

# A Sustainable Preparation of Functional Perylenophanes by Domino Metathesis

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# Abstract

A sustainable four-step synthesis of soluble perylenophanes for applications as fluorescent optical functional materials is presented and even allows upscaling because of starting with technical bulk products. Thus, terminal alkenylnitriles were alkylated reduced to amines, condensed with perylenetetracarboxylic bisanhydride and cyclised to cyclophanes by means of double cross metathesis in yields until 69% of isolated dyes. The first metathesis by means of the second-generation Hoveyda-Grubbs-catalyst brings the remaining reactive olefinic groups close together favouring the ring-closure to the cyclophanes where the locked neighboring of chromophores in a skew arrangement induce strong exciton interactions. The latter cause an increased the Stokes' separation by means of a moderate hypsochromic shift of light absorption and a stronger bathochromic shift of fluorescence. Various applications such as for lasers, photonics, solar collectors or in analytics are discussed.

# **Keywords**

Optical Materials, Functional Dyes, Fluorescence, Exciton Interaction, Metathesis

# **1. Introduction**

The interaction of two or more chromophores offers many possibilities for modern optoelectronics [1] and functional materials because various optical effects can be generated where the perylene dyes [2] such as 1 [3] and other *peri*-arylenes [4] are suitable components because of their high chemical and photochemical stability and fluorescence quantum yields. Moreover, one single optical transition of these chromophores in the visible spectral region favors the planning, construction and operation of functional multichromophoric assemblies. The elec-

tronic interaction of two chromophores induces spectral shifts of the initial absorption to two new positions known as the Davydov splitting [5] [6]. Thus, a more bathochromic  $\alpha$ -transition and a more hypsochromic  $\beta$ -transition are obtained instead of the light absorption of the individual chromophores; see Figure 1, left.

There are two fundamental arrangements of the transition moments of two or more chromophores with (i) coplanarity known as *H*-orientation [7] according to the initially described hypsochromically absorbing aggregates and (ii) linear shift known as *J*-arrangement [8]; see **Figure 1**, right.

The *H*-orientation induces an *anti*-synchronous electron movement according to Förster's analysis [9] because of Coulomb interactions; this is schematically indicated in **Figure 1** with an arbitrary flashlight distribution of charges. The electrostatic interactions remain still somewhat disfavorable because the comparably short distance of equal charges; thus, the transition energy of the individual chromophores increases for the *H* orientation and causes a hypsochromic shift of light absorption. The *H*-arrangement lowers the molar absorptivity because of an effective shortening the compact molecular antenna for two chromophores. Moreover, the point symmetry compensates the transition moment and thus, suppresses fluorescence. The *J*-arrangement with linearly shifted chromophores induces a synchronous electron movement with more favorable attractive Coulomb interactions, lowers the transition energy, causes a bathochromic shift, increases the molar absorptivity because the extended antenna and allows fluorescence.

A skew-type arrangement of chromophores activates both transitions so that



**Figure 1.** Left: Energy levels of two interacting chromophores and resulting Davydov splitting in the middle with the resulting electronic *a* and  $\beta$  transitions. Middle: Basic orientations of transition moments, coplanar in *H* (bottom,  $\beta$ ) and linearly shifted in *J* arrangements (top, *a*). Indication of a momentaneous charge distribution by "+" and "–". Right: Formula **2**.

the initial absorption of the isolated chromophores appears to be split in two bands: Davydov splitting. The intensities of the individual bands depend from the exact orientation of the transition moments of the involved chromophores.

Aggregates such as H and J arrangement of chromophores are only weakly held together by non-covalent interactions and are labile concerning dissociation such as with dilution. A higher stability can be obtained with covalently linked chromophores, preferently forming cyclophanes such as 2 [10]. However, synthesis of such cyclophanes proved to be complicated for complex chromophores and upscaling of 2 is difficult because of simultaneous and stoichiometric addition of two solids under dilution conditions. Moreover, the limited solubility of 2 means an obstacle for applications in homogeneous media. An efficient method for the preparation of such cyclophanes with increased solubility would bring about appreciable progress.

#### 2. Results and Discussions

Here we applied olefin metathesis [11] [12] [13] [14] [15] for the efficient, economic and sustainable synthesis of bichromophoric perylenetetracarboxylic bisimides dyes (dyads) because of catalysed carbon-carbon linking where special optic effects are expected as a consequence of the interacting chromophores in such molecules. Firstly, we studied the linking of simple alkylene-substituted perylene carboxamides by metathesis; however, the generally very low solubility of perylenebiscarboximides means an obstacle for such bimolecular reactions. Thus, we introduced solubility-increasing groups and firstly attached the 2,5-di-*tert*-butyl substituent [2] to one nitrogen atom of perylenbiscarboximide and an allyl group as the terminal olefine to the other; the nitrogen atoms form ideal positions for the ring-formation because of orbital nodes [16] in HOMO and LUMO causing an electronic decoupling of substituents at these positions. However, metathesis with second-generation Hoveyda-Grupps-catalyst (4) [17] gave only low yields of a few percents. Obviously, the solubility of the staring material is still too low for efficient coupling.



As a consequence, we introduced the more efficiently solubilising 7-tridecyl group in **3** and obtained 10% of the dyad **5** as a *cis/trans* mixture as was also found for all other products of metathesis (only the *trans* isomer of **5** is shown).



The analogous coupling of the 4-vinylphenyl derivative **6** for the generation of the more rigid stilbene as the spacer gave higher yields; however, a sparingly soluble pigment-like material **7** was obtained with limited use for investigation and application in homogeneous solution. A prolongation of the swallow-tail substituents to octylnonyl (**6a** and **7a**) and further to nonyldecyl (**6b** and **7b**) did not sufficiently improve the solubility. Furthermore, we introduced geminal alkyl



Figure 2. X-ray crystal structure analyses. Left: The starting material 14 for 15 and 16 (kn237). Right: The starting material 21 for 22 (kn095).

groups [18] in 8 into the linker between the two chromophores and an even longer chain in 10 and could improve the solubility by the prolongation of the interlinking chain in 9 and 11, respectively; however, such compounds exhibit

an unexpected and for 11 even more pronounced tendency of the degradation of the central connecting chain as a consequence of the contact to air. Resuming, the coupling of the simple allyl derivative **3** with a 7-tridecyl group at one nitrogen atom gave best results and indicates that metathesis is generally applicable for the synthesis of dyads. As a consequence, we investigated ring-closing metathesis because of higher proximity of the reacting olefinic groups.

Thus, we firstly connected in 12 two chromophores with an N-hydroxyethyl group by means of etherification in a one-pot reaction with methanesulphonic acid chloride. The nitrogen atoms at the opposite sides of the chromophores were attached to terminal olefinic alkyl groups where geminal alkyl substituents were applied for solubility increasing. Ring-closing metathesis to 13 was realised by means of second-generation Hoveyda-Grupps-catalyst (4); however, the solubility of the material was still comparably restrainingly low. Moreover, two steps with moderate yields were necessary for the preparation of a cyclophane. For further improvement, we targeted two consecutive metatheses as a Domino reaction in one pot and replaced the hydroxyethyl group in the starting material for 13 by an allyl group in 14; for structural details see Figure 2, left. However, a direct metathesis gave a complex mixture of products containing 15 and 16 both as *cis/trans* mixtures. As a consequence, we allowed to react the symmetrically substituted perylene dyes 17, 19 and 21 with  $N_{N}$ -2-butyl-2- $\omega$ -alkenylpentyl groups in metathesis with 4 and obtained the corresponding for applications sufficiently soluble cyclophanes 18, 20 and 22 as cis/ trans mixtures with very similar properties; for structural details of the starting material 21 for 22, see Figure 2, right. Comparably satisfying yields of cyclophanes were obtained as high as 69% of 22. No polymeric material could be detected indicating the favoring of the second metathesis as a consequence of the neighbourship of the chromophores after the first metathesis.





The yields of isolated pure material of such Domino reactions increase with the flexibility of the generated cyclophanes where 50% were obtained for the compact **18**, 57% for **20** with a larger mash and even 69% for **22** with a still larger ring. A prolongation of the alkyl chains in the swallow-tail system or a replacement by *iso*-propyl groups appreciably decreases the yields of cyclophanes presumably caused by a less compact arrangement for the second and ring-closing metathesis as a Domino reaction. Resuming, the cyclophanes **18**, **20**, and **22** are preferred for special optical applications. As a consequence, a sustainable, efficient, economic and upscalable access to the starting materials **23** for metathesis would bring about further progress.

Thus, we started synthesis with the alkylation [19] of  $\omega$ -akenyl nitriles with 1-iodobutane by means of LDA (lithium diisopropylamide) in a laboratory synthesis according to **Figure 3**; an efficient upscaling is possible applying alkyl bromides with sodium and sodium amide, respectively, in liquid ammonia according to Ref. [20] in a solvent-recycling chain of batches [21]. The alkylated nitrile was reduced with complex hydrides such as lithium aluminiumhydride or even catalytic with hydrogen to the primary amine and the latter condensed with the technical mass product perylene-3,4:9,10-tertacarboxylicbisahydride in melt imidazole [22] [23] with the addition of zinc acetate to obtain **23** with n = 1, 2 and 3.

Special optic effects [9] are expected as a consequence of the interaction of chromophores [24] in the dyads (bichromophores). However, the UV/Vis spectra of the open-chain dyad 5 are nearly identic with the spectra of 1 (Figure 4, left spectrum, red and green curves). Obviously, the long distance of the individual chromophores allows only slight exciton interactions [25]. Thus, a more tight arrangement of the chromophores was targeted for stronger interactions. Two chromophores linked with an ether group and tied close together by ring-closing



**Figure 3.** Synthesis of the starting materials for metathesis: **23**, n = 1 until 3 by means of alkylation of terminal alkenyl nitriles, reduction and condensation. i) C<sub>4</sub>H<sub>9</sub>I, LDA; ii) LiAlH<sub>4</sub>; iii) Perylene-3,4:9,10-tetracarboxylicbisanhydride, zinc acetate, imidazole.



**Figure 4.** Left spectrum: UV/Vis absorption (left) and fluorescence (right) spectra in chloroform. Green curves: **5**, red cuves: **1** for comparison. Right spectrum: UV/Vis absorption (left, magenta) and fluorescence (right, blue) spectra of **13** in chloroform.

metathesis in the cyclophane 13 form a skew arrangement where there are optical transitions with a major H-component (hypsochromic  $\beta$  transition) and a minor J-component (bathochromic a transition); compare Ref. [26] for similar arrangements in micelles. As a consequence, the more hypsochromically absorbing  $\beta$  transition dominates the absorption spectrum (Figure 4, right spectrum, magenta curve, left, more hypsochromic compared with the red curve of 1 in the left spectrum); however, fluorescence is suppressed because of symmetry according to Förster's [9] analysis. On the other hand, the minor J-component with more bathochromic transitions allows fluorescence and causes the broad fluorescence spectrum at longer wavelengths shown in Figure 4 (right spectrum, blue curve, right). Overall, the Stokes' shift of **13** is increased compared with **1**; however, the still comparably low solubility of 13 means still an obstacle for many optoelectronic applications. Moreover, the two-step ring-closure is unfavorable for the overall yield. As a consequence the products 15 and 16 of a double one pot metathesis (domino metathesis) both as mistures of cis/trans isomers were investigated as an alternative.

15 and 16 could be separated by means of preparative T.L.C. and gave the surprising result of nearly identic UV/Vis absorption and fluorescence spectra although the chomophore-linking chains are different; see Figure 5, left spectrum. Moreover, the spectra resemble 13 both in absorption and fluorescence. Thus, a similar arrangement of the chromophores in 13, 15 and 16 seems to be induced by their interactions for sufficiently flexible ring chains. The solubility of 15 and 16 is still comparably low and the side chains of the compounds slowly degrade in solution by the contact with air. As a consequence, further investigations were focused on the well-accessible compounds 18, 20, and 22 where four geminal alkyl groups are more efficiently solubilising. The UV/Vis absorption spectra of 18, 20 and 22 are similar to 2 and all are hypsochromically shifted compared with 1; Figure 5, right spectrum. The shapes are typical of perylenes in *H*-arrangements such as the cyclophanes 2 and 13 and indicate the domination of this component for light absorption. The comparably strong fluorescence of 18, 20 and 22 are attributed to the *J* component of the skew arrangement



**Figure 5.** Left spectrum: UV/Vis absorption (left) and fluorescence (right) spectra in chloroform. Red curves: **15**, green curves: **16**. Right spectrum: UV/Vis absorption (left) and fluorescence (right) spectra in chloroform, *E* and *I* normalised to 2. Red curves: **18**, green curves: **20**, blue curves: **22** and yellow curves normalised to 1: **1** for comparison.

of the chromophores; this is allowed according to Förster's analysis, whereas the *H* transition is suppressed because of symmetry. As a consequence, the *H* transition dominates concerning light absorption and the energy of excitation is intramolecularly transferred to the J transition for emission resulting in an increased Stokes' shift; the latter exhibits an alternating behaviour with the lengths of the chromophores-connecting chains. A very large Stokes' shift is obtained for 18 with a fluorescence maximum at 637.0 nm, a medium large shift for 20 at 582.8 nm and again a very large shift for 22 at 638.3 nm. Thus, two different main types of stable arrangements of chromophores seem to be reached for 18 and 22 and some other for 20. Further discussions are concentrated to the more readily soluble cyclophanes 20 and 22 because of the still comparably low solubility of 18. The high fluorescence quantum yield of 20 and 22 both of nearly 70% in combination with larges Stokes' shifts make these dyads of interest for fluorescence applications where the position of the fluorescence maximum can be controlled by the chain lengths of the connection of the two chromophores. Further stabilisation of the peryleneocyclophanes is possible by catalytic hydrogenation.

# 3. Conclusions

Cyclophanes of perylenebiscarboximides (perylene dyes), firstly described [10] with linear alky spacers, exhibit an increasing interest concerning redox properties [27] [28], photoswitches [29], guest host detectors and triplet generators [30] and detectors for aromatics [31] where comparably complicated starting materials and the necessary dilution principle for preparation [32] [33] mean obstacles for synthesis, upscaling and applications. The here described efficient and sustainable preparation of perylenocyclophanes in particular **20** and **22** from versatile terminal olefinic nitriles, alkylation and reduction with bulk reagents, condensation with the mass product perylene tetracarbocylic bisanhydride and subsequent ring-closing metathesis allows not only efficient synthesis but also technical upscaling so that applications as fluorescent dyes with large Stokes' shift such as for solar collectors [34] [35] [36] become feasible.

#### 4. Experimental

#### 4.1. Spectroscopy

IR spectra: Perkin Elmer 1420 Ratio Recording Infrared Spektrometer, FT 1000; UV/Vis spectra: Varian Cary 5000 and Bruins Omega 20; fluorescence spectra: Perkin Elmer FS 3000 (totally corrected); CD spectroscopy: Jasco J810 Spectropolarimeter, spectral bandwidth 0.5 nm, integration time 0.5 and 1 s, data interval 0.2 nm; NMR spectroscopy: Varian Vnmrs 600 (600 MHz); mass spectrometry: Finnigan MAT 95. Crystal structures: The data for **kn095** and **kn237** have been collected at 200 K on a Nonius Kappa CCD equipped with a graded multilayered X-ray optics mirror (MoK $\alpha$  radiation). The structures have been solved with SHELXS and refined with SHELXL [36]. The hydrogen atoms have been added in ideal geometry riding on their parent atoms. In kn237, the disorder in a side chain has been described by a split model. All split atoms have been refined isotropically. The ratio of the site occupation factors refined to 0.69/0.31. The figure shows the main part only. The data have been deposited with the CCDC and can be obtained free of charge via

<u>https://www.ccdc.cam.ac.uk/structures/</u>: **kn095** CCDC 1900229 (2,9-bis-(2,2-dibutylhept-6-enyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquinline-1,3,8,10-tetraone), **kn237** CCDC 1900230 (2-allyl-9-(2,2-dibutylhept-6-enyl)anthra[2,1,9-*def*; 6,5,10-*d'e'f*]-diisoquinoline-1,3,8,10-tetraone). Figures are created with ORTEP [37] at the 50% ellipsoid prabability level.

#### 4.2. Chemicals

Imidazole (RN 288-32-4) and perylene-3,4:9,10-tetracarboxylic bisanhydride (RN 128-69-8) were ordered from BASF. Perylene-3,4,9,10-tetracarboxylic-3, 4-anhydride-9,10-(1-hexylheptylimide) was prepared according to the literature [38].

**2,2-Dibutylhex-5-enenitrile** [39]: Diisopropylamine (6.89 mL, 9.48 mmol) in anhydrous THF (45 mL) under argon atmosphere at 0°C was subsequently treated dropwise with a solution of 2.5 m 1-butyllithium in hexane (37.9 mL, 94.8 mmol), 5-hexenenitrile (5.00 mL, 43.1 mmol) and 1-iodobutane (10.8 mL, 94.8 mmol) in anhydrous THF (40 mL, tetrahydrofurane), stirred at 0°C for 2 h, allowed to warm at room temperature, stirred for 16 h, cautiously hydrolysed (100 mL distilled water), extracted with diethylether, washed with distilled water (100 mL), saturated brine (50 mL) and 2 N aqueous HCl (50 mL), dried with magnesiumsulphate and distilled. Yield 5.25 g (59%), b.p. 71°C/1.6·10<sup>-2</sup> mbar,  $n_D^{20} = 1.376$ . IR (KBr):  $\tilde{v} = 3079.9$  w, 2957.9 vs, 2937.4 vs, 2864.3 vs, 2230.9 w, 1833.0 w, 1728.7 w, 1642.4 m, 1467.8 m, 1458.4 m, 1417.4 w, 1381.1 w, 1342.9 w, 1302.3 w, 1265.2 w, 1159.0 w, 1106.3 w, 993.3 w, 913.0 m, 731.9 w, 646.2 w, 557.1 cm<sup>-1</sup> w. <sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.86$  (*t*, 1 H, <sup>3</sup>*J* = 7.1 Hz), 1.29 (m, 6 H,

6 CH<sub>2</sub>), 1.52 (m, 8 H, 4 CH<sub>2</sub>), 2.08 (m, 2 H, CH<sub>2</sub>), 4.91 (m, 1 H, R = CH<sub>2</sub>), 4.98 (m, 1 H, R = CH<sub>2</sub>), 5.72 ppm (m, 1 H, CH). <sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.5, 22.5, 28.3, 35.0, 35.4, 40.0 (C<sub>quart.</sub>), 114.9 (CH<sub>2</sub> olefin.), 123.3 (CN), 136.8 ppm (CH<sub>2</sub> olefin.). MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 208 (5) [*M*<sup>+</sup> + H], 153 (24) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>7</sub>], 151 (28) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>], 110 (100) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>5</sub> - C<sub>4</sub>H<sub>9</sub>], 97 (67) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>] - C<sub>4</sub>H<sub>7</sub>].

2-But-3-envl-2-hexyloctanenitrile: Diisopropylamine (2.6 mL, 90 mmol) in anhydrous THF (40 mL) was allowed to react with a solution of 1-butyllithium (36.0 mL, 90.0 mmol, 2.5 m), 5-hexenenitrile (4.70 mL, 40.9 mmol) and 1-iodohexane (13.3 mL, 90.0 mmol) in anhydrous THF (40 mL) according to 2,2-dibutylhex-5enenitrile. Yield 7.94 g (73%) colorless oil, b.p.  $100^{\circ}$ C- $102^{\circ}$ C/ $1 \times 10^{-3}$  mbar,  $n_{D}^{20}$ = 1.454. IR (KBr):  $\tilde{v}$  = 3079.6 w, 2931.2 vs, 2859.9 vs, 2230.6 w, 1826.5 w, 1730.3 w, 1642.3 m, 1459.0 m, 1416.7 w, 1379.0 w, 1303.8 w, 1078.1 w, 993.6 w, 912.9 m, 759.9 w, 724.6 w, 648.0 w, 556.0 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.89$  (t, 6 H,  ${}^{3}J_{H,H} = 6.8$  Hz, 2 CH<sub>3</sub>), 1.29-1.41 (m, 16 H, 8 CH<sub>2</sub>), 1.52 -1.65 (m, 6 H, 3 CH<sub>2</sub>), 2.11-2.20 (m, 2 H, CH<sub>2</sub>), 4.97-5.09 (m, 2 H, CH<sub>2, olefin</sub>), 5.73 - 5.84 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.0, 22.5, 24.2, 28.7, 29.3, 31.5, 35.3, 36.1, 40.4 (C<sub>quart</sub>), 115.3 (CH<sub>2, olefin</sub>), 124.0 (CN), 137.6 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) m/z (%): 264 (4) [M<sup>+</sup> + H], 263 (4) [M<sup>+</sup>], 262 (5)  $[M^{\dagger} - H]$ , 206 (22)  $[M^{\dagger} - C_4 H_9]$ , 192 (21)  $[M^{\dagger} - C_5 H_{11}]$ , 179 (43)  $[M^{\dagger} - C_5 H_{11}]$  $C_6H_{13}$ ], 138 (100)  $[M^+ - C_6H_{13} - C_3H_5]$ , 125 (35)  $[M^+ - C_6H_{13} - C_4H_7]$ , 97 (26)  $[M^{+} - 2 \times C_{6}H_{13}], 55 (17) [C_{4}H_{9}].$ 

**2-But-3-enyl-2-octyldecanenitrile:** Diisopropylamine (12.7 mL 90.2 mmol) in anhydrous THF (45 mL), a solution of 1-butyllithium (36.1 mL, 90.2 mmol, 2.5 m); 5-hexenenitrile (4.76 ml, 41.0 mmol) and 1-iodoctane (22.3 ml, 133 mmol; 3 eq.) in anhydrous THF (50 mL) were allowed to react according to 2,2-dibutylhex-5-enenitrile. Yield 10.7 g (82%) light yelowish, viscous oil, b.p. 140°C-144°C/1 × 10<sup>-3</sup> mbar,  $n_D^{20} = 1.457$ . - IR (KBr):  $\tilde{\nu} = 3079.7$  w, 2926.9 vs, 2856.0 s, 2230.9 w, 1731.3 w, 1642.5 w, 1465.6 m, 1378.3 w, 1157.5 w, 1071.5 w, 992.3 w, 912.6 w, 711.4 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.89$  (t,  ${}^{3}J_{\rm H,H} = 6.9$  Hz, 6 H, 2 CH<sub>3</sub>), 1.28 - 1.31 (m, 20 H, 10 CH<sub>2</sub>), 1.40 - 1.41 (m, 4 H, 2 CH<sub>2</sub>), 1.54 - 1.58 (m, 4 H, 2 CH<sub>2</sub>), 1.62 - 1.65 (m, 2 H, CH<sub>2</sub>), 2.15 - 2.18 (m, 2 H, CH<sub>2</sub>), 4.99 - 5.01 (m, 2 H, CH<sub>2, olefin.</sub>), 5.77 - 5.84 ppm (m, 1 H, CH<sub>olefin.</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 14.0$ , 22.5, 24.1, 29.1, 29.3, 29.6, 31.7, 35.3, 36.0, 40.4 (C<sub>quart.</sub>), 115.2 (CH<sub>2, olefin.</sub>), 123.9 (CN), 137.1 ppm (CH<sub>olefin.</sub>). MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 318 (4) [*M*<sup>+</sup> - H], 207 (46) [*M*<sup>+</sup> - C<sub>8</sub>H<sub>17</sub>], 166 (100) [*M*<sup>+</sup> - C<sub>8</sub>H<sub>17</sub> -C<sub>3</sub>H<sub>5</sub>], 95 (15) [*M*<sup>+</sup> - 2 × C<sub>8</sub>H<sub>17</sub>], 55 (60) [*M*<sup>+</sup> - 2 × C<sub>8</sub>H<sub>17</sub> - C<sub>3</sub>H<sub>5</sub>].

