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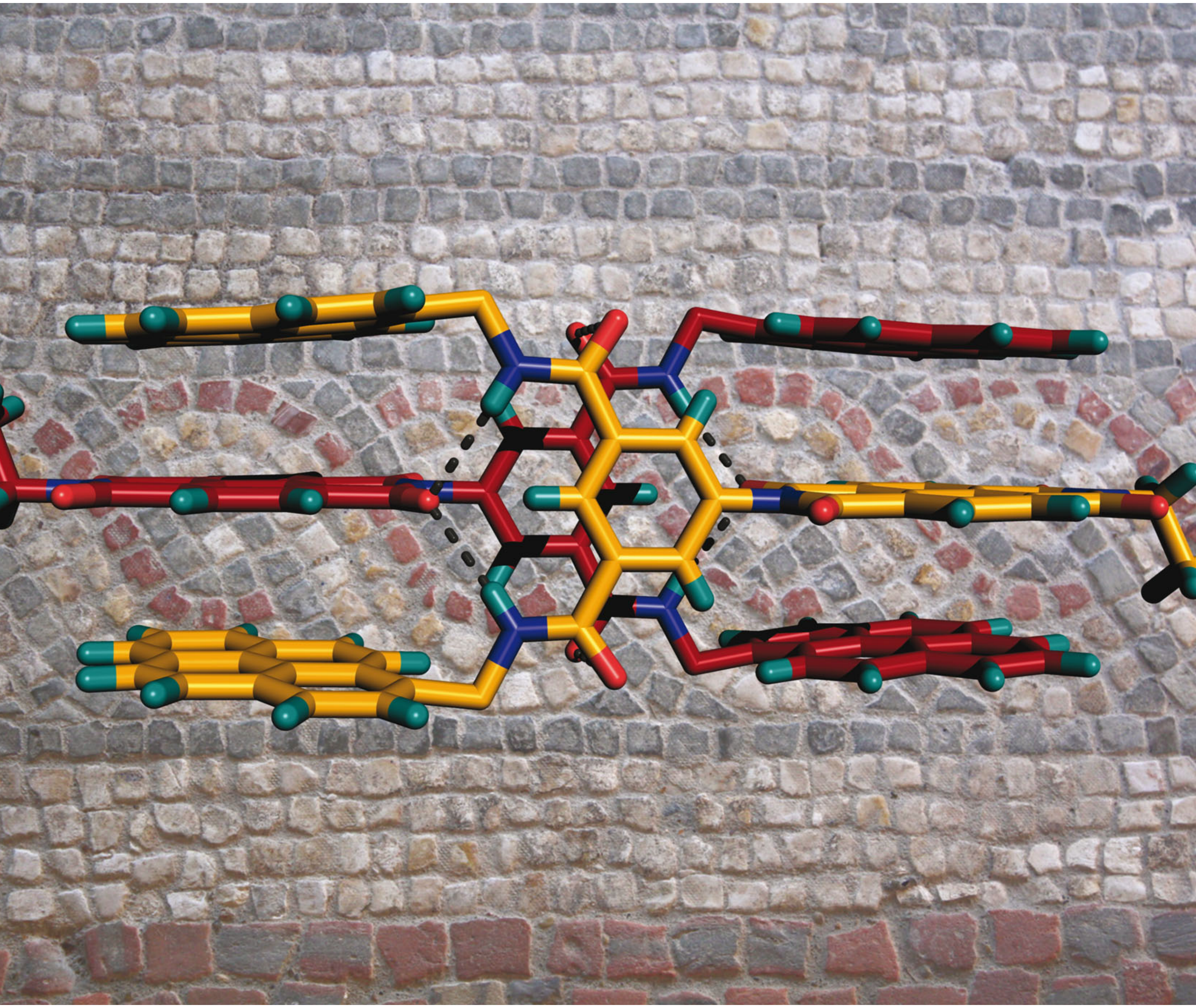

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Mutual binding of polymer end-groups by complementary π–π-stacking: a molecular "Roman Handshake"†

