DOI: 10.1002/chem.200600874

Perylenophthalocyanines

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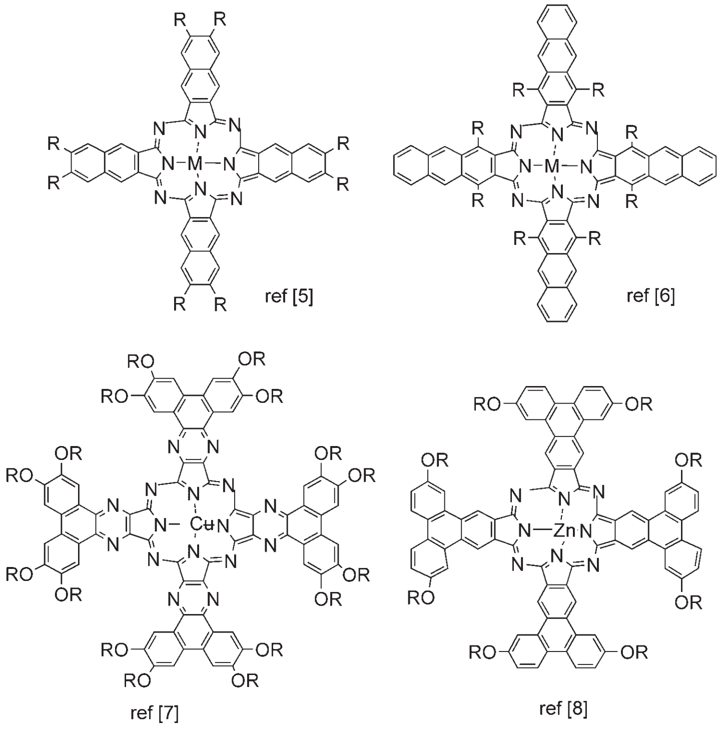
Abstract: The first perylenophthalocyanines have been synthesised using a Diels–Alder reaction between dialkylperylenes and fumaronitrile as the key step towards the dinitrile precursors. As expected the octaalkylperylenophthalocyanines show red-shifted absorption spectra. They are high melting solids that do not display mesophase behaviour at accessible temperatures. A 3:1 phthalocyanine/perylenophthalocyanine hybrid material, prepared by a mixed macrocyclisation reaction, presents an unusual board-like molecular profile. Its absorption maxima lie between those observed for the parent phthalocyanines and the symmetrical perylenophthalocyanines. The spectrum shows a characteristic split Q-band due to the reduced symmetry of the core. This material is non-mesogenic but is sufficiently soluble to permit processing and characterisation. The ^{1}H NMR spectrum indicates that at least two of the appended alkyl chains are displaced out of the macrocycle plane and lie in its shielding region—an arrangement that disfavours the face-to-face packing required for mesophase formation.

Keywords: liquid crystals • materials science • pericyclic reactions • perylenes • phthalocyanines

Introduction

Phthalocyanines are important molecular materials because of the potential for such molecules to form the functional component of optoelectronic devices.[1,2] Their use in such applications typically requires a combination of molecular (e.g. optical absorption/band gap, redox) and bulk (e.g. processability, self-assembly, mesophase formation) properties. For this reason a large number of phthalocyanine derivatives have been prepared. Some phthalocyanines are discotic liquid crystals,[3] an important sub-class of liquid crystals to emerge since their discovery almost 30 years ago.[4] Phthalocyanine itself can be modified extensively to tune both molecular and bulk properties. Such modifications can focus on a combination of variation of the (organic) core structure (e.g. introduction of substituents to change absorption and/or solubility properties) and central metal ion (more than 70 elements can be introduced). Extension of the aromatic core has also been investigated (Scheme 1).[5–8] The extended π system so-produced leads to tuning of the molecular properties, and careful choice of derivative also permits their processing (solubility) and self-assembly (mesophase) properties. Such extended systems that retain mesophase behaviour are termed macrodiscotic materials.[9]



Scheme 1. Examples of π-extended phthalocyanines.

