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Conformational Modulation of Sequence Recognition in Synthetic Macromolecules

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Experimental Section

1. Materials and Methods. Synthetic procedures were performed under an atmosphere of dry nitrogen unless otherwise specified. Commercial solvents and reagents were used without purification unless otherwise stated. *N,N*-dimethylacetamide (DMAc) was distilled over calcium hydride before use. Compounds **3**,^{S1} **4**,^{S2} **1**,^{S3} **2**,^{S3} **5**,^{S4} and **8**,^{S5} and homopolymer **10**^{S6} were prepared according to literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Proton and ¹³C NMR spectra were recorded on Bruker AV-700 and DPX-250 MHz spectrometers. Chemical shifts are reported in ppm relative to TMS, and multiplicities as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Matrix-assisted, laser desorption/ionisation, time-of-flight (MALDI-TOF) mass spectra were obtained using an SAI LT3 LaserTof spectrometer with a 1,8,9-trihydroxyanthracene as matrix and sodium trifluoroacetate as cationising agent. Infra-red spectra were recorded on a Perkin Elmer 1700 FTIR spectrometer using Nujol or thin polymer films cast from *N,N*-dimethylformamide (DMF). UV-visible absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrometer. Elemental analyses were provided by Medac Ltd. Melting points and polymer glass transition temperatures were measured under nitrogen by differential scanning calorimetry (DSC) using a Mettler DSC 20 system, at a heating rate of 10 °C/min. Inherent viscosities (η_{inh}) of polyimides were measured at 25 °C in a thermostatted water bath on 0.1% polymer solutions in 1-methylpyrrolidinone (NMP) using a Schott-Geräte CT-52 semi-automated viscometer and AVS 470 measurement system. Molecular weights of polyimides relative to polystyrene standards were determined by gel permeation chromatography (GPC) on a Polymer Laboratories PL-220 instrument equipped with a differential refractive index detector and 2 x PL-gel 10 mm mixed-B columns. Analyses were carried out in DMF/LiBr solution (0.05 M in LiBr) at 60 °C, at a flow rate of 1.0 mL min⁻¹ and with an injection volume of 100 μ L. Samples were run in DMF/LiBr (0.05 M) at a concentration of 1 mg mL⁻¹, and both solvent and sample solutions were filtered through a 0.02 mm PTFE membrane prior to injection. Computational modeling (molecular mechanics with charge-equilibration) was carried out using the *Cerius2* suite of programs (v.3.5, Accelrys Inc., San Diego) with the Dreiding II force field,^{S7} parametrized for aromatic polymer

systems.^{S8} Atomic coordinates for modeled structures are given, in electronic format, as PDB files. Single crystal X-ray data for **6** were measured using Cu-K α radiation on a Siemens P4 diffractometer at 293 K, and for [**4+6**] on an Oxford Diffraction X-Calibur Gemini diffractometer with Cu-K α radiation at 150 K. Details of crystal data, data collection, structure solution and refinement are given below and, in electronic format, in the associated CIF files.

2. Synthetic Procedures.

4,4'-bis[4-(3-aminophenoxy)benzoyl]biphenyl (5):^{S4} A mixture of 3-aminophenol (3.274 g, 30.0 mmol), 4,4'-bis(4-fluorobenzoyl)biphenyl (3.98 g, 10.0 mmol), potassium carbonate (2.764 g, 20.0 mmol), *N,N*-dimethylacetamide (DMAc, 140 mL) and toluene (60 mL) was heated to reflux under nitrogen, with Dean-Stark distillation of water. After 3 h the toluene was distilled off and the temperature raised to 160 °C. After a further 4 h the reaction mixture was cooled to room temperature, poured into water (600 mL) and the precipitate was filtered off. After washing with water and then methanol, the solid was dried at 100 °C for 2 h and purified by chromatography (2% methanol in dichloromethane) to give pale yellow, crystalline **5**. Yield 4.5 g, 78% ; m.p. 221 °C; ¹H NMR (DMSO-*d*₆, 250 MHz) δ 7.97 (d, *J* = 8.5 Hz, 4H), 7.87 (d, *J* = 8.3 Hz, 4H), 7.84 (d, *J* = 8.8 Hz, 4H), 7.11 (d, *J* = 8.8 Hz, 4H), 7.10 (t, *J* = 8.1 Hz, 2H), 6.39 (m, 2H), 6.33 (t, *J* = 2.2 Hz, 2H), 6.27 (m, 2H), 5.39 (br, 4H) ppm; ¹³C NMR (DMSO-*d*₆, 62.5 MHz) δ 194.4, 161.8, 156.2, 151.1, 142.9, 137.3, 132.6, 131.4, 130.7, 130.6, 127.5, 117.4, 110.9, 107.2, 105.3 ppm; IR (Nujol): 3416 (ν N-H), 1643 (ν C=O), 1240 (ν C-O-C), 853, 832, 765, 749 cm⁻¹; MS (CI): *m/z* = 577 [M+H]⁺.