**2-Butyl-2-vinylhexanenitrile:** Diisopropylamine (11.5 mL, 82.1 mmol) in anhydrous THF (40 mL), a solution of 1-butyllithium (32.8 mL, 82.1 mmol, 2.5 m), allylcyanide (2.50 g, 37.3 mmol) and 1-iodobutane (9.34 mL, 82.1 mmol) in anhydrous THF (45 mL) were allowed to react according to 2,2-dibutylhex-5-enenitrile. Yield 1.54 g (23%) colorless liquid, b.p.  $43^{\circ}$ C/8 ×  $10^{-3}$  mbar,  $n_D^{20}$  = 1.441. IR (KBr):  $\tilde{\nu}$  = 3088.0 w, 2959.3 vs, 2936.9 vs, 2864.4 vs,

2237.2 w, 1853.1 w, 1736.3 w, 1639.5 w, 1468.0 m, 1411.5 w, 1381.0 w, 1343.3 w, 1302.5 w, 1260.7 w, 1158.5 w, 1111.7 w, 1066.6 w, 989.5 m, 925.1 m, 785.1 w, 753.2 w, 731.2 w, 695.8 w, 587.5 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.89$  (t,  ${}^{3}J_{\rm H,\rm H} = 7.0$  Hz, 6 H, 2 CH<sub>3</sub>), 1.24 - 1.52 (m, 10 H, 5 CH<sub>2</sub>), 1.63 - 1.73 (m, 2 H, CH<sub>2</sub>), 5.22 - 5.25 (m, 2 H, CH<sub>2</sub>, olefin.), 5.42 - 5.44 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 13.8$ , 22.6, 27.0, 38.6, 46.1 (C<sub>quart.</sub>), 116.5 (CH<sub>2</sub>, olefin.), 121.5 (CN), 137.2 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 180 (4) [*M*<sup>+</sup> + H], 153 (4) [*M*<sup>+</sup> - C<sub>2</sub>H<sub>3</sub>], 136 (5) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>], 123 (100) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>], 108 (37) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub> - C<sub>2</sub>H<sub>3</sub>], 94 (22) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub> - C<sub>2</sub>H<sub>3</sub>], 80 (50) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub> - C<sub>3</sub>H<sub>7</sub>].

**2-Allyl-2-butylhexanenitrile:** Diisopropylamine (15.3 mL, 109 mmol) in anhydrous THF (50 mL), a solution of 1-butyllithium (43.6 mL, 109 mmol), 2.5 m), 4-pentenenitrile (4.90 g, 49.6 mmol) and 1-iodobutane (12.4 mL, 109 mmol) in anhydrous THF (45 mL) were allowed to react according to 2,2-dibutylhex-5-enenitrile. Yield 8.31 g (87%) colorless liquid, b.p.  $62^{\circ}$ C- $64^{\circ}$ C/ $1 \times 10^{-2}$  mbar,  $n_D^{20} = 1.447$ . IR (KBr):  $\tilde{\nu} = 3081.0$  w, 2958.8 vs, 2937 vs, 2864.5 s, 2231.9 w, 1737.5 w, 1642.6 w, 1467.9 m, 1417.8 w, 1381.6 w, 1342.7 w, 994.9 m, 920.8 m, 732.2 w, 565.1 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.92$  (t, <sup>3</sup>*J* = 7.1 Hz, 6 H, 2 CH<sub>3</sub>), 1.28 - 1.46 (m, 8 H, 4 CH<sub>2</sub>), 1.51 - 1.59 (m, 4 H, 2 CH<sub>2</sub>), 2.31 - 2.34 (m, 2 H, CH<sub>2</sub>), 5.13 - 5.21 (m, 2 H, CH<sub>2</sub>), 5.73 - 5.87 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 13.9$ , 22.8, 26.4, 35.7, 40.3, 40.4 (C<sub>quart</sub>), 119.6 (CH<sub>2, olefin</sub>), 123.8 (CN), 131.9 ppm (CH<sub>olefin</sub>). - MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 194 (4) [*M*<sup>\*</sup> + H], 150 (100) [*M*<sup>\*</sup> - C<sub>3</sub>H<sub>7</sub>], 137 (17) [*M*<sup>\*</sup> - C<sub>4</sub>H<sub>9</sub>], 110 (22) [*M*<sup>\*</sup> - C<sub>3</sub>H<sub>5</sub>], 55 (11) [*M*<sup>\*</sup> - C<sub>4</sub>H<sub>9</sub> - C<sub>3</sub>H<sub>7</sub>], 40 (33) [*M*<sup>\*</sup> - 2 × C<sub>4</sub>H<sub>9</sub> - C<sub>3</sub>H<sub>5</sub>].

2,2-Dibutylhept-6-enenitrile: Diisopropylamine (14.1 mL, 101 mmol) in anhydrous THF (45 mL), a solution of 1-butyllithium (40.4 mL, 101 mmol, 2.5 m), 6-heptenenitrile (5.00 g, 45.8 mmol) and 1-iodobutane (11.4 mL, 101 mmol) in anhydrous THF (30 mL) were allowed to react according to 2,2-dibutylhex-5enenitrile. Yield 9.04 g (89%) colorless oil, b.p.  $85^{\circ}$ C/1·10<sup>-3</sup> mbar,  $n_D^{20} = 1.451$ . IR (KBr):  $\tilde{v}$  = 3080.3 w, 2957.2 vs, 2929.9 vs, 2872.0 s, 2860.5 s, 2230.6 w, 1666.3 m, 1636.9 m, 1535.0 w, 1466.5 m, 1414.1 w, 1378.3 w, 1260.9 w, 1235.9 w, 1155.8 w, 1095.9 w, 1003.9 w, 910.5 m, 802.1 w, 729.3 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 0.92 (t, <sup>3</sup>*J* = 7.0 Hz, 6 H, 2 CH<sub>3</sub>), 1.29 - 1.39 (m, 8 H, 4 CH<sub>2</sub>), 1.48 - 1.55 (m, 8 H, 4 CH<sub>2</sub>), 2.07 (q,  ${}^{3}J = 6.5$  Hz, 2 H, CH<sub>2</sub>), 4.95 - 5.05 (m, 2 H, CH<sub>2. olefin.</sub>), 5.71 - 5.84 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 13.8, 22.8, 23.5, 26.3, 33.6, 35.5, 35.8, 40.4 (C<sub>quart</sub>), 115.1 (CH<sub>2. olefin</sub>), 124.2 (CN), 137.8 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) m/z (%): 222 (1) [M<sup>+</sup> - H], 165 (33)  $[M^{+} - C_4H_9]$ , 153 (4)  $(M^{+} - C_5H_9]$ , 122 (100)  $[M^{+} - C_4H_9 - C_3H_7]$ , 110  $(M^{\dagger} - C_5H_9 - C_3H_7], 55 (9) [M^{\dagger} - 2 \times C_4H_9 - C_4H_7], 41 (18) [M^{\dagger} - 2 \times C_4H_9 - C_4H_7]$  $C_{5}H_{0}$ ].

**2,2-Diisopropylbut-3-enenitrile (method 1):** Diisopropylamine (23.1 mL, 164 mmol) in anhydrous THF (50 mL), a solution of 1-butyllithium (65.6 mL, 164 mmol, 2.5 m), allylcyanide (5.00 g, 74.5 mmol) und 2-iodopropane (6.40 mL, 164 mmol) in anhydrous THF (50 mL) were allowed to react according to

2,2-dibutylhex-5-enenitrile. Yield 940 mg (8%) colorless liquid, b.p.  $25^{\circ}$ C- $26^{\circ}$ C/1 ×  $10^{-3}$  mbar (for the further characterisation see **method 2**).

2,2-Diisopropylbut-3-enenitrile (method 2): Lithiumhexamethyldisilazane (100 mL, 0.1 m solution) under argon atmosphere was cooled at 0°C and treated dropwise with stirring within 20 min with a solution of allylcyanide (3.05 g, 45.5 mmol) in anhydrous THF (15 mL) and then with 2-iodopropane (17.0 g, 100 mmol), stirred at 0°C for 90 min, allowed to warm slowly at room temperature, stirred for 16 h, cautiously hydrolised with distilled water (50 mL), treated drop wise with 2 N aqueous HCl (100 mL, strong evolution of foam), extracted with diethylether (3 × 100 mL), dried with magnesiumsulphate, evaporated and distilled. Yield 1.18 g (10%) colorless liquid, b.p. 62 - 63°C/20 mbar,  $n_D^{20} = 1.447$ . IR (KBr):  $\tilde{\nu}$  = 3087.1 w, 2969.3 vs, 2938.0 m, 2878.8 m, 2234.6 w, 1639.9 w, 1466.8 m, 1412.9 w, 1390.9 m, 1375.4 w, 1315.7 w, 1260.2 w, 1203.7 w, 1171.6 w, 1063.5 w, 994.2 m, 925.5 m, 803.0 w, 699.0, 672.0 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ , 25°C):  $\delta = 0.93$  (d,  ${}^{3}J = 6.8$  Hz, 6 H, 2 CH<sub>3</sub>), 1.05 (d,  ${}^{3}J = 6.7$  Hz, 6 H, 2 CH<sub>3</sub>), 2.03 (sept.,  ${}^{3}J$  = 6.8 Hz, 2 H, 2 CH<sub>aliphat</sub>), 5.33 - 5.39 (m, 1 H, CH<sub>olefin</sub>), 5.44 - 5.47 ppm (m, 2 H, CH<sub>2, olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 17.3, 18.4, 31.6, 55.7 (C<sub>quart.</sub>), 118.7 (CH<sub>2, olefin.</sub>), 120.4 (CN), 132.6 ppm (CH<sub>olefin.</sub>). MS  $(\text{DEI}^+/70 \text{ eV}) \ m/z \ (\%): 152 \ (0.2) \ [M^+ + \text{H}], 109 \ (64) \ [M^+ - \text{C}_3\text{H}_7], 94 \ [M^+ - \text{C}_3\text{H}_7]$  $- CH_3$ , 67 (10)  $[M^+ - 2 \times C_3H_7]$ , 41 (13)  $[M^+ - 2 \times C_3H_7 - C_2H_3]$ .

2,2-Diisopropylhex-5-enenitrile: Diisopropylamine (12.7 mL, 90.2 mmol) in anhydrous THF (45 mL), a solution of 1-butyllithium (36.1 mL, 90.2 mmol, 2.5 m), 5-hexenenitrile (3.90 g, 41.0 mmol) and 2-iodopropane (9.00 mL, 90.2 mmol) in anhydrous THF (40 mL) were allowed to react according to 2,2-dibutylhex-5enenitrile. Yield 4.51 g (62%) colorless liquid, b.p. 56°C-58°C/1 × 10<sup>-3</sup> mbar,  $n_D^{20} = 1.455$ . IR (KBr):  $\tilde{v} = 3079.7$  w, 2971.8 vs, 2880.5 m, 2228.7 w, 1736.2 w, 1642.5 m, 1471.0 m, 1417.6 w, 1392.3 m, 1375.9 w, 1309.5 w, 1175.0 w, 1130.7 w, 992.9 w, 913.7 m, 757.9 w, 698.0 w, 617.4 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.97 - 1.00$  (m, 6 H, 2 CH<sub>3</sub>), 1.06 - 1.08 (m, 6 H, 2 CH<sub>3</sub>), 1.51 - 1.58 (m, 2 H, CH<sub>2</sub>), 1.92 - 2.06 (m, 2 H, 2 CH), 2.16 - 2.25 (m, 2 H, CH<sub>2</sub>), 4.94 - 5.09 (m, 2 H, CH<sub>2, olefin</sub>), 5.71 - 5.84 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  = 17.5, 18.8, 29.5, 31.7, 32.6, 49.1 ( $C_{\text{quart.}}$ ), 115.0 ( $\text{CH}_{2, \text{ olefin.}}$ ), 122.2 (CN), 137.3 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 180 (1) [*M*<sup>+</sup> + H], 164 (3)  $[M^{+} - CH_{3}], 137 (5) [M^{+} - C_{3}H_{7}], 122 (8) [M^{+} - C_{3}H_{7} - CH_{3}], 110 (10) [M^{+} - C_{3}H_{7}], 122 (8) [M^{+} - C_{3}H_{7}], 120 (10) [M^{+}$  $C_{3}H_{7} - 2 \times CH_{3}$ ], 96 (100)  $[M^{+} - 2 \times C_{3}H_{7}]$ , 55 (8)  $[M^{+} - 2 \times C_{3}H_{7} - C_{3}H_{5}]$ , 41 (19)  $[M^{\dagger} - C_4 H_7 - 2 \times C_3 H_7].$ 

**2,2-Dibutylhex-5-enylamine:** Lithiumaluminiumhydride (1.54 g, 40.5 mmol) under nitrogen atmosphere was disperged in anhydrous diethylether (110 mL) and treated dropwise and stirring with 1,1-dibutylhex-5-enenitrile (5.25 g, 25.3 mmol) in anhydrous diethylether (20 mL), heated under reflux for 3 h, allowed to cool, treated dropwise with 30% aqueous NaOH (10 mL), diluted with distilled water (50 mL), collected with the organic phase, extracted with brine (20 mL), dried with magnesiumsulphate, evaporated and distilled in vacuo. Yield

3.54 g (66%) colorless liquid, b.p. 65°C-66°C/1.2 × 10<sup>-2</sup> mbar,  $n_D^{20} = 1.459$ . IR (KBr):  $\tilde{\nu} = 3391.2$  w, 3306 w, 3076.5 w, 2956.7 vs, 2929.9 vs, 2861.3 vs, 1819.1 w, 1640.4 m, 1580.3 m, 1468.0 m, 1378.8 m, 1292.2 m, 1141.7 w, 1067.7 w, 993.7 w, 907.8 m, 815.7 w, 729.1 w, 636.2 w, 557.2 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.83$  (t, <sup>3</sup>J = 7.3 Hz, 6 H, 2 CH<sub>3</sub>), 1.05 - 1.10 (m, 8 H, 4 CH<sub>2</sub>), 1.17 - 1.23 (m, 6 H, 2 CH<sub>3</sub>), 1.84 - 1.88 (m, 2 H, CH<sub>2</sub>), 2.39 (s, 2 H, N-CH<sub>2</sub>), 4.83 - 4.94 (m, 2 H, CH<sub>2</sub>, olefin.), 5.70 - 5.77 ppm (m, 1 H, CH<sub>olefin</sub>.). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 14.0$ , 23.5, 25.0, 27.4, 33.6, 34.0, 38.7, 47.0 (CH<sub>2</sub>-N), 113.7 (CH<sub>2</sub>, olefin.), 139.3 ppm (CH<sub>olefin</sub>.). MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 212 (6) [*M*<sup>+</sup> + H], 196 (42) [*M*<sup>+</sup> - NH<sub>2</sub>], 154 (61) [*M*<sup>+</sup> - NH<sub>2</sub> - C<sub>3</sub>H<sub>5</sub>], 140 (56) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>7</sub> - NH<sub>2</sub>], 97 (81) [*M*<sup>+</sup> - 2 × C<sub>4</sub>H<sub>9</sub>], 83 (91) [*M*<sup>+</sup> - 2 × C<sub>4</sub>H<sub>9</sub> - NH<sub>2</sub>], 69 (100) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>7</sub> - C<sub>4</sub>H<sub>9</sub> - CH<sub>2</sub>NH<sub>2</sub>].

2-But-3-envl-2-hexyloctylamine: Lithiumaluminiumhydride (1.76 g, 46.5 mmol) in anhydrous diethylether (110 mL), 2-but-3-enyl-2-hexyloctanenitrile (7.90 g, 30.0 mmol) in anhydrous diethylether (40 mL) and subsequently 30% aqueous NaOH (15 mL) were allowed to react as was described for 2,2-dibutylhex-5envlamine. Yield 5.58 g (70%) colorless oil, b.p. 96 - 98°C/1·10<sup>-3</sup> mbar,  $n_D^{20}$  = 1.462. IR (KBr):  $\tilde{\nu}$  = 3076.8 w, 2956.1 s, 2928.1 vs, 2858.6 s, 1725.0 w, 1640.4 w, 1467.1 m, 1378.2 w, 1300.7 w, 1070.5 w, 993.7 w, 908.0 m, 815.5 w, 724.1 w, 636.9 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.86$  (t, <sup>3</sup>J = 6.8 Hz, 6 H, 2 CH<sub>3</sub>), 1.13 - 1.29 (m, 22 H, 11 CH<sub>2</sub>), 1.86 - 1.94 (m, 2 H, CH<sub>2</sub>), 2.43 (s, 2 H, CH<sub>2</sub>-N), 4.87 - 5.01 (m, 2 H, CH<sub>2, olefin</sub>), 5.72 - 5.86 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.0, 22.6, 22.8, 27.5, 30.2, 31.8, 33.7, 34.4, 38.9, 47.1 (CH<sub>2</sub>-N), 113.8 (CH<sub>220lefin</sub>), 139.5 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) m/z (%): 266 (10)  $[M^{+} - H]$ , 252 (58)  $[M^{+} - NH_{2}]$ , 238 (35)  $[M^{+} - CH_{4}N_{1}$  196 (61)  $[M^{*} - C_{5}H_{11}]$ , 182 (100)  $[M^{*} - C_{6}H_{13}]$ , 151  $[M^{*} - C_{6}H_{13} - CH_{4}N]$ , 111  $[M^{*} - C_{6}H_{13}]$  $C_6H_{13} - C_5H_{11}$ , 97 (81)  $[M^{+} - 2 \times C_6H_{13}]$ , 83 (79)  $[M^{+} - 2 \times C_6H_{13} - NH_{2}]$ , 69 (71)  $[M^{+} - 2 \times C_{6}H_{13} - CH_{4}N], 55 (52) [M^{+} - 2 \times C_{6}H_{13} - C_{2}H_{6}N].$ 

**2-But-3-enyl-2-octyldecylamine:** Lithiumaluminiumhydride (1.84 g, 48.5 mmol) in anhydrous diethylether (130 mL), 2-but-3-enyl-2-octyldecanenitrile (10.0 g, 31.3 mmol) in anhydrous diethylether (30 mL) and subsequently 30% aqueous NaOH (20 mL) were allowed to react as was described for 2,2-dibutylhex-5-enylamine. Yield 8.56 g (85%) colorless, very viscous oil, b.p. 115°C-120°C/1 ×  $10^{-3}$  mbar,  $n_D^{20} = 1.463$ . - IR (KBr):  $\tilde{V} = 3076.8$  w, 2955.8 s, 2926.4 vs, 2855.4 s, 1736.5 w, 1640.6 w, 1467.1 m, 1378.2 w, 1299.3 w, 1069.9 w, 992.8 w, 907.8 m, 814.9 w, 722.0 w, cm<sup>-1</sup> 636.9 w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.85$  (t, <sup>3</sup>*J* = 6.7 Hz, 6 H, 2 CH<sub>3</sub>), 1.12 - 1.24 (m, 30 H, 15 CH<sub>2</sub>), 1.85 - 1.93 (m, 2 H, CH<sub>2</sub>), 2.42 (s, 2 H, CH<sub>2</sub>–N), 4.85 - 5.00 (m, 2 H, CH<sub>2</sub>, olefin.), 5.71 - 5.84 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 14.0$ , 22.6, 22.8, 27.5, 29.3, 29.6, 30.5, 31.8, 33.7, 34.4, 38.4, 47.1 (CH<sub>2</sub>–N), 113.8 (CH<sub>2</sub>, olefin.), 139.4 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 322 (11) [*M*<sup>+</sup> – H], 308 (34) [*M*<sup>+</sup> – NH<sub>2</sub>], 294 (45) [*M*<sup>+</sup> – C<sub>8</sub>H<sub>17</sub> – C<sub>7</sub>H<sub>15</sub>], 97 (83) [*M*<sup>+</sup> – 2 × C<sub>8</sub>H<sub>17</sub>], 83 (68) [*M*<sup>+-</sup> 2 × C<sub>8</sub>H<sub>17</sub> – NH<sub>2</sub>],

69 (52)  $[M^{+} - 2 \times C_8 H_{17} - C H_4 N]$ , 55 (41)  $[M^{+} - 2 \times C_8 H_{17} - C_2 H_6 N]$ .

