Poly(1,1-bis(dialkylamino)propan-1,3-diyl)s; conformationally-controlled oligomers bearing electroactive groups†

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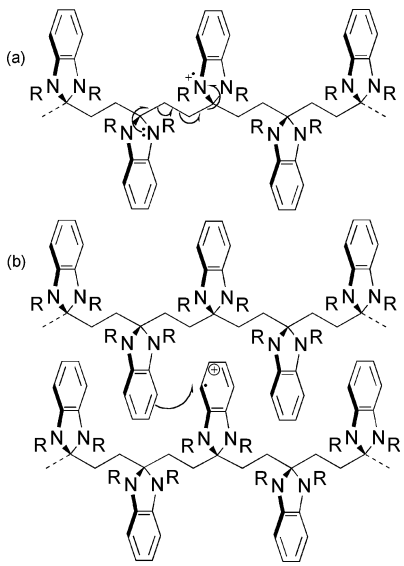
The design of polymers with repeating $[C(NR_2)_2CH_2CH_2]$ units which may simultaneously provide conformational control and contain repeating electroactive centres is discussed; $(NR_2)_2$ groups would be ideally provided by *ortho*-phenylenediamine derivatives, with 1,8-diaminonaphthalenes as alternatives. Oligomers containing 1,8-bis(methylamino)naphthalenes, up to the hexamer, were obtained by condensation of oligomers of $CH_3[COCH_2CH_2]_nCOCH_3$ with 1,8-bis(methylamino)naphthalene, but attempts to prepare related oligomers from 1,2-bis(alkylamino)benzenes were unsuccessful, as only terminal ketone groups could be converted to aminals. Evidence for a strong preference for all-*anti* conformations of the main chain in the naphthalenediamine oligomers is provided by ring current effects on ^{1}H NMR shifts, and by X-ray structures, which also provide evidence of intercalation in the solid state. Electrochemical studies of these oligomers show irreversible oxidation of oligomers in solution, but oxidation of longer oligomers leads to the deposition of a reddish-pink insoluble material which shows two reversible oxidation waves. Possible interpretation of these results is discussed.

Introduction

Conducting and semi-conducting polymers are an active research area, with most useful materials being based on extended π-systems. In this paper we explore the synthesis of some oligomers that might provide materials whose conductivity would be based on quite different mechanisms. We were intrigued that one of two possible charge-hopping mechanisms[1–3] might operate (Scheme 1 below), with polymers and oligomers based on the structure **1**. Given a highly ordered chain conformation (see below), through-bond electron transfer *via* the perfectly aligned (all-*anti*) –$[CH_2CH_2]$– links might be rapid (Scheme 1(a)), in spite of their saturated nature. In addition (or alternatively), these compounds have the potential to organise themselves into intercalated structures, see Scheme 1(b), so that under appropriate conditions, direct through-space electron transfer *via* the stacked π-systems might be efficient.

In earlier work, we showed that $[Ar_2CCH_2CH_2]_n$ polymers (Ar_2 = 2,2′-biphenylyl) possess essentially straight (all-*anti*) chains, and developed routes to oligomers such as **2** and related polymers involving novel anionic ring-opening polymerisation of spiro[cyclopropane-1,9′-fluorene].[4,5] The original aim of the work described in this paper was therefore the preparation of polymers such as **1**, in which the 1,2-bis(alkylamino)benzene units should provide similar conformational control to 2,2′-biphenylyl units, but would also be electroactive. Derivatives of *N*,*N*′-dialkyl-*o*-phenylenediamines are readily oxidised to long-lived radical cations and even dications,[6–10] and these have been incorporated into other novel polymeric structures.[11] In this paper, we describe our attempts to prepare oligomers and polymers related to **1**, and preliminary studies of their structure and electrochemistry.



Scheme 1 (a) Possible through-bond electron transfer for partially charged **1**; (b) Possible through-space electron transfer in stacked (intercalated) structures based on **1**.

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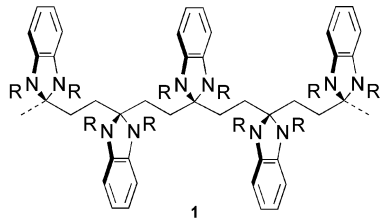

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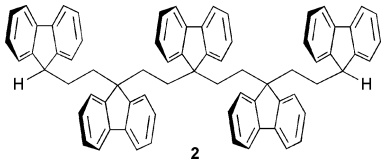

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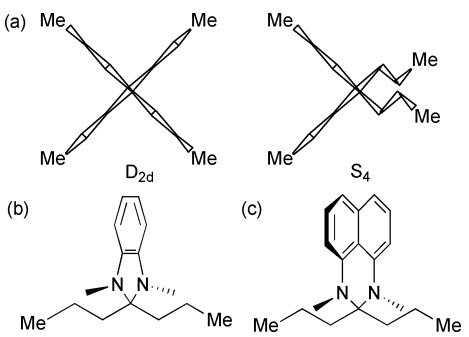
Results and discussion

Design

Quaternary centres have profound effects on the conformations of both the adjacent set of bonds and also the set of bonds one atom away. More distant bonds are normally unaffected. These effects have been analysed in detail elsewhere,[5,12] but they result in a compound like 4,4-dipropylheptane having two conformations which are strongly preferred to all others, Scheme 2(a). Two conformations is one too many(!) for most control purposes, but if one of the chains is made rigid, this problem can be overcome, as we showed for the fluorene-based oligomers **2**.[4,5] Thus, the conformation shown in Scheme 2(b) for 2,3-dihydro-1,3-dimethyl-2,2-dipropyl-1*H*-benzo[*d*]imidazole is more stable than any other by 10.1 kJ mol^{-1}, according to a Merck Molecular Force Field (MMFF) conformational search, while the conformation shown for 2,3-dihydro-1,3-dimethyl-2,2-dipropyl-1*H*-perimidine (Scheme 2(c)) is preferred by 10.9 kJ mol^{-1}. Actually the aromatic rings in both (b) and (c) are somewhat canted due to the pyramidisation at the nitrogen atoms but this does not compromise the conformational control of the main chain. Note however that the presence of any substituents on the first two carbon atoms of the R groups creates additional non-bonded interactions and so partially destroys the conformational control.

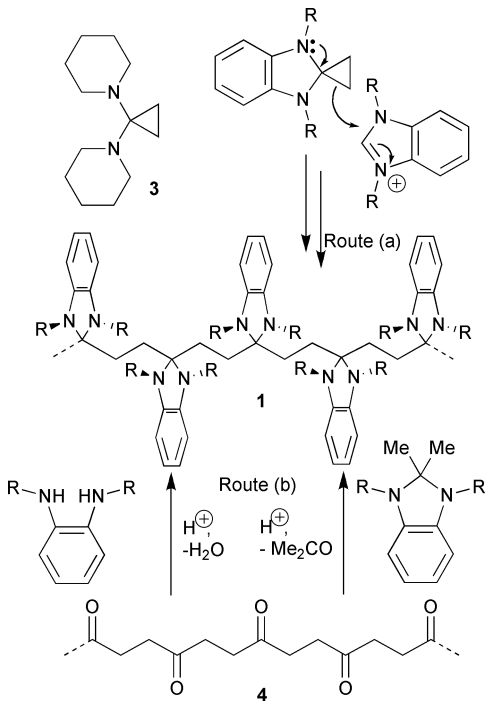


Scheme 2 Preferred conformations of (a) 4,4-dipropylheptane (b) 2,3-dihydro-1,3-dimethyl-2,2-dipropyl-1*H*-benzo[*d*]imidazole, (c) 2,3-dihydro-1,3-dimethyl-2,2-dipropyl-1*H*-perimidine.

We have shown that, in a polymeric structure, repeating quaternary centers need to be placed either 3 or 4 atoms apart in order to retain conformational control over all bonds in the chain, while not introducing other steric interactions.[4,5] Thus polymers like **1** should exhibit all-*anti* main chains.

Synthetic routes

We initially envisioned two routes to oligomers and polymers like **1** (Scheme 3).



Scheme 3 Routes to polymers **1**; (a) Cationic ring-opening polymerisation of spiro-1,1-diaminocyclopropanes, and (b) aminal formation from oligomeric/polymeric ketones **5**.

