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Mutual complexation between π - π stacked molecular tweezers

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ABSTRACT

Aromatic and heterocyclic molecules which form electronically-complementary π - π stacked complexes have recently found extensive application in functional materials, molecular machines, and stimuli-responsive supramolecular polymers. Here we describe the design and synthesis of model compounds that self-assemble through complementary stacking motifs, paralleling those postulated to exist in high-molecular weight, healable, supramolecular polymer systems. Complexation studies using ¹H NMR and UV-vis spectroscopy indicated formation of a complementary complex between a π -electron rich dipyranyl tweezer-motif and a tweezer-like, π -electron deficient bis-diimide. The binding stoichiometry in solution between the chain-folding diimide and the pyrenyl derivative was equimolar with respect to the two binding motifs and the resulting association constant was measured at $K_a = 1200 \pm 90 \text{ M}^{-1}$. Single crystal X-ray analysis of this "tweezer-tweezer" complex showed a low-energy conformation of the triethylenedioxy linker within the bis-diimide chain-fold. Interplanar separations of 3.4 – 3.5 Å were found within the π -stacks, and supporting hydrogen bonds between pyrenyl amide NH groups and diimide carbonyl oxygens were identified.

INTRODUCTION

Molecules which exhibit highly directional but non-covalent interactions are the essential components in a supramolecular chemist's armoury. Such interactions have been used to design and build self-assembled supramolecular architectures for a wide variety of potential applications.^{1,2} Low molecular weight species capable of specific, dynamic and addressable interactions have thus been synthesised and deployed in a range of different fields,³ and in the present context, π - π stacking interactions have been the subject of

numerous synthetic and theoretical investigations.⁴⁻⁶ Hunter and Sanders, for example, have proposed⁷ an elegant model of the charge distribution in π -systems to explain the strong geometrical requirements for interactions between aromatic and other planar molecules. This model is based on competing electrostatic interactions between the π -electrons of one component and the aromatic σ -framework of the other ($-/+$, attractive), and between the two π -systems ($-/-$, repulsive) and two σ -frameworks ($+/+$, repulsive).⁸ The model also accounts successfully for the strong face-to-face interactions observed⁹ when complementary electron withdrawing and donating aromatic substituents are present in the supramolecular assembly. Complementary π - π stacking can be utilised synthetically to template the formation of covalent bonds.¹⁰ Stoddart and co-workers have exploited this technique to great effect in the synthesis of mechanically interlocked molecules such as rotaxanes and catenanes, leading to the formation of intricate molecular assemblies,¹¹ molecular switches¹² and molecular machines^{13,14} Thermally addressable copolymers have been synthesised by Iverson and co-workers¹⁵⁻²⁰ with alternating donor and acceptor species that produce reversibly stacked arrangements in solution and the solid state. This type of arrangement often results in strong absorption in the visible range, arising from charge-transfer between the HOMO of the donor and the LUMO of the acceptor.²¹ However, as noted by Hunter and Sanders, charge transfer in this situation is a consequence, rather than a cause, of complementary π - π stacking. We ourselves have previously reported diimide-based macrocycles^{22,23} which allow the self-assembly of complementary "small-molecule" π - π stacked motifs, as well as polymer blends in which supramolecular π - π stacking results in the formation of self-assembled and intrinsically healable materials.²⁴⁻³⁶

Earlier computational studies³⁷ predicted that two π -electron deficient naphthalene diimide moieties separated by a flexible linker derived from 2,2'-(ethylenedioxy)bis(ethylamine), and with simple *N*-methyl substituents as the terminal units (for ease of computation), should give rise to a chain-folding motif that would exhibit complementary face-to-face π - π stacking interactions with a π -electron rich, pyrenyl tweezer-molecule (Figure 1). An average interplanar stacking distance of ca. 3.5 Å between the two complexing species, close to the optimum van der Waals contact distance, was predicted from this molecular mechanics study. The calculated interplanar separations were consistent with values found experimentally for related pyrenyl tweezers/ether-imide-sulfone macrocycles,³⁸ naphthalene/naphthalene diimide catenanes,³⁹ and naphthalene/naphthalene diimide co-crystals.¹⁵

