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-
The electronic 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
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, preferably 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 perylenbicarboximides 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 perylenbicarboximide 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 starting 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 octynonyl (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-ω-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 ω-akynyl 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 alkyted 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-tetracarboxylicbisahydride 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) C₄H₉I, LDA; ii) LiAlH₄; iii) Perylene-3,4,9,10-tetracarboxylicbisahydride, zinc acetate, imidazole.
metathesis in the cyclophane 13 form a skew arrangement where there are optical transitions with a major H-component (hypsochromic β transition) and a minor J-component (bathochromic α transition); compare Ref. [26] for similar arrangements in micelles. As a consequence, the more hypsochromically absorbing β 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 mixtures 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 identical UV/Vis absorption and fluorescence spectra although the chromophore-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
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 alkyl 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 tetracarboxylic 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 Spectrometer, FT 1000; UV/Vis spectra: Varian Cary 5000 and Bruin 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 (MoKα 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 https://www.ccdc.cam.ac.uk/structures/

kn095 CCDC 1900229 (2,9-bis-(2,2-dibutylhept-6-enyl)anthra[2,1,9-def;6,5,10-d’e’f’]diisoquinoline-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 probability 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 magnesium sulphate and distilled. Yield 5.25 g (59%), b.p. 71°C/1.6·10⁻² mbar, \( n_D^{20} = 1.376 \). IR (KBr): \( \tilde{\nu} = 3079.9 \) w, 2957.9 vs, 2937.4 vs, 2864.3 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⁻¹ w. \( ^1H \) NMR: (300 MHz, CDCl₃): \( \delta = 0.86 \) (t, 1 H, \( J = 7.1 \) Hz), 1.29 (m, 6 H, 2,2-Di-butylhex-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 magnesium sulphate and distilled. Yield 5.25 g (59%), b.p. 71°C/1.6·10⁻² mbar, \( n_D^{20} = 1.376 \). IR (KBr): \( \tilde{\nu} = 3079.9 \) w, 2957.9 vs, 2937.4 vs, 2864.3 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⁻¹ w. \( ^1H \) NMR: (300 MHz, CDCl₃): \( \delta = 0.86 \) (t, 1 H, \( J = 7.1 \) Hz), 1.29 (m, 6 H,
6 CH₂), 1.52 (m, 8 H, 4 CH₂), 2.08 (m, 2 H, CH₂), 4.91 (m, 1 H, R = CH₂), 4.98 (m, 1 H, R = CH₂), 5.72 ppm (m, 1 H, CH). ¹³C NMR: (75 MHz, CDCl₃): δ = 13.5, 22.5, 28.3, 35.0, 35.4, 40.0 (C quart.), 114.9 (CH₂ olefin.), 123.3 (CN), 136.8 ppm (CH₂ olefin.). MS: (DEI⁺/70 eV): m/z (%): 208 (5) [M⁺ + H], 153 (24) [M⁺ − C₄H₇], 151 (28) [M⁺ − C₃H₅ − C₄H₉], 97 (67) [M⁺ − C₄H₉ − C₄H₇].

2-But-3-enyl-2-hexloctanenitrile: 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 mL), 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-5-enenitrile. Yield 7.94 g (73%) colorless oil, b.p. 100 °C-102 °C/1 × 10⁻³ mbar, nD²⁰ = 1.454. IR (KBr): ν = 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, 110.0 w, 993.6 w, 912.9 m, 759.9 w, 724.6 w, 648.0 w, 556.0 cm⁻¹ w. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.89 (t, 6 H, 3JH,H = 6.8 Hz, 2 CH₃), 1.29 - 1.41 (m, 16 H, 8 CH₂), 1.52 - 1.65 (m, 6 H, 3 CH₂), 2.11 - 2.20 (m, 2 H, CH₂), 4.97 - 5.09 (m, 2 H, CH₂, olefin.), 5.73 - 5.84 ppm (m, 1 H, CH olefin.). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 14.0, 22.5, 24.2, 28.7, 31.5, 35.3, 36.1, 40.4 (C quart.), 115.3 (CH₂ olefin.), 124.0 (CN), 137.6 ppm (CH olefin.). MS (DEI⁺/70 eV) m/z (%): 264 (4) [M⁺ + H], 263 (4) [M⁺], 262 (5) [M⁺ − H], 206 (22) [M⁺ − C₄H₉], 192 (21) [M⁺ − C₅H₁₁], 179 (43) [M⁺ − C₆H₁₃], 138 (100) [M⁺ − C₆H₁₃ − C₃H₅], 125 (35) [M⁺ − C₆H₁₃ − C₄H₇], 97 (26) [M⁺ − 2 × C₆H₁₃], 55 (17) [C₄H₉].

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 (4.70 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 yellowish, viscous oil, b.p. 140 °C-144 °C/1 × 10⁻³ mbar, nD²⁰ = 1.457. - IR (KBr): ν = 3079.7 w, 2926.9 vs, 2856.0 s, 1642.5 w, 1465.6 w, 1378.3 w, 1157.5 w, 1071.5 w, 992.3 w, 912.6 w, 711.4 cm⁻¹ w. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.89 (t, 6 H, 3JH,H = 6.9 Hz, 6 H, 2 CH₃), 1.28 - 1.31 (m, 20 H, 10 CH₂), 1.40 - 1.41 (m, 4 H, 2 CH₂), 1.54 - 1.58 (m, 4 H, 2 CH₂), 1.62 - 1.65 (m, 2 H, CH₂), 2.15 - 2.18 (m, 2 H, CH₂), 4.99 - 5.01 (m, 2 H, CH₂ olefin.), 5.77 - 5.84 ppm (m, 1 H, CH₂ olefin.). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 14.0, 22.5, 24.2, 28.7, 29.3, 31.5, 35.3, 36.1, 40.4 (C quart.), 115.3 (CH₂ olefin.), 124.0 (CN), 137.6 ppm (CH₂ olefin.). MS (DEI⁺/70 eV) m/z (%): 264 (4) [M⁺ + H], 263 (4) [M⁺], 262 (5) [M⁺ − H], 206 (22) [M⁺ − C₄H₉], 192 (21) [M⁺ − C₅H₁₁], 179 (43) [M⁺ − C₆H₁₃], 138 (100) [M⁺ − C₆H₁₃ − C₃H₅], 125 (35) [M⁺ − C₆H₁₃ − C₄H₇], 97 (26) [M⁺ − 2 × C₆H₁₃], 55 (17) [C₆H₁₃].

2-Butyl-2-vinylhexanenitrile: Diisopropylamine (11.5 mL, 82.1 mmol) in anhydrous THF (45 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 °C/8 × 10⁻³ mbar, nD²⁰ = 1.441. IR (KBr): ν = 3088.0 w, 2959.3 vs, 2936.9 vs, 2864.4 vs,
2237.2 w, 1853.1 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, 1066.6 w, 989.5 m, 925.1 m, 785.1 w, 753.2 w, 731.2 w, 695.8 w, 587.5 cm –1 w. 1H NMR (300 MHz, CDCl 3, 25˚C): δ = 0.89 (t, 3JH,H = 7.0 Hz, 6 H, 2 CH3), 1.24 - 1.52 (m, 10 H, 5 CH2), 1.63 - 1.73 (m, 2 H, CH2), 5.22 - 5.25 (m, 2 H, CH 2, olefin.), 5.42 - 5.44 ppm (m, 1 H, CH olefin.). 13C NMR (75 MHz, CDCl3, 25˚C): δ = 13.8, 22.6, 27.0, 38.6, 46.1 (C quart.), 116.5 (CH2 olefin.), 121.5 (CN), 137.2 ppm (CH olefin.). MS (DEI+/70 eV) m/z (%): 180 (4) [M+ + H], 153 (4) [ M+ − C2H3], 136 (5) [ M+ − C3H7], 123 (100) [ M+ − C4H9], 108 (37) [M+ − C3H7 − C2H3], 94 (22) [M+ − C4H9 − C2H3], 80 (50) [M+ − C4H9 − C3H7].

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 ˚C-64˚C/1 × 10–2 mbar, 20 Dn = 1.447. IR (KBr): ν = 3081.0 w, 2958.8 vs, 2937 vs, 2864.5 s, 2231.9 w, 1737.5 w, 1642.6 w, 1467.9 m, 1381.6 w, 1342.7 w, 994.9 m, 920.8 m, 802.1 w, 729.3 cm –1 w. 1H NMR (300 MHz, CDCl3, 25˚C): δ = 0.92 (t, 3J = 7.1 Hz, 6 H, 2 CH 3), 1.28 - 1.46 (m, 8 H, 4 CH 2), 1.51 - 1.59 (m, 4 H, 2 CH 2), 2.31 - 2.34 (m, 2 H, CH2), 5.13 - 5.21 (m, 2 H, CH 2, olefin.), 5.73 - 5.84 ppm (m, 1 H, CH olefin.). 13C NMR (75 MHz, CDCl 3, 25˚C): δ = 13.9, 22.8, 26.4, 35.7, 40.3, 40.4 (C quart.), 119.6 (CH 2, olefin.), 123.8 (CN), 131.9 ppm (CH olefin.). MS (DEI’/70 eV) m/z (%): 194 (4) [M+ + H], 150 (100) [ M+ − C3H7], 137 (17) [M+ − C4H9], 110 (22) [ M+ − C3H7 − C3H5], 55 (11) [ M+ − C4H9 − C3H7 − C3H5], 40 (33) [ M+ − 2 × C 4H9 − C3H5].