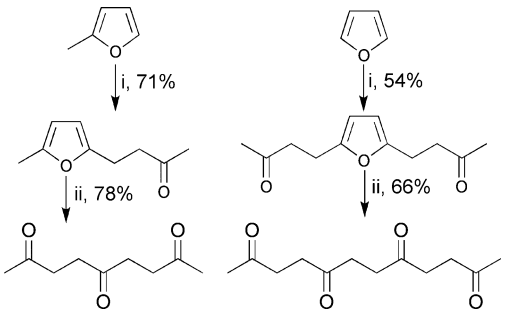
1,1-Bis(dialkylamino)cyclopropanes are very reactive towards electrophiles, and so might undergo cationic ring-opening polymerisation. Unfortunately, preliminary experiments using the known[13] 1,1-bis-piperidinocyclopropane **3** showed that several imidazolium ions were not strong enough electrophiles to cause ring opening, so this route was not pursued further.

Polymer **1** might be prepared alternatively by polyaminal formation from the ethylene/CO copolymer **4** (Scheme 3(b)). Two obvious problems with the second route are (a) incomplete aminal formation, and (b) the insolubility of the ethylene/CO copolymer. The ethylene/propylene/CO terpolymer is more soluble, but would destroy some of the designed conformational control. Fortunately, several low-molecular-mass oligomers with the repeating [$COCH_2CH_2$] unit are known, and could provide a test of the feasibility of route (b).

Preparation of $CH_3[COCH_2CH_2]_nCOCH_3$ oligomers

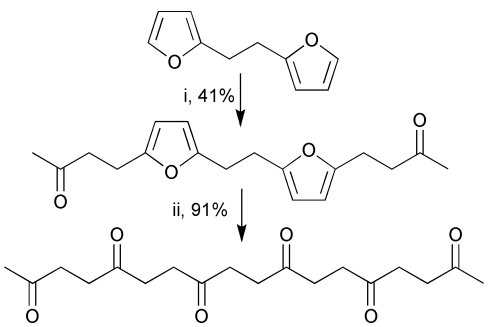
In order to explore route (b) in Scheme 3, we required a series of $CH_3[COCH_2CH_2]_nCOCH_3$ oligomers. A repetitive synthesis that might be extended to any desired chain length would be ideal, but we have been unable to devise a suitable scheme. However, acetonylacetone ($n = 1$) is readily available, and the literature

describes a number of methods[14–16] for the synthesis of polyketones with repeating [CH_2CH_2CO] units. We elected to use procedures described by Poirier[17,18] for the preparation of 2,5,8-nonanetrione and 2,5,8,11-dodecanetetraone using methylfuran and furan as respective starting materials (Scheme 4).



Scheme 4 Preparation of 2,5,8-nonanetrione and 2,5,8,11-dodecanetetraone. *Reagents and conditions*: (i) Methyl vinyl ketone, $BF_3{\cdot}Et_2O$, EtOH, $MeNO_2$, –20 °C; (ii) HCl, H_2O, 100 °C.

We extended these methods to prepare 2,5,8,11,14,17-octadecanehexaone from 2-[2-(2-furyl)ethyl]furan (Scheme 5). 2-[2-(2-furyl)ethyl]furan was prepared from furoin *via* reduction to deoxyfuroin with chlorotrimethylsilane and sodium iodide in acetonitrile, followed by a modified Wolff–Kishner reduction, as described by Wenkert *et al.*[19]

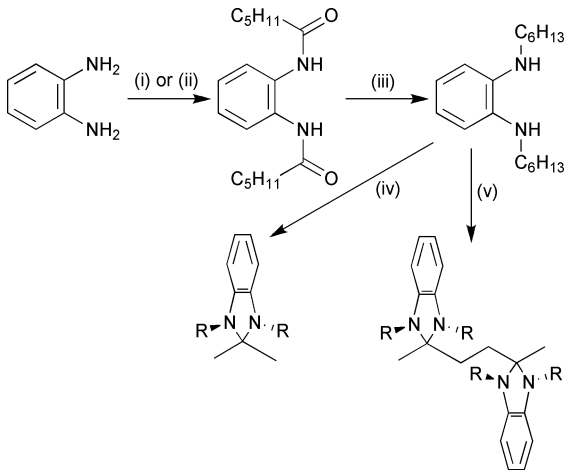


Scheme 5 Preparation of 2,5,8,11,14,17-octadecanehexaone. *Reagents and conditions*: (i) Methyl vinyl ketone, $BF_3{\cdot}Et_2O$, EtOH, $MeNO_2$, –20 °C; (ii) HCl, H_2O, 100 °C.

Attempted preparation of polyaminals from *N*,*N*′-dialkyl-*o*-phenylenediamines

We hoped that it would be possible to prepare polyaminals from polyketones **4** by reaction with a range of diamines (*e.g.* **5** in Scheme 3), or their simple aminal deriviatives (*e.g.* **6**). While a number of electroactive diamines might be considered,[8,20–22] *o*-phenylenediamines were our preferred choice of diamines for the synthesis of target oligomers due to the established stability of their radical cations.

Initially, hexyl chains were chosen as R groups because we anticipated that the solubility of the oligomeric aminals would be a problem; these groups would still provide maximum conformational control. *N*,*N*′-Dihexyl-*o*-phenylenediamine was prepared and converted to the monomer and dimer acetals as shown in Scheme 6.



Scheme 6 Preparation of *N*,*N*′-dihexyl-1,2-benzenediamine and monomer and dimer aminals. *Reagents and conditions*: (i) $CH_3(CH_2)_4$-COCl, Et_3N, 84%; (ii) $(CH_3(CH_2)_4CO)_2O$, 78%; (iii) $LiAlH_4$, THF, –40 to 66 °C, 86%; (iv) Me_2CO, HOAc, 87%; (v) acetonylacetone, *p*-toluenesulfonic acid, toluene, Dean–Stark trap, 79%.

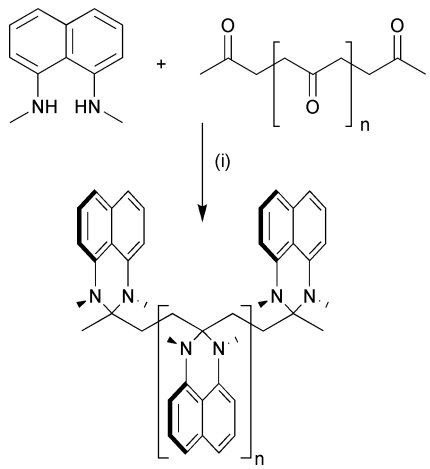
At this point, a major problem was encountered. Reaction with 2,5,8-nonanetrione, under Dean–Stark conditions only led to low yields (~15%) of product in which only the terminal carbonyl groups were converted to aminals; no significant amount (<2%) of product involving aminal formation at the central carbonyl groups could be detected, even after 1 week of refluxing. The same problems were encountered in attempts to synthesise the tetramer using 2,5,8,11-dodecanetetraone. Although the 5-*endo*-trig cyclisation is formally not allowed by Baldwin's rules, many 5-membered ring acetals and aminals have been prepared in acidic conditions. We initially believed that the hexyl groups might be causing the problem, but repetition of this work with ethyl groups produced the same results; internal carbonyl groups could not be converted to aminals.

We therefore turned our attention to compounds containing 1,8-naphthalenediamine units, in spite of the fact that these were known not to be electroactive in the same way as *o*-phenylenediamines.

Preparation of oligomers containing 1,8-naphthalenediamine units

N,*N*′-Dimethyl-1,8-naphthalenediamine, prepared *via* N-methylation of perimidine followed by hydrolysis,[23] was readily converted to aminals with both acetone and 3-pentanone. More significantly, fully protected polyaminals could be prepared from all the $CH_3[COCH_2CH_2]_nCOCH_3$ oligomers in excellent yields (Scheme 7). We can offer no simple explanation why polyaminal formation is much more favourable with the apparently bulkier naphthalenediamines, although the 6-*endo*-trig nature of the cyclisation step may play its part.

These polyaminals were found to be quite soluble in chloroform and dichloromethane, and could be crystallised by diffusion of ether or pentane into $CHCl_3$ solutions. Although not strictly correct, we will refer to these oligomers from now on as monomers, dimers, trimers, *etc.* for simplicity.



Scheme 7 Preparation of oligomeric aminals containing 1,8-naphthalenediamine units. *Reagents and conditions*: (i) $CH_3[COCH_2CH_2]_n$-$COCH_3$ oligomer, *p*-toluenesulfonic acid, toluene, Dean–Stark trap, 82–93%.