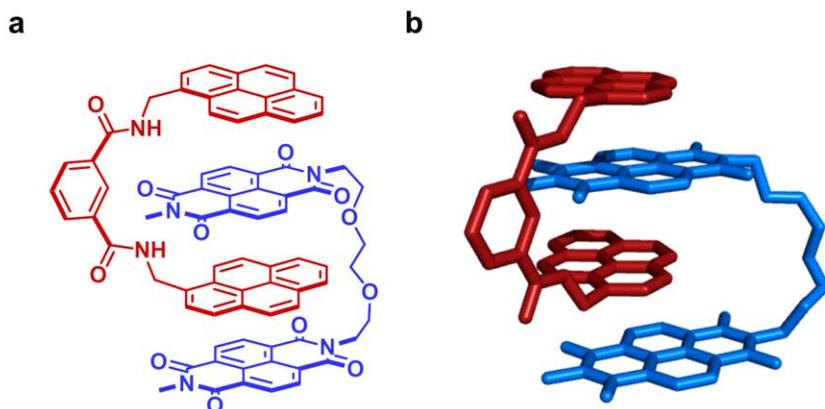


Figure 1. (a) Molecular formula and (b) energy-minimized molecular model of a chain-folding bis-diimide (shown in blue) complexing to a bis-pyrenyl tweezer (shown in red).³⁷

Here we report the synthesis and characterisation of a small-molecule "tweezer-tweezer" type model for the complexation postulated to occur in certain healable materials.²⁴⁻³⁶ The discrete complex formed between the two tweezer-molecules was investigated both spectroscopically in solution and crystallographically in the solid state, and the resulting association constant and binding mode were analysed. Each component in the complex binds to the other in precisely the same "tweezer" fashion, and their interaction can thus best be described as "mutual complexation". These results provide a deeper understanding of the π - π stacking interactions which drive the self-assembly of supramolecular polymers.

EXPERIMENTAL

Methods and Materials. Reagents and solvents were purchased from Sigma Aldrich or Fisher Scientific and were used without further purification, with the exception of chloroform which was dried by distillation from calcium hydride under argon. ¹H NMR (700 or 400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on a Bruker Avance III AV700 or Bruker Nanobay 400 spectrometers using CDCl₃/trifluoroacetic acid (9:1 v/v) with TMS as internal standard or DMSO-*d*₆ as solvents. Infrared (IR) spectroscopic analysis was carried out using a Perkin Elmer 100 FT-IR instrument with diamond-ATR sampling accessory and samples either as solids or oils. UV-visible spectra were measured with a Varian Cary 300 spectrophotometer with heating attachment, using 1 cm² quartz cuvettes, in the wavelength range 350 - 800 nm. Mass spectra were collected using a ThermoFisher Orbitrap XL (ESI) instrument. Melting points were measured by DSC under nitrogen using a Mettler 823e instrument, at a heating rate of 10 °C min⁻¹. The bis-pyrenyl tweezer compound **2** was prepared as described in the literature.⁴⁰ Single crystal X-ray data were measured on Beamline I19 at Diamond Light Source using synchrotron radiation (0.6889 Å).⁴¹

Preparation of the bis-imide-dianhydride intermediate. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (4.02 g, 1.5×10^{-2} mol) was dissolved in KOH solution (4.04 g, 7.2×10^{-2} mol, in 800 mL water) over 1 hour to afford a dark brown solution. The solution was acidified to pH 6.3 using 1M H₃PO₄ before the addition of 2,2' (ethylenedioxy)bis(ethylamine) (1.12 g, 7.5×10^{-3} mol) and subsequent stirring for 20 minutes. The solution was re-acidified to pH 6.4 (1M H₃PO₄) and heated at 110 °C for 20 hours. After cooling to room temperature, acetic acid (20 mL) was added and the mixture was stirred for 30 minutes. The solid was then refluxed in acetic anhydride for 20 hours before being filtered off and dried at 50 °C overnight to afford the bis-diimide dianhydride (4.01 g, 83%). Mpt = 304-307 °C; FT-IR $\nu_{\max}/\text{cm}^{-1}$: 3083, 2959, 1790, 1768, 1708, 1672, 1580, 1449, 1372, 1330, 1287, 1187, 1108, 1056, 1033, 762; ¹H NMR (400 MHz, CDCl₃/TFA 6:1 v/v): δ (ppm) = 8.89-8.84 (8H, s, Ar-H); 4.49 (4H, t, $J = 5.5$ Hz, OCH₂CH₂N); 3.97 (4H, t, $J = 5.5$ Hz, OCH₂CH₂N); 3.88 (4H, s, CH₂OCH₂CH₂OCH₂), ¹³C NMR (100 MHz, CDCl₃/TFA 6:1 v/v): δ (ppm) = 163.3, 161.6, 161.2, 160.8, 160.4, 159.5, 133.6, 131.9, 128.8, 127.3, 126.8, 122.9, 69.6, 67.9, 39.6; ESI-MS: m/z calc. for C₃₄H₂₀O₁₂N₂Na, 671.0914; found: 671.0905.

