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Easy synthesis of liquid crystalline perylene derivatives

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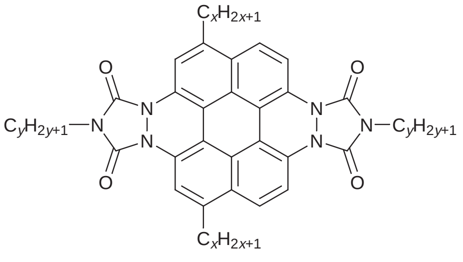
Mesophase forming chromophores are an important challenge of material science. This article describes the synthesis of new perylene mesogenes **10**. The materials were obtained by twofold Diels–Alder reactions of our recently published 1 : 1 isomeric mixture of 3,9- and 3,10-dialkylperylenes with *N*-heptadecyltriazoline-3,5-diones. In contrast to the analogous derivatives **1** published earlier by our group (see reference 3), the new compounds **10** are prepared by a more efficient synthetic route and on a larger scale. Furthermore the characteristics of the liquid crystalline behavior of both materials are compared.

Liquid crystalline chromophores combine the properties of dyes and the characteristics of liquid crystals. This combination is of particular interest for the design of photoconductive and NLO-active materials[1] and the construction of light emitting diodes.[2] Additional requirements are thermal and photochemical stability, the existence of a stable mesophase over a broad temperature range and of course, ready synthetic accessibility.



P*x*-*y* (**1**)

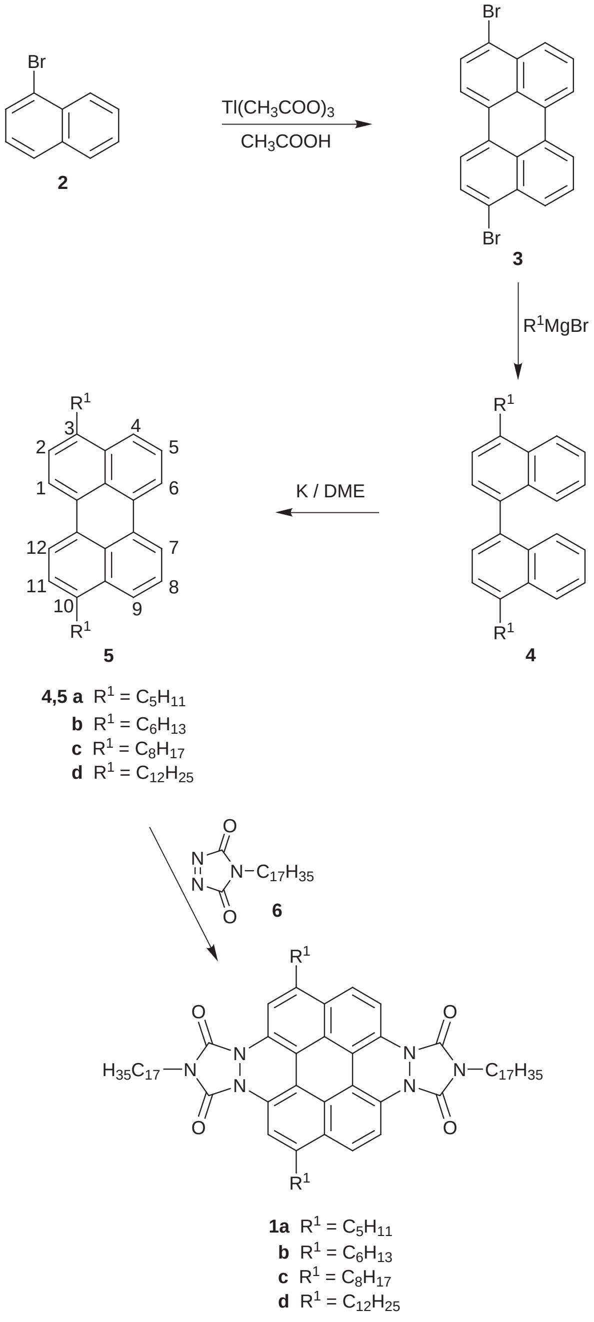
The perylene mesogens P*x*-*y* (**1**) were originally synthesized in our group by twofold Diels–Alder reaction of 3,10-dialkylperylenes **5** with *N*-alkyltriazolinediones **6**.[3] P*x*-*y* is an abbreviation used for simplicity, with P meaning perylene, *x* indicating the length of the alkyl chain attached to the perylene core and *y* the length of the alkyl chain of the urazole unit.

