JOURNAL OF
Materials
CHEMISTRY

Liquid crystalline perylene-3,4-dicarboximide derivatives with high thermal and photochemical stability

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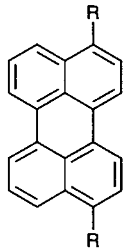
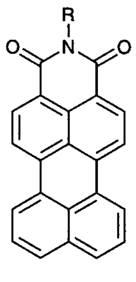
Three new perylene-3,4-dicarboximide chromophores **5a–c** have been synthesized. They are characterized by high extinction coefficients and excellent thermal and photochemical stability. They display liquid crystallinity and exhibit several discotic phases depending upon temperature and substitution pattern.

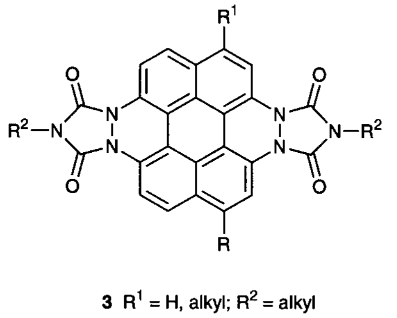
Perylenes **1** and perylene-3,4-dicarboximides **2** are well-known chromophores combining high extinction coefficients and nearly quantitative quantum yields of fluorescence with outstanding photochemical and thermal stability.[1,2] Several other perylene derivatives offer the additional advantage of exhibiting photoconductivity in the solid state.[3,4] Despite their advantages, perylene derivatives suffer from their limited processability (*i.e.* solubility in organic solvents and film forming behaviour). This could, however, be overcome by the introduction of solubilizing alkyl chains. Alkyl chains have a dual role, since they increase the solubility in organic solvents but can also induce the mesogenic behaviour of the substituted perylene derivatives.[5] Recently, we have presented the perylene derivatives **3** bearing four alkyl chains which form discotic mesophases.[6] The discotic mesogens such as **3** are of particular importance as functional materials since they combine liquid crystallinity with the chromophoric properties of perylene. In this paper, we present a new class of T-shaped discotic mesogens **5a–c** based on the perylene-3,4-dicarboximide core on which two or three alkyl chains are grafted.



1 R = H, alkyl



2 R = alkyl, aryl



3 R^1 = H, alkyl; R^2 = alkyl

Results and Discussion

Synthesis and characterization

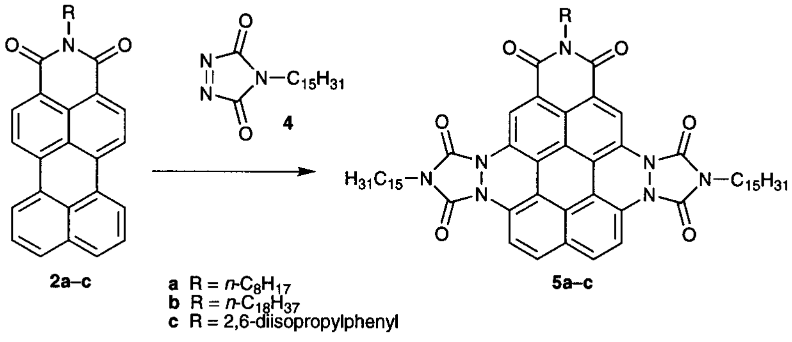
The synthesis of the perylene derivatives **5a–c** (Scheme 1) is based on the Diels–Alder reaction of the *N*-alkylated 1,2,4-triazoline-3,5-dione **4**[6a] with various *N*-substituted perylenedicarboximides **2a–c**.[7] The reaction was carried out at high temperatures (boiling *m*-xylene). Due to the instability of the *N*-alkylated 1,2,4-triazoline-3,5-dione **4** under these conditions and the low reactivity of peryleneimide **2** as a diene, it was necessary to add a large excess of **4** (10 portions of 10 equiv. each) over the whole reaction time to achieve a high conversion. The high oxidation potential of *N*-alkylated 1,2,4-triazoline-3,5-dione **4** allows the adducts to be dehydrogenated to the corresponding aromatic compounds **5a–c** *in situ*. Perylenes **5a–c** were first purified by extracting impurities with hot methanol. Compounds **5a**,**b** were further recrystallized from chloroform whereas compound **5c** was chromatographed on silica gel with methylene chloride as eluent. The chromophores **5a–c** were obtained in 80% yield independent of the nature of the substituents and the purification method. The characterization was achieved by field desorption mass spectrometry (FD-MS), UV–VIS, ^{1}H NMR and ^{13}C NMR spectroscopy and was found to be in good agreement with the proposed structures **5a–c**. No trace of side products could be observed by the aforementioned characterization techniques and by thin layer chromatography, which is a particularly sensitive method for chromophores. Therefore the purity was assessed to be over 99%.