Preparation of the phenyl-terminated chain-folding bis-diimide (1). The bis-diimide dianhydride intermediate (0.20 g, 3.0×10^{-4} mol) and aniline (0.06 g, 6.3×10^{-4} mol) were dissolved in DMSO (5 mL) and heated under reflux for 18 hours under nitrogen before cooling to room temperature and filtering. The filtrand was washed with diethyl ether (20 mL) and chloroform (10 mL) and dried to afford **1** as a tan powder (0.17 g, 68%). Mpt = 344-349 °C, FT-IR $\nu_{\max}/\text{cm}^{-1}$: 1708, 1661, 1582, 1452, 1247, 1197; ¹H NMR, (CDCl₃/TFA 6:1 v/v, 400 MHz): δ (ppm) = 8.86 (8H, AA'XX' system Ar-H, diimide), 7.62-7.55 (6H, m, Ar-H, *N*-phenyl), 7.35-7.29 (4H, m Ar-H, *N*-phenyl), 4.51 (4H, t, $J = 5.5$ Hz, OCH₂CH₂N), 3.98 (4H, t, $J = 5.5$ Hz, OCH₂CH₂N), 3.89 (4H, s, CH₂OCH₂CH₂OCH₂); ¹³C NMR (CDCl₃/TFA 6:1 v/v, 100 MHz): δ (ppm) = 164.3, 163.7, 162.1, 161.7, 161.2, 160.8, 133.3, 132.4, 131.9, 130.1, 128.1, 127.1, 126.8, 126.3, 69.7, 68.0, 39.6; ESI-MS: m/z calc. for C₄₆H₃₀N₄O₁₀, 798.1949; found: 798.1956.

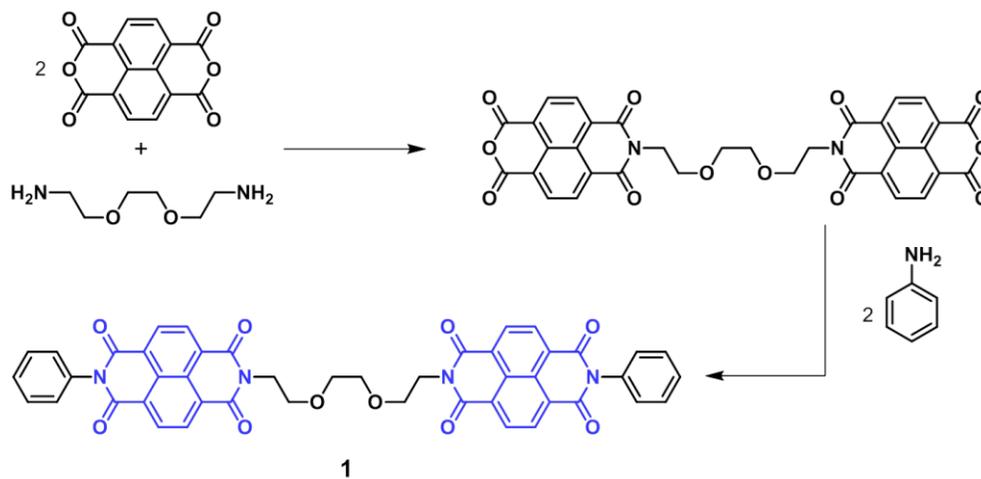
Single crystal X-ray structure. A diffraction grade crystal of complex [**1** + **2**] was grown by vapour diffusion of water into a 1:1 solution of **1** and **2** in a 6:1 v/v mixture of chloroform and trifluoroacetic acid (TFA). Data for [**1**+**2**] were collected on the single crystal beamline I19 at the Diamond synchrotron, Harwell, Didcot, UK, at 150 K to overcome problems of fast desolvation, solvent disorder, and weak scattering of the crystals. CrystalClear (Rigaku) was used for data collection and CrysAlisPro (Agilent) was used for data reduction. The structures were solved by charge flipping using Superflip.⁴² All structures were refined with full-matrix least-squares on F^2 using CRYSTALS.⁴³ The nitro group on the pyrenyl tweezer was disordered over two sites and was refined using parts and thermal restraints.