**2-Butyl-2-vinylhexylamine:** Lithiumaluminiumhydride (460 mg, 12.1 mmol) in anhydrous diethylether (30 mL), 2-butyl-2-vinylhexanenitrile (1.40 g, 7.81 mmol) in anhydrous diethylether (8 mL) and subsequently 30% aqueous NaOH (5 mL) were allowed to react as was described for 2,2-dibutylhex-5-enylamine. Yield 791 mg (55%) colorless liquid, b.p. 43 - 44°C/1·10<sup>-3</sup> mbar,  $n_D^{20}$  = 1.455. IR (KBr):  $\tilde{\nu}$  = 3080.8 w, 2957.2 vs, 2929.9 vs, 2860.5 s, 1666.3 m, 1636.9 w, 1535.0 w, 1466.5 m, 1414.1 w, 1378.3 m, 1260.9 w, 1235.9 w, 1095.9 w, 1003.9 w, 910.5 m, 802.1 w, 729.3 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 0.86 (t, <sup>3</sup>*J* = 7.1 Hz, 6 H, 2 CH<sub>3</sub>), 1.08 - 1.32 (m, 12 H, 6 CH<sub>2</sub>), 2.49 (s, 2 H, CH<sub>2</sub>–N), 4.86 - 4.93 (m, 1 H, CH<sub>2, olefin</sub>), 5.07 - 5.11 (m, 1 H, CH<sub>2, olefin</sub>), 5.51 - 5.60 (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.0, 23.5, 25.4, 33.3, 43.9, 47.8 (CH<sub>2</sub>–N), 113.6 (CH<sub>2, olefin</sub>), 145.4 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) *m*/*z* (%): 184 (6) [*M*<sup>+</sup> + H], 154 (43) [*M*<sup>+</sup> - CH<sub>4</sub>N], 126 (100) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub> - NH<sub>2</sub>], 41 (51) [*M*<sup>+</sup> - 2 × C<sub>4</sub>H<sub>9</sub> - CH<sub>4</sub>N].

**2-Allyl-2-butylhexylamine:** Lithiumaluminiumhydride (2.52 g, 66.5 mmol) in anhydrous diethylether (150 mL), 2-allyl-2-butylhexanenitrile (8.30 g, 42.9 mmol) in anhydrous diethylether (40 mL) and subsequently 30% aqueous NaOH (20 mL) were allowed to react as was described for 2,2-dibutylhex-5-enylamine. Yield 5.98 g (71%) colorless liquid, b.p. 66°C-68°C/1 × 10<sup>-3</sup> mbar,  $n_D^{20}$  = 1.459 - IR (KBr):  $\tilde{\nu}$  = 3074.4 w, 2956.9 vs, 2929.8 vs, 2861.2 s, 1728.5 w, 1638.2 w, 1580.3 w, 1467.6 m, 1379.2 w, 1299.8 w, 1103.7 w, 996.2 w, 911.4 w, 815.7 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 0.89 (t, <sup>3</sup>*J* = 7.0 Hz, 6 H, 2 CH<sub>3</sub>), 1.15 - 1.33 (m, 12 H, 6 CH<sub>2</sub>), 1.94 - 1.98 (m, 2 H, CH<sub>2</sub>), 2.44 (s, 2 H, CH<sub>2</sub>–N), 4.99 - 5.06 (m, 2 H, CH<sub>2,olefin</sub>), 5.70 - 5.84 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.1, 23.6, 25.2, 34.1, 39.4, 39.5, 47.4 (CH<sub>2</sub>–N), 116.7 (CH<sub>2,olefin</sub>), 135.1 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) *m/z* (%): 197 (19) [*M*<sup>+</sup>], 182 (100) [*M*<sup>+</sup> - NH<sub>2</sub>], 168 (5) [*M*<sup>+</sup> - CH<sub>4</sub>N], 140 (14) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>], 69 (3) [*M*<sup>+</sup> - 2 × C<sub>4</sub>H<sub>9</sub> - NH<sub>2</sub>], 57 (16) [*M*<sup>+</sup> - 2 × C<sub>4</sub>H<sub>9</sub> - CH<sub>4</sub>N].

**2,2-Dibutylhept-6-enylamine:** Lithiumaluminiumhydride (2.35 g, 61.7 mmol) in anhydrous diethylether (150 mL), 2,2-dibutylhept-6-enenitrile (8.80 g, 39.8 mmol) in anhydrous diethylether (40 mL) and subsequently 30% aqueous NaOH (20 mL) were allowed to react as was described for 2,2-dibutylhex-5-enylamine. Yield 7.31 g (81%) colorless liquid, b.p. 82°C-84°C/2 × 10<sup>-3</sup> mbar,  $n_D^{20} = 1.461$ . IR (KBr):  $\tilde{\nu} = 3076.9$  w, 2956.0 vs, 2930.1 vs, 2861.2 s, 1871.8 w, 1640.3 m, 1467.5 m, 1378.5 w, 1297.2 w, 1069.1 w, 992.3 w, 909. m, 814.9 w, 730.0 w, 642.7 w, 556.3 cm<sup>-1</sup> w. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.88$  (t, <sup>3</sup>*J* = 7.2 Hz, 6 H, 2 CH<sub>3</sub>), 1.11 - 1.29 (m, 16 H, 8 CH<sub>2</sub>), 1.97 - 2.04 (m, 2 H, CH<sub>2</sub>), 2.43 (s, 2 H, CH<sub>2</sub>–N), 4.91 - 5.03 (m, 2 H, CH<sub>2</sub>, olefin.), 5.72 - 5.86 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 14.1$ , 22.4, 23.6, 25.2, 33.9, 34.2, 34.6, 38.3, 47.2 (CH<sub>2</sub>–N), 114.4 (CH<sub>2, olefin</sub>), 139.0 ppm (CH<sub>olefin</sub>). MS (DEI<sup>+</sup>/70 eV) m/z (%): 225 (4) [ $M^{+}$ ], 194 (5) [ $M^{+}$  – CH<sub>4</sub>N], 168 (24) [ $M^{+}$  – C<sub>4</sub>H<sub>9</sub>], 111 (40)

$$\begin{split} & [M^{*}-2\times C_{4}H_{9}],\,97\,\,[M^{*}-2\times C_{4}H_{9}-NH_{2}],\,83\,\,(100)\,\,[M^{*}-2\times C_{4}H_{9}-CH_{4}N],\\ & 69\,\,(96)\,\,[M^{*}-2\times C_{4}H_{9}N-C_{2}H_{6}N],\,55\,\,(100)\,\,[M^{*}-2\times C_{4}H_{9}-C_{3}H_{8}N],\,40\,\,(29)\\ & [M^{*}-2\times C_{4}H_{9}-C_{4}H_{10}N]. \end{split}$$

**2,2-Diisopropylbut-3-enylamine:** Lithiumaluminiumhydride (366 mg, 9.64 mmol) in anhydrous diethylether (30 mL), 2,2-diisopropylbut-3-enenitrile (940 mg, 6.22 mmol) in anhydrous diethylether (10 mL) and subsequently 30% aqueous NaOH (10 mL) were allowed to react as was described for 2,2-dibutylhex-5-enylamine. Yield 282 mg (29%) colorless liquid, b.p.  $26^{\circ}$ C/3.2 ×  $10^{-2}$  mbar. IR (KBr):  $\tilde{v} = 3081.6$  w, 2966.2 vs, 2877.7 m, 1660.8 w, 1634.4 w, 1466.3 m, 1413.8 w, 1389.7 m, 1260.2 w, 1171.4 w, 1064.0 w, 1010.0 w, 926.1 m, 804.8 w, 698.3 w, 671.5 cm<sup>-1</sup> w.

2,2-Diisopropylhex-5-enylamine; alternative synthesis: A 70% solution of sodium-bis(2-methoxyethoxo)aluminiumdihydride in toluene (13.7 g, 47.8 mmol) under nitrogen atmosphere was diluted with anhydrous toluene (4 mL), reaed under reflux, treated dropwise within 15 min with a solution of 2,2-diisopropylhex-5enenitrile (3.42 g, 19.1 mmol) in anhydrous toluene (3 mL), refluxed for 4 h, cooled to 0°C, treated with 30% aqueous NaOH (15 mL), diluted with distilled water (100 mL), extracted with diethylether ( $3 \times 150$  mL), washed with distilled water (2  $\times$  200 mL), dried with magnesium sulphate, evaporated and distilled in vacuo. Yield 2.43 g (53%) colorless liquid, b.p. 98°C-100°C/22 mbar,  $n_D^{20}$  = 1.478. IR (KBr):  $\tilde{v}$  = 3076.1 w, 3020.0 w, 2961.9 vs, 2880.5 s, 1640.4 m, 1580.3 m, 1468.9 m, 1385.0 m, 1296.1 m, 1166.9 w, 1066.7 w, 992.5 w, 969.2 w, 908.6 w, 815.7 w, 721.2 w, 660.2 cm<sup>-1</sup> w. MS (DEI<sup>+</sup>/70 eV) m/z (%): 184 (3)  $[M^+ + H]$ , 168 (4)  $[M^{\dagger} - NH_2], 152$  (7)  $[M^{\dagger} - CH_4N], 140$  (100)  $[M^{\dagger} - C_3H_7], 123$  (23)  $[M^{\dagger} - C_4N_2], 133$  (23)  $[M^{\dagger} - C_4N$  $C_{3}H_{7} - NH_{2}$ ], 109 (47)  $[M^{+} - C_{3}H_{7} - CH_{4}N]$ , 97 (77)  $[M^{+} - 2 \times C_{3}H_{7}]$ , 83 (57)  $[M^{t} - 2 \times C_{3}H_{7} - NH_{2}], 69 (90) [M^{t} - 2 \times C_{3}H_{7} - CH_{4}N], 55 (95) [C_{4}H_{7}], 43 (45)$  $[C_{3}H_{7}].$ 

2,9-Bis-(2,2-dibutylhex-5-envl)anthra[2,1,9-def,6,5,10-d'e'f]diisoquinolin e-1,3,8,10-tetraone (19): Perylene-3,4:9,10-tetracarboxylicbisanhydride (60 mg, 1.18 mmol) under argon was treated with imidazole (4.5 g), the quantity of a micro spatulum of zincacetate dihydrate, heated at 140°C, treated dropwise with 2,2-dibutylhex-5-enylamine (1.00 g, 4.74 mmol), stirred at 140°C for 4 h, still warm treated with ethanol (50 mL), precipitated with 2 N aqueous HCl, diluted with distilled water (100 mL), extracted with chloroform, dried with magnesium sulphate, evaporated and purified by column separation (silica gel, chloroform/ethanol 80:1). Yield 869 mg (94%) reddish orange solid with a metallic lustre, m.p. > 250°C.  $R_{\rm f}$  value (silica gel; CHCl<sub>3</sub>/EtOH 80:1) = 0.45. - IR: (KBr):  $\tilde{V}$  = 2956.1 s, 2924.5 vs, 2854.2 vs, 1702.4 m, 1661.4 m, 1595.7 m, 1579.3 w, 1462.5 m, 1405.1 w, 1378.1 w, 1335.5 m, 1250.6 w, 1158.2 w, 1124.8 w, 907.4 w, 810.6 w, 748.5 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.90$  (t, <sup>3</sup>J = 7.1 Hz, 12 H, 4 CH<sub>3</sub>), 1.25 - 1.36 (m, 24 H, 12 CH<sub>2</sub>), 1.38 - 1.41 (m, 4 H, 2 CH<sub>2</sub>), 2.11 - 2.14 (m, 4 H, 2 CH2), 4.25 (s, 4 H, 2 N-CH2), 4.89 - 4.19 (m, 2 H, CH2, olefin), 4.99 - 5.02 (2 H, CH<sub>2. olefin</sub>), 5.79 - 5.86 (m, 2 H, CH<sub>olefin</sub>), 8.59 - 8.67 ppm (m, 8 H, CH<sub>aromat</sub>). <sup>13</sup>C

NMR (150 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 14.2$ , 23.7, 25.7, 28.3, 35.7, 35.9, 40.8, 45.6, 113.8, 123.0, 123.5, 126.5, 129.3, 131.4, 134.6, 139.8, 164.3 ppm. UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max} (\varepsilon) = 457.5$  (18700), 488.4 (51000), 524.9 nm (84700). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max} (I_{rel}) = 533$  (1.00), 575 nm (0.36). Fluorescence quantum yield ( $\lambda_{exc} = 488$  nm,  $E_{483 \text{ nm/l cm}} = 0.0259$ , reference: 2,9-bis-(1-hexylheptyl)-anthra[2,1,9-*def*;6,5,10*d'e'f*]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 0.99. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 778 (100) [*M*<sup>+</sup>], 723 (21) [*M*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>], 598 (27) [*M*<sup>+</sup> -C<sub>13</sub>H<sub>25</sub>], 585 (12) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub>], 418 (67) [*M*<sup>+</sup> - 2 × C<sub>13</sub>H<sub>25</sub>], 404 (25) [*M*<sup>+</sup> -C<sub>13</sub>H<sub>25</sub> - C<sub>14</sub>H<sub>27</sub>], 390 (6) [*M*<sup>+</sup> - 2 × C<sub>14</sub>H<sub>27</sub>]. C<sub>52</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub> (778.5): Calcd. C 80.17, H 8.02, N 3.60; found C 79.99, H 8.05, N 3.62.

2,9-Bis-(2-but-3-enyl-2-hexyloctyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquin oline-1,3,8,10-tetraone: Pervlene-3,4: 9,10-tetracarboxylicbisanhydride (1.00 g, 2.55 mmol), imidazole (6.0 g), 2-but-3-enyl-2-hexyloctylamine (2.73 g, 10.2 mmol) and ethanol (15 mL) were allowed to react analogously to 2,9-bis-(2,2dibutylhex-5-enyl)anthra-[2,1,9-*def*;6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone, precipitated with 2 N aqueous HCl (80 mL), extracted with chloroform dried with magnesium sulphate and purified by column separation (silica gel, chloroform, colum 700 × 54 mm). Yield 1.69 g (74%) bright red glossy solid, m.p. 130°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>) = 0.52. IR: (KBr):  $\tilde{V}$  = 3077 4 w, 2954.7 vs, 2929.7 vs, 2857.8 s, 1701.8 s, 1661.5 vs, 1595.6 vs, 1579.0 m, 1507.7 w, 1458.7 m, 1438.4 m, 1405.4 m, 1377.4 m, 1335.8 s, 1251.0 m, 1216.4 w, 1178.1 w, 1159.4 w, 1125.8 w, 995.1 w, 908.7 m, 853.5 m, 811.2 m, 796.0 w, 750.0 w, 723.4 w, 673.9 w, 633.2 w, 581.8 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.87$  (t, <sup>3</sup>J = 6.8Hz, 12 H, 4 CH<sub>3</sub>), 1.26 - 1.33 (m, 40 H, 20 CH<sub>2</sub>), 1.37 - 1.40 (m, 4 H, 2 CH<sub>2</sub>), 2.10 - 2.14 (m, 4 H, 2 CH<sub>2</sub>), 4.24 (s, 4 H, N-CH<sub>2</sub>), 4.89 - 4.91 (m, 2 H, CH<sub>2, olefin</sub>), 4.98 - 5.01 (2 H, CH<sub>2, olefin</sub>), 5.79 - 5.85 (m, 2 H, CH<sub>olefin</sub>), 8.54 - 8.63 ppm (m, 8 H, CH<sub>aromat</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 13.9, 22.5, 23.3, 27.9, 30.2, 31.7, 35.3, 36.0, 40.5, 45.3, 113.6, 122.8, 123.3, 126.2, 129.0, 131.3, 134.3, 139.7, 164.0 ppm. UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max}$  (*E*) = 457.7 (0.22), 488.7 (0.60), 525.2 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}(I_{rel}) = 533$  (1.00), 575 nm (0.36). Fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 488 nm,  $E_{483 \text{ nm/l cm}}$  = 0.0401, reference: 2,9-bis-(1- hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline- 1,3,8,10-tetraone (1) with  $\Phi$ = 1.00 [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 890 (100) [ $M^{+}$ ], 835 (22) [ $M^{+}$  - $C_4H_7$ ], 654 (39)  $[M^{+} - C_{17}H_{33}]$ , 641 (17)  $[M^{+} - C_{18}H_{35}]$ , 599 (8)  $[M^{+} - C_{18}H_{35} - C_{18}H_{35}]$  $C_{3}H_{7}$ ], 418 (62)  $[M - 2 \times C_{17}H_{33}]$ , 404 (31)  $[M^{+} - C_{17}H_{33} - C_{18}H_{35}]$ , 391 (11)  $[M^{+}]$  $-2 \times C_{18}H_{35}$ ].

**2,9-Bis-(2-but-3-enyl-2-octyldecyl)anthra[2,1,9-***def*,**6,5,10-***d'e'f***]**diisoquin oline-1,3,8,10-tetraone: Perylene-3,4: 9,10-tetracarboxylicbisanhydride (500 mg, 1.27 mmol), imidazole (3.5 g), 2-but-3-enyl-2-octyldecylamine (65 g, 5.10 mmol) and ethanol (15 mL) were allowed to react analogously to 2,9-bis-(2-but-3-enyl-2-hexyloctyl)anthra-[2,1,9-*def*,**6**,5,10-*d'e'f***]**diisoquinoline-1,3,8,10-tetrao ne. The reaction product was purified by column separation (silica gel, chloroform). Yield 875 mg (69%) dark red, glossy solid, m.p. 105°C.  $R_{\rm f}$  (silica gel,

CHCl<sub>3</sub>/iso-hexane 10:1) = 0.63. IR (KBr):  $\tilde{v}$  = 3078.7 w, 2919.3 vs, 2852.5 s, 1688.5 m, 1651.6 s, 1593.3 m, 1577.3 m, 1506.5 w, 1482.0 w, 1453.6 w, 1435.0 m, 1402.9 m, 1378.4 w, 1351.2 m, 1331.8 s, 1247.7 m, 1215.3 w, 1174.0 w, 1155.0 w, 1121.4 w, 1007.1 w, 900.0 m, 873.3 w, 849.8 m, 810.0 m, 795.6 w, 748.4 m, 721.7 w, 658.2 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 0.86 (t, <sup>3</sup>*J* = 6.9 Hz, 12 H, 4 CH<sub>3</sub>), 1.24 - 1.32 (m, 56 H, 28 CH<sub>2</sub>), 1.38 - 1.40 (m, 4 H, 2 CH<sub>2</sub>), 2.10 - 2.14 (m, 4 H, 2 CH<sub>2</sub>), 4.23 (s, 4 H, N-CH<sub>2</sub>), 4.83 - 4.91 (m, 2 H, CH<sub>2 olefin</sub>), 4.98 - 5.02 (m, 2 H, CH<sub>2. olefin</sub>), 5.79 - 5.86 (m, 2 H, CH<sub>olefin</sub>), 8.53 - 8.62 ppm (m, 8 H, CH<sub>ar</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.1, 22.7, 23.5, 28.2, 29.4, 29.6, 30.7, 31.9, 35.6, 36.2, 40.7, 44.6, 113.8, 123.0, 123.5, 126.3, 129.2, 131.4, 134.4, 139.8, 164.2 ppm. UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max}$  ( $\varepsilon$ ) = 457.0 (19300), 488.8 (52200), 524.0 nm (85100). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $I_{rel}$ ) = 534 (1.00), 576.3 (0.52), 621.3 nm (0.12). Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{488 \text{ nm/l cm}}$  = 0.0256, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diiso-quinoline-1,3,8,10-tetr aone (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 1002 (100) [ $M^+$  – H], 947 (23)  $[M^{t} - C_{4}H_{7}]$ , 710 (45)  $[M^{t} - C_{21}H_{41}]$ , 697 (20)  $[M^{t} - C_{22}H_{43}]$ , 418 (72)  $[M^{\dagger} - 2 \times C_{21}H_{41}]$ , 404 (35)  $[M^{\dagger} - C_{21}H_{41} - C_{22}H_{43}]$ , 391 (12)  $[M^{\dagger} - 2 \times C_{21}H_{41}]$ C22H43]. C68H94N2O4 (1003.5): Calcd. C 81.39, H 9.44, N 2.79; found C 81.17, H 9.57, N 2.99.