The major disadvantage of the P*x*-*y* systems (**1**) was the lengthy synthesis of the 3,10-dialkylperylenes **5**, which were used in the subsequent twofold Diels–Alder reaction. Starting from 1-bromonaphthalene (**2**), the products **5** were obtained through a three-step synthesis in good yields, however the intermediates required tedious purification methods and the reactions were restricted to small scales. An additional problem of this route was the use of highly toxic thallium salts.

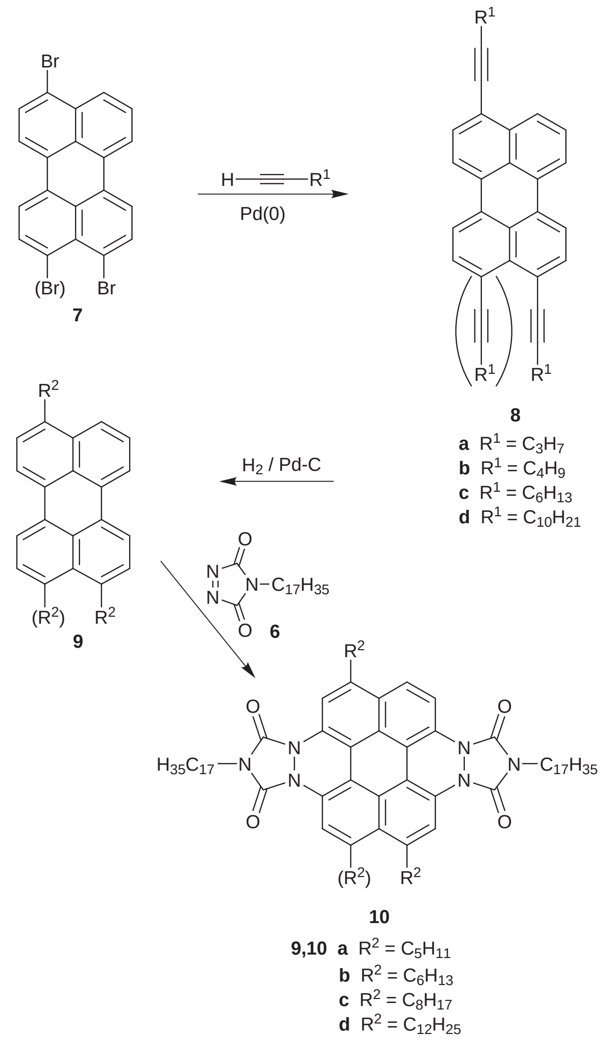
Herein we describe a new and easy route for the preparation of the new liquid crystalline perylene derivatives **10**.

Results and discussion

The synthesis started with a twofold bromination of perylene. This reaction yielded a 1 : 1 isomeric mixture of 3,9- and 3,10-dibromoperylene which could not be separated by column chromatography or HPLC.[4] Due to the fact that this isomeric mixture was used in the subsequent Hagihara-coupling, one also obtained an isomeric mixture of 3,9- and 3,10-dialkyl substituted perylenes **9**. In our experiments, however, this mixture of isomers showed no significant differences in solubility, absorption and reactivity in comparison with the pure 3,10-isomer **5**.[4] The advantage of this method is the simplicity of the procedure and its suitability for large-scale synthesis.



Scheme 1



Scheme 2

For this reason we used the isomeric mixture **9** for the preparation of the new liquid crystalline perylenes **10**.

