Design, synthesis and computational modelling of aromatic tweezer-molecules as models for chain-folding polymer blends

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ABSTRACT

Novel 'tweezer-type' complexes that exploit the interactions between π-electron-rich pyrenyl groups and π-electron deficient diimide units have been designed and synthesised. The component molecules leading to complex formation were accessed readily from commercially available starting materials through short and efficient syntheses. Analysis of the resulting complexes, using the visible charge-transfer band, revealed association constants that increased sequentially from 130 to 11,000 M^{-1} as increasing numbers of π–π-stacking interactions were introduced into the systems. Computational modelling was used to analyse the structures of these complexes, revealing low-energy chain-folded conformations for both components, which readily allow close, multiple π–π-stacking and hydrogen bonding to be achieved. In this paper, we give details of our initial studies of these complexes and outline how their behaviour could provide a basis for designing self-healing polymer blends for use in adaptive coating systems.

1. Introduction

Materials chemistry has seen an explosion of interest in polymers with tuneable properties in recent years. One of the many driving forces for this research has been the desire to produce polymers with healable or even self-healing characteristics.[1] Polymers of this type are typified by their ability to re-organise their molecular architecture in response to a controllable external stimulus such as heat, light or an electric field.[2] Thus, if subjected to stress or even fracture, the material is able to recover the physical properties of the original system. Significant progress towards the goal of self-healing polymers has been made by several groups. Notably, Wudl et al. have synthesised epoxy resins containing diene (furan) and dieneophile (maleimide) residues.[3] These components are able to react via a thermally reversible Diels–Alder reaction to heal any structural damage within the resin. Thus, should a crack form in the material, the system can be subjected to a thermal annealing process during which time new covalent bonds form between monomers between either side of the crack and the material can regain its mechanical properties.

An alternative approach to self-healing polymers has been investigated by White et al.[4] In these systems, the bulk polymer contains a dispersion of microcapsules filled with a monomeric 'healing agent'. Should a crack propagate through the polymer, it ruptures the microcapsules, releasing the monomer into the crack. The healing agent is then polymerised by contact with a catalyst, which is also impregnated within the bulk material, thus sealing the crack with new polymer.

In contrast to these covalent-bond-forming approaches to heal a fracture in a polymeric material, it has recently been shown that non-covalent bonds may be used to effect healing processes within supramolecular polymer materials.[5] Supramolecular materials generally comprise low to medium molecular weight species that form extended polymeric architectures via non-covalent interactions.[6] Such self-assembled materials have been found to exhibit physical properties similar to those of high molecular weight polymers, including high viscosity[7] and a high storage modulus.[8] It has been postulated[5] that, in polymer systems of this type, a fracture will propagate via dissociation of the weaker supramolecular bonds between the components, rather than by scission of the stronger covalent bonds within these units. In this model, as the components of the material remain chemically unaltered during the fracturing process, application of a suitable stimulus may allow the supramolecular array to re-assemble and so ultimately restore the original properties of the material.

Studies by Sijbesma and Meijer have shown that high binding constants $(>10^7 \, M^{-1})$ are required to generate stable and processable supramolecular polymers.[9] However, in addition to the requirement for high binding efficiencies between the recognition

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units of the monomeric components, the purity of the monomers used also constrains the ability to produce materials with properties consistent with high molecular weight polymers.[7]

As part of a programme working towards the development of healable and self-healing polymers, we are investigating whether a blend of two interacting oligomeric components, in which one of the species possesses multiple but equivalent binding sites, will enable the generation of 'infinite' supramolecular arrays. A supramolecular polymer of this type would possess a cross-linked architecture and should therefore be tolerant of minor quantities of impurities such as mono-functional components. In order to realise self-assembling, supramolecular polymer systems of this type, we are exploiting the well-known 'charge-transfer' (π–π-stacking) interaction between π-electron-deficient naphthalene tetracarboxylic diimide or pyromellitic diimide moieties and π-electron-rich species such as pyrenyl or alkoxynaphthalenyl residues.[10] Complexes between such species have previously been employed to synthesise a diverse range of systems ranging from small-molecule catenanes[11] and clips or 'tweezer'-type molecules,[12] to extended oligomeric and polymeric complexes.[13] Notable contributions in this field have been reported by Iverson et al. who produced a series self-complementary, chain-folding 'aedemers',[14] and the interactions occurring in double stranded 'zipper' type supramolecular polymeric complexes have also been studied.[15] More recent investigations by Colquhoun et al. have explored the interactions between small, pyrene-based tweezer-molecules and high molecular weight, chain-folding polyimides.[16]

Utilising the chain-folding concept to provide multiple binding sites embedded in an oligo-imide backbone, it should be possible to 'cross-link' these low molecular weight entities (non-covalently) with telechelic pyrenyl-terminated oligomers via π–π-stacking and hydrogen bonding interactions, to produce potentially healable supramolecular materials. As part of our programme to generate oligomeric, multi-receptor systems featuring chain-folding aromatic diimide units and pyrene-functionalised chains, we set out to gain a detailed understanding of the interactions between these two recognition motifs. Specifically, we sought to answer the following questions: (i) what is the simplest chain-folding motif that can be synthesised and analysed; and (ii) is it possible to modulate the strength of the interactions between pyrenyl moieties and the chain-folding diimide to generate complexes with 'designed-in' binding constants? The present report details the rational design and synthesis of a series of well-defined models for the proposed chain-folding host polyimides and a study of their interactions with a variety of pyrene-based guest molecules.

2. Results and discussion

2.1. Computational modelling

Key to success of the proposed two-component, complementary polymer blend is the design of the chain-folding, diimide-oligomer host system. It is vital that the separation of the π-electron deficient imide groups allows them to attain the correct spatial configuration in order to form a strong tweezer-like complex with a pyrenyl unit. An additional design consideration is that the systems studied should be accessible from readily available starting materials through short and efficient syntheses routes if materials of genuine utility are to be obtained. This approach ensures that the complexation data, structural understanding and synthetic insights gained through the present model studies can be transferred with confidence to analogous but more complex higher molecular weight materials.