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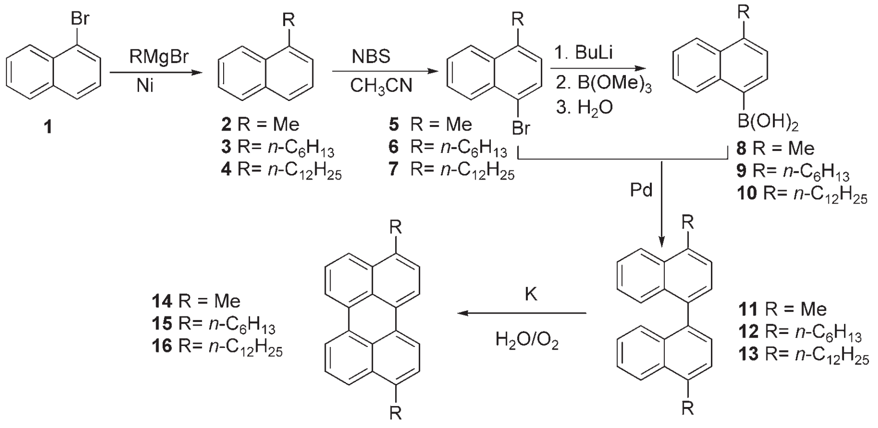
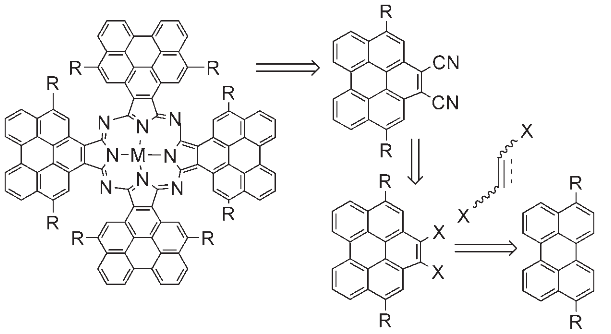
Results and Discussion

Herein we report the first examples of substituted perylenophthalocyanines—the most π-extended phthalocyanines reported to date. Perylene is itself an important unit in organic materials chemistry[10] and we reasoned that coupling to functional phthalocyanine cores could lead to new and optimised properties as well as providing a way to investigate the structural limits within which this class of material retains mesophase behaviour. The synthesis of such perylenophthalocyanines is not trivial and, as with most phthalocyanine syntheses, the primary challenge lies in the preparation of their phthalonitrile precursors. We reasoned that the synthesis of the required substituted perylene dinitriles could be achieved by a Diels–Alder reaction between a substituted perylene and suitable dienophile (Scheme 2). A number of such Diels–Alder reactions on the parent perylene[11,12] itself and on dialkylperylenes[13,14] (using powerful dienophiles in this case) have been reported.



Scheme 3. Synthesis of dialkylperylenes. NBS = *N*-bromosuccinimide.

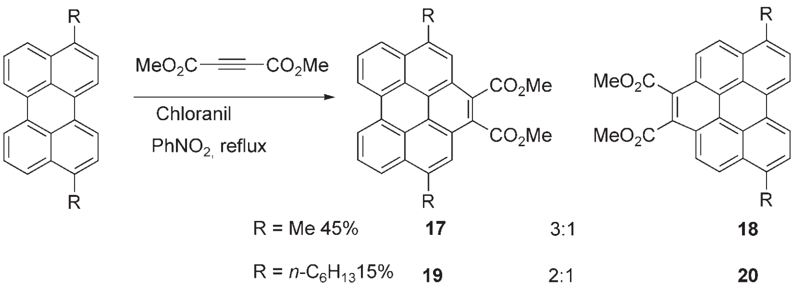


Scheme 2. Retrosynthesis of perylenophthalocyanines and the Diels–Alder reaction between a substituted perylene and a suitable dienophile as key step.