Modelling oligomers containing 1,8-naphthalenediamine units

For comparison with the X-ray structure discussed below, the 1,8-naphthalenediamine oligomers were modelled with the PM3 semi-empirical method in Spartan.[24] First, conformational searches were performed for the dimer and trimer using the MMFF. As expected, this showed that conformations with an all-*anti* main chain were the lowest energy by a substantial margin. It was not possible to extend these searches to the tetramer or hexamer, but the all-*anti* conformers were modelled, first with the MMFF, and then using PM3. The preferred structures are shown in Fig. 1. Note that the aromatic moieties are tilted with respect to the main chain, reflecting pyramidalisation of the nitrogen atoms. It was found that structures with the nitrogen lone pairs on the terminal 1,8-naphthalenediamine units pointing inwards were preferred to alternatives where these pointed outwards, and this is in accord with the X-ray structures (see below). We were concerned whether PM3 gave a good account of the geometry around the nitrogen atoms in these structures. The simple monomer, 2,2-diethyl-1,3-dimethyl-2,3-dihydro-1*H*-perimidine showed very similar ground-state geometry at the PM3 and B3LYP/6-31G* level, but the calculated ring-inversion barrier was higher (38 kJ mol^{-1}) with DFT than PM3 (20 kJ mol^{-1}).

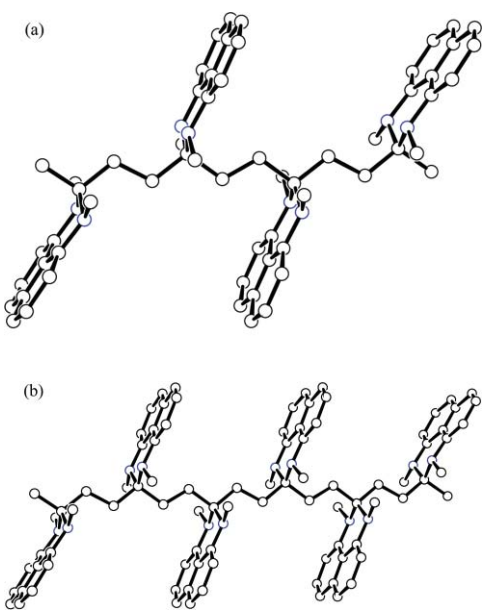


Fig. 1 Calculated structures for the (a) tetramer, and (b) hexamer.

NMR data for oligomers derived from *N*,*N*′-dimethyl-1,8-naphthalenediamine

The ^{1}H NMR spectrum of the hexamer is shown in Figs. 2(a) and (b).

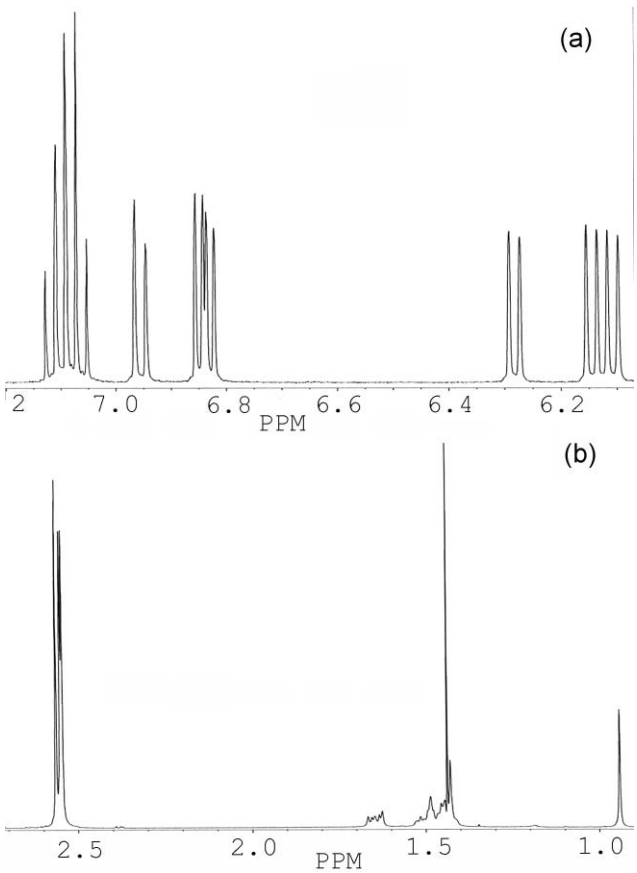


Fig. 2 ^{1}H NMR spectrum of the hexamer; (a) aromatic region, (b) aliphatic region.

In the aromatic region, the doublets at δ 6.1–6.3 ppm represent the *ortho* protons in the naphthalene ring. *Para* protons are represented by three doublets at δ 6.8–7.0 ppm, while the *meta* protons are at δ 7.0–7.2 ppm. The differential shielding within these groups must result from ring current effects from distant aromatic rings; those in the central naphthalene unit likely being shifted furthest upfield. Fig. 2(b) displays the aliphatic protons; the peaks at δ 0.96 ppm (terminal CH_3s) and the three peaks at δ 2.7 ppm (N–Me) are singlets. The peaks at δ 1.4–1.7 ppm are complex multiplets representing the 20 protons in the chain. ^{1}H NMR chemical shifts for other monomers and oligomers are listed in Table 1.

Table 1 ^{1}H NMR chemical shifts of protons in monomers and oligomers

	Molecule					
	Me_2C (monomer)	Et_2C (monomer)	**8** (dimer)	**9** (trimer)	**10** (tetramer)	**11** (hexamer)
C_q–CH_3	1.4	—	1.31	1.19	1.09	0.96
CH_2	—	—	1.93	1.66–1.71	1.61–1.67	1.45–1.55
CH_2	—	—	1.93	1.93–1.97	1.79–1.85	1.64–1.70
N–CH_3	2.97	2.96	2.76	2.77	2.71	2.59
ortho-H$^{(terminal)}$	6.6	6.4	6.47	6.45	6.42	6.3
ortho-H$^{(central)}$	—	—	—	6.22	6.26	6.15
meta-H$^{(terminal)}$	—	—	7.26	7.7	7.24	7.11
meta-H$^{(central)}$	—	—	—	7.20	7.24	7.11
para-H$^{(terminal)}$	—	—	7.26	7.15	7.11	6.98
para-H$^{(central)}$	—	—	—	7.02	7.03	6.86

In general, the longer the chain size, the more shielded almost all the protons become. Thus the terminal methyl groups of the chain are at 1.4 ppm for the model monomer but are steadily shifted upfield to 0.96 ppm for the hexamer. Methylene protons in the main chain become more shielded due to ring current shielding by the naphthalene units in the chain, as do the N–Me groups and this pattern is also replicated in the aromatic protons, with the central oligomer units shifted more than the terminal ones. This information corresponds with our published data on the fluorene oligomers **2**, but, perhaps because the naphthalene units are displaced more to either side of the main chains, the shifts are less dramatic than for the fluorenes.

X-Ray structural data for oligomers derived from *N*,*N*′-dimethyl-1,8-naphthalenediamine

X-Ray diffraction data was collected for crystals of the dimer, trimer, tetramer and hexamer. We will discuss these structures in turn, but note that the conformations become more regular as the chain grows longer, encouraging the idea that the internal section of an extended polymer would have a highly controlled conformation, as intended.

The dimer (CCDC 709694†) crystallised in the orthorhombic space group $Pna2_1$ and one crystallographically independent molecule was found in the unit cell. Anomalous scattering was insufficient to determine the absolute structure but we were able to locate and refine hydrogens without positional constraints. The dimer (Fig. 3) is not as conformationally controlled as we had expected. There is significant twisting along the chain as evidenced by the C1–C2–C3–C4 dihedral angle of *ca.* 58°. This is perhaps due to packing forces. The naphthalene diamine units are not perpendicular to the main chain, and the nitrogen atoms are quite pyramidal. These factors undoubtedly also contribute to the low degree of conformational control of the main C_6 chain in the solid-state structure.

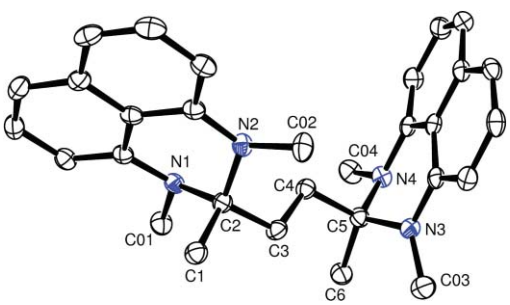


Fig. 3 Solid-state structure of the dimer **8**. Thermal ellipsoids are shown at a 50% probability level. Hydrogens have been omitted for clarity.