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-5-enenitrile. Yield 9.04 g (89%) colorless oil, b.p. 85 ˚C/1·10–3 mbar, 20 Dn = 1.451. IR (KBr): ν = 3080.3 w, 2957.2 vs, 2929.9 vs, 2872.0 s, 2860.5 s, 2230.6 w, 1666.3 m, 1639.5 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 w, 802.1 w, 729.3 cm –1 w. 1H NMR (300 MHz, CDCl3, 25˚C): δ = 0.92 (t, 3J = 7.0 Hz, 6 H, 2 CH3), 1.29 - 1.39 (m, 8 H, 4 CH2), 1.48 - 1.55 (m, 8 H, 4 CH2), 2.07 (q, 3J = 6.5 Hz, 2 H, CH3), 4.95 - 5.05 (m, 2 H, CH2 olefin.), 5.71 - 5.84 ppm (m, 1 H, CH olefin.), 13C NMR (75 MHz, CDCl3, 25˚C): δ = 13.8, 22.8, 23.5, 26.3, 33.6, 35.5, 35.8, 40.4 (C quart.), 115.1 (CH2 olefin.), 124.2 (CN), 137.8 ppm (CH olefin.). MS (DEI’/70 eV) m/z (%): 222 (1) [ M+ − H], 165 (33) [ M+ − C3H7], 153 (4) [ M+ − C4H9], 122 (100) [ M+ − C4H9 − C3H7], 110 ( M+ − C4H9 − C3H7), 55 (9) [ M+ − 2 × C 4H9 − C3H7], 41 (18) [ M+ − 2 × C 4H9 − C3H7].

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°C-26°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 hydrolysed with distilled water (50 mL), treated dropwise 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): \( \nu = 3087.1 \text{ w}, 2969.3 \text{ vs}, 2938.0 \text{ m}, 2878.8 \text{ m}, 2234.6 \text{ w}, 1639.9 \text{ w}, 1466.8 \text{ w}, 1412.9 \text{ w}, 1390.9 \text{ m}, 1375.4 \text{ w}, 1315.7 \text{ w}, 1203.2 \text{ w}, 1171.6 \text{ w}, 1063.5 \text{ w}, 994.2 \text{ m}, 925.5 \text{ m}, 803.0 \text{ w}, 699.0, 672.0 \text{ cm}^{-1} \). ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 0.93 (d, \( 3J = 6.8 \text{ Hz}, 6 \text{ H}, 2 \text{ CH₃} \)), 1.05 (d, \( 3J = 6.7 \text{ Hz}, 6 \text{ H}, 2 \text{ CH₃} \)), 2.03 (sept., \( 3J = 6.8 \text{ Hz}, 2 \text{ H}, 2 \text{ CH₃} \), aliphat.), 5.33 - 5.39 (m, 1 H, CH olefin.), 5.44 - 5.47 ppm (m, 2 H, CH₂, olefin.). ¹³C NMR (75 MHz, CDCl₃, 25°C): δ = 17.3, 18.4, 31.6, 55.7 (C quart.), 118.7 (CH₂ olefin.), 120.4 (CN), 132.6 ppm (CH olefin.). MS (DEI'70 eV) m/z (%): 152 (0.2) [M⁺ + H], 109 (64) [M⁺ − C₃H₇], 94 [M⁺ − C₃H₇ − CH₃], 67 (10) [M⁺ − 2 × C₃H₇], 41 (13) [M⁺ − 2 × C₃H₇ − C₂H₃].

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-5-enenitrile. Yield 4.51 g (62%) colorless liquid, b.p. 56°C-58°C/1 × 10⁻³ mbar, \( n_D^{20} = 1.455 \). IR (KBr): \( \nu = 3079.7 \text{ w}, 2971.8 \text{ vs}, 2880.5 \text{ m}, 2228.7 \text{ w}, 1736.2 \text{ w}, 1642.5 \text{ m}, 1471.0 \text{ m}, 1417.6 \text{ w}, 1392.3 \text{ m}, 1375.9 \text{ w}, 1309.5 \text{ w}, 1175.0 \text{ w}, 1107.1 \text{ w}, 992.9 \text{ w}, 913.7 \text{ m}, 757.9 \text{ w}, 698.0 \text{ w}, 617.4 \text{ cm}^{-1} \text{ w} \). ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 0.97 - 1.00 (m, 6 H, 2 CH₃), 1.06 - 1.08 (m, 6 H, 2 CH₂), 1.51 - 1.58 (m, 2 H, CH₂), 1.92 - 2.06 (m, 2 H, 2 CH₂), 2.16 - 2.25 (m, 2 H, CH₂), 4.94 - 5.09 (m, 2 H, CH₂ olefin.), 5.71 - 5.84 ppm (m, 1 H, CH olefin.). ¹³C NMR (75 MHz, CDCl₃, 25°C): δ = 17.5, 18.8, 29.5, 31.7, 32.6, 49.1 (C quart.), 115.0 (CH₂ olefin.), 122.2 (CN), 137.3 ppm (CH₂ olefin.). MS (DEI'70 eV) m/z (%): 180 (1) [M⁺ + H], 164 (3) [M⁺ − CH₃], 137 (5) [M⁺ − C₃H₇], 122 (8) [M⁺ − C₃H₇ − CH₂], 110 (10) [M⁺ − C₃H₇ − 2 × CH₂], 96 (100) [M⁺ − 2 × C₃H₇], 55 (8) [M⁺ − 2 × C₃H₇ − C₂H₃], 41 (19) [M⁺ − C₄H₇ − 2 × C₃H₇].

2,2-Dibutylhex-5-enylamine: Lithiumaluminiumhydride (1.54 g, 40.5 mmol) under nitrogen atmosphere was dispersed in anhydrous diethylether (110 mL) and treated dropwise with 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 × 10⁻² mbar, $n_D^{20} = 1.459$. IR (KBr): $\tilde{\nu} = 3391.2$ w, 3306 w, 3076.5 m, 2956.7 vs, 2929.9 vs, 2861.2 m, 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⁻¹ w. $^1$H NMR (600 MHz, CDCl₃, 25°C): $\delta = 0.83$ (t, $^3J = 7.3$ Hz, 6 H, 2 CH₃), 1.05 - 1.10 (m, 8 H, 4 CH₂), 1.17 - 1.23 (m, 6 H, 2 CH₂), 1.84 - 1.88 (m, 2 H, CH₂), 2.39 (s, 2 H, N–CH₂), 4.83 - 4.94 (m, 2 H, CH₂ olefin.), 5.70 - 5.77 ppm (m, 1 H, CH olefin.). $^{13}$C NMR (150 MHz, CDCl₃, 25°C): $\delta = 14.0, 23.5, 25.0, 27.4, 33.6, 34.0, 38.7, 47.0$ (CH₂-N), 113.7 (CH₂ olefin.), 139.3 ppm (CH olefin.). MS (DEI⁺/70 eV) m/z (%): 212 (6) [M⁺ + H⁺], 196 (42) [M⁺ − NH₂], 154 (61) [M⁺ − NH₂ − C3H₅], 140 (56) [M⁺ − C4H₇ − NH₂], 97 (81) [M⁺ − 2 × C4H₉], 83 (91) [M⁺ − 2 × C4H₉ − NH₂], 69 (100) [M⁺ − C₆H₁₃ − C₄H₇ − CH₂NH₂].

**2-But-3-enyl-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-5-enylamine. Yield 5.58 g (70%) colorless oil, b.p. 96 - 98°C/1·10⁻³ 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, 1299.3 w, 1069.9 w, 992.8 w, 907.8 m, 814.9 w, 722.0 w, 636.9 cm⁻¹ w. $^1$H NMR (300 MHz, CDCl₃, 25°C): $\delta = 0.86$ (t, $^3J = 6.8$ Hz, 6 H, 2 CH₃), 1.13 - 1.29 (m, 22 H, 11 CH₂), 1.86 - 1.94 (m, 2 H, CH₂), 2.43 (s, 2 H, CH₂-N), 4.87 - 5.01 (m, 2 H, CH₂ olefin.), 5.72 - 5.86 ppm (m, 1 H, CH olefin.). $^{13}$C NMR (75 MHz, CDCl₃, 25°C): $\delta = 14.0, 22.6, 22.8, 27.5, 30.2, 31.8, 33.7, 34.4, 38.9, 47.1$ (CH₂-N), 113.8 (CH₂ olefin.), 139.5 ppm (CH olefin.). MS (DEI⁺/70 eV) m/z (%): 266 (10) [M⁺ − H⁺], 252 (58) [M⁺ − NH₂], 238 (35) [M⁺ − CH₄N⁺], 196 (61) [M⁺ − C₆H₁₃], 182 (100) [M⁺ − C₈H₁₇], 151 [M⁺ − C₆H₁₃ − CH₂-N], 111 [M⁺ − C₈H₁₇ − C₆H₁₃], 97 (81) [M⁺ − 2 × C₆H₁₃], 83 (79) [M⁺ − 2 × C₆H₁₃ − NH₂], 69 (100) [M⁺ − C₆H₁₃ − C₉H₁₇ − CH₂NH₂].

**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): $\tilde{\nu} = 3076.8$ w, 2955.8 s, 2924.8 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⁻¹ 636.9 w. $^1$H NMR (300 MHz, CDCl₃, 25°C): $\delta = 0.85$ (t, $^3J = 6.7$ Hz, 6 H, 2 CH₃), 1.12 - 1.24 (m, 30 H, 15 CH₂), 1.85 - 1.93 (m, 2 H, CH₂), 2.42 (s, 2 H, CH₂-N), 4.85 - 5.00 (m, 2 H, CH₂ olefin.), 5.71 - 5.84 ppm (m, 1 H, CH olefin.). $^{13}$C NMR (75 MHz, CDCl₃, 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 (CH₂-N), 113.8 (CH₂ olefin.), 139.4 ppm (CH olefin.). MS (DEI⁺/70 eV) m/z (%): 322 (11) [M⁺ − H⁺], 308 (34) [M⁺ − NH₂], 294 (45) [M⁺ − CH₄N⁺], 210 (100) [M⁺ − C₆H₁₇], 139 (34) [M⁺ − C₈H₁₇ − C₆H₁₃], 111 (52) [M⁺ − C₉H₁₇ − C₈H₁₇], 97 (83) [M⁺ − 2 × C₆H₁₃], 83 (68) [M⁺ − 2 × C₆H₁₇ − NH₂].
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69 (52) \([M^* − 2 \times C_8H_{17} − CH_2N], 55 (41) \([M^* − 2 \times C_8H_{17} − C_2H_6N]).

