

Liquid crystalline coronene derivatives

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The synthesis of liquid crystalline coronenediimides **9** and coronenemonoimide **10** is described in detail and the mesophases are investigated. A large intracolumnar charge carrier mobility of *ca.* 0.2 cm² Vs⁻¹ has been found for the discotic mesophase of the coronenemonoimide **10** using the pulse-radiolysis time-resolved microwave conductivity technique. The large mobility, together with the room temperature liquid crystallinity, make this compound an attractive candidate for applications as the electron transport layer in molecular electronic devices.

Introduction

Derivatives of perylene (**1**) such as perylene-3,4:9,10-tetracarboxydiimides **2** or perylene-3,4-dicarboximides **3** (see Scheme 1) are important dyes and pigments due to their outstanding chemical, thermal and photochemical stability.¹ In addition to conventional uses, perylenes **1–3** are used as so called functional dyes in applications such as reprographic processes,² fluorescent solar collectors,³ photovoltaic cells,⁴ optical switches⁵ and lasers.⁶ With the synthesis of terrylene-tetracarboxydiimides **4**⁷ and quaterylene-tetracarboxydiimides **5** as well as benzoylterrylenedicarboximides **6**⁸ new highly stable dyes with attractive properties became available. In addition, liquid crystalline perylene derivatives could be provided such as *e.g.* **7** and **8**⁹ and suitably substituted perylenetetracarboxydiimides **2**.¹⁰ Such liquid crystalline dyes show important functional properties (*e.g.* photoconductivity) originating from the combination of liquid crystallinity and absorption in the visible region.¹¹

We recently reported the synthesis of coronenetetracarboxydiimides **9**,¹² which were prepared in a few steps from perylenetetracarboxydiimides **2** in high yields. The new dyes **9** constituted further examples of chromophores with liquid crystalline properties like the above mentioned perylene derivatives **2**, **7** and **8**. Based on the readily available and extremely robust perylenediimide chromophore, the aim of this research work was to provide new liquid crystalline derivatives with different spectral properties. Therefore we proceeded to investigate the coronenediimides **9** and also tried to synthesize further coronene derivatives such as the coronenemonoimide **10**. We present here our synthetic work towards the coroneneimides in detail and give some of the physical data such as X-ray diffraction spectra and charge carrier mobilities.

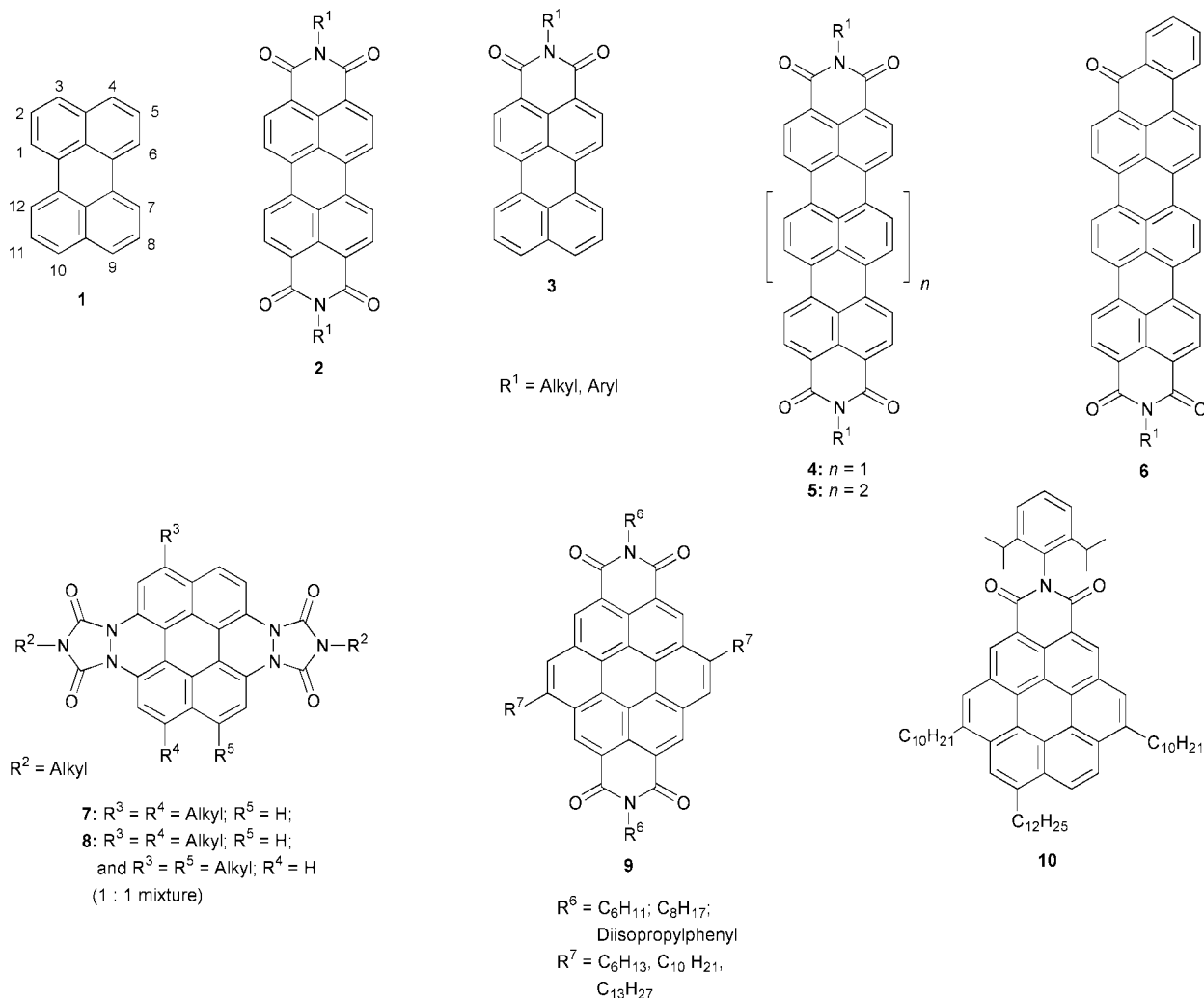
Results and discussion

The whole story started with a surprise (see Scheme 2): the *N,N'*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxydiimide **13a** was treated with dodec-1-yne employing the reaction conditions used for the functionalization of 3,9(10)-dibromoperylene or 9-bromoperylene-3,4-dicarboximides;¹³ thereby, piperidine, the base used in the palladium catalyzed reaction, acted as a nucleophile, thus substituting the bromine atoms in the bay-region of the perylene derivative **13a** to give the isolated products **15** and **16** and a third reaction product, a

yellow compound, which was characterized as coronene derivative **9a**. A possible explanation for the occurrence of product **9a** is a spontaneous cyclization of the expected product **14a** under the reaction conditions; the detailed mechanism of this cyclization is still unknown.

As we were interested in the new yellow chromophores **9** and wanted to investigate these coronene derivatives with respect to their chromophoric and possible liquid crystalline properties, we searched for a route to synthesize **9** in a more selective way. First of all, one had to prevent the nucleophilic attack of piperidine in the bay-region of the perylenediimides **13**. The use of a tertiary nitrogen base such as triethylamine or a sterically hindered piperidine derivative as the base in the Hagihara coupling proved to be successful. As shown in Scheme 3 the products of the palladium catalyzed reaction of **13** with an alkyne in this case were the bisalkynyl substituted perylenediimides **14**, and only very small amounts (<5%) of the coronenediimides **9** were isolated. The products **14** were characterized by NMR and UV/Vis spectroscopy, FD mass spectrometry and elemental analysis. In the ¹H NMR the presence of two isomers of **14** (*N,N'*-dialkyl-1,7-dialkynyl-perylene-3,4:9,10-tetracarboxydiimide and *N,N'*-dialkyl-1,6-dialkynylperylene-3,4:9,10-tetracarboxydiimide) could be observed. Integration of the signals showed that the ratio of the two isomers is 94%:6%. Due to the symmetry of both isomers, an assignment of the signals to the individual isomers was not possible. Each dibromoperlenediimide **13** is known to consist of two isomers as well, but for **13** the separate integration of the characteristic signals proved to be impossible. We believe that in the bromination of **11** the 1,7-isomer of **12** is the preferred product and as **13** arises from **12** by just substituting the bromine atoms, the 1,7-dialkynyl substituted perylenediimides should be the major products as well. There is no way of separating the isomers of **13** or **14** on a larger scale, so the isomeric mixtures were used as such.¹⁴

The next step in the synthesis of the coronenediimides **9** was the controlled cyclization of **14**. Several reaction conditions for initiating the cyclization were tested. The presence of a base seemed to be necessary, but the use of potassium hydroxide or *tert*-butoxide caused saponification of the imide function of **14**. Finally, the use of the strong, but non-nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) resulted in a color change from red to yellow as expected for the formation of **9**. FD-mass spectrometry as well as NMR and UV/Vis spectroscopy proved that **9** had been formed. Similar to the case of **13**



Scheme 1 Important dyes with perylene and coronene units.

and **14**, the aromatic region of the ^1H -NMR spectrum shows the presence of two isomers of **9**. In the UV/Vis spectra of **14d** (Fig. 1a) an absorption band at 552 nm with the typical perylene fine structure can be observed. The coronene derivative **14d** does not absorb in that region, but shows three absorption bands in the visible – a weak band at 511 nm and stronger bands at 338 and 428 nm which give rise to yellow color. The absorption bands at 511 and 428 nm show the typical perylene vibrational structure while the short wavelength absorption at 338 nm does not.¹⁵

Various derivatives of **9** were synthesized following the route described above (Scheme 3). During these experiments, a severe limitation of the cyclization reaction was observed in that sterically demanding substituents such as *tert*-butyl (**14c**) or phenyl (**14i**) next to the triple bond of **14** prevented the formation of the corresponding coronenediimide **9**.

Disc shaped molecules such as the above mentioned perylene derivatives **7** and **8** having an extended planar π -system and mobile alkyl chains often show liquid crystalline behaviour.⁹ The coronenediimides **9** were therefore investigated with regard to mesophase formation.