Trimer crystals (CCDC 709695†), obtained by slow diffusion of pentane into a chloroform solution, were very weakly diffracting due to extensive disorder. The cause of this is clear: channels of *ca.* 12 Å in diameter propagate along the crystallographic *c*-axis and provide such an effective means of escape for the co-crystallized solvent ($CHCl_3$) that removal of the crystal from the mother liquor results in immediate collapse of the lattice (Fig. 4). Nevertheless, the structure was solved in the tetragonal space group $P\bar{4}2_1c$ using standard direct methods, and 2.5 crystallographically independent trimer units were found in the asymmetric unit (one lies astride a two-fold rotation axis). Although the structure is insufficiently resolved to merit detailed analysis of geometric parameters, as with the dimer, conformational control along the central C_9 chain appears limited.

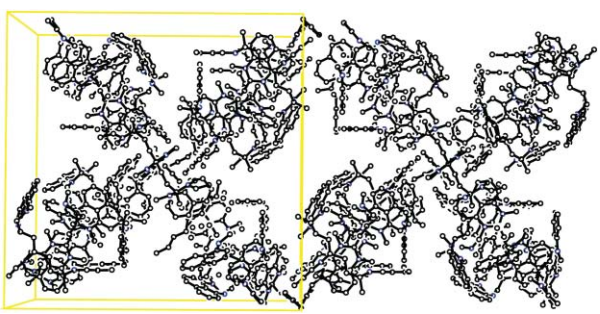


Fig. 4 Packing diagram for the trimer **9** as viewed down the crystallographic *c*-axis.

The solid-state structure of the tetramer (CCDC 709696†) is shown in Fig. 5 and that of the hexamer in Fig. 6.

The tetramer was crystallised from chloroform–hexane, and both solvents are present in the lattice as slightly disordered solvates. The hexamer (CCDC 709697†) was crystallised from chloroform–diethyl ether, and well-ordered molecules of the latter occupy the clefts between adjacent naphthalene units on the same side of the main chain in the structure, as can be seen in Fig. 7.

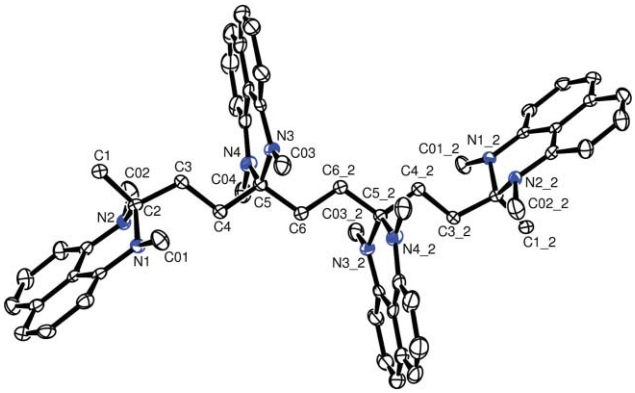


Fig. 5 Solid-state structure of the tetramer **10**. Thermal ellipsoids are shown at a 50% probability level. Hydrogens have been omitted for clarity. The symmetry operator for generating equivalent atoms (_2) is: $1 - x$, $1 - y$, $1 - z$.

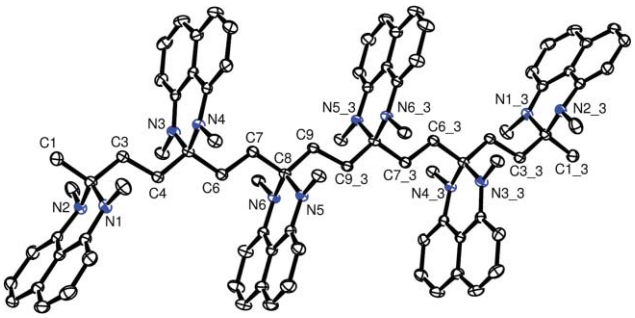


Fig. 6 Solid-state structure of the hexamer **11**. Thermal ellipsoids are shown at a 50% probability level. Hydrogens have been omitted for clarity. The symmetry operator for generating equivalent atoms (_3) is: $2 - x$, $1 - y$, $2 - z$.

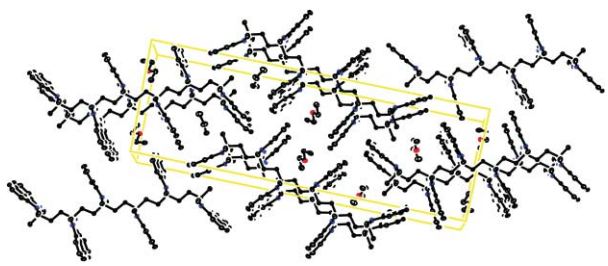


Fig. 7 Packing diagram for the hexamer as viewed down the crystallographic *a*-axis.

In spite of this, there is a limited amount of intercalation between naphthalenes from adjacent molecules.

The oligomer chains in both the tetramer and hexamer are all-*anti* as expected from our calculations: the carbon-backbone dihedral angles in the solid-state structures range from 164(1)° (between the two outer naphthalenediamines in the tetramer) to 180(1)°. It is interesting to compare these structures with the PM3 models. In both, the outer naphthalenediamines have strongly pyramidal nitrogen atoms pointing inwards. However, the internal naphthalenediamines are much closer to being perpendicular to the main chain, and their nitrogen atoms are significantly more planar (sum of angles around nitrogen ~358° for the inner rings in the tetramer and ~354° in the hexamer). The detailed structures are undoubtedly influenced by packing forces, and these can apparently force the inner nitrogen close to planarity. Nevertheless, it does seem clear that conformational control is stronger towards the interior of the chain, and that in an extended polymer, the inner portion would resemble our proposed model quite closely.

Attempted polymer synthesis

Ethylene/propylene/CO terpolymer was refluxed with *N*,*N*′-dimethyl-1,8-naphthalenediamine with a catalytic amount of *p*-toluenesulphonic acid in toluene. The mixture was refluxed for a number of weeks, but no conversion of ketone to aminal groups could be detected by infra-red spectroscopy and the majority of the product after refluxing for this time was starting material. A number of related procedures were tried with no success. We presume that the difficulty is the extreme insolubility of the polymeric ketone.

Cyclic voltammetry of oligomeric derivatives of 1,3-dialkyl-2,2-disubstituted 2,3-dihydro-1*H*-perimidines

One of our principal aims in making the compounds of the type previously described was to study their redox chemistry and electrochemical behaviour. As described above, we were unable to prepare suitable derivatives of *N*,*N*′-dialkyl-*o*-phenylenediamines. While the related polyaminals derived from *N*,*N*′-dimethyl-1,8-naphthalenediamine could be prepared, simple derivatives of *N*,*N*′-dialkyl-1,8-naphthalenediamine unfortunately do not show reversible oxidation. One possible way out would be to make derivatives of corresponding oligomers derived from 1,4,5,8-tetraaminonaphthalenes, since these have been shown to undergo reversible oxidation.[20–22] However, synthesis of these molecules is complicated, so this was not pursued. In spite of all the anticipated difficulties, the electrochemical behaviour of the dimer, trimer, tetramer and hexamers derived from *N*,*N*′-dialkyl-1,8-naphthalenediamines was investigated. The monomers 1,2,2,3-tetramethyl-2,3-dihydro-1*H*-perimidine, and 2,2-diethyl-1,3-dimethyl-2,3-dihydro-1*H*-perimidine were also examined for comparison.

All the compounds above behaved essentially similarly during initial oxidation scans, each showing completely irreversible oxidation waves at +0.55 ± 0.1 V *versus* SCE. However, with the trimer **9** (Fig. 8), tetramer **10**, and hexamer **11** (but not the dimer **8** (inset in Fig. 8) or monomers), new reversible waves were observed which grew on repeated cycling. A red insoluble material was deposited on the electrode at the same time. For trimer **9** (Fig. 8), a pair of reversible peaks appeared at *ca.* –0.1 and +0.1 V that increased in intensity with cycling, the peak current density for the oxidation of the oligomer decreased with cycling as the electrode became coated with polymer. For the tetramer **10**, the pair of reversible peaks appeared at *ca.* –0.15 and +0.1 V. It was noticed that the peak height of the latter was 2–3 times that of the former; peak separations were about 0.1 V. Finally, for the hexamer **11**, the pair of reversible peaks again appeared at *ca.* –0.15 and +0.1 V, but now the wave at *ca.* +0.1 V was more than 3 times bigger than the one at *ca.* –0.15 V.