**2-Butyl-2-vinylhexylamine:** Lithium aluminium hydride (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-ynylamine. Yield 791 mg (55%) colorless liquid, b.p. 43 – 44˚C/1·10–3 mbar, \(\eta^2_D = 1.455\). 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\(^{-1}\) w. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25˚C): \(\delta = 0.86\) (t, \(^3J = 7.1\) Hz, 6 H, 2 CH\(_3\)), 1.08 - 1.32 (m, 12 H, 6 CH\(_2\)), 2.49 (s, 2 H, CH\(_2–N\)), 4.86 - 4.93 (m, 1 H, CH\(_2\)), 5.07 - 5.11 (m, 1 H, CH\(_2\)), 5.51 - 5.60 (m, 1 H, CH\(_2\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 25˚C): \(\delta = 14.0, 23.5, 25.4, 33.3, 43.9, 47.8\) (CH\(_2–N\)), 113.6 (CH\(_2\)), 145.4 ppm (CH\(_2\)). MS (DEI+/70 eV) m/z (%): 184 (6) \([M^* + H]\), 154 (43) \([M^* − CH_4N]\), 126 (100) \([M^* − C_4H_9]\), 112 (56) \([M^* − C_4H_9 − NH_2]\), 70 (94) \([M^* − 2 \times C_4H_9]\), 55 (68) \([M^* − 2 \times C_4H_9 − CH_4N]\).

**2-Allyl-2-butylhexylamine:** Lithium aluminium hydride (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-ynylamine. Yield 5.98 g (71%) colorless liquid, b.p. 66 ˚C-68˚C/1 × 10–3 mbar, \(\eta^2_D = 1.459\). IR (KBr): \(\tilde{\nu} = 3074.4\) w, 2956.9 vs, 2930.1 vs, 2861.2 s, 1728.5 w, 1638.2 w, 1580.3 w, 1467.6 m, 1392.9 w, 1299.8 w, 1103.7 w, 996.2 w, 911.4 w, 815.7 cm\(^{-1}\) w. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25˚C): \(\delta = 0.89\) (t, \(^3J = 7.0\) Hz, 6 H, 2 CH\(_3\)), 1.15 - 1.33 (m, 12 H, 6 CH\(_2\)), 1.94 - 1.98 (m, 2 H, CH\(_2\)), 2.44 (s, 2 H, CH\(_2–N\)), 4.99 - 5.06 (m, 2 H, CH\(_2\)), 5.70 - 5.84 ppm (m, 1 H, CH\(_2\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 25˚C): \(\delta = 14.1, 23.6, 25.2, 34.1, 39.4, 39.5, 47.4\) (CH\(_2\)), 116.7 (CH\(_2\)), 135.1 ppm (CH\(_2\)). MS (DEI+/70 eV) m/z (%): 197 (19) \([M^*]\), 182 (100) \([M^* − NH_2]\), 168 (5) \([M^* − CH_2N]\), 140 (14) \([M^* − C_4H_9]\), 69 (3) \([M^* − 2 \times CH_2 − NH_2]\), 57 (16) \([M^* − 2 \times C_4H_9 − CH_2N]\).

**2,2-Dibutylhept-6-enylamine:** Lithium aluminium hydride (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-ynylamine. Yield 7.31 g (81%) colorless liquid, b.p. 82 ˚C-84˚C/2 × 10–3 mbar, \(\eta^2_D = 1.461\). IR (KBr): \(\tilde{\nu} = 3076.9\) w, 2956.0 vs, 2930.1 vs, 2861.2 s, 1871.8 w, 1640.3 m, 1465.7 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\(^{-1}\) w. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25˚C): \(\delta = 0.88\) (t, \(^3J = 7.2\) Hz, 6 H, 2 CH\(_3\)), 1.11 - 1.29 (m, 16 H, 8 CH\(_2\)), 1.97 - 2.04 (m, 2 H, CH\(_2\)), 2.43 (s, 2 H, CH\(_2–N\)), 4.91 - 5.03 ppm (m, 1 H, CH\(_2\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 25˚C): \(\delta = 14.1, 22.4, 23.6, 25.2, 33.9, 34.2, 34.6, 38.3, 47.2\) (CH\(_2–N\)), 114.4 (CH\(_2\)), 139.0 ppm (CH\(_2\)). MS (DEI+/70 eV) m/z (%): 225 (4) \([M^*]\), 194 (5) \([M^* − CH_2N]\), 168 (24) \([M^* − C_4H_9]\), 111 (40)
$[\text{M}−2\times\text{C}_4\text{H}_9]$, 97 $[\text{M}−2\times\text{C}_4\text{H}_9−\text{NH}_2]$, 83 (100) $[\text{M}−2\times\text{C}_4\text{H}_9−\text{CH}_4\text{N}]$, 69 (96) $[\text{M}−2\times\text{C}_4\text{H}_9\text{N}−\text{C}_2\text{H}_6\text{N}]$, 55 (100) $[\text{M}−2\times\text{C}_4\text{H}_9−\text{C}_3\text{H}_8\text{N}]$, 40 (29) $[\text{M}−2\times\text{C}_4\text{H}_9−\text{C}_4\text{H}_{10}\text{N}]$.

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 ˚C/3.2 × 10⁻² mbar. IR (KBr): $\nu = 3081.6$ 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, $698.3$ w, $671.5$ cm⁻¹ 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-5-enenitrile (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 × 150 mL), washed with distilled water (2 × 150 mL), dried with magnesiumsulphate, evaporated and distilled in vacuo. Yield 2.43 g (53%) colorless liquid, b.p. 98 ˚C-100˚C/22 mbar, $\delta_{D}^{20} = 1.478$. IR (KBr): $\nu = 3076.1$ 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⁻¹ w. MS (DEI+/70 eV) m/z (%): 184 (3) [M⁺ + H], 168 (4) [M⁺−NH₂], 152 (7) [M⁺−CH₄N], 140 (100) [M⁺−C₃H₇], 123 (23) [M⁺−C₃H₇−NH₂], 109 (47) [M⁺−2×C₃H₇], 97 (77) [M⁺−2×C₄H₉], 83 (57) [M⁺−2×C₄H₉−NH₂], 69 (90) [M⁺−2×C₄H₉−CH₄N], 55 (95) [C₄H₇], 43 (45) [C₄H₇].

2,9-Bis-(2,2-dibutylhex-5-enyl)anthra[2,1,9-def6,5,10-d’e’f’]diisoquinoline-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 magnesiumsulphate, 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. $R$ value (silica gel; CHCl₃/EtOH 80:1) = 0.45. - IR (KBr): $\nu = 2956.1$ s, 2924.5 vs, 2854.2 vs, 1702.4 m, 1661.4 m, 1595.7 m, 1579.3 m, 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⁻¹ w. 1H NMR (600 MHz, CDCl₃, 25˚C): $\delta = 0.90$ (t, $^3J = 7.1$ Hz, 12 H, 4 CH₃), 1.25 - 1.36 (m, 24 H, 12 CH₂), 1.38 - 1.41 (m, 4 H, 2 CH₂), 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, CH₂,olefin.), 5.79 - 5.86 (m, 2 H, CH₂,olefin.), 8.59 - 8.67 ppm (m, 8 H, CH aromat.). 13C
NMR (150 MHz, CDCl₃, 25°C): δ = 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 (CHCl₃): λmax (ε) = 457.5 (18700), 488.4 (51000), 524.9 nm (84700). Fluorescence (CHCl₃): λmax (Irel) = 533 (1.00), 575 nm (0.36). Fluorescence quantum yield (λexc = 488 nm, E₄₈₃ nm/1 cm = 0.0259, reference: 2,9-bis-(1-hexylheptyl)-anthra[2,1,9-def,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 0.99. MS: (DEI+/70 eV): m/z (%): 778 (100) [M+], 723 (21) [M+ − C4H9], 598 (27) [M+ − C13H25], 585 (12) [M+ − C13H25], 418 (67) [M' − 2 × C13H25], 404 (25) [M' − C13H25 − C14H27], 390 (6) [M' − 2 × C14H27]. C52H62N2O4 (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,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone: Perylene-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-(2,2-dibutylhex-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, column 700 × 54 mm). Yield 1.69 g (74%) bright red glossy solid, m.p. 130°C. Rf-value (silica gel, CHCl₃) = 0.52. IR: (KBr): ν = 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⁻¹ w. 1H NMR (600 MHz, CDCl₃, 25°C): δ = 0.87 (t, 3J = 6.8 Hz, 12 H, 4 CH₃), 1.26 - 1.33 (m, 40 H, 20 CH₂), 1.37 - 1.40 (m, 4 H, 2 CH₂), 2.10 - 2.14 (m, 4 H, 2 CH₂), 4.24 (s, 4 H, N –CH2), 4.89 - 4.91 (m, 2 H, CH₂, olefin.), 4.98 - 5.01 (2 H, CH₂, olefin.), 5.79 - 5.85 (m, 2 H, CH₂, olefin.), 8.54 - 8.63 ppm (m, 8 H, CHaromatic.). 13C NMR (150 MHz, CDCl₃, 25°C): δ = 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 (CHCl₃) λmax (ε) = 457.7 (0.22), 488.7 (0.60), 525.2 nm (1.00). Fluorescence (CHCl₃): λmax (Irel) = 533 (1.00), 575 nm (0.36). Fluorescence quantum yield (λexc = 488 nm, E₄₈₃ nm/1 cm = 0.0401, reference: 2,9-bis-(1-hexylheptyl)-anthra[2,1,9-def,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00. MS: (DEI'/70 eV): m/z (%): 890 (100) [M+], 835 (22) [M' − C13H25], 654 (39) [M' − C17H33], 641 (17) [M' − C18H35], 599 (8) [M' − C19H37 − C13H25], 418 (62) [M' − 2 × C13H25], 391 (11) [M' − 2 × C18H35].