Computational modelling studies (charge-compensated molecular mechanics, using a custom-modified version of the Dreiding II force field, Cerius3.5, Accelrys Inc., San Diego) revealed that separating two naphthalene tetracarboxylic diimide units with a short but highly flexible spacer-group derived from commercially available 2,2′-(ethylenedioxy)bis(ethylamine) (1) would allow the imides to adopt the correct spatial orientation to generate the 'chain-folded-tweezer' motif required for strong face-to-face binding to pyrene (Fig. 1). For ease of computation, the model for the diimide tweezer 2 contained simple methyl substituents at the imide termini. Encouragingly, the interplanar separation between the atoms of the diimide units and pyrene 3 within the complex was found to be close to van der Waals contact distances, at ca. 3.5 Å—consistent with values observed in the solid state structures of related tweezers[12] and catenanes[11] and also with those found in the co-crystals of pyrene and diimide derivatives.[14a]

Whilst this simulation was most encouraging, it was apparent that if 1:1 complexation between tweezer diimide 2 and pyrene 3 occurred as predicted, each of the π-electron-poor diimide units in tweezer 2 would only be able to maintain one face-to-face interaction with the π-electron-rich pyrene guest. However, to increase the number of associative interactions between the species, a simple approach would be to employ the amide-based, pyrenyl tweezer-molecule 4, which we have studied extensively over recent years.[12,16] Modelling the 'tweezer–tweezer' complex, which could potentially be formed between compounds 2 and 4 strongly supported this approach, and suggested that both the pyrenyl groups of 4 would be able to form strong, associative, face-to-face interactions with the new bis-diimide tweezer 2. Moreover,
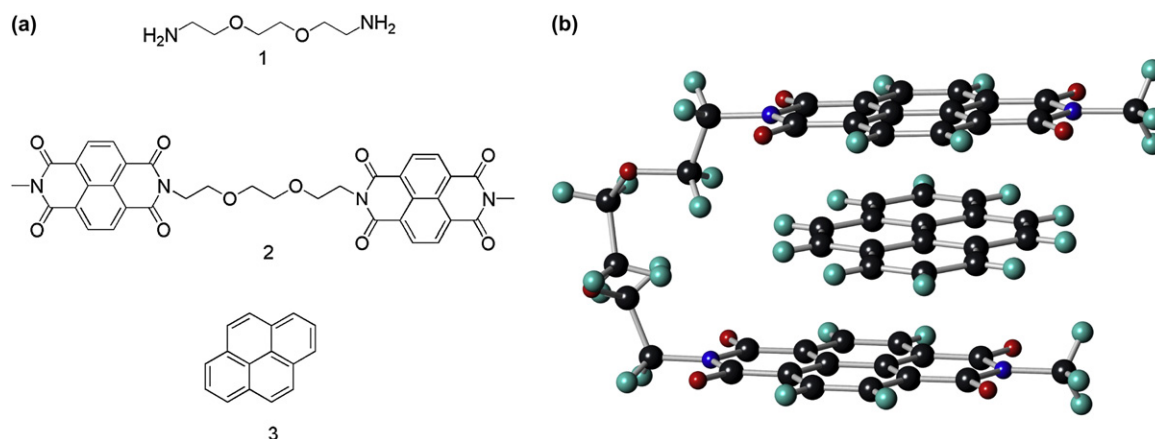

Figure 1. Structure of diimide tweezer **2** (a) and minimised model of the tweezer-type complex between the bis-diimide **2** and pyrene (b). Interplanar spacings between the π-systems average ∼3.5 Å.

additional binding forces should result from the pair of convergent hydrogen bonds (NH···O=2.01, 2.39 Å) predicted to occur between the two amide –NH– groups of **4** and one of the carbonyl groups of **2** (Fig. 2).

Extending this concept still further, the oligomeric diimides, for which compound **2** is designed to be a model, would contain several repetitions of the bis-diimide chain-folding motif along the backbone. This structural repeat would offer the potential for a third diimide unit to complete a second chain-fold around the bis-pyrenyl tweezer and thus bind both faces of *each* pyrenyl moiety of **4**, so further increasing the overall strength of binding between π-electron-rich and π-electron-poor components. An energy-minimised model of a complex between the trimeric diimide (**5**), wherein each of the diimide units is separated by a 2,2′-(ethyl-enedioxy)bis(ethylamine) residue (see **1** in Fig. 3), and the bis-pyrenyl tweezer-molecule **4** showed that a second chain-fold could indeed be achieved quite readily. This system could thus meet our aim of producing a model chain-folding polyimide from the minimum number of low-cost, commercially available starting materials.

2.2. Synthesis and binding studies

Guided by the computational modelling studies of the complex between the diimide tweezer **2** and pyrene (**3**) it was evident that, to realise even the simplest such system in practice, it would be necessary to synthesise a bis-diimide in which each of the diimide units is unsymmetrically substituted. Simple addition of the required mono- and di-amine to naphthalene dianhydride **6** would result in a statistical distribution of products, which in turn would necessitate extensive purification to isolate the desired compound, resulting in low yields of the target compound. To circumvent this problem, the reaction conditions described by Buncel et al. were employed.[17] Thus, by carrying out the reaction stepwise, first in water with careful control of pH (Scheme 1), unsymmetrically substituted diimides may be obtained in good yields (typically ca. 75%). In the present work, application of this procedure enabled the synthesis of diacid imide **7** in excellent yield (85%, Scheme 1). The branched amine **8** was chosen as a commercial analogue of the so-called 'swallow tail' hydrocarbons, which have been used to promote solubility in related systems.[18] Diacid **7** was used directly
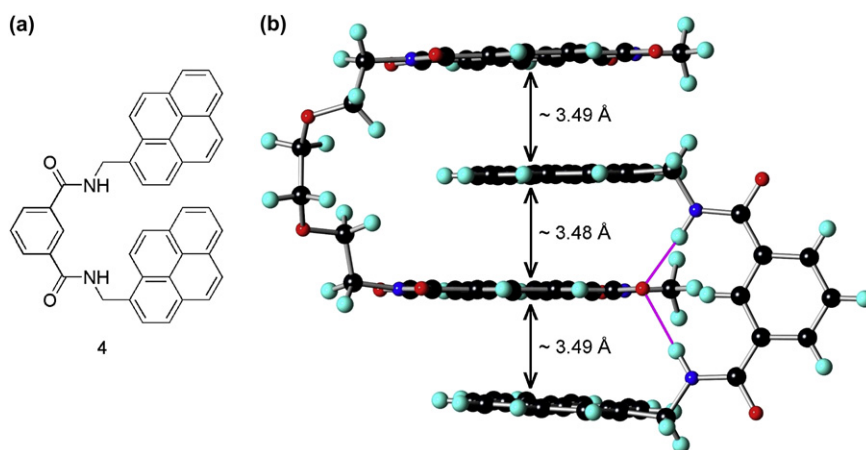