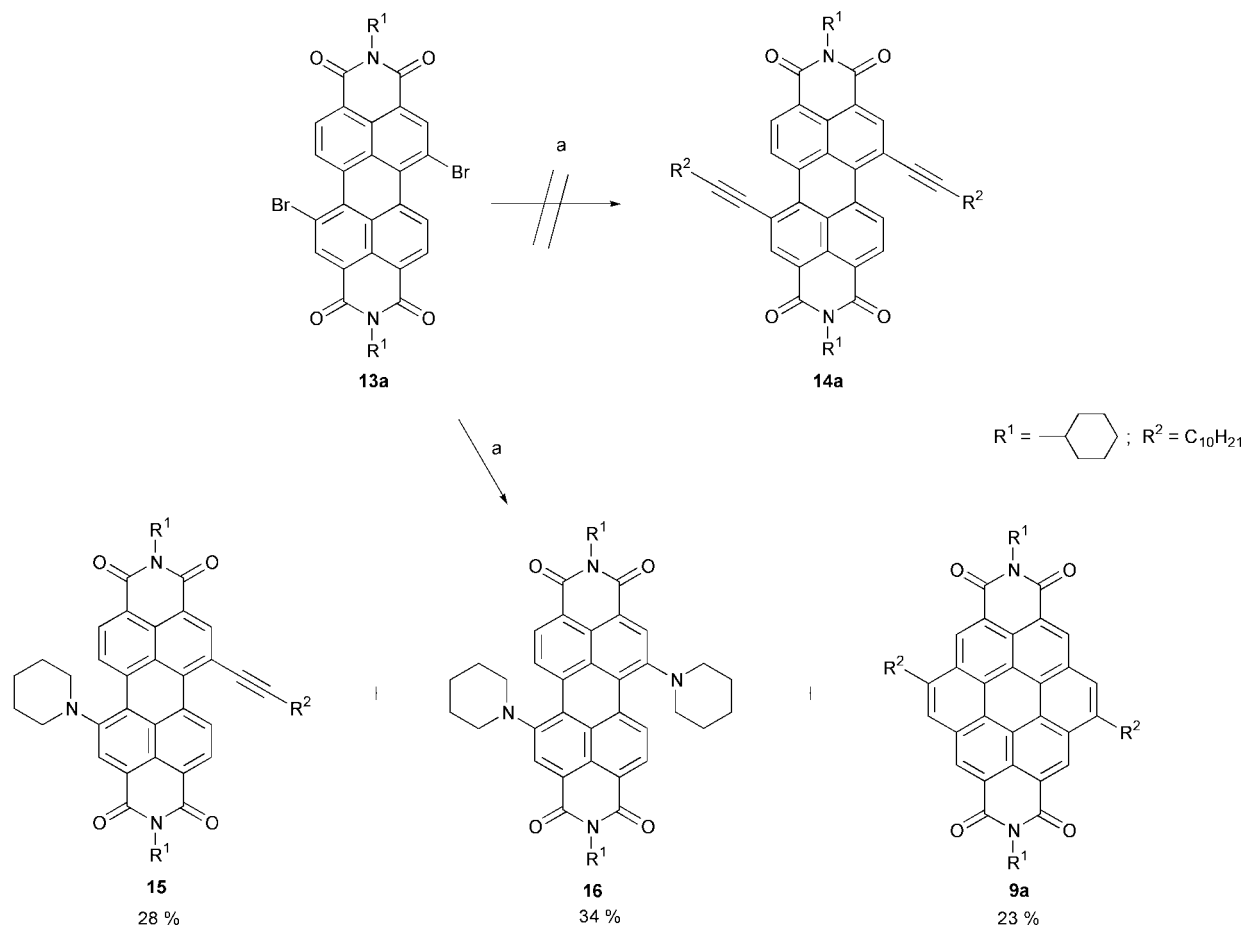
First of all, DSC traces of the substances **9** were monitored. Fig. 2 shows a typical example (**9e**): At 191 °C a phase transition can be observed. Polarizing microscopy proved that this corresponds to the transition into the mesophase, as characteristic textures could be observed for **9e** for temperatures above 191 °C. Table 1 summarizes the transition temperatures for the different derivatives of **9**. For some

derivatives, having short alkyl chains at the coronene core (**9b**, **9d**) or bulky *N*-substituents (**9g**), the formation of a mesophase could not be observed.

The accurate identification of the mesophases was performed by X-ray diffraction. The characteristic signals for a columnar discotic mesophase (Col_{ho}) formed by the liquid crystalline derivatives of **9** can be seen in Fig. 3.

The alkyl chains give rise to the reflexion at $2\theta = 17.6^\circ$ (halo reflexion). The (001) reflexion can be seen at $2\theta = 25^\circ$, corresponding to an intracolumnar distance of 3.6 Å. From the very strong (100) reflexion at $2\theta = 4.4^\circ$ the intercolumnar distance of about 20 Å can be calculated. The hexagonal order of the columns is proved by the weak (110) reflexion at $2\theta = 7.7^\circ$. Similar diffraction patterns were obtained for all other liquid crystalline coronenediimides **9**. The optical behaviour of **9** in polymer films resulting from the formation of aggregates depending on the concentration of **9** in those films was discussed in an earlier publication.¹²

One major disadvantage for possible applications of the liquid crystals **9** is their very high temperatures for transition into the mesophase (between 177 and 266 °C). The variation of the alkyl chains at the coronene core or the imide nitrogen atom gave a decrease in the melting temperature of about 90 °C (from 266 (**9d**) to 177 °C (**9f**)). But even a melting temperature of 177 °C is much too high for investigations such as measurements of charge carrier mobilities in the mesophase. Another way of influencing the melting temperature is the variation of the chromophore itself. Therefore the



Scheme 2 Reaction products of the Hagihara coupling in the bay region of *N,N'*-dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**): **a**: dodec-1-yne, THF–piperidine (1 : 1), 8 mol% [Pd(PPh₃)₄], 10 mol% CuI, 60 °C, 4 h.

tribromoperylenemonoimide **18** was subjected to the same reaction conditions like the earlier described dibromoperylenediimides **13** (Scheme 4).

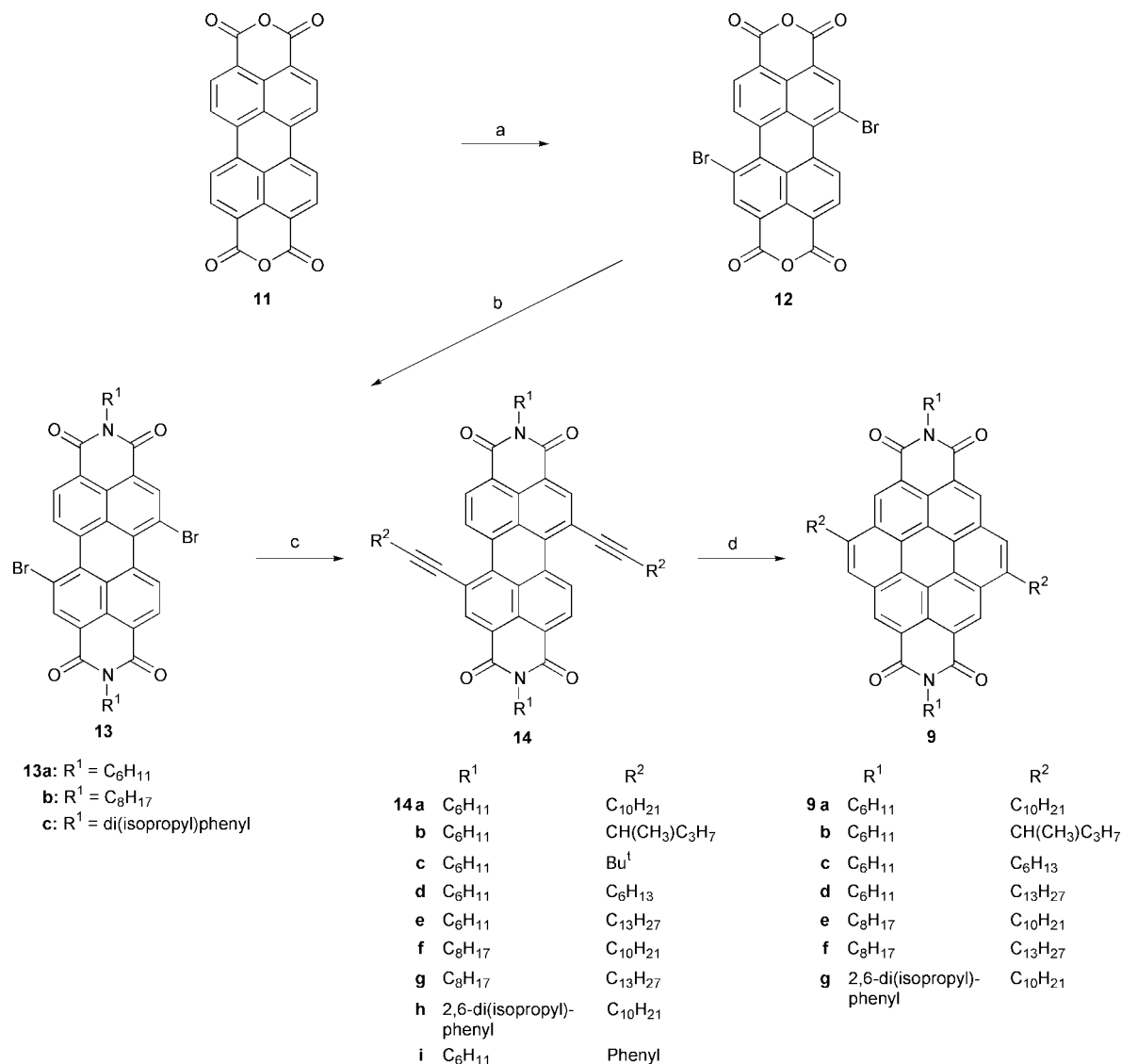
N-(2,6-Diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide (**18**) was synthesized from *N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**17**)¹⁶ by treating **17** with elemental bromine. Minor amounts of tetrabromoperylenemonoimide were present as an impurity in the crude material and could be separated by column chromatography. Hagihara coupling of **18** with dodec-1-yne was performed as described above, but lower reaction temperatures were employed as the reaction occurred much faster than for the dibromoperylenediimides **13**. It is worth mentioning, that (in contrast to the dialkynyl substituted perylenediimides **14**) only one isomer of **19** was isolated, as could be proved by NMR spectroscopy. The bromination of **17** works regioselectively and only the 1,6,9-tribromoperylene-3,4-dicarboximide **18** was obtained. In the aryl–alkyne coupling the alkyne substituents are exchanged for the bromine atoms, resulting selectively in the 1,6,9-trialkynylperylene-3,4-dicarboximide **19**. Compound **19** is a dark red substance with an absorption in chloroform solution at 549 nm, and a fluorescence maximum at 571 nm (*Stokes* shift 19 nm). When **19** was subjected to the reaction conditions of the base induced cyclization, the triple bond in the 9-position of the perylenemonoimide **19** was not affected and the coronenemonoimide derivative **20**, still containing a triple bond, was isolated. The triple bond was then hydrogenated¹³ with elemental hydrogen in the presence of palladium on charcoal to give product **10**. Fig. 4 shows the UV/Vis spectra of coronenediimide **9c** (Fig. 4a) and coronenemonoimide **10** (Fig. 4b). The same absorption bands as for **9** can be seen in

the spectrum of the coronenemonoimide **10** except that positions of the bands are shifted to lower wavelengths.

As in the case of the coronenediimides **9**, the coronenemonoimide **10** was first investigated by DSC which showed a phase transition at 160 °C (Fig. 5). Polarizing microscopy then revealed that this is the transition from the mesophase to the isotropic melt, as one could see characteristic structures for temperatures below 160 °C, and for temperatures over 160 °C the image turned black. This means that compound **10** is liquid crystalline at room temperature and that the transition temperature into the mesophase must be below 0 °C, which is significantly lower than for the coronenediimides **9**. X-Ray-diffraction of compound **10** also showed the characteristic peaks of a columnar mesophase (Col_{ho}), the reflexions are summarized in Table 2. In addition X-ray diffractograms of compounds **19** (*T*_i = 135 °C) and **20** (*T*_i = 269 °C) were measured and their reflexions, which were characteristic for a columnar mesophase are presented in Table 2.

The synthesis of coronenemonoimide **10** thus yielded a substance showing a columnar discotic mesophase at room temperature. This made an investigation of the charge carrier mobility in the mesophase possible.

The one-dimensional, intracolumnar charge carrier mobility for compound **10**, measured using the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC), is shown as a function of temperature in Fig. 6. The value of $\Sigma\mu_{1D}$ is close to 0.2 cm² Vs^{−1} at room temperature. The mobility increases gradually with increasing temperature up to a value of ca. 0.3 cm² Vs^{−1} just below 160 °C at which a transition to the isotropic liquid phase was proposed to occur. At this temperature an abrupt decrease of approximately 20% occurs.



Scheme 3 Synthesis of coronenediimides **9**: **a**: Br_2 , 100% H_2SO_4 , 40 °C, 12 h, 90–95%; **b**: R^1NH_2 , CH_3COOH , NMP, 85 °C, 8 h, 88–95%; **c**: $R^2C\equiv CH$, 8 mol% $[Pd(PPh_3)_4]$, 10 mol% CuI , THF– Et_3N (1 : 1), 80 °C, 14 h, 85–95%; **d**: DBU, toluene, 100 °C, 12 h, 95–100%. (NMP = *N*-methylpyrrolidone; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.)

This decrease is much smaller than has been previously found at the mesophase to isotropic liquid phase transition for other discotic materials.¹⁷ We conclude that the “isotropic” phase of **10** still retains a high degree of columnar order and may in fact be more correctly considered to be a highly fluid mesophase rather than an isotropic liquid.