2,9-Bis-(2-butyl-2-vinylhexyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline -1,3,8,10-tetraone: Perylene-3,4: 9,10-tetracarboxylicbisanhydride (658 mg, 1.68 mmol), imidazole (6.0 g), 2-butyl-2-vinylhexylamine (700 mg, 3.82 mmol) and ethanol (25 mL) were allowed to react analogously to 2,9-bis-(2,2-dibutylhex-5envl)anthra[2,1,9-def;6,5,10- d'e'f]diisoquinoline-1,3,8,10-tetraone. The reaction product was purified by column separation (silica gel, chloroform/ethanol 60:1). Yield 928 mg (78%) reddish orange, sparingly soluble powder, m.p. > 250°C.  $R_{\rm f}$ value (silica gel, CHCl<sub>3</sub>/EtOH 60:1) = 0.73. IR (KBr):  $\tilde{v}$  = 3080.6 w, 2956.6 m, 2932.1 m, 2870.5 m, 1700.9 vs, 1660.3 vs, 1595.0 s, 1578.8 m, 1507.9 w, 1458.1 w, 1438.0 m, 1404.5 m, 1356.6 m, 1335.6 s, 1253.0 m, 1218.5 w, 1165.8 w, 1120.1 w, 1010.2 w, 913.2 w, 853.1 w, 810.8 m, 796.0 w, 755.5 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.95$  (t, <sup>3</sup>J = 7.3 Hz, 12 H, 4 CH<sub>3</sub>), 1.22 - 1.46 (m, 24 H, 12 CH<sub>2</sub>), 4.26 (s, 4 H, 2 CH<sub>2</sub>), 4.74 - 4.76 (m, 2 H, CH<sub>2 olefin</sub>), 4.88 - 4.90 (m, 2 H, CH<sub>2. olefin</sub>), 5.81 - 5.86 (m, 2 H, CH<sub>2</sub>), 8.59 - 8.65 ppm (m, 8 H, CH<sub>aromat</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.2, 23.6, 23.8, 25.7, 34.0, 44.7, 45.9, 112.6, 123.1, 123.5, 126.5, 129.2, 131.5, 134.6, 145.0, 164.1 ppm. UV/Vis (CHCl<sub>3</sub>)  $\lambda_{\rm max}$  $(\varepsilon) = 457.1 (19400), 487.8 (52700), 524.4 \text{ nm} (87900).$  Fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  $(I_{rel}) = 532.8 (1.00), 574.3 (0.52), 624.3 \text{ nm} (0.14)$ . Fluorescence quantum yield (λexc = 487 nm, E 487 nm/1 cm = 0.0319, reference: 2,9-bis-(1-h-exylheptyl)anthra[2,1,9-def ;6,5,10-d'e'f ]di-isoquinoline-1,3,8,10-tetraone (1) with  $\Phi =$ 1.00 [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 722 (65)  $[M^{+}]$ , 666 (43)  $[M^{+}]$  $C_4H_9$ ], 569 (100)  $[M^+ - C_{11}H_{21}]$ , 557 (69)  $[M^+ - C_{12}H_{23}]$ , 500 (23)  $[M^+ - C_{12}H_{23} - C_{12}H_{23}]$  $C_4H_9$ ], 416 (25)  $[M^+ - 2 \times C_{11}H_{21}]$ , 404 (87)  $[M^+ - C_{11}H_{21} - C_{12}H_{23}]$ , 390 (62)  $[M^+$  $-2 \times C_{12}H_{23}$ ]. -  $C_{48}H_{54}N_2O_4$  (723.0): Calcd. C 79.74, H 7.53, N 3.87; found C

#### 79.47, H 7.59, N 3.78.

2,9-Bis-(2-allyl-2-butylhexyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (17): Perylene-3,4: 9,10-tetracarboxylicbisanhydride (1.00 g, 2.55 mmol), imidazole (6.0 g), 2-allyl-2-butyl-hexylamine (2.01 g, 10.2 mmol) and ethanol (15 mL) were allowed to react analogously to 2,9-bis-(2,2dibutylhex-5-enyl)anthra[2,1,9-def;6,5,10- d'e'f]diisoquinoline-1,3,8,10-tetraone. The reaction product was purified by column separation (silica gel, chloroform/ethanol 60:1). Yield 1.43 g (75%) bright orange powder, m.p. > 250°C. R<sub>f</sub> value (silica gel; CHCl<sub>3</sub>/EtOH 60:1) = 0.53. IR: (KBr):  $\tilde{v}$  = 3071.5 w, 2952.4 m, 2929.4 m, 2867.9 m, 1691.4 s, 1650.2 vs, 1591.5 s, 1576.3 m, 1506.0 w, 1464.4 w, 1435.9 m, 1401.9 m, 1386.2 w, 1370.1 w, 1357.6 w, 1333.8 s, 1248.0 m, 1216.0 w, 1200.0 w, 1158.2 w, 1125.8 w, 1103.1 w, 1071.7 w, 1016.7 w, 1001.9 w, 988.5 w, 970.5 w, 898.8 w, 868.6 w, 851.8 w, 810.3 m, 793.3 w, 747.6 m, 710.5 w, 658.9 cm<sup>-1</sup> w. <sup>1</sup>H NMR(600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.90$  (t, <sup>3</sup>J = 7.1 Hz, 12 H, 4 CH<sub>3</sub>), 1.26 - 1.38 (m, 24 H, 12 CH<sub>2</sub>), 2.14 (d,  ${}^{3}J$  = 7.1 Hz, 4 H, 2 CH<sub>2</sub>), 4.26 (s, 4 H, 2 N-CH2), 4.92 - 4.94 (m, 2 H, CH2 olefin,), 5.00 - 5.02 (m, 2 H, CH2 olefin,), 5.90 -5.97 (m, 2 H, CH<sub>olefin</sub>), 8.60 - 8.66 ppm (m, 8 H, CH<sub>aromat</sub>). <sup>13</sup>C NMR (150 MHz,  $CDCl_3$ , 25°C):  $\delta$  = 16.4, 25.9, 27.8, 38.3, 43.0, 43.1, 48.0, 119.0, 125.2, 125.7, 128.7, 131.5, 133.7, 136.8, 137.4, 166.6 ppm. UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max}$  (E) = 458.2 (0.22), 489.1 (0.60), 525.6 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $I_{rel}$ ) = 534.5 (1.00), 577.0 (0.52), 621.8 nm (0.12). Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{488 \text{ nm/l cm}} = 0.0323$ , reference: 2,9-bis-(1-hexylheptyl)anthra [2,1,9-def,6,5,10d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS:  $(\text{DEI}^+/70 \text{ eV}): m/z$  (%): 750 (99)  $[M^+]$ , 709 (57)  $[M^+ - C_3H_5]$ , 584 (32)  $[M^+ - C_3H_5]$  $C_{12}H_{23}$ ], 571 (34) [ $M^{+} - C_{13}H_{25}$ ], 543 (12).

2,9-Bis-(2,2-dibutylhept-6-envl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoli ne-1,3,8,10-tetraone (21): Perylene-3,4: 9,10-tetracarboxylicbisanhydride (1.00 g, 2.55 mmol), imidazole (5.0 g), 2,2-dibutylhept-6-enylamine (2.30 g, 10.2 mmol) and ethanol (25 mL) were allowed to react analogously to 2,9-bis-(2,2dibutylhex-5-enyl)anthra[2,1,9-def;6,5,10- d'e'f]diisoquinoline-1,3,8,10-tetraone. The reaction product was purified by column separation (silica gel, chloroform/ethanol 100:1). Yield 1.77 g (86%) reddish orange small plates, m.p. 239°C.  $R_{\rm f}$  value (silica gel, CHCl<sub>3</sub>) = 0.49. IR (KBr):  $\tilde{\nu}$  = 3076.8 w, 2955.6 m, 2932.4 m, 2863.8 m, 1698.7 vs, 1660.2 vs, 1594.8 s, 1578.5 m, 1507.9 w, 1457.1 w, 1438.7 m, 1404.7 m, 1335.9 s, 1252.4 m, 1217.1 w, 1160.6 w, 1125.6 w, 1102.8 w, 1013.0 w, 909.1 w, 854.2 w, 811.4 m, 796.0 w, 752.1 w, 632.9 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz,  $CDCl_3$ , 25°C):  $\delta = 0.89$  (t,  ${}^{3}J = 7.0$  Hz, 12 H, 4 CH<sub>3</sub>), 1.25 - 1.32 (m, 28 H, 14 CH2), 1.42 - 1.47 (m, 4 H, 2 CH2), 2.00 - 2.03 (m, 4 H, 2 CH2), 4.23 (s, 4 H, N-CH2), 4.89 - 4.91 (m, 2 H, CH2, olefin.), 4.96 - 4.99 (m, 2 H, CH2, olefin.), 5.78 -5.85 (m, 2 H, CH<sub>olefin</sub>), 8.53 - 8.62 ppm (m, 8 H, CH<sub>aromat</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C): *δ* = 14.2, 23.1, 23.8, 25.7, 34.8, 35,8, 40.7, 45.6, 114.2, 123.0, 123.5, 126.4, 129.2, 131.3, 134.4, 139.2, 164.2 ppm. UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max}$  (E) = 457.1 (0.22), 488.1 (0.60), 524.5 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}(I_{rel}) = 533.0$ 

(1.00), 574.5 (0.52), 623.5 nm (0.12). Fluorescence quantum yield ( $\lambda_{exc} = 487$  nm,  $E_{487 \text{ nm/l cm}} = 0.0296$ , 2,9-bis-(1-hexyl- heptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*] diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 806 (100) [ $M^{t} - H$ ], 612 (43) [ $M^{t} - C_{14}H_{27}$ ], 599 (11) [ $M^{t} - C_{15}H_{29}$ ], 418 (56) [ $M^{t} - 2 \times C_{14}H_{27}$ ], 404 (19) [ $M^{t} - C_{14}H_{27} - C_{15}H_{29}$ ], 391 (6) [ $M^{t} - 2 \times C_{15}H_{27}$ ].  $C_{54}H_{66}N_2O_4$  (807.1): Calcd. C 80.36, H 8.24, N 3.47; fund C 79.94, H 8.11, N 3.48.

2,9-Bis-(2,2-diisopropylbut-3-enyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquin oline-1,3,8,10-tetraone: Pervlene-3,4: 9,10-tetracarboxylicbisanhydride (176 mg, 450 µmol), imidazole (1.5 g), 2,2-diisopropylbut-3-enylamine (280 mg, 1.80 mmol) and ethanol (15 mL) were allowed to react analogously to 2,9-bis-(2,2dibutylhex-5-enyl)anthra-[2,1,9-*def*,6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone. The reaction product was purified by column separation (silica gel, chloroform/ethanol 40:1). Yield 13 mg (4%) sparingly soluble brick red solid, m.p. > 250°C.  $R_{\rm f}$  value (silica gel; CHCl<sub>3</sub>/EtOH 40:1) = 0.80. IR (KBr):  $\tilde{\nu}$  = 3079.2 w br., 2958.1 m, 2877.2 m, 1697.5 s, 1651.3 vs, 1591.2 s, 1578.0 m, 1506.9 w, 1465.3 w, 1434.6 m, 1404.1 m, 1379.0 m, 1359.5 m, 1331.8 s, 1246.8 m, 1214.2 w, 1161.9 w, 1127.1 w, 1099.0 w, 1004.3 w, 913.1 w, 850.6 w, 809.8 m, 792.9 w, 751.8 m, 711.9 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 0.95 - 1.00 (m, 24 H, 8 CH<sub>3</sub>), 2.15 - 2.20 (m, 4 H, 4 CH<sub>aliphat</sub>), 4.48 (s, 4 H, 2 N-CH<sub>2</sub>), 4.96 - 4.99 (m, 2 H, CH<sub>2. olefin.</sub>), 5.18 - 5.20 (m, 2 H, CH<sub>2, olefin.</sub>), 5.92 - 5.97 (m, 2 H, CH<sub>olefin.</sub>), 8.64 - 8.72 ppm (m, 8 H, CH<sub>aromat</sub>). UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max}$  (*E*) = 457.8 (0.22), 488.6 (0.60), 525.0 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 534.5 (1.00), 577.0 (0.52), 635.8 nm (0.12). – Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{483 \text{ nm/1 cm}}$  = 0.0318, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def, 6,5,10-d'e'f]-diisoquinoline- 1,3,8,10-tetraone (1) with  $\Phi = 1.00 [40]$ : 1.00. MS (DEI<sup>+</sup>/70 eV): m/z(%): 666 (22)  $[M^{+}]$ , 623 (23)  $[M^{+} - C_{3}H_{7}]$ , 541 (35)  $[M^{+} - C_{9}H_{17}]$ , 529 (35)  $[M^{+} - C_{9}H_{17}]$ , 529 (35)  $[M^{+} - C_{9}H_{17}]$  $C_{10}H_{19}$ ], 418 (19)  $[M^{+} - 2 \times C_{9}H_{17}]$ , 404 (98)  $[M^{+} - C_{9}H_{17} - C_{10}H_{19}]$ , 391 (100)  $[M^+ - 2 \times C_{10}H_{19}].$ 

**2,9-Bis-(2,2-diisopropylhex-5-enyl)anthra[2,1,9-***def***;6,5,10-***d'e'f***]***diisoqui* **noline-1,3,8,10-tetraone:** Perylene-3,4: 9,10-tetracarboxylicbisanhydride (100 mg, 255 µmol), imidazole (2.0 g), 2,2-diisopropylhex-5-enylamine (140 mg, 765 µmol) and ethanol (15 mL) were allowed to react analogously to 2,9-bis-(2,2-dibutylhex-5-enyl)anthra[2,1,9-*def***;6,5,10-***d'e'f***]**diisoquinoline-1,3,8,10-tetraone. The reaction product was purified by column separation (silica gel, chloroform/ ethanol 60:1). Yield 70 mg (38%) brick red solid, m.p. > 250°C. *R*<sub>f</sub> value (silica gel; CHCl<sub>3</sub>/EtOH 60:1) = 0.74. IR (KBr):  $\tilde{v}$  = 2964.3 m, 2880.1 m, 1694.6 s, 1650.5 vs, 1591.2 s, 1577.8 m, 1507.5 w, 1434.5 w, 1404.2 m, 1379.2 w, 1358.9 w, 1334.4 s, 1248.5 m, 1214.9 w, 1162.8 w, 1128.1 w, 1100.0 w, 1039.9 w, 972.0 w, 906.2 w, 851.4 w, 810.1 m, 793.5 w, 750.3 m, 712.1 cm<sup>-1</sup> w. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 0.98 - 1.05 (m, 24 H, 8 CH<sub>3</sub>), 1.20 - 1.27 (m, 8 H, 4 CH<sub>2</sub>), 2.16 - 2.22 (m, 4 H, 4 CH<sub>aliphat</sub>.), 4.52 (s, 4 H, 2 N-CH<sub>2</sub>), 4.84 - 4.86 (m, 2 H, CH<sub>2</sub>, olefin.), 4.91 - 4.94 (m, 2 H, CH<sub>2</sub>), 5.36 - 5.40 (m, 2 H, CH<sub>olefin</sub>.), 8.63 - 8.71 ppm (m, 8 H, CH<sub>aromat.</sub>). UV/Vis (CHCl<sub>3</sub>)  $\lambda_{max}$  (*E*) = 457.8 (0.22), 488.6 (0.60), 525.0 nm (1.00). – Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*<sub>rel</sub>) = 535.0 (1.00), 578.0 (0.52), 626.5 nm (0.12). Fluorescence quantum yield ( $\lambda_{exc}$  = 489 nm, *E*<sub>489 nm/1 nm</sub> = 0.0240, reference: 2,9-bis-(1-hexyl-heptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetr aone (1) with  $\Phi$  = 1.00 [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 722 (82) [*M*<sup>+</sup>], 679 (42) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>], 570 (36) [*M*<sup>+</sup> - C<sub>11</sub>H<sub>21</sub>], 557 (58) [*M*<sup>+</sup> - C<sub>12</sub>H<sub>23</sub>], 418 (100) [*M*<sup>+</sup> - 2 × C<sub>11</sub>H<sub>21</sub>], 404 (80) [*M*<sup>+</sup> - C<sub>11</sub>H<sub>21</sub> - C<sub>12</sub>H<sub>23</sub>], 391 (51) [*M*<sup>+</sup> - 2 × C<sub>12</sub>H<sub>23</sub>]. HMRS (C<sub>48</sub>H<sub>54</sub>N<sub>2</sub>O<sub>4</sub>): Calcd. *m/z*: 722.408, found *m/z*: 722.406.

2-(2,2-Dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e' f]diisoquinoline-1,3,8,10-tetraone (21): 9-(2-Hydroxyethyl)2-benzopyrano [6',5'4':10,5,6] anthra[2,1,9-def]isoquinoline-1,3,8,10-tetraone (600 mg, 1.38 mmol), imidazole (5 g) and the quantity of a microspatulum of zinc acetate dihydrate under argon atmosphere were melt, stirred at 140°C, slowly treated with 2,2-dibutylhept-6-envlamine (396 mg, 1.76 mmol), further stirred at 140°C for 3 h, allowed to cool treated with ethanol (15 mL), precipitated with 2 N aqueous HCl, collected by vacuum filtration (D4 glass filter), dried in air and purified by column separation (1000 mL silica gel, glas column 800 × 42 mm, chloroform/ethanol 30:1). Yield 742 mg (84%) reddish brown solid, m.p. > 250°C. R-value (silica gel, CHCl<sub>3</sub>/EtOH 20:1) = 0.12. IR (ATR):  $\tilde{v}$  = 3523.4 (w), 3074.3 (w), 2953.5 (m), 2930.9 (m), 2862.2 (m), 1693.5 (s), 1646.2 (vs), 1593.4 (s), 1577.1 (m), 1506.8 (w), 1438.1 (w), 1403.5 (w), 1336.3 (m), 1251.2 (w), 1169.4 (w), 1126.3 (w), 1059.7 (w), 908.0 (w), 856.9 (w), 808.8 (m), 793.9 (w), 744.1 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.89$  (t, <sup>3</sup>*J*(H,H) = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 1.24 - 1.33 (m, 14 H, 7 × CH<sub>2</sub>), 1.42 - 1.47 (m, 2 H, CH<sub>2</sub>), 2.01 (q,  ${}^{3}/(H,H) = 7.3$  Hz, 2 H, C<sub>q</sub>-CH<sub>2</sub>), 4.07 (t,  ${}^{3}/(H,H) = 5.2$  Hz, 2 H, N-CH<sub>2</sub>-CH<sub>2</sub>), 4.22 (s, 2 H, N-CH<sub>2</sub>-C<sub>g</sub>), 4.50 (t,  ${}^{3}/(H,H) = 5.2$  Hz, 2 H, HO-CH2), 4.96 - 4.97 (m, 1 H, CH2010, 4.99 - 5.00 (m, 1 H, CH2010, 5.78 -5.85 (m, 1 H, CH<sub>olefin</sub>), 8.42 - 8.46 (m, 4 H,  $4 \times$  CH<sub>pervlene</sub>), 8.52 - 8.53 (m, 2 H,  $2 \times$ CH<sub>perylene</sub>), 8.60 - 8.62 ppm (m, 2 H,  $2 \times CH_{prylene}$ . <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 14.2, 23.1, 23.8, 25.8, 34.8, 35.8, 35.9, 40.7, 43.0, 45.7, 61.5,$ 114.3, 122.8, 122.9, 123.2, 123.6, 129.0, 129.4, 131.2, 131.5, 134.0, 134.8, 139.2, 164.1 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $I_{rel}$ ) = 458.8 (0.22), 490.0 (0.60), 526.4 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 535.5 (1.00), 577.3 (0.54), 625.3 nm (0.13). Fluorescence quantum yield ( $\lambda_{\text{exc}} = 488 \text{ nm}, E_{488 \text{ nm/lcm}} = 0.0344$ , reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetra one (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 642 (100) [ $M^{+}$ ], 448 (64)  $[M^{+} - C_{14}H_{27}]$ , 433 (23)  $[M^{+} - C_{15}H_{29}]$ , 405 (98)  $[M^{+} - C_{14}H_{27} - C_{2}H_{5}O]$ , 390 (13)  $[M^{\dagger} - C_{15}H_{29} - C_{2}H_{5}O]$ . HMRS  $(C_{41}H_{42}N_{2}O_{5})$ : Calcd. *m/z*: 642.3094; found *m/z*: 642.3099.

**2-(1-Hexylheptyl)-9-(6-hydroxypentyl)anthra[2,1,9-***def***;6,5,10-***d'e'f'***]diis oquinoline-1,3,8,10-tetraone:** 9-(1-Hexylheptyl)-2-benzopyrano[6',5'4':10,5, 6]anthra[2,1,9-*def*]-isoquinoline-1,3,8,10-tetraone (300 mg, 0.523 mmol), 5-amino-1-pentanol (80.9 mg (0.784 mmol), imidazole (3.5 g), the quantity of a microspatulum of zincacetate dihydrate, acetic acid (40 mL, replacement of ethanol) and 2 N aqueous HCl (60 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxy-ethyl)anthra[2,1,9-def,6,5,10-d'e'f]diiso quinoline-1,3,8,10-tetraone and purified by colun separation (800 mL of silica gel, gas column 780 × 44 mm, chloroform/ethanol 20:1). Yield 290 mg (84%) light red powder, m.p. > 250°C. R-value (silica gel, CHCl<sub>3</sub>/EtOH 20:1) = 0.12. IR (KBr):  $\tilde{v} = 3468.1$  (w,br.), 2928.1 (w), 2858.1 (w), 1697.1 (s), 1657.1 (vs), 1595.5 (m), 1578.7 (w), 1507.8 (w), 1439.4 (w), 1404.5 (m), 1342.5 (m), 1253.2 (w), 1176.2 (w), 1126.9 (w), 1107.9 (w), 853.1 (w), 810.5 (m), 747.5 (m), 627.0 (w), 432.6 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.83$  (t, <sup>3</sup>/(H,H) = 7.0 Hz, 6 H,  $2 \times CH_3$ ), 1.19 - 1.38 (m, 16 H,  $8 \times CH_2$ ), 1.67 - 1.72 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 1.80 - 1.90 (m, 4 H, 2 × CH<sub>2</sub>), 2.22 - 2.28 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 3.69 (t,  ${}^{3}$ *J*(H,H) = 6.4 Hz, 2 H, N-CH<sub>2</sub>), 4.24 - 4.25 (m, 2 H, CH<sub>2</sub>-OH), 5.16 - 5.21 (m, 1 H, a-CH), 8.59 - 8.68 ppm (m, 8 H,  $8 \times CH_{pervlene}$ ). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 14.0, 22.6, 23.3, 26.9, 27.9, 29.2, 31.8, 32.4, 40.4, 54.8, 62.8, 123.0, 123.1, 123.2, 126.4, 126.5, 129.4, 129.6, 131.2, 131.5, 131.9, 134.4, 134.8, 163.5 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 458.9 (17800), 489.9 (49000), 526.4 nm (82000). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 532.9 (1.00), 576.3 (0.54), 625.3 nm (0.13). Fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 489 nm,  $E_{489 \text{ nm/l cm}}$  = 0.0242, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetra one (1) with  $\Phi = 1.00 \, [40]$ : 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 658 (85)  $[M^{+}]$ , 641 (13)  $[M^+ - OH]$ , 573 (6)  $[M^+ - C_6H_{13}]$ , 476 (100)  $[M^+ - C_{13}H_{27}]$ , 459 (11)  $[M^+ - C_{13}H_{27}]$  $C_{13}H_{27} - OH$ ], 390 (69) [ $M^+ - C_{13}H_{27} - C_5H_{11}O$ ].  $C_{41}H_{42}N_2O_5$  (642.3): Calcd. C 76.57, H 7.04, N 4.25; found C 76.31, H 7.06, N 4.07.