Analogous to the already mentioned P*x*-*y* **1** the new liquid crystalline perylenes are abbreviated as Pi*x*-*y* **10**. The 'i' stands for isomeric mixture of 3,9- and 3,10-substituted dialkylperylenes **9**. To prepare the Pi*x*-*y* **10**, the 3,9(10)-dibromoperylene **7** was coupled with *n*-alkynes using a palladium catalyzed reaction in 98–100% yield.[4] Subsequent hydrogenation of the triple bonds afforded the 3,9(10)-dialkylperylenes **9** in quantitative yield.[4] As in the case of 3,10-dialkylperylenes **5** these were then reacted with *N*-heptadecyltriazoline-3,5-dione **6** in boiling xylene in a twofold Diels–Alder reaction in both bay-regions of the dialkylperylenes **9** to yield the blue Pi*x*-*y* **10** diaddition products in 95–98% yield.[3] The materials show good solubility in organic solvents. The purification steps were much easier than in the case of the P*x*-*y* compounds **1**, the dibromoperylene **7** and the dialkyne substituted derivatives **8** could be recrystallized and the dialkylperylenes **9** were used for the next reaction without further purification. Unlike the P*x*-*y* derivatives **1**, with the alkyl substituents at the 3,10-positions, the Pi*x*-*y* **10** consist of a 1 : 1 isomeric mixture of the 3,9- and 3,10-substituted species. Analogous to the 3,9(10)-dibromoperylene (**7**), all attempts to separate the two isomers of the Pi*x*-*y* **10** were unsuccessful. Characterization of the Pi*x*-*y* materials **10** 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 structures **10**. No trace of side products was observed by the aforementioned characterization techniques or by thin layer chromatography, which is a particularly sensitive method for chromophores.

The published liquid crystalline perylenes P*x*-*y* (**1**) are blue solids showing a maximum of absorption of $\lambda_{max} = 585$ nm. With X-ray diffraction we showed in earlier publications that the majority of P*x*-*y* derivatives **1** form discotic phases.[3] Through the variation of the alkyl chains at the perylene core and/or the urazole units the characteristics of the mesophase can be controlled. With no or short alkyl chains ($x < 3$) attached to the *peri*-positions of the perylene core (*e.g.* P0–17) smectic phases are obtained.[3] The transition temperatures are also affected if one varies the length of the alkyl chains of the 3,5-dioxotriazole units attached to the perylene. All P*x*-*y* derivatives **1** form remarkably stable (broad) mesophases (*e.g.* P12–11 is liquid crystalline in the temperature region between −23 and 373 °C) due to their pronounced form anisotropy shown by deuteron ^{2}H NMR spectroscopy. The results of ^{2}H NMR spectroscopy indicated that the five-membered, heterocyclic ring clearly deviates from a coplanar conformation. This nonplanarity could cause an entanglement between neighboring perylene units, resulting in an increased phase width of the P*x*-*y* compounds **1**.[3] Similar entanglements were found to be the reason for the increased stability of the mesophase formed by ester substituted triphenylenes.[5]

The new compounds Pi*x*-*y* **10** show an absorption spectrum with $\lambda_{max} = 585$ nm ($\varepsilon \approx 20\,000$ l mol^{-1} cm^{-1}), which is the same as for P*x*-*y* **1**. Similar to P*x*-*y* **1** the Pi*x*-*y* derivatives **10** form mesophases, which qualitatively were detected by polarizing microscopy. The materials show birefringence and shearability, both typical of liquid crystals. The transition temperatures of **10** were determined by calorimetric (DSC) measurements.

From comparision of the transition temperatures of the different Pi*x*-*y* derivatives **10** (Table 1, right column) it is clear that derivatives with the same alkyl chain length at the urazole unit ($y = 17$) show decreasing transition temperatures into the mesophase with increasing length of the alkyl chain attached to the perylene core. In addition to this trend, the isotropization temperature increases, *i.e.* the mesophase range broadens. This trend is exactly the same as in the case of the P*x*-*y* compounds **1**.

Comparison of the transition temperatures of Pi*x*-*y* **10** with P*x*-*y* **1** (Table 1) reveals that the Pi*x*-*y* **10** have slightly lower melting points than the P*x*-*y* **1**. Isotropization temperatures are similar, if both classes of compounds have the same alkyl chains attached to the perylene core (*i.e.* same *x*). The differences in the transition temperatures into the mesophase (T_m) are especially pronounced when *x* is small. For example Pi5–17 **10a** melts at 47 °C while P5–17 **1a** shows the transition into the mesophase at 89 °C, a difference of 42 °C. In summary, the fact that the melting temperature T_m decreases while the isotropization temperature T_i is almost the same for the