The UV–VIS spectra of the blue perylene imide derivatives **5a–c** are qualitatively identical, *i.e.* two absorptions in the visible range are observed (Fig. 1). Depending on the substituents, the maximum of the shortest wavelength absorption ranges from $\lambda_{max} = 663$ to 668 nm and for the longest wavelength absorption from $\lambda_{max} = 705$ to 725 nm.

If the longest wavelength absorption maximum at $\lambda_{max} = 725$ nm is considered for the sake of comparison, one notices a bathochromic shift of 220 nm relative to the synthetic precursor, the perylene imides **2** ($\lambda_{max} = 505$ nm), or of 145 nm relative to the previously reported mesogens **3** ($\lambda_{max} = 580$ nm). The large bathochromic shifts observed for the chromophore **5a–c** are due to its two auxochromic groups, *i.e.* the carboxylic imide and the urazole substituents, linked together by the perylene core, create an extended π-system.

Thermal and photochemical stability

The thermal stability of **5a–c** was investigated by thermogravimetric analysis. The perylene imides **5a–c** exhibit a high thermal stability, up to 400 °C, and no mass loss was observed for any substitution pattern. The photostability of the chromophores **5a–c** was tested in two separate series of experiments. First, non-degassed chloroform solutions of the chromophores **5a–c** and the parent perylene imide **2c** as reference material were exposed to UV light (366 nm).[8a] After 7 d no significant bleaching was observed for the chromophores **5a–c** and the



Scheme 1

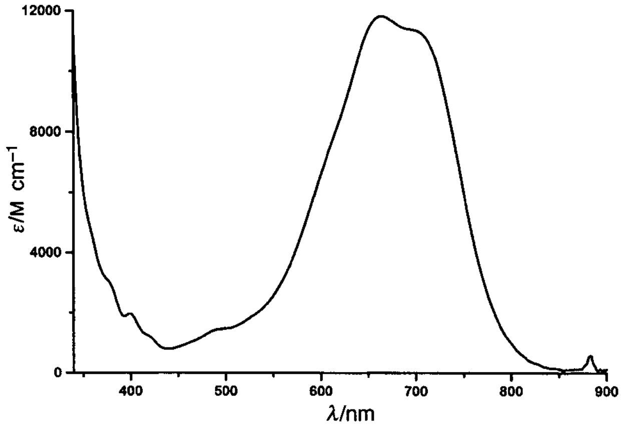


Fig. 1 UV–VIS absorption spectrum of **5a** in $CHCl_3$

Table 1 Visible absorption maxima (λ_{max}) and extinction coefficients (ε) of **2c** and **5a–c** measured in chloroform at room temperature

compound	λ_{max}/nm	ε/l mol^{-1} cm^{-1}
2c	505	32 100
5a	668,705	10 800, 10 100
5b	663, 705	9900, 9400
5c	668, 725	9300, 8900

reference perylene **2c**. The second photostability test, the so-called Xenotest 4509,[1,8b] indicated no change of extinction coefficient for chromophores **5a–c** even after 7 d of irradiation. Transparent samples of polyvinyl chloride and polystyrene coloured with chromophores **5a–c** showed no significant bleaching even after 1000 h of irradiation. The long wavelength absorption, the high extinction coefficient and the excellent thermal and photochemical stability of perylene imides **5a–c** suggest an application in paints, varnishes and thermoplastics.[9] It is anticipated that the presence of two or three long alkyl chains in perylene imides **5a–c** will enhance the compatibility with polyolefins and lead to a dispersion at the molecular level of the dye in the thermoplastic matrix.