Macrocycles: A solution of diamine **5** (1.442g, 2.5 mmol) and pyromellitic dianhydride (0.545 g, 2.5 mmol) in dry DMAc (180 mL) was added via syringe pump over 18 h to refluxing DMAc (70 mL) under nitrogen. After a further 2 h the reaction mixture was cooled to room temperature, poured into water (400 mL) and the precipitate was filtered off. After washing with water and then with methanol, the solid was dried and purified by column chromatography (2% ethyl acetate in dichloromethane) to

give, after evaporation and drying under vacuum, very pale yellow, crystalline **6**. Macrocycle **7** was obtained analogously, using 1,4,5,8-naphthalenetetracarboxylic dianhydride in place of pyromellitic dianhydride. Both macrocycles retained ca. 0.1 equivalents of dichloromethane (as evidenced by ^1H NMR), even after extended drying under vacuum.

Macrocycle **6**: Yield 30 mg, 1.6%; m.p. 481 °C; ^1H NMR (CDCl_3/TFA , 250 MHz) δ 8.55 (s, 2H), 7.89 (d, $J = 8.7$ Hz, 4H), 7.83 (d, $J = 8.7$ Hz, 4H), 7.72 (d, $J = 8.8$ Hz, 4H), 7.65 (t, $J = 8.2$ Hz, 2H), 7.40 (m, 2H), 7.36 (m, 2H), 7.34 (d, $J = 8.8$ Hz, 4H), 7.14(t, $J = 2.1$ Hz, 2H) ppm; ^{13}C NMR (CDCl_3/TFA , 62.5 MHz) δ 202.25, 166.05, 160.17, 157.84, 145.08, 137.53, 137.04, 133.67, 132.58, 132.30, 131.58, 131.51, 127.73, 121.11, 120.53, 120.13, 119.91, 114.61 ppm; MS (CI): $m/z = 759.0$ $[\text{M}+\text{H}]^+$. Anal. Calc. for $\text{C}_{48}\text{H}_{26}\text{N}_2\text{O}_8 \cdot 0.1\text{CH}_2\text{Cl}_2$ C 75.30, H 3.44, N 3.65 %; found C 75.00, H 3.45, N 3.48 %.

Macrocycle **7**: Yield 30 mg, 1.4%; m.p. 549 °C; ^1H NMR (CDCl_3/TFA , 250 MHz) δ 8.97 (s, 2H), 7.76 (d, $J = 8.5$ Hz, 4H), 7.71 (t, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 6.6$ Hz, 4H), 7.63 (d, $J = 8.4$ Hz, 4H), 7.49 (m, 2H), 7.37 (d, $J = 8.7$ Hz, 4H), 7.23 (m, 2H), 7.00 (t, $J = 2.1$ Hz, 2H) ppm; ^{13}C NMR (62.5 MHz) δ 202.20, 164.46, 158.42, 158.24, 145.18, 136.84, 134.24, 134.12, 133.15, 132.32, 132.23, 131.96, 127.80, 127.55, 127.25, 123.46, 121.34, 120.12, 114.04 ppm; MS (MALDI-TOF): $m/z = 831$ $[\text{M}+\text{Na}]^+$. Anal. Calc. for $\text{C}_{52}\text{H}_{22}\text{N}_2\text{O}_8 \cdot 0.1\text{CH}_2\text{Cl}_2$: C 76.57, H 3.48, N 3.43; found C 76.59, H 3.73, N 3.48%.