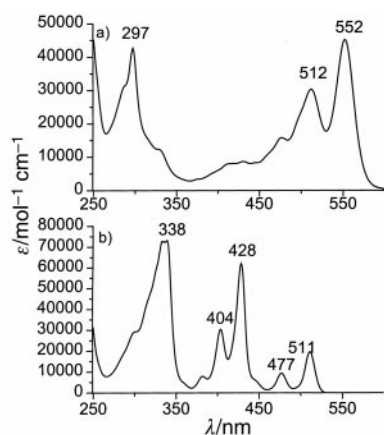


Fig. 1 UV/Vis-spectra of a) **14d** ($CHCl_3$); b) **9c** ($CHCl_3$).

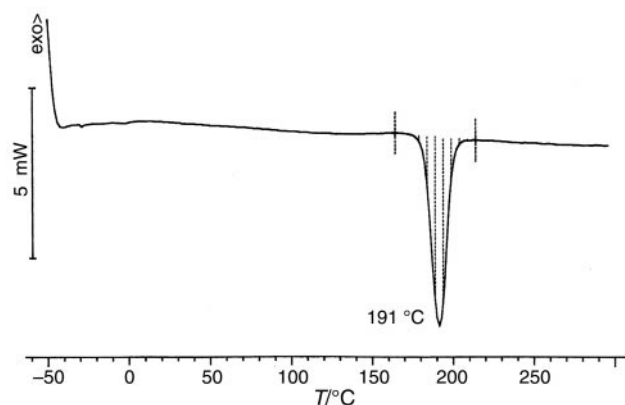


Fig. 2 DSC trace of **9e** (10 K min^{-1}).

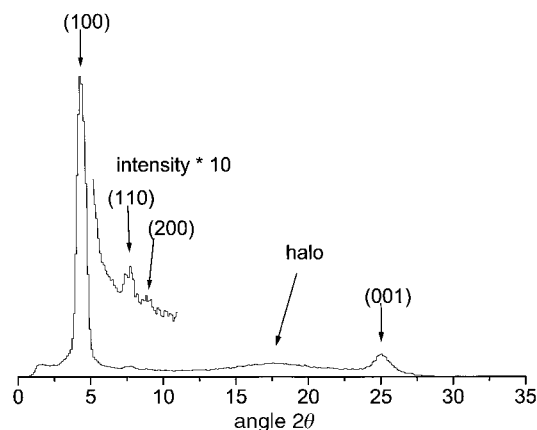


Fig. 3 X-Ray diffraction of **9e** at 200 °C.

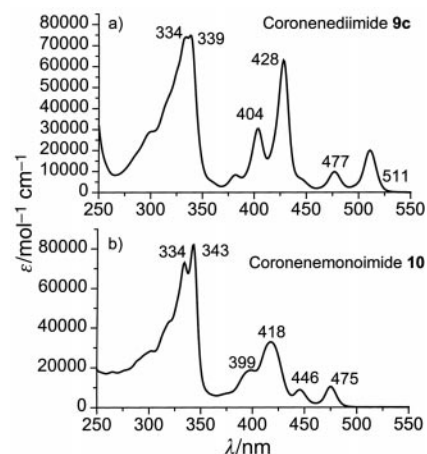


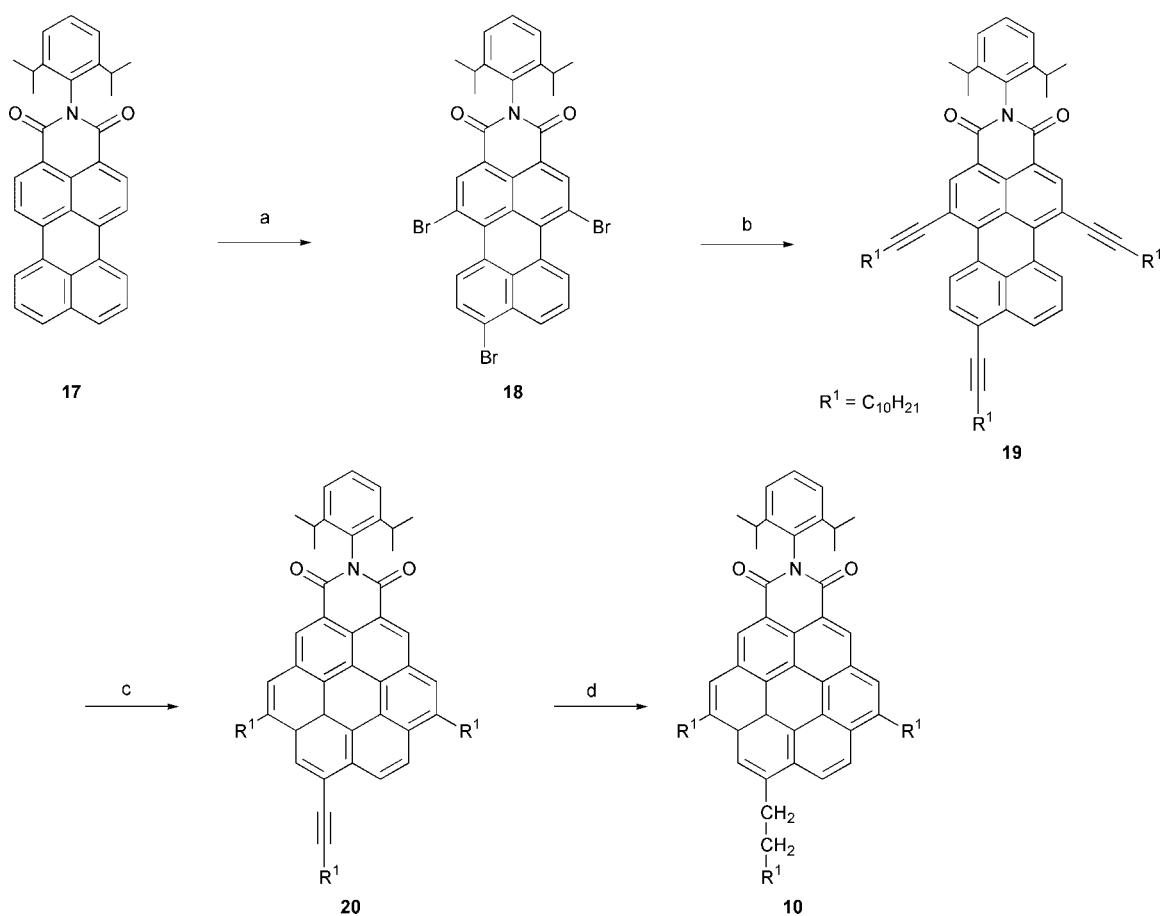
Fig. 4 UV/Vis spectra of a) coronenediimide **9c**; b) coronenemonoimide **10**.

Table 1 Melting points of coronenediimide derivatives **9**

R ²	R ¹ = C ₆ H ₁₁	R ¹ = C ₈ H ₁₇	R ¹ = diisopropylphenyl
C ₆ H ₁₃	9a > 350 ^a	—	—
CH(CH ₃)C ₃ H ₇	9b > 350 ^a	—	—
C ₁₀ H ₂₁	9c Cr 245 Col _{ho}	9e Cr 192 Col _{ho}	9g Cr 277 I
C ₁₃ H ₂₇	9d Cr 266 Col _{ho}	9f Cr 177 Col _{ho}	—

^aMesophase could not be observed.

for the imido derivatives of perylene **7** and **8**.¹⁹ Imido substituted aromatic compounds are of interest for practical applications because they have been shown to have *n*-type, *i.e.* electron conducting, semiconductive characteristics²⁰ in contrast to the more usual *p*-type, hole transport, behaviour of other discotic materials. The coronenemonoimide derivative studied in the present work is of particular interest because of its liquid crystalline properties even at room temperature and the fact that it has a readily accessible fluid phase which makes possible the ready processing of thin film device structures.



Scheme 4 Synthesis of coronenemonoimide **10**: a: Br₂, CHCl₃, reflux, 6 h, 86%; b: R¹C≡CH, 8 mol% [Pd(PPh₃)₄], 10 mol% CuI, THF–Et₃N (1 : 1), 60 °C, 12 h, 80%; c: DBU, toluene, 100 °C, 24 h, 65%; d: H₂, Pd-C, THF, 22 °C, 1 h, 90%.

Table 2 X-Ray diffraction peaks of a) **10** at 110 °C; b) **19** at 97 °C; c) **20** at 127 °C

Reflexion	10 2 θ =	19	20
(100)	4.60	4.42	4.46
(110)	7.96	—	7.72
(001)	24.20	24.86	25.00
Halo	18	15–22	15–22

Experimental section

Equipment and materials

NMR spectra were recorded on Bruker DPX 250, Bruker AMX 300 and Bruker 500 DRX spectrometers (at room temperature, unless otherwise noted); the operating frequencies are given with the data. FD mass spectra were recorded on a VG instruments ZAB2-SE-FPD. IR-spectra (KBr method) were recorded on a Nicolet FT-IR 320 spectrometer. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 9 spectrometer, and fluorescence spectra were measured on a Spex Fluorolog 2 Type F 212 spectrometer. Column chromatography was performed on silica gel (Merck, Geduran Si60), mesh size 70–230. Thermogravimetric analyses were performed on a Mettler TG 50 thermobalance. Elemental analyses were performed by the Department of Chemistry and Pharmacy of the University, Mainz.

All commercially available reagents and solvents were used without further purification unless otherwise stated. THF was distilled from potassium. Hydrogen gas was purchased from Linde and used without further purification.

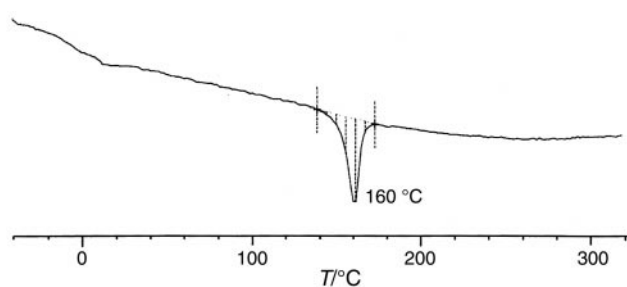
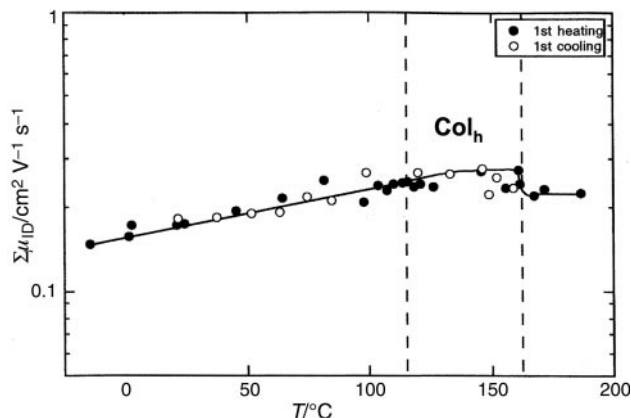
Measurement of charge transport properties

The charge transport properties of coronenemonoimide **10** were investigated using the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC). In brief, a uniform, micromolar concentration of charge carriers is formed in the material by a nanosecond pulse of ionizing radiation (3 MeV electrons from a Van de Graaff accelerator). Microwaves (26–38 GHz) are used to quantitatively probe (without the need of electrode contacts) the radiation-induced conductivity within the sample. The precise experimental methodology and data reduction procedures have been reported previously.^{17b–d,21}

The one-dimensional, intracolumnar charge carrier mobility was determined from the end-of-pulse conductivity per unit dose, $\Delta\sigma_{\text{eop}}/D$ ($\text{Sm}^2 \text{J}^{-1}$), using the relationship

$$\Sigma\mu_{1D} = 3 \frac{\Delta\sigma_{\text{eop}}}{D} \cdot \frac{E_p}{W_p} \quad (1)$$

In eqn. (1) E_p (eV) is the average energy per initial ionization event and W_p is the probability that ion-pairs survive to the end of the pulse. Using the model described previously^{17c,21} values of 25 and 0.37 eV were used for E_p and W_p respectively. The factor of 3 in eqn. (1) takes into account the fact that the

**Fig. 5** DSC-trace of **10** (10 K min^{−1}).**Fig. 6** Charge carrier mobility of **10** as a function of temperature (measured by pulse-radiolysis time resolved microwave conductivity technique (PR-TRMC)).

organised columnar domains within the present bulk samples are randomly orientated and that charge transport is expected to be highly anisotropic and to occur almost exclusively along the axis of the macrocyclic stacks. The mobility sum, $\Sigma\mu_{1D} = \mu(+) + \mu(-)$, is used in eqn. (1) since the PR-TRMC technique does not allow the determination of the separate contributions of the positive and negative charge carriers to the radiation-induced conductivity.