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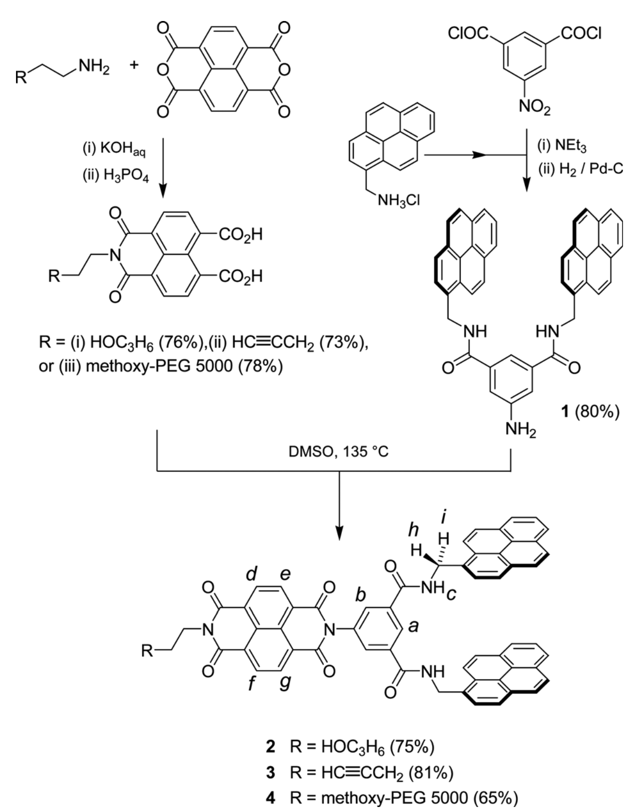
Self-complementary tweezer-molecules based on a naphthalenediimide core self-assemble into supramolecular dimers through mutual π–π-stacking and hydrogen bonding. The resulting motif is extremely stable in solution ($K_a = 10^5\ M^{-1}$), and its attachment to one terminal position of a poly(ethylene glycol) chain leads to a doubling of the polymer's apparent molecular weight.

Systems in which aromatic π–π-stacking interactions enable the assembly of complex, multi-component molecular architectures have given rise to important fields of supramolecular chemistry since the initial discoveries in this area some 30 years ago.[1] In particular, the exploitation of π-electron-accepting, tetracationic cyclophanes as π–π-stacking host molecules has led to the synthesis of charged catenanes, rotaxanes, redox-driven switches and molecular logic gates, *via* templated self-assembly.[2] Similarly, π-electron-accepting macrocycles based on aromatic diimides such as 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) have afforded neutral catenanes and rotaxanes from analogous self-templated reactions.[3]

In addition, a wide range of novel π–π-stacked supramolecules has been obtained using molecular "tweezers" or "clips"[4] which bind electron-poor π-systems between a pair of π-electron-rich arms. A number of clip-type systems also show evidence for strong self-association in aqueous solution driven by hydrophobic interactions,[5] or in the solid state.[6] Most recently, a self-complementary tweezer-type molecule was reported to assemble into π–π-stacked dimers in the solid state, but no evidence could be found for self-association in solution.[7] Self-complementary *hydrogen-bonding* motifs, leading to supramolecular polymers, are of course well-known through the work of Meijer,[8] Zimmerman,[9] and others.[10]

We have recently shown that complementary π–π-stacking has significant potential both for the design of healable, supramolecular polymer blends,[11] and for the development of molecular-level information processing, whereby tweezer-type molecules show sequence-selective binding to triplet sequences in aromatic copolyimides.[12] Here we report that the novel amino-functional tweezer-molecule **1** (Scheme 1) may be attached to a 1,4,5,8-naphthalenetetracarboxylic diimide residue to afford *self*-complementary tweezer-molecules **2** and **3** and a tweezer-functionalised PEG-derivative **4** that shows supramolecular length-doubling in solution.



Scheme 1 Synthesis of the amino-functional tweezer-molecule **1**, the self-complementary imido-tweezers **2** and **3**, and the corresponding tweezer-end-capped polymer **4**.

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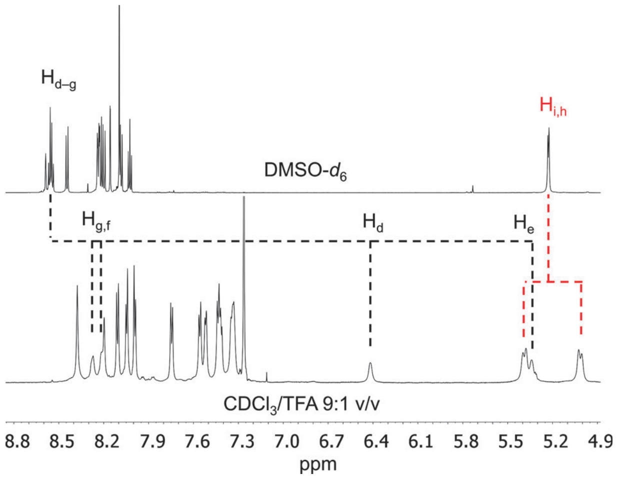

Fig. 1 Comparative ^1H NMR spectra of **3** ($R = CH_2C{\equiv}CH$) in d_6-DMSO and $CDCl_3$/TFA (9 : 1 v/v). Note the very large self-complexation-induced resonance shifts and magnetic inequivalencies for protons H^d and H^e in the spectrum when $CDCl_3$/TFA is used as solvent.