2,9-Bis-(2-but-3-enyl-2-octyldecyl)anthra[2,1,9-def,5,10-d'e'f']diisoquinoline-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,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone. The reaction product was purified by column separation (silica gel, chloroform). Yield 875 mg (69%) dark red, glossy solid, m.p. 105°C. Rf (silica gel,
CHCl₃/iso-hexane 10:1) = 0.63. IR (KBr): \( \nu = 3078.7 \text{ w}, 2919.3 \text{ vs}, 2852.5 \text{ s}, 1688.5 \text{ m}, 1651.6 \text{ s}, 1593.3 \text{ m}, 1577.3 \text{ m}, 1506.5 \text{ w}, 1452.0 \text{ w}, 1435.0 \text{ m}, 1402.9 \text{ m}, 1378.4 \text{ w}, 1313.8 \text{ s}, 1247.7 \text{ m}, 1215.3 \text{ w}, 1174.0 \text{ w}, 1155.0 \text{ w}, 1121.4 \text{ w}, 1007.1 \text{ w}, 900.0 \text{ m}, 873.8 \text{ w}, 849.8 \text{ w}, 810.0 \text{ m}, 795.6 \text{ w}, 748.4 \text{ m}, 721.7 \text{ w}, 658.2 \text{ cm}^{-1} \text{ w}. \)

1H NMR (600 MHz, CDCl₃, 25°C): \( \delta = 0.86 \text{ (t, } 3J = 6.9 \text{ Hz, } 12 \text{ H, } 4 \text{ CH}_3), 1.24 - 1.32 \text{ (m, } 56 \text{ H, } 28 \text{ CH}_2), 1.38 - 1.40 \text{ (m, } 4 \text{ H, } 2 \text{ CH}_2), 2.10 - 2.14 \text{ (m, } 4 \text{ H, } 2 \text{ CH}_2), 4.23 \text{ (s, } 4 \text{ H, N–CH}_2), 4.83 - 4.91 \text{ (m, } 2 \text{ H, CH}_2 \text{, olefin.), 4.98 - 5.02 \text{ (m, } 2 \text{ H, CH}_2 \text{, olefin.), 5.79 - 5.86 \text{ (m, } 2 \text{ H, CH}_2 \text{, olefin.), 8.53 - 8.62 \text{ ppm (m, } 8 \text{ H, CH}_ar.). \)

13C NMR (150 MHz, CDCl₃, 25°C): \( \delta = 14.1, 22.7, 23.5, 28.2, 29.4, 29.6, 31.7, 31.9, 35.6, 36.2, 40.7, 44.6, 113.0, 123.0, 123.5, 126.3, 129.2, 131.4, 134.4, 139.8, 164.2 \text{ ppm. UV/Vis (CHCl}_3\text{) } \lambda_{max} (\varepsilon) = 457.0 \text{ (19300), 488.8 \text{ (52200), 524.0 nm (85100). Fluorescence (CHCl}_3\text{) } \lambda_{max} (\varepsilon) = 547.0 \text{ (19300), 488.8 \text{ (52200), 524.0 nm (85100). Fluorescence quantum yield ( } \lambda_{exc} = 488 \text{ nm, } E_{488 \text{ nm/1 cm}} = 0.0256, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with } \Phi = 1.00 [40]): 1.00. MS: (DEI+/70 eV): m/z (%): 1002 \text{ (100) } [M+ – H], 947 \text{ (23) } [M+ – C_4H_7], 710 \text{ (45) } [M+ – C_6H_4], 697 \text{ (20) } [M+ – C_22H_{43}], 418 \text{ (72) } [M+ – 2 \times C_{21}H_{41}], 404 \text{ (35) } [M+ – C_{21}H_{41} – C_{22}H_{43}], 391 \text{ (12) } [M+ – 2 \times C_{22}H_{43}]. \}

C_{68}H_{94}N_2O_4 (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-def6,5,10-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-5-enyl)anthra[2,1,9-def6,5,10-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. Rf value (silica gel, CHCl₃/EtOH 60:1) = 0.73. IR (KBr): \( \nu = 3080.6 \text{ w}, 2956.6 \text{ m}, 2932.1 \text{ m}, 2870.5 \text{ m}, 1700.9 \text{ vs}, 1660.3 \text{ vs}, 1578.8 \text{ m}, 1507.9 \text{ w}, 1451.8 \text{ w}, 1438.0 \text{ m}, 1404.5 \text{ m}, 1356.6 \text{ m}, 1355.6 \text{ s}, 1253.0 \text{ m}, 1218.5 \text{ w}, 1165.8 \text{ w}, 1120.1 \text{ w}, 1010.2 \text{ w}, 913.2 \text{ w}, 851.3 \text{ m}, 810.8 \text{ m}, 796.0 \text{ w}, 755.5 \text{ cm}^{-1} \text{ w}. \)

1H NMR (600 MHz, CDCl₃, 25°C): \( \delta = 0.95 \text{ (t, } 3J = 7.3 \text{ Hz, } 12 \text{ H, } 4 \text{ CH}_3), 1.22 - 1.46 \text{ (m, } 24 \text{ H, } 12 \text{ CH}_2), 4.26 \text{ (s, } 4 \text{ H, } 2 \text{ CH}_2), 4.74 - 4.76 \text{ (m, } 2 \text{ H, CH}_2 \text{, olefin.), 4.88 - 4.90 \text{ (m, } 2 \text{ H, CH}_2 \text{, olefin.), 5.81 - 5.86 \text{ (m, } 2 \text{ H, CH}_2 \text{), 8.59 - 8.65 \text{ ppm (m, } 8 \text{ H, CH}_aremat.). \)

13C NMR (150 MHz, CDCl₃, 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 \text{ ppm. UV/Vis (CHCl}_3\text{) } \lambda_{max} (\varepsilon) = 457.1 \text{ (19400), 487.8 \text{ (52700), 524.4 nm (87900). Fluorescence (CHCl}_3\text{) } \lambda_{max} (\varepsilon) = 534 \text{ (1.00), 576.3 (0.52), 621.3 nm (0.12). Fluorescence quantum yield ( } \lambda_{exc} = 488 \text{ nm, } E_{488 \text{ nm/1 cm}} = 0.0256, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with } \Phi = 1.00 [40]): 1.00. MS: (DEI+/70 eV): m/z (%): 722 \text{ (65) } [M+], 666 \text{ (43) } [M+ – C_4H_9], 569 \text{ (100) } [M+ – C_{11}H_{21}], 557 \text{ (69) } [M+ – C_{12}H_{23}], 500 \text{ (23) } [M+ – C_{12}H_{23} – C_{21}H_{41}], 416 \text{ (25) } [M+ – 2 \times C_{11}H_{21}], 404 \text{ (87) } [M+ – C_{11}H_{21} – C_{12}H_{23}], 390 \text{ (62) } [M+ – 2 \times C_{12}H_{23}]. \text{ C}_{68}H_{94}N_2O_4 (723.0): Calcd. C 81.39, H 9.44, N 2.79; found C 81.17, H 9.57, N 2.99.
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-(2,2-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 1.43 g (75%) bright orange powder, m.p. > 250 °C. Rf value (silica gel; CHCl$_3$/EtOH 60:1) = 0.53. IR (KBr): $\nu$ = 3071.5 w, 2952.4 m, 2929.4 m, 2867.9 m, 1691.4 s, 1650.2 vs, 1576.3 m, 1506.0 w, 1464.4 w, 1435.9 m, 1401.9 m, 1373.0 s, 1367.2 w, 1359.2 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, 917.4 w, 868.6 w, 851.8 w, 810.3 w, 793.3 w, 747.6 m, 710.5 w, 658.9 cm$^{-1}$ w. $^1$H NMR(600 MHz, CDCl$_3$, 25°C): $\delta$ = 0.90 (t, $^3J$ = 7.1 Hz, 12 H, 4 CH$_3$), 1.26 - 1.38 (m, 24 H, 12 CH$_2$), 2.14 (d, $^3J$ = 7.1 Hz, 4 H, 2 CH$_2$), 4.26 (s, 4 H, 2 N–CH$_2$), 4.93 - 4.96 (m, 2 H, CH$_2$-olefin$_1$), 5.00 - 5.02 (m, 2 H, CH$_2$-olefin$_2$), 5.90 - 5.97 (m, 2 H, CH-olefin), 8.60 - 8.66 ppm (m, 8 H, CH$_2$-aromat.). $^{13}$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$_3$) $\lambda_{max}$ (E) = 458.2 (0.22), 489.1 (0.60), 525.6 nm (1.00). Fluorescence (CHCl$_3$): $\lambda_{max}$ ($I_{rel}$) = 534.5 (1.00), 577.0 (0.52), 621.8 nm (0.12). Fluorescence quantum yield ($\lambda_{exc}$ = 488 nm, $E_{488\text{ nm}}/1\text{ cm}$ = 0.0323, 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+/70 eV): m/z (%): 750 (99) [ M+], 709 (57) [ M+ − C$_3$H$_5$], 584 (32) [ M+ − C$_{12}$H$_{23}$], 571 (34) [ M+ − C$_{13}$H$_{25}$], 543 (12).