Crystal data. (C₄₆H₃₀N₄O₁₀)(C₄₂H₂₇N₃O₄), $M_r = 1436.46$, triclinic, P-1. $a = 13.761(8)$, $b = 15.925(10)$, $c = 18.611(10)$ Å, $\alpha = 66.96(3)$, $\beta = 71.71(4)$, $\gamma = 76.72(4)^\circ$. $V = 3537.0(18)$ Å³, $T = 150$ K, $Z = 2$, $D_c = 1.349$

g cm^{-3} , $\mu(\text{synchrotron} - 0.6889 \text{ \AA}) = 0.093 \text{ mm}^{-1}$, $F(000) = 1492$. Independent measured reflections 15129. $R_1 = 0.1082$, $wR_2 = 0.1509$ for 5766 independent observed reflections [$2\theta \leq 25^\circ$, $I > 2 \sigma(I)$]. The electron density present in the centre of the macrocycle could not be identified and so was modelled using PLATON SQUEEZE.⁴⁴ There was a residual electron density of 132 electrons, which could correspond to many combinations of water and trifluoroacetic acid molecules (as used in the crystal-growing process) in a $P1$ unit cell. CCDC 1576798.

RESULTS AND DISCUSSION

To understand the supramolecular binding between the chain-folding diimide units and pyrenyl residues present in a number of recently reported polymers that show intrinsic healability, the complexation of a simple chain-folding bis-diimide with a bis-pyrenyl tweezer was investigated. A simple two-step synthesis of the bis-diimide was chosen, based on desymmetrisation of 1,4,5,8-naphthalenetetracarboxylic dianhydride. An unsymmetrical bis-diimide (**1**) was thus synthesised under pH-controlled conditions using the procedure described by Ghadiri *et al.*,⁴⁵ whereby an intermediate bis-imide dianhydride was obtained from 2,2'-(ethylenedioxy)bis(3-ethylamine) and naphthalene dianhydride (Scheme 1). The bis-imide dianhydride was then end-capped with aniline via conventional thermal imidisation³⁷ to yield the desired chain-folding bis-diimide **1** (Scheme 1) as a pale red solid. In order to explore the complexation behaviour of **1** in solution and in the solid state, a bis-pyrenyl molecular tweezer **2** (Figure 2) was synthesised as described in an earlier publication.⁴⁰ The choice of a nitro-substituted tweezer (**2**) for these studies was based on experience showing that complexes of this molecule afforded better-quality single crystals than those of the corresponding unsubstituted tweezer.



Scheme 1. Synthesis of the chain-folding bis-diimide **1** via desymmetrisation of 1,4,5,8-naphthalenetetracarboxylic dianhydride. Reaction conditions are described in the Experimental section.