Mesophase behaviour

The Diels–Alder adducts **5a–c** exhibit liquid crystalline behaviour although they possess only two or three alkyl chains as compared to the previously reported mesogens **3**.[6] Examination by polarizing microscopy reveals birefringence and low shear resistance for the high-temperature mesophases of **5a–c** giving evidence of the formation of liquid crystalline phases. Yet the observed textures were not specific. The transition temperatures and enthalpies of compounds **5a–c** upon heating (**5a,b**: recorded between −20 and 340 °C) and cooling (**5a,b**: recorded between 340 and −20 °C) were obtained by differential scanning calorimetry (DSC) and are collected in Tables 2 and 3.

Table 2 Transition temperatures and transition enthalpies of mesogens **5a–c** upon heating, scan rate 10 °C min^{-1}

compound	transition temperature/°C^a	transition enthalpies/J g^{-1b}
5a	11, 211	13.2, 4.3
5b	36, 186	37.9, 5.3
5c	210, 217, 293, 315	4.5^c, -5.3^c, 10.5, 2.9

^{a}Error ± 2 °C. ^{b}Error ± 0.5 J g^{-1}. ^{c}Error ± 2 J g^{-1}.

Table 3 Transition temperatures and transition enthalpies of mesogens **5a–c** upon cooling, scan rate −10 °C min^{-1}

compound	transition temperature/°C^a	transition enthalpies/J g^{-1b}
5a	200, 0	4.2, 12.2
5b	177, 26	5.6, 34.8
5c	315, 132	2.9, 3.5

^{a}Error ± 2 °C. ^{b}Error ± 0.5 J g^{-1}.

DSC-traces of **5c** were recorded in the range −40 and 340 °C upon heating and cooling. The data of Table 2 (Table 3) were obtained from the second heating (cooling) curve and are reproducible, at 10 °C min^{-1}, the second and third heating (cooling) curve of each compound being identical. The heating and cooling curves of mesogens **5a,b** are comparable. The isotropization temperatures could not be determined (max. temperature of operation of the optical microscope's heating stage is 320 °C, highest operation temperature of the diffractometer sample holder is about 280 °C). Most likely, the high-temperature LC phases of **5a,b** exist until the onset of decomposition. For **5c**, no X-ray scattering studies could be done at temperatures above the transition peak at 315 °C. Therefore, it remains unclear whether this peak correlates with the isotropization of the substance.

Two mesophases are observed for mesogens **5a,b**. Upon heating, the first mesophase ranges from 11 to 211 °C and from 36 to 186 °C for **5a** and **5b**, respectively. The higher-temperature mesophase was observed from 211 °C (186 °C) for **5a** (**5b**) to the highest examination temperature, *i.e.* 300 °C for polarizing microscopy and about 280 °C for X-ray scattering. Upon cooling, sample **5a** showed two transitions at 200 and at 0 °C and for sample **5b** at 177 and at 26 °C. Thus, the transitions recorded upon cooling occurred at approximately 10 °C below those recorded upon heating.