Polymers: Copolymer **11**. Diamines **5** (0.288 g, 0.50 mmol) and **8** (0.324 g, 0.50 mmol) were dissolved in DMAc (4 mL) by stirring at room temperature, and pyromellitic dianhydride (0.218 g, 1.0 mmol) was then added in one portion. The dianhydride gradually dissolved and the mixture became viscous after 0.5 h. The pale yellow solution was stirred for a further 20 h, then transferred to a Petri dish and heated at 80 °C under vacuum for 2 h to remove the solvent. The resulting film of polyamic acid was imidized by heating sequentially under nitrogen at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min and finally at 250 °C for 30 min. The resulting polyimide film was dissolved in DMF and the solution added dropwise to stirring methanol to give uniform beads of copolymer **11**, which were

again reprecipitated from DMF in methanol, and finally dried at 80 °C for 4 h. Homopolymer **9**^{S4} was similarly obtained using only diamine **5** in place of the mixture of diamines **5** and **8**.

Copolymer **11**: Yield 0.755 g, 95%; T_g 268 °C, $\eta_{inh} = 0.62$ dL g⁻¹; $M_n = 15,000$, $M_w = 36,000$; ¹H NMR (CDCl₃/TFA 6:1 v/v, 250 MHz) δ 8.56 (s), 8.54 (s), 8.52 (s), 8.04 (d, $J = 8.5$ Hz), 7.98–7.92 (m), 7.83 (d, $J = 8.4$ Hz), 7.74 (d, $J = 8.5$ Hz), 7.66–7.56 (m), 7.35–7.16 (m) ppm; ¹³C NMR (CDCl₃/ TFA, 6:1 v/v, 62.5 MHz) δ 200.0, 165.7, 165.6, 162.3, 162.1, 155.9, 155.4, 144.8, 144.5, 140.3, 137.1, 137.0, 136.2, 133.7, 133.6, 131.8, 131.7, 131.3, 131.1, 130.2, 128.6, 128.1, 127.6, 123.1, 122.8, 120.0, 118.5, 117.9 ppm; IR: 1777, 1731 ($\nu_{C=O_{imide}}$), 1650 ($\nu_{C=O_{ketone}}$), 1371 (ν_{C-N}), 1242(ν_{C-O-C}), 835, 725 cm⁻¹.

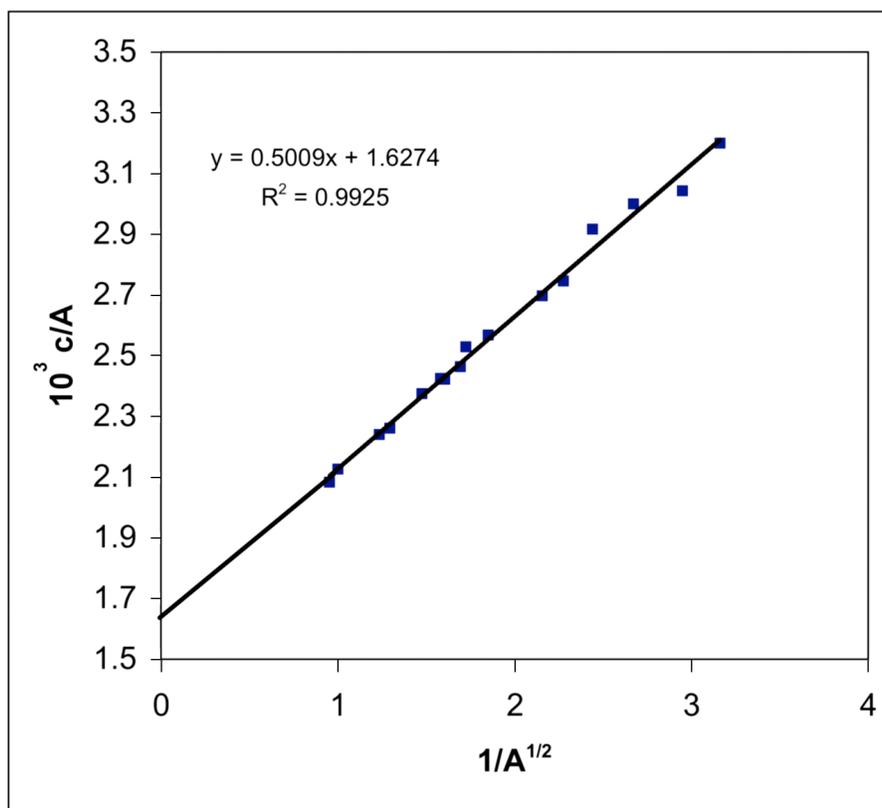
Homopolymer **9**: Yield: 0.728 g, 96%; T_g 249 °C, $\eta_{inh} = 0.71$ dL g⁻¹; $M_n = 12,500$, $M_w = 32,000$; ¹H NMR (CDCl₃/TFA, 6:1 v/v, 250 MHz) δ 8.56 (s), 7.93 (d, $J = 8.7$ Hz), 7.83 (d, $J = 8.4$ Hz), 7.63 (t, $J = 8.0$ Hz), 7.36–7.30 (m), 7.20 (d, $J = 8.8$ Hz) ppm; ¹³C NMR (CDCl₃/TFA 6:1 v/v, 62.5 MHz) δ 200.1, 165.7, 156.0, 144.8, 137.1, 136.1, 133.7, 131.6, 131.3, 131.0, 127.6, 122.8, 120.0, 118.4, 117.9 ppm; IR: 1777, 1737 ($\nu_{C=O_{imide}}$), 1650 ($\nu_{C=O_{ketone}}$), 1371 (ν_{C-N}), 1241(ν_{C-O-C}), 834, 724 cm⁻¹.