When solutions of the chain-folding bis-diimide **1** and bis-pyrenyl molecular tweezer **2** were mixed using chloroform/trifluoroacetic acid (TFA) as solvent, a deep red solution was formed. The color results from a strong charge-transfer absorption³⁷ in the visible (Figure S8), centred at 529 nm as noted previously for related systems.^{31–35,37,46–48} Use of the strong proton-donor TFA as co-solvent was necessary because of the relative insolubility of bis-diimide **1** in more common aprotic or protic solvent systems. The absorption at 529 nm is indicative of π - π -stacking-induced charge transfer from the HOMO of the π -electron-rich pyrenyl moiety **2** to the LUMO of the π -electron-deficient, chain-folding diimide **1**. The formation of complex [**1+2**] was further investigated by ¹H NMR spectroscopy over a range of stoichiometries (see SI). Very large upfield complexation shifts ($\Delta\delta$ up to 1.8 ppm) were observed for the aromatic proton resonances of both the π -electron-rich pyrenyl groups and the π -electron-poor naphthalene diimide residues (Figure S9). This can be attributed to mutual ring-current shielding between the intercalating pyrenyl units and the chain-folding bis-diimide, confirming the presence of complementary π - π stacking supramolecular interactions in solution. Conversely, the *downfield* complexation shifts ($\Delta\delta$ ca. 0.3 ppm) of both resonances associated with nitroarene residue of **2** on complexation with the bis-diimide **1** suggest that, in the complex [**1+2**], the nitroarene ring must lie edge-on to the diimide residue, i.e. within its *deshielding* zone.⁷ As shown below, these conclusions regarding the supramolecular geometry of [**1+2**] in solution are in complete accord with the structure of the complex in the solid state, determined by single crystal X-ray analysis.

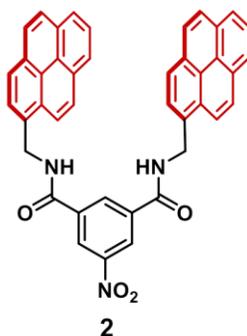


Figure 2. Bis-pyrenyl molecular tweezer **2** used in the present work.⁴²

The association constant for complex [**1 + 2**] was determined by UV-Vis spectroscopy using the dilution method described by Neilsen *et al.* (see SI).²⁸ First, the binding stoichiometry was identified (Figure 3a) by the continuous variation method.⁴⁹ The maximum at 0.5 mol fraction in the resulting Job plot showed that an equimolar complex between **1** and **2** is formed in solution, as predicted by the earlier computational model.³⁷ The association constant was then evaluated from the intensity of the charge

transfer absorption band (λ_{\max}) at equimolar stoichiometry of **1** and **2**, measured at decreasing concentration (Figure 3b). This procedure yielded an association constant (K_a) of $1200 (\pm 90) \text{ M}^{-1}$.

Confirmation of the π -stacking geometry and stoichiometry of complex [**1** + **2**] was provided by single crystal X-ray analysis of the complex (Figure 4). The resulting structure shows the bis-diimide (**2**) folding around the pyrenyl tweezer-molecule (**1**), resulting in three complementary donor-acceptor π - π stacking interactions within each supramolecular assembly.

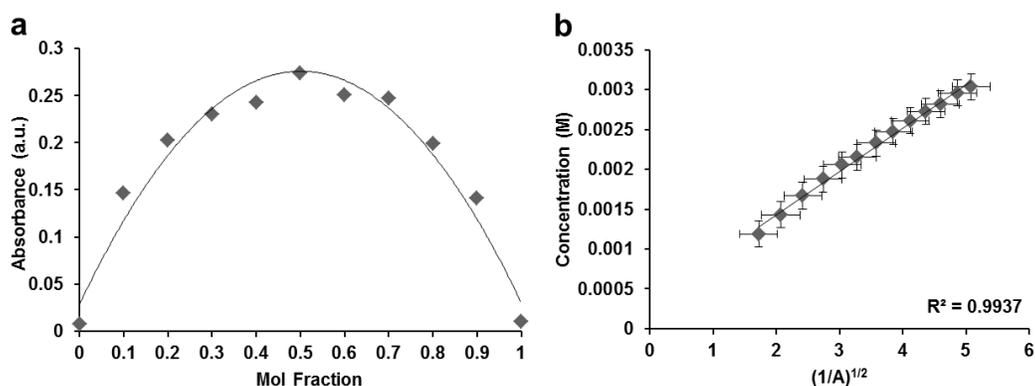


Figure 3: (a) Job plot and (b) UV-Vis binding study using the dilution method for measuring the association constant K_a of the complex formed between **1** and **2** (error bars show standard error).