Table 1 Comparison of the phase transition temperatures of P*x*-*y* and Pi*x*-*y* derivatives (Cryst = crystalline, Iso Liq = isotropic liquid) measured with differential scanning calometry (DSC); all data taken from the 2nd heating cycle, scan rate 10 °C min^{-1}

x	P*x*-17	Pi*x*-17
5	**1a** Cryst 89 Col$_{ho}$ 226 Iso Liq (°C)	**10a** Cryst 47 Col$_{ho}$ 238 Iso Liq (°C)
6	**1b** Cryst 76 Col$_{ho}$ 245 Iso Liq (°C)	**10b** Cryst 32 Col$_{ho}$ 243 Iso Liq (°C)
8	**1c** Cryst 57 Col$_{ho}$ 288 Iso Liq (°C)	**10c** Cryst 29 Col$_{ho}$ 287 Iso Liq (°C)
12	**1d** Cryst 16 Col$_{ho}$ 316 Iso Liq (°C)	**10d** Cryst 14 Col$_{ho}$ 320 Iso Liq (°C)

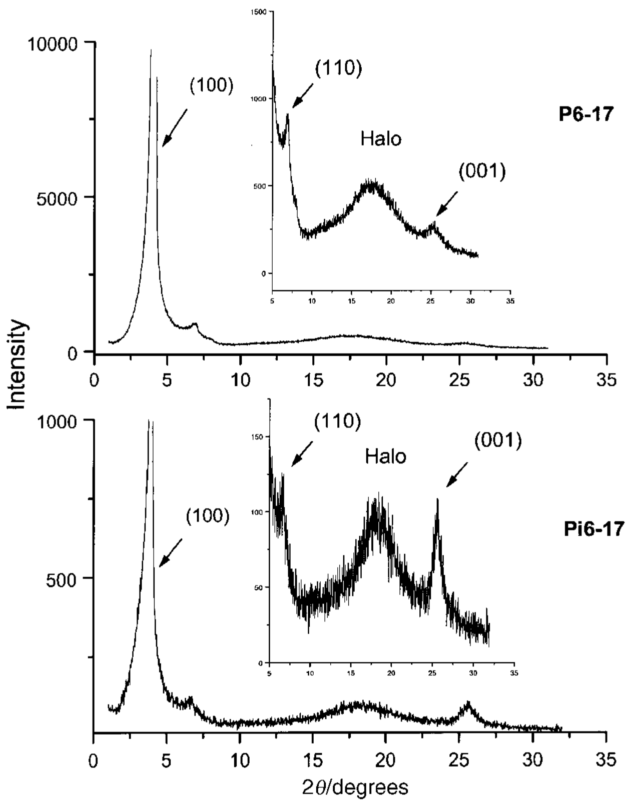


Fig. 1 Small-angle X-ray diffractograms of P6–17 (**1b**) at 127 °C and Pi6–17 (**10b**) at 140 °C.

corresponding P*x*-*y* materials **1**, leads to even broader mesophases for the Pi*x*-*y* **10**. This effect might be caused by the slightly higher irregularity in the case of the new Pi*x*-*y* compounds **10** due to the presence of an isomeric mixture.

The mesophases of **10** were characterized by small-angle X-ray scattering. Similar to the corresponding P*x*-17 compounds **1a–d**, all the Pi*x*-17 derivatives **10a–d** form discotic phases with hexagonal superstructure (Col$_{\mathrm{ho}}$). Fig. 1 shows the characteristic scattering peaks of a Col$_{\mathrm{ho}}$ phase for P6–17 **1b** as well as for Pi6–17 **10b**.

The intense (100)-reflections at $2\theta=4.05°$ (P6–17 **1b**) and $2\theta=3.95°$ (Pi6–17 **10b**) correspond to an intercolumnar distance of approximately 22 Å in both cases. Each derivative shows the (001)-reflection at $2\theta=25.5°$ which indicates an intracolumnar distance of 3.5 Å. The hexagonal superstructure of both substances was proven from the (110)-reflection occurring at $2\theta=7.00°$ (P6–17 **1b**) and $2\theta=6.85°$ (Pi6–17 **10b**).