The nature of the high temperature mesophases of **5a**,**b**, characterized by X-ray diffraction, are comparable and are therefore discussed together. A common feature of the X-ray diffractograms of **5a,b** is the presence of a diffuse halo, characteristic of the liquid-like organization of the alkyl chains. The high-temperature mesophase of **5a**, examined at 240 °C (second heating), may most likely possess a hexagonal columnar order

(D_{ho} phase) as indicated by (110)- and (001)-Bragg reflections at about $2\theta = 6.4$ and 26.0°, corresponding to an intercolumnar distance of 27.4 Å and an intracolumnar distance of 3.4 Å, respectively (the characteristic reflections are marked in Fig. 2). The (100) reflection is observed at about $2\theta = 3.7°$, corresponding to a *d*-spacing of about 23.9 Å between adjacent (100) planes. A weak (200) reflection is found at about $2\theta = 7.5°$ (11.7 Å). The ratio between the experimental *d*-spacings of the (110) and the (100) reflection is 0.573, and therefore in good agreement with the theoretical value (0.577) for hexagonal discotic mesophases;[10] as postulated by theory, the *d*-spacings of the (100), (110) and (200) reflections have the ratio $1:1/\sqrt{3}:1/2$. Accordingly, the X-ray diffractogram of the high-temperature mesophase of **5b** exhibits characteristic (110)- and (001)-Bragg reflections at about $2\theta = 6.6$ and 26.0°, corresponding to an intercolumnar distance of about 27 Å and an intracolumnar distance of 3.4 Å, respectively. The (100)-Bragg reflection is observed at about $2\theta = 3.7°$ (*d*-spacing 23.7 Å), the (200)-reflection is situated at about $2\theta = 7.6°$. As in the case of **5a**, the observed reflections are in agreement with an ordered hexagonal discotic mesophase (D_{ho} phase) [(100)/(110)/(200)-*d*-spacings in $1:1/\sqrt{3}:1/2$ ratio]. The intercolumnar distances of the high-temperature mesophase **5a**,**b** as derived from the scattering angles in the diffractograms are independent of the length of the alkyl chains of the amide function, R = *n*-octyl and *n*-octadecyl for **5a** and **5b**, respectively. Assuming constant density and intracolumnar spacing, the ratio of intercolumnar distances of the C_{18} and C_8 derivatives should be 1.065 : 1. However, this gives rise to a difference of 2θ for the two reflections of only 0.2° which is within the experimental error considering the width and asymmetry of the (100) reflection (Fig. 2). In addition, it can be expected that short side chains cannot be packed as efficiently as longer ones in a columnar packing arrangement so that the density of C_8 could be lower than that of C_{18}.

The X-ray diffractograms of the low-temperature mesophase of **5a**,**b**, recorded at 150 °C display, at wide angles, the (001)-Bragg reflection at $2\theta = 26.0°$ corresponding to an intracolumnar distance of 3.4 Å. Moreover, a diffuse halo of liquid-like organization of the alkyl chains is observed. The diffractograms of **5a** in the small-angle regime exhibit besides the (100)-Bragg reflection at about $2\theta = 3.7°$ (24.0 Å), two additional reflections at $2\theta = 6.4°$ (13.7 Å) and 7.6 ° (11.6 Å). The less intense first-order reflection at smaller angles of 2.8° (31.6 Å) shows that the material is not uniformly organized at this temperature. The reflections at 6.4 and 3.7° exhibit a *d*-spacing ratio of 0.571, compared with the theoretical value of 0.577 for a hexagonal discotic phase. These peaks can be assigned to (110)- and (100)-Bragg reflections, showing that the sample possesses mostly hexagonal discotic order. The diffractogram of **5b** at 150 °C exhibits reflections at about $2\theta = 2.7°$ (32.7 Å), 3.6° (24.5 Å), 5.0° (17.7 Å), 6.3° (14.0 Å), 7.4° (12.0 Å), and 26.1° (3.4 Å). From these observations, the low-temperature mesophases of **5b** must be assigned to a more complex (columnar) structure whereas the high-temperature mesophase exhibits a strict hexagonal columnar order (D_{ho} phase). We did not succeed in indexing the diffraction pattern of the low-temperature-phase.