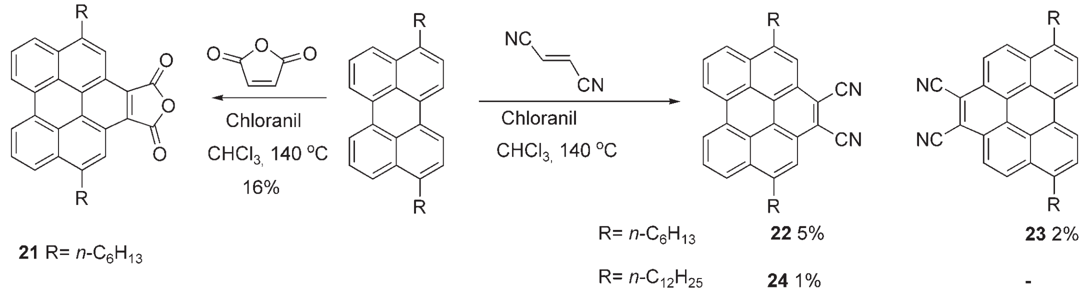
Dialkylperylene intermediates were prepared following a similar route that of Müllen et al.[13] 4,4′-Dialkyl-1,1′-binaphthalenes were synthesised most conveniently using a Suzuki cross-coupling reaction between the precursor naphthylbromides and boronic acids (Scheme 3).[15] The binaphthalenes were converted to the corresponding perylene by treatment with potassium metal in DME[16] followed by simple aqueous workup. The synthesis was initially performed to give dimethylperylene **14**[17] as a simple derivative to allow investigation of subsequent Diels–Alder reactions.

The Diels–Alder reaction of dimethylperylene **14** was initially attempted by using dimethylacetylene dicarboxylate (DMAD) as dienophile, reasoning that, if successful in this general approach, the esters could be converted to nitriles. Treatment of **14** with DMAD and chloranil (employed to oxidise the intermediate Diels–Alder adduct) in refluxing nitrobenzene[11] afforded a mixture of addition products **17** and **18** in 45% yield (ca. 3:1; Scheme 4). However, the same reaction with the dihexylperylene **15** produced a significantly reduced yield of adducts (15%, 2:1 **19**:**20**) after optimisation. No starting material was recovered from these reactions which typically produced significant quantities of black degradation products. The quantity/rate of degradation appears to be directly related to the length/bulk of the appended alkyl chains. Furthermore, the product (coronene) from double Diels–Alder addition to both bays was not observed in either reaction.

The reaction of perylenes with alternative dienophiles was then investigated. Reaction of **15** with maleic anhydride (which is known to react with perylene itself[18]) produced a modest yield (16%) of the adduct **21** (Scheme 5). The material proved to be only sparingly soluble and therefore difficult to purify and handle. It appeared that the forcing conditions required for the Diels–Alder reaction on long-chain dialkylperylenes also led to decomposition resulting in consis-



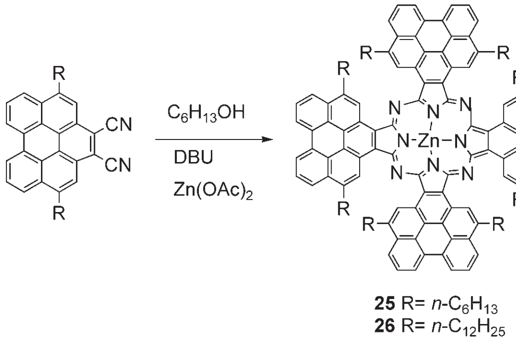
Scheme 4. The Diels–Alder reaction between dialkylperylenes and DMAD.



Scheme 5. The Diels–Alder reaction employing maleic anhydride and fumaronitrile.