Conclusions

The isomeric mixture Pi*x*-*y* **10** forms very stable liquid crystalline phases similar to the known P*x*-*y* derivatives **1**, and therefore, exhibit the same attractive physical properties. Besides the fact that the mesophases are slightly broader, the new perylene mesogens Pi*x*-*y* **10** have almost the same liquid crystalline properties as the P*x*-*y* derivatives **1**. Due to the ease of preparation of the Pi*x*-*y* derivatives **10**, larger amounts of the liquid crystalline chromophores can be synthesized, which makes them readily available for different investigations and applications. This was one of the requirements for microwave conductivity detections, which will be presented in a following paper.[6]

Table 2 Small-angle X-ray scattering-reflections of P6–17 **1b** at 127 °C and Pi6–17 **10b** at 140 °C

	P6–17 **1b**	Pi6–17 **10b**
(100)	$2\theta=4.05°$	$2\theta=3.95°$
(110)	$2\theta=7.00°$	$2\theta=6.85°$
(001)	$2\theta=25.5°$	$2\theta=25.5°$

As terminal difunctionalized dialkylperylenes **11** can be synthesized in a similar way to the dialkylperylenes,[3] the improved route presented here offers a possibility for the preparation of functionalized Pi*x*-*y* derivatives **10** as well, if functionalized alkynes are employed in the coupling reactions. In contrast, the synthesis of 3,10-substituted and terminal functionalized dialkylperylenes starting from 1-bromonaphthalene (**2**) (Scheme 1) is not possible, since the functional groups are incompatible with the cyclization conditions. The functional Pi*x*-*y* **10** compounds can then be used to build up liquid crystalline perylene polymers, which is a major goal of our present work.

Experimental

Measurements

^{1}H NMR: Varian Gemini 200 (200 MHz), Bruker AC 300 (300 MHz), Bruker AMX 500 (500 MHz). ^{13}C NMR: Varian Gemini 200 (50.32 MHz), Bruker AC 300 (75.48 MHz), Bruker AMX 500 (125.80 MHz). UV–VIS: Perkin-Elmer Lambda 9, Perkin-Elmer Lambda 15. FD-MS: ZAB2-SE-FPD (VG Instruments). Melting points (uncorrected): Büchi melting point apparatus. Thermal analysis: Mettler DSC 30 differential scanning calorimeter. Thin layer chromatography (TLC): Ready-to-use silica gel 60 F$_{254}$ plates (Merck). Column chromatography: Silica gel, particle size 70–230 mesh (Merck, Geduran Si 60) and aluminium oxide (Merck, Geduran AL 90) using the eluents indicated. The argon used was passed through an oxygen scavenger (BTS catalyst, BASF AG), silica gel and KOH pellets. THF, piperidine, DME and DMF were purified and dried according to standard procedures.[7] Hydrogen gas was purchased from Linde and used without further purification. The small-angle X-ray diffractograms were measured on a Siemens Kristallflex D-500 diffractometer (beam divergence 0.3), equipped with a hot stage. Cu-Kα radiation was selected by a graphite crystal monochromator. All samples were heated to measurement temperature and kept at this temperature for 30 min prior to measurement (measurement time ~2 h).

Synthesis

3,9- and 3,10-Dialkylperylenes (1 : 1 isomeric mixture). The different 3,9(10)-dialkylperylenes were prepared according to our recently published procedure: 'New synthetic routes to alkyl-substituted and functionalized perylenes'.[4]

***N*-Heptadecyltriazoline-3,5-dione (6).** Heptadecyltriazolinedione **6** was obtained in a five-step reaction starting from stearic acid employing the procedure described by Saville.[8]

Synthesis of P*x*-*y* (1)

4,4′-Dibromo-1,1′-binaphthyl (3). 10 g Thallium trifluoroacetate and 7.6 g 1-bromonaphthalene were dissolved in 150 ml trifluoroacetic acid and stirred at room temperature for 3 h. The color of the reaction mixture gradually turned from deep purple to gray and the product precipitated. After addition of 150 ml of water the crude product was filtered through a Büchner funnel, dried under vacuum, recrystallized from dioxane and chromatographed over a short column (silica gel–petroleum ether) The product crystallized as white needles and could be isolated in 38% yield (2.9 g), melting point: 216 °C; ^{1}H-NMR (200 MHz, CDCl$_3$): $\delta=8.36$–8.32 (d; 2 H, $^3J=8$ Hz, 2 Ar-H), 7.99–7.95 (d; 2 H, $^3J=8$ Hz, 2 Ar-H), 7.57–7.53 (m; 2 H, 2 Ar-H), 7.35–7.24 (m; 6 H, 6 Ar-H); ^{13}C-NMR

(50 MHz, $CDCl_3$): $\delta = 137.72$, 133.90, 132.02, 129.49, 128.20, 127.90, 127.51, 123.00. FD-MS (8 kV): *m*/*z* = 410.00 (100%) [M^+].