The DSC trace of compound **5c**, at a scan rate of 10 °C min^{-1}, reveals an unexpectedly rich phase behaviour (Tables 2 and 3). Upon heating an initial endothermic transition is observed at 210 °C, directly followed by an exothermic transition at 217 °C. Two other endothermic transitions occur at 293 and 315 °C. Upon cooling, only two exothermic transitions are observed at 315 and 132 °C. The transition at 293 °C is accompanied by the formation of an optically anisotropic liquid crystalline phase with low shear resistance as evidenced by polarizing microscopy. However, the resulting texture is not specific. Upon cooling from the high-temperature mesophase, no textural change was observed while the viscosity increased sharply indicating that the sample is supercooled. Interestingly enough, no birefringence is observed above 315 °C, suggesting isotropization. The nature of the phases has been investigated by X-ray diffraction. However, since our X-ray scattering setup does not allow investigation of the sample over 280 °C, we have heated up the sample to 305 °C in a hot air stream and frozen it rapidly. The so-obtained supercooled sample was then analysed by X-ray scattering. The diffractogram exhibits only one small-angle reflection at $2\theta = 3.9°$ (22.6 Å). Additionally, the trace displays an unsymmetrical halo in the range from about 10–22 Å, plus one pronounced reflection at approximately 26° (3.4 Å) which should be attributed to the distance of the aromatic cores between neighbouring molecules. Clearly, the replacement of an alkyl side chain by a more rigid diisopropyl substituent for **5c** has a dramatic influence on the phase behaviour, since (110) and (200) reflections—typical of hexagonal ordering—are not seen in the small-angle regime of the liquid crystalline high-temperature phase. Together, the X-ray data and the observation of low shear resistance by polarizing microscopy of **5c** corroborate the existence of a liquid crystalline phase above 293 °C. However, the X-ray diffraction patterns at 100 and 240 °C look similar and indicate mesomorphic order at both temperatures of measurements. Specifically, an intense reflection in the small-angle regime was observed at about $2\theta = 3.0°$ (29.8) and 2.8° (32.1) at 100 and 240 °C, respectively. Additionally, the X-ray diffraction patterns display unsymmetrical halos in the range from about $2\theta \sim 15$ to $\sim 23°$ and one pronounced reflection at approximatively 25.5° (3.5 Å) corresponding to the distance of the aromatic cores between neighbouring molecules.

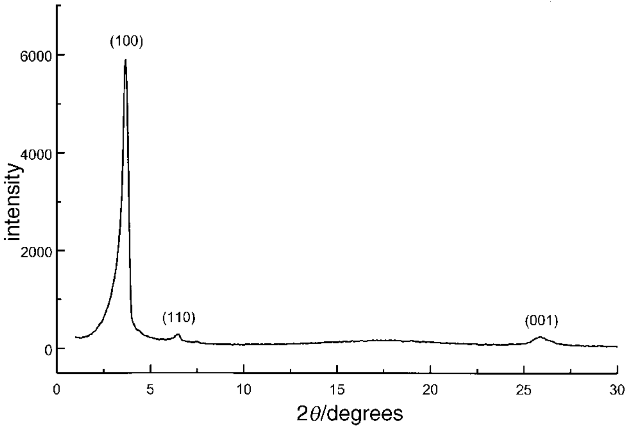


Fig. 2 X-Ray diffractogram of **5a** at 240 °C

Conclusions

A new class of T-shaped perylene-3,4-dicarboximide chromophores **5a–c** has been obtained *via* a short and efficient synthetic pathway. They combine several key properties: (*i*) liquid crystalline behaviour over wide temperature ranges, (*ii*) high thermal and photochemical stability, and (*iii*) intense absorptions at long wavelengths. This unique set of properties makes them potential candidates for photoconductive materials. Other high-tech applications of **5a–c** as functional dyes in optical recording and thermal written display can also be envisaged.

This research was supported by BASF AG and the Bundesministerium für Bildung und Forschung of the Federal Republic of Germany.