2-{2-(2-Ethoxyethyl)-9-(1-nonyldecyl)anthra[2,1,9-def;6,5,10-d'e'f]diis oquinoline-1,3,8,10-tetraon}-9-(1-nonyldecyl)anthra[2,1,9-def;6,5,10-d'e'f] diisoquinoline-1,3,8,10-tetraone: 2-(2-Hydroxyethyl)-9-(1-nonyldecyl) anthra [2,1,9-def;6,5,10-d'e'f] diisoquinoline-1,3,8,10-tetraone (140 mg, 0.200 mmol) under argon atmosphere was dissolved in anhydrous chloroform (5 mL), treated with triethylamine (61 mg, 0.60 mmol) and then with (2-cyanoethyl)-N,Ndiisopropylphosphonamidechloride (122 mg, 0.553 mmol), stirred at room tmperature for 18 h, diluted with chloroform (120 mL), three times shaken with 5% aqueous NaHCO3 (80 mL each), dried with magnesium sulphate and purified two times by column separation (1000 mL silica gel, chlorofor/acetone 10:1, glas column 700  $\times$  55 mm, fraction 4), Yield 30 mg (22%) dark red solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/acetone 10:1) = 0.06. IR (ATR):  $\tilde{v}$  = 2921.2 (vs), 2852.1 (s), 1748.9 (w), 1696.4 (s), 1653.8 (vs), 1592.9 (s), 1577.0 (m), 1506.6 (w), 1436.0 (w), 1403.6 (m), 1338.8 (s), 1247.4 (m), 1194.0 (w), 1175.5 (w), 1125.5 (w), 1065.1 (w), 1005.6 (w), 851.1 (w), 808.5 (m), 788.1 (w), 744.0 cm<sup>-1</sup> (m). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.83$  (t, <sup>3</sup>/(H,H) = 7.0 Hz, 12 H,  $4 \times CH_3$ ), 1.22 - 1.41 (m, 56 H, 28 CH<sub>2</sub>), 1.87 - 1.95 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 2.20 -2.29 (m, 4 H,  $\beta$ -CH<sub>2</sub>), 4.53 (t,  $^{3}$ /(H,H) = 5.1 Hz, 4 H, 2 × N-CH<sub>2</sub>-CH<sub>2</sub>), 4.62 (t,  ${}^{3}$ *J*(H,H) = 5.2 Hz, 4 H, 2 × CH<sub>2</sub>O), 5.12 - 5.19 (m, 2 H, 2 × *a*-CH), 8.00 - 8.02 (m,

2 H, 2 × CH<sub>perylene</sub>), 8.11 - 8.13 (m, 2 H, 2 × CH<sub>perylene</sub>), 8.24 - 8.26 (m, 2 H, 2 × CH<sub>perylene</sub>), 8.39 - 8.45 ppm (m, 2 H, 2 × CH<sub>perylene</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 14.1, 22.7, 27.1, 29.3, 29.6, 31.9, 32.3, 39.1, 54.9, 65.0, 122.4, 122.5, 122.7, 125.7, 128.9, 129.0, 131.0, 133.5, 134.1, 163.0 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 459.0 (0.23), 490.0 (0.63), 527.0 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 573.8 (1.00), 577.0 (0.52), 625.3 nm (0.13). Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{488 nm/1 cm}$  = 0.0271, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1, 9-*def*;6,5,10- *d'e'f*]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi$  = 1.00 [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 1383 (< 1) [*M*<sup>*t*</sup>], 1366 (< 1) [*M*<sup>*t*</sup> - HO], 1257 (< 1) [*M*<sup>*t*</sup> - C<sub>9</sub>H<sub>19</sub>], 1100 (< 1) [*M*<sup>*t*</sup> - C<sub>9</sub>H<sub>19</sub> - OH], 700 (64) [*M*<sup>*t*</sup> - C<sub>45</sub>H<sub>51</sub>N<sub>2</sub>O<sub>4</sub>], 684 (39) [*M*<sup>*t*</sup> - C<sub>45</sub>H<sub>51</sub>N<sub>2</sub>O<sub>5</sub>], 432 (4) [*M*<sup>*t*</sup> - C<sub>45</sub>H<sub>51</sub>N<sub>2</sub>O<sub>4</sub> - C<sub>9</sub>H<sub>19</sub>], 418 (74) [*M*<sup>*t*</sup> - C<sub>45</sub>H<sub>51</sub>N<sub>2</sub>O<sub>5</sub> - C<sub>9</sub>H<sub>19</sub>].

2-(2-Bromethyl)-9-(1-nonyldecyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquin oline-1,3,8,10-tetraone: 2-(2-Hydroxyethyl)-9-(1-nonyldecyl)anthra[2,1,9-*def*; 6,5,10-*d'e'f'*]diiso-quinoline-1,3,8,10-tetraone (100 mg, 0.143 mmol) was dissolved in chloroform (6 mL), treated with phosphorustribromide (193 mg, 0.713 mmol), heated to reflux with stirring for 4 h, cooled to 0°C, precipitated with methanol (25 mL), collected by vacuun filtration (D4 micro glass filter) and purified by column separation (500 mL silica gel, chloroform/ethylacetate 30:1, glass column 500 × 44 mm, second fraction). Yield 30 mg (27%) dark red solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOAc 30:1) = 0.64. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 0.82 (t, <sup>3</sup>/(H,H) = 6.4 Hz, 6 H, 2 × CH<sub>3</sub>), 1.18 -1.36 (m, 28 H, 14 × CH<sub>2</sub>), 1.81 - 1.97 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 2.17 - 3.71 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 3.71 (t, <sup>3</sup>/(H,H) = 7.0 Hz, 2 H, CH<sub>2</sub>–Br), 4.61 (t, <sup>3</sup>/(H,H) = 7.0 Hz, 2 H, N–CH<sub>2</sub>), 5.18 (m, 1 H, CH), 8.40 - 8.62 ppm (m, 8 H, 8 × CH<sub>perviene</sub>).

2-Amino-9-(2-but-3-enyl-2-octyldecyl)-anthra[2,1,9-def;6,5,10-d'e'f]diis oquinoline-1,3,8,10-tetraone: 9-Amino-2-benzopyrano-[6',5'4':10,5,6]anthra [2,1,9-def]iso-quinoline-1,3,8,10-tetraone (700 mg, 1.72 mmol), 2-but-3-enyl-2octyldecylamine (5c, 836 mg, 2.58 mmol), imidazole (4.0 g), the quantity of a micro spatulum of zincacetate dihydrate, ethanol (15 mL) and 2 N aqueous HCl (100 mL) were allowed to react analogously to 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone, dried in vacuo with calciumchloride and then with phosphorous(V)oxid and purified by column separation (800 mL silica gel, chloroform/ethanol 30:1, glass column 780 × 44 mm). Yield 579 mg (47%) dark red solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 30:1) = 0.10. IR (ATR):  $\tilde{\nu}$  = 3329.9 (w), 3243.5 (w), 3073.7 (w), 2921.7 (vs), 2851.6 (s), 1696.7 (vs), 1652.1 (vs), 1592.6 (vs), 1576.3 (m), 1507.3 (w), 1456.9 (w), 1436.0 (w), 1402.3 (m), 1367.5 (m), 1339.7 (s), 1301.1 (m), 1251.2 (m), 1201.2 (w), 1171.2 (w), 1123.9 (w), 991.0 (w), 903.3 (w), 850.1 (w), 807.9 (m), 793.9 (w), 756.9 (w), 737.8 (m), 666.6 cm <sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.86$  (t, <sup>3</sup>/(H,H) = 6.9 Hz, 6 H, 2 × CH<sub>3</sub>), 1.24 - 1.40 (m, 30 H, 15 × CH<sub>2</sub>), 2.10 - 2.14 (m, 2 H, CH<sub>2</sub>), 4.24 (s, 2 H, N-CH2), 4.90 - 4.91 (m, 1 H, CH2.olefin.), 4.99 - 5.02 (m, 1 H, CH2.olefin.), 5.79 - 5.85

(m, 1 H, CH<sub>olefin</sub>), 8.51 - 8.64 ppm (m, 8 H, 8 × CH<sub>perylene</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 14.2, 22.7, 23.6, 28.2, 29.4, 29.7, 30.8, 32.0, 35.6, 36.3, 40.8, 45.7, 113.9, 122.3, 122.9, 123.4, 123.8, 126.0, 127.9, 129.1, 131.4, 131.6, 134.0, 135.1, 139.8, 160.1, 164.1 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 460 (0.24), 491.6 (0.62), 528.4 nm (1.00). Fluorescence (CHCl<sub>3</sub>): No emission detected. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 711 (21) [*M*<sup>+</sup>], 696 (13) [*M*<sup>+</sup> – NH<sub>2</sub>], 419 (100) [*M*<sup>+</sup> – C<sub>21</sub>H<sub>41</sub>], 404 (76) [*M*<sup>+</sup> – C<sub>22</sub>H<sub>43</sub>], 390 (28) [*M*<sup>+</sup> – C<sub>22</sub>H<sub>43</sub> – NH<sub>2</sub>]. HMRS (C<sub>46</sub>H<sub>54</sub>N<sub>3</sub>O<sub>4</sub>): Calcd. m/z: 712.411 [*M*<sup>+</sup> + H]; found m/z: 712.410.

2-Allyl-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3, **8,10-tetraon(3):** 9-(1-Hexylheptyl)-2-benzopyrano [6',5'4':10,5,6]anthra[2,1, 9-def jisoquinoline-1,3,8,10-tetraone (500 mg, 0.872 mmol) the quantity of a microspatulum of zincacetate dihydrate, acetic acid (80 mL, replacement of ethanol), imidazole (8.0 g), allylamine (65.0 mg, 1.14 mmol) and 2 N aqueous HCl (100 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-t etraone and purified by column separation (800 mL of silica gel, chloroform/ ethanol 30:1, glas column 780 × 44 mm). Yield 405 mg (76%) light red solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 30:1) = 0.63. IR (KBr):  $\tilde{V}$  = 2954.6 (m), 2926.7 (s), 2856.6 (m), 1770.3 (w), 1698.2 (s), 1659.2 (s), 1595.1 (s), 1578.5 (m), 1506.7 (w), 1482.2 (w), 1456.2 (w), 1436.1 (m), 1404.4 (m), 1376.1 (m), 1345.4 (s), 1251.7 (m), 1216.0 (w), 1193.9 (w), 1174.7 (m), 1156.3 (w), 1125.9 (w), 1106.7 (w), 997.7 (w), 930.5 (w), 852.0 (w), 810.2 (m), 796.2 (w), 786.2 (w), 747.9 (m), 723.9 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$ = 0.83 (t,  ${}^{3}/(H,H)$  = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 1.21 - 1.37 (m, 16 H, 8 × CH<sub>2</sub>), 1.88 (m, 2 H, a-CH<sub>2</sub>), 2.25 (m, 2 H, a-CH<sub>2</sub>), 4.83 (d, 2 H,  ${}^{3}f$ (H,H) = 5.9 Hz, N-CH<sub>2</sub>), 5.19 (m, 1 H, N-CH), 5.25 (m, 1 H, CH<sub>2.0lefin</sub>), 5.37 (m, 1 H, CH<sub>2.0lefin</sub>), 6.02 (m, 1 H, CH<sub>olefin</sub>), 8.55 - 8.66 ppm (m, 8 H, 8 × CH<sub>pervlene</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 16.0, 24.6, 28.9, 31.2, 33.7, 34.4, 44.6, 56.8, 120.0, 124.9, 125.1, 128.3, 128.5, 131.5, 133.1, 133.5, 133.9, 136.3, 136.8, 165.1 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  (E) = 458 (0.22), 489 (0.60), 526 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  (I) = 535 (1.00), 579 nm (0.41). Fluorescence quantum yield (CHCl<sub>3</sub>,  $\lambda_{exc}$  = 488 nm,  $E_{488 \text{ nm/l cm}} = 0.0285$ ; reference: 2,9-bis-(1-hexylheptyl)anthra-[2,1,9-*def*;6,5,10d'e'f]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS (DEI<sup>+</sup>/70 eV): m/z (%): 612 (62)  $[M^+]$ , 430 (100)  $[M^+ - C_{13}H_{26}]$ , 415 (67)  $[430 - CH_3]$ , 390 (3)  $[M^{+} - C_{13}H_{26} - C_{3}H_{4}]$ . HMRS  $(C_{40}H_{40}N_{2}O_{4})$ : Calcd. *m/z*: 612.299; found *m/z*: 612.300.

2-(2,2-Dibutylhex-5-enyl)-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*] diisoquinoline-1,3,8,10-tetraone (8): 9-(1-Hexylheptyl)-2-benzopyrano[6',5'4': 10,5,6] anthra[2,1,9*def*]isoquinoline-1,3,8,10-tetraone (2, 100 mg, 0.174 mmol) 2,2-dibutylhex-5-enylamine (80.0 mg, 0.348 mmol), imidazole (2.70 g), the quantity of a microspatulum of zincacetate dihydrate, ethanol (10 mL) and 2 N aqueous HCl (50 mL) were allowed to react as was described for 2-(2,2dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquinoli ne-1,3,8,10-tetraone and purified by medium pressure chromatography (silica gel, chloroform 25 mL·min<sup>-1</sup>, column  $36 \times 460$  mm). Yield 869 mg (94%) light red powder, m.p. > 250°C. R-value (silica gel, CHCl<sub>3</sub>) = 0.39. IR (KBr):  $\tilde{V}$  = 3436.5 (m, br.), 2955.5 (s), 2928.9 (s), 2858.8 (m), 1698.8 (vs), 1659.5 (vs), 1595.2 (vs), 1578.5 (m), 1506.2 (w), 1456.4 (w), 1436.5 (w), 1405.7 (m), 1337.4 (vs), 1252.5 (m), 1213.4 (w), 1175.3 (w), 1125.2 (w), 1106.8 (w), 995.8 (w), 908.8 (w), 852.2 (w), 810.6 (m), 748.4 cm<sup>-1</sup> (m). <sup>1</sup>H NMR (600 Mhz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$ = 0.83 (t,  ${}^{3}/(H,H)$  = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 0.89 (t,  ${}^{3}/(H,H)$  = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 1.19 - 1.38 (m, 28 H, 14 × CH<sub>2</sub>), 1.38 - 1.41 (m, 2 H, CH<sub>2</sub>), 1.84 - 1.90 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 2.10 - 2.14 (m, 2 H, CH<sub>2</sub>), 2.23 - 2.28 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 4.25 (s, 2 H, CH2), 4.89 - 4.91 (m, 1 H, CH2.olefin), 4.99 - 5.02 (m, 1 H, CH2.olefin), 5.16 - 5.21 (m, 1 H,  $\alpha$ -CH), 5.79 - 5.86 (m, 1 H, CH<sub>olefin</sub>), 8.61 - 8.69 ppm (m, 8 H, 8  $\times$ CH<sub>nervlene</sub>). <sup>13</sup>C NMR (151 Mhz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 15.4$ , 15.5, 23.9, 25.1, 27.1, 28.3, 29.5, 30.6, 33.1, 33.7, 36.8, 37.2, 42.0, 46.8, 56.1, 115.2, 124.2, 124.9, 127.9, 130.7, 131.0, 132.5, 133.3, 136.0, 141.1, 165.7 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$ (E) = 458.2 (0.22), 489.0 (0.60), 525.4 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}} (I) =$ 532.2 (1.00), 576.5 (0.35) nm. Fluorescence quantum yield ( $\lambda_{exc}$  = 487 nm,  $E_{487}$  $_{nm/1 cm} = 0.0440$ , reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS (DEI<sup>+</sup>/70 eV): m/z (%): 766 (45)  $[M^{+}]$ , 586 (30)  $[M^{+} - C_{12}H_{24} - CH_{2}]$ , 404 (100)  $[M^{+} - C_{26}H_{50}]$ , 390 (49)  $[404 - CH_2]$ . HMRS ( $C_{51}H_{63}N_2O_4$ ): Calcd. m/z: 767.478  $[M^+ + H]$ ; found *m/z*: 767.478.

2-(2-But-3-enyl-2-hexyloctyl)-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d' e'f']diisoquinoline-1,3,8,10-tetraone: 9-(1-Hexylheptyl)-2-benzopyrano[6',5'4': 10,5,6] anthra[2,1,9-def]isoquinoline-1,3,8,10-tetraone (107 mg, 0.187 mmol), 2-but-3-enyl-2-hexyloctyl-amine (100 mg, 0.373 mmol), imidazole (2.5 g), ethanol, (10 mL) and 2 N aqueous HCl (75 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def;6,5, 10-d'e'f]diisoquinoline-1,3,8,10-tetraone and purified by column separation (750 mL of silica gel, chloroform and then 350 mL of silica gel, dichloromethane, column 600  $\times$  34 mm). Yield 109 mg (76%) light red solid, m.p. > 250°C.  $R_{\rm c}$ -value (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) = 0.55. IR (KBr):  $\tilde{\nu}$  = 2953.8 (m), 2924.8 (s), 2854.4 (m), 1696.1 (s), 1652.1 (vs), 1594.2 (s), 1578.1 (m), 1507.0 (w), 1456.6 (w), 1434.9 (w), 1404.8 (m), 1333.9 (s), 1252.6 (m), 1211.7 (w), 1174.9 (w), 1123.7 (w), 1107.5 (w), 993.0 (w), 904.8 (w), 850.7 (w), 808.0 (m), 745.8 (m), 669.8 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.83$  (t, <sup>3</sup>*J*(H,H) = 7.0 Hz, 6 H,  $2 \times CH_3$ , 0.87 (t,  ${}^{3}/(H,H) = 6.8$  Hz, 6 H,  $2 \times CH_3$ ), 1.20 - 1.36 (m, 36 H, 18 × CH<sub>2</sub>), 1.38 - 1.41 (m, 2 H, CH<sub>2</sub>), 1.84 - 1.89 (m, 2 H, β-CH<sub>2</sub>), 2.10 - 2.14 (m, 2 H,  $C_a$ -CH<sub>2</sub>), 2.22 - 2.28 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 4.25 (s, 2 H, N-CH<sub>2</sub>-C<sub>a</sub>), 4.89 - 4.92 (m, 1 H, CH<sub>2.olefin</sub>), 4.98 - 5.02 (m, 1 H, CH<sub>2.olefin</sub>), 5.16 - 5.21 (m, 1 H, a-CH), 5.79 -5.86 (m, 1 H, CH<sub>olefin</sub>), 8.63 - 8.69 ppm (m, 8 H,  $8 \times CH_{pervlene}$ ). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS): δ = 14.0, 22.6, 22.7, 23.5, 26.9, 29.2, 30.4, 31.8, 31.9, 32.4, 35.6, 36.2, 40.8, 54.8, 113.8, 123.4, 123.5, 126.5, 129.4, 129.7, 131.5, 134.7,

139.8, 164.4 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 458.0 (0.22), 489.4 (0.60), 525.8 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 534.0 (1.00), 576.0 (0.50), 624.8 nm (0.11). Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{488 \text{ nm/1 cm}}$  = 0.0282, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*,6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-

tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 822 (86) [ $M^{t}$ ], 767 (21) [ $M^{t} - C_{4}H_{7}$ ], 586 (35) [ $M^{t} - C_{17}H_{33}$ ], 573 (16) [ $M^{t} - C_{18}H_{35}$ ], 404 (100) [ $M^{t} - C_{13}H_{27} - C_{17}H_{33}$ ], 391 (27) [ $M^{t} - C_{13}H_{27} - C_{18}H_{35}$ ]. HMRS ( $C_{55}H_{71}N_{2}O_{4}$ ): Calcd. m/z: 823.541 [ $M^{t} + H$ ]; found m/z: 823.547.