Synthesis of *N,N'*-dialkyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimides **13** (procedure A)

A mixture of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (**12**) (10 g; 18 mmol) and NMP (450 ml) were heated to 85 °C. Glacial acetic acid (6.2 g; 0.1 mol) and the amine (55 mmol) were added slowly. After stirring at 85 °C for 12 h the mixture was cooled to room temperature and the product was isolated by filtration and washed with methanol.

***N,N'*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**).** 1,7-Dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (**12**) (10 g; 18 mmol) and cyclohexylamine (5.34 g; 54 mmol) were reacted as described in procedure A to yield the red compound (**13a**) (10.25 g; 80%). Mp > 250 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ = 9.47 (d, ³*J*(H,H) = 8 Hz, 2 H; H-6, H-12), 8.86 (s, 2 H; H-2, H-8), 8.63 (d, ³*J*(H,H) = 8 Hz, 2 H; H-5, H-11), 5.00 (m, 2 H; 2 N-CH), 2.53 (m, 4 H; 4 CH_{cyclohex}), 1.91 (m, 4 H; 4 CH_{cyclohex}), 1.75 (m, 6 H; 6 CH_{cyclohex}), 1.47 (m, 4 H; 4 CH_{cyclohex}), 1.34 (m, 2 H; 2 CH_{cyclohex}); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 163.65 (C=O), 163.10 (C=O), 138.22, 138.07, 133.20, 133.02, 130.08, 129.63, 128.87, 128.49, 127.40, 124.24, 123.82, 121.02, 54.59, 30.10, 29.50, 26.98, 25.92; UV/Vis (CHCl₃): λ_{max} (ϵ) = 526 (57300), 490 (40000), 459 (14970), 390 (6800), 272 (30200), 264 nm (28950 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 526 nm): λ_{em} = 547 nm; MS (8 kV; FD): *m/z* = 710.8 (100%) [*M*⁺] (calcd. 710.04); IR (KBr): (cm^{−1}) = 2930, 2926, 2851, 1700, 1698, 1659, 1588, 1452, 1419, 1398, 1361, 1327, 1301, 1257, 1239, 1166, 1156, 1143, 1115, 984, 979, 659, 630, 624, 806, 691, 603.

***N,N'*-Di(*n*-octyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13b**).** 1,7-Dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (**12**) (10 g, 18 mmol) and *n*-octylamine (7.1 g, 54 mmol) were reacted as described in procedure A to yield the red compound (**13b**) (11.4 g; 82%). Mp > 250 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ = 9.29 (d, ³*J*(H,H) = 8 Hz, 2 H; H-6, H-12), 8.72 (s, 2 H; H-2, H-8), 8.50 (d, ³*J*(H,H) = 8 Hz, 2 H; H-5, H-11), 4.12 (t, ³*J*(H,H) = 7 Hz, 4 H; 2 N-CH₂), 1.70 (m, 4 H; 2 CH₂), 1.41–1.23 (m, 20 H; 10 CH₂), 0.87 (t, ³*J*(H,H) = 7 Hz, 6 H; 2 CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 162.70, 162.18,

137.83, 137.72, 132.68, 132.53, 129.64, 129.04, 128.41, 126.81, 123.24, 122.79, 120.74, 40.78, 31.94, 29.42, 29.34, 28.10, 27.24, 22.75, 13.94. UV/Vis (CHCl₃): λ_{max} (ϵ) = 526 (56590), 490 (38200), 459 (15040), 390 (6640), 272 (30130), 264 nm (29190 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, exc.: 526 nm): λ_{em} = 547 nm; MS (8 kV, FD): m/z = 770.0 (100%) [M^+] (calcd. 770.13); C₄₀H₄₀Br₂N₂O₄ (772.57): calcd.: C 62.19, H 5.22, Br 20.69, N 3.63, O 8.28%; found C 61.77, H 5.31, Br 20.64, N 3.54%.

N,N-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide **13c** (procedure B)

1,7-Dibromoperylene-3,4,9,10-tetracarboxylic dianhydride (**12**) (12 g, 22 mmol) and 2,6-diisopropylaniline (17.73 g, 0.1 mol) were heated to 160 °C in propionic acid (280 ml). After stirring in an argon atmosphere at this temperature for 16 h the warm solution was filtered. The product precipitated after addition of water to the filtrate and was isolated by filtration. The crude product was washed with water until neutral and dried *in vacuo* over P₂O₅ to give the diimide (**13c**) (15 g, 78%). Mp > 250 °C; ¹H NMR (250 MHz, CD₂Cl₂): δ = 9.60 (d, ³*J* (H,H) = 8 Hz, 2 H; H-6, H-12), 9.01 (s, 2 H; H-2, H-8), 8.78 (d, ³*J* (H,H) = 8 Hz, 2 H; H-5, H-11), 7.54 (t, ³*J* (H,H) = 8 Hz, 2 H), 7.38 (d, ³*J* (H,H) = 8 Hz, 4 H), 2.75 (septet, ³*J* (H,H) = 7 Hz, 4 H; 4 CH₃isopropyl), 1.15 (d, ³*J* (H,H) = 7 Hz, 12 H; 4 (CH₃)isopropyl); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 163.51, 163.04, 146.42, 138.85, 138.74, 133.93, 133.70, 131.07, 130.86, 130.72, 130.08, 130.02, 129.22, 128.82, 128.11, 124.54, 123.61, 123.21, 121.39, 29.61, 24.10; UV/Vis (CHCl₃): λ_{max} (ϵ) = 527 (53100), 491 (36380), 459 (14570), 390 (6350), 260 nm (32120 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, exc.: 526 nm): λ_{em} = 547 nm; MS (8 kV, FD): m/z = 868.5 (100%) [M^+] (calcd. 866.13).

Reaction of *N,N*-dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) with dodec-1-yne in the presence of piperidine (Scheme 2)

N,N-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (500 mg, 0.7 mmol) was dissolved in a mixture of dry THF (150 ml) and dry triethylamine (150 ml) in an argon atmosphere. Pd(PPh₃)₄ (32 mg, 0.03 mmol) and CuI (6.5 mg, 0.02 mmol) were added under argon atmosphere. Dodec-1-yne (466 mg, 2.8 mmol) was added with a syringe through a septum. After stirring at 80 °C for 12 h the mixture was poured into the same amount of diluted cold HCl (HCl:H₂O = 1:3) and the product was extracted with dichloromethane. The organic layer was extracted with water until the aqueous layer was neutral. The crude reaction mixture was separated by column chromatography on silica gel (CH₂Cl₂). The products **9a** (23%), **15** (28%) and **16** (34%) were isolated (percentages after column chromatography). Analytical data for **9a** see below. Analytical data for **15** (major isomer): ¹H NMR (500 MHz, CD₂Cl₂): δ = 10.56 (d, ³*J* (H,H) = 9 Hz, 1 H; aromatic H), 9.27 (s, 1 H; aromatic H), 9.09 (s, 1 H; aromatic H), 8.78 (d, ³*J* (H,H) = 9 Hz, 1 H; aromatic H), 8.72 (d, ³*J* (H,H) = 9 Hz, 1 H; aromatic H), 8.28 (d, ³*J* (H,H) = 9 Hz, 1 H; aromatic H), 5.17 (m, 2 H, 2 N-CH₂cyclohex), 3.45 (m, 4 H, 2 CH₂-N_{piperidine}), 2.83–2.65 (m, 6 H; =CH₂, 2 CH₂CH₂-N_{piperidine}), 1.99–1.75 (m, 18 H; 9 CH₂), 1.55–1.25 (m, 20 H; 10 CH₂), 0.85 (t, ³*J* (H,H) = 7 Hz, 3 H, CH₃). UV/Vis (dioxane): λ_{max} (ϵ) = 528 (15060), 463 (20130), 282 nm (30052 l mol⁻¹ cm⁻¹); MS (8 kV, FD): m/z = 802.00 (100%) [M^+] (calcd. 801.45); Analytical data for **16**: ¹H NMR (250 MHz, CD₂Cl₂): δ = 9.60 (d, ³*J* (H,H) = 9 Hz, 2 H; aromatic H), 8.44 (s, 2 H; aromatic H), 8.37 (d, ³*J* (H,H) = 9 Hz, 2 H; aromatic H), 5.00 (m, 2 H, 2 N-CH₂cyclohex), 3.55–3.38 (m, 4 H, 4 CH₂piperidine), 3.05–2.86 (m, 4 H, 4 CH₂piperidine), 3.73–2.48 (m, 4 H, 4 CH₂cyclohex), 2.08–1.25 (m, 28

H, 12 CH₂piperidine and 16 CH₂cyclohex); UV/Vis (CHCl₃): λ_{max} (ϵ) = 675 (broad) (10385), 445 (10232), 280 nm (20501 l mol⁻¹ cm⁻¹); MS (8 kV, FD): m/z = 720.50 (100%) [M^+] (calcd. 720.37).

Reaction of *N,N*-dialkyl-1,7-dialkynylperylene-3,4,9,10-tetracarboxydiimides **14** with alkynes in the presence of triethylamine (Scheme 3)

Dibromoperylene **13** (3 mmol) was dissolved in a mixture of dry THF (250 ml) and dry triethylamine (250 ml) in an argon atmosphere. Pd(PPh₃)₄ (347 mg, 0.3 mmol) and CuI (46 mg, 0.24 mmol) were added under argon atmosphere. The alkyne (12 mmol, 4 equivalents) was added with a syringe through a septum. After stirring at 80 °C for 12 h the mixture was poured into the same amount of cold dilute HCl (HCl:H₂O = 1:3) and the product was extracted with dichloromethane. The organic layer was extracted with water until the aqueous layer was neutral. The crude product was purified by column chromatography on silica gel (CH₂Cl₂).

N,N-Dicyclohexyl-1,7-di(dodec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14a**). *N,N*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (3 g, 4.2 mmol) and dodec-1-yne (2.6 g, 15.6 mmol) were reacted as described for (**14**) to yield (**14a**) (3.3 g, 89%). Mp 175 °C; ¹H NMR (500 MHz, CDCl₃): δ = 9.98 (d, ³*J* (H,H) = 8 Hz, 2 H; H-6, H-12), 8.62 (s, 2 H; H-2, H-8), 8.50 (d, ³*J* (H,H) = 8 Hz, 2 H; H-5, H-11), 5.00 (tt, ³*J*₁ (H,H) = 12 Hz, ³*J*₂ (H,H) = 4 Hz, 2 H; 2 N-CH), 2.62 (t, ³*J* (H,H) = 7 Hz, 4 H; 2 =CH₂), 2.57 (m, 4 H; 4 CH₂cyclohex), 1.92 (m, 8 H; 4 CH₂cyclohex, 2 CH₂), 1.75 (m, 10 H; 6 CH₂cyclohex, 2 CH₂), 1.55–1.24 (m, 30 H; 12 CH₂ and 6 CH₂cyclohex), 0.86 (t, ³*J* (H,H) = 7 Hz, 6 H, 2 CH₃). ¹³C NMR (125 MHz, CDCl₃): δ = 163.53 (C=O), 163.28 (C=O), 137.84, 133.64, 133.17, 129.84, 127.09, 127.06, 126.51, 123.18, 122.21, 120.56, 101.67 (C=C), 82.40 (C=C), 54.02 (CH-N), 31.92, 29.64, 29.34, 29.27, 29.25, 29.11, 28.32, 26.59, 25.48, 22.68, 20.30, 14.09 (CH₃); UV/Vis (CHCl₃): λ_{max} (ϵ) = 552 (45870), 511 (28300), 476 (14800), 297 nm (41720 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, exc.: 552 nm): λ_{em} = 571 nm; MS (8 kV, FD): m/z = 882.3 (100%) [M^+] (calcd. 882.53); C₆₀H₇₀N₂O₄ (883.22): calcd. C 81.59, H 7.99, N 3.17, O 7.25%; found C 81.19, H 8.02, N 3.04%.