Experimental

Measurements

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 300, and Bruker AMX 500 spectrometer. The thermal analysis was carried out using a Mettler DSC 30 differential scanning calorimeter. Thermogravimetric analysis was conducted with a Mettler TG50 thermobalance. UV–VIS absorption spectra were recorded on a Perkin Elmer Lambda 9. A photostability test was carried out with a Camag laboratory lamp having an emission centred around 366 nm. Quartz cuvettes containing the dye solutions were placed at a distance of 10 cm from the lamp and photostability was monitored by UV–VIS absorption spectroscopy. The Xenotest 450 was carried out in the Farbenlaboratorium of BASF AG, with a radiation power of 810 W m^{-2} with $\lambda < 800$ nm. The X-ray diffractograms were measured on a Siemens Kristalloflex D-500 diffractometer (beam divergence 0.3°) equipped with a hot stage. Cu-Kα radiation was selected by a graphite crystal monochromator. Samples **5a,b** (**5c**) have been annealed at 240 °C (280 °C) for 30 min, chilled to room temp. and maintained at this temperature for 1 h. Then, all the samples were heated to measurement temperature and kept at this temperature for 30 min prior to measurement (measurement time ~2 h).

Solvents and reagents

The solvents were used as commercial p.a. quality (*i.e.* purity measured by gas chromatography >99.5%). *N*-Alkyl triazolinediones **4** were synthesized according to the literature.[5,6] *N*-octylperylene-3,4-dicarboximide **2a** and *N*-octadecylperylene-3,4-dicarboximide **2b** were prepared according to a general procedure.[8] *N*-(2,6-Diisopropylphenyl)perylene-3,4-dicarboximide **2c** was supplied by BASF AG.

Synthesis

Since the synthetic procedures of perylene derivatives **5a–c** are all similar, only that of **5a** is given as a representative example.

Perylene monoimide **2a** (200 mg, 0.46 mmol) was added to 20 ml of *m*-xylene. This suspension was brought to reflux and a large excess of 1,2,4-triazoline-3,5-dione **4** (5 g, 43.4 mmol) was added in portions of 0.5 g every 6 min. The course of the reaction was monitored by thin layer chromatography on silica gel with methylene chloride as eluent: perylene monoimide **2a**: orange red spot, $R_F = 0.6$; monofunctionalized perylene (never isolated): blue spot, $R_F = 0.15$; title product **5a**: blue spot, $R_F = 0.1$. The reaction mixture was refluxed until no more perylene monoimide **2a** and monofunctionalized perylene could be observed. Then, the reaction mixture was poured in 150 ml of hot methanol and filtered. The solid residue was purified by a two-fold extraction with hot methanol, followed by a recrystallization from chloroform affording 385 mg of the title compound **5a** in 80% yield. Since the perylene derivative **5c** could not be recrystallized, it was purified by column chromatography on silica gel with methylene chloride as eluent.

Characterization

Note that the ^{1}H and ^{13}C NMR chemical shifts of the aromatic and of the aliphatic protons in the vicinity of the aromatic core of **5a–c** were found to be slightly concentration and temperature dependent. This is presumably attributed to aggregation. *J* Values are in Hz.

Perylene monoimide 5a. δ_H (300 MHz, 80 °C, 5.7 mmol l^{-1}, $C_2D_2Cl_4$) 8.53 (s, 2H, H-2,5), 7.85 (d, *J* 8.5, 2H, H-8,11), 7.13 (d, *J* 8.5, 2H, H-9,10), 3.98 (m, 2H, α-CH$_2$, C_8H_{15}), 3.68 (m, 4H, α-CH$_2$, $C_{15}H_{31}$), 1.82 (m, 4H, β-CH$_2$, $C_{15}H_{31}$), 1.70 (m; 2H, β-CH$_2$, C_8H_{15}), 1.5–1.1 (m, 58H), 0.9 (m; 9H; CH$_3$). δ_C (125 MHz, 80 °C, 57.3 mmol l^{-1}, $C_2D_2Cl_4$) 161.24, 144.50, 144.26, 133.25, 132.45, 130.62, 127.22, 122.38, 118.04, 117.24, 114.75, 110.66, 41.21, 40.49, 32.12, 32.07, 29.94, 29.93, 29.87, 29.86, 29.82, 29.75, 29.52, 29.48, 29,43, 29.38, 27.78, 27.45, 27.03, 22.86, 14.26. FD-MS: *m*/*z* 1047.3 (M$^+$, 100%). UV–VIS: λ_{max}(CHCl$_3$)/nm (ε/mol^{-1} cm^{-1}) 668 (10 800 l), 705 (10 100 l).