The interplanar pyrene/diimide separations in the complex [**1** + **2**] are in the range $3.42 - 3.49 \text{ \AA}$. These are essentially van der Waals contacts and are typical of those found in complementary π - π stacked complexes (Figure 4). The diimide residues are essentially parallel whereas the two pyrenyl species are tilted slightly towards one other, as also found in related structures^{40,50-52} (see SI, Figure S12).

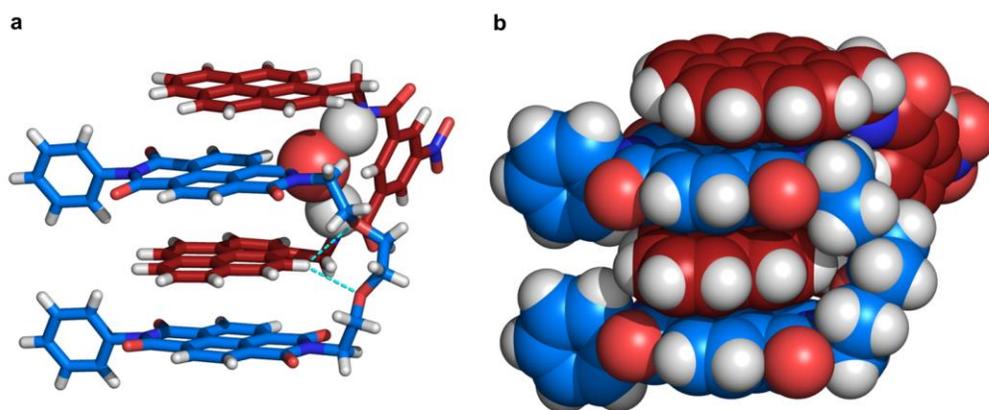


Figure 4: X-ray structure of the 1:1 complex between bis-diimide **1** and bis-pyrenyl tweezer **2**. (a) Stick representation of complex [**1** + **2**], with hydrogen bonds between the amide NH groups of the tweezer molecule and a carbonyl oxygen of a diimide residue highlighted as van der Waals spheres ($\text{N}\cdots\text{O}$ distances are 3.01 and 3.14 Å).

Weak CH \cdots O interactions between the oxygens of the triethylenedioxy chain linking the two diimide residues and a pyrenyl CH hydrogen are also shown as cyan dashed lines (C \cdots O distances are 3.48 and 3.51 Å); (b) Space-filling representation of the complex (atoms shown at van der Waals radii) highlighting the complementary π - π -stacking contacts between aromatic carbon atoms of the pyrenyl and NDI residues.

Reinforcing the π - π stacking interactions are hydrogen bonds between **1** and **2** (Figure 4a). The primary hydrogen bonding mode is between the NH groups of the amide bonds in the bis-pyrenyl tweezer and a carbonyl oxygen of the diimide, but in addition there is evidence for weak CH_{pyrene} \cdots O_{ether} hydrogen bonding, since the pyrenyl residue located within the cavity of the diimide chain-fold is in relatively close contact with the ether oxygens (Figure 4b). The nitroarene subunit of **2** lies edge-on to a complexing naphthalenediimide residue of **1**, exactly as predicted by the NMR analysis above. As shown in Figure 5c, a view of complex [**1** + **2**] along the crystallographic *a*-direction demonstrates that the diimide residues are essentially superimposable, with no net rotation between them. In contrast, the two pyrenyl residues are rotated by ca. 90° with respect to one other (Figure 5b). When considering the relative positions of the π -electron rich and π -electron deficient residues, (Figure 5d-5f) it is important to note that the pyrenyl groups "P1" and "P2" are in two very different environments, with P2 sandwiched between the two diimide residues of **1**, and P1 on the exterior face of one of the diimides (Figure 5a). The pyrenyl unit P1 is offset and rotated by approximately 17° with respect to its adjacent diimide residue (Figure 5d).

