Mutual complexation between π-π stacked molecular tweezers

Article

Supplemental Material

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Supporting Information

Mutual complexation between π-π stacked molecular tweezers

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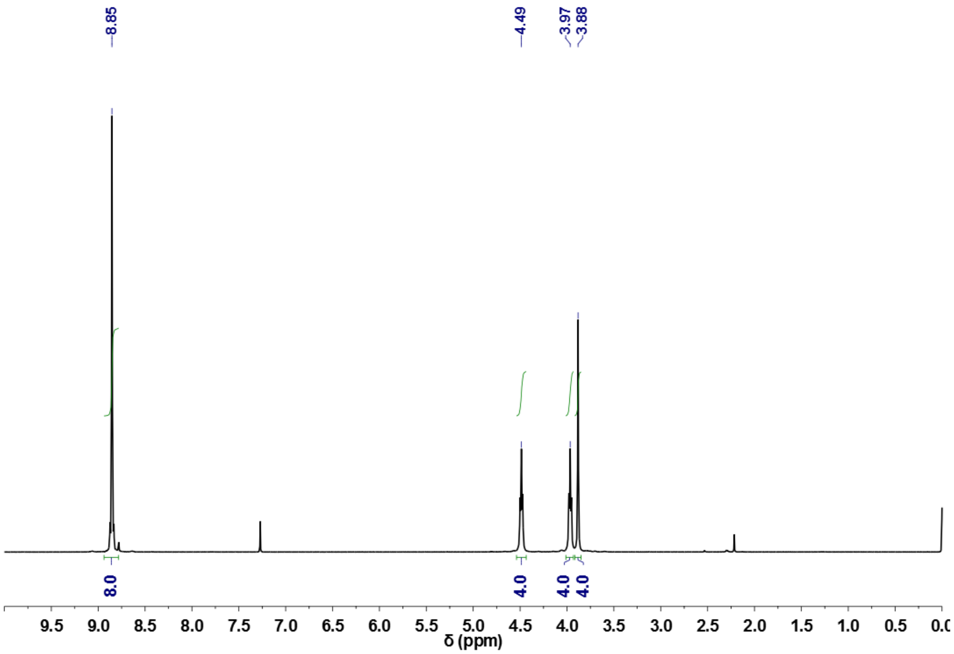

Figure S1: ^{1}H NMR spectrum of the bis-diimide dianhydride intermediate (Scheme 1).

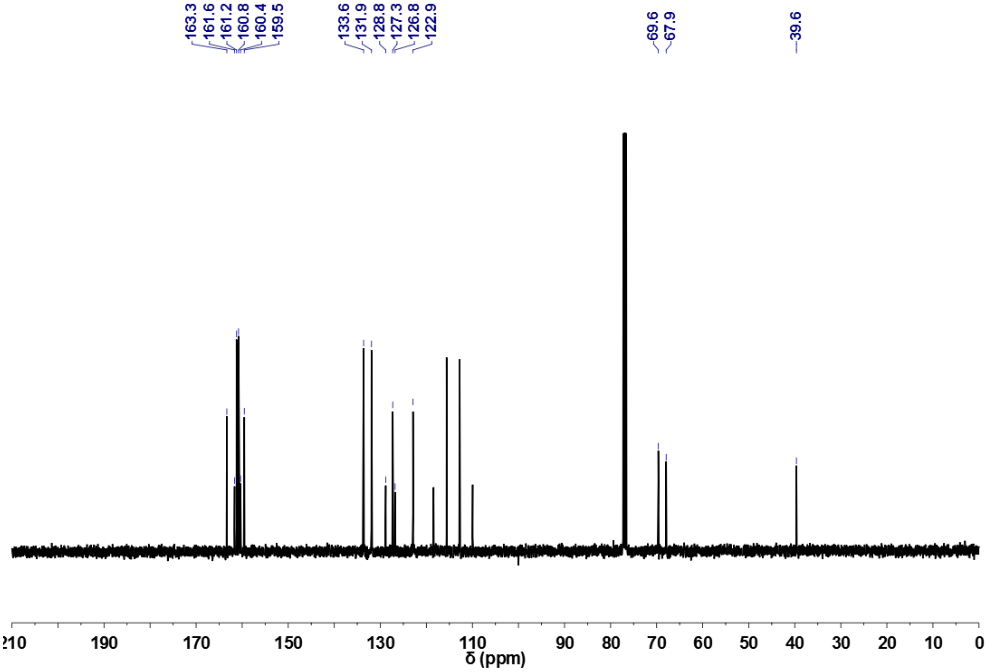

Figure S2: ^{13}C NMR spectrum of the bis-diimide dianhydride intermediate (Scheme 1).