Figure 2. Molecular formula of the bis-pyrenyl tweezer-molecule **4** (a) and an energy-minimised model of its complex with the bis-diimide **2** (b). Interplanar spacings shown are the average distances of pyrenyl carbons from the mean planes of the diimide units. Hydrogen bonds (NH···O) are shown in magenta.
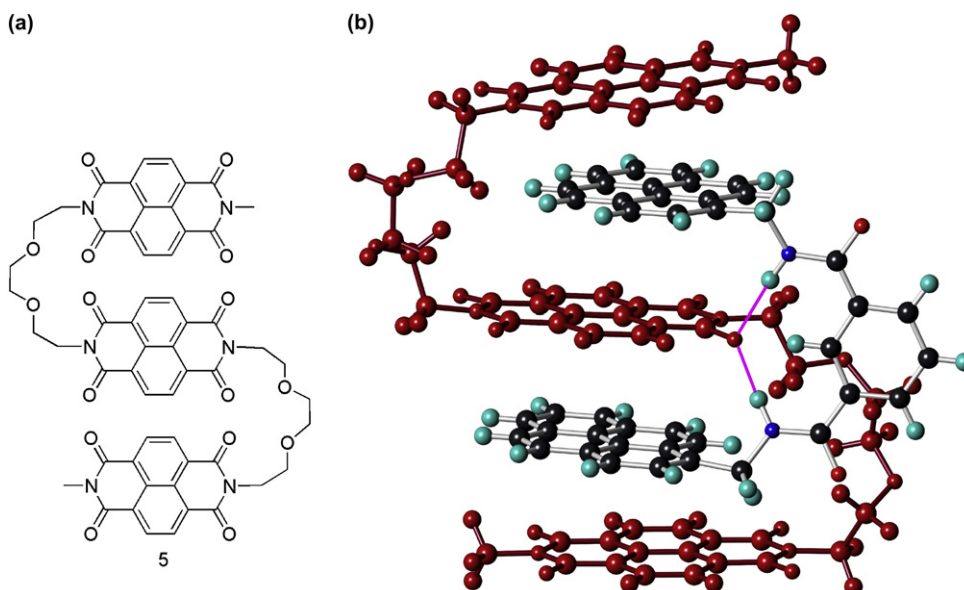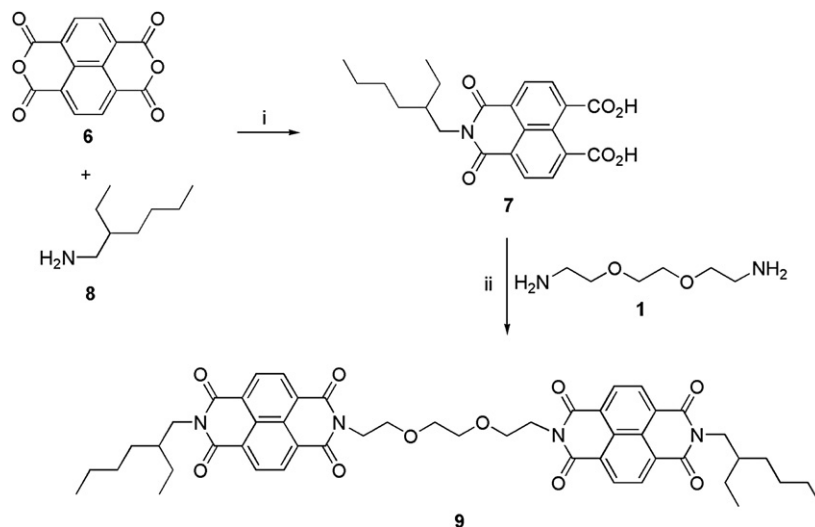

Figure 3. Structure of tris-diimide (a) and energy-minimised model of the complex formed between the trimeric diimide **5** and the bis-pyrenyl tweezer **4** (b). Molecule **5** is shown in red, to distinguish it more clearly from tweezer **4**. Hydrogen bonds (NH···O) are shown in magenta.

Scheme 1. Synthesis of bis-diimide tweezer **9**. Reagents and conditions: (i) H$_2$O, pH=6.2, 110 °C, 24 h, 85%; (ii) DMAc, 125 °C, 18 h, 82%.

to synthesise the model tweezer-type compound **9** (82% yield) by reaction with 0.5 mol equiv of 2,2′-(ethylenedioxy)bis(ethylamine).

As noted above, the model complex between **2** and **3** (see Fig. 1) was originally energy-minimised using pyrene as the π-electron-rich species. However, pyrene itself was judged to be an over-simplified analogue for the pyrenyl-end-capped oligo-amides, which we propose to use in the construction of supramolecular network polymers. Therefore, we synthesised the benzamidomethyl-substituted pyrene **10** as a more realistic π-electron-rich component. This was obtained straightforwardly via condensation of benzoyl chloride (**11**) with 1-pyrenemethylamine hydrochloride (**12**) (Scheme 2).

With the model host and guest compounds **9** and **10** in hand, it was possible to study the binding of the components under controlled conditions. Simply mixing chloroform solutions of the two components afforded a deep red solution resulting from a strong charge-transfer band, centred on 530 nm, which is diagnostic of a complementary, aromatic, π–π-stacked complex.[10] Moreover, titration of the pyrenyl derivative **10** against a fixed concentration of tweezer-compound **9** (Fig. 4) in CDCl$_3$ revealed a significant upfield shift (up to 0.6 ppm at equimolar concentration **9** and **10**) of the ^{1}H NMR resonance corresponding to the four 'naphthalene' protons of tweezer-molecule **9**. This shift is accompanied by a progressive increase in the complexity of the resonances, which changes from an apparent singlet in the starting material (**9**) to an apparent AA′BB′ spin pattern (two distorted doublets) at equimolar concentrations of the components (Fig. 4). There are clearly two chemically distinct protons in **9**, one type adjacent to the 'terminal' imide units and the other adjacent to the 'internal' imides. An AA′BB′ pattern would therefore be expected for **9**. However, in the uncomplexed molecule, the environments of these protons are evidently indistinguishable and hence their associated resonances coincide, with complete loss of coupling information. Complexation with compound **10** must then result in the two different types of 'naphthalene' proton experiencing different degrees of ring-current shielding by the pyrenyl residue. Association and dissociation are obviously fast on the NMR timescale, but even so the

averaged environments of the 'naphthalene' protons, when **9** is complexed to **10**, are quite different so that their associated resonances no longer coincide.

A Job plot, using results from UV/vis spectroscopy based on the charge-transfer absorption band at 530 nm (Fig. 5a) confirmed formation of a 1:1 complex between the pyrenyl derivative **10** and the bis-diimide tweezer **9**, supporting the stoichiometry predicted for the modelled complex. The association constant for the complex was found to be 130($\pm$20) M^{-1} by the UV/vis dilution method[19] (Fig. 5b).