N,N-Dicyclohexyl-1,7-bis(3-methylhex-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14b**). *N,N*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (1 g, 1.4 mmol) and 3-methylhex-1-yne (405 mg, 4.22 mmol) were reacted as described for (**14**) to yield (**14b**) (950 mg, 91%). Mp > 250 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ = 10.13 (d, ³*J* (H,H) = 8 Hz, 2 H; H-6, H-12), 8.65 (s, 2 H; H-2, H-8), 8.55 (d, ³*J* (H,H) = 8 Hz, 2 H; H-5, H-11), 4.99 (m, 2 H; 2 N-CH), 2.92 (m, 2 H; 2 CH), 2.54 (m, 4 H; 4 CH₂cyclohex), 1.91 (m, 4 H; 4 CH₂cyclohex), 1.76–1.43 (m, 20 H; 12 CH₂cyclohex and 4 CH₂), 1.41 (d, ³*J* (H,H) = 6.7 Hz, 6 H; 2 CH₃), 1.01 (t, ³*J* (H,H) = 7 Hz, 6 H; 2 CH₃); ¹³C NMR (125 MHz, CDCl₃): δ = 163.52, 163.34, 137.83, 133.82, 133.34, 129.85, 127.20, 127.03, 126.78, 123.01, 122.05, 120.70, 105.57, 82.31, 53.88, 38.42, 28.93, 26.97, 26.38, 25.28, 20.67, 20.30, 13.88; UV/Vis (CHCl₃): λ_{max} (ϵ) = 552 (47320), 511 (27990), 476 (15030), 297 nm (41870 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, exc.: 552 nm): λ_{em} = 571 nm; MS (8 kV, FD): m/z = 742.4 (100%) [M^+] (calcd. 742.37).

N,N-Dicyclohexyl-1,7-bis(3,3-dimethylbut-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14c**). *N,N*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (500 mg, 0.7 mmol) and *tert*-butylethyne (230 mg, 2.8 mmol) were reacted as described for (**14**) (reaction temperature 50 °C) and the red product (**14c**) was isolated (463 mg, 92%). Mp 217 °C; ¹H

NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ = 10.09 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 8.68 (s, 2 H; H-2, H-8), 8.58 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 5.01 (m, 2 H; 2 CH-N), 2.55 (m, 4 H; 4 $\text{CH}_{\text{cyclohex}}$), 1.91 (m, 4 H; 4 $\text{CH}_{\text{cyclohex}}$), 1.74 (m, 6 H; 6 $\text{CH}_{\text{cyclohex}}$), 1.45 (m, 22 H; 4 $\text{CH}_{\text{cyclohex}}$, 6 CH_3), 1.32 (m, 2 H; 2 $\text{CH}_{\text{cyclohex}}$); ^{13}C NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 50 °C): δ = 164.02, 163.83, 138.19, 134.39, 133.89, 130.25, 127.79, 127.59, 127.27, 123.64, 122.64, 121.22, 109.29, 81.48, 54.48, 34.90, 30.72, 29.93, 29.48, 29.18, 29.90, 25.80; UV/Vis (CHCl_3): λ_{max} (ϵ) = 552 (45680), 511 (27020), 476 (14960), 297 nm ($41310 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 552 nm): λ_{em} = 571 nm; MS (8 kV, FD): m/z = 715.2 (100%) [M^+] (calcd. 714.34).

***N,N'*-Dicyclohexyl-1,7-di(oct-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (14d).** *N,N'*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (750 mg, 1 mmol) and oct-1-yne (467 mg, 4 mmol) were reacted as described for (**14**) to give the red product **14d** (750 mg, 92%). Mp 221 °C; ^1H NMR (500 MHz, CD_2Cl_2): δ = 9.03 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 7.85 (s, 2 H; H-2, H-8), 7.73 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 4.91 (m, 2 H; 2 N-CH), 2.58 (m, 6 H; 2 $\equiv\text{CH}_2$, 4 $\text{CH}_{\text{cyclohex}}$), 2.00 (m, 8 H; 4 $\text{CH}_{\text{cyclohex}}$, 2 CH_2), 1.78 (m, 10 H; 6 $\text{CH}_{\text{cyclohex}}$, 2 CH_2), 1.48 (m, 14 H; 4 CH_2 und 6 $\text{CH}_{\text{cyclohex}}$), 1.00 (t, 3J (H,H) = 7 Hz, 6 H; 2 CH_3); ^{13}C NMR (75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ = 163.12, 162.91, 137.46, 133.03, 132.47, 129.45, 126.53, 126.39, 125.96, 122.65, 121.70, 120.11, 101.97, 81.95, 53.82, 31.15, 28.73, 28.04, 26.41, 22.42, 20.04, 13.99; UV/Vis (CHCl_3): λ_{max} (ϵ) = 552 (46210), 511 (28900), 476 (15050), 297 nm ($41320 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 552 nm): λ_{em} = 571 nm; MS (8 kV, FD): m/z = 770.3 (100%) [M^+] (calcd. 770.41).

***N,N'*-Dicyclohexyl-1,7-di(pentadec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (14e).** *N,N'*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (1 g, 1.4 mmol) and pentadecyne (880 mg, 4.23 mmol) were reacted as described for (**14**) and the red product (**14e**) (1.1 g, 81%) was isolated. Mp 164 °C; ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.01 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 7.81 (s, 2 H; H-2, H-8), 7.70 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 4.93–4.78 (m, 2 H; 2 CH-N), 2.56–2.39 (m, 8 H; 2 CH_2 , 4 $\text{CH}_{\text{cyclohex}}$), 1.98–1.20 (m, 60 H; 22 CH_2 , 16 $\text{CH}_{\text{cyclohex}}$), 0.81 (t, 3J (H,H) = 7 Hz, 6 H; 2 CH_3); ^{13}C NMR (75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ = 163.25, 163.05, 137.60, 133.32, 132.82, 129.67, 126.71, 126.25, 122.80, 121.86, 120.35, 101.81, 82.00, 53.84, 31.71, 29.52, 29.48, 29.23, 29.16, 29.06, 29.04, 28.92, 28.09, 26.41, 22.51, 20.06, 14.02; UV/Vis (CHCl_3): λ_{max} (ϵ) = 552 (47320), 511 (27990), 476 (15030), 297 nm ($41870 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 552 nm): λ_{em} = 571 nm; MS (8 kV, FD): m/z = 966.3 (100%) [M^+] (calcd. 966.63).

***N,N'*-Di(*n*-octyl)-1,7-di(dodec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (14f).** *N,N'*-Di(*n*-octyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13b**) (2.5 g, 3.2 mmol) and dodec-1-yne (2.12 g, 12.8 mmol) were reacted as described for (**14**) to yield the red product (**14f**) (2.74 g, 91%). Mp 168 °C; ^1H NMR (500 MHz, CD_2Cl_2): δ = 9.56 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 8.21 (s, 2 H; H-2, H-8), 8.07 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 4.09 (m, 8 H; 2 CH_2 -N, 2 CH_2), 1.1 (m, 56 H; 28 CH_2), 0.91 (m, 12 H; 4 CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 162.92, 162.71, 137.74, 133.74, 132.72, 129.62, 128.97, 128.32, 128.15, 126.88, 126.81, 126.68, 126.29, 122.72, 122.25, 121.73, 121.37, 120.47, 120.26, 103.12, 82.63, 41.10, 40.86, 32.39, 32.32, 30.26, 30.21, 30.17, 30.12, 30.09, 29.91, 29.81, 29.73, 28.79, 27.66, 23.17, 23.12, 20.73, 14.33, 14.29; UV/Vis (CHCl_3): λ_{max} (ϵ) = 552 (47030), 511 (29640), 476 (15680), 297 nm ($42420 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 552 nm): λ_{em} = 571 nm; MS (8 kV, FD): m/z = 942.4 (100%) [M^+] (calcd. 942.63); IR (KBr): (cm^{-1}) = 3028, 3022,

2959, 2926, 2868, 2853, 1711, 1670, 1622, 1595, 1467, 1456, 1406, 1384, 1362, 1336, 1241, 912, 740; $\text{C}_{64}\text{H}_{82}\text{N}_2\text{O}_4$ (943.36): calcd. C 81.49, H 8.76, N 2.97, O 6.78%; found C 79.93, H 8.73, N 2.85%.

***N,N'*-Di(*n*-octyl)-1,7-di(pentadec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (14g).** *N,N'*-Di(*n*-octyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13b**) (3 g, 3.8 mmol) and pentadec-1-yne (3.2 g, 15.5 mmol) were reacted as described for (**14**). The red product (**14g**) (3.5 g, 89%) was isolated. Mp 152 °C; ^1H NMR (500 MHz, CD_2Cl_2): δ = 9.33 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 8.03 (s, 2 H; H-2, H-8), 7.85 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 4.07 (m, 8 H; 2 CH_2 -N, 2 CH_2), 1.95–1.18 (m, 68 H; 34 CH_2), 0.90 (m, 12 H; 4 CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 163.02, 162.87, 138.03, 134.12, 132.93, 129.93, 129.13, 128.73, 128.52, 127.08, 127.01, 126.98, 126.63, 122.97, 122.58, 122.03, 121.72, 120.80, 120.53, 103.83, 83.03, 41.31, 41.08, 32.84, 32.41, 30.28, 30.25, 30.19, 30.13, 30.09, 29.95, 29.90, 29.83, 29.75, 28.83, 27.72, 23.21, 23.15, 20.77, 14.34, 14.28; UV/Vis (CHCl_3): λ_{max} (ϵ) = 552 (46580), 511 (29130), 476 (15240), 297 nm ($40980 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 552 nm): λ_{em} = 572 nm; MS (8 kV, FD): m/z = 1026.7 (100%) [M^+], 2054.3 (70%) [M_2^+], 3081.4 (20%) [M_3^+] (calcd. 1027.7).

***N,N'*-Bis(2,6-diisopropylphenyl)-1,7-di(dodec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (14h).** *N,N'*-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13c**) (3 g, 3.46 mmol) and dodec-1-yne (1.72 g, 10.38 mmol) were reacted as described for (**14**) to give the product (**14h**) (3.1 g, 85%). Mp 191 °C; ^1H NMR (500 MHz, CD_2Cl_2): δ = 10.25 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 8.84 (s, 2 H; H-2, H-8), 8.74 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 7.57 (t, 3J (H,H) = 8 Hz, 2 H), 7.43 (d, 3J (H,H) = 8 Hz, 4 H), 2.75 (septet, 3J (H,H) = 7 Hz, 4 H; 4 $\text{CH}_{\text{isopropyl}}$), 2.68 (t, 3J (H,H) = 7.3 Hz, 4 H; 2 CH_2), 1.94 (m, 4 H; 2 CH_2), 1.78 (m, 4 H; 2 CH_2), 1.61–1.19 (m, 24 H; 12 CH_2), 1.17 (d, 3J (H,H) = 7 Hz, 12 H; 4 (CH_3)_{isopropyl}), 0.83 (t, 3J (H,H) = 7 Hz, 6 H; 2 CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 164.21, 163.79, 146.31, 146.27, 142.37, 138.47, 136.93, 133.97, 131.40, 131.29, 130.80, 130.58, 129.71, 129.45, 128.47, 126.62, 125.72, 124.27, 124.21, 123.05, 122.39, 122.14, 121.62, 121.14, 103.30, 83.07, 31.99, 29.69, 29.64, 29.60, 29.48, 29.40, 29.37, 29.34, 28.60, 23.90, 23.82, 22.74, 20.58, 13.93; UV/Vis (CHCl_3): λ_{max} (ϵ) = 552 (46980), 511 (27790), 476 (14980), 297 nm ($40329 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 552 nm): λ_{em} = 572 nm; MS (8 kV, FD): m/z = 1039.2 (100%) [M^+] (calcd. 1038.63); $\text{C}_{72}\text{H}_{82}\text{N}_2\text{O}_4$ (1069.52): calcd. C 83.10, H 8.29, N 2.62, O 5.98%; found C 82.79, H 8.22, N 2.56%.