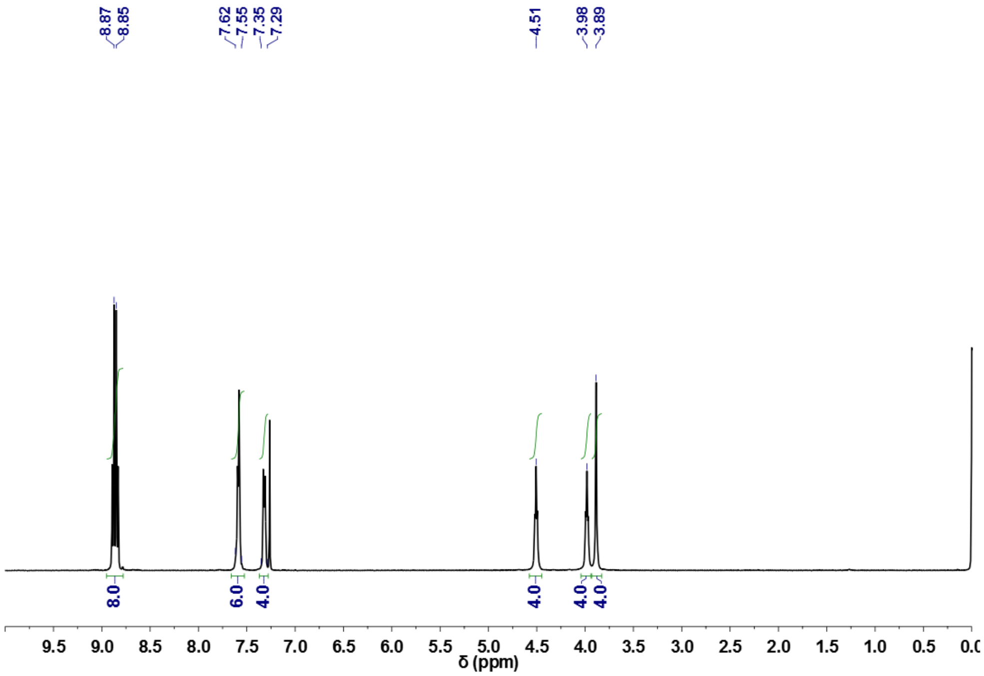

Figure S3: ^{1}H NMR spectrum of the phenyl-terminated chain-folding bis-diimide **1**.