Whilst these preliminary binding assays for complexation between **9** and **10** were encouraging, the relatively low binding constant would certainly not be sufficient to translate into the formation of stable supramolecular polymers. To enhance the binding constant, we next investigated complexation between the bis-diimide tweezer-molecule (**9**) and the bis-pyrenyl tweezer-compound **4**. Mixing the two tweezer-type molecules **4** and **9** produced a deep red solution as a result of a strong absorption band centred on 538 nm. A Job plot based on this absorption revealed that the complex was formed in a 1:1 ratio of **4** to **9**, in accordance with the proposed mode of binding (Fig. 6a). Encouragingly, the binding constant for **4** with **9** with was found to be 3500($\pm$400) M^{-1} (Fig. 6b), more than an order of magnitude greater than that observed between the mono-pyrene derivative **10** and the bis-diimide **9** (Fig. 5b).

To assess the binding characteristics of an oligomeric, chain-folding imide with the pyrenyl tweezer-molecule **4**, we next synthesised a trimeric diimide, analogous to the system modelled in our initial computational studies. The target trimeric diimide **16** was thus synthesized as shown in Scheme 3. Mono-protection of 2,2′-(ethylenedioxy)bis(ethylamine) afforded the known[20] trityl (Tr) protected amine **13**, using a large excess of the diamine to reduce the quantity of unwanted bis-protected amine formed. Addition of amine **13** to diacid **7**, followed by deprotection with trifluoroacetic acid, furnished the desymmetrised naphthalene-diimide **15** in good yield (76%, two steps). The synthesis was completed by condensation of 2 equiv of amine **15** with naphthalene
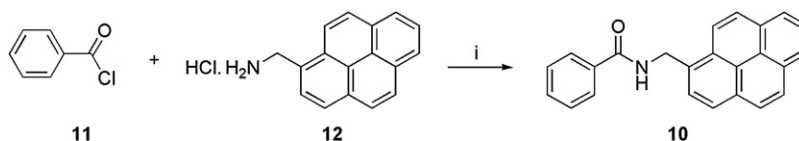
Scheme 2. Synthesis of model compound **10**. Reagents and conditions: (i) Et$_3$N, CHCl$_3$, 10 min, 80% yield.
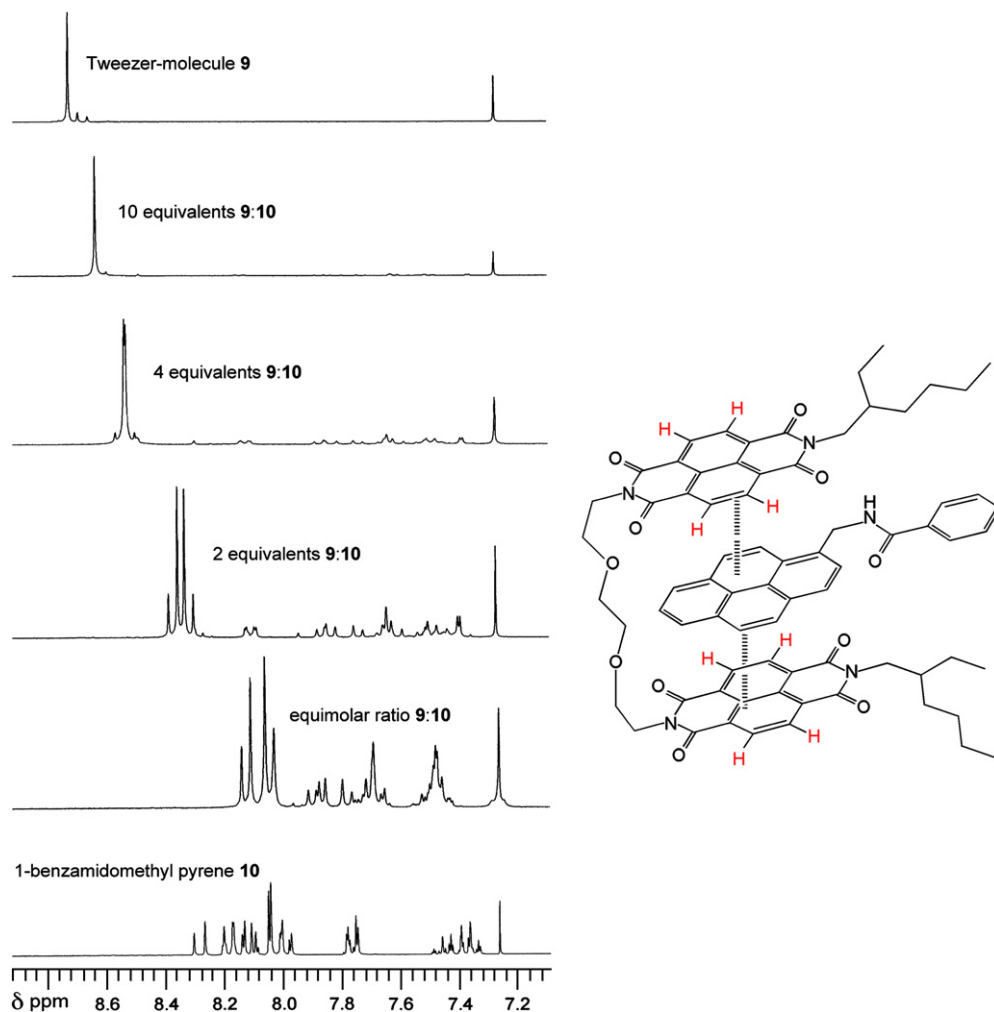
Figure 4. Titration of the guest pyrenyl compound **10** against the bis-diimide tweezer **9**, as monitored by ^{1}H NMR spectroscopy (250 MHz, CDCl$_3$; note residual CHCl$_3$ resonance at 7.25 ppm).

tetracarboxylic dianhydride to furnish the target trimer **16** in 75% yield.