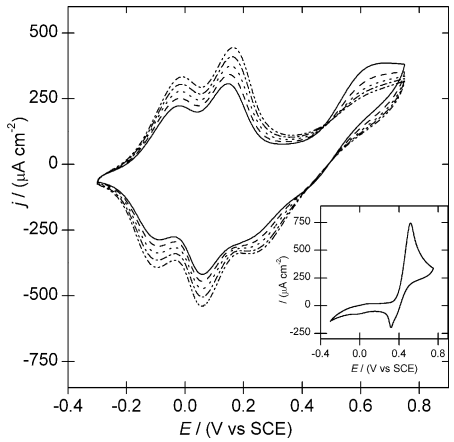


Fig. 8 Cyclic voltammograms of the trimer **9** and the dimer **8** (inset). The *I*–*V* curves were recorded at a scan rate of 50 mV s^{-1}.

These results suggested that some kind of aggregation or polymerisation process was occurring, and so we examined one of these oligomers, using a transparent indium tin oxide electrode suitable for spectroelectrochemical studies. It was found that a pinkish-red, conducting, film was deposited on the electrode, and an electronic spectrum of this film, in the reduced state, was obtained (Fig. 9).

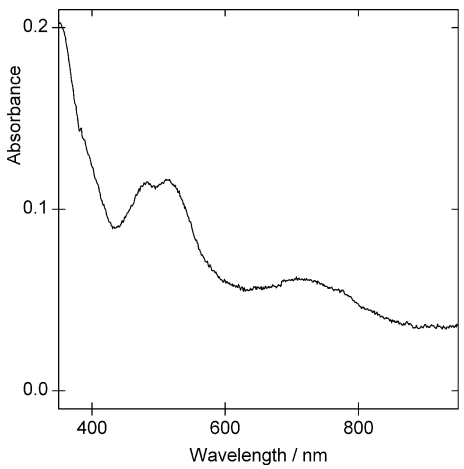
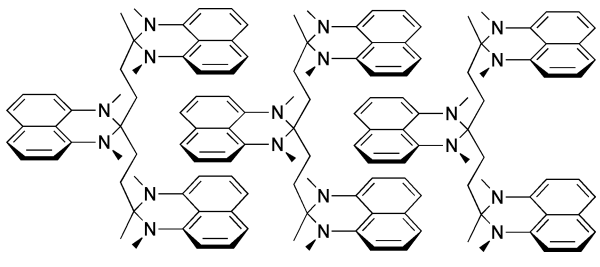


Fig. 9 UV–visible spectrum of the polymer deposited on an ITO electrode during a cyclic voltammetric study of the trimer **9**.

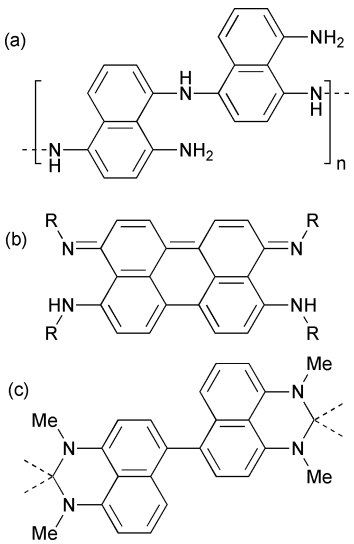
Possible structures for the conducting film

Without more detailed studies, it is only possible to speculate about the nature of this polymer film. As discussed previously, these oligomers were designed to be able to intercalate and/or stack. The formation of a conducting polymer film through non-covalent interactions of this type would be novel and worthy of extended study. Therefore, it can be pointed out that conducting films are only formed from trimer **9** onwards, and this is surely the smallest oligomer which could form a stable intercalated structure, as shown in Scheme 8.

An alternative view would be that some form of covalent polymerisation process is occurring to lay down the polymer film. Polyanilines have received considerable attention, prepared by chemical, electrochemical and even enzymatic oxidation of anilines. These studies have been extended to the oxidative polymerisation of many aromatic diamines,[25] including 1,8-diaminonaphthalene. The proposed[26] structure for poly(1,8-diaminonaphthalene) is shown in Scheme 9(a). This structure has both 1,4- and 1,5-linked naphthalenes, although there is no clear evidence which supports this, and formation of corresponding structures from our oligomers would require rupture of the aminal units or demethylation. 1,8-Diaminonaphthalenes can undergo oxidative dimerisation to 4,9-diaminoperylenequinone-3,10-diimines,[27] admittedly under rather different conditions (see Scheme 9(b)). This suggests the possibility of a polymer structure based on 4,4-coupling of the naphthalene units as another alternative. Such a linkage would be expected to give a stable radical cation, as shown in Scheme 9(c), but could get oxidised further to a perylene derivative. It is noteworthy that the electronic spectrum of the polymer film is relatively similar to that reported for 4,9-diaminoperylenequinone-3,10-diimines.[27]



Scheme 8 Possible intercalation.



Scheme 9 (a) Suggested structure for poly(1,8-diaminonaphthalene)[26]; (b) Structure of 4,9-diaminoperylenequinone-3,10-diimines[27]; (c) Suggested structure for a 4,4-linked unit in the oxidised film.

Conclusions

A series of oligomeric polyaminals derived from *N*,*N*′-dimethyl-1,8-naphthalenediamine up to the hexamer **11** were prepared. Attempts to prepare the corresponding oligomers with

N,*N*′-dialkyl-*o*-phenylenediamine-derived pendant groups were frustrated by the unreactivity of internal ketone groups of polyketones towards aminal formation with these diamines. This result with the apparently less bulky diamine is puzzling. The naphthalene-derived oligomeric polyaminals proved to be quite tractable, and were characterised using NMR spectroscopy and X-ray diffraction. The conformational preference for all-*anti* main chains increases with chain length, and the structures show interesting alignments of the aryl groups and signs of intercalation. However, these oligomers do not show simple oxidation behaviour, but form deposits on the electrode, suggesting that some form of electropolymerisation is occurring.

Experimental

General procedures

^{1}H and ^{13}C NMR spectra were recorded on JEOL Eclipse 400 or JNM-GX400 spectrometers. Chemical shifts (δ) are quoted in parts per million downfield from tetramethylsilane (TMS). Coupling constants (J) are expressed in Hertz (Hz). The following abbreviations for multiplicities have been used: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (qn) quintet, (sp) septet, and (m) multiplet. The abbreviation (br) is used as a prefix if the signal showed broadening. When broadening was very large, the range is given.

Low-resolution mass spectra (m/z) were recorded in the Fast Atom Bombardment (FAB), Electron Impact (EI) (70 eV) or Chemical Ionisation (CI) modes using a Fisons VG Analytical Autospec spectrometer with only molecular ions (M^+ or $[M + H]^+$), and major peaks being reported with intensities being quoted as percentages of the base peak. High-resolution EI and CI mass determinations were performed on the same instrument as the corresponding low-resolution spectra.

Elemental combustion analyses were performed using a Perkin–Elmer 240C elemental analyser and were performed by the staff of the microanalytical department at the School of Chemistry, University of Bristol.

GC-MS was performed using an Agilent 6890 apparatus equipped with a capillary column HP-5MS (HP190915–433, 5% phenyl pethyl siloxane, 30 m × 250 μm × 0.25 μm nominal) under the following conditions: helium 1 mL min^{-1} (constant-flow mode), injector 250 °C (splitless mode), detector EI (Agilen MSD 5973), oven 70 °C (3 min), 15 °C min^{-1} (15.3 min), 300 °C (18 min) unless otherwise specified.

4-(5-Methyl-2-furyl)-2-butanone, 2,5,8-nonanetrione, 4-[5-(3-oxobutyl)-2-furyl]-2-butanone, and 2,5,8,11-dodecanetetraone were prepared using the procedures of Poirier and Dujardin.[17,18] Preparative details for 1,2-di(2-furyl)-1-ethanone,[19] 2-[2-(2-furyl)-ethyl]furan,[19] *N*-[2-(acetylamino)phenyl]acetamide, *N*,*N*-diethyl-1,2-benzenediamine, *N*-[2-(hexanoylamino)phenyl]hexanamide, *N*,*N*-dihexyl-1,2-benzenediamine, 2-methyl-1*H*-perimidine,[28] 1,2-dimethyl-1*H*-perimidine,[23] 1,2-dimethylperimidinyl methiodide,[23] and 1,2,2,3-tetramethyl-2,3-dihydro-1*H*-perimidine[29] are in the ESI†.