The ^1H NMR spectrum of **3** in DMSO-d_6 confirmed the structure shown in Scheme 1, but showed no evidence for the expected intermolecular π–π-stacking. In particular, the four diimide protons (H^d, H^e, H^f and H^g in Scheme 1) appear as a very narrow A,A′,B,B′ system at 8.54 ppm, with no upfield shifts or separations that could be associated with aromatic ring-current shielding. However, the potent solvating effects of DMSO are well known to diminish or even abolish many supramolecular interactions,[13] whereas associations through π–π-stacking are generally unaffected, or even mildly enhanced, by proton-donor solvents such as $CDCl_3$/hexafluoropropan-2-ol or $CDCl_3$/trifluoroacetic acid.[14]

In keeping with this, the ^1H NMR spectrum of **3** in $CDCl_3$/trifluoroacetic acid (9 : 1 v/v) showed very striking evidence of intermolecular π–π-stacking, with the four diimide protons now appearing as four separate resonances, spanning a *very* wide chemical shift range (*ca.* 3 ppm; Fig. 1). The position of one diimide resonance in particular (at 5.35 ppm) signifies extensive ring-current shielding by pyrenyl units, as this represents a 3.1 ppm upfield shift from its position in DMSO-d_6 (ESI,† Fig. S7). Moreover, the chemically-equivalent methylene protons H^h and H^i of **3** (Scheme 1) are now represented by two distinct doublets (*gem*-CH_2, J = 14 Hz) separated by *ca.* 0.4 ppm.

The magnetic inequivalence of three chemically equivalent pairs of protons (H^d and H^f; H^e and H^g; and H^h and H^i) must reflect restricted rotation about the *N*-aryl and pyrenyl-CH_2 bonds respectively. These inequivalencies are not observed in the corrresponding spectrum in DMSO-d_6, so that the conformational restrictions can only arise from strong intermolecular association in $CDCl_3$/trifluoroacetic acid, with exchange between molecular pairs being frozen on the NMR timescale. The ^1H NMR spectra of compounds **2** and **3** in this solvent system showed no change in chemical shifts on dilution, implying a very high self-association constant. A K_a value of 100 000 [$\pm$10 000] M^{-1} was eventually determined for dimerisation of **3** using the UV-visible dilution method.[15] This association constant is amongst the highest ever recorded for a π–π-stacked complex in a non-aqueous solvent.[16]

Single crystal X-ray analysis (see ESI†) of the alkynyl-functional compound **3** confirmed that the molecule forms a centrosymmetric, supramolecular dimer with multiple, complementary π–π-stacking and hydrogen bonding interactions between the two molecules (Fig. 2). The overall supramolecular motif is very reminiscent of the type of handshake used in ancient Rome – a mutual grip of the wrist[17] – and here it seems to represent a similarly firm molecular clasp. The inequivalencies identified by ^1H NMR analysis are completely consistent with the dimeric structure found in the solid state. In particular, one diimide proton (H^e, colour-coded green in Fig. 2b) is positioned such that it would experience much greater ring-current shielding than the others, so that this proton can be identified with the very high-field diimide resonance referred to above (δ = 5.35 ppm; $\Delta\delta$ = 3.10 ppm relative to its position in DMSO-d_6).

Polymer **4**, derived from an amino-terminated methoxy-PEG of nominal MW 5000 (Scheme 1; also ESI,† Fig. S10), shows much greater solubility than either **2** or **3**, being soluble in a wide range of solvents including water, acetone, toluene, chloroform and DMSO. Solvatochromism of the charge-transfer band is observed,[14a] with a shift in peak absorbance of **4**, from 520 nm in toluene to 570 nm in water, leading to an observable change in colour from deep red to olive green (ESI,† Fig. S11). Polymer **4** also undergoes non-covalent association and consequent length-doubling in chloroform, as shown (i) by ^1H NMR spectroscopy (ESI,† Fig. S8 and S9: proton inequivalencies are very similar to those described above for **3**), (ii) by an intense charge-transfer absorption at 520 nm, and most importantly (iii) by its molecular weight distribution from GPC in chloroform (Fig. 3). The two clearly-defined peaks represent M_n values of *ca.* 4.9 kDa and 11.5 kDa, corresponding to single- and double-length polymer chains respectively, so that polymer **4** – in this solvent – could be described as a dynamic block copolymer

