self-complexing tweezer molecule **3** (700 MHz, CDCl_3/TFA , 9:1 v/v), highlighting the intermolecular cross-peak between isophthaloyl (8.38 ppm) and pyrenyl (8.15 ppm) protons. In the solid state these form the closest intermolecular proton-proton contacts (ca. 2.4 Å), as shown in the lower image.

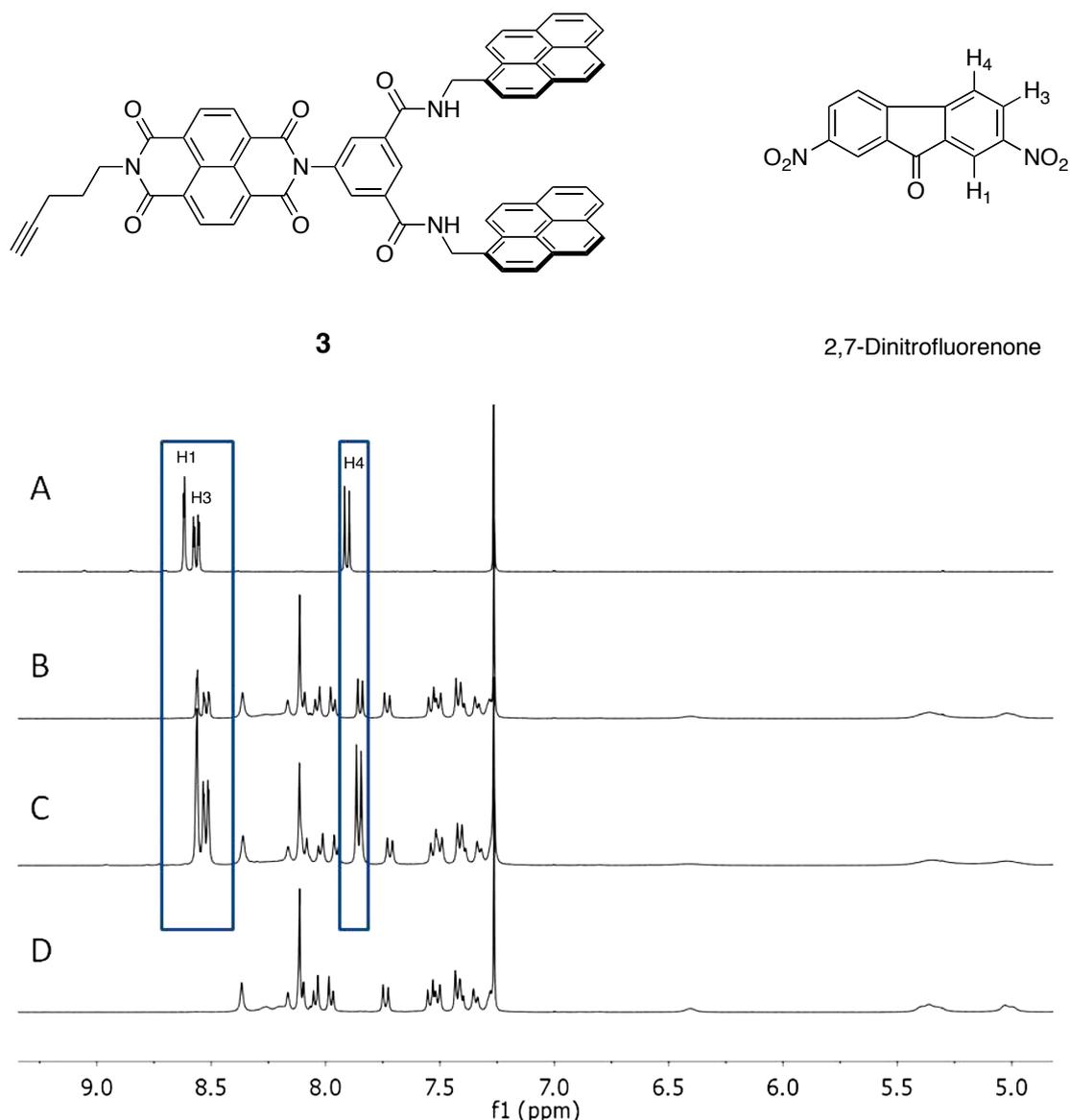


Fig. S14. ¹H NMR spectra (CDCl₃/TFA, 10:1 v/v) of:

- (A) 2,7-dinitrofluorenone;
- (B) 2,7-dinitrofluorenone plus tweezer-molecule **3** (mol ratio = 1.5:1 respectively);
- (C) 2,7-dinitrofluorenone plus tweezer-molecule **3** (mol ratio = 5:1 respectively);
- (D) Tweezer-molecule **3**.

Spectra B, C and D are of tweezer-molecule **3** at a concentration of 5.0 mg/mL. The signals for **3** are essentially identical in each spectrum. Only very small complexation shifts are observed for the 2,7-dinitrofluorenone resonances (ca. 0.06 ppm). As these shifts show no dependence on the molar ratio of the two components, it is possible that they are due solely to nonspecific complexation with the *outer* surfaces of the pyrenyl residues in the dimer of **3**.

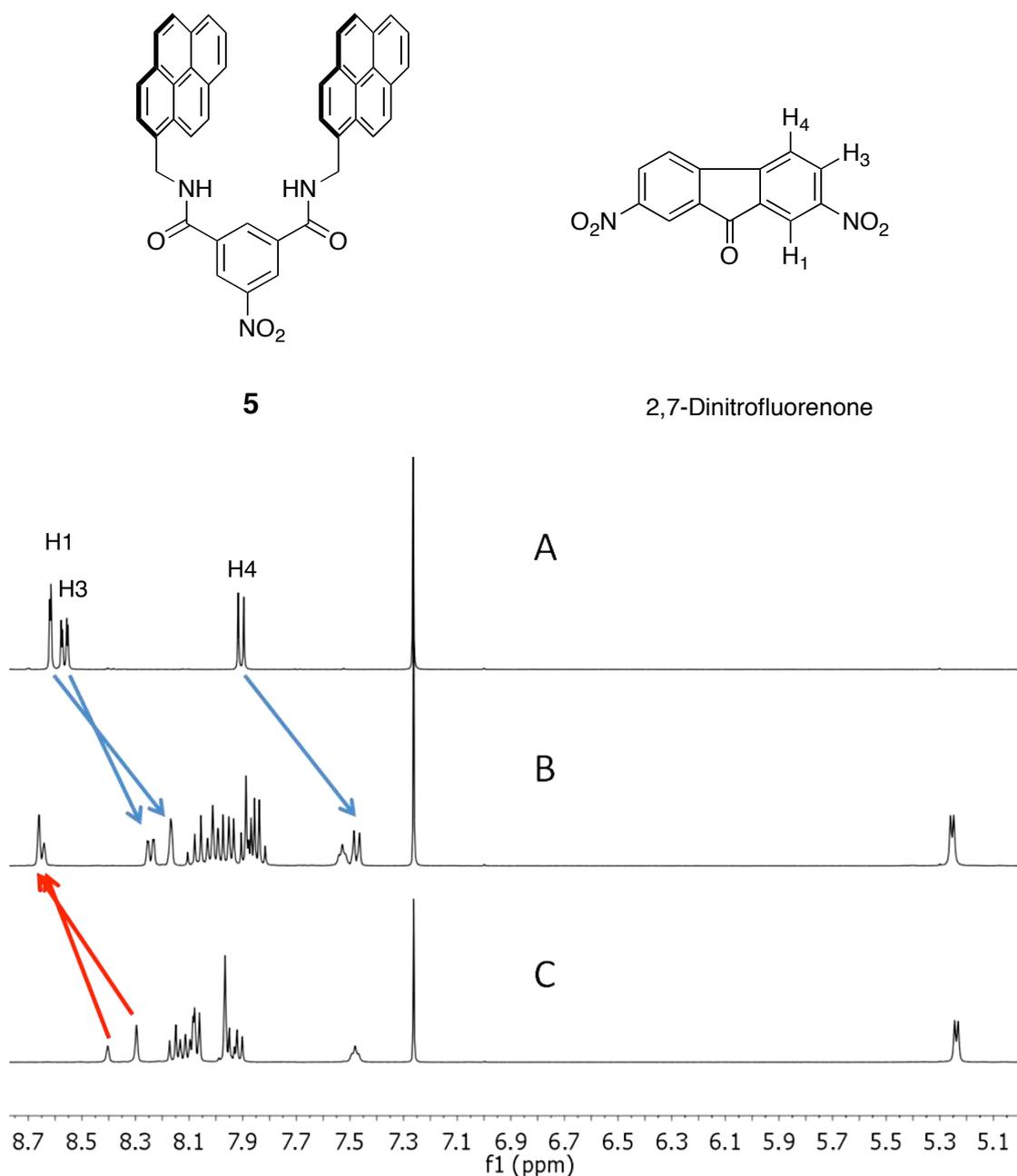


Fig. S15. ¹H NMR spectra (CDCl₃/TFA, 10:1 v/v) of:

- (A) 2,7-dinitrofluorenone;
- (B) 2,7-dinitrofluorenone plus tweezer-molecule **5** (mol ratio 1.3:1 respectively);
- (C) Tweezer-molecule **5**.

Spectra B and C are of tweezer-molecule **5** at a concentration of 3.0 mg/mL. The upfield complexation shifts observed for the 2,7-dinitrofluorenone resonances are up to 0.5 ppm, i.e. an order of magnitude greater than those observed with the self-complexing tweezer-molecule **3** (Fig. S13).