4-(5-[2-[5-(3-Oxobutyl)-2-furyl]ethyl]-2-furyl)-2-butanone. A solution of but-3-en-2-one (1.57 g, 22.4 mmol) was added to a mixture of 2-[2-(2-furyl)ethyl]furan (1.84 g, 11.2 mmol) and nitromethane (30 mL) in a flask under nitrogen with stirring. The solution was cooled to −20 °C and a solution of boron trifluoride etherate (0.64 g, 4.48 mmol) in ethanol (1.03 g, 22.4 mmol) was prepared in a separate flask under nitrogen. The catalyst was added dropwise to the solution at −20 °C with stirring resulting in a red colour. Stirring was continued for 90 min at which the brown solution was warmed to −10 °C and $NaHCO_3$ (saturated solution, 30 mL) was added. The product was extracted with dichloromethane (4 × 40 mL), dried over $MgSO_4$, filtered, concentrated *in vacuo* and purified by flash column chromatography (silica gel 60H, hexane–diethyl ether, 30 : 70) to afford the desired product as a white crystalline powder (1.39 g, 41%). M.p. 57–58 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.16 (6 H, s), 2.73–2.89 (8 H, m), 2.88 (4 H, s), 5.86 (4 H, s); ^{13}C NMR (100 MHz; $CDCl_3$) δ 22.4 & 26.9 (C-1′, -4′, 2t), 29.9 (C-1, q), 41.9 (C-3′, t), 105.7 (C-3, -4, 4d), 152.9 & 153.5 (C-2, -5, 4 s), 207.4 (C-2′, 2 s); MS m/z (EI) 302 (M^+, 21), 151 (100), 107 (24), 94 (13) 81 (29) 55 (9); Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found C, 71.38; H, 7.39; IR (ATR) ν_{max}/cm^{-1} 2920 (C–H & C=C), 1712 (C=O), 1567 (C=C), 1161 (C–O–C).

2,5,8,11,14,17-Octadecanehexaone. 3 M HCl (8.5 mL) was added to a solution of 4-(5-2-[5-(3-oxobutyl)-2-furyl]ethyl-2-furyl)-2-butanone (0.50 g, 1.65 mmol) with stirring. The solution was refluxed for 2 h and the product was extracted with dichloromethane (4 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the desired product. Further purification involved crystallisation from hot ethanol, affording a white crystalline powder (0.51 g, 91%). M.p. 142–143 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.05 (6 H, s), 2.59 (4 H, s), 2.61 (8 H, 2 s); ^{13}C NMR (100 MHz; $CDCl_3$) δ 29.7 (C-1, q), 36.0 (t), 36.8 (t), 37.2 (t), 207.2 (C-2, s), 208.1 (C-5, -8, 2 s); MS m/z (EI) 338 (M^+, 1), 320 (2), 302 (2), 267 (14) 249 (16) 211 (58), 165 (54), 151 (87), 127 (97), 107 (54), 99 (100), 71 (41), 55 (50); Anal. Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74. Found C, 64.00; H, 7.62; IR (ATR) ν_{max}/cm^{-1} 2911 (C–H), 1691 (C=O), 1172 (C–O).

1,3-Dihexyl-2,2-dimethyl-2,3-dihydro-1*H*-benzo[*d*]imidazole. Acetic acid (55 μL, 0.90 mmol) was added to a solution of *N*,*N*-dihexyl-1,2-benzenediamine (2.48 g, 9.0 mmol) in acetone (20 mL) with stirring under nitrogen. The solution was refluxed for 20 h. The acetone was removed under reduced pressure and diethyl ether (40 mL) was added. The solution was washed with water (2 × 30 mL), dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The resulting black oil was purified by column chromatography (neutral alumina, hexane–ethyl acetate, 95 : 5) to afford the desired product as a brown solid (2.48 g, 87%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.89 (6 H, t, J = 7.0 Hz), 1.27 (6 H, s), 1.30–1.40 (12 H, m), 1.62 (4 H, m), 2.95 (4 H, t, J = 7.3 Hz), 6.17 (2 H, dd, J = 3.3, 2.9 Hz), 6.50 (2 H, dd, J = 3.0, 3.3 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ 14.2 (C-6′, 2q), 22.6 (C-5′, 2t), 22.8 (C-4′, 2t), 27.2 (C-1, 2q), 29.6 (C-3′, 2t), 31.8 (C-2′, 2t), 43.9 (C-1′, 2t), 86.9 (C-2, s), 102.9 (C-4, -7, 2d), 117.2 (C-5, -6, 2d), 140.5 (C-3a, -8, 2q); MS m/z (EI) 316 (M^+, 22), 301 (100), 272 (20), 229 (26), 217 (15), 201 (21), 159 (14), 145 (30), 133 (26), 119 (20), 55 (10); HRMS found 316.2884, $C_{21}H_{36}N_2$ requires 316.2879. IR (ATR) ν_{max}/cm^{-1} 2926 (C–H), 1312 (^{tert}amine) & 1174, 1109, 874 (1,2-disubstituted benzene).

2-[2-(1,3-Dihexyl-2-methyl-2,3-dihydro-1*H*-benzo[*d*]imidazol-2-yl)ethyl]-1,3-dihexyl-2-methyl-2,3-dihydro-1*H*-benzo[*d*]imidazole 7. Dimer **7** was prepared from *N*,*N*-dihexyl-1,2-benzenediamine (1.21 g, 4.38 mmol), acetonylacetone (0.25 g, 2.19 mmol) and *p*-toluenesulphonic acid (83.0 mg, 0.44 mmol) in toluene (20 mL). The solution was refluxed under nitrogen for 20 h using a flask provided with a condenser and a Dean–Stark trap. The toluene was removed under reduced pressure and dichloromethane (30 mL) was added. The solution was washed with $NaHCO_3$ (saturated solution, 2 × 20 mL), water (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a black oil. This oil was purified by column chromatography (neutral alumina, hexane–ethyl acetate, 99 : 1) to afford green crystals which were recrystallised from hot methanol, precipitating the desired product as fine white crystals (1.09 g, 79%). M.p. 83–84 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.83 (12 H, t, J = 6.8 Hz), 1.12 (6 H, s), 1.25 (28 H, br m), 1.54 (4 H, s), 1.61 (8 H, m), 2.90 (8 H, m), 6.03 (4 H, dd, J = 3.1, 3.4 Hz), 6.41 (4 H, dd, J = 3.2, 3.2 Hz)); ^{13}C NMR (100 MHz; $CDCl_3$) δ 14.1 (C-6′, 4q), 22.8 (C-5′, 4t), 24.1 (C-1, 4q), 27.3 (C-4′, 4t), 29.0 (C-3′, 4t), 31.0 (C-′2, 2t), 31.8 (C-2′, 4t), 43.6 (C-1′, 4t), 88.3 (C-2, 2 s), 101.7 (C-4, -7, 2d), 116.7 (C-5, -6, 2d), 140.6 (C-3a, -7a, 4 s); MS *m*/*z* (EI) 631 (M^+, 2), 313 (32), 301 (100) 145 (9), 133 (8); HRMS found 630.5609, $C_{42}H_{70}N_4$ requires 630.5601; Anal. Calcd for $C_{42}H_{70}N_4$: C, 79.94; H, 11.18; N, 8.88. Found C, 80.48; H, 11.13; N, 9.11; IR (ATR) ν_{max}/cm^{-1} 2925 (C–H), 1300 (^{tert}amine) & 1159, 1119, 870 (1,2-disubstituted benzene).

2-[2-(1,3-Diethyl-2-methyl-2,3-dihydro-1*H*-benzo[*d*]imidazol-2-yl)ethyl]-1,3-diethyl-2-methyl-2,3-dihydro-1*H*-benzo[*d*]imidazole. The dimer was prepared from *N*,*N*-diethyl-1,2-benzenediamine (1.45 g, 8.84 mmol), acetonylacetone (0.50 g, 4.42 mmol) and *p*-toluenesulphonic acid (168.0 mg, 0.88 mmol) in toluene (15 mL). The solution was refluxed under nitrogen for 20 hours using a flask provided with a condenser and a Dean–Stark trap. The toluene was removed under reduced pressure and dichloromethane (30 mL) was added. The solution was washed with $NaHCO_3$ (saturated solution, 2 × 20 mL), brine (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a black oil. This oil was purified by column chromatography (neutral alumina, hexane–dichloromethane, 85:15) to afford the desired product as a blue solid. This blue powder was recrystallised from isopropyl alcohol (1.53 g, 85%). M.p. 140–142 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.19 (6 H, s), 1.23 (12 H, t, J = 7.0), 1.72 (4 H, s), 2.98 – 3.19 (8 H, m), 6.16 (4 H, dd, J = 3.4, 2.9 Hz), 6.49 (4 H, dd, J = 3.4, 3.4 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ 14.3 (C-2′, q), 23.1 (C-1, q), 31.1 (C-′2, t), 37.2 (C-1′, t), 88.6 (C-2, s), 102.0 (C-4, -7, d), 116.9 (C-5, -6, d), 140.2 (C-3a, 7a, s); MS *m*/*z* (EI) 406 (M^+, 12), 201 (12) 189 (100), 160 (20), 145 (28), 133 (25), 119 (6), 92 (10); HRMS found 406.3089, $C_{26}H_{38}N_4$ requires 406.3096; IR (ATR) ν_{max}/cm^{-1} 2980 (C–H), 1330 (^{tert}amine), 1165, 1112, 929 (1,2-disubstituted benzene).