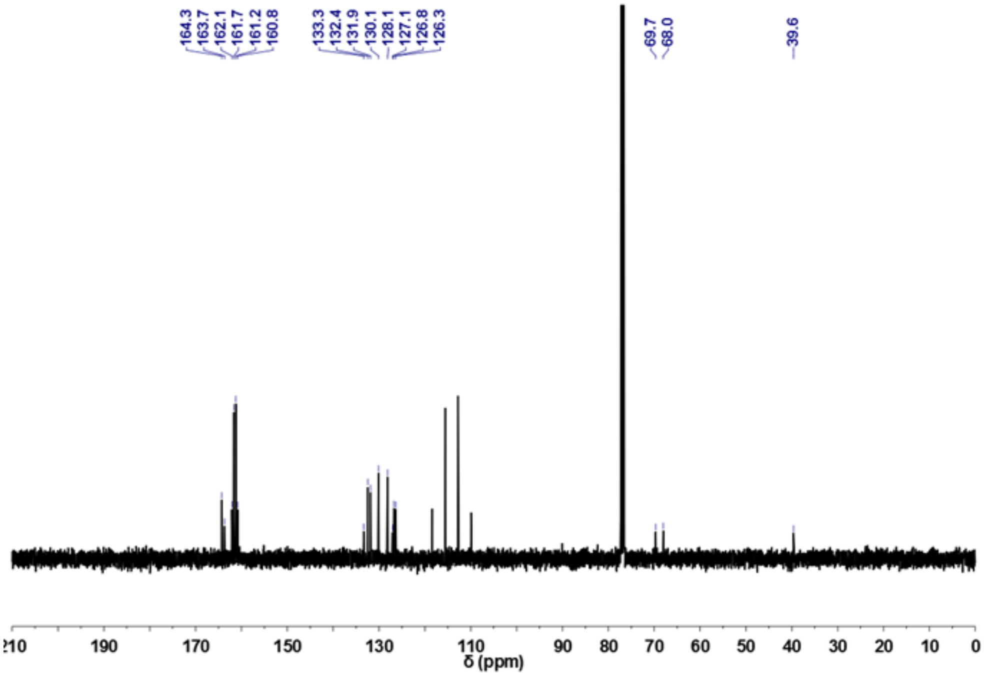

Figure S4: ^{13}C NMR spectrum of the phenyl-terminated chain-folding bis-diimide **1**.

Synthesis of bis-pyrenyl tweezer (2)[S1]

5-Nitro-isophthalic acid (0.40 g, 1.9 × 10^{-3} mol) was refluxed in thionyl chloride (5 mL). After 4 hours, excess thionyl chloride was evaporated under reduced pressure. The resulting solid residue was then dissolved in dry $CHCl_3$ (10 mL) under argon. Pyrenemethylamine hydrochloride (1.034 g, 3.8 × 10^{-3} mol) was added as a slurry in dry $CHCl_3$ (5 mL). Triethylamine (2 mL) was added dropwise to the stirred reaction mixture. The suspension was then diluted with dry $CHCl_3$ (3 mL) and stirred under argon for 24 hours at ambient temperature. The resulting yellow precipitate was then filtered and washed with $CHCl_3$ (75 mL) and hot water (150 mL). The precipitate was then filtered off and washed with copious volumes of water and dried under vacuum (100°C, 24 hours) to yield a yellow solid (0.532 g, 44%). m.p. 314 °C. FT-IR ν_{max}/cm^{-1} 3265, 1651, 1623, 1559, 1534, 1447, 1415, 1452, 1317, 1305, 1290, 1284, 1255; ^{1}H NMR, (DMSO-d_6, 400 MHz): δ (ppm) = 9.70, [2H, t, *J*= 5.5 Hz, $CH_2NHC(O)$], 8.93 [1H, t, *J* = 1.4 Hz, Ar-*H* (*para* to NO_2)], 8.87 [2H, d, *J* = 1.4 Hz, Ar-*H* (*ortho* to NO_2)], 8.49 [2H, d, *J* = 9.3 Hz, Ar-*H* (Pyr)], 8. 27-8.21 [8H, m, Ar-*H* (Pyr)], 8.12-8.11 [6 H, m, Ar-*H* (Pyr), 8.06-8.02 [2 H, m, Ar-*H* (Pyr)], 5.27 [4H, d, J = 5.4 Hz, $CH_2NHC(O)$]; ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) = 163.6, 147.9, 135.8, 132.2, 130.7, 130.2, 128.2, 127.6, 127.3, 127.1, 126.2, 125.3, 125.2, 124.7, 124.4, 124.0, 123.9, 123.2, 41.4.