2-(1-Hexylheptyl)-9-(2,2-dibutylhept-6-enyl)anthra[2,1,9-def;6,5,10-d'e'f' diisoquinoline-1,3,8,10-tetraone (10): 9-(1-Hexylheptyl)-2-benzopyrano-[6', 5'4': 10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10-tetraone (103 mg, 180 µmol) 2,2-dibutylhept-6-envlamine (53 mg, 0.23 mmol), imidazole (2.7 g) ethanol (10 mL) and 2 N aqueous HCl (50 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxy-ethyl)anthra[2,1,9-def;6,5,10-d'e'f]diiso quinoline-1,3,8,10-tetraone and purified by column separation (500 mL of silica gel, chloroform, column 500 × 44 mm). Yield 121 mg (86%) light red, shiny solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>) = 0.37. IR (KBr):  $\tilde{\nu}$  = 2954.0 (m), 2926.7 (m), 2856.9 (m), 1696.5 (s), 1652.7 (vs), 1594.5 (m), 1578.1 (w), 1507.3 (w), 1456.9 (w), 1435.5 (w), 1405.2 (w), 1334.8 (s), 1253.6 (m), 1212.1 (w), 1175.8 (w), 1123.9 (w), 1107.0 (w), 996.8 (w), 906.2 (w), 850.8 (w), 808.3 (m), 746.3 (m), 669.7 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 0.83  $(t, {}^{3}/(H,H) = 6.8 \text{ Hz}, 6 \text{ H}, 2 \times \text{CH}_{3}), 0.89 (t, {}^{3}/(H,H) = 6.8 \text{ Hz}, 6 \text{ H}, 2 \times \text{CH}_{3}), 1.22$ - 1.36 (m, 30 H, 15 × CH<sub>2</sub>), 1.41 - 1.49 (m, 2 H, CH<sub>2</sub>), 1.82 - 1.91 (m, 2 H, CH<sub>2</sub>), 1.99 - 2.04 (m, 2 H, CH<sub>2</sub>), 2.20 - 2.29 (m, 2 H, CH<sub>2</sub>), 4.24 (s, 2 H, N-CH<sub>2</sub>-C<sub>2</sub>), 4.89 - 5.01 (m, 2 H, CH<sub>2.0lefin</sub>), 5.15 - 5.23 (m, 1 H, CH), 5.77 - 5.87 (m, 1 H,  $CH_{olefin}$ ), 8.63 - 8.69 ppm (m, 8 H, 8 ×  $CH_{pervlene}$ ). <sup>13</sup>C NMR (150 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 14.0, 14.1, 22.6, 23.1, 23.8, 25.7, 26.9, 29.2, 31.7, 32.4, 34.8, 35.9, 40.7, 45.6, 54.8, 114.2, 123.0, 123.1, 123.6, 126.6, 129.3, 129.6, 131.5, 134.6, 139.2, 164.3 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 458.0 (0.22), 488.8 (0.61), 525.4 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 533.5 (1.00), 575.8 (0.52), 623.8 nm (0.12). Fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 488 nm,  $E_{488 \text{ nm/l cm}}$  = 0.0294, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def,6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetra one (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 780 (51) [ $M^{+}$ ], 711 (8)  $[M^{+} - C_{5}H_{9}]$ , 586 (28)  $[M^{+} - C_{14}H_{27}]$ , 576 (14)  $[M^{+} - C_{15}H_{29}]$ , 404 (100)  $[M^{+} - C_{14}H_{27}]$  $C_{13}H_{27} - C_{14}H_{27}$ ], 390 (23)  $[M^{+} - C_{13}H_{27} - C_{15}H_{29}]$ . HMRS  $(C_{52}H_{65}N_2O_4)$ : Calcd. m/z: 781.494 [ $M^{+}$  + H]; found m/z: 781.496.

**2-(1-Octylnonyl)-9-(4-vinylphenyl)anthra[2,1,9-***def***;6,5,10-***d'e'f***]diisoqui noline-1,3,8,10-tetraone (6a)**: 9-(1-Ocytlnonyl)-2-benzopyrano[6',5'4':10,5,6] anthra[2,1,9-*def*]iso-quinoline-1,3,8,10-tetraone (494 mg, 0.784 mmol) 4-vinylaniline (121 mg, 1.02 mmol), imidazole (6.0 g) the quantity of a microspatulum of zincacetate dihydrate, acetic acid (120 mL, replacement of ethanol) and 2 N aqueous HCl (100 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-t etraone (42) and purified by column separation (800 mL of silica gel, chloroform/ethanol 30:1, glas column grobes 780 × 44 mm). Yield 362 mg (63%) light red solid, m.p. > 250°C.  $R_{\rm f}$ -value (alumina, CHCl<sub>3</sub>) = 0.49. IR (KBr):  $\tilde{\nu}$  = 3091.5 (w), 2954.2 (m), 2925.0 (m), 2854.5 (m), 1698.4 (s), 1658.4 (vs), 1594.6 (s), 1578.2 (m), 1510.3 (w), 1483.5 (w), 1465.6 (w), 1433.8 (w), 1404.8 (m), 1343.9 (s), 1301.8 (w), 1254.9 (m), 1197.0 (w), 1176.7 (w), 1137.9 (w), 1124.8 (w), 1112.7 (w), 988.2 (w), 970.0 (w), 908.6 (w), 846.4 (w), 810.5 (m), 798.2 (w), 746.6 (m), 722.1 (w), 617.6 (w), 592.5 (w), 499.1 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.83$  (t,  ${}^{3}$ /(H,H) = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 1.20 - 1.38 (m, 24 H, 12 × CH<sub>2</sub>), 1.85 - 1.91 (m, 2 H, β-CH<sub>2</sub>), 2.22 - 2.28 (m, 2 H, β-CH<sub>2</sub>), 5.16 -5.21 (m, 1 H, a-CH<sub>2</sub>), 5.30 (m, 1 H, CH<sub>2.0lefin</sub>), 5.82 - 5.85 (m, 1 H, CH<sub>2.0lefin</sub>), 6.79 - 6.84 (m, 1 H,  $CH_{olefin}$ ), 7.32 - 7.33 (m, 2 H, 2 ×  $CH_{arvl}$ ), 7.60 - 7.62 (m, 2 H, 2 ×  $CH_{arv}$ ), 8.61 - 8.72 ppm (m, 8 H, 8 ×  $CH_{pervlene}$ ). <sup>13</sup>C NMR (150 MHz,  $CDCl_3$ , 25°C, TMS): δ = 14.1, 22.6, 27.0, 29.2, 29.5, 31.8, 32.4, 54.8, 115.1, 123.0, 123.3, 124.2, 126.4, 126.6, 127.2, 128.7, 129.5, 129.8, 131.1, 131.8, 134.3, 135.1, 136.1, 138.3, 163.5, 164.5 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 459.4 (0.22), 490.2 (0.60), 526.8 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 535.3 (1.00), 579.0 (0.53), 626.3 nm (0.13). Fluorescence quantum yield ( $\lambda_{exc}$  = 489 nm,  $E_{489 \text{ nm/l cm}}$  = 0.0372; reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diiso- quinoline-1, 3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 730 (20)  $[M^{t}]$ , 617 (2)  $[M^{t} - C_{8}H_{17}]$ , 492 (100)  $[M^{t} - C_{17}H_{35}]$ . HMRS ( $C_{49}H_{50}N_{2}O_{4}$ ): Calcd. *m/z*: 731.384 [*M*<sup>+</sup> + H]; found *m/z*: 731.382.

2-Allyl-9-(1-nonyldecyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8, **10-tetraone:** 9-(1-Nonyldecyl)-2-benzopyrano[6',5'4':10,5,6]anthra[2,1,9-*def*] isoquinoline-1,3,8,10-tetraone (300 mg, 0.456 mmol), imidazole (7.0 g), allylamine (150 mg, 2.63 mmol), the quantity of a microspatulum of zincacetate dihydrate, acetic acid (100 mL, replacement of ethanol) and 2 N aqueous HCl (150 mL, precipitation with ice-cooling) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxy-ethyl)anthra[2,1,9-def,6,5,10-d'e'f]diiso quinoline-1,3,8,10-tetraone and purified by column separation (500 mL of alumina, chloroform/*n*-pentane 2:1, glass column 500 × 44 mm and then 800 mL of silica gel, chloroform/ethanol 80:1, glass column 780 × 44 mm). Yield 112 mg (35%) dark red solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 80:1) = 0.19. IR (KBr):  $\tilde{\nu}$  = 2924.1 (s), 2853.6 (m), 1698.5 (s), 1658.7 (s), 1595.5 (s), 1578.0 (m), 1506.2 (w), 1436.2 (w), 1404.2 (m), 1376.5 (w), 1346.0 (m), 1252.4 (m), 1175.0 (w), 1096.2 (w), 993.6 (w), 937.0 (w), 851.4 (w), 809.9 (m), 795.4 (w), 746.9 cm<sup>-1</sup> (m). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.83$  (t, <sup>3</sup>/(H,H) = 7.0 Hz, 6 H,  $2 \times CH_3$ ), 1.20 - 1.27 (m, 28 H,  $14 \times CH_2$ ), 1.87 (m, 2 H,  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2 H, a-CH<sub>2</sub>), 4.84 (d,  ${}^{3}$ /(H,H) = 5.8 Hz, 2 H, N-CH<sub>2</sub>), 5.18 (m, 1 H, N-CH), 5.25 (d, <sup>3</sup>/(H,H) = 10.5 Hz, 1 H, CH<sub>2,olefin</sub>.), 5.37 (d, <sup>3</sup>/(H,H) = 16.3, 1 H,  $CH_{2,olefin.}$ ), 6.02 (m, 1 H,  $CH_{olefin.}$ ), 8.59 - 8.68 ppm (m, 8 H, 8 ×  $CH_{perylene}$ ). UV/Vis  $(CHCl_3): \lambda_{max} (E) = 459 (0.23), 489 (0.60), 526 nm (1.00). Fluorescence (CHCl_3):$  $\lambda_{\text{max}}$  (I) = 533 (1.00), 577 nm (0.37). Fluorescence quantum yield (CHCl<sub>3</sub>,  $\lambda_{\text{exc}}$  =

487 nm,  $E_{487 \text{ nm/l cm}} = 0.0304$ ; reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*; 6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS (DEI<sup>+</sup>/70 eV): *m/z* (%): 696 (78) [*M*<sup>+</sup>], 430 (100) [*M*<sup>+</sup> - C<sub>19</sub>H<sub>38</sub>], 415 (46) [430 - CH<sub>3</sub>]. HMRS (C<sub>46</sub>H<sub>52</sub>N<sub>2</sub>O<sub>4</sub>): Calcd. *m/z*: 696.393; found *m/z*: 696.394.

2-(1-Nonyldecyl)-9-(4-vinylphenyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoqui noline-1,3,8,10-tetraone (6b): Variant I: 9-(1-Nonyldecyl)-2-benzopyrano[6', 5'4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (500 mg, 0.760 mmol), imidazole (6.0 g), 4-amino-styrene (161 mg, 1.35 mmol), the quantity of a microspatulum of zincacetate dihydrate, acetic acid (80 mL, replacement of ethanol) and 2 N aqueous HCl (100 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-envl)-9-(2-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e'f] diisoquinoline-1,3,8,10-tetraone and purified by column separation (800 mL silica gel, chloroform, glass column 780 × 44 mm). Yield 281 mg (49%) dark red solid. Variant II: 9-(4-Phenylacrylsäure)-2-benzopyrano[6',5'4': 10,5,6]anthra [2,1,9-def]isoquinoline-1,3,8,10-tetraone (400 mg, 0.744 mmol), 1-nonyldecylamine (274 mg, 0.967 mmol) imidazole (6.0 g), the quantity of a microspatulum of zincacetate dihydrate, acetic acid (100 mL, replacement of ethanol) and 2 N aqueous HCl (120 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl)-anthra-[2,1,9-def,6,5,10-d'e'f]diis oquinoline-1,3,8,10-tetraone and purified by column separation (500 mL of silica gel, chloroform, glass colmn 500 × 44 mm). Yield < 1%, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>) = 0.43. IR (KBr):  $\tilde{\nu}$  = 3092.1 (m), 2954.3 (m), 2924.5 (s), 2854.0 (m), 1698.6 (s), 1658.6 (s), 1594.6 (s), 1578.1 (m), 1510.5 (m), 1483.3 (w), 1465.6 (w), 1433.9 (m), 1404.6 (m), 1344.2 (s), 1302.0 (w), 1255.2 (s), 1197.0 (w), 1177.4 (m), 1137.9 (w), 1125.1 (w), 1113.5 (w), 988.1 (w), 963.5 (w), 921.3 (w), 847.5 (w), 810.5 (m), 798.2 (m), 757.9 (w), 746.6 (m), 722.1 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 0.83 (t, <sup>3</sup>/(H,H) = 7.1 Hz, 6 H, 2 × CH<sub>3</sub>), 1.21 - 1.32 (m, 28 H, 14 × CH<sub>2</sub>), 1.84 - 1.90 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 2.22 - 2.28 (m, 2 H,  $\beta$ -CH<sub>2</sub>), 5.19 (m, 1 H,  $\alpha$ -CH), 5.35 (d, <sup>3</sup>/(H,H) = 10.9 Hz, 1 H, CH<sub>2 olefin</sub>),  $5.84 (d, {}^{3}/(H,H) = 17.6 Hz, 1 H, CH_{2.0lefin}), 6.81 (dd, {}^{3}/(H,H) = 17.6, 10.9 Hz, 1 H,$  $CH_{olefin}$ ), 7.32 (d,  ${}^{3}f(H,H) = 8.3$  Hz, 2 H,  $CH_{arvl}$ ), 7.61 (d,  ${}^{3}f(H,H) = 8.3$  Hz, 2 H,  $CH_{arv}$ ), 8.62 - 8.73 ppm (m, 8 H, 8 ×  $CH_{pervlene}$ ). <sup>13</sup>C NMR (151 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 14.4, 32.0, 27.3, 29.6, 29.8, 30.0, 32.2, 32.7, 55.1, 115.5, 123.4, 123.6, 126.7, 127.0, 127.5, 129.0, 129.9, 130.2, 132.2, 134.6, 134.7, 135.5, 136.4, 138.6, 163.9 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 459 (0.22), 490 (0.60), 527 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 534 (1.00), 578 nm (0.40). Fluorescence quantum yield (CHCl<sub>3</sub>,  $\lambda_{exc}$  = 489 nm,  $E_{489 \text{ nm/1 cm}}$  = 0.0319; reference: 2,9-bis-(1hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]: 1.00. MS (DEI<sup>+</sup>/70 eV): m/z (%): 758 (27) [ $M^{+}$ ], 492 (100) [ $M^{+}$  - $C_{19}H_{38}$ ], 373 (16)  $[C_{24}H_7NO_4]$ . HMRS  $(C_{51}H_{55}N_2O_4)$ : Calcd. *m/z*.759.416  $[M^+ +$ H]; found *m/z*: 759.418.

**2-Allyl-9-(2,5-di-***tert*-butylphenyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquin oline-1,3,8,10-tetraone:9-(2,5-Di-*tert*-butylphenyl)-2-benzopyrano[6',5'4':10,

5,6]anthra[2,1,9-def]-isoquinoline-1,3,8,10-tetraone (120 mg, 0.207 mmol), imidazole (3.0 g), allylamine (35 mg (0.63 mmol), the quantity of a microspatulum of zincacetate dihydrate, ethanol (40 mL) and 2 N aqueous HCl (120 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6envl)-9-(2-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tet raone and purified by column separation (500 mL of silica gel, chloroform/ethanol 30:1, glass column 500 × 44 mm). Yield: 71 mg (55%) dark red solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 30:1) = 0.21. IR (KBr):  $\tilde{\nu}$ = 2961.5 (m), 2924.2 (m), 1701.0 (m), 1663.1 (m), 1594.3 (m), 1578.7 (m), 1507.5 (w), 1435.8 (w), 1402.1 (m), 1359.5 (m), 1252.8 (w), 1177.8 (w), 1125.7 (w), 997.5 (w), 854.3 (w), 826.5 (w), 811.6 (w), 794.1 (w), 750.2 (w), 734.0 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 1.23$  (s, 9 H, *tert*-butyl), 1.27 (s, 9 H, *tert*-butyl), 4.79 (d,  ${}^{3}f(H,H) = 5.9$  Hz, 2 H, N–CH<sub>2</sub>), 5.19 (d,  ${}^{3}f(H,H) = 10.3$  Hz, 1 H, CH<sub>2.olefin</sub>), 5.31 (d, <sup>3</sup>/(H,H) = 17.0 Hz, 1 H, CH<sub>2.olefin</sub>), 5.97 (m, 1 H, CH<sub>olefin</sub>), 6.97 (s, 1 H, CH<sub>arvl</sub>), 7.41 (d,  ${}^{3}/(H,H) = 8.6$  Hz, 1 H, CH<sub>arvl</sub>), 7.53 (d,  ${}^{3}/(H,H) = 8.6$ Hz, 1 H, CH<sub>arvl</sub>), 8.60 - 8.71 ppm (m, 8 H, CH<sub>pervlene</sub>). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 458 (0.22), 490 (0.60), 526 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 534 (1.00), 575 (0.35), 622 nm (0.06). Fluorescence quantum yield (CHCl<sub>3</sub>,  $\lambda_{exc}$  = 488 nm,  $E_{488 \text{ nm/l cm}} = 0.0571$ ; reference: 2,9-bis-(1-hexylheptyl)anthra- [2,1,9-*def*;6,5,10d'e'f diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS (DEI<sup>+</sup>/70 eV): m/z (%): 618 (3)  $[M^{t}]$ , 561 (100)  $[M^{t} - C_{4}H_{9}$  (isobutene)], 545 (7) [561 -CH<sub>3</sub>]. HMRS (C<sub>41</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>): Calcd. *m/z*: 618.252; found *m/z*: 618.253.

2-Allyl-9-(2,2-dibutyl-hept-6-enyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquin oline-1,3,8,10-tetraone (14): 9-Allyl-2-benzopyrano[6',5'4':10,5,6]anthra [2,1, 9-def jisoquinoline-1,3,8,10-tetraone (1.00 g, 2.32 mmol), imidazole (5.0 g); 2,2-dibutylhept-6-envlamine (672 mg, 2.78 mmol), the quantity of a microspatulum of zincacetate dihydrate, ethanol (15 mL) and 2 N aqueous HCl (80 mL) were allowed to react as was described for 2-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl) anthra[2,1,9-*def*,6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone and purified by column separation (800 mL of silica gel, chloroform/ethanol 50:1, glass column  $800 \times 42$  mm) and then 500 mL of alumina, chloroform/ethanol 50:1, glass column 780 × 44 mm). The material was dissolved in the minimal amount of chloroform and treated with vapour of methanol at room temperature for isothermal distillation. Yield 807 mg (54%) red needles, m.p. > 250°C. R-value (alumina;  $CHCl_3$  = 0.38. IR (ATR):  $\tilde{v}$  = 2928.8 (s), 2858.9 (m), 1692.8 (s), 1652.1 (vs), 1591.5 (s), 1507.1 (w), 1433,5 (m), 1403.7 (m), 1368.7 w, 1325.2 (s), 1246.0 (m), 1179.7 (w), 1091.5 (w), 1011.2 (w), 925.4 (w), 849.2 (w), 808.6 (m), 792.5 (w), 748.6 (m), 655.5 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 0.89 (t,  ${}^{3}$ /(H,H) = 7.1 Hz, 6 H, 2 × CH<sub>3</sub>), 1.25 - 1.35 (m, 14 H, 7 × CH<sub>2</sub>), 1.42 - 1.47 (m, 2 H, CH<sub>2</sub>), 2.00 (m, 2 H, CH<sub>2</sub>), 4.22 (s, 2 H, N-CH<sub>2</sub>), 4.84 (d, 2 H,  ${}^{3}f(H,H) = 5.9$ Hz, N-CH2), 4.89 - 4.90 (m, 1 H, CH2.olefin.), 4.91 - 4.92 (m, 1 H, CH2.olefin.), 4.96 -4.97 (m, 1 H, CH<sub>2.0lefin</sub>), 4.99 - 5.00 (m, 1 H, CH<sub>2.0lefin</sub>), 5.24 - 5.25 (m, 1 H, CH<sub>2,olefin</sub>), 5.26 - 5.27 (m, 1 H, CH<sub>2,olefin</sub>), 5.36 - 5.37 (m, 1 H, CH<sub>2,olefin</sub>), 5.39 -

5.40 (m, 1 H, CH<sub>2,0lefin</sub>.), 5.78 - 5.85 (m, 1 H, CH<sub>olefin</sub>.), 6.00 - 6.07 (m, 1 H, CH<sub>olefin</sub>.), 8.55 - 8.57 (m, 4 H, CH<sub>aromat</sub>.), 8.61 - 8.83 (m, 2 H, CH<sub>aromat</sub>.), 8.66 - 8.67 ppm (m, 2 H, CH<sub>aromat</sub>.). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 14.4, 23.3, 24.0, 26.0, 35.1, 36.1, 36.2, 40.9, 42.8, 114.5, 118.2, 123.1, 123.3, 123.4, 123.9, 126.5, 126.7, 129.4, 130.0, 131.6, 131.7, 132.2, 134.5, 135.0, 139.4, 163.3, 164.4 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 456.8 (18100), 488.0 (49700), 524.4 nm (82500). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (I) = 533.0 (1.00), 574.5 (0.52), 623.5 nm (0.12). Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{488 \text{ nm/1 cm}}$  = 0.0306, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]-diisoquinoline-1,3,8,10-tetr aone (1) with  $\Phi$  = 1.00 [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 638 (90) [*M*<sup>+</sup>], 444 (100) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub>], 429 (35) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub> - CH<sub>3</sub>], 415 (8) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub> - 2 × CH<sub>3</sub>]. C<sub>42</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub> (638.8): Calcd. C 78.97, H 6.96, N 4.39; found C 78.89, H 6.63, N 4.40.