***N*,*N*′-Dimethyl-1,8-naphthalenediamine.** Nitrogen was bubbled through a solution of potassium hydroxide (145.6 g, 2.60 mol) in ethanol (800 mL) for 5 min. 1,2-Dimethylperimidinyl methiodide (58.45 g, 0.17 mol) was added in one portion to the alkaline ethanolic solution and the resultant solution was refluxed under nitrogen. After 3 h, the reaction mixture was cooled and diluted with water to yield a final volume of 2.5 L. The resulting solution was neutralised with glacial acetic acid until the pH was weakly basic to litmus. A brown solid precipitated out during this time. The solid was filtered, washed with water and dried under reduced pressure to yield the desired amine. The crude material was purified by column chromatography (neutral alumina, hexane–dichloromethane, 60 : 40) to afford the desired product as a light-brown solid (20.8 g, 66%). M.p. 102–103 °C (Lit.,[30] 101°C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 2.81 (6 H, s), 5.40 (2 H, br s), 6.52 (2 H (H 2 & 7), br dd, J = 7.3, 1.0 Hz), 7.18 (2 H (H 4 & 5), br dd, J = 8.3, 1.5 Hz), 7.24 (2 H (H 3 & 6), br dd, J = 8.0, 7.6 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ 32.3 (C-1′, q), 106.6 (C-2, d), 117.1 (C-8a, s), 119.3 (C-4, d), 126.6 (C-3, d), 137.0 (C-1, s), 147.9 (C-8a, s); MS *m*/*z* (EI) 186 (M^+, 100), 168 (83) 154 (57), 143 (23), 127 (38), 115 (46); Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found C, 77.52; H, 7.60; N, 14.75; IR (ATR) ν_{max}/cm^{-1} 3354 (aromatic ^{sec}N–H), 3052 (aromatic C–H), 2902 (aliphatic C–H), 1300 (^{sec}amine), 1585, 806 & 752 (1,2,3-trisubstituted aromatic).

2,2-Diethyl-1,3-dimethyl-2,3-dihydro-1*H*-perimidine. To a solution of *N*,*N*′-dimethyl-1,8-naphthalenediamine (0.62 g, 3.33 mmol) and pentan-3-one (0.32 g, 0.37 mmol) in toluene (10 mL) was added *p*-toluenesulphonic acid (63.3 mg, 0.33 mmol) in a flask under nitrogen with stirring. The solution was refluxed for 20 h in the presence of 4 Å molecular sieves. The toluene was removed under reduced pressure and dichloromethane (20 mL) was added. The solution was washed with $NaHCO_3$ (saturated solution, 2 × 15 mL), water (2 × 15 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown solid. This solid was purified by column chromatography (neutral alumina, hexane–dichloromethane, 80 : 20) to afford the desired product as a white solid (0.75 g, 80%). M.p. 97–98 °C.

1,2,3-Trimethyl-2-[2-(1,2,3-trimethyl-2,3-dihydro-1*H*-2-perimidinyl)ethyl]-2,3-dihydro-1*H*-perimidine 8. Dimer **8** was prepared from a solution of *N*,*N*′-dimethyl-1,8-naphthalenediamine (0.34 g, 1.81 mmol), acetonylacetone (0.10 g, 0.90 mmol) and *p*-toluenesulphonic acid (17.2 mg, 0.09 mmol) in toluene (5 mL). The solution was refluxed under nitrogen for 20 h using a flask provided with a condenser and a Dean–Stark trap. The toluene was removed under reduced pressure and dichloromethane (20 mL) was added. The solution was washed with $NaHCO_3$ (saturated solution, 2 × 15 mL), water (2 × 15 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown solid. This brown solid was purified by column chromatography (neutral alumina, hexane–dichloromethane, 70 : 30) to afford a white powder. Further purification involved crystallisation from hot ethanol or dissolving in a minimum amount of toluene and crystallisation by slow diffusion of pentane, precipitating colourless crystals (1.76 g, 89%). M.p. 147–150 °C.

2-(2-[1,3-Dimethyl-2-[2-(1,2,3-trimethyl-2,3-dihydro-1*H*-2-perimidinyl)ethyl]-2,3-dihydro-1*H*-2-perimidinylethyl)]-1,2,3-trimethyl-2,3-dihydro-1*H*-perimidine 9. Trimer **9** was prepared from a solution of *N*,*N*′-dimethyl-1,8-naphthalenediamine (0.62 g, 3.34 mmol), 2,5,8-nonanetrione (0.14 g, 0.83 mmol) and *p*-toluenesulphonic acid (16.0 mg, 0.08 mmol) in toluene (5 mL). The solution was refluxed under nitrogen for 20 h using a flask provided with a condenser and a Dean–Stark trap. The toluene was removed under reduced pressure and dichloromethane (20 mL) was added. The solution was washed with $NaHCO_3$ (saturated

solution, 2 × 15 mL), water (2 × 15 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown solid. This brown solid was purified by column chromatography (neutral alumina, dichloromethane) to afford the desired product as a white powder. Further purification involved dissolving in a minimum amount of chloroform and crystallising by slow diffusion of pentane, precipitating fine colourless crystals (0.47 g, 84%). M.p. 268–269°C.

Tetramer 10. Tetramer **10** was prepared from a solution of *N*,*N*′-dimethyl-1,8-naphthalenediamine (1.85 g, 9.96 mmol), 2,5,8,11-dodecanetetraone (0.50 g, 2.21 mmol) and *p*-toluenesulphonic acid (42 mg, 0.22 mmol) in toluene (10 mL). The solution was refluxed under nitrogen for 20 h using a flask provided with a condenser and a Dean–Stark trap. The toluene was removed under reduced pressure and dichloromethane (30 mL) was added. The solution was washed with $NaHCO_3$ (saturated solution, 2 × 20 mL), water (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown solid. This brown solid was purified by column chromatography (neutral alumina, dichloromethane) to afford the desired product as a white powder. Further purification involved dissolving in a minimum amount of chloroform and crystallising by slow diffusion of pentane, precipitating fine colourless crystals (1.62 g, 82%). M.p. 159–160 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.09 (6 H, s), 1.61–1.67 & 1.79–1.85 (8 H, m), 1.69 (4 H, s), 2.70 (12 H, s), 2.71 (12 H, s), 6.26 (4 H, br d, $J = 7.8$ Hz), 6.42 (4 H, br d, $J = 7.5$ Hz), 7.03 (4 H, br d, $J = 8.3$ Hz), 7.11 (4 H, br d, $J = 8.3$ Hz), 7.24 (12 H, br dd, $J = 8.5$, 7.9 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ 19.3 (C-1, q), 30.1 (C-1, t), 31.0 (C-2, t), 32.8 (C-1, q), 33.4 (C-1, q), 75.0 (C-2, s), 78.2 (C-2, s), 100.7 (C-4, d), 105.2 (C-4, d), 110.5 (C-9b, s), 114.3 (C-9b, s), 115.6 (C-6, d) 117.1 (C-6, d), 126.9 (C-5, d), 127.3 (C-5, d), 133.7 (C-6a, s), 133.9 (C-6a, s), 141.8 (C-3a, s), 142.5 (C-3a, s); MS *m*/*z* (FAB) 899 ([M + H]$^+$, 2) 660 (16), 435 (38), 223 (12), 211 (100), 196 (43) 182 (9), 168 (14); Anal. Calcd for $C_{60}H_{66}N_8$: C, 80.14; H, 7.40; N, 12.46. Found C, 80.53; H, 7.74; N, 12.40; IR (ATR) ν_{max}/cm^{-1} 3049 (aromatic C–H), 2861 (aliphatic C–H), 1329 (^{tert}amine), 1575, 803 & 749 (1,2,3-trisubstituted aromatic).