***N,N'*-Dicyclohexyl-1,7-bis(2-phenylethynyl)perylene-3,4,9,10-tetracarboxydiimide (14i).** *N,N'*-Dicyclohexyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (**13a**) (500 mg, 0.7 mmol) and phenylethyne (300 mg, 2.94 mmol) were reacted as described for (**14**) to yield the red product (**14i**) (460 mg, 87%). Mp 165 °C; ^1H NMR (500 MHz, CHCl_3): δ = 10.08 (d, 3J (H,H) = 8 Hz, 2 H; H-6, H-12), 8.84 (s, 2 H; H-2, H-8), 8.69 (d, 3J (H,H) = 8 Hz, 2 H; H-5, H-11), 7.64 (m, 4 H; 4 H-Ph), 7.46 (m, 6 H; 6 H-Ph), 5.04 (m, 2 H; 2 N-CH), 2.56 (m, 4 H; 4 $\text{CH}_{\text{cyclohex}}$), 1.91 (m, 4 H; 4 $\text{CH}_{\text{cyclohex}}$), 1.76 (m, 6 H; 6 $\text{CH}_{\text{cyclohex}}$), 1.45 (m, 4 H; 4 $\text{CH}_{\text{cyclohex}}$), 1.35 (m, 2 H; 2 $\text{CH}_{\text{cyclohex}}$); UV/Vis (CHCl_3): λ_{max} (ϵ) = 573 (38630), 531 (24850), 494 nm ($10750 \text{ l mol}^{-1} \text{ cm}^{-1}$); fluorescence emission (CHCl_3 , exc.: 572 nm): λ_{em} = 590 nm; MS (8 kV, FD): m/z = 754.5 (100%) [M^+] (calcd. 754.28).

Synthesis of *N,N'*-dialkyl-5,11-dialkylcoronene-2,3,8,9-tetracarboxydiimides (**9**) (Scheme 3)

N,N'-Dialkyl-1,7-dialkynylperylene-3,4,9,10-tetracarboxydiimide (**14**) (1 mmol) were dissolved in *m*-xylene (or toluene) (400 ml). The solution was deoxygenated by bubbling with argon. DBU

(0.6 ml) was added through a septum with a syringe. The reaction mixture was stirred at 100–110 °C for 20 h. After cooling to room temperature, the solution was poured into ice cold dilute HCl and the product was extracted with dichloromethane. The organic layer was washed with water until neutral, dried over MgSO₄ and the solvent evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel–CH₂Cl₂).

***N,N'*-Dicyclohexyl-5,11-didecylcoronene-2,3,8,9-tetracarboxydiimide (9a).** *N,N'*-Dicyclohexyl-1,7-di(dodec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14a**) (1 g, 1.13 mmol) was reacted as described for (**9**) to yield the yellow product (**9a**) (950 mg, 95%). DSC: $T_m = 245\text{ }^\circ\text{C}$; $T_i > 300\text{ }^\circ\text{C}$; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.24$ (s, 2 H; H-1, H-7), 8.99 (s, 2 H; H-4, H-10), 8.06 (s, 2 H; H-6, H-12), 5.33 (m, 2 H; 2 CH-N), 3.40 (t, ³*J* (H,H) = 7 Hz, 4 H; 2 Ar-CH₂), 2.87 (m, 4 H; 4 CH_{cyclohex}), 2.15 (m, 4 H; 4 CH_{cyclohex}), 1.90 (m, 6 H; 6 CH_{cyclohex}), 1.71–1.29 (m, 34 H; 6 CH_{cyclohex}, 14 CH₂), 0.88 (t, ³*J* (H,H) = 7 Hz, 6 H; 2 CH₃); ¹³C NMR (75 MHz, C₂D₂Cl₄, 50 °C): $\delta = 164.35$, 164.13, 140.17, 128.42, 127.76, 127.17, 126.37, 124.62, 121.01, 120.83, 120.65, 120.54, 119.76, 118.38, 54.40, 33.17, 31.71, 30.62, 29.72, 29.54, 29.48, 29.42, 29.15, 26.68, 25.52, 22.48, 13.95; UV/Vis (CHCl₃): λ_{max} (ϵ) = 511 (19744), 477 (9435), 428 (62092), 404 (30463), 382 (7933), 338 (73176), 334 nm (72780 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 477 nm): $\lambda_{\text{em}} = 517$ nm; MS (8 kV, FD): $m/z = 882.4$ (100%) [M^+] (calcd. 883.22); C₆₀H₇₀N₂O₄ (883.22): calcd. C 81.59, H 7.99, N 3.17, O 7.25%; found C 80.85, H 8.01, N 3.09%.

***N,N'*-Dicyclohexyl-5,11-bis(1-methylbutyl)coronene-2,3,8,9-tetracarboxydiimide (9b).** *N,N'*-Dicyclohexyl-1,7-bis(3-methylhex-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14b**) (500 mg, 0.67 mmol) was reacted as described for (**9**) to yield (**9b**) (445 mg, 89%) as an orange substance. Mp > 300 °C; ¹H NMR (500 MHz, CHCl₃): $\delta = 10.01$ (s, 1 H; H_{arom.}), 9.97 (s, 1 H; H_{arom.}), 9.71 (s, 1 H; H_{arom.}), 9.67 (s, 1 H; H_{arom.}), 8.85 (s, 1 H; H_{arom.}), 8.82 (s, 1 H; H_{arom.}), 5.26 (m, 2 H; CH-N), 4.38 (m, 2 H; 2 CH-Ar), 2.82 (m, 4 H; 4 CH_{cyclohex}), 2.25–1.40 (m, 30 H; 16 CH_{cyclohex}, 4 CH₂, 2 CH₃), 1.06 (t, ³*J* (H,H) = 7 Hz, 3 H; CH₃), 1.00 (t, ³*J* (H,H) = 7 Hz, 3 H; CH₃); ¹³C NMR (75 MHz, C₂D₂Cl₄): $\delta = 165.12$, 164.82, 146.43, 146.32, 129.93, 129.34, 129.27, 128.36, 128.32, 125.51, 125.16, 123.25, 123.16, 121.95, 121.90, 121.65, 121.62, 121.45, 121.42, 121.17, 120.61, 120.53, 54.32, 40.58, 40.35, 34.52, 34.44, 29.25, 26.60, 25.45, 22.30, 22.04, 20.86, 20.80, 20.73, 14.27, 14.21; UV/Vis (CHCl₃): λ_{max} (ϵ) = 511 (18470), 477 (8990), 428 (61570), 404 (29080), 382 (7590), 338 (73870), 334 nm (72460 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 477 nm): $\lambda_{\text{em}} = 517$ nm; MS (8 kV, FD): $m/z = 742.4$ (100%) [M^+] (calcd. 742.38).

***N,N'*-Dicyclohexyl-5,11-dihexylcoronene-2,3,8,9-tetracarboxydiimide (9c).** *N,N'*-Dicyclohexyl-1,7-di(oct-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14d**) (500 mg, 0.65 mmol) was reacted as described for (**9**) to yield the orange product **9c** (480 mg, 96%). Mp > 300 °C; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.44$ (s, 2 H; H-1, H-7), 9.18 (s, 2 H; H-4, H-10), 8.26 (s, 2 H; H-6, H-12), 5.35 (m, 2 H; 2 CH-N), 3.52 (t, ³*J* (H,H) = 8 Hz, 4 H; 2 Ar-CH₂), 2.86 (m, 4 H; 4 CH_{cyclohex}), 2.12 (m, 8 H; 4 CH_{cyclohex}, 2 CH₂), 2.02–1.88 (m, 6 H; 6 CH_{cyclohex}), 1.72–1.38 (m, 18 H; 6 CH_{cyclohex}, 6 CH₂), 0.96 (t, ³*J* (H,H) = 7 Hz, 6 H; 2 CH₃); ¹³C NMR (500 MHz, CDCl₃): $\delta = 164.85$, 164.61, 140.71, 128.97, 128.43, 127.78, 125.16, 124.67, 121.84, 121.35, 121.26, 121.08, 120.59, 51.51, 33.69, 31.77, 31.36, 31.22, 29.64, 29.53, 26.86, 25.71, 22.74, 14.10; UV/Vis (CHCl₃): λ_{max} (ϵ) = 511 (18660), 477 (9070), 428 (61690), 404 (29270), 382 (7680), 338 (73480), 334 nm (72769 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 477 nm): $\lambda_{\text{em}} = 517$ nm; MS (8 kV, FD): $m/z = 770.3$ (100%) [M^+] (calcd. 770.41).

***N,N'*-Dicyclohexyl-5,11-di(tridecyl)coronene-2,3,8,9-tetracarboxydiimide (9d).** *N,N'*-Dicyclohexyl-1,7-di(tridec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14e**) (1 g, 1.04 mmol) was reacted as described for (**9**) to yield the yellow product (**9d**) (945 mg, 95%). DSC: $T_m = 266\text{ }^\circ\text{C}$, $T_i > 300\text{ }^\circ\text{C}$; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.29$ (s, 2 H; H-1, H-7), 9.04 (s, 2 H; H-4, H-10), 8.10 (s, 2 H; H-6, H-12), 5.34 (m, 2 H; 2 CH-N), 3.42 (t, ³*J* (H,H) = 8 Hz, 4 H; 2 Ar-CH₂), 2.87 (m, 4 H; 4 CH_{cyclohex}), 2.15 (m, 8 H; 4 CH_{cyclohex}, 2 CH₂), 1.93 (m, 6 H; 6 CH_{cyclohex}), 1.75–1.25 (m, 46 H; 6 CH_{cyclohex}, 20 CH₂), 0.85 (t, ³*J* (H,H) = 7 Hz, 6 H; 2 CH₃); ¹³C NMR (125 MHz, CDCl₃): $\delta = 164.71$ (C=O), 164.47 (C=O), 140.49, 128.73 (CH), 128.73, 128.12, 127.49 (CH), 124.90 (CH), 121.39, 121.12, 120.97, 120.86, 120.16, 118.75, 109.71, 54.55 (CH-N), 33.60, 31.93, 31.15, 30.02, 29.77, 29.68, 29.66, 29.52, 29.38, 26.87, 25.72, 22.69, 14.10 (CH₃); UV/Vis (CHCl₃): λ_{max} (ϵ) = 511 (19231), 477 (9250), 428 (61780), 404 (29760), 382 (7790), 338 (73350), 334 nm (72760 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 477 nm): $\lambda_{\text{em}} = 517$ nm; MS (8 kV, FD): $m/z = 966.7$ (100%) [M^+] (calcd. 966.63); C₆₆H₈₂N₂O₄ (967.38): calcd. C 81.94, H 8.54, N 2.90, O 6.62%; found C 81.90, H 8.53, N 2.89%.