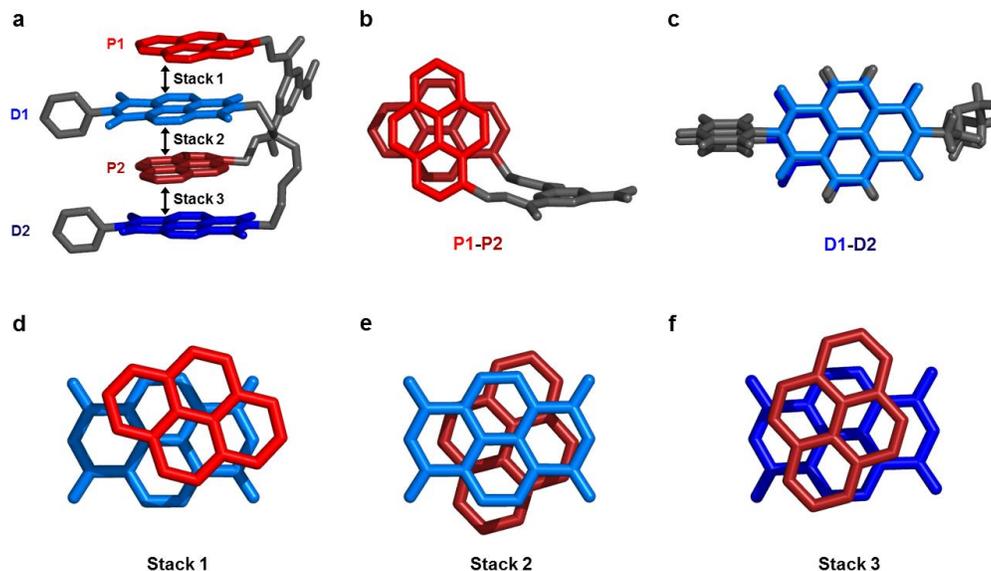


Figure 5: Multiple π - π -stacking within the complex formed by **1** and **2**, showing (a) the crystal structure with each electronically complementary motif labelled; (b) the relative arrangement of the two parallel pyrenyl moieties P1 and P2 in **2**; (c) the relationship (eclipsed) between the two diimide moieties in **1**; and (d-f) the individual relationships within the complex, demonstrating overlap of complementary moieties in the three labelled stacks. There is also a fourth complementary stack between P1 and D2 (in an adjacent complex), as shown in Figure 6.

However, as shown in Figures 5e and 5f, the pyrenyl residue P2 is rotated by approximately 74° with respect to both diimide residues (D1 and D2). It has been suggested that the stacking interaction between NDI and pyrene may involve direct overlap of the HOMO of pyrene with the LUMO of the diimide, as a consequence of the congruent shapes of the two molecules,⁵³ but such an interaction would require an "eclipsed" arrangement of the two complementary residues which is not evident in any of the interactions shown in Figure 5. Indeed, the very different geometric relationships between the diimide residues and pyrenes P1 and P2 in **[1 + 2]** suggest that there is no strong preference for any particular rotational arrangement in such complexes.

Finally, it is important to consider the extended packing of the complex in the crystal. The bis-diimide **1** and bis-pyrenyl tweezer **2** mutually intercalate to form complex **[1 + 2]**, and the complexes pack parallel to the *a* axis of the unit cell forming an infinite π - π stack through the crystal (Figure 6a) containing alternating "donor" and "acceptor" units. The unit cell contains two centrosymmetrically-related complexes, both aligned with their π -stacking directions parallel to *a*, so that the "outside" pyrenyl residue of each complex stacks against a diimide residue of a complex in the next unit cell. The unit cell *a* axis length of 13.76 Å corresponds to four interplanar separations averaging 3.44 Å, three of which are within the complex, and the fourth represents the stacking between complexes in adjacent unit cells.