Hexamer 11. Hexamer **11** was prepared from a solution of *N*,*N*′-dimethyl-1,8-naphthalenediamine (0.54 g, 2.90 mmol), 2,5,8,11,14,17-octadecanehexaone (0.14 g, 0.41 mmol) and *p*-toluenesulphonic acid (7.8 mg, 0.04 mmol) in toluene (4 mL). The solution was refluxed under nitrogen for 20 h using a flask provided with a condenser and a Dean–Stark trap. The toluene was removed under reduced pressure and dichloromethane (30 mL) was added. The solution was washed with $NaHCO_3$ (saturated solution, 2 × 20 mL), water (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a brown solid. This brown solid was purified by column chromatography (neutral alumina, dichloromethane) to afford the desired product as a white powder. Further purification involved dissolving in a minimum amount of chloroform and crystallising by slow diffusion of diethyl ether, precipitating fine colourless crystals (0.52 g, 93%). M.p. 185–188 °C.

X-Ray crystallography

Crystals were inspected under a binocular microscope fitted with a polarising attachment. Suitable crystals were then coated with epoxy resin, mounted on a glass fibre and quickly transferred to a Bruker-AXS SMART or PROTEUM (CCD area-detector) diffractometer under a stream of cold N_2 gas. Preliminary scans were taken to assess crystal quality, lattice symmetry, ideal exposure time *etc.* prior to collecting a sphere or hemisphere (for low- and high-symmetry crystal systems respectively) of diffraction intensity data using SMART operating software.[31] Intensities were then integrated from several series of exposures (each exposure covering 0.3° in ω), merged and corrected for Lorentz and polarisation effects using SAINT software.[32] Solutions were generated by conventional heavy-atom Patterson or direct methods and refined by full-matrix non-linear least squares on all F^2 data, using SHELXS-97 and SHELXL software respectively (as implemented in the SHELXTL suite of programs).[33] Empirical absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.[34] All structures were refined until convergence (max shift/esd <0.01) and in each case, the final Fourier difference map showed no chemically sensible features. Crystallographic refinement parameters are summarised in Table 2.

Dimer 8. All hydrogens were located in the Fourier difference. map and refined without positional constraints. Anomalous scattering was not sufficient to determine absolute configuration.

Trimer 9. As discussed in the text, crystals of the trimer **9** are extensively disordered due to rapid solvent loss on removal from the mother liquor, which in turn causes partial collapse of the crystal lattice. The data obtained was measured from a pre-cooled crystal, which was transferred rapidly from the mother liquor to the cryostream, and it constitutes the best of numerous attempts. In the large channels between the stacked trimer units were located *ca.* three $CHCl_3$ solvent molecules (per asymmetric unit). However, these were so poorly resolved that attempts to model their geometries and positional disorder were abandoned in favour of removing their scattering contributions using the SQUEEZE routine in PLATON.[35] These solvents have been included in the moiety formula. The 2.5 fragments of trimer located in the asymmetric unit are also poorly resolved. Rigid-body constraints were applied for many of the naphthalenyl rings during the early stages of refinement to enforce sensible geometries. These were then replaced by extensive distance, similarity and planarity restraints (DFIX, SAME and FLAT) for the final stages of refinement. Hydrogens were placed in calculated positions and refined with riding constraints and with isotropic displacement parameters 1.2× or 1.5× their parent carbons (for sp^2 and sp^3 carbons respectively). Methyl hydrogens were, however, not included in the model as reliable positions could not be determined. We stress that the structure of the trimer **9** does not merit detailed analysis beyond establishing its basic atomic connectivity.

Tetramer 10. All hydrogen atoms were placed in calculated positions and refined with riding constraints and isotropic displacement parameters fixed at 1.2× or 1.5× their parent carbons (for sp^2 and sp^3 carbons respectively). The bond length of one C(sp^3)–C(sp^3) in a partially disordered hexane solvate was restrained (DFIX) to a target value of 1.53(1) Å.

Hexamer 11. Aromatic hydrogens were placed in calculated positions and refined with riding constraints and isotropic

Table 2 Crystal data and refinement parameters for the dimer **8**, trimer **9**, tetramer **10** and hexamer **11**

Complex	Dimer	Trimer·1.2$CHCl_3$	Tetramer·2$CHCl_3$·C_6H_{14}	Hexamer·4$C_4H_{10}O$
Empirical formula	$C_{30}H_{30}N_4$	$C_{46.2}H_{51.2}Cl_{3.6}N_6$	$C_{65}H_{75}Cl_6N_8$	$C_{106}H_{138}N_{12}O_4$
Formula weight/g mol^{-1}	450.61	818.15	1181.03	1644.28
Temperature/K	100(2)	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073	1.54178
Crystal system	Orthorhombic	Tetragonal	Triclinic	Monoclinic
Space group	$Pna2_1$	$P\bar{4}2_1c$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions/Å	$a = 11.836(2)$	$a = 30.277(4)$	$a = 13.395(3)$	$a = 8.6359(7)$
	$b = 16.170(3)$	$b = 30.277(4)$	$b = 13.920(3)$	$b = 40.315(8)$
	$c = 12.621(3)$	$c = 25.361(5)$	$c = 18.238(4)$	$c = 13.478(3)$
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 82.99(3)°$	$\alpha = 90°$
	$\beta = 90°$	$\beta = 90°$	$\beta = 74.76(3)°$	$\beta = 107.58(1)°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 63.01(3)°$	$\gamma = 90°$
Volume/$Å^3$	2415.5(8)	23248(7)	2923.8(14)	4473.4(13)
Z (Z')	4 (1)	20 (2.5)	2 (1)	2 (0.5)
Density (calculated)/mg m^{-3}	1.239	1.169	1.342	1.221
Absorption coefficient/mm^{-1}	0.074	0.269	0.343	0.577
$F(000)$	968	8632	1246	1780
Crystal size/mm	$0.3 \times 0.1 \times 0.1$	$0.2 \times 0.2 \times 0.15$	$0.4 \times 0.3 \times 0.3$	$0.3 \times 0.2 \times 0.05$
q range for data collection	2.05–27.48°	1.05–22.50°	2.32–27.44°	2.19–70.48°
Index ranges	$-14 \leq h \leq 15$	$-32 \leq h \leq 32$	$-15 \leq h \leq 15$	$-10 \leq h \leq 10$
	$-13 \leq k \leq 20$	$-24 \leq k \leq 32$	$-16 \leq k \leq 16$	$-47 \leq k \leq 49$
	$-16 \leq l \leq 15$	$-27 \leq l \leq 23$	$-21 \leq l \leq 21$	$-16 \leq l \leq 16$
Reflections collected	16500	88405	26699	35123
Independent reflections	5171 [$R_{int} = 0.0565$]	15215 [$R_{int} = 0.0930$]	10253 [$R_{int} = 0.0201$]	8399 [$R_{int} = 0.0337$]
Data/restraints/parameters	5171/1/443	15215/972/511	10253/1/723	8399/0/755
Goodness-of-fit on F^2	$S = 0.944$	$S = 1.629$	$S = 1.008$	$S = 0.956$
R indices [for reflections with $I > 2s(I)$][a,b]	$R_1 = 0.0428$, $wR_2 = 0.0854$	$R_1 = 0.1808$, $wR_2 = 0.4508$	$R_1 = 0.0791$, $wR_2 = 0.2112$	$R_1 = 0.0367$, $wR_2 = 0.0960$
R indices (for all data)[a,b]	$R_1 = 0.0487$, $wR_2 = 0.0875$	$R_1 = 0.2136$, $wR_2 = 0.4742$	$R_1 = 0.0922$, $wR_2 = 0.2168$	$R_1 = 0.0429$, $wR_2 = 0.0987$
Weighting scheme[b]	$a = 0.0395$, $b = 0.0000$	$a = 0.2000$, $b = 0.0000$	$a = 0.0895$, $b = 10.8805$	$a = 0.0701$, $b = 0.0000$
Largest diff. peak and hole/e $Å^{-3}$	0.214 and –0.233	0.616 and –0.490	1.455 and –0.789	0.267 and –0.242

[a] Structure was refined on F_o^2 using all data; the value of R_1 is given for comparison with older refinements based on F_o with a typical threshold of $F \geq 4\sigma(F)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_o^2]/3$.

displacement parameters fixed at 1.2× their parent carbons. All aliphatic hydrogens were located in the Fourier difference map and refined without constraints.

Electrochemistry

Cyclic voltammograms were recorded on an Autolab potentiostat (Ecochemie, Netherlands) operating in three-electrode mode. A platinum or ITO working electrode, a saturated calomel reference electrode and a platinum gauze counter electrode were immersed in dichloromethane solutions containing 5×10^{-3} mol dm^{-3} of oligomer and 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate.

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