2-{2-(2,2-Dibutylhept-6-enyl)-9-(2-ethoxyethyl)anthra[2,1,9-def;6,5,10-d 'e f']diisoquinoline-1,3,8,10-tetraon}-9-(2,2-dibutylhept-6-enyl)-anthra[2, 1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (12): 2-(2,2-Dibutyl-hept-6envl)-9-(2-hydroxyethyl)-anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-te traone (700 mg, 1.09 mmol) was dissolved in refluxing dichloromethane (450 mL), treated with diisopropylethylamine (7 mL, dark red solution), treated dropwise with methanesulfonicchloride (3.0 mL, 39 mmol), heated with reflux for 3 h, allowed to cool, treated with distilled water (250 mL) shaken with 2 N aqueous HCl (150 mL), evaporated, dissolved in the minimal amount of chloroform, precipitated with methanol, colled by vaccum filtration (D4 micro glass filter), dried in air and purified by column separation (100 mL of silica gel, chloroform/ethanol 30:1, second fraction, glass column 800 × 44 mm, and a second column separation with silica gel, chloroform/ethanol 30:1). Yield 496 mg (72%) red, only sparingly soluble solid, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 30:1) = 0.12. IR (ATR):  $\tilde{v}$  = 3519.7 (w,br.), 3070.6 (w), 2952.7 (m), 2928.8 (m), 2859.8 (m), 1692.9 (s), 1645.4 (vs), 1592.8 (vs), 1576.3 (m), 1506.1 (w), 1482.1 (w), 1457.2 (w), 1437.6 (m), 1402.9 (m), 1355.7 (s), 1248.4 (m), 1199.2 (w), 1169.2 (w), 1125.9 (w), 1059.5 (w), 1024.5 (w), 907.6 (w), 855.8 (w), 808.7 (m), 793.6 (w), 744.0 (m), 667.9 (w), 640.2 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.89$  (t, <sup>3</sup>/(H,H) = 7.1 Hz, 12 H, 4 × CH<sub>3</sub>), 1.25 -1.35 (m, 28 H, 14 CH<sub>2</sub>), 1.42 - 1.48 (m, 4 H,  $2 \times$  CH<sub>2</sub>), 2.00 - 2.03 (m, 4 H,  $2 \times$  $C_{a}$ -CH<sub>2</sub>), 4.04 (t, <sup>3</sup>/(H,H) = 5.2 Hz, 4 H, 2 × N-CH<sub>2</sub>-CH<sub>2</sub>), 4.24 (s, 4 H, 2 × N-CH<sub>2</sub>), 4.51 (t,  ${}^{3}/(H,H) = 5.4$  Hz, 4 H, 2 × CH<sub>2</sub>-OH), 4.89 - 4.91 (m, 2 H, 2 ×  $CH_{2,olefin.}$ ), 4.96 - 4.99 (m, 2 H, 2 ×  $CH_{2,olefin.}$ ), 5.78 - 5.85 (m, 2 H, 2 ×  $CH_{olefin.}$ ), 8.58 - 8.70 ppm (m, 16 H,  $16 \times CH_{pervlene}$ ). <sup>13</sup>C NMR (150 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 14.2, 23.0, 23.7, 25.7, 34.8, 35.8, 35.9, 40.7, 43.0, 45.6, 61.4, 114.2,$ 122.7, 122.8, 123.2, 123.5, 125.9, 126.1, 128.9, 129.3, 131.0, 131.4, 133.8, 134.6, 139.2, 164.0 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 458.6 (0.23), 489.6 (0.61), 526.2 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 537.8 (1.00), 577.8 (0.52), 625.5 nm (0.13). Fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 488 nm,  $E_{488 \text{ nm/l cm}}$  = 0.0274; reference:

2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetra one (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 1267 (< 1) [ $M^+$ ], 642 (100)  $[M^{+} - C_{41}H_{41}N_{2}O_{4}]$ , 626 (24)  $[M^{+} - C_{41}H_{41}N_{2}O_{5}]$ , 448 (64)  $[M^{+} - C_{41}H_{41}N_{2}O_{5}]$  $C_{41}H_{41}N_2O_4 - C_{14}H_{27}$ , 405 (99)  $[M^{+} - C_{41}H_{41}N_2O_4 - C_{15}H_{29}]$ . HMRS  $(C_{82}H_{82}N_4O_9)$ : Calcd. *m/z*: 1266.608; found *m/z*: 1266.609. Byproduct I: 2-(2,2-Dibutylhept-6-enyl)-9-(2-methoxyethyl)anthra[2,1,9-def,6,5,10-d'e'f'] diisoquinoline-**1,3,8,10-tetraone**): Yield 39 mg (5%) red solid, m.p. > 250°C. *R*<sub>-</sub>value (silica gel, CHCl<sub>3</sub>/EtOH 30:1) = 0.12. IR (ATR):  $\tilde{v}$  = 3069.3 (w), 2953.6 (m), 2929.38 m), 2860.5 (m), 1694.9 (s), 1650.8 (vs), 1593.0 (s), 1577.2 (m), 1506.6 (w), 1482.1 (w), 1437.4 (m), 1403.3 (m), 1335.7 (s), 1247.3 (m), 1198.6 (w), 1173.9 (w), 1158.3 (w), 1112.7 (w), 1064.1 (w), 1015.7 (w), 909.7 (w), 852.7 (w), 808.7 (m), 794.0 (w), 744.8 (m), 668.1 (w), 640.5 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 0.89$  (t, <sup>3</sup>/(H,H) = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 1.26 - 1.46 (m, 14 H, 7 × CH<sub>2</sub>), 2.00 - 2.03 (m, 2 H, C<sub>q</sub>-CH<sub>2</sub>), 3.42 (s, 3 H, OCH<sub>3</sub>), 3.78 (t,  ${}^{3}/(H,H) = 5.3$ Hz, 2 H, N-CH<sub>2</sub>-CH<sub>2</sub>), 4.23 (s, 2 H, N-CH<sub>2</sub>), 4.48 (t,  ${}^{3}/(H,H) = 5.3$  Hz, 2 H, MeO-CH<sub>2</sub>), 4.89 - 4.91 (m, 1 H, CH<sub>2.olefin</sub>), 4.96 - 5.00 (m, 1 H, CH<sub>2.olefin</sub>), 5.78 -5.85 ppm (m, 1 H, CH<sub>olefin</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 14.4, 24.0, 25.9, 35.1, 36.2, 39.7, 40.9, 45.8, 59.1, 69.8, 114.5, 123.1, 123.3, 131.5, 131.7, 134.5, 134.9, 139.4, 163.7, 164.4 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 458.4 (0.23), 489.4 (0.61), 525.8 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (I) = 534.8 (1.00), 578.0 (0.54), 626.3 nm (0.13). Fluorescence quantum yield ( $\lambda_{exc}$  = 488 nm,  $E_{488}$  $_{nm/1 cm} = 0.02590$ ; reference: 2,9-bis-(1-hexylheptyl)anthra[2,1, 9-def;6,5,10d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$ ): 1.00. MS: (DEI<sup>+</sup>/70 eV): m/z (%): 656 (66)  $[M^{+}]$ , 587 (21)  $[M^{+} - C_{5}H_{9}]$ , 462 (39)  $[M^{+} - C_{14}H_{27}]$ , 449 (38)  $[M^{t} - C_{15}H_{29}], 404 (100) [M^{t} - C_{14}H_{27} - C_{3}H_{7}O], 390 (26) [M^{t} - C_{15}H_{29} - C_{15}H_{29}]$ C<sub>3</sub>H<sub>7</sub>O]. HMRS (C<sub>42</sub>H<sub>44</sub>N<sub>2</sub>O<sub>5</sub>): Calcd. *m/z*: 656.325; found *m/z*: 656.326. Byproduct II: 2-(2,2-Dibutylhept-6-enyl)-9-(2-chlorethyl)anthra- [2,1,9-def, 6,5,10-d'e'f] diisoquinoline-1,3,8,10-tetraone (50): Yield 51 mg (8%) red powder, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel; CHCl<sub>3</sub>/EtOH 30:1) = 0.12. IR (ATR):  $\tilde{v}$  = 3068.9 (w), 2952.2 (m), 2932.6 (m), 2868.7 (m), 1695.4 (s), 1658.9 (vs), 1612.7 (w), 1592.7 (s), 1578.3 (m), 1507.4 (w), 1482.0 (w), 1457.9 (w), 1435.8 (m), 1404.1 (m), 1378.3 (m), 1355.8 (m), 1329.2 (s), 1251.9 (m), 1180.0 (w), 1161.3 (w), 1124.0 (w), 1097.4 (w), 1015.1 (m), 964.1 (w), 906.4 (w), 855.5 (m), 807.3 (m), 794.0 (m), 744.4 (m), 668.3 (w), 643.3 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 0.89 (t, <sup>3</sup>/(H,H) = 7.0 Hz, 6 H, 2 × CH<sub>3</sub>), 1.25 - 1.35 (m, 14 H,  $7 \times CH_2$ ), 1.42 - 1.47 (m, 2 H,  $CH_2$ ), 2.00 - 2.03 (m, 2 H,  $C_g$ - $CH_2$ ), 3.90 (t,  ${}^{3}$ /(H,H) = 6.8 Hz, 2 H, N-CH<sub>2</sub>-CH<sub>2</sub>), 4.23 (s, 2 H, N-CH<sub>2</sub>), 4.61 (t,  ${}^{3}$ /(H,H) = 6.8 Hz, 2 H, CH<sub>2</sub>-Cl), 4.89 - 4.92 (m, 1 H, CH<sub>2.0lefin</sub>), 4.96 - 5.00 (m, 1 H, CH<sub>0lefin</sub>), 5.78 - 5.85 (m, 1 H, CH $_{\rm olefin}$ ), 8.55 - 8.68 ppm (m, 8 H, 8  $\times$  CH $_{\rm pervlene}$ ).  $^{13}C$  NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 14.4, 23.3, 24.0, 26.0, 35.1, 36.1, 40.7, 40.9, 41.6, 45.9, 114.5, 123.0, 123.1, 123.5, 124.0, 129.4, 131.5, 131.9, 134.3, 135.2, 139.4, 163.5, 164.4 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 458.8 (0.22), 489.6 (0.60), 526.0 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 535.0 (1.00), 577.5 (0.53),

624.5 nm (0.12). Fluorescence quantum yield ( $\lambda_{exc} = 488$  nm,  $E_{nm/1 cm} = 0.0393$ ; reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*,6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 660 (62) [*M*<sup>+</sup>], 626 (71) [*M*<sup>+</sup> - Cl], 466 (95) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub>], 432 (100) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub> -Cl], 404 (54) [*M*<sup>+</sup> - C<sub>14</sub>H<sub>27</sub> - C<sub>2</sub>H<sub>4</sub>Cl], 390 (15) [*M*<sup>+</sup> - C<sub>15</sub>H<sub>29</sub> - C<sub>2</sub>H<sub>4</sub>Cl]. HMRS (C<sub>41</sub>H<sub>41</sub>ClN<sub>2</sub>O<sub>4</sub>): Calcd. *m/z*: 660.276; found *m/z*: 660.277.

2-(1-Hexylheptyl)-9-{4-(2-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d' e' f'*] diisoquino-

line-1,3,8,10-tetraon-9-yl)but-2-enyl}anthra[2,1,9-def,6,5,10-d'e'f]diisoguin oline-1,3,8,10-tetraone(5):2-Allyl-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f' ]diisoquinoline-1,3,8,10-tetraone (300 mg,490 µmol) under argon atmosphere was disperged in dichloromethane (10 mL), heated to 50°C, treated with second -generation Hoveyda-Grubbs-catalyst (3, 42 mg, 50 µmol darkening of the reaction mixture) heated to reflux for 2 h (red precipitate), evaporated in vacuo, treated with a small amount of chloroform and purified by column separation (800 mL of silica gel, chloroform/ethanol 40:1, glass column 780 × 44 mm, second red fraction after the starting material). Yield 112 mg (19%) reddish brown, sparingly soluble solid (cis/trans-mixture), m.p. > 250°C. R-value (silica gel, CHCl<sub>3</sub>/EtOH 40:1) = 0.22 (*cis*-isomer), 0.24 (*trans*-isomer). IR (KB\$r):  $\tilde{V}$  = 2925.1 (m), 2854.8 (m), 1697.4 (m), 1655.7 (m), 1594.6 (m), 1436.0 (w), 1404.0 (m), 1339.9 (m), 1249.5 (w), 1170.4 (w), 851.9 (w), 810.3 (w), 747.0 cm<sup>-1</sup> (w). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS): *cis*-isomer:  $\delta = 0.83$  (t, <sup>3</sup>/(H,H) = 7.0 Hz, 12 H,  $4 \times CH_3$ , 1.16 - 1.41 (m, 32 H, 16 × CH<sub>2</sub>), 1.83 - 1.89 (m, 4 H, 2 ×  $\beta$ -CH<sub>2</sub>), 2.21 - 2.28 (m, 4 H,  $2 \times \beta$ -CH<sub>2</sub>), 5.15 - 5.21 (m, 2 H,  $2 \times \alpha$ -CH), 5.24 - 5.25 (m, 4 H,  $2 \times \text{N-CH}_2$ ), 5.86 - 5.88 (m, 2 H,  $2 \times \text{CH}_{\text{olefin}}$ ), 8.57 - 8.74 ppm (m, 16 H, 16 × CH<sub>pervlene</sub>); *trans*-isomer:  $\delta = 0.83$  (t, <sup>3</sup>/(H,H) = 7.9 Hz, 12 H, 4 × CH<sub>3</sub>), 1.16 - 1.41 (m, 32 H, 16 × CH<sub>2</sub>), 1.83 - 1.89 (m, 4 H, 2 ×  $\beta$ -CH<sub>2</sub>), 2.21 - 2.28 (m, 4 H, 2 ×  $\beta$ -CH<sub>2</sub>), 4.83 - 4.84 (m, 4 H, 2 × N-CH<sub>2</sub>), 5.15 - 5.21 (m, 2 H, 2 ×  $\alpha$ -CH), 6.09 -6.11 (m, 2 H, CH  $_{\rm olefin})$ , 8.57 - 8.74 ppm (m, 16 H, 16  $\times$  CH  $_{\rm pervlene})$ . UV/Vis  $(CHCl_3): \lambda_{max}$  (E) = 459.8 (0.23), 490.2 (0.63), 527.2 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 534.0 (1.00), 576.0 nm (0.35). Fluorescence quantum yield  $(\lambda_{\text{exc}} = 488 \text{ nm}, E_{488 \text{nm/lcm}} = 0.0448; \text{ reference: 2,9-bis-(1-hexylheptyl)anthra[2,1, methods]}$ 9-*def*,6,5,10-*d'e'f*]diiso-quinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 1.00. MS (DEI+/70 eV): m/z (%): 1197 (51) [ $M^{+}$ ], 1014 (58) [ $M^{+} - C_{13}H_{27}$ ], 833 (100)  $[M^{t} - 2 \times C_{13}H_{26}]$ , 815 (33), 624 (22)  $[M^{t} - C_{37}H_{35}N_{2}O_{4}]$ , 611 (12)  $[M^{t} - C_{37}H_{35}N_{2}O_{4}]$  $C_{38}H_{37}N_2O_4$ ], 572 (11) [ $M^{+} - C_{41}H_{41}N_2O_4$ ], 442 (92) [ $M^{+} - C_{37}H_{35}N_2O_4 - C_{13}H_{27}$ ], 429 (15)  $[M^{+} - C_{38}H_{37}N_{2}O_{4} - C_{13}H_{26}], 417$  (56)  $[M^{+} - C_{39}H_{37}N_{2}O_{4} - C_{13}H_{26}], 416$ (21)  $[M^{\dagger} - C_{39}H_{38}N_2O_4 - C_{13}H_{26}], 403$  (8)  $[M^{\dagger} - C_{40}H_{39}N_2O_4 - C_{13}H_{26}], 390$  (92)  $[M^{\dagger} - C_{41}H_{40}N_2O_4 - C_{13}H_{26}], 373 (30) [M^{\dagger} - C_{41}H_{41}N_3O_4 - C_{13}H_{27}], 347 (36) [M^{\dagger}]$  $-C_{41}H_{41}N_3O_4 - C_{13}H_{26} - CO]$ , 345 (13), 69 (15), 55 (17). HMRS ( $C_{78}H_{76}N_4O_8$ ): Calcd. *m/z*: 1196.566; found *m/z*: 1196.561.

2-(2,5-Di-*tert*-butylphenyl)-9-{4-(2-(2,5-di-*tert*-butylphenyl)anthra[2,1,9 -*def*;6,5,10-*d' e' f'*]diisoquinoline-1,3,8,10-tetraon-9-yl)but-2-enyl}anthra[2, 1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone:2-Allyl-9-(2,5-di-tert-bu tylphenyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone(50.0 mg, 80.8 µmol) under argon atmosphere was dissolved in dichloromethane (5 mL), treated with second-generation Hoveyda-Grubbs-catalyst (3, 9.15 mg, 14.6 µmol), heated to reflux for 20 h, terated with further second-generation Hoveyda-Grubbs-catalyst (5 mg, 8  $\mu$ mol = 10 Mol %), heated to reflux for further 7 h, stirred at room temperature for 36 h, quenched by the addition of chloroform (10 mL) and distilled water (10 mL) stirred for 1 h shaken two timed with a misture of chloroform/water 1:1 with the collection of the organic phaseand purified by medium pressure chromatography (silica gel, chloroform/ethanol 40:1 at 10 mL·min<sup>-1</sup>, column 36 × 460 mm, second red fraction, and a second chromatography with silica gel, chloroform/ethanol 30:1). Yield 5.1 mg (5%) dark red, pigment-like powder.  $R_{\rm f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 40:1) = 0.17. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 459.8 (0.22), 491.0 (0.58), 529.0 nm (1.00). Fluorescence  $(CHCl_3): \lambda_{max}$  (I) = 540.5 (1.00), 578.0 (0.74), 626.5 nm (0.17). Fluorescence quantum yield ( $\lambda_{exc}$  = 489 nm,  $E_{488 \text{ nm/lcm}}$  = 0.0233; reference: 2,9-bis-(1hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00 \ [40]$ ): 1.00. MS (DEI<sup>+</sup>/70 eV): m/z (%): 1151 (24)  $[M^{+} - C_4H_8]$ , 573 (28), 521 (100)  $[M^{+} - C_{46}H_{43}N_{2}O_{4}]$ , 505 (15)  $[M^{+} - C_{47}H_{47}N_{2}O_{4}]$ . HMRS  $(C_{80}H_{65}N_{4}O_{8})$ : Calcd. *m/z*: 1209.480 [*M*<sup>+</sup> + H]; found *m/z*: 1209.479.

2-(1-Octylnonyl)-9-{4'-(2-(1-octylnonyl)anthra[2,1,9-def;6,5,10-d' e' f'] diisoquino-

line-1,3,8,10-tetraon-9-yl)-stilben-4-yl}anthra[2,1,9-*def*;6,5,10-*d' e' f*]diis oquino-

line-1,3,8,10-tetraone(7a):2-(1-Octylnonyl)-9-(4-vinylphenyl)anthra[2,1,9-def, (65,10-d'e'f') diiso-quinoline-1,3,8,10-tetraone (**6a**, 203 mg, 278 µmol) under argon atmosphere was dissolved in refluxing chloroform (20 mL), treated with second-generation Hoveyda-Grubbs-catalyst (3, 11.7 mg, 13.8 µmol) heated with stirring (bath 80°C) for 1 h and further 12 h at room temperature (no detectable reaction), treated with futher second-generation Hoveyda-Grubbs-catalyst (3, 13.0 mg, 15.3 µmol) heated to reflux for 8 h (formation of a pigment-like red precipitate), collected by vacuum filtration (D4 micro glass filter) and thoroughly washed with hot chloroform to remove staring materials and by-products. Yield 66 mg (17%) red pigment, m.p. > 250°C. IR (KBr):  $\tilde{v}$  = 2952.7 (m), 2924.0 (s), 2853.6 (m), 1698.2 (s), 1660.1 (s), 1594.4 (s), 1578.3 (m), 1513.8 (m), 1483.7 (w), 1464.7 (w), 1433.5 (m), 1405.6 (m), 1342.8 (s), 1303.9 (w), 1254.0 (m), 1195.6 (m), 1174.8 (m), 1136.8 (w), 1124.2 (w), 1111.4 (w), 1019.7 (w), 963.5 (w), 853.0 (w), 835.9 (w), 811.7 (m), 798.8 (m), 747.3 (m), 616.1 (w), 549.9 (w), 491.5 (w), 430.5 cm<sup>-1</sup> (w). UV/Vis (H<sub>2</sub>SO<sub>4</sub>):  $\lambda_{max}$  (*E*) = 404.8 (0.10), 557.8 (0.58), 602.4 nm (1.00). Fluorescence (H<sub>2</sub>SO<sub>4</sub>):  $\lambda_{max}$  (*I*) = 623.0 nm (1.00). MS (FAB<sup>+</sup>/70 eV): m/z (%): 1433 [M<sup>+</sup>], 879, 823, 801, 765, 749, 731, 613, 460, 391, 307, 154.