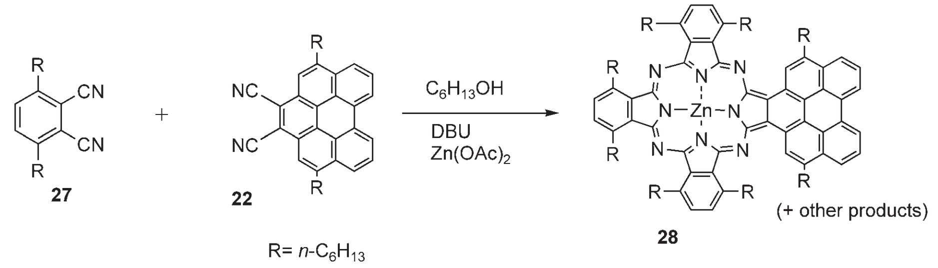
tently low yields. Several further steps were required to convert the intermediates to the required dinitriles so the routes were considered unsuitable. Ideally the nitrile groups should be inserted during the Diel–Alder reaction by employing a suitable dienophile. The obvious candidate is dicyanoacetylene, but this was not considered because it is known to be explosive. Attention therefore focused on fumaronitrile, an easily handled dienophile which has been employed in the synthesis of some simple phthalocyanine precursors.[19] The Diels–Alder reaction was therefore performed between dihexylperylene **15** and fumaronitrile (excess) with chloranil in a minimal volume of chloroform in a sealed tube at 140 °C (optimised conditions). Significant decomposition was again observed but the two isomeric Diels–Alder adducts **22** and **23** could be isolated in low yields (5 % and 2 % respectively) providing sufficient material (**22**) for subsequent phthalocyanine synthesis. Performing the same reaction with didodecylperylene resulted in an even lower yield (1 %) of dinitrile **24**.

Synthesis of the first perylenophthalocyanine was achieved by heating dinitrile **22** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and zinc acetate in refluxing hexanol (Scheme 6).[20] The perylenophthalocyanine proved to be only sparingly soluble in all solvents used and was formed alongside many side products/impurities making purification challenging. Perylenophthalocyanine **25** was eventually isolated by Soxhlet extraction (using THF) and careful reprecipitation, and characterised primarily by MALDI mass spectrometry (molecular ion at 2044). NMR spectra could not be obtained for the material, even at significantly elevated temperatures, due to its low solubility and tendency to aggregate. Polarising optical microscopy showed that **25** is not mesogenic at accessible temperatures and has a melting point above 300 °C. The dodecyl analogue **26** was similarly prepared and briefly investigated. Its properties appear similar to the shorter chain analogue; it is also non-mesogenic below 300 °C. Although it is marginally more soluble than **25**, the material aggregates strongly, making chromatographic separation difficult and NMR spectra unobtainable.



Scheme 6. Synthesis of perylenophthalocyanines **25** and **26**.

We therefore decided to investigate the synthesis of hybrid phthalocyanine/perylenophthalocyanine materials by cyclising perylene dinitrile **22** with dialkylphthalonitrile **27** (Scheme 7).[18] The 3:1 unsymmetrical material is particularly interesting because it presents an unusual board-like molecular architecture. We reasoned also that such derivatives would prove easier to handle and characterise. The cyclisation was therefore performed using a 9:1 mixture of **27** and **22** with DBU and zinc acetate in refluxing hexanol to afford a mixture of products. MALDI mass spectrometry clearly indicated the presence of all possible products and the desired 3:1 hybrid **28** could be isolated by column chromatography. Like the symmetrical perylenophthalocyanine **25**, **28** shows strong aggregation in solution. Nevertheless it was possible to obtain a ^{1}H NMR spectrum at 70 °C that shows some interesting features (Figure 1). Signals for hydrogens on or close to the aromatic core are broadened significantly



Scheme 7. Synthesis of board-shaped hybrid phthalocyanine **28**, by statistical cyclisation between dinitriles **22** and **27**.