3. ¹H NMR studies of the binding of **3** and **4** to polyimides **9**, **10**, **11** and macrocycles **6** and **7**.

A stock solution of each macrocycle (4 mM) or each polyimide (4 mM with respect to total imide residues) in either CDCl₃/trifluoroacetic acid (6:1 v/v) or CDCl₃/hexafluoropropan-2-ol (6:1 v/v) was prepared in a 5 mL volumetric flask, and 0.8 mL of this solution was added to an NMR tube using a micropipette. The solution was slowly evaporated under a nitrogen flow and the residue was dried at 80 °C under vacuum for 4 h. A solution of tweezer molecule **3** or **4** in the same solvent, having the required concentration of tweezer, was prepared in a 5 mL volumetric flask. An aliquot of this solution (0.8 mL) was added to the NMR tube by micropipette and mixed well to re-dissolve the model di-imide or polyimide before carrying out NMR analysis. Peak assignments were made by reference to chemical shift data for known cyclic and linear oligo-imides, by 2-D (COSY) analyses, by evaluation of integrals, and by tracking incremental changes in peak positions on progressive addition of the tweezer-molecule.

4. Measurement of the association constant K_a for tweezer-molecule **3** with polyimide **9**.

A charge-transfer absorption resulting from complexation between **3** and **9** was observed at 497 nm, and this absorption was used to determine the binding constant by the UV-visible dilution method.^{S9}



A = absorbance

c = concentration (mole L⁻¹) of imide units (equimolar with tweezer)

Intercept, $y_0 = 1.627 \times 10^3$; Slope, $\alpha = 0.501$

$$K_a = y_0/\alpha^2 = 6,486 \text{ M}^{-1} \text{ (estimated error = 10\%)}$$

So that: $K_a = 6.5 (\pm 0.7) \times 10^3 \text{ M}^{-1}$

Figure S1. Association constant plot (UV-vis dilution method) for polymer **9** with tweezer-molecule **3** in CHCl₃/hexafluoropropan-2-ol (6:1, v/v).