Perylene monoimide 5b. δ_H (500 MHz, 80 °C, 5.0 mmol l^{-1}, $C_2D_2Cl_4$) 8.53 (s, 2H, H-2,5), 7.68 (br, 2H, H-8,11), 6.97 (br, 2H, H-9,10), 3.91 (br, 2H, α-CH$_2$, $C_{18}H_{37}$), 3.62 (br, 4H, α-CH$_2$, $C_{15}H_{31}$), 1.80 (br, 4H, β-CH$_2$, $C_{15}H_{31}$), 1.67 (br, 2H, β-CH$_2$, C_8H_{15}), 1.5–1.2 (br, 78 H), 0.89 (br, 9 H). δ_C (125 MHz, 80 °C, 50.4 mmol l^{-1}, $C_2D_2Cl_4$) 161.13, 144.60, 144.35, 133.24, 132.23, 130.70, 127.23, 124.51, 123.41, 122.89, 122.62, 117.87, 117.14, 114.68, 110.72, 41.26, 40.57, 32.03, 29.83, 29.67, 29.50, 29.40, 29.30, 28.04, 27.66, 27.49, 27.03, 22.70, 13.98. FD-MS: *m*/*z* 1189.0 (M$^+$, 100%), 2376.7 (M^{2+}, 15%). UV–VIS: λ_{max}(CHCl$_3$)/nm (ε/mol^{-1} cm^{-1}) 663 (9900 l), 705 (9400 l).

Perylene monoimide 5c. δ_H (300 MHz, 100 °C, 5.5 mmol l^{-1}, $C_2D_2Cl_4$) 8.72 (s, 2H, H-2,5), 8.10 (d, *J* 8.8, 2 H, H-8,11), 7.40 (t, *J* 7.8, 1H, H-phenyl), 7.25 (d, *J* 7.8, 2 H, H-phenyl), 7.20 (d, *J* 8.8, 2H, H-9,10), 3.69 (m, 4H, α-CH$_2$, $C_{15}H_{31}$), 2.70 (m, *J* 6.7, 2H, CH, Pr^i), 1.80 (m, 4H, β-CH$_2$, $C_{15}H_{31}$), 1.5–1.2 (br, 48H), 1.17 (d, *J* 6.7, 12H, CH$_3$, Pr^i), 0.9 (m, 6 H, CH$_3$, $C_{15}H_{31}$). δ_C (75 MHz, 100 °C, 54.7 mmol l^{-1}, $C_2D_2Cl_4$) 161.69, 146.01, 144.80, 144.73, 133.73, 132.17, 131.12, 130.95, 129.63, 127.21, 124.95, 124.15, 124.10, 124.00, 123.14, 118.81, 118.02, 114.79, 111.28, 40.59, 32.05, 29.83, 29.75, 29.63, 29.45, 29.43, 29.25, 27.70, 26.94, 24.23, 22.76, 14.11. FD-MS: *m*/*z* 1096.2 (M$^+$, 100%), 2192.9 (M^{2+}, 16%), 3290.7 (M^{3+}, 40%). UV–VIS: λ_{max}(CHCl$_3$)/nm (ε/mol^{-1} cm^{-1}) 668 (9300 l), 725 (8900 l).

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Paper 7/05910H; *Received* 12*th August*, 1997