4,4′-Di(*n*-hexyl)-1,1′-binaphthyl (4). 8.0 g (12.1 mmol) 4,4′-Dibromo-1,1′-binaphthyl (**3**) and 200 mg Ni(dppe)Cl_2 (dppe = diphenylphosphinoethane) were suspended in 50 ml of dry ether under an argon atmosphere. 9.16 g (48.40 mmol) Butylmagnesium bromide in 20 ml ether were added at room temperature with a syringe through a septum. The reaction mixture was stirred at room temperature until it began to reflux spontaneously. When the solution started to cool it was heated to reflux for 18 h. The cooled reaction mixture was hydrolyzed by addition of 5 ml of methanol. The solvent was evaporated and the crude product dried under vacuum and purified by chromatography with silica gel and pentane as eluent. The yield was 7.95 g (93%) of white crystals, mp: 56 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.17$–8.14 (d; 2 H, $^3J = 8$ Hz, 2 Ar-H), 7.60–7.41 (m; 8 H, 8 Ar-H), 7.36–7.21 (m; 2 H, 2 Ar-H), 3.21–3.08 (t; 4 H, $^3J = 7$ Hz, 2 Ar-CH_2), 1.98–1.80 (m; 4 H, 2 Ar-CH_2-CH_2), 1.56–1.30 (m; 12 H, 6 CH_2), 0.99–0.85 (t; 6 H, $^3J = 7$ Hz, 2 CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta =$ 139.22, 137.64, 133.99, 132.52, 128.20, 128.11, 126.00, 125.92, 125.86, 124.55, 33.81, 32.74, 31.24, 30.09, 23.66, 14.70. IR: $\tilde{\nu} =$ 2961, 1379, 849, 763 cm^{-1}. FD-MS (8 kV): *m*/*z* = 422.68 [M^+].

3,10-Di(*n*-hexyl)perylene (5). 2 g (4.7 mmol) 4,4′-Bis-*n*-hexyl-1,1′-binaphthyl (**4**) were dissolved in 50 ml dimethoxyethane (DME) (dried over potassium) under an argon atmosphere. 2 g potassium was added in small pieces in an argon stream. The reaction mixture was stirred in the dark at room temperature for 2 days and monitored by thin layer chromatography. After completion of the reaction the excess potassium was removed carefully and the solution was stirred under an oxygen atmosphere for 1 day. The color changed from deep blue to orange indicating the oxidation of the perylene anions. The DME was removed by distillation and the crude product purified by column chromatography (silica gel–CH_2Cl_2), mp: 131 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.19$–8.17 (d; 2 H, $^3J = 8$ Hz, 2 Ar-H), 8.08–8.05 (d; 2 H, $^3J = 8$ Hz, 2 Ar-H), 7.87–7.84 (d; 2 H, $^3J = 8$ Hz, 2 Ar-H), 7.51–7.45 (dd; 2 H, $^3J = 8$ Hz, 2 Ar-H), 7.31–7.29 (d; 2 H, $^3J = 8$ Hz, 2 Ar-H), 3.01–2.96 (t; 4 H, $^3J = 7$ Hz, 2 Ar-CH_2), 1.80–1.70 (m; 4 H, 2 Ar-CH_2-CH_2), 1.50–1.32 (m; 12 H, 6 CH_2), 0.92–0.87 (t; 6 H, $^3J = 7$ Hz, 2 CH_3). ^{13}C-NMR (75 MHz, d_8-THF): $\delta =$ 138.32, 132.91, 131.94, 129.57, 128.77, 126.62, 126.05, 123.57, 119.83, 33.24, 31.66, 30.45, 29.40, 22.54, 13.95. UV (Dioxan): λ_{max} (ε) = 451nm (16595), 423nm (12882), 401 nm (5754). FD-MS (8 kV): *m*/*z* = 420.52 (100%) [M^+].