5. X-ray Analyses: Summary Crystal Data. Single crystals of macrocycle **6** (yellow needles) were grown by vapor diffusion of hexane into a solution of **6** in chloroform/trifluoroacetic acid, and crystals of [**4+6**] (red prisms) were obtained from an equimolar solution of the two components in chloroform/hexafluoropropan-2-ol. *Crystal data for 6*: $C_{48}H_{26}N_2O_8$ $M_r = 758.71$, monoclinic, $C2/c$, $a = 30.384(4)$, $b = 18.213(3)$, $c = 12.900(2)$ Å, $\beta = 95.380(10)^\circ$. $V = 7107.4(17)$ Å³, $T = 293(2)$ K, $Z = 8$, $D_c = 1.42$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.800$ mm⁻¹, $F(000) = 3136$. Independent measured reflections 5284. $R_1 = 0.057$, $wR_2 = 0.145$ for 3558 independent observed reflections [$2\theta \leq 60^\circ$, $I > 2\sigma(I)$]. Average $I/\sigma(I) = 0.0969$. CCDC 834642. *Crystal data for [4+6]*: [$C_{41}H_{27}N_3O_2 + C_{48}H_{26}N_2O_8$], $M_r = 1352.43$, monoclinic, $P2_1/n$, $a = 15.9918(2)$, $b = 35.2582(5)$, $c = 26.4571(3)$ Å, $\beta = 102.2610(10)^\circ$. $V = 14577.4(3)$ Å³, $T = 150(2)$ K, $Z = 8$, $D_c = 1.23$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 0.655$ mm⁻¹, $F(000) = 5616$. Independent measured reflections 20752. $R_1 = 0.1122$, $wR_2 = 0.2697$ for 12793 independent observed reflections [$2\theta \leq 61.062^\circ$, $I > 2\sigma(I)$]. Average $I/\sigma(I) = 0.1238$. CCDC 834129.

Table S1. Crystal data and refinement for macrocycle 6 (CCDC 834642).

Identification code	Macrocycle 6
Formula	C ₄₈ H ₂₆ N ₂ O ₈
Formula weight	758.71
Temperature	293 K
Diffractometer, wavelength	Siemens P4, 1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 30.384(4) Å α = 90° b = 18.213(3) Å β = 95.380(10)° c = 12.9003(15) Å γ = 90°
Volume, Z	7107.4(17) Å ³ , 8
Density (calculated)	1.418 Mg/m ³
Absorption coefficient	0.800 mm ⁻¹
F(000)	3136
Crystal colour / morphology	Yellow needles
Crystal size	0.80 x 0.13 x 0.10 mm ³
θ range for data collection	2.83 to 60.03°
Index ranges	-26 ≤ h ≤ 34, -16 ≤ k ≤ 20, -9 ≤ l ≤ 14
Reflns collected / unique	5393 / 5284 [R(int) = 0.0183]
Reflns observed [F > 4σ(F)]	3558
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5284 / 0 / 523
Goodness-of-fit on F ²	0.999
Final R indices [F > 4σ(F)]	R1 = 0.0572, wR2 = 0.1448
R indices (all data)	R1 = 0.0884, wR2 = 0.1602
Largest diff. peak, hole	0.191, -0.175 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.000

Table S2. Crystal data and refinement for complex [4+6] (CCDC 834129)

Identification code	Complex [4+6]
Formula	[C41 H27 N3 O2] + [C48 H26 N2 O8]
Formula weight	1352.43
Temperature	150 K
Diffractometer, wavelength	Agilent Gemini Ultra, 1.54180 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 15.9918(2) Å $\alpha = 90^\circ$ b = 35.2582(5) Å $\beta = 102.261(1)^\circ$ c = 26.4571(3) Å $\gamma = 90^\circ$
Volume, Z	14577.4(3) Å ³ , 8
Density (calculated)	1.232 Mg/m ³
Absorption coefficient	0.655 mm ⁻¹
F(000)	5616
Crystal colour / morphology	Red prisms
Crystal size	0.16 x 0.11 x 0.04 mm ³
φ range for data collection	3.60 to 61.06°
Index ranges	-17 ≤ h ≤ 17, 0 ≤ k ≤ 39, 0 ≤ l ≤ 28
Reflns collected / unique	20752 / 20752 [R(int) = 0.028]
Reflns observed [F > 2s(F)]	12793
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	20648 / 4459 / 1844
Goodness-of-fit on F ²	0.9523
Final R indices [F > 2s(F)]	R1 = 0.1122, wR2 = 0.2697
R indices (all data)	R1 = 0.1406, wR2 = 0.3069
Largest diff. peak, hole	1.10, -0.80 eÅ ⁻³
Mean and maximum shift/error	0.018 and 0.174