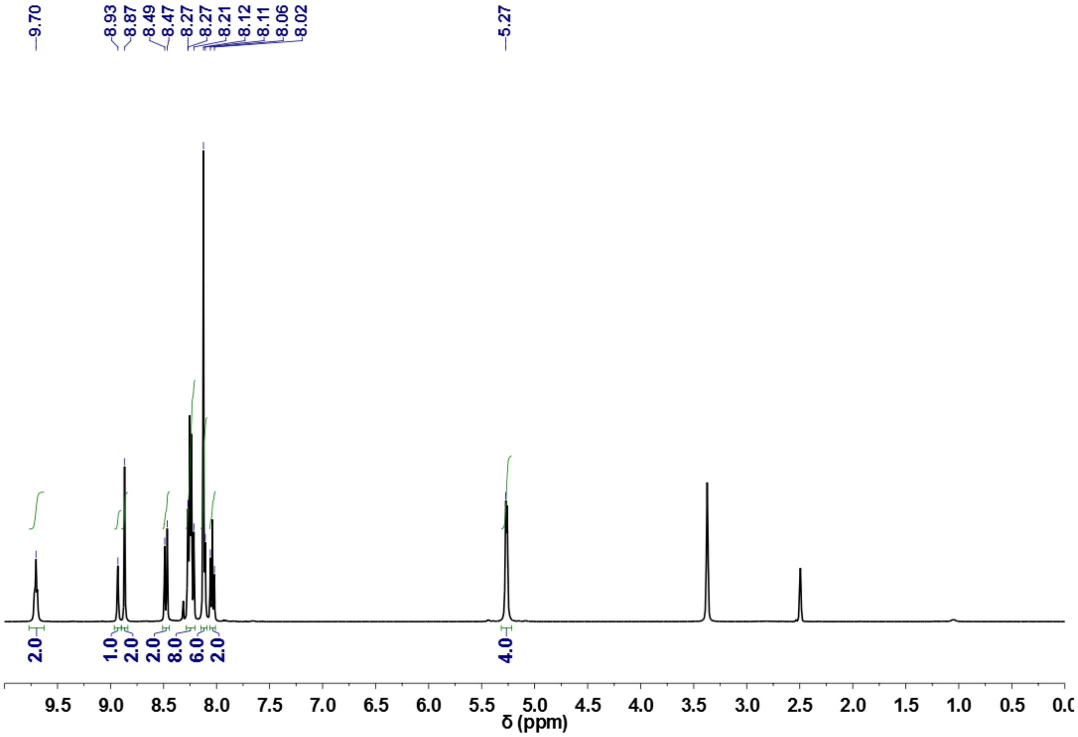

Figure S5: ^{1}H NMR spectrum of the bis-pyrenyl tweezer **2**.

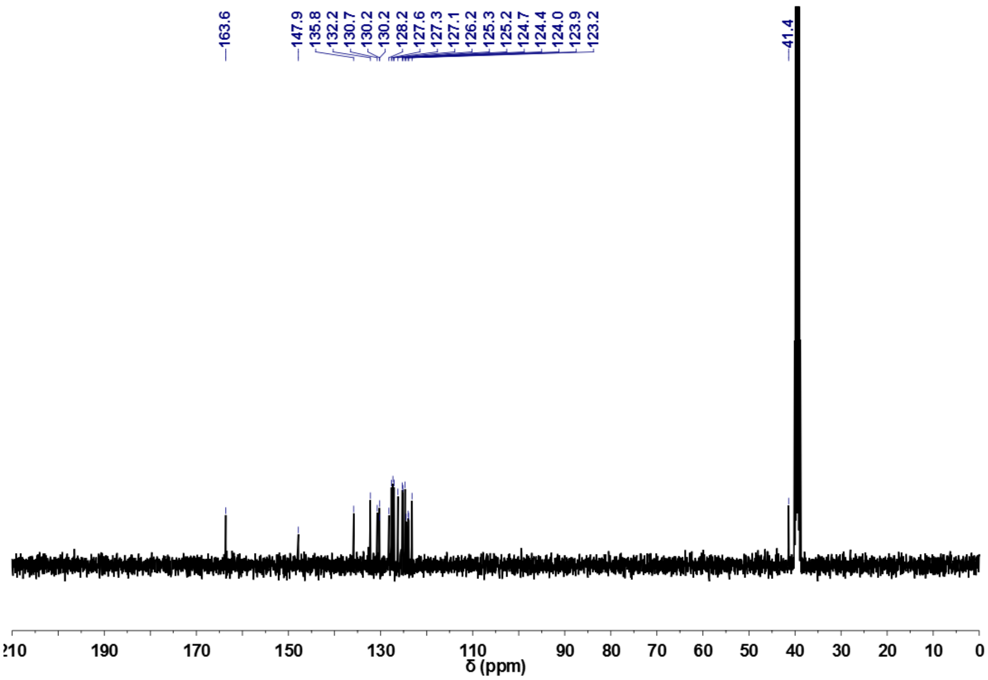

Figure S6: ^{13}C NMR spectrum of the bis-pyrenyl tweezer **2**.