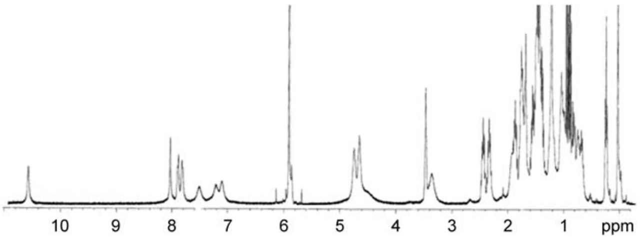
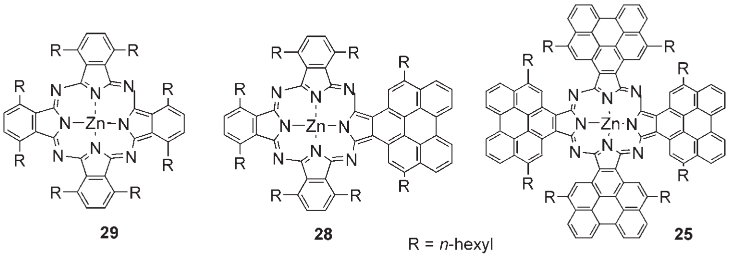


Figure 1. ^{1}H NMR spectrum of the board-shaped hybrid phthalocyanine **28**.

due to aggregation, but are well separated. One signal, presumably for the perylene proton adjacent to the alkyl substituent, is dramatically deshielded and appears at $\delta = 10.7$ ppm. The most intriguing observation, however, appears in the shielded region of the spectrum where a triplet corresponding to two methyl groups is seen at $\delta = 0.2$ ppm. This clearly indicates that two alkyl chains are forced away from the macrocycle plane and lie in its shielding region. Such an arrangement makes face-to-face packing unfavourable. It is unsurprising, therefore, that the material does not display a mesophase and melts directly to the isotropic liquid at 290 °C. Attempts to grow crystals suitable for X-ray crystallography to interrogate the structure more precisely have so far been unsuccessful (fibrous crystals or amorphous solids are produced).

It is interesting to compare the absorption spectra of the new compounds with a typical phthalocyanine (Figure 2). As expected the most π-extended phthalocyanine, symmetrical perylenophthalocyanine **25**, shows λ_{max} at 797 nm, significantly red-shifted (approximately 100 nm) compared to zinc octaalkylphthalocyanine phthalocyanine **29**. The absorption spectrum for hybrid phthalocyanine/perylenophthalocyanine **28** shows peaks that lie between those observed for the parent phthalcyanines and the symmetrical perylenophthalocyanines (λ_{max} at 746 nm and 706 nm). The spectrum shows a characteristic split Q-band due to the reduced symmetry of the core; its fluorescence spectrum (excited at 745 nm) shows a small Stokes shift with maximum emission at 756 nm.



29 **28** **25**

R = *n*-hexyl

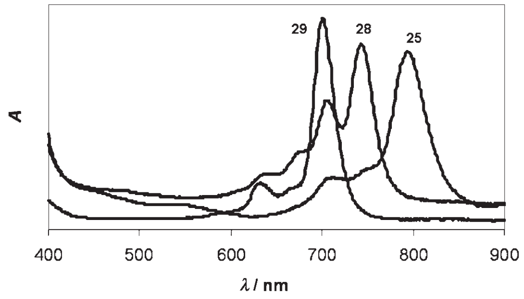


Figure 2. Comparison of the absorption spectra (normalised) of the perylenophthalocyanines (**25**, **28**) with an octaalkylphthalocyanine (**29**) showing the progressive red-shift due to extended conjugation.

Conclusion

In conclusion, the first perylenophthalocyanines have been synthesised and, as expected, show red-shifted absorption spectra. They are high melting solids that do not display mesophase behaviour at accessible temperatures. A 3:1 phthalocyanine/perylenophthalocyanine hybrid material presents an unusual board-like molecular profile. This material is non-mesogenic but is sufficiently soluble to permit processing and characterisation. The ^{1}H NMR spectrum indicates that at least two of the appended alkyl chains are displaced out of the macrocycle plane and lie in its shielding region—an arrangement that disfavours the face-to-face packing required for mesophase formation.