2,9-Bis-(2,2-dibutylhept-6-enyl)anthra[2,1,9-def;6,5,10-d’e’f’]diisoquinoline-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-(2,2-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 100:1). Yield 1.77 g (86%) reddish orange small plates, m.p. 239 °C. Rf value (silica gel, CHCl$_3$, 25°C): $\delta$ = 0.90 (t, $^3J$ = 7.1 Hz, 12 H, 4 CH$_3$), 1.26 - 1.38 (m, 24 H, 12 CH$_2$), 2.14 (d, $^3J$ = 7.1 Hz, 4 H, 2 CH$_2$), 4.26 (s, 4 H, 2 N–CH$_3$), 4.90 - 4.94 (m, 2 H, CH$_2$-olefin$_1$), 5.00 - 5.02 (m, 2 H, CH$_2$-olefin$_2$), 5.90 - 5.97 (m, 2 H, CH-olefin), 8.60 - 8.66 ppm (m, 8 H, CH$_2$-aromat.). $^{13}$C NMR (150 MHz, CDCl$_3$, 25°C): $\delta$ = 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$_3$) $\lambda_{max}$ (E) = 457.1 (0.22), 488.1 (0.60), 524.5 nm (1.00). Fluorescence (CHCl$_3$): $\lambda_{max}$ ($I_{rel}$) = 533.0...
(1.00), 574.5 (0.52), 623.5 nm (0.12). Fluorescence quantum yield ($\lambda_{\text{exc}} = 487$ nm, $E_{487 \text{ nm}/1 \text{ cm}} = 0.0296$, 2,9-bis-(1-hexyl-heptyl)anthra[2,1,9-def6,5,10-d'e']diisoquinoline-1,3,8,10-tetraone (1) with $\Phi = 1.00$ [40]): 1.00. MS: (DEI+/70 eV): $m/z$ (%): 806 (100) [$M^+ - H$], 612 (43) [$M^+ - C_{14}H_{27}$], 599 (11) [$M^+ - C_{15}H_{29}$], 418 (56) [$M^+ - 2 \times C_{15}H_{29}$], 404 (19) [$M^+ - C_{14}H_{27} - C_{15}H_{29}$], 391 (6) [$M^+ - 2 \times C_{15}H_{27}$]. C$_{54}$H$_{66}$N$_2$O$_4$ (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-def6,5,10-d'e']diisoquinoline-1,3,8,10-tetraone: Perylene-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-(2,2-dibutylhex-5-enyl)anthra[2,1,9-def6,5,10-d'e']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$_f$ value (silica gel; CHCl$_3$/EtOH 40:1) = 0.80. IR (KBr): $\nu$ = 3079.2 w, 2958.1 m, 2877.2 m, 1697.5 s, 1651.3 vs, 1591.2 s, 1578.0 m, 1465.3 w, 1434.6 m, 1404.1 m, 1359.5 m, 1359.0 m, 1331.8 s, 1248.6 m, 1214.2 w, 1161.9 w, 1127.1 w, 1099.0 w, 1004.3 w, 913.1 w, 850.8 w, 809.8 m, 792.9 w, 751.8 m, 711.9 cm$^{-1}$ w. $^1$H NMR (600 MHz, CDCl$_3$, 25˚C): $\delta = 0.95$ - 1.00 (m, 24 H, 8 CH$_3$), 2.15 - 2.20 (m, 4 H, 4 CH$_2$, aliph.), 4.48 (s, 4 H, 2 N–CH$_2$), 4.96 - 4.99 (m, 2 H, CH$_2$, olefin.), 5.18 - 5.20 (m, 2 H, CH$_2$, olefin.), 5.92 - 5.97 (m, 2 H, CH$_2$, olefin.), 8.64 - 8.72 ppm (m, 8 H, CH aromat.). UV/Vis (CHCl$_3$) $\lambda_{\text{max}}$ (E) = 457.8 (0.22), 486.6 (0.60), 525.0 nm (1.00). Fluorescence (CHCl$_3$): $\lambda_{\text{max}}$ ($I_{\text{rel}}$) = 534.5 (1.00), 577.0 (0.52), 635.8 nm (0.12). Fluorescence quantum yield ($\lambda_{\text{exc}} = 488$ nm, $E_{488 \text{ nm}/1 \text{ cm}} = 0.0318$, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def6,5,10-d'e']diisoquinoline-1,3,8,10-tetraone (1) with $\Phi = 1.00$ [40]): 1.00. MS (DEI+/70 eV): $m/z$ (%): 666 (22) [$M^+$], 623 (23) [$M^+ - C_{14}H_{27}$], 541 (35) [$M^+ - C_{15}H_{29}$], 529 (35) [$M^+ - C_{16}H_{31}$], 418 (19) [$M^+ - 2 \times C_{15}H_{29}$], 404 (98) [$M^+ - C_{14}H_{27} - C_{15}H_{29}$], 391 (100) [$M^+ - 2 \times C_{15}H_{27}$].

2,9-Bis-(2,2-diisopropylhex-5-enyl)anthra[2,1,9-def6,5,10-d'e']diisoquinoline-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-def6,5,10-d'e']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$_f$ value (silica gel; CHCl$_3$/EtOH 60:1) = 0.74. IR (KBr): $\nu$ = 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, 1126.8 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$^{-1}$ w. $^1$H NMR (600 MHz, CDCl$_3$, 25˚C): $\delta = 0.98$ - 1.05 (m, 24 H, 8 CH$_3$), 1.20 - 1.27 (m, 8 H, 4 CH$_2$), 2.16 - 2.22 (m, 4 H, 4 CH$_2$, aliph.), 4.52 (s, 4 H, 2 N–CH$_2$), 4.84 - 4.86 (m, 2 H, CH$_2$, olefin.), 4.91 - 4.94 (m, 2 H, CH$_3$), 5.36 - 5.40 (m, 2 H, CH$_2$, olefin.), 8.63 - 8.71 ppm (m, 8 H, 8 CH$_2$).
CHaromat). UV/Vis (CHCl₃) λ<sub>max</sub> (E) = 457.8 (0.22), 488.6 (0.60), 525.0 nm (1.00).

- Fluorescence (CHCl₃): λ<sub>max</sub> (I<sub rel>) = 535.0 (1.00), 578.0 (0.52), 626.5 nm (0.12).

Fluorescence quantum yield (λ<sub>exc</sub> = 489 nm, E<sub>489 nm / 1 cm</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-tetraone (1) with Φ = 1.00 [40]): 1.00. MS: (DEI +/70 eV): m/z (%): 722 (82) [M⁺], 679 (42) [M⁺ – C₆H₆], 570 (36) [M⁺ – C₇H₁₄], 557 (58) [M⁺ – C₈H₂₀], 418 (100) [M⁺ – 2 × C₇H₁₄ – C₈H₂₀], 404 (80) [M⁺ – C₇H₁₄ – C₈H₂₀], 391 (51) [M⁺ – 2 × C₈H₂₀].

HMRS (C₄₈H₅₄N₂O₄): Calcd. m/z: 722.408, found m/z: 722.406.

2-(2,2'-Dibutylhept-6- enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (21): 9-(2-Hydroxyethyl)2-benzopyrano[6',5':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-enylamine (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<sub>V</sub>-value (silica gel, CHCl₃/EtOH 20:1) = 0.12. IR (ATR): ν<sub>max</sub> = 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), 1363.6 (m), 1251.2 (w), 1169.4 (w), 1126.3 (w), 1059.7 (w), 908.0 (w), 856.9 (w), 793.9 (w), 744.1 cm<sup>-1</sup> (w). ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.89 (t, 3J(H,H) = 7.0 Hz, 6 H, 2 × CH₃), 1.24 - 1.33 (m, 14 H, 7 × CH₂), 1.42 - 1.47 (m, 2 H, CH₂), 2.01 (q, 3J(H,H) = 7.3 Hz, 2 H, Cq–CH₂), 4.07 (t, 3J(H,H) = 5.2 Hz, 2 H, N–CH₂–CH₂), 4.22 (s, 2 H, N–CH₂–Cq), 4.50 (t, 3J(H,H) = 5.2 Hz, 2 H, HO–CH₂), 4.96 - 4.97 (m, 1 H, CH₂olefin.), 4.99 - 5.00 (m, 1 H, CH₂olefin.), 5.78 - 5.85 (m, 1 H, CH₂olefin.), 8.42 - 8.46 (m, 4 H, 4 × CH<sub>perylene</sub>), 8.52 - 8.53 (m, 2 H, 2 × CH<sub>perylene</sub>), 8.60 - 8.62 ppm (m, 2 H, 2 × CH<sub>perylene</sub>). ¹³C NMR (150 MHz, CDCl₃, 25°C, TMS): δ = 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 (CHCl₃): λ<sub>max</sub> (I<sub rel>) = 458.8 (0.22), 490.0 (0.60), 526.4 nm (1.00). Fluorescence (CHCl₃): λ<sub>max</sub> (I) = 535.5 (1.00), 577.3 (0.54), 625.3 nm (0.13). Fluorescence quantum yield (λ<sub>exc</sub> = 488 nm, E<sub>488 nm / 1 cm</sub> = 0.0344, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00. MS: (DEI⁺/70 eV): m/z (%): 642 (100) [M⁺], 448 (64) [M⁺ – C₉H₁₇], 433 (23) [M⁺ – C₁₀H₂₃], 405 (98) [M⁺ – C₁₁H₂₅ – C₆H₆], 390 (13) [M⁺ – C₁₂H₂₉ – C₆H₆]. HMRS (C₄₁H₄₂N₂O₅): Calcd. m/z: 642.3094; found m/z: 642.3099.