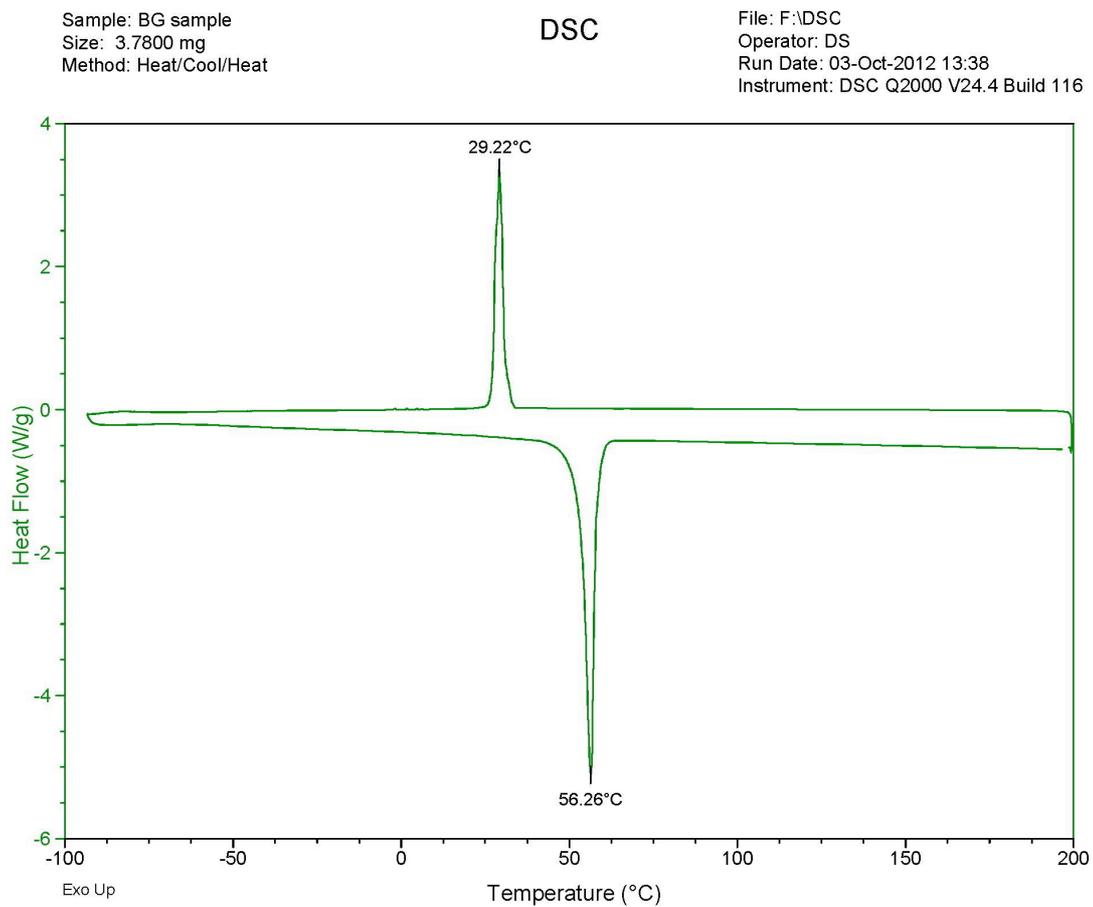


Fig. S16. DSC Thermogram of supramolecular polymer **4**. The lower trace shows the heating curve (10 °C min⁻¹) and the upper trace the cooling curve (10 °C min⁻¹).

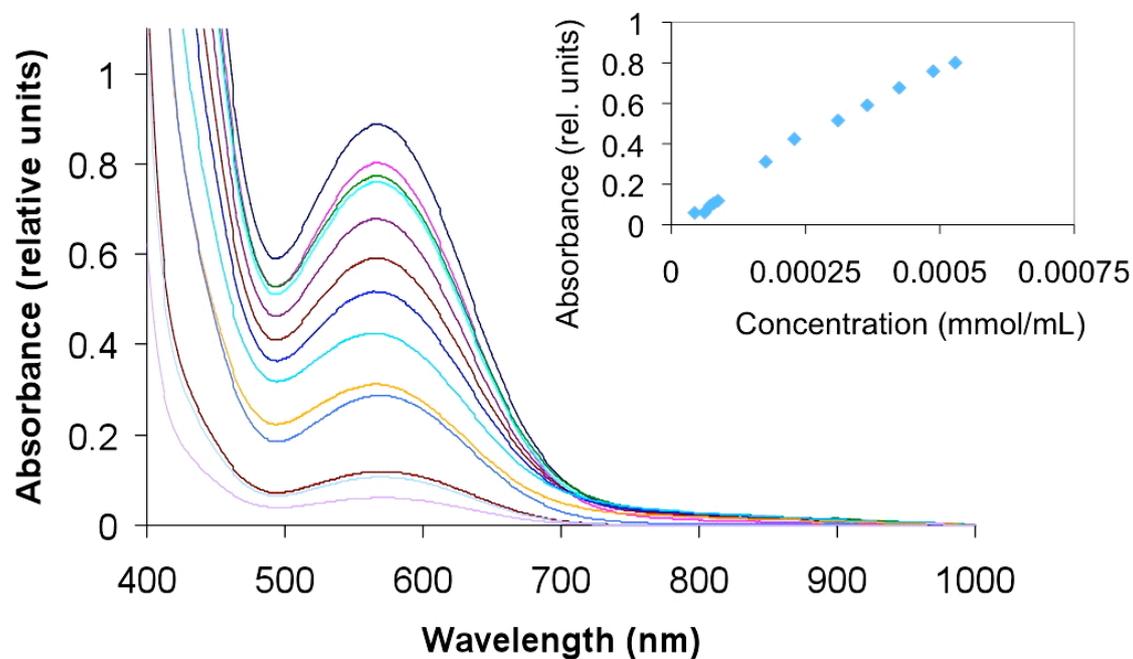


Fig. S17. Raw data used in the determination of the dimerisation constant, K_a , for tweezer-molecule **3** using the UV-vis dilution method,³ based on the charge transfer band at 565 nm in $\text{CHCl}_3/\text{CF}_3\text{COOH}$ (9:1, v/v). Data were analysed using the program *DynaFit*.⁴

³ M. B. Nielsen, J. O. Jeppesen, J. Lau, C. Lomholt, D. Damgard, J. P. Jacobsen, J. Becher and J. F. Stoddart, *J. Org. Chem.*, 2001, **66**, 3559.