Experimental Section

17 and 18: 3,10-Dihexylperylene **15** (1.00 g, 2.36 mmol), chloranil (0.58 g, 2.36 mmol) and DMAD (5.10 g, 0.036 mol) were stirred in refluxing nitrobenzene (3 mL) for 2 h. After cooling, the mixture was purified by column chromatography (silica gel, CH_2Cl_2/light petroleum) and recrystallisation from ethanol. **17**: Yield 0.12 g, 10%; m.p. 144–145 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.93$ (t, $J = 7.0$ Hz, 6H), 1.25–1.56 (m, 12H), 1.85–1.93 (m, 4H), 3.23 (t, $J = 7.7$ Hz, 4H), 4.16 (s, 6H), 8.03 (dd, $J = 7.9$, 7.7 Hz, 2H), 8.18 (s, 2H), 8.32 (d, $J = 7.9$ Hz, 2H), 8.96 ppm (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$, 22.8, 29.7, 30.4, 31.8, 34.1, 53.0, 121.3, 123.2, 123.6, 124.3, 125.1, 125.2, 127.2, 127.6, 131.2, 131.6, 139.5, 169.5 ppm; $\tilde{\nu}_{max}$ (Nujol) = 1732 cm^{-1}; HR-MS (FAB): calcd for $C_{38}H_{40}O_4 + [NH_4^+]$: 578.3270; found: 578.3271; **18**: Yield 0.065 g, 5%; m.p. 161–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 6.8$ Hz, 6H), 1.25–1.55 (m, 12H), 1.84–1.89 (m, 4H), 3.30 (t, $J = 7.8$ Hz, 4H), 4.15 (s, 6H), 7.92 (d, $J = 8.2$ Hz, 2H), 8.20 (d, $J = 9.5$ Hz, 2H), 8.38 (d, $J = 9.5$ Hz, 2H), 8.93 ppm (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$, 22.7, 29.6, 31.6, 31.9, 33.6, 51.8, 120.9, 124.3, 125.2, 125.4, 126.3, 127.9, 128.6, 129.3, 130.1, 131.2, 138.9, 169.4 ppm; $\tilde{\nu}_{max}$ (Nujol) = 1730 cm^{-1}; HR-MS (FAB): calcd for $C_{38}H_{40}O_4 + [NH_4^+]$: 578.3270; found: 578.3269.

21: 3,10-Dihexylperylene **15** (1.00 g, 2.36 mmol), chloranil (0.58 g, 2.36 mmol), maleic anhydride (3.54 g, 0.036 mol) and $CHCl_3$ (2 mL) were heated in a sealed tube at 140 °C for 96 h. After cooling, the mixture was purified by column chromatography (silica gel, CH_2Cl_2/light petroleum) and recrystallisation from pentanol.

22: Yield 0.19 g, 16%; m.p. >300 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 70 °C): δ=0.80 (t, J=7.0 Hz, 6H), 1.13–1.31 (m, 12H), 1.50–1.75 (m, 4H), 3.07 (t, J=7.7 Hz, 4H), 8.03 (dd, J=8.2, 7.9 Hz, 2H), 8.21 (d, J=8.2 Hz, 2H), 8.35 (s, 2H), 8.85 ppm (d, J=7.9 Hz, 2H); $\tilde{\nu}_{max}$ (Nujol)=1830, 1761 cm^{-1}; HR-MS (EI): calcd for $C_{36}H_{34}O_3$: 514.2508; found: 514.2515.