***N,N'*-Di(*n*-octyl)-5,11-didecylcoronene-2,3,8,9-tetracarboxydiimide (9e).** *N,N'*-Di(*n*-octyl)-1,7-di(dodec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14f**) (1 g, 1.06 mmol) was reacted as described for (**9**) to yield the yellow product (**9e**) (895 mg, 90%). DSC: $T_m = 191\text{ }^\circ\text{C}$, $T_i > 300\text{ }^\circ\text{C}$; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.28$ (s, 2 H; H-1, H-7), 9.06 (s, 2 H; H-4, H-10), 8.22 (s, 2 H; H-6, H-12), 4.41 (t, ³*J* (H,H) = 8 Hz, 4 H; 2 N-CH₂), 3.48 (t, ³*J* (H,H) = 8 Hz, 4 H; 2 Ar-CH₂), 2.03–1.91 (m, 8 H; 4 CH₂), 1.66–1.57 (m, 8 H; 4 CH₂), 1.51–1.23 (m, 40 H; 20 CH₂), 0.92–0.84 (m, 12 H; 4 CH₃); ¹³C NMR (125 MHz, C₂D₂Cl₄, 70 °C): $\delta = 163.54$, 163.31, 140.28, 128.39, 127.86, 127.22, 126.46, 124.50, 121.15, 120.56, 120.21, 119.92, 118.54, 40.87, 33.11, 31.66, 31.63, 30.50, 29.73, 29.49, 29.43, 29.21, 29.08, 28.18, 27.21, 22.41, 13.82; UV/Vis (CHCl₃): λ_{max} (ϵ) = 512 (20120), 478 (9640), 428 (60240), 404 (29820), 382 (7950), 338 (70560), 332 (71050 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 477 nm): $\lambda_{\text{em}} = 518$ nm; MS (8 kV, FD): $m/z = 942.5$ (100%) [M^+] (calcd. 942.63); C₆₄H₈₂N₂O₄ (943.36): calcd. C 81.49, H 8.76, N 2.97, O 6.78%; found C 81.39, H 8.68, N 2.94%.

***N,N'*-Di(*n*-octyl)-5,11-di(tridecyl)coronene-2,3,8,9-tetracarboxydiimide (9f).** *N,N'*-Di(*n*-octyl)-1,7-di(pentadec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14g**) (1.5 g, 1.4 mmol) was reacted as described for (**9**) to yield the yellow product (**9f**) (895 mg, 90%). DSC: $T_m = 177\text{ }^\circ\text{C}$, $T_i > 300\text{ }^\circ\text{C}$; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.50$ (s, 2 H; H-1, H-7), 9.26 (s, 2 H; H-4, H-10), 8.40 (s, 2 H; H-6, H-12), 4.46 (t, ³*J* (H,H) = 8 Hz, 4 H; 2 CH₂-N), 3.60 (t, ³*J* (H,H) = 8 Hz, 4 H; 2 Ar-CH₂), 2.10–1.90 (m, 8 H; 4 CH₂), 1.65–1.25 (m, 60 H; 30 CH₂), 0.91–0.84 (m, 12 H; 4 CH₃); ¹³C NMR (125 MHz, CDCl₃): $\delta = 163.83$, 163.52, 140.35, 128.54, 127.95, 127.34, 126.63, 124.70, 121.32, 120.73, 120.43, 120.08, 118.74, 40.89, 33.60, 33.12, 31.68, 31.65, 31.16, 30.51, 29.71, 29.45, 29.23, 29.09, 28.19, 27.25, 22.42, 13.81; UV/Vis (CHCl₃): λ_{max} (ϵ) = 511 (20210), 477 (9660), 428 (60670), 404 (30040), 382 (7990), 338 (70830), 332 nm (71980 l mol^{−1} cm^{−1}); fluorescence emission (CHCl₃, exc.: 477 nm): $\lambda_{\text{em}} = 511$ nm; MS (8 kV, FD): $m/z = 1026.7$ (100%) [M^+] (calcd. 1026.72); C₇₀H₉₄N₂O₄ (1027.52): calcd. C 81.82, H 9.22, N 2.73, O 6.23%; found C 81.76, H 9.25, N 2.64%.

***N,N'*-Bis(2,6-diisopropylphenyl)-5,11-didecylcoronene-2,3,8,9-tetracarboxydiimide (9g).** *N,N'*-Bis(2,6-diisopropylphenyl)-1,7-di(dodec-1-ynyl)perylene-3,4,9,10-tetracarboxydiimide (**14h**) (1.5 g, 1.45 mmol) was reacted as described for (**9**) to yield the yellow product (**9g**) (1.35 g, 90%). Mp 227 °C; ¹H NMR (500 MHz, C₂D₂Cl₄, 100 °C): $\delta = 10.21$ (s, 2 H; H-1, H-7), 9.96 (s, 2 H; H-4, H-10), 9.05 (s, 2 H; H-6, H-12), 7.48 (t, ³*J*

(H,H)=8 Hz, 2 H; 2 Ar-H), 7.35 (d, 3J (H,H)=8 Hz, 4 H; 4 Ar-H), 3.88 (t, 3J (H,H)=8 Hz, 4 H; 2 Ar-CH₂), 2.95 (septet, 3J (H,H)=7 Hz, 4 H; 4 CH₃isopropyl), 2.19 (m, 4 H; 2 CH₂), 1.66 (m, 4 H; 2 CH₂), 1.46 (m, 4 H; 2 CH₂), 1.36–1.20 (m, 32 H; 10 CH₂, 4 (CH₃)isopropyl), 0.78 (t, 3J (H,H)=7 Hz, 6 H; 2 CH₃); ^{13}C NMR (125 MHz, C₂D₂Cl₄, 100 °C): δ =165.40, 165.14, 146.49, 142.71, 131.95, 131.15, 130.63, 130.07, 129.85, 129.13, 127.41, 124.99, 124.48, 123.80, 123.64, 122.62, 122.42, 122.35, 34.41, 34.35, 32.19, 32.03, 30.27, 29.95, 29.93, 29.85, 29.59, 29.48, 24.48, 24.46, 24.33, 24.20, 22.92, 4.30; UV/Vis (CHCl₃): λ_{max} (ϵ)=511 (19890), 477 (8920), 429 (69050), 404 (30810), 382 (6960), 338 (71810), 333 nm (76770 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, exc.: 477 nm): λ_{em} =518 nm; MS (8 kV, FD): m/z =1039.0 (100%) [M^+] (calcd. 1038.63); C₇₂H₈₂N₂O₄ (1039.45): calcd. C 83.20, H 7.95, N 2.70, O 6.16%; found C 82.72, H 8.26, N 2.73%.

Synthesis of coronenemonoimides (10)

Tribromoperylenemonoimide (18). *N*-(2,6-Diisopropylphenyl)-perylene-3,4-dicarboximide (17) (10 g, 21 mmol) was dissolved in chloroform (1.5 l), bromine (60 ml) was added dropwise and the mixture was stirred for 6 h at reflux temperatures. After cooling to room temperature the solution was added to a vigorously stirred mixture of water (3 l), KOH (25 g) and Na₂SO₂ (15 g). KOH and Na₂SO₂ were added carefully in portions until the color changed from brown to bright orange. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic solutions were dried over MgSO₄ and the solvent was evaporated leaving the crude product (13 g, 86%), which was then purified in portions of 4 g each by column chromatography (silica gel, petroleum ether: CH₂Cl₂=1:1). Mp >300 °C; ^1H NMR (250 MHz, CD₂Cl₂): δ =9.42 (d, 3J (H,H)=8 Hz, 1 H; Ar-H), 9.21 (d, 3J (H,H)=8 Hz, 1 H; Ar-H), 8.92 (s, 1 H; Ar-H), 8.91 (s, 1 H; Ar-H), 8.51 (d, 3J (H,H)=8 Hz, 1 H; Ar-H), 8.04 (d, 3J (H,H)=8 Hz, 1 H; Ar-H), 7.89 (m, 1 H; Ar-H), 7.53 (t, 3J (H,H)=7 Hz, 1 H; Ph-H), 7.36 (d, 3J (H,H)=7 Hz, 2 H; 2 Ph-H), 2.75 (m, 2 H; 2 CH₃isopropyl), 1.21 (d, 3J (H,H)=7 Hz, 6 H; 2 (CH₃)isopropyl); ^{13}C NMR (75 MHz, CD₂Cl₂): δ =162.75, 146.14, 138.37, 135.49, 135.27, 131.61, 130.97, 130.88, 130.74, 130.28, 129.94, 129.76, 129.73, 129.05, 127.63, 127.07, 126.85, 126.39, 124.24, 121.07, 121.02, 119.28, 119.07, 29.29, 23.78; MS (8 kV, FD): m/z =716.0 (100%) [M^+] (calcd. 714.94); C₃₄H₂₄NO₂Br₃ (718.28): calcd. C 56.85, H 3.37, N 1.95, Br 33.37, O 4.45%; found C 56.56, H 3.50, N 1.92, Br 32.75%.

***N*-(2,6-Diisopropylphenyl)-1,6,9-tri(dodec-1-ynyl)perylene-3,4-dicarboximide (19).** *N*-(2,6-Diisopropylphenyl)-1,6,9-tribromoperylenedicarboximide (18) (1 g, 1.4 mmol) was dissolved in a mixture of dry THF (250 ml) and dry triethylamine (250 ml) in an argon atmosphere. Pd(PPh₃)₄ (194 mg, 1.68 mmol, 12 mol%) and CuI (40 mg, 2.1 mmol, 15 mol%) were added under argon atmosphere. Finally dodec-1-yne (903 mg, 5.4 mmol) was added *via* syringe through a septum. After stirring at 60 °C for 12 h the mixture was poured into the same amount of cold dilute HCl (HCl:H₂O=1:3) and the product was extracted with dichloromethane. The organic layer was extracted with water until the aqueous layer was neutral. The crude product was purified by column chromatography on silica gel (CH₂Cl₂-petroleum ether=1:1) to yield pure (19) (1.1 g, 80%) as red powder. ^1H NMR (500 MHz, CDCl₃): δ =9.90 (d, 3J (H,H)=8 Hz, 1 H; H-12), 9.78 (d, 3J (H,H)=8 Hz, 1 H; H-7), 8.72 (s, 1 H; H-2 or H-5), 8.71 (s, 1 H; H-2 or H-5), 8.45 (d, 3J (H,H)=8 Hz, 1 H; H-10), 7.69 (m, 2 H; H-8, H-11), 7.45 (t, 3J (H,H)=8 Hz, 1 H; Ph-H), 7.30 (d, 3J (H,H)=8 Hz, 2 H; 2 Ph-H), 2.70 (septet, 3J (H,H)=7 Hz, 2 H; 2 CH₃isopropyl), 2.62–2.53 (m, 6 H; 3 CH₂=), 1.75–1.67 (m, 6 H; 3 CH₂), 1.56–1.47 (m, 6 H; 3 CH₂), 1.38–1.23 (m, 36 H; 18 CH₂), 1.14 (d, 3J (H,H)=7 Hz, 12 H; 4 (CH₃)isopropyl), 0.87–0.82 (m, 9

H; 3 CH₃); ^{13}C NMR (125 MHz, CDCl₃): δ =163.45, 145.73, 138.47, 138.45, 137.15, 136.85, 133.27, 130.82, 129.83, 129.53, 129.50, 128.85, 128.75, 128.57, 128.08, 127.37, 127.16, 126.16, 125.08, 124.01, 119.76, 118.92, 99.21, 97.86, 97.64, 82.62, 82.56, 78.92, 31.89, 29.60, 29.58, 29.54, 29.32, 29.30, 29.22, 29.17, 29.09, 28.84, 28.38, 23.96, 22.66, 20.10, 19.97, 14.07; UV/Vis (CHCl₃): λ_{max} (ϵ)=549 (61230), 519 (49160), 343 (34300), 285 nm (47200 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, exc.: 520 nm): λ_{em} =589 nm; MS (8 kV, FD): m/z =973.7 (100%) [M^+] (calcd. 973.67); C₇₀H₈₇NO₂ (974.46): calcd. C 86.28, H 9.00, N 1.44, O 3.28%; found C 86.27, H 8.97, N 1.37%.