6. Comparison of the X-ray structure of [4+6] with that of [3+1]

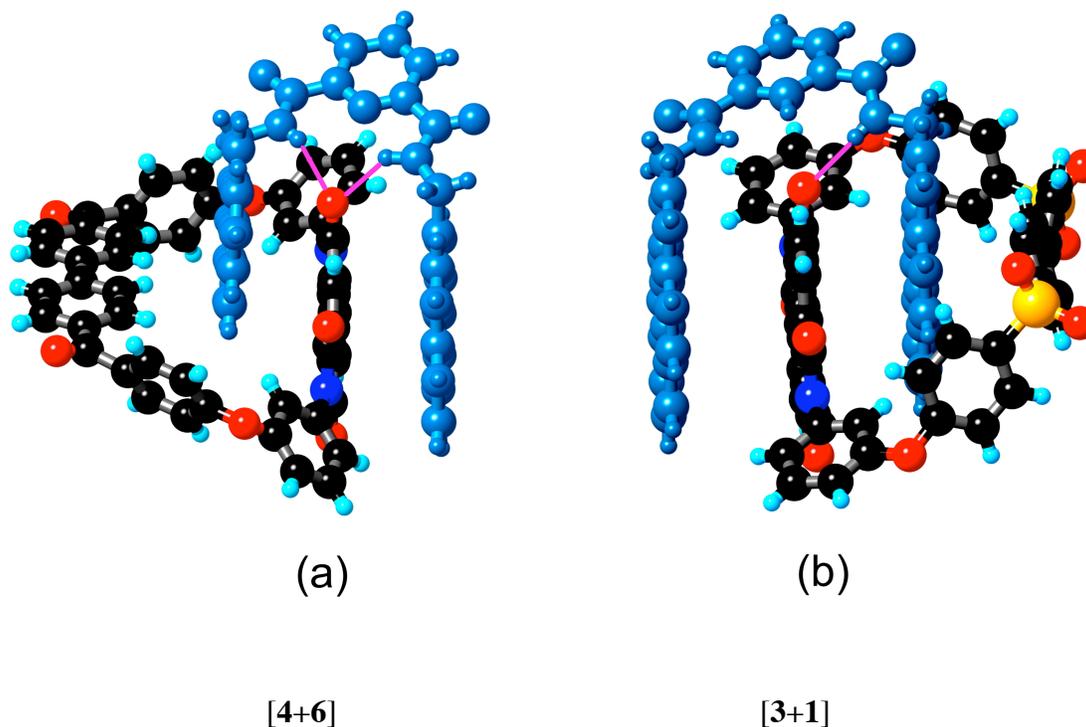


Figure S2. Images (a) and (b) illustrate the different degrees of π - π -overlap achieved between the diimide unit and the "internal" pyrenyl tweezer-arm in complexation of the imide-ketone macrocycle **6** with tweezer-molecule **4**, and in complexation of the imide-sulfone macrocycle **1** with tweezer-molecule **3** (ref. S1). The "in-plane" orientation of the 4,4'-biphenylene residue in [4+6] blocks access to the macrocyclic cavity and so limits the degree of achievable π - π -overlap between the "internal" pyrenyl residue of the tweezer and the diimide unit. In contrast, the "out-of-plane" orientation of the 4,4'-biphenylene residue in [3+1] permits the "internal" pyrenyl unit to enter the cavity and so achieve optimal, complementary π - π -overlap with both the diimide residue *and* the aromatic rings of the 4,4'-biphenylenedisulfone unit. Hydrogen bonds in [4+6] (shown in magenta): NH----OC = 2.22, 2.26 Å and N-H-O = 151, 156°.