Twofold Diels–Alder reaction of the dialkylperylenes 5 or 9 with *N*-heptadecyltriazolinedione 6 (Method A). 250 mg of dialkyl substituted perylene derivative **5** or **9** were dissolved in 25 ml of *m*-xylene and heated to reflux. A fourfold excess of *N*-heptadecyltriazolinedione **6** was added to the solution in small portions and the reaction monitored by thin layer chromatography until the starting material (yellow) and the monoadduct (red) vanished. When the reaction was completed the hot solution was poured into 200 ml of methanol. The precipitate was collected by filtration, redissolved in dichloromethane and added dropwise to hot ethanol. The hot solution was filtered and the product isolated as a blue solid which was further purified by chromatography over silica gel with dichloromethane as eluent.

P6–17 (1b). Synthesis was performed using Method A: 250 mg (0.60 mmol) 3,10-di(*n*-hexyl)perylene and 1.2 g (3.57 mmol) *N*-heptadecyltriazolinedione (**6**) yielded 615 mg (94%) of the deep blue product. DSC: $T_m = 76$ °C, $T_i = 245$ °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): $\delta = 8.04$–8.02 (d; 2 H, $^3J = 8.8$ Hz, 2 Ar-H), 7.97 (s, 2 H, 2 Ar-H), 7.40–7.10 (m; 2 H, 2 Ar-H), 3.72–3.65 (t; 4 H, $^3J = 6.7$ Hz, CH_2-N), 2.72–2.55 (m; 4 H, 2 Ar-CH_2), 1.82–1.78 (m; 4 H, 2 CH_2), 1.70–1.63 (m; 4 H, 2 CH_2), 1.55–1.18 (m; 68 H, 34 CH_2), 0.92–0.81 (m; 12 H, 4 CH_3). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 110 °C): $\delta =$ 145.02, 144.98, 144.48, 141.18, 129.98, 129.83, 126.39, 125.02, 124.96, 113.82, 113.70, 113.15, 110.98, 41.33, 40.50, 32.86, 32.20, 32.09, 29.93, 29.53, 29.16, 28.10, 28.03, 27.59, 27.17, 27.13, 26.70, 22.83, 22.69, 13.93. UV (CH_2Cl_2): λ_{max} (ε) = 585 nm (11252), 539 nm (8542), 503 nm (4465). FD-MS (8 kV): *m*/*z* = 1091.00 (100%) [M^+].

Synthesis of the Pi*x*–*y* compounds

Pi5–17 (10a). Synthesis was performed using Method A: 250 mg (0.63 mmol) 3,9(10)-di(*n*-pentyl)perylene (**9a**) and 1.3 g (3.85 mmol) *N*-heptadecyltriazolinedione (**6**) yielded 630 mg (94%) of the deep blue product. DSC: $T_m = 47$ °C, $T_i =$ 238 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): $\delta = 8.21$–8.16 (m; 2 H, 2 Ar-H), 8.10 (s, 2 H, 2 Ar-H), 7.47–7.40 (m; 2 H, 2 Ar-H), 3.71–3.66 (t; 4 H, $^3J = 6.7$ Hz, CH_2-N), 2.70–2.55 (m; 4 H, 2 Ar-CH_2), 1.78–1.76 (m; 4 H, 2 CH_2), 1.63–1.60 (m; 4 H, 2 CH_2), 1.50–1.15 (m; 64 H, 32 CH_2), 0.89–0.86 (m; 12 H, 4 CH_3). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 110 °C): $\delta =$ 144.69, 144.63, 144.51, 141.10, 130.01, 129.80, 126.43, 125.01, 124.93, 113.83, 113.67, 113.13, 110.89, 41.23, 40.12, 32.87, 32.21, 32.11, 29.90, 29.51, 29.15, 28.10, 27.98, 27.58, 27.17, 27.12, 26.70, 22.83, 22.71, 14.23. UV (CH_2Cl_2): λ_{max} (ε) = 585 nm (10593), 539 nm (8912), 503 nm (3876). FD-MS (8 kV): *m*/*z* = 1063.0 (100%) [M^+].