Mixing solutions of the bis-pyrenyl tweezer **4** and trimer **16** produced a deep red solution as a result of a strong charge-transfer band centred on 539 nm signifying complex formation. A Job plot based on this absorption maximum revealed that the complex forms in a 1:1 ratio of **4** to **16**, with a binding constant of 11,000($\pm$2000) M^{-1} (Fig. 7), an increase of a further factor of 3 compared to that for the tweezer–tweezer complex between **4** and **9** (Fig. 6).
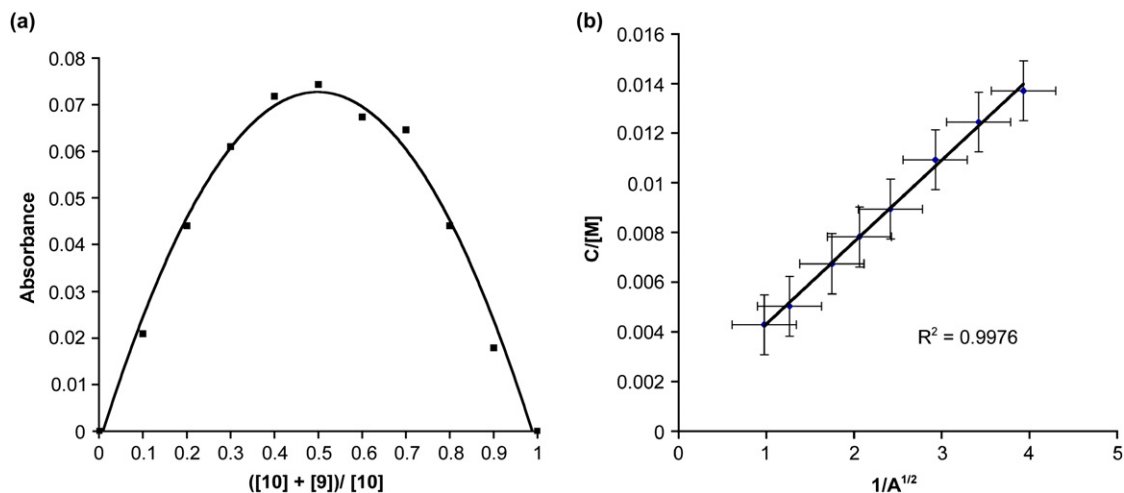

Figure 5. Job plot (a) and UV/vis binding study (b) using the dilution method, for complex formation between **9** and **10** (error bars show standard error).
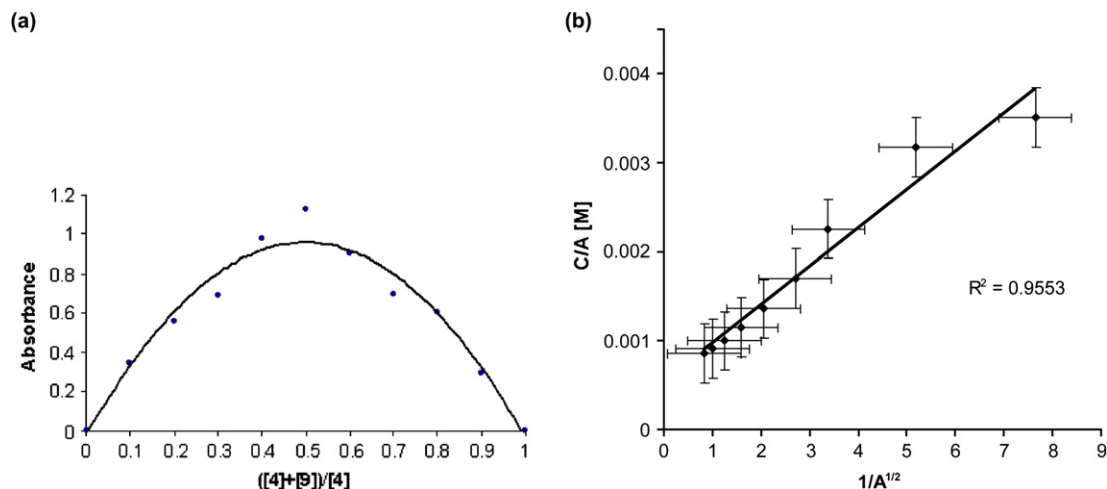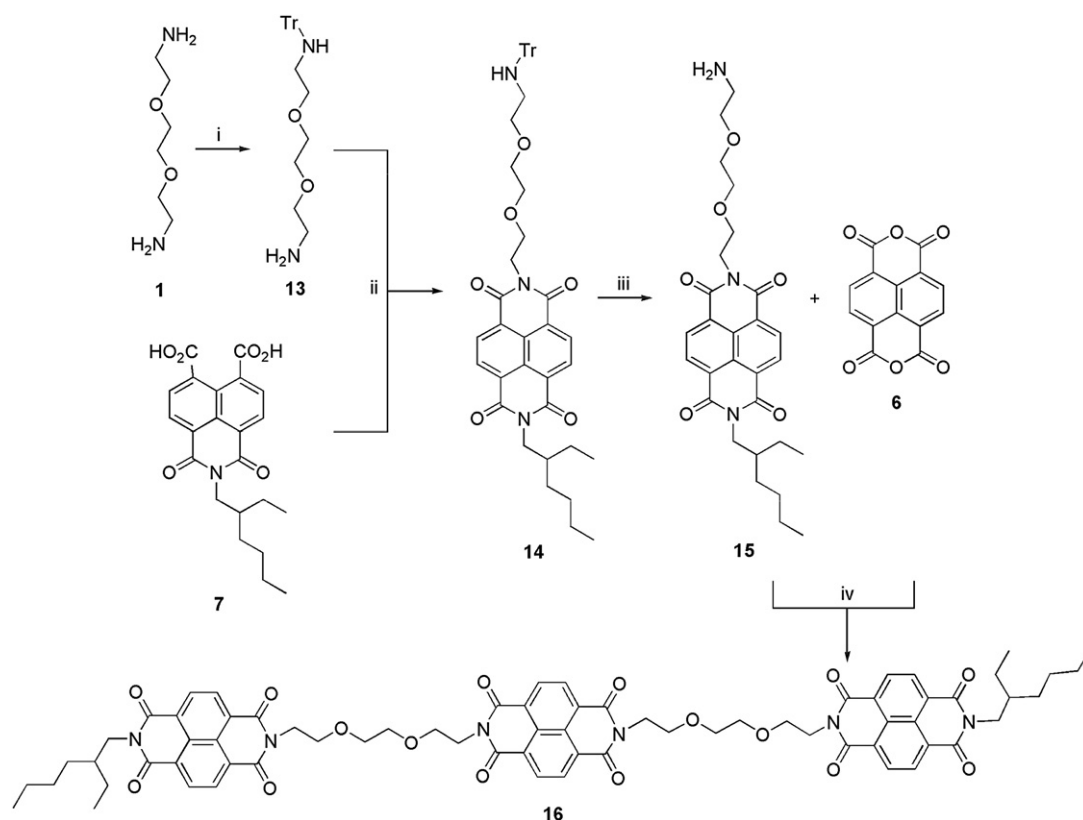
Figure 6. Job plot (a) and UV/vis binding study (b) using the dilution method, for complex formation between **4** and **9** (error bars show standard error).