7. ^1H NMR titration data for tweezer-molecule **3** with homopolymers **9** and **10**

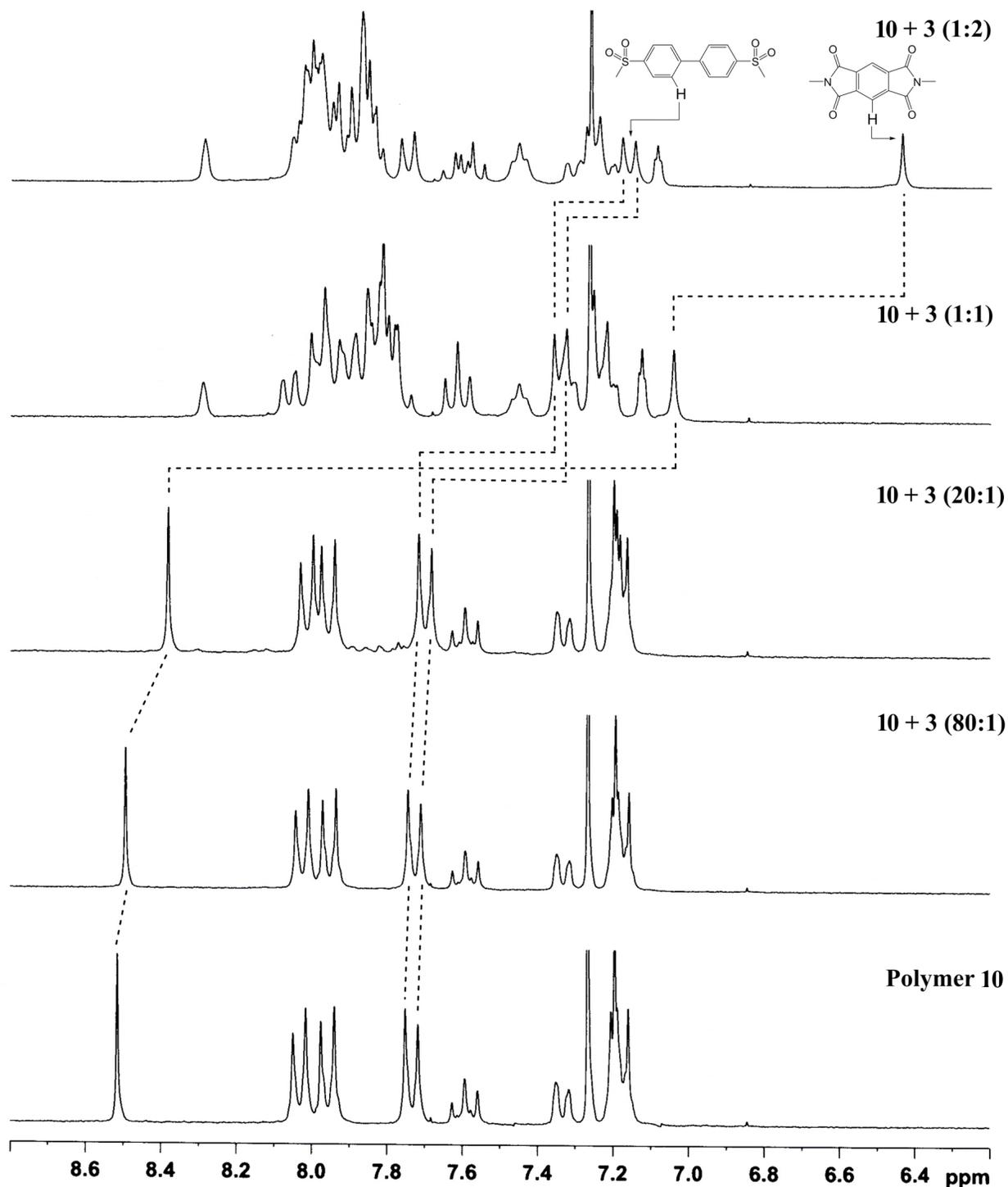


Figure S3. ^1H NMR spectra (250 MHz, CDCl_3/TFA , 6:1, v/v) of poly(imide-sulfone) **10**, alone and in the presence of 1.25, 5, 100 and 200 mol% (relative to diimide residues) of tweezer-molecule **3**. Resonances arising from pyromellitimide and biphenyl protons, as shown, undergo dramatic upfield complexation shifts as a result of aromatic ring-current shielding by the pyrenyl groups of **3**.