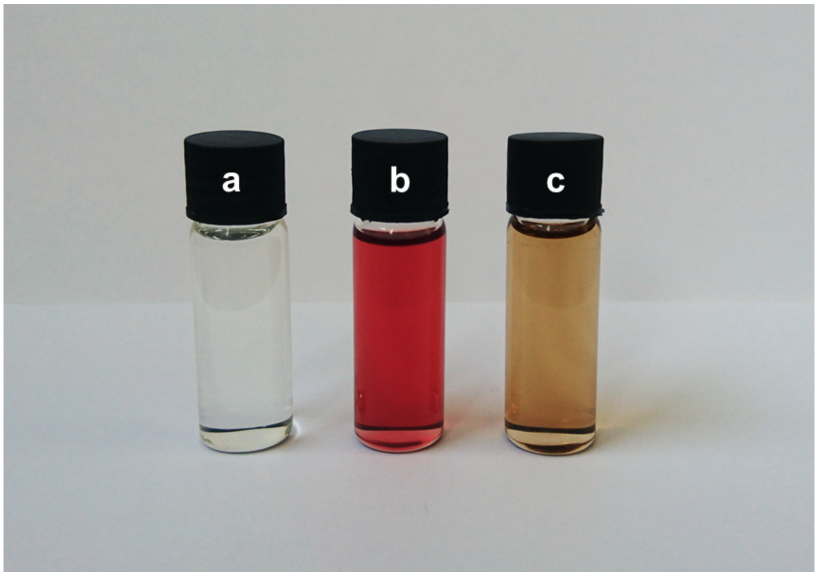

Figure S7: Solutions of (a) the chain-folding bis-diimide (**1**), (b) the 1:1 complex [**1** + **2**], and (c) the bis-pyrenyl tweezer-molecule (**2**). In each case the solvent is $CHCl_3$/TFA, 6:1 v/v.

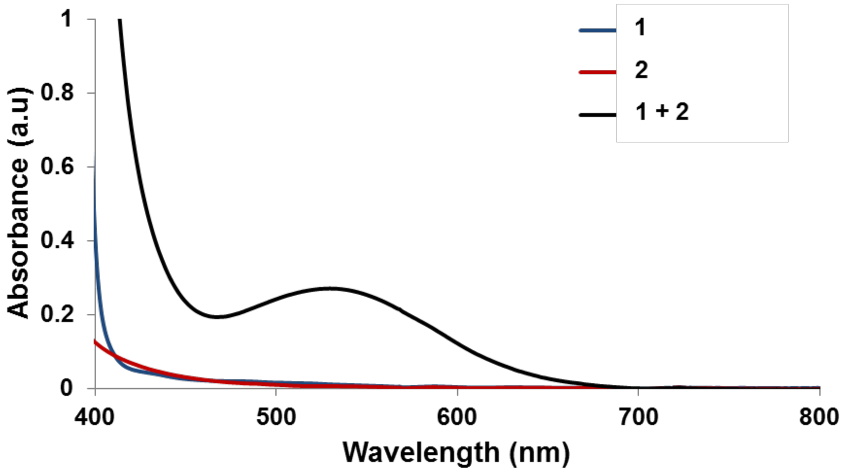

Figure S8: UV-vis spectra of **1** and **2** individually, and of the 1:1 complex [**1** + **2**].