Scheme 3. Synthesis of trimeric diimide **16**. (i) Tr–Cl (0.1 equiv), Et₃N, CH₂Cl₂, rt, 73%; (ii) DMAc, 125 °C, 18 h, 80%; (iii) TFA/CH₂Cl₂ (1:10 v/v), 3 h, rt, 95%; (iv) DMAc, 125 °C, 18 h, 75%.

3. Conclusions

A new chain-folding tweezer-molecule comprising two π-electron deficient naphthalene tetracarboxylic diimide units separated by a short ethylene glycol spacer has been designed and synthesised, and the binding characteristics of this type of receptor with π-electron-rich pyrenyl guest molecules has been evaluated. Computational modelling predicted that stable complexes should be formed and indeed strong charge-transfer absorption bands were observed on mixing the diimide host and pyrenyl guests in solution. Binding assays revealed that by increasing both the number of π-electron deficient naphthalene-diimide units and π-electron-rich, pyrene-based moieties, in conjunction with the use of appropriate flexible spacers between the receptor sites, it was possible to generate stable assemblies with binding constants up to 11,000 M⁻¹. The results of this initial study are very encouraging and tend to confirm our hypothesis that the binding motifs described could form the basis of a new class of supramolecular polymer blends based on non-covalent networks.
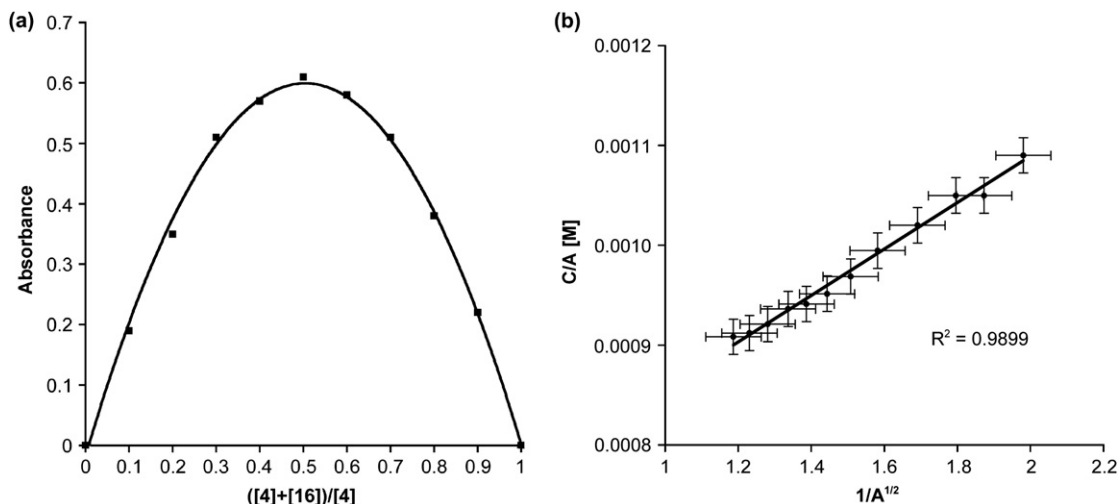
Figure 7. Job plot (a) and UV/vis binding study (b) using the dilution method, for complex formation between **4** and **16** (error bars show standard error).

4. Experimental

4.1. General

Reagents were purchased from either Aldrich or Acros and were used as received without further purification. Solvents were used as supplied, with the exception of chloroform ($CHCl_3$), which was distilled under nitrogen from calcium hydride. DMAc (99.8% anhydrous) was purchased from Aldrich and used as received. NMR spectra were recorded on Bruker AC250 operating at 250 MHz and 62.5 MHz for ^1H and ^{13}C nuclei, respectively, or Bruker AMX400 operating at 400 MHz and 100 MHz for ^1H and ^{13}C nuclei, respectively. The residual protic signal from the deuterated solvent or tetramethylsilane was used as internal reference. Infrared (IR) spectroscopic analyses were performed on a Perkin–Elmer 17 20-X Infrared Fourier Transform spectrometer on KBr disks using a thin film for sample preparation. Matrix-assisted laser desorption–ionisation time-of-flight mass spectra (MALDI-TOF MS) were obtained using a Scientific Analysis Instruments LT3 LaserTof (Manchester, UK) spectrometer using dithranol as the matrix. A typical sample preparation is described as follows: 3 μL of a solution of the analyte in chloroform (1–10 mg mL^{-1}) was combined with 10–20 μL of the freshly prepared matrix (40 mg mL^{-1} in $CHCl_3$) in a mini-vial, and from the mixture was taken an aliquot, which was transferred onto a sample plate and left to air dry prior to analysis. Mass spectra (MS) were obtained from a Finnigan MAT95 (CI) or a Waters LCT Premier (ESI). UV/vis absorption measurements were performed in a 1 cm^2 quartz cuvettes on a double-beam Perkin–Elmer Lambda 25 spectrophotometer interfaced with UV WinLab software, in the wavelength range 400–700 nm, employing a scan speed of 120 nm min^{-1}, with a slit width of 1 nm. Spectra were recorded using samples dissolved in analytical grade chloroform mixed 6:1 with hexafluoroisopropanol and blank-corrected for the possible absorption of the solvent. Elemental analyses were provided by Medac UK Ltd.

4.2. Computational modelling

Computational modelling studies using charge-compensated molecular mechanics were carried out with a custom-modified version of the Dreiding II force field in *Cerius2* (version 3.5, Accelrys Inc., San Diego) running on an SGI-O2 workstation. Customisation of the force field involved constrained planarisation of the naphthalene tetracarboxylic diimide and pyrenyl residues in order to

reduce the number of variable parameters during minimisation. Starting models were generated with pre-folded conformations based—where possible—on known X-ray structures[12,16] and were brought together by simple docking procedures prior to energy-minimisation. While the final structures obtained in this work clearly represent genuine energy-minima, a more detailed computational study involving extended conformational searching would be required to prove that these structures unambiguously represent *global* minima.

4.3. Binding studies

Binding constants were determined according to the UV/vis dilution method described in detail by Stoddart et al.[19] This methodology requires measurement of the charge-transfer absorption band arising from complex formation between equimolar quantities of the π-electron-rich and π-electron-deficient species at varying concentrations. The concentration range was chosen to ensure that the maximum absorption measured during the experiment remained below 1 absorbance unit, and thus within the range where the Beer–Lambert law is applicable. The following concentration ranges were used: **9/10**=0.004500–0.000887 mol L^{-1}; **9/4**=0.001250–0.000060 mol L^{-1}; **16/4**=0.000645–0.000278 mol L^{-1}. The error bars shown in Figures 5b, 6b and 7b represent standard errors of estimate.