22 and 23: 3,10-Dihexylperylene **15** (1.00 g, 2.36 mmol), chloranil (0.58 g, 2.36 mmol), fumaronitrile (2.0 g, 0.036 mol) and $CHCl_3$ (2 mL) were heated in a sealed tube at 140 °C for 96 h. After cooling, the mixture was purified by column chromatography (silica gel, CH_2Cl_2/light petroleum) and recrystallisation from pentanol. **22**: Yield 0.05 g, 5%; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, J=7.2 Hz, 6H), 1.39–1.61 (m, 12H), 1.81–1.87 (m, 4H), 3.12 (t, J=7.3 Hz, 4H), 7.75 (s, 2H), 8.11 (dd, J=8.0, 7.3 Hz, 2H), 8.26 (d, J=8.0 Hz, 2H), 8.89 ppm (d, J=7.3 Hz, 2H); $\tilde{\nu}_{max}$ (Nujol)=2221 cm^{-1}; HR-MS (EI): calcd for $C_{36}H_{34}N_2$: 494.2722; found: 494.2723; **23**: Yield 0.02 g, 2%; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (t, J=7.1 Hz, 6H), 1.25–1.56 (m, 12H), 1.77–1.84 (m, 4H), 3.16 (t, J=7.4 Hz, 4H), 7.53 (d, J=9.2 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 7.84 (d, J=9.2 Hz, 2H), 8.53 Hz (d, J=8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 22.6, 29.5, 31.1, 31.7, 33.2, 109.9, 115.3, 121.3, 122.3, 122.5, 125.9, 126.6, 127.8, 128.2, 129.2, 129.3, 139.3 ppm; $\tilde{\nu}_{max}$ (Nujol)=2225 cm^{-1}; HR-MS (EI): calcd for $C_{36}H_{34}N_2$: 494.2722; found: 494.2705.

24: Synthesised as above; Yield 1%, m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, J=7.3 Hz, 6H), 1.25–1.61 (m, 36H), 1.81–1.92 (m, 4H), 3.28 (t, J=6.6 Hz, 4H), 7.75 (s, 2H), 8.18 (dd, J=7.9, 7.1 Hz, 2H), 8.45 (d, J=7.9 Hz, 2H), 9.12 (d, J=7.1 Hz, 2H); $\tilde{\nu}_{max}$ (Nujol) =2224 cm^{-1}; HR-MS (EI): calcd for $C_{48}H_{58}N_2$: 662.4600; found: 662.4596.

25: Dinitrile **22** (0.30 g, 0.60 mmol), DBU (0.06 g, 0.40 mmol) and zinc acetate (0.02 g, 0.15 mmol) were stirred in refluxing hexanol for 24 h. After the mixture had been cooled, the precipitate was filtered off, extracted (Soxhlet) with pyridine/THF and reprecipitated repeatedly (THF). Yield 12 mg, 4%, m.p. >300 °C; λ_{max} (THF)=797 nm (ε= 1.36×10^5); MS (MALDI): m/z: 2044 ([M]$^+$, 100%).

28: Dinitrile **22** (0.30 g, 0.6 mmol), 3,6-dihexylphthalonitrile **27** (1.61 g, 5.4 mmol), DBU (0.70 g, 4.5 mmol) and zinc acetate (0.6 g, 2.6 mmol) were stirred in refluxing hexanol for 24 h. After the mixture had been cooled, the precipitate was filtered off and purified by column chromatography (silica gel, CH_2Cl_2/light petroleum, THF/light petroleum) and recrystallisation from THF/MeOH). Yield 16 mg, 5%; m.p. 290 °C; ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 70 °C): 0.23 (t, J=7.3 Hz, 6H), 0.74–1.88 (m, 68H), 2.05–2.43 (m, 8H), 3.29–3.41 (brs, 4H), 4.45–4.90 (3×brs, 12H), 7.03–7.45 (3×brs, 6H), 7.78–7.85 (2×brm, 4H), 8.00 (brs, 2H), 10.51 ppm (brs, 2H); λ_{max} (THF) = 746 nm (ε=1.73×10^5); MS (MALDI): m/z: 1449 ([M]$^+$).

Acknowledgements

Support from the EPSRC Mass Spectrometry Service Centre (Swansea) is gratefully acknowledged.

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Received: June 21, 2006