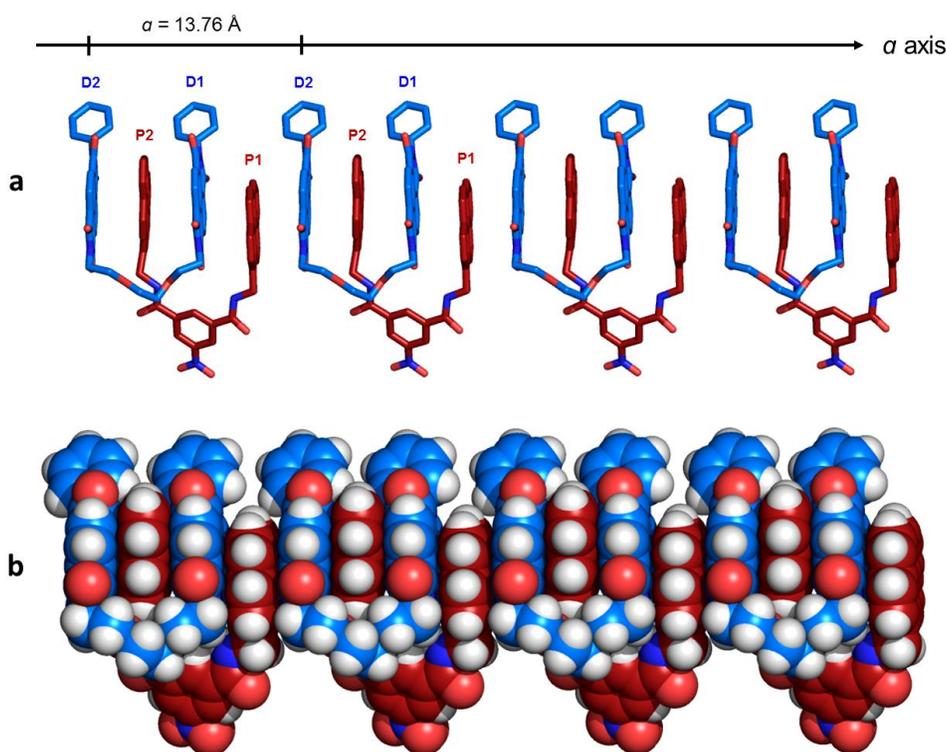


Figure 6: Packing in the crystal structure of [**1** + **2**], viewed perpendicular to the *a* axis. (a) Stick representation of four unit cells. The unit cell *a* axis length of 13.76 Å corresponds to four interplanar separations averaging 3.44 Å. The interacting π -systems are labelled as in Figure 5; (b) Space filling representation in the same orientation, with hydrogen atoms included.

CONCLUSIONS

A chain-folding molecule comprising a pair of naphthalene tetracarboxylic diimide units separated by a flexible triethylenedioxy linking unit has been evaluated for its ability to form a multiply π - π stacked complex with a bis-pyrenyl-tweezer molecule, both in solution and in the solid state. Solution ^1H NMR spectroscopy studies clearly demonstrated the existence of π - π stacking interactions and UV-vis spectroscopic analysis using the charge-transfer band indicates formation of a 1:1 complex in solution. Single crystal X-ray analysis confirmed the formation, in the solid state, of a discrete 1:1 complex between the chain-folding diimide and the bis-pyrenyl tweezer. In the crystal structure, interplanar separations between complementary π -systems (diimide and pyrene) are within the van der Waals separation required for the formation of donor-acceptor π - π stacking interactions. Evidence of hydrogen bonding between tweezer-amide NH groups and diimide carbonyl residues is observed, and weak $\text{CH}\cdots\text{O}$ hydrogen bonds may be present between ether-oxygens of the chain-folding diimide spacer and hydrogen atoms on the pyrenyl moieties. These results confirm and extend previous hypotheses relating to the binding motifs in certain polymeric, self-healing materials.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF, Structure Factors, Checkcif report) for the structure of [**1** + **2**]. ^1H and ^{13}C NMR spectra for **1** and **2**, and for their complexation in solution. UV-vis spectroscopic data and measurement of the association constant for complex [**1** + **2**]. Hirshfeld analysis of π - π -stacking in complex [**1** + **2**]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Mutual complexation between π - π stacked molecular tweezers

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Model compounds that self-assemble through complementary π - π -stacking interactions, paralleling those in high-molecular weight, healable, supramolecular polymers, are described. Complexation studies and association constant determination in solution demonstrate formation of an equimolar complex between two complementary species. Single crystal X-ray analysis of this "tweezer-tweezer" complex show interplanar separations of 3.4 – 3.5 Å within the π -stacks, as well as supporting hydrogen bonds.