4.4. Diacid imide 7

1,4,5,8 Naphthalene tetracarboxylic dianhydride (2.00 g, 7.46 mmol) was dissolved in a solution of KOH (1.96 g) in water (350 mL) and the resulting brown solution was acidified to pH 6.3 with H_3PO_4 (1 M). 2-Ethyl hexylamine (962 mg, 7.46 mmol) was added and the solution was re-acidified to pH 6.4 with H_3PO_4 (1 M), then heated to 110 °C for 16 h. After cooling to room temperature, the cloudy solution was filtered and the filtrate was acidified with AcOH (5 mL), which produced a cream precipitate. After stirring for 20 min, the solid was collected by filtration and dried under vacuum at 50 °C to give **7** as a cream powder (2.52 g, 85%). Mp 173–174 °C (decomp.); ^1H NMR ($CDCl_3/CF_3CO_2H$, 250 MHz) δ=8.65 (2H, AA'XX', Ar–H), 8.18 (2H, AA'XX', Ar–H), 4.04–3.86 (2H, m, NCH_2CH), 1.86–1.81 (1H, m, $CH_2CH(CH_2)_2$), 1.28–1.22 (8H, m, 4×CH_2), 0.89–0.81 (6H, m, 2×CH_3); ^{13}C NMR ($CDCl_3/CF_3CO_2H$, 250 MHz) δ=168.5, 163.5, 137.0, 130.6, 129.6, 128.9, 125.8, 124.8, 43.8, 37.5, 30.4, 28.5, 23.9, 22.8, 14.3, 10.8. IR ν_{max}(KBr)/cm^{-1} 3418, 2956, 2921, 2858,

1702, 1697, 1592, 1450, 1390, 1347, 1298, 1232. ESI-MS (negative ion mode) m/z calcd for $C_{22}H_{22}NO_6$: 396.1447, found: 396.1466. Anal. Calcd for $C_{22}H_{23}NO_6 \cdot 1/2H_2O$: C, 65.01; H, 5.95; N, 3.45. Found: C, 64.73; H, 5.60; N, 3.40%.

4.5. Bis-diimide tweezer 9

A solution of diacid **7** (100 mg, 0.287 mmol) and diamine **1** (21.3 mg, 0.144 mmol) in DMAc (2.5 mL) and toluene (0.25 mL) were stirred at 135 °C for 20 h. After cooling to room temperature, the dark solution was added dropwise to a stirred mixture of chloroform/methanol (10 mL 1:1 v/v). After 10 min, the resulting suspension was collected by filtration and dried at 70 °C under vacuum to give bis-diimide tweezer **9** (103 mg, 82%) as a peach coloured solid. Mp 223–224 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ=8.69 (8H, s, Ar–H), 4.36 (4H, t, J=5.9 Hz, 2×(CO$_2$)NCH_2CH$_2$), 4.12 (2H, dd, J=5.2 and 9.1 Hz, 2×(CO)$_2$NCHHCH), 4.05 (2H, dd, J=7.0, 13.0 Hz, 2×(CO)$_2$NCHHCH), 3.77 (4H, t, J=5.8 Hz, 2×OCH_2CH$_2$), 3.66 (4H, s, OCH$_2$CH_2), 1.95–1.84 (2H, m, CH$_2$CH(CH$_2$)$_2$), 1.43–1.20 (16H, m, 8×CCH_2C), 0.94–85 (12H, m, 4×CH_3); ^{13}C NMR (CDCl$_3$, 67.5 MHz) δ=163.1, 162.8, 130.99, 130.96, 127.01, 126.98, 70.6, 68.1, 45.0, 39.9, 38.3, 31.1, 29.1, 24.4, 23.5, 14.5, 11.0; IR ν_{max}(KBr)/cm^{-1} 2950, 2914, 2872, 1705, 1659, 1581,1453,1375,1333,1241. ESI-MS m/z calcd for $C_{50}H_{54}N_4O_{10}$: 871.3918; found: 871.3943. Anal. Calcd for $C_{50}H_{54}N_4O_{10} \cdot H_2O$: C, 67.55; H, 6.35; N, 6.30%. Found: C, 67.70; H, 6.06; N, 6.39%.

4.6. N-Pyren-1-ylmethyl-benzamide 10

To a solution of 1-pyrenemethylamine hydrochloride **11** (0.268 g, 1.00 mmol) and dry triethylamine (2 mL, 14.4 mmol) in dry chloroform (50 mL) was added a solution of benzoyl chloride **12** (0.280 g, 0.231 mL, 2.00 mmol) with stirring over a period of 5 min. The reaction was poured into n-hexane (200 mL). A pale yellow precipitate was formed and filtered off under vacuum. The crude product was washed well with hydrochloric acid solution 0.5 M (20 mL), water (50 mL) and acetone (10 mL). A white solid **10** (0.2681 g, 80% yield) was obtained and dried under high vacuum pump. Mp 198 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 7.98–8.33 (9H, m, Py–H), 7.34–7.78 (5H, m, Ar–H), 6.48 (br, NH), 5.34–5.32 (2H, d, NHCH_2–Py, J=5.2 Hz); ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 167.58, 134.68, 131.98, 131.73, 131.64, 131.29, 131.13, 129.55, 129.00, 128.78, 128.03, 127.75, 127.74, 127.42, 126.55, 125.86, 125.81, 125.46, 125.21, 125.09, 123.19, 43.01; IR ν_{max}(KBr)/cm^{-1} 3350, 1665, 1500; HRMS (CI): $C_{24}H_{17}NO$ m/z calcd: 335.1310; found: 335.1313.