2-(1-Hexylheptyl)-9-(6-hydroxypentyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone: 9-(1-Hexylheptyl)-2-benzopyrano[6',5':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’]diisoquinoline-1,3,8,10-tetraone and purified by column 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. Rf-value (silica gel, CHCl3/EtOH 20:1) = 0.12. IR (KBr): ν = 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), 1079.9 (w), 853.1 (w), 810.5 (m), 674.5 (m), 627.0 (w), 432.6 cm–1 (w). 1H NMR (600 MHz, CDCl3, 25˚C, TMS): δ = 0.83 (t, 3J(H,H) = 7.0 Hz, 6 H, 2 × CH3), 1.19 - 1.38 (m, 16 H, 8 × CH2), 1.67 - 1.72 (m, 2 H, β-CH2), 1.80 - 1.90 (m, 4 H, 2 × CH2), 2.22 - 2.28 (m, 2 H, β-CH2), 3.69 (t, 3J(H,H) = 6.4 Hz, 2 H, N –CH2), 4.24 - 4.25 (m, 2 H, CH2–OH), 8.59 - 8.68 ppm (m, 8 H, 8 × CH perylene). 13C NMR (150 MHz, CDCl3, 25˚C, TMS): δ = 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 (CHCl3): λmax (ε) = 458.9 (17800), 489.9 (49000), 526.4 nm (82000). Fluorescence (CHCl3): λmax (I) = 532.9 (1.00), 576.3 (0.54), 625.3 nm (0.13). Fluorescence quantum yield (λexc = 489 nm, E489 nm/1 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-tetraone (1) with Φ = 1.00 [40]): 1.00. MS: (DEI+/70 eV): m/z (%): 658 (85) [M+], 641 (13) [M+ − OH], 573 (6) [M' − C9H15], 476 (100) [M' − C13H27], 459 (11) [M' − C13H27 − OH], 390 (69) [M' − C13H27 − C6H13O]. C41H42N2O5 (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-Dibutylhept-6-enyl)-9-(2-hydroxy-ethyl)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 (6 1 mg, 0.60 mmol) and then with (2-cyanoethyl)-N,N-diisopropylphosphonamidechloride (122 mg, 0.553 mmol), stirred at room temperature 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, chloroform/acetone 10:1, glas column 700 × 55 mm, fraction 4), Yield 30 mg (22%) dark red solid, m.p. > 250˚C. Rf-value (silica gel, CHCl3/acetone 10:1) = 0.06. IR (ATR): ν = 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 –1 (m). 1H NMR (600 MHz, CDCl3, 25˚C, TMS): δ = 0.83 (t, 3J(H,H) = 7.0 Hz, 12 H, 4 × CH3), 1.22 - 1.41 (m, 56 H, 28 CH2), 1.87 - 1.95 (m, 4 H, β-CH2), 4.53 (t, 3J(H,H) = 5.1 Hz, 4 H, 2 × N–CH2–CH2), 4.62 (t, 3J(H,H) = 5.2 Hz, 4 H, 2 × CH2O), 5.12 - 5.19 (m, 2 H, 2 × α-CH), 8.00 - 8.02 (m,
2 H, 2 × CH₉perylen), 8.11 - 8.13 (m, 2 H, 2 × CHperylen), 8.24 - 8.26 (m, 2 H, 2 × CHperylen), 8.39 - 8.45 ppm (m, 2 H, 2 × CHperylen). ¹³C NMR (150 MHz, CDCl₃, 25°C, TMS): δ = 14.1, 22.7, 27.1, 29.3, 30.6, 31.9, 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 (CHCl₃): λₘₐₓ (Ε) = 459.0 (0.23), 490.0 (0.63), 527.0 nm (1.00). Fluorescence (CHCl₃): λₘₐₓ (Ι) = 573.8 (1.00), 577.0 (0.52), 625.3 nm (0.13). Fluorescence quantum yield (Iₑₓc = 488 nm, E₄₈₈ nm/1 cm = 0.0271, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def6,5,10-’def’]diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00.

MS: (DEI+70 eV): m/z (%): 1383 (< 1) [ M+], 1366 (< 1) [ M+ − HO], 1257 (< 1) [M+ − C₉H₁₉], 1100 (< 1) [ M+ − C₉H₁₉ − OH], 700 (64) [ M+ − C₆H₅N₂O₄], 684 (39) [ M+ − C₆H₅N₂O₅], 432 (4) [M+ − C₆H₅N₂O₄ − C₉H₁₉], 418 (74) [ M+ − C₆H₅N₂O₅ − C₉H₁₉].

2-(2-Bromethyl)-9-(1-nonyldecyl)anthra[2,1,9-def6,5,10-’d’e’T]diisoquinoline-1,3,8,10-tetraene: 2-(2-Hydroxyethyl)-9-(1-nonyldecyl)anthra[2,1,9-def6,5,10-’d’e’T]diisoquinoline-1,3,8,10-tetraene (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 vacuum 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. Rₖ-value (silica gel, CHCl₃/EtOAc 30:1) = 0.64. ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.82 (t, 3J(H,H) = 6.4 Hz, 6 H, 2 × CH₃), 1.18 - 1.36 (m, 28 H, 14 × CH₂), 1.81 - 1.97 (m, 2 H, β-CH₂), 2.17 - 3.71 (m, 2 H, β-CH₂), 3.71 (t, 3J(H,H) = 7.0 Hz, 2 H, CH₂–Br), 4.61 (t, 3J(H,H) = 7.0 Hz, 2 H, N–CH₂), 5.18 (m, 1 H, CH), 8.40 - 8.62 ppm (m, 8 H, 8 × CHperylen).

2-Amino-9-(2-but-3-enyl-2-octyldecyl)-anthra[2,1,9-def6,5,10-’d’e’T]diisoquinoline-1,3,8,10-tetraene: 9-Amino-2-benzopyrano-[6´,5´4´:10,5,6]anthra[2,1,9-def6,5,10-’d’e’T]diisoquinoline-1,3,8,10-tetraene (700 mg, 1.72 mmol), 2-but-3-enyl-2-octyldecylamine (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-def6,5,10-’d’e’T]diisoquinoline-1,3,8,10-tetraene, 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. Rₖ-value (silica gel, CHCl₃/EtOH 30:1) = 0.10. IR (ATR): ν = 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⁻¹ (w).

¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.86 (t, 3J(H,H) = 6.9 Hz, 6 H, 2 × CH₃), 1.24 - 1.40 (m, 30 H, 15 × CH₂), 2.10 - 2.14 (m, 2 H, CH₂), 4.24 (s, 2 H, N–CH₂), 4.90 - 4.91 (m, 1 H, CH₂olefin.), 4.99 - 5.02 (m, 1 H, CH₂olefin.), 5.79 - 5.85
(m, 1 H, CH_{defn.}), 8.51 - 8.64 ppm (m, 8 H, 8 × CH_perylene). 13C NMR (150 MHz, CDCl_3, 25°C, TMS): δ = 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_3): λ_{max} (E) = 460 (0.24), 491.6 (0.62), 528.4 nm (1.00). Fluorescence (CHCl_3): No emission detected. MS: (DEI'/70 eV): m/z (%): 711 (21) [M^+], 696 (13) [M^+ − NH_2], 419 (100) [M^+ − C_{12}H_{24}], 404 (76) [M^+ − C_{13}H_{26}], 390 (28) [M^+ − C_{13}H_{26} − NH_2]. HMRS (C_{46}H_{54}N_{3}O_{4}): Calcd. m/z: 712.411 [M^+ + H]; found m/z: 712.410.

2-Allyl-9-(1-hexylheptyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3): 9-(1-Hexylheptyl)-2-benzopyrano [6’,5’4’:10,5,6]anthra[2,1,9-def]isoquinoline-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-def6,5,10-d'e']diisoquinoline-1,3,8,10-tetraone 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_f-value (silica gel, CHCl_3/EtOH 30:1) = 0.63. IR (KBr): ν = 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), 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⁻¹ (w). 1H NMR (600 MHz, CDCl_3, 25°C, TMS): δ = 0.83 (t, 3J(H,H) = 7.0 Hz, 6 H, 2 × CH₃), 1.21 - 1.37 (m, 16 H, 8 × CH₂), 1.88 (m, 2 H, α-CH₂), 2.25 (m, 2 H, α-CH₂), 4.83 (d, 2 H, 3J(H,H) = 5.9 Hz, N-CH₂), 5.19 (m, 1 H, N-CH), 5.25 (m, 1 H, CH_{olefin.}), 5.37 (m, 1 H, CH_{olefin.}), 6.02 (m, 1 H, CH_{defn.}), 8.55 - 8.66 ppm (m, 8 H, 8 × CH_perylene). 13C NMR (151 MHz, CDCl_3, 25°C, TMS): δ = 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_3): λ_{max} (E) = 458 (0.22), 489 (0.60), 526 nm (1.00). Fluorescence (CHCl_3): λ_{max} (I) = 535 (1.00), 579 nm (0.41). Fluorescence quantum yield (CHCl_3, λ_{exc} = 458 nm, E_{458 nm}/1 cm = 0.0285; reference: 2,9-bis-(1-hexylheptyl)anthra-[2,1,9-def6,5,10-d'e']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00. MS (DEI'/70 eV): m/z (%): 612 (62) [M^+], 430 (100) [M^+ − C_{12}H_{24}], 415 (67) [430 − CH₂], 390 (3) [M^+ − C_{12}H_{24} − C_{2}H₄]. 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-def6,5,10-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-(2,2-dibutylhept-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def6,5,10-d'e']diisoquinoli
ne-1,3,8,10-tetraone and purified by medium pressure chromatography (silica gel, chloroform 25 mL min⁻¹, column 36 × 460 mm). Yield 869 mg (94%) light red powder, m.p. > 250°C. Rf-value (silica gel, CHCl₃) = 0.39. IR (KBr): ν = 3436.5 (m, br.), 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), 1374.7 (vs), 1252.5 (m), 1175.3 (w), 1125.2 (w), 1106.8 (w), 995.8 (w), 908.8 (w), 852.2 (w), 810.6 (m), 748.4 cm⁻¹ (m). 1H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.83 (t, 3J(H,H) = 7.0 Hz, 6 H, 2 × CH₃), 0.89 (t, 3J(H,H) = 7.0 Hz, 6 H, 2 × CH₃), 1.19 - 1.38 (m, 28 H, 14 × CH₂), 1.38 - 1.41 (m, 2 H, CH₂), 1.84 - 1.90 (m, 2 H, β-CH₂), 2.10 - 2.14 (m, 2 H, CH₂), 2.23 - 2.28 (m, 2 H, β-CH₂), 4.25 (s, 2 H, CH₂), 4.89 - 4.91 (m, 2 H, CH₂, olefin.), 5.16 - 5.21 (m, 1 H, α-CH), 5.79 - 5.86 (m, 1 H, CH olefin.), 8.61 - 8.69 ppm (m, 8 H, 8 × CH perylene). 13C NMR (151 Mhz, CDCl₃, 25°C, TMS): δ = 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, 133.3, 136.0, 141.1, 165.7 ppm. UV/Vis (CHCl₃): λmax (E) = 458.2 (0.22), 475.2 (0.50), 489.0 (0.60), 525.4 nm (1.00). Fluorescence (CHCl₃): λmax (I) = 532.2 (1.00), 576.5 (0.35) nm. Fluorescence quantum yield (λexc = 487 nm, E₄₈₇ = 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 Φ = 1.00 [40]): 1.00. MS (DEI +/70 eV): m/z (%): 766 (45) [M⁺], 586 (30) [M⁺ − C₁₂H₂₄ − CH₂], 404 (100) [M⁺ − C₂₆H₇₀], 390 (49) [404 − CH₂]. HMRS (C₅₁H₆₃N₂O₄): Calcd. m/z: 767.478 [M⁺ + H]; found m/z: 767.478.
139.8, 164.4 ppm. UV/Vis (CHCl₃): λₘₐₓ (Ε) = 458.0 (0.22), 489.4 (0.60), 525.8 nm (1.00). Fluorescence (CHCl₃): λₘₐₓ (Φ) = 534.0 (1.00), 576.0 (0.50), 624.8 nm (0.11). Fluorescence quantum yield (λₑₓc = 488 nm, E₄₈₈ nm/1 cm = 0.0282, reference: 2,9-bis-(1-hexylethyl)anthra[2,1,9-def6,5,10- d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00. MS: (DEI+/70 eV): m/z (%): 822 (86) [M⁺], 767 (21) [M⁻ C₅H₇], 586 (35) [M⁻ C₁₄H₂₇], 573 (16) [M⁻ C₁₅H₂₉], 404 (100) [M⁻ C₁₃H₂₇ - C₁₇H₃₃], 391 (27) [M⁻ C₁₃H₂₇ - C₁₈H₃₅]. HMRS (C₅₂H₆₅N₂O₄): Calcd. m/z: 823.494 [M⁺ + H]; found m/z: 823.547.