***N*-(2,6-Diisopropylphenyl)-6,11-didecyl-8-dodecynyl-2,3-coronenedicarboximide (20).** Trialkynylperylene (19) (1.9 g, 1.95 mmol) was dissolved in toluene (600 ml) and the solution was deaerated by bubbling with argon. DBU (3.1 ml) were added with a syringe through a septum. After stirring for 24 h at 110 °C the solution was poured into the same amount of diluted HCl (HCl:H₂O=1:3) and the product was extracted with dichloromethane. The organic layer was dried over MgSO₄ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (CH₂Cl₂-petroleum ether=1:1) and the yellow product was isolated (1.25 g, 65%). DSC: T_i =269 °C; ^1H NMR (500 MHz, C₂D₂Cl₄, 100 °C): δ =9.83 (s, 1 H; H_{arom.}), 9.80 (s, 1 H; H_{arom.}), 9.39 (d, 3J (H,H)=9 Hz, 1 H; H_{arom.}), 9.09 (s, 1 H; H_{arom.}), 9.07 (d, 3J (H,H)=9 Hz, 1 H; H_{arom.}), 8.86 (s, 1 H; H_{arom.}), 8.81 (s, 1 H; H_{arom.}), 7.51 (t, 3J (H,H)=8 Hz, 1 H; H-b), 7.38 (d, 3J (H,H)=8 Hz, 2 H; 2 H-a), 3.75 (t, 3J (H,H)=8 Hz, 2 H; Ar-CH₂), 3.70 (t, 3J (H,H)=7.7 Hz, 2 H; Ar-CH₂), 3.01 (septet, 3J (H,H)=6.5 Hz, 2 H; 2 CH₃isopropyl), 2.84 (t, 3J (H,H)=7.5 Hz, 2 H; CH₂=), 2.18–2.12 (m, 4 H; 2 CH₂), 1.96–1.93 (m, 2 H; CH₂), 1.78–1.60 (m, 6 H; 3 CH₂), 1.55–1.26 (m, 36 H; 18 CH₂), 1.24 (d, 3J (H,H)=7 Hz, 12 H; 4 (CH₃)isopropyl), 0.89–0.83 (m, 9 H; 3 CH₃); ^{13}C NMR (125 MHz, C₂D₂Cl₄, 100 °C): δ =165.62, 165.59, 146.51, 139.98, 139.42, 132.38, 130.54, 130.26, 129.86, 129.52, 128.73, 128.22, 128.16, 127.98, 127.92, 126.97, 126.86, 124.32, 123.63, 123.42, 123.38, 123.36, 123.26, 122.87, 122.60, 122.05, 121.20, 120.80, 120.72, 98.56, 80.19, 34.41, 34.13, 32.21, 32.15, 31.64, 31.42, 30.26, 30.18, 29.97, 29.95, 29.92, 29.90, 29.75, 29.64, 29.61, 29.55, 29.54, 29.47, 24.39, 22.92, 22.88, 20.51, 14.27, 14.25; UV/Vis (CHCl₃): λ_{max} (ϵ)=480 (12070), 450 (11850), 426 (40180), 403 (23250), 345(60010), 335 nm (81150 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, λ_{exc} =426 nm): λ_{em} =486 nm; MS (8 kV, FD): m/z =974.0 (100%) [M^+] (calcd. 973.67).

***N*-(2,6-Diisopropylphenyl)-6,11-didecyl-8-dodecylcoronene-2,3-dicarboximide (10).** Coronenemonoalkyne (20) (390 mg, 0.4 mmol) was dissolved in THF (200 ml) and the solution was deaerated by alternately evacuating and flushing with argon several times. Palladium on charcoal (200 mg) was added under argon atmosphere, and the flask was evacuated and then flushed with hydrogen gas. The reaction mixture was stirred at room temperature and the course of the hydrogenation was monitored by FD mass spectrometry. After 1 h the reaction was complete and the solution was filtered through Celite and the solvent was evaporated. The crude product was dissolved in CHCl₂ and on addition of methanol the yellow product (350 mg, 90%) precipitated. DSC: T_i =160 °C; ^1H NMR (500 MHz, C₂D₂Cl₄, 100 °C): δ =9.82 (s, 1 H; H_{arom.}), 9.80 (s, 1 H; H_{arom.}), 9.15 (d, 3J (H,H)=9 Hz, 1 H; H-9 or H-10), 9.08 (d, 3J (H,H)=9 Hz, 1 H; H-9 or H-10), 8.88 (s, 1 H; H_{arom.}), 8.84 (s, 1 H; H_{arom.}), 8.82 (s, 1 H; H_{arom.}), 7.47 (t, 3J (H,H)=8 Hz, 1 H; Ph-H), 7.34 (d, 3J (H,H)=8 Hz, 2 H; 2 Ph-H), 3.78–3.69 (m, 6 H; 3 Ar-CH₂), 2.96 (septet, 3J (H,H)=7 Hz, 2 H; 2 CH₃isopropyl), 2.17–2.08 (m, 6 H; 3 CH₂), 1.65–1.62 (m, 6 H; 3 CH₂), 1.50–1.45 (m, 6 H; 3 CH₂), 1.39–1.19 (m, 46 H; 17 CH₂, 4 (CH₃)isopropyl), 0.82 (t, 3J (H,H)=7 Hz, 9 H; 3 CH₃); ^{13}C NMR (125 MHz, C₂D₂Cl₄, 100 °C): δ =166.72, 147.52,

141.34, 140.77, 140.54, 133.45, 131.41, 131.29, 131.16, 130.47, 129.14, 128.81, 128.75, 125.58, 125.28, 125.10, 124.88, 124.71, 124.30, 124.22, 124.05, 124.01, 122.72, 122.23, 121.63, 121.29, 35.87, 35.36, 33.14, 32.89, 32.60, 31.26, 31.22, 30.91, 30.71, 30.53, 25.37, 23.86, 15.23; UV/Vis (CHCl₃): λ_{max} (ϵ) = 475 (10480), 446 (8860), 418 (33020), 399 (18760), 343 (82030), 334 nm (73010 l mol⁻¹ cm⁻¹); fluorescence emission (CHCl₃, λ_{exc} = 415 nm): λ_{em} = 482 nm; MS (8 kV, FD): m/z = 977.9 (100%) [M⁺] (calcd. 977.70); IR (KBr): (cm⁻¹) = 3067, 3033, 2958, 2923, 2852, 1706, 1666, 1629, 1595, 1468, 1443, 1337, 1260, 1191, 1097, 1057, 1019, 923, 865, 800, 766, 721; C₇₀H₉NO₂ (978.49): calcd. C 85.92, H 9.37, N 1.43, O 3.27%; found C 85.35, H 9.41, N 1.39%.

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References

- 1 F. Graser and E. Hädicke, *Liebigs Ann. Chem.*, 1980, 1994; F. Graser and E. Hädicke, *Liebigs Ann. Chem.*, 1980, 483; Y. Nagao and T. Misono, *Dyes Pigm.*, 1984, **5**, 171; A. Rademacher, S. Märkle and H. Langhals, *Chem. Ber.*, 1982, **115**, 2927; H. Zollinger, *Color Chemistry*, 2nd ed., VCH, Weinheim, 1991; R. M. Christie, *Polym. Int.*, 1994, **34**, 351.
- 2 H. O. Loufty, A. M. Hor, P. Kazmaler and M. J. Tarn, *J. Imag. Sci.*, 1989, **33**, 151.
- 3 G. Seybold and G. Wagenblast, *Dyes Pigm.*, 1989, **11**, 303; H. Langhals, *Nachr. Chem. Tech. Lab.*, 1980, **28**, 716.
- 4 D. Schlottwein, D. Wöhrle, E. Kaarmann and U. Melville, *Chem. Mater.*, 1994, **6**, 3.
- 5 M. P. O'Neil, M. P. Niemczyk, W. A. Svec, D. Gosztola, G. L. Gaines and M. R. Wasielewski, *Science*, 1992, **257**, 63.
- 6 R. Reisfeld and G. Seybold, *Chimia*, 1990, **44**, 295; M. Sandrai, L. Hadel, R. R. Sauers, S. Husain, K. Krogh-Jespersen, J. D. Westbrook and G. R. Bird, *J. Phys. Chem.*, 1992, **96**, 7988; R. Gvishi, R. Reisfeld and Z. Burshtein, *Z. Chem. Phys. Lett.*, 1993, **213**, 338.
- 7 H. Quante and K. Müllen, *Angew. Chem.*, 1995, **107**, 1487; H. Quante and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1323.
- 8 F. O. Holtrup, G. R. J. Müller, H. Quante, S. De Feyter, F. De Schryver and K. Müllen, *Chem. Eur. J.*, 1997, **3**, 219.
- 9 D. Pressner, C. Göltner, H.-W. Spiess and K. Müllen, *Ber. Bunsenges. Phys. Chem.*, 1993, **97**, 1362; C. Göltner, D. Pressner, K. Müllen and H.-W. Spiess, *Angew. Chem.*, 1993, **105**(11), 1722; C. Göltner, D. Pressner, K. Müllen and H.-W. Spiess, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**(11), 1660; P. Schlichting, U. Rohr and K. Müllen, *J. Mater. Chem.*, 1998, **8**, 2651.
- 10 R. A. Cormier and B. A. Gregg, *Chem. Mater.*, 1998, **10**, 1309.
- 11 H. Bengs, F. Closs, T. Frey, D. Funhoff, H. Ringsdorf and K. Siemensmeyer, *Liq. Cryst.*, 1993, **15**(5), 565; D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141; D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and D. Siemensmeyer, *Phys. Rev. Lett.*, 1993, **70**(4), 457; F. Closs, K. Siemensmeyer, T. Frey and D. Funhoff, *Liq. Cryst.*, 1993, **14**(3), 629.
- 12 U. Rohr, P. Schlichting, A. Böhm, M. Groß, K. Meerholz, C. Bräuchle and K. Müllen, *Angew. Chem.*, 1998, **110**(10), 1463; U. Rohr, P. Schlichting, A. Böhm, M. Groß, K. Meerholz, C. Bräuchle and K. Müllen, *Angew. Chem., Int. Ed.*, 1998, **37**(10), 1434.
- 13 P. Schlichting, U. Rohr and K. Müllen, *Liebigs Ann./Recl.*, 1997, 395.
- 14 In all schemes only the major isomer of **9**, **12**, **13** and **14** is shown.
- 15 Semiempirical calculations made by Dr P. Erk (BASF AG) could relate the absorption bands with the electronic transitions: P. Schlichting, PhD thesis, University of Mainz, 1998.
- 16 Synthesis of perylenemonoimides: Y. Nagao and T. Misono, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1191; Y. Nagao and T. Misono, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1575.
- 17 P. G. Schouten, J. M. Warman, M. P. de Haas, M. A. Fox and H. Pan, *Nature*, 1991, **353**, 736; P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelinck, R. J. M. Nolte, M. J. Kopijn, J. W. Zwikker, M. K. Engel, M. Hanack, Y. H. Chang and W. T. Ford, *J. Am. Chem. Soc.*, 1994, **116**, 6880; A. M. van de Craats, P. G. Schouten and J. M. Warman, *EKISHO, J. Jap. Liq. Cryst. Soc.*, 1998, **2**, 12; A. M. van de Craats, J. M. Warman, M. P. de Haas, J. Simmerer, D. Haarer and P. Schumacher, *Adv. Mater.*, 1996, **8**, 823.
- 18 A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison and K. Müllen, *Adv. Mater.*, 1999, **17**, 1469.
- 19 A. M. van de Craats, J. M. Warman, P. Schlichting, U. Rohr, Y. Geerts and K. Müllen, *Synth. Met.*, 1999, **102**, 1550.
- 20 G. Horowitz, F. Kouki, P. Spearman, D. Fichou, C. Nogues and X. Pan, *Adv. Mater.*, 1996, **8**, 242; P. Ranke, I. Bleyl, J. Simmerer, D. Haarer, A. Bacher and H. W. Schmidt, *Appl. Phys. Lett.*, 1997, **71**, 1332.
- 21 P. G. Schouten, J. M. Warman and M. P. de Haas, *J. Phys. Chem.*, 1993, **97**, 9863.