⁴ P. Kuzmic, *Anal. Biochem.* 1996, **237**, 260.

Crystallographic data for **3**

$C_{61}H_{38}N_4O_6$, $M_r = 1024.45$, triclinic, space group $P-1$, $a = 12.0004(12)$, $b = 12.2208(12)$, $c = 18.0893(17)$ Å, $\alpha = 85.468(7)$, $\beta = 71.607(6)$, $\gamma = 83.252(7)^\circ$, $V = 2497.4(4)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.362$ g cm⁻³, $\lambda = 0.7749$ Å, $\mu = 0.08$ mm⁻¹, $T = 100$ K, crystal dimensions $0.1 \times 0.1 \times 0.08$ mm³, 13713 unique reflections were measured on Beamline 11.3.1 at the Advanced Light Source, Berkeley, California with a maximum 2θ value of 47.90° . Refinement with SHELXL gave a conventional R -factor of 0.0941 (weighted R_2 0.2720 and goodness of fit 1.136) following removal of disordered solvent using the SQUEEZE program in PLATON. One of the pyrene rings was fitted as disordered using the FRAG option in SHELXL. The respective maximum and minimum electron densities were 0.44 and -0.40 e Å³. The data for **3** have been deposited as CCDC 866020 and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

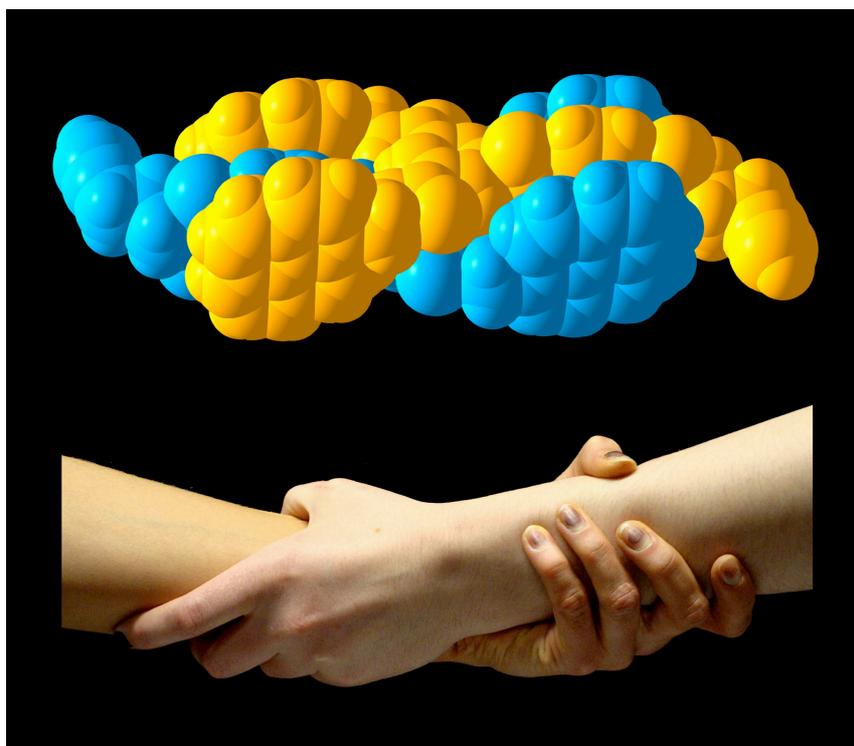


Fig. S18. X-ray structure of the self-complexing tweezer-molecule **3** (above) showing its resemblance to the classical "Roman" handshake (below).