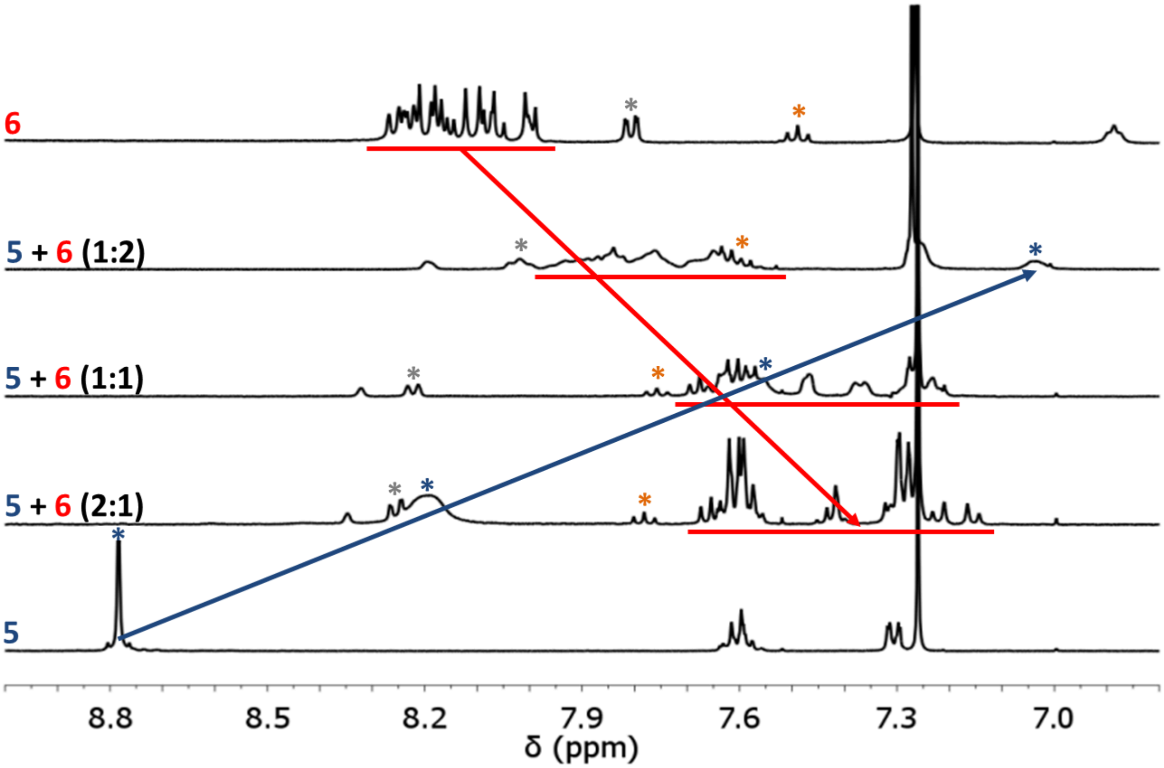

Figure S9: Partial ^{1}H NMR spectra (400 MHz) of chain-folding diimide **1**, bis-pyrenyl tweezer **2** and blends of **1** with **2** at different molar ratios showing upfield shifts of both the diimide (**blue**) and pyrenyl (**red**) resonances. (Spectra obtained in $CDCl_3$/TFA, 9:1 v/v). The broad nature of the proton resonances for both π-electron-rich and π-electron deficient species in the bound state suggests that the system is approaching slow exchange on the NMR timescale. Note also the *downfield* shifts of resonances (* and *) associated with the nitroarene residue of component **2**, implying (as demonstrated in the X-ray structure of [**1**+**2**]) that the nitroarene group must lie within the ring-current *deshielding* zone of a complexing diimide residue.

Measurement of association constant

The association constant for [**1** + **2**] was determined by UV-vis spectroscopy according to the method described by Stoddart *et al*. First, a Job plot was constructed by titrating **1** against **2** (Figure S10), which established that the complex is indeed equimolar as predicted. Next, the intensity of the charge transfer absorption associated with complexation of equimolar quantities of the π-electron-rich and π-electron-deficient species was measured at decreasing total concentration. The concentration range was chosen in order to maintain absorbance of below 1 absorbance unit, values thus being within the Beer-Lambert limit. The concentration range used was: [**1** + **2**] = 0.000400-0.000111 M.

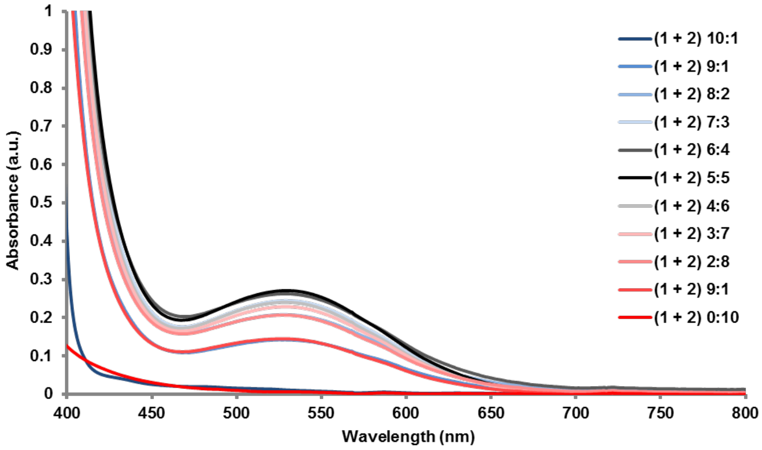

Figure S10: UV-Vis spectra showing the titration of **1** vs. **2** used to construct the Job plot.