Pi6–17 (10b). Synthesis was performed using Method A: 250 mg (0.60 mmol) 3,9(10)-di(*n*-hexyl)perylene (**9b**) and 1.2 g (3.57 mmol) *N*-heptadecyltriazolinedione (**6**) yielded 620 mg (95%) of the deep blue product. DSC: $T_m = 32$ °C, $T_i =$ 243 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): $\delta = 8.03$–8.01 (d; 2 H, $^3J = 8.8$ Hz, 2 Ar-H), 7.96 (s, 2 H, 2 Ar-H), 7.50–7.20 (m; 2 H, 2 Ar-H), 3.71–3.66 (t; 4 H, $^3J = 6.7$ Hz, CH_2-N), 2.69–2.55 (m; 4 H, 2 Ar-CH_2), 1.83–1.78 (m; 4 H, 2 CH_2), 1.70–1.65 (m; 4 H, 2 CH_2), 1.56–1.18 (m; 68 H, 34 CH_2), 0.91–0.83 (m; 12 H, 4 CH_3). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 110 °C): $\delta = 145.01$, 144.93, 144.21, 141.20, 129.98, 129.80, 126.35, 125.01, 124.93, 113.80, 113.72, 113.13, 110.89, 41.30, 40.10, 32.81, 32.19, 32.01, 29.91, 29.52, 29.16, 28.10, 28.02, 27.58, 27.15, 26.99, 26.68, 22.81, 22.70, 13.90. UV (CH_2Cl_2): λ_{max} (ε) = 585 nm (10903), 539 nm (8937), 503 nm (4003). FD-MS (8 kV): *m*/*z* = 1091.20 (100%) [M^+].

Pi8–17 (10c). Synthesis was performed using Method A: 250 mg (0.52 mmol) 3,9(10)-di(*n*-octyl)perylene (**9c**) and 1.06 g (3.14 mmol) *N*-heptadecyltriazolinedione (**6**) yielded 560 mg (94%) of the deep blue product. DSC: $T_m = 29$ °C, $T_i =$ 287 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): $\delta = 8.20$–8.15 (m; 2 H, 2 Ar-H), 8.09 (s, 2 H, 2 Ar-H), 7.48–7.40 (m; 2 H, 2 Ar-H), 3.71–3.65 (t; 4 H, $^3J = 6.7$ Hz, 2 CH_2-N), 2.82–2.70 (m; 4 H, 2 Ar-CH_2), 1.81–1.71 (m; 4 H, 2 CH_2), 1.70–1.59 (m; 4 H, 2 CH_2), 1.45–1.18 (m; 76 H, 38 CH_2), 0.90–0.78 (m; 12 H, 4 CH_3). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 110 °C): $\delta =$ 144.98, 144.96, 144.47, 141.21, 130.01, 129.97, 129.85, 126.38, 126.36, 125.02, 124.98, 113.81, 113.72, 113.13, 110.91, 41.32, 40.18, 32.85, 32.18, 32.07, 29.96, 29.87, 29.53, 29.38, 29.16, 28.13, 28.08, 27.63, 27.45, 27.16, 26.73, 22.85, 22.78, 22.70, 14.03. UV (CH_2Cl_2): λ_{max} (ε) = 585 nm (10102), 539 nm (8946), 503 nm (4203). FD-MS (8 kV): *m*/*z* = 1146.5 (100%) [M^+].

Pi12–17 (10d). Synthesis was performed using Method A: 250 mg (0.42 mmol) 3,9(10)-di(*n*-dodecyl)perylene (**9d**) and 0.86 g (2.55 mmol) *N*-heptadecyltriazolinedione (**6**) yielded 492 mg (93%) of the deep blue product. DSC: $T_m = 14$ °C, $T_i =$

320 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 110 °C): $\delta = 8.10$–8.00 (m; 2 H, 2 Ar-H), 8.00 (s, 2 H, 2 Ar-H), 7.35–7.10 (broad; 2 H, 2 Ar-H), 3.71–3.68 (t; 4 H, $^3J = 8$ Hz, 2 CH_2-N), 2.65 (broad; 4 H, 2 Ar-CH_2), 1.82–1.78 (t; 4 H, $^3J = 8$ Hz, 2 CH_2), 1.64–1.60 (t; 4 H, $^3J = 7$ Hz, 2 CH_2), 1.48–1.22 (m; 92 H, 46 CH_2), 0.89–0.86 (t; 12 H, $^3J = 6$ Hz, 4 CH_3). UV (Dioxan): λ_{max} (ε) = 585 nm (11165), 539 nm (9034), 503 nm (4235). FD-MS (8 kV): $m/z = 1259.00$ (100%) [M^+].

References

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