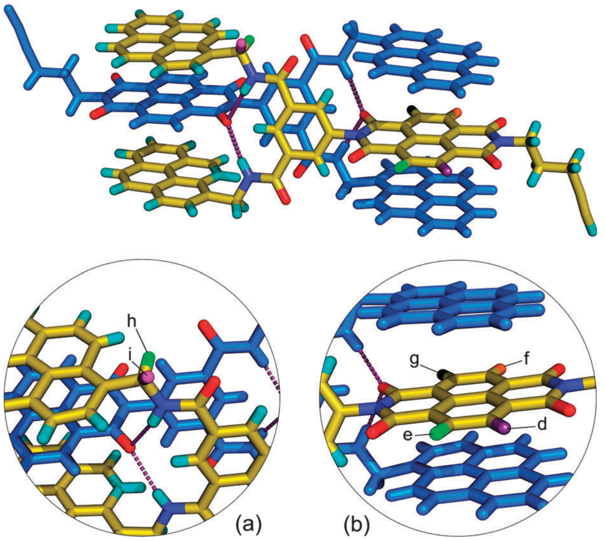

Fig. 2 Single crystal X-ray structure of the imido-tweezer-molecule **3** (centrosymmetric, supramolecular dimer). The upper view illustrates the two triple-π-stacks resulting from dimer formation and shows hydrogen bonds (in magenta) between amide NH and diimide C=O units. The lower views show how dimerisation leads to magnetic inequivalence (a) of geminal CH_2 protons (*h* and *i*, green/magenta), and (b) of chemically equivalent pairs of protons in the naphthalenedimide residue (*e* and *g*, green/black; *d* and *f*, purple/orange).

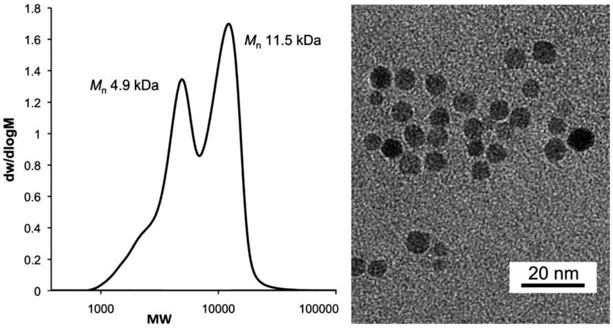

Fig. 3 Left: GPC trace for polymer **4** in chloroform, calibrated against PEG standards; the two peaks correspond to single-length and double-length chains arising from association *via* the "Roman Handshake". Right: transmission electron micrograph showing micellar nanoparticles of polymer **4** on a graphene oxide support.

[PEG–"Roman Handshake"–PEG]. Conversely, in DMF-LiBr as eluent, only a single peak corresponding to unassociated chains was observed, confirming the conclusion from NMR analysis that, in the present system, dipolar aprotic solvents are powerful inhibitors of supramolecular dimerisation.

In aqueous solution, dimerisation of polymer **4** is clearly evident from the strong charge-transfer absorption in the visible at 570 nm (ESI,† Fig. S11), but **4** also seems to aggregate to form micellar-type structures in water. Aqueous GPC thus shows peaks at $M_n \approx$ 4500 Da (unimers) and $\approx$ 120000 Da (self-assembled nanostructures; ESI,† Fig. S12). However, no GPC peak associated with the dimer is observed in water, suggesting that in aqueous solution the dimers themselves undergo a further assembly process to form micelles. This is corroborated by unstained TEM analysis (Fig. 3) of dried samples on graphene oxide supports,[18] which shows well-defined, spherical assemblies with diameters in the size-range 6–8 nm. Analysis by dynamic light scattering also confirmed that nanoscale structures (*ca.* 20 nm) were present in aqueous solution although, as is often found for PEO-based systems,[19] larger aggregates (*ca.* 200 nm) were also found.

We have thus demonstrated a powerful new self-assembling molecular motif based on electronically-complementary π–π-stacking interactions and hydrogen bonding, and have shown its potential for effective enhancement of polymer molar mass.

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