4.7. Trityl protected diimide 14

A stirred solution of 2-{2-[2-(trityl-amino)-ethoxy]-ethoxy}-ethylamine **13** (195 mg, 0.500 mmol) and diacid imide **7** (199 mg, 0.500 mmol) were dissolved in DMAc (5 ml) and toluene (0.5 mL) and heated at 135 °C for 16 h. After cooling to room temperature, chloroform (50 mL) was added to the dark suspension and washed with water (4×20 mL) and brine (20 mL) before being dried over MgSO$_4$, filtered and the solvent removed under reduced pressure. The resulting black oil was added dropwise into methanol and stirred rapidly for 10 min, producing a cream precipitate, which was collected by filtration and subjected to column chromatography (gradient 1:9 to 1:1 EtOAc/hexane) to give **14** as a tan solid (319 mg, 85%). Mp 131–132 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ=8.68 (4H, m, 4×Naphthalene–H), 7.46–7.09 (15H, m, Ar–H), 4.42 (2H, t, J=5.8 Hz, (CO$_2$)NCH_2CH$_2$), 4.16 (1H, dd, J=7.7 and 12.9 Hz, (CO)$_2$NCHHCH), 4.10 (1H, dd, J=6.0 and 12.9 Hz, (CO)$_2$NCHHCH), 3.80 (2H, t, J=5.8 Hz, OCH_2CH$_2$), 3.67–3.64 (2H, m, OCH$_2$CH_2), 3.57–3.45 (6H, m, 2H, 2×OCH_2CH$_2$ and NHCH_2CH$_2$), 2.27 (2H, t, J=5.4 Hz, NHCH$_2$CH_2), 2.00–1.90 (3H, br m, CH$_2$NH_2 and CH$_2$CH(CH$_2$)$_2$), 1.44–

1.24 (8H, m, 4×CH_2), 0.97–0.85 (m, 6H, 2×CH_3); ^{13}C NMR (CDCl$_3$, 62.5 MHz) δ=163.0, 162.7, 146.0, 131.0, 128.7, 127.8, 126.69, 126.66, 126.59, 126.46, 126.21, 71.4, 70.6, 70.2, 70.0, 67.8, 44.5, 43.0, 39.5, 37.9, 30.6, 28.5, 24.0, 23.0, 14.0, 10.5; IR ν_{max}(KBr)/cm^{-1} 3439, 2959, 2929, 2870, 1708, 1664, 1583, 1450, 1380, 1332, 1244, 1115. HRMS (CI): $C_{47}H_{49}N_3O_6$ m/z calcd: 751.3621; found: 751.3628. Anal. Calcd for $C_{47}H_{49}N_3O_6$: C, 75.08; H, 6.57; N, 5.59%. Found: C, 75.29; H, 6.69; N, 5.51%.

4.8. Amino diimide 15

Trityl protected diimide **14** (250 mg, 0.333 mmol) was dissolved in a stirred mixture of dichloromethane (15 mL) and trifluoroacetic acid (0.5 mL). After 3 h at room temperature, a saturated aqueous solution of NaHCO$_3$ (5 mL) was added dropwise and the organic layer separated, washed again with aqueous NaHCO$_3$ (2×5 mL) and water (5 mL) before the organic layer was dried over MgSO$_4$, filtered and the solvent removed under reduced pressure to give an orange solid, which was subjected to column chromatography (gradient chloroform to 7:1:0.1 chloroform/methanol/triethylamine) to give **15** (153 mg, 90%) as a tan solid. Mp 179–180 °C (decomp.) ^{1}H NMR (CDCl$_3$, 250 MHz) δ=8.67 (m, 4H, Ar–H), 4.38 (2H, t, J=5.8 Hz, (CO$_2$)NCH_2CH$_2$), 4.16 (1H, dd, J=7.7 and 13.0 Hz, (CO)$_2$NCHHCH), 4.10 (1H, dd, J=13.0 and 7.3 Hz, (CO)$_2$NCHHCH), 3.79 (2H, t, J=5.8 Hz, OCH_2CH$_2$), 3.65–3.61 (2H, m, 2H, OCH$_2$CH_2), 3.54–3.50 (2H, m, OCH_2CH$_2$), 3.41 (2H, t, J=5.1 Hz, OCH$_2$CH_2), 2.79–2.74 (2H, m, CH_2NH$_2$), 2.27 (br, 2H, NH_2), 1.95–1.84 (1H, m, CH$_2$CH(CH$_2$)$_2$), 1.40–1.17 (8H, m, 4×CH_2), 0.89–0.78 (6H, m, 2×CH_3); ^{13}C NMR (CDCl$_3$, 62.5 MHz) δ=163.5, 163.3, 131.42, 130.37, 127.0, 126.8, 73.0, 70.7, 70.4, 68.3, 45.0, 41.8, 39.0, 38.3, 31.1, 29.0, 24.4, 23.4, 14.5, 11.0. IR ν_{max}(KBr)/cm^{-1} 3416, 2955, 2870, 1700, 1661, 1579, 1452, 1333, 1241, 1093, 766. ESI-MS m/z calcd for $C_{28}H_{36}N_3O_6$: 510.2604, found: 510. 2601.

4.9. Tris-diimide 16

A solution of amino diimide **15** (50.0 mg, 0.0982 mmol) and 1,4,5,8 naphthalene dicarboxylicanhydride (12.5 mg, 0.0468 mmol) were stirred at 135 °C for 20 h in a solution of DMAc (2.5 mL) and toluene (0.25 mL). After cooling to room temperature, the dark solution was added dropwise into chloroform/methanol mix (5 mL, 1:1, v/v), which was stirred rapidly for 10 min. The resulting suspension was collected by filtration and dried under vacuum at 70 °C, then subjected to column chromatography (gradient chloroform to chloroform/methanol (20:1 v/v)) to give tris-diimide **16** (43 mg, 75%) as a tan solid. Mp 257–260 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ=8.89 (8H, s, Ar–H), 8.51 (4H, s, Ar–H), 4.33 (8H, t, J=5.6 Hz, 4×(CO$_2$)NCH_2CH$_2$), 4.12 (2H, dd, J=13.0 and 7.8 Hz, (CO)$_2$NCHHCH), 4.08 (2H, dd, J=13.0 and 7.5 Hz, (CO)$_2$NCHHCH), 3.76 (8H, t, J=5.6 Hz, 4×OCH_2CH$_2$), 3.67 (8H, s, 4×OCH$_2$CH_2), 1.94–1.87 (2H, m, CH$_2$CH(CH$_2$)$_2$), 1.42–1.23 (16H, m, 8×CH_2), 0.89–0.78 (12H, m, 4×CH_3); ^{13}C NMR (CDCl$_3$/(CF$_3$)$_2$CHOH, 100 MHz) δ=163.6, 163.3, 163.2, 131.2, 126.72, 126.69, 126.59, 126.4, 126.3, 69.9, 67.9, 44.8, 39.5, 37.9, 30.6, 28.6, 24.0, 23.0, 14.0, 10.5; IR ν_{max}(KBr)/cm^{-1} 2954, 2912, 2875, 1707, 1663, 1580,1452, 1241; ESI-MS m/z calcd for $C_{70}H_{70}N_6O_{16} \cdot$Na: 1273.4746; found: 1273.4778. Anal. Calcd for $C_{70}H_{70}N_6O_{16} \cdot H_2O$: C, 66.23; H, 5.72; N, 6.62%. Found: C, 66.48; H, 5.76; N, 6.54%.

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