2-(1-Hexylethyl)-9-(2,2-dibutyleth-6-enyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (10): 9-(1-Hexylethyl)-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-dibutyleth-6-enylamine (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-dibutyleth-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-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. Rₙ-value (silica gel, CHCl₃) = 0.37. IR (KBr): ν = 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), 1211.2 (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⁻¹ (w). ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.83 (t, 3J(H,H) = 6.8 Hz, 6 H, 2 × CH₃), 0.89 (t, 3J(H,H) = 6.8 Hz, 6 H, 2 × CH₃), 1.22 - 1.36 (m, 30 H, 15 × CH₂), 1.41 - 1.49 (m, 2 H, CH₂), 1.82 - 1.91 (m, 2 H, CH₂), 1.99 - 2.04 (m, 2 H, CH₂), 2.20 - 2.29 (m, 2 H, CH₂), 4.24 (s, 2 H, N–CH₂–Cq), 4.89 - 5.01 (m, 2 H, CH₂olefin.), 5.15 - 5.23 (m, 1 H, CH), 5.77 - 5.87 (m, 1 H, CHolefin.), 8.63 - 8.69 ppm (m, 8 H, 8 × CH perylene). ¹³C NMR (150 MHz, CDCl₃, 25°C, TMS): δ = 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 (CHCl₃): λₘₐₓ (Ε) = 458.0 (0.22), 488.8 (0.61), 525.4 nm (1.00). Fluorescence (CHCl₃): λₘₐₓ (Φ) = 533.5 (1.00), 575.8 (0.52), 623.8 nm (0.12). Fluorescence quantum yield (λₑₓc = 488 nm, E₄₈₈ nm/1 cm = 0.0294, reference: 2,9-bis-(1-hexylethyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetra one (1) with Φ = 1.00 [40]): 1.00. MS: (DEI'/70 eV): m/z (%): 780 (51) [M⁺], 711 (8) [M⁻ C₅H₇], 586 (28) [M⁻ C₁₄H₂₇], 576 (14) [M⁻ C₁₅H₂₉], 404 (100) [M⁻ C₁₃H₂₇ - C₁₇H₃₃], 391 (27) [M⁻ C₁₃H₂₇ - C₁₈H₃₅]. HMRS (C₅₂H₆₅N₂O₄): Calcd. m/z: 781.494 [M⁺ + H]; found m/z: 781.496.
etraone (42) and purified by column separation (800 mL of silica gel, chloroform/ethanol 30:1, glass column groves 780 × 44 mm). Yield 362 mg (63%) light red solid, m.p. > 250°C. Rf-value (alumina, CHCl₃) = 0.49. IR (KBr): ν = 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⁻¹ (w). ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.83 (t, 3J(H,H) = 7.0 Hz, 6 H, 2 × CH₃), 1.20 - 1.38 (m, 24 H, 12 × CH₂), 1.85 - 1.91 (m, 2 H, β-CH₂), 2.22 - 2.28 (m, 2 H, β-CH₂), 5.16 - 5.21 (m, 1 H, α-CH₂), 5.30 (m, 1 H, CH₂olefin.), 5.82 - 5.85 (m, 1 H, CH₂olefin.), 6.79 - 6.84 (m, 1 H, CH₂olefin.), 7.32 - 7.33 (m, 2 H, 2 × CH aryl), 7.60 - 7.62 (m, 2 H, 2 × CH aryl), 8.61 - 8.72 ppm (m, 8 H, 8 × CH perylene). ¹³C NMR (150 MHz, CDCl₃, 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 (CHCl₃): λmax (Ε) = 459.4 (0.22), 490.2 (0.60), 526.8 nm (1.00). Fluorescence (CHCl₃): λmax (ε) = 459.4 (0.22), 490.2 (0.60), 526.8 nm (1.00). Fluorescence quantum yield (CHCl₃, λexc = 489 nm, E₄₈₉ nm/1 cm = 0.0372; reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00. MS: (DEI +/70 eV): m/z (%): 730 (20) [M⁺], 617 (2) [ M⁺ − C₈H₁₇], 492 (100) [ M⁺ − C₁₇H₃₅]. HMRS (C₄₉H₅₀N₂O₄): Calcd. m/z: 731.384 [M⁺ + H]; found m/z: 731.382.
487 nm, $E_{487 \text{ nm/1 cm}} = 0.0304$; 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’/70 eV): $m/z$ (%): 696 (78) [M'], 430 (100) [M' − C$_{19}$H$_{38}$], 415 (46) [430 − CH$_{3}$]. HMRS (C$_{46}$H$_{52}$N$_{2}$O$_{4}$): Calcd. $m/z$: 696.393; found $m/z$: 696.394.

2-((1-Nonyldecyl)-9-(4-vinylphenyl)anthra[2,1,9-def;5,10-d’e’f’]diisoquinoline-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 zinc acetate 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-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 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 zinc acetate 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’]diisoquinoline-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. Rf-value (silica gel, CHCl$_3$) = 0.43. IR (KBr): $\nu = 3092.1$ (m), 2954.3 (m), 2924.5 (s), 2854.0 (m), 1698.6 (s), 1658.6 (s), 1594.6 (s), 1578.1 (s), 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), 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$^{-1}$ (w).

$^1$H NMR (600 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 0.83 (t, $^3J(H,H) = 7.1$ Hz, 6 H, 2 × CH$_3$), 1.21 - 1.32 (m, 28 H, 14 × CH$_2$), 1.84 - 1.90 (m, 2 H, $\beta$-CH$_2$), 2.22 - 2.28 (m, 2 H, $\beta$-CH$_2$), 5.19 (m, 1 H, $\alpha$-CH), 5.35 (d, $^3J(H,H) = 10.9$ Hz, 1 H, CH$_2$olefin), 5.84 (d, $^3J(H,H) = 17.6$ Hz, 1 H, CH$_2$olefin), 6.81 (dd, $^3J(H,H) = 17.6$, 10.9 Hz, 1 H, CH$_2$olefin), 7.32 (d, $^3J(H,H) = 8.3$ Hz, 2 H, CH$_2$aryl), 7.61 (d, $^3J(H,H) = 8.3$ Hz, 2 H, CH$_2$aryl), 8.62 - 8.73 ppm (m, 8 H, 8 × CH$_2$perylened). $^1$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, 135.6, 138.6, 163.9 ppm. UV/Vis (CHCl$_3$): $\lambda_{max}$ (E) = 459 (0.22), 490 (0.60), 527 nm (1.00). Fluorescence (CHCl$_3$): $\lambda_{max}$ (I) = 534 (1.00), 578 nm (0.40). Fluorescence quantum yield (CHCl$_3$): $\lambda_{max}$ ($E$) = 489 nm, $E_{489 \text{ nm/1 cm}} = 0.0319$; reference: 2-(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’/70 eV): $m/z$ (%): 758 (27) [M'], 492 (100) [M' − C$_{19}$H$_{38}$], 373 (16) [C$_{24}$H$_{48}$NO$_{4}$]. HMRS (C$_{51}$H$_{55}$N$_{2}$O$_{4}$): 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;5,10-d’e’f’]diisoquinoline-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-6-enyl)-9-(2-hydroxyethyl)anthra[2,1,9-def,5,10-d'e']diisoquinoline-1,3,8,10-tetraone 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. Rf-value (silica gel, CHCl₃/EtOH 30:1) = 0.21. IR (KBr): ν = 2961.5 (m), 2924.2 (m), 1701.0 (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), 753.0 cm⁻¹ (w). 1H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 1.23 (s, 9 H, tert-butyl), 1.27 (s, 9 H, tert-butyl), 4.79 (d, 3J(H,H) = 5.9 Hz, 2 H, N–CH₂), 5.19 (d, 3J(H,H) = 10.3 Hz, 1 H, CH₂,olefin.), 5.31 (d, 3J(H,H) = 17.0 Hz, 1 H, CH₂,olefin.), 6.97 (s, 1 H, CH₃), 7.41 (d, 3J(H,H) = 8.6 Hz, 1 H, CH₃), 7.53 (d, 3J(H,H) = 8.6 Hz, 1 H, CH₃), 8.60 - 8.71 ppm (m, 8 H, CH perylene). UV/Vis (CHCl₃): λmax (E) = 458 (0.22), 490 (0.60), 526 nm (1.00). Fluorescence (CHCl₃): λmax (I) = 534 (1.00), 575 (0.35), 622 nm (0.06). Fluorescence quantum yield (CHCl₃, λexc = 488 nm, Ey= 0.0571; reference: 2,9-bis-(1-hexylheptyl)anthra- [2,1,9-def,5,10-d'e']diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 1.00. MS (DEI+/70 eV): m/z (%): 618 (3) [ M+], 561 (100) [ M+ − C₄H₉ (isobutene)], 545 (7) [561 − CH₃]. HMRs (C₄₁H₃₄N₂O₄): Calcd. m/z: 618.252; found m/z: 618.253.