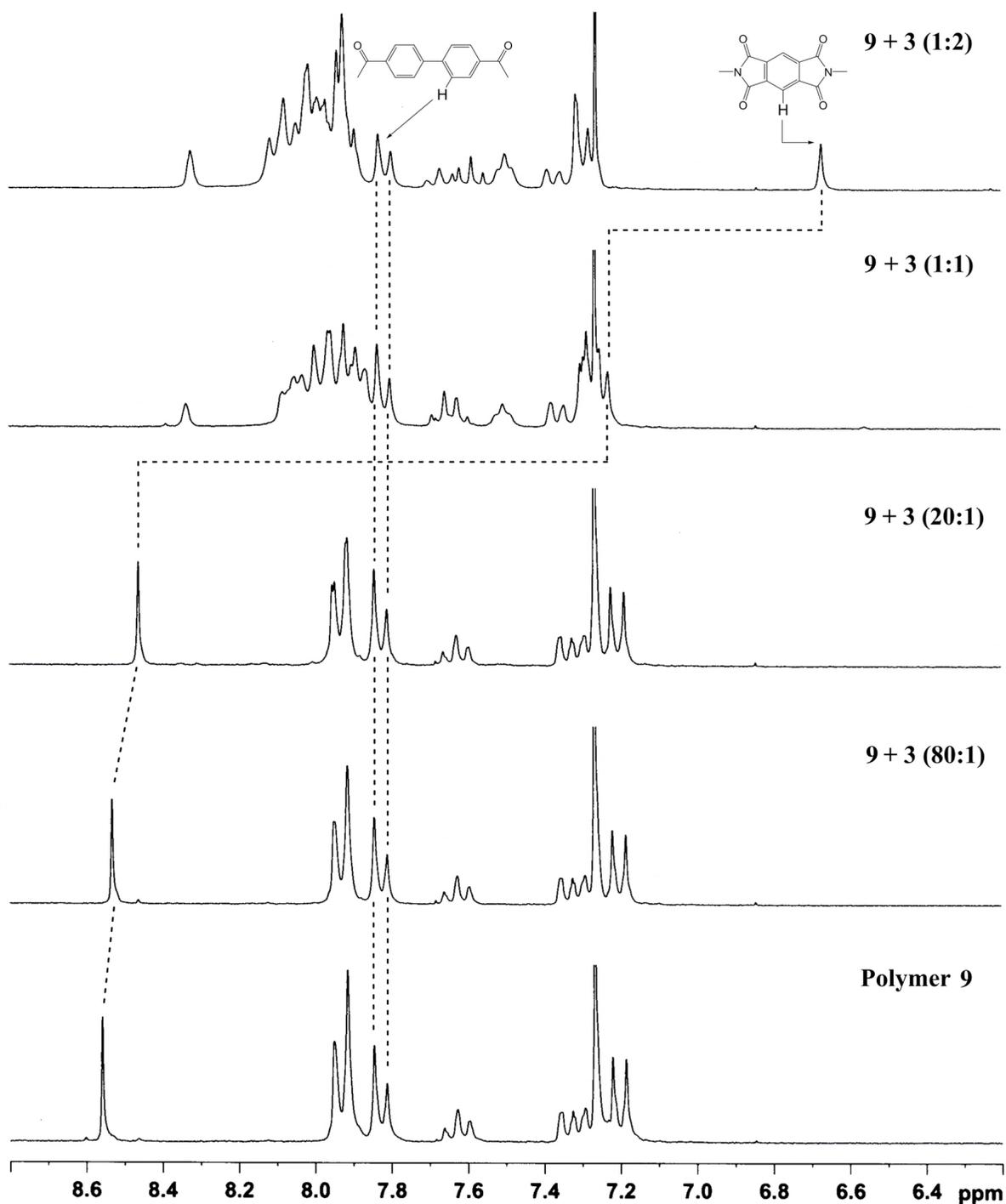


Figure S4. ^1H NMR spectra (250 MHz, CDCl_3/TFA , 6:1, v/v) of poly(imide-ketone) **9**, alone and in the presence of 1.25, 5, 100 and 200 mol% (relative to diimide residues) of tweezer-molecule **3**. The singlet resonance arising from the pyromellitimide protons, as shown, undergoes a dramatic upfield complexation shift as a result of aromatic ring-current shielding by the pyrenyl groups of **3**, but the doublet associated with the protons *ortho* to the biphenyl linkage is unaffected (c.f. Figure S1).

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