2-(1-Nonyldecyl)-9-{4'-(2-(1-nonyldecyl)anthra[2,1,9-def;6,5,10-d'e'f

]diiso-

# quinline-1,3,8,10-tetraon-9-yl)-stilben-4-yl}anthra[2,1,9-*def*,6,5,10-*d' e' f*]diisoquino-

line-1,3,8,10-tetraone(7b):2-(1-Nonyldecyl)-9-(4-vinylphenyl)anthra[2,1,9-d ef,6,5,10-d'e'f]diiso-quinoline-1,3,8,10-tetraone (6b,150 mg, 198 µmol) under argon atmosphere was dissolved in chloroform (10 mL), treated with second-generation Hoveyda-Grubbs-catalyst (3, 37.4 mg, 44.0 µmol) heated with reflux (bath 80°C) for 7 h (beginning of the formation of a precipiate of very fine, light red neddles after 2 h), stirred at room temperature for 14 h and with reflux for 5 h, collected by vacuum filtration (D4 micro glass filter) and washed with hot chloroform for removing staring matrials and by-products. Yield 12 mg (4%) dark red pigment, m.p. > 250°C. IR (KBr):  $\tilde{\nu}$  = 2923.5 (m), 2852.8 (m), 1698.0 (s), 1660.1 (s), 1594.4 (s), 1578.1 (m), 1513.8 (w), 1465.0 (w), 1433.9 (w), 1405.4 (m), 1343.4 (s), 1254.3 (m), 1175.2 (m), 1124.4 (w), 963.7 (w), 852.9 (w), 811.7 (m), 798.9 (w), 747.2 (m), 549.9 cm<sup>-1</sup> (w). UV/Vis (H<sub>2</sub>SO<sub>4</sub>):  $\lambda_{max}$  (E) = 317.6 (0.30), 402.8 (0.12), 556.8 (0.58), 601.8 nm (1.00). Fluorescence (H<sub>2</sub>SO<sub>4</sub>):  $\lambda_{\text{max}}$  (*I*) = 631.5 nm (1.00). MS (FAB<sup>+</sup>/70 eV): m/z (%): 1490 [*M*<sup>+</sup>], 1378, 1225, 1071, 919, 835  $[M^{\dagger} - C_{43}H_{46}N_2O_4]$ , 829, 793, 759  $[M^{\dagger} - C_{49}H_{49}N_2O_4]$ , 749, 733, 613, 596, 460, 307, 154.

2-(1-Hexylheptyl)-9-{1-(2,2,13-tributyl-13-((1-hexylheptyl)anthra[2,1,9def;6,5,10-d' e' f' ]diisoquinoline-1,3,8,10-tetraon)methyl)heptadec-7-enyl}anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone(9):2-(2,2-Dibu tylhex-5-enyl)-9-(1-hexylheptyl)-anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3 ,8,10-tetraone (8, 50.0 mg, 65.2 µmol) under argon atmosphere were dissolved in dichloromethane (10 mL), treated with second-generation Hoveyda-Grubbscatalyst (3, 7.6 mg, 12 µmol), heated under reflux for 11 h, stirred at room temperature for 12 h, quenched by the addition of chloroform (15 mL), distilled water (10 mL) and acetic acid (15 mL), stirred for 2 h, shaken three times with distilled water (25 mL each), evaporated and purified by medium pressure chromatography (silica gel, chloroform/ethanol 60:1 at 35 mL·min<sup>-1</sup>, red fraction, column  $36 \times 460$  mm and a second medium pressure chromatography. Yield 3.0 mg (3%) red solid.  $R_{f}$ -value (silica gel, CHCl<sub>3</sub>/EtOH 40:1) = 0.17. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (*E*) = 461.6 (0.29), 491.8 (0.75), 527.4 nm (1.00). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 536.8 (1.00), 579.8 nm (0.74). MS (DEI<sup>+</sup>/70 eV): m/z (%): 1504 (2) [ $M^{+}$ ], 711 (74) [ $M^{+} - C_{53}H_{65}N_{2}O_{4}$ ], 404 (86) [ $M^{+} - C_{62}H_{81}N_{2}O_{4}$ - C<sub>13</sub>H<sub>27</sub>], 390 (100) [404 - CH<sub>2</sub>].

2-(1-Hexylheptyl)-9-{1-(2,2,9-tributyl-9-((1-hexylheptyl)anthra[2,1,9-*def* ;6,5,10-*d' e' f'*]diisoquinoline-1,3,8,10-tetraon)methyl)tridec-5-enyl}anthra[ 2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone(11):2-(1-Hexylheptyl) -9-(2,2-dibutylhept-6-enyl)-anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diiso-quinoline-1,3,8,10 -tetraone (10, 100 mg, 0.128 mmol) under argon atmosphere was dissolved in tetrahydrofurane (20 mL), treated with second-generation Hoveyda-Grubbs-catalyst (3, 13 mg, 21  $\mu$ mol), stirred at room temperature for 18 h, precipitated with methanol, collected by vacuum filtration, dried at 110°C in air and purifid by column separation (silica gel, chloroform). A pure fraction again forms a spectrum of side products. MS (ESI<sup>+</sup>/70 eV): m/z (%): 1091 (23), 915 (16), 457 (100).

2,9-Bis-{2,9-bis-([2,2,9,9-tetrabutyl-dec-5-en-10-yl]yl)anthra[2,1,9-def;6, 5,10-d'e'f' diisoquinoline-1,3,8,10-tetraone anthra [2,1,9-def;6,5,10-d'e'f' dii soquinoline-1,3,8,10-tetraone(22):2,9-Bis-(2,2-dibutyl-hex-5-enyl)anthra[2,1,9def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (21, 100 mg, 128 µmol) was dissolved in warm dichloromethane (100 mL, clear solution)), treated with second-generation Hoveyda-Grubbs-catalyst (3, 16 mg, 26 µmol, 1,3-bis-(2,4,6trimethylphenyl)-2-imidazolidinylidene)dichloro(2-isopropoxy-phenylmethyl phenylmethylene)ruthenium), stirred at 40°C for 5 d, allowed to cool, precipitated with methanol (100 mL), collected by vacuum filtration (D4 glas filter), washed with methanol until colorless washings, dissolved in a minimal amount of chloroform, purified by medium pressure column chromatography (500 mL of silica gel, chloroform/ethanol 60:1, second, red band), and precipitated with methanol. Yield 55.0 mg (57%) dark red solid, m.p. >250°C. R<sub>f</sub> value (silica gel; CHCl<sub>3</sub>/EtOH 80:1) = 0.15. IR (KBr):  $\tilde{v}$  = 3502.2 w br., 1953.8 s, 2927.6 s, 2858.7 s, 1697.7 vs, 1656.6 vs, 1593.9 s, 1578.0 m, 1507.1 w, 1436.6 m, 1404.2 m, 1376.1 w, 1332.3 s, 1250.2 m, 1217.0 w, 1178.2 w, 1159.3 w, 1125.2 w, 1015.8 w, 976.7 w, 851.7 w, 809.2 m, 795.8 w, 747.0 cm<sup>-1</sup> m. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 0.84 - 1.75$  (m, 84 H, 8 CH<sub>3</sub> + 30 CH<sub>2</sub>), 2.25 - 2.39 (m, 4 H, 2 CH<sub>2</sub>), 3.85 - 4.42 (m, 12 H, 4 N-CH<sub>2</sub>R + 4 CH<sub>olefin</sub>), 7.08 - 7.20 (m, 4 H, CH<sub>arom</sub>), 7.52 -7.54 (m, 2 H, CH<sub>arom</sub>), 7.70 - 7.73 (m, 2 H, CH<sub>arom</sub>), 7.82 - 8.65 ppm (m, 8 H, CH<sub>arom.</sub>). UV CHCl<sub>3</sub>:  $\lambda_{max}$  ( $\varepsilon$ ) = 468.4 (27300), 494.4 (62800), 530.2 nm (56700). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}(I_{rel}) = 533.8$  (0.90), 582.8 nm (1.00). Fluorescence quantum yield ( $\lambda_{exc}$  = 493 nm,  $E_{483 \text{ nm/1 cm}}$  = 0.00997, reference: 2,9-bis-(1-hexylheptyl) anthra[2,1,9-def, 6,5,10-d'e'f]diisoquinoline-1,3,8,10- tetraone (1) with  $\Phi = 1.00$ [40]): 75%. MS (DEI/70 eV): m/z (%):1500 (4) [ $M^{+}$ ], 778 (31) [ $M^{+}$  - $C_{48}H_{56}N_2O_4$ ], 723 (37)  $[M^+ - C_{52}H_{60}N_2O_4]$ , 585 (32)  $[M^+ - C_{48}H_{56}N_2O_4 - C_{14}H_{27}]$ , 418 (45)  $[M^{+} - C_{48}H_{56}N_{2}O_{4} - 2 \times C_{13}H_{25}], 404 (100) [M^{+} - C_{48}H_{56}N_{2}O_{4} - C_{13}H_{25}]$  $-C_{14}H_{27}$ ], 391 (57)  $[M^{+} - C_{48}H_{56}N_{2}O_{4} - 2 \times C_{14}H_{27}]$ . HRMS  $(C_{100}H_{116}N_{4}O_{8})$ : Calcd. 1500.8794, found 1500.8788.

2,9-Bis-{2,9-bis-([2,2,7,7-tetrabutyloct-4-en-8-yl]yl)anthra[2,1,9-*def*;6,5,1 0-*d'e'f*]diisoquinoline-1,3,8,10-tetraone}anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoq uinoline-1,3,8,10-tetraone(20):2,9-Bis-(2-allyl-2-butylhexyl)anthra[2,1,9-*def*;6, 5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone (19, 100 mg, 133 µmol) under argon atmoshere was dissolved with warming in dry THF (125 mL), treated with second-generatio-Hoveyda-Grubbs catalyst (3, 13 mg, 20 µmol; 15 mol%), stirred at 60°C for 18 h (orange fluorescent mixture); stirred at room temperarure for 31 h, concentrated in vacou, recipitated with methanol, collected by vacuum filtration (D4 glas filter), dried at 110°C, purified by column separation (500 mL powder of silica gel, chloroform/ethanol 60:1, column,500 × 44 mm) and purified by preparative TLC (silica gel, chloroform). Yield 48 mg (50%) dark red pigment, m.p. > 250°C.  $R_{\rm f}$ -value (silica gel; CHCl<sub>3</sub>/EtOH 60:1) = 0.24. IR (ATR):  $\tilde{\nu}$  = 2954.3 (m), 2927.9 (s), 2859.2 (m), 1697.4 (vs), 1654.8 (vs), 1593.5 (s), 1577.9 (m), 1507.1 (w), 1482.4 (w), 1455.6 (w), 1436.4 (m), 1404.0 (m), 1375.9 (m), 1332.6 (s), 1249.5 (m), 1217.9 (w), 1177.3 (w), 1160.7 (w), 1101.8 (w), 1014.3 (w), 972.0 (w), 850.4 (w), 809.1 (m), 795.6 (w), 747.4 (m), 671.9 (w), 638.0 cm<sup>-1</sup> (w). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\rm max}$  (E) = 467.4 (0.52) (sh.), 490.6 (1.00), 527.4 nm (0.78). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{\rm max}$  (I) = 529.8 (0.21), 637.0 nm (1.00). MS: (DEI<sup>+</sup>/70 eV): m/z (%): 1444 (9) [ $M^+$ ], 1265 (3) [ $M^+$  – C<sub>13</sub>H<sub>24</sub>], 1252 (3) [ $M^+$  – C<sub>14</sub>H<sub>26</sub>].

2,9-Bis-{2,9-bis-([2,2,11,11-tetrabutyldodedec-6-en-12-yl]yl)anthra[2,1,9 -def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone}anthra[2,1,9-def;6,5,10-d' e'f]diisoquinoline-1,3,8,10-tetraone:2,9-Bis-(2,2-dibutylhept-6-enyl)anthra[2,  $1,9-def_{6}(5,5,10-d'e'f')$  diiso-quinoline-1,3,8,10-tetraone (100 mg, 124 µmol) under argon atmosphere was dissolved in dry THF (150 mL), treated with secondgeneration-Hoveyda-Grubs catalyst (3, 10 mg, 16 µmol; 13 Mol%), stirred at room temperature for 24 h, concentrated in vacuo, precipitated with methanol, thoroughly washed with methanol, dried in air (110°C, 16 h), purifid by column separation (800 mL powder of silica gel, 800 × 44 mm column, chloroform/ethanol 60:1) and purified by preparative TLC (silica gel, chloroform). Yield 67 mg (69%) dark red pigment, m.p. > 250°C. R-value (silica gel; CHCl<sub>3</sub>/EtOH 60:1) = 0.24. IR (ATR):  $\tilde{v}$  = 2954.3 (s), 2927.9 (s), 2859.2 (m), 1697.4 (vs), 1654.8 (vs), 1593.6 (s), 1577.9 (m), 1507.1 (w), 1482.4 (w), 1455.6 (w), 1436.4 (m), 1404.0 (m), 1332.6 (s), 1249.5 (m), 1217.9 (w), 1177.3 (w), 1160.7 (w), 1101.8 (w), 1014.3 (w), 972.0 (w), 912.1 (w), 850.4 (w), 809.1 (m), 795.6 (w), 747.4 (m), 671.9 (w), 638.0 cm<sup>-1</sup> (w). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 465.4 (0.48) (sh.), 490.6 (1.00), 527.6 nm (0.89). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 536.0 (0.11), 638.3 nm (1.00). Fluorescence quantum yield ( $\lambda_{exc}$  = 493 nm,  $E_{493m/1 cm}$  = 0.0100, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]-diisoquinoline-1,3,8,10-tetraone (1) with  $\Phi = 1.00$  [40]): 0.75. MS: (DEI<sup>+</sup>/70 eV): m/z(%): 1557 (5)  $[M^{\dagger}]$ , 543 (5)  $[M^{\dagger} - C_{69}H_{94}N_2O_4]$ , 529 (6)  $[M^{\dagger} - C_{70}H_{94}N_2O_4]$ .

2-But-3-enyl-2-hexyloctyl-9-{2-but-3-enyl-2-hexyloctyl-9-([2,2,9,9-tetrab utyl-dedec-6-en-10-yl]yl)anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8, 10-tetraone}anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone:2, 9-Bis-(2-but-3-enyl-2-hexyloctyl)anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3 ,8,10-tetraone (50 mg, 56 µmol) under argon atmosphere was dissolved in dry THF (175 mL), treated with second-generation Hoveyda-Grubbs-catalyst (**3**, 10 mg, 16 µmol; 13 Mol%), stirred at room temperature for 24 h, concentrated in vacuo, precipitated with methanol, collected by vacuum filtration, thoroughly washed with methanol, dried in air (110°C, 16 h), purified by column separation (800 mL powder of silica gel, 800 × 44 mm column, dichloromethane) and further purified by preparative TLC (silica gel, chloroform).

**2-(2,2'-Ethoxyethan-diyl)-9-(1,12-(2,2,11,11-tetrabutyl)dodec-6-en-diyl) bis-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone(13):**2-{2-(2,2-Dibutylhept-6-enyl)--9-(2-ethoxyethyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoq uinoline-1,3,8,10-tetraon}-9-(2,2-dibutylhept-6-enyl)anthra[2,1,9-def;6,5,10-d'e'f diisoquinoline-1,3,8,10-tetraone (12, 200 mg, 0.158 mmol), second-generation Hoveyda-Grubbs-catalyst (3, 20 mg, 32 µmol; 20 Mol%) and THF (250 mL) were allowed to react as was described for 2,9-bis-{2,9-bis-([2,2,11,11-tetrabutyldodedec-6-en-12-yl]yl)anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone}anth ra[2,1,9-def,6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone, stirred at room temperature for 24 h and purified by column separation (800 mL of silica gel, chloroform/ ethanol 15:1, glass column  $800 \times 44$  mm) and further by medium pressure chromatography (silica gel, chloroform, column  $36 \times 460$  mm,  $25 \text{ mL} \cdot \text{min}^{-1}$ ). Yield 10 mg (10%) dark red pigment, m.p. > 250°C. R-value (silica gel; CHCl<sub>3</sub>/EtOH 10:1) = 0.54. IR (ATR):  $\tilde{V}$  = 3479.4 (m,br.), 2952.3 (s), 2930.3 (s), 2865.1 (m), 1693.2 (vs), 1598.4 (vs), 1593.3 (vs), 1577.4 (s), 1507.6 (w), 1438.4 (m), 1403.9 (m), 1336.0 (s), 1247.4 (m), 1167.8 (w), 1126.0 (w), 1054.2 (w), 852.8 (w), 808.5 (m), 794.3 (w), 744.4 (m), 668.0 (w), 641.1 cm<sup>-1</sup> (w). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (*E*) = 466.6 (0.44), 493.8 (1.00), 529.8 nm (0.84). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  $(I) = 537.5 (0.70), 584.5 (0.77), 628.5 \text{ nm} (1.00). \text{ MS: } (\text{DEI}^+/70 \text{ eV}): m/z (\%):$ 1223 (< 1)  $[M^{+} - CH_{3}]$ , 1182 (< 1)  $[M^{+} - C_{4}H_{9}]$ , 530 (10)  $[C_{34}H_{30}N_{2}O_{4}]$ , 460 (13)  $[C_{28}H_{16}N_2O_5]$ , 432 (58)  $[C_{26}H_{12}N_2O_5]$ , 404 (100)  $[C_{25}H_{10}N_2O_4]$ , 390 (88)  $[C_{24}H_8N_2O_4].$ 

2-(1,8-(2,2-Dibutyl)oct-6-en-diyl)-9-(1,8-(7,7-dibutyl)oct-2-en-diyl)bis-a nthra[2,1,9-def;6,5,10-d' e' f ] diisoquinoline-1,3,8,10-tetraone (15) and 2-(1,4but-2-en-diyl)-9-(1,12-(2,2,11,11-tetrabutyl)dodec-6-en-diyl)bisanthra[2,1, 9-def;6,5,10-d' e' f ]diisoquinoline-1,3,8,10-tetraone(16):2-Allyl-9-(2,2-dib utyl-hept-6-enyl)anthra[2,1,9-def; 6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (14, 100 mg, 0.157 mmol), second-generation Hoveyda-Grubbs-catalyst (3, 20 mg, 32 µmol, 20 Mol%) and THF (150 mL) were allowed to react as was described for 2,9-bis-{2,9-bis-([2,2,11,11-tetrabutyldodedec-6-en-12-yl]yl) anthra[2,1,9-def, 6,5,10-*d'e'f*]diisoquinoline-1,3,8,10-tetraone}anthra[2,1,9-*def*;6,5,10-*d'e'f*]diisoq uinoline-1,3,8,10-tetraone, stirred at room temperature for 24 h and purified by column separation (silica gel, chloroform). Yield 17 mg (17%) of a mixture of both isomers, m.p. > 250°C. IR (ATR):  $\tilde{v}$  = 2952.7 (m), 2930.2 (m), 2862.7 (m), 1696.8 (vs), 1653.8 (vs), 1593.3 (vs), 1578.0 (m), 1507.0 (w), 1482.1 (w), 1436.0 (m), 1403.7 (m), 1331.0 8m), 1248.1 (m), 1218.3 (w), 1195.8 (w), 1173.4 (w), 1125.4 (w), 1095.3 (w), 1012.1 (w), 974.0 (w), 927.1 (w), 886.4 (w), 851.3 (w), 808.8 (m), 795.3 (w), 746.0 (m), 641.6 cm<sup>-1</sup> (w). The isomers were separated by chromatography by means of fine silica gel (800 mL of silica gel 40 to 60 µm, chloroform/ethanol 20:1, glasss column 800 × 44 mm). Isomer I: (2-(1,8-(2,2-Dibutyl)oct-6-en-diyl)-9-(1,8-(7,7-dibutyl)oct-2-en-diyl)bis-anthra[2,1,9-def;6,5, 10-d' e' f' diisoquinoline-1,3,8,10-tetraone): Yield 5 mg (5%) dark red podwer.  $R_{\rm r}$ -value (silica gel; CHCl<sub>3</sub>/EtOH 20:1) = 0.46. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\rm max}$  (E) = 492.2 (1.00), 528.8 nm (0.80). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 534.5 (0.31), 628.0 nm (1.00). Fluorescence quantum yield ( $\lambda_{exc}$  = 491 nm,  $E_{491 \text{ nm/1 cm}}$  = 0.0126 cm<sup>-1</sup>, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline- 1,3,8,10tetraone (1) with Φ = 1.00 [40]): 0.69. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 1220 (<1) [*M*<sup>+</sup>], 1182 (<1) [*M*<sup>+</sup> - C<sub>3</sub>H<sub>4</sub>], 1138 (<1) [*M*<sup>+</sup> - 2 × C<sub>3</sub>H<sub>7</sub>], 443 (18) [C<sub>28</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>], 404 (85) [*M*<sup>+</sup> - C<sub>25</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>], 391 (100) [C<sub>24</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>]. **Isomer II**: (2-(1,4-But-2-en-diyl)-9-(1,12-(2,2,11,11-tetrabutyl)dodec-6-en-diyl)bisanthra[2,1,9-*def*;6,5, 10-*d' e' f'*]diisoquinoline-1,3,8,10-tetraone): Yield 5 mg (5%) dark red powder. *R*<sub>f</sub>-value (silica gel; CHCl<sub>3</sub>/EtOH 20:1) = 0.29. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{max}$  (*E*) = 492.0 (1.00), 528.8 nm (0.78). Fluorescence (CHCl<sub>3</sub>):  $\lambda_{max}$  (*I*) = 535.0 (0.36), 630.5 nm (1.00). Fluorescence quantum yield ( $\lambda_{exc}$  = 491 nm, *E*<sub>491nm/1cm</sub> = 0.0154 cm<sup>-1</sup>, reference: 2,9-bis-(1-hexylheptyl)anthra-[2,1,9-*def*;6,5,10-*d'e'f*]diisoqui-noline-1,3,8,10-tetraone (1) with Φ = 1.00 [13]): 0.88. MS: (DEI<sup>+</sup>/70 eV): *m/z* (%): 1220 (1) [*M*<sup>+</sup>], 1138 (1) [*M*<sup>+</sup> - 2 × C<sub>3</sub>H<sub>7</sub>], 443 (20) [C<sub>28</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>], 404 (82) [*M*<sup>+</sup> -C<sub>25</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>], 391 (100) [C<sub>24</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>].

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# **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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