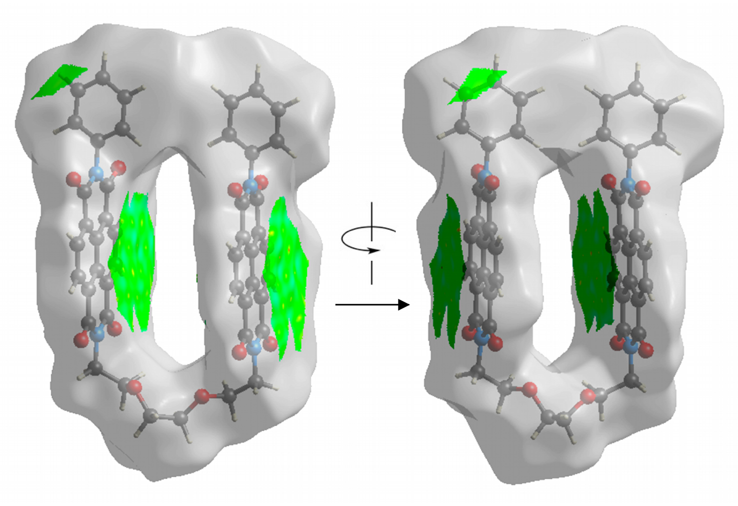

Figure S11: Hirshfeld surface[S2] for the chain-folded bis-diimide component **1**, viewed from two different angles to show both faces of each diimide residue. Regions of the molecule showing close π-π-stacking between the diimide residues shown and the pyrenyl residues of the tweezer-molecule **2** (not shown) are highlighted in green. Three such regions of contact are *within* the supramolecular assembly [**1** + **2**], with the fourth highlighted region representing contact *between* such assemblies along the crystallographic *a*-direction.

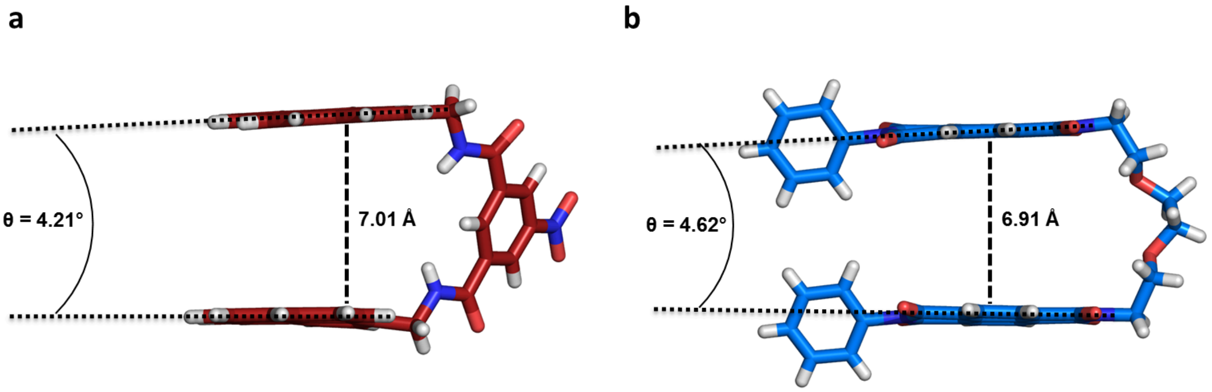

Figure S12: Measurements from the crystal structure of [**1** + **2**]. (a) the divergence of the pyrenyl residues from parallel in **2** (taken from the pyrene mean planess) and the lateral separation (pyrene centroid to centroid) in **2**, and (b) the divergence of the diimide residues from parallel in **1** (taken from the diimide mean planes) and the lateral separation (diimide centroid to centroid) in **1**.

References to Supporting Information

(S1) Greenland, B. W.; Bird, M. B.; Burattini, S.; Cramer, R.; O'Reilly, R. K.; Patterson, J. P.; Hayes, W.; Cardin, C. J.; Colquhoun, H. M. *Chem. Commun.* **2013**, *49* (5), 454–456.

(S2) McKinnon, J. J.; Spackman, M. A.; Mitchell, A. S. *Acta Cryst.* **2004**, *B60*, 627–668.