2-allyl-9-(2,2-dibutyl-hept-6-enyl)anthra[2,1,9-def,5,10-d'e']diisoquinoline-1,3,8,10-tetraone (14): 9-Allyl-2-benzopyrano[6´,5´4´:10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10-tetraone (1.00 g, 2.32 mmol), imidazole (5.0 g), 2,2-dibutylhept-6-enylamine (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']diisoquinoline-1,3,8,10-tetraone and purified by column separation (800 mL of silica gel, chloroform/ethanol 50:1, glass column 800 × 42 mm) and then 500 mL of alumina, chloroform/ethanol 50:1, purified by 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. Rf-value (alumina; CHCl₃) = 0.38. IR (ATR): ν = 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⁻¹ (w). 1H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 0.89 (t, 3J(H,H) = 7.1 Hz, 6 H, 2 × CH₃), 1.25 - 1.35 (m, 14 H, 7 × CH₂), 1.42 - 1.47 (m, 2 H, CH₂), 2.00 (m, 2 H, CH₂), 4.22 (s, 2 H, N–CH₂), 4.89 - 4.90 (m, 1 H, CH₂olefin.), 4.91 - 4.92 (m, 1 H, CH₂olefin.), 4.96 - 4.97 (m, 1 H, CH₂olefin.), 4.99 - 5.00 (m, 1 H, CH₂olefin.), 5.24 - 5.25 (m, 1 H, CH₂olefin.), 5.26 - 5.27 (m, 1 H, CH₂olefin.), 5.36 - 5.37 (m, 1 H, CH₂olefin.), 5.39 -
5.40 (m, 1 H, CH\textsubscript{olefin}), 5.78 - 5.85 (m, 1 H, CH\textsubscript{olefin}), 6.00 - 6.07 (m, 1 H, CH\textsubscript{aromat}), 8.55 - 8.57 (m, 4 H, CH aromatic), 8.61 - 8.83 (m, 2 H, CH aromatic), 8.66 - 8.67 ppm (m, 2 H, CH aromatic). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}, 25°C, TMS): δ = 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\textsubscript{3}): λ\textsubscript{max} (ε) = 456.8 (18100), 488.0 (49700), 524.4 nm (82500).

Fluorescence (CHCl\textsubscript{3}): λ\textsubscript{max} (I) = 533.0 (1.00), 574.5 (0.52), 623.5 nm (0.12).

UV/Vis (CHCl\textsubscript{3}): λ\textsubscript{max} (ε) = 456.8 (18100), 488.0 (49700), 524.4 nm (82500).

Fluorescence (CHCl\textsubscript{3}): λ\textsubscript{max} (I) = 533.0 (1.00), 574.5 (0.52), 623.5 nm (0.12).

Fluorescence quantum yield (λ\textsubscript{exc} = 488 nm, E\textsubscript{488 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-tetraceta (1) with Φ = 1.00 [40]): 1.00.

MS: (DEI:+/70 eV): m/z (%): 638 (90) [ M+], 444 (100) [M+ − C\textsubscript{14}H\textsubscript{27}], 429 (35) [M+ − C\textsubscript{14}H\textsubscript{27} − CH\textsubscript{3}], 415 (8) [M+ − C\textsubscript{14}H\textsubscript{27} − 2 × CH\textsubscript{3}]. C\textsubscript{42}H\textsubscript{42}N\textsubscript{2}O\textsubscript{4} (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-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e'f']-diisoquinoline-1,3,8,10-tetraceta]-9-(2,2-dibutylhept-6-enyl)-anthra[2,1,9-def;6,5,10-d'e'f']-diisoquinoline-1,3,8,10-tetraceta (12): 2-(2,2-Dibutyl-hept-6-enyl)-9-(2-hydroxyethyl)-anthra[2,1,9-def;6,5,10-d'e'f']-diisoquinoline-1,3,8,10-tetraceta (700 mg, 1.09 mmol) was dissolved in refluxing dichloromethane (450 mL), treated with diisopropylethylamine (7 mL, dark red solution), treated dropwise with methanesulfonic chloride (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 vacuum 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\textsubscript{f}-value (silica gel, CHCl\textsubscript{3}/EtOH 30:1) = 0.12. IR (ATR): ν = 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\textsuperscript{−1} (w). 1H NMR (600 MHz, CDCl\textsubscript{3}, 25°C, TMS): δ = 0.89 (t, J(H,H) = 7.1 Hz, 12 H, 4 × CH\textsubscript{3}), 1.25 - 1.35 (m, 28 H, 14 CH\textsubscript{2}), 1.42 - 1.48 (m, 4 H, 2 × CH\textsubscript{2}), 2.00 - 2.03 (m, 4 H, 2 × C\textsubscript{q}−CH\textsubscript{2}), 4.04 (t, J(H,H) = 5.2 Hz, 4 H, 2 × N−CH\textsubscript{2}−CH\textsubscript{3}), 4.12 (s, 4 H, 2 × N−CH\textsubscript{3}), 4.51 (t, J(H,H) = 5.4 Hz, 4 H, 2 × CH\textsubscript{2}−OH), 4.89 - 4.91 (m, 2 H, 2 × CH\textsubscript{olefin}), 4.96 - 4.99 (m, 2 H, 2 × CH\textsubscript{olefin}), 5.78 - 5.85 (m, 2 H, 2 × CH\textsubscript{olefin}), 8.58 - 8.70 ppm (m, 16 H, 16 × CH\textsubscript{perylene}). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}, 25°C, TMS): δ = 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\textsubscript{3}): λ\textsubscript{max} (E) = 458.6 (0.23), 489.6 (0.61), 526.2 nm (1.00). Fluorescence (CHCl\textsubscript{3}): λ\textsubscript{max} (I) = 537.8 (1.00), 577.8 (0.52), 625.5 nm (0.13). Fluorescence quantum yield (λ\textsubscript{exc} = 488 nm, E\textsubscript{488 nm}/1 cm = 0.0274; reference:
2,9-bis-(1-hexylheptyl)anthra[2,1,9-def,5,10-d’e’]diisoquinoline-1,3,8,10-tetraone (1) with $\Phi = 1.00$ [40]: 1.00. MS: (DEI+/70 eV): $m/z$ (%): 1267 (< 1) [M]+, 642 (100) [$M’ - C_{41}H_{41}N_2O_4$], 626 (24) [$M’ - C_{41}H_{41}N_2O_3$], 448 (64) [$M’ - C_{41}H_{41}O_4$ - C_{14}H_{27}], 405 (99) [$M’ - C_{41}H_{41}O_4$ - C_{15}H_{29}]. HMRS ($C_{42}H_{44}N_2O_5$): Calcd. $m/z$: 1266.608; found $m/z$: 1266.609. 

Byproduct I: 2-(2,2-Dibutylhept-6-etyl)-9-(2-methoxyethyl)anthra[2,1,9-def,5,10-d’e’] diisoquinoline-1,3,8,10-tetraone: Yield 39 mg (5%) red solid, m.p. > 250˚C. Rf-value (silica gel, CHCl$_3$/EtOH 30:1) = 0.12. IR (ATR): $\nu = 3069.3$ (w), 2953.6 (m), 2929.3 (m), 2860.5 (m), 1694.9 (s), 1650.8 (vs), 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), 794.8 (w), 744.8 (m), 668.1 (w), 640.5 cm$^{-1}$ (w). $^1$H NMR (600 MHz, CDCl$_3$, 25˚C, TMS): $\delta = 0.89$ (t, $^3J(H,H) = 7.0$ Hz, 6 H, 2 × CH$_3$), 1.26 - 1.46 (m, 14 H, 7 × CH$_2$), 2.00 - 2.03 (m, 2 H, C$_q$–CH$_2$), 3.42 (s, 3 H, OCH$_3$), 3.78 (t, $^3J(H,H) = 5.3$ Hz, 2 H, N–CH$_2$–CH$_2$), 4.23 (s, 2 H, N–CH$_2$), 4.48 (t, $^3J(H,H) = 5.3$ Hz, 2 H, MeO–CH$_2$), 4.89 - 4.91 (m, 1 H, CH$_2$, olefin.), 4.96 - 5.00 (m, 1 H, CH$_2$, olefin.), 5.78 - 5.85 ppm (m, 1 H, CH olefin.). $^{13}$C NMR (150 MHz, CDCl$_3$, 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$_3$): $\lambda_{max}$ (E) = 458.4 (0.23), 489.4 (0.61) nm (1.00). Fluorescence (CHCl$_3$): $\lambda_{max}$ (I) = 534.8 (1.00), 578.0 (0.54), 626.3 nm (0.13). Fluorescence quantum yield ($\lambda_{exc} = 488$ nm, $E_{488 \mu m/1 cm}$ = 0.02590; reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def,5,10-d’e’]diisoquinoline-1,3,8,10-tetraone (1) with $\Phi = 1.00$): 1.00. MS: (DEI+/70 eV): $m/z$ (%): 656 (66) [$M’$], 587 (21) [$M’ - C_5H_9$], 462 (39) [$M’ - C_{14}H_{27}$], 449 (38) [$M’ - C_{14}H_{27}$], 404 (100) [$M’ - C_{14}H_{27}$ – C$_2$H$_2$O], 390 (26) [$M’ - C_{13}H_{28}$ – C$_2$H$_2$O]. HMRS ($C_{42}H_{44}N_2O_5$): Calcd. $m/z$: 656.325; found $m/z$: 656.326.

Byproduct II: 2-(2,2-Dibutylhept-6-etyl)-9-(2-chlorethyl)anthra[2,1,9-def,5,10-d’e’] diisoquinoline-1,3,8,10-tetraone (50): Yield 51 mg (8%) red powder, m.p. > 250˚C. Rf-value (silica gel, CHCl$_3$/EtOH 30:1) = 0.12. IR (ATR): $\nu = 3069.3$ (w), 2953.6 (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$^{-1}$ (w). $^1$H NMR (600 MHz, CDCl$_3$, 25˚C, TMS): $\delta = 0.89$ (t, $^3J(H,H) = 7.0$ Hz, 6 H, 2 × CH$_3$), 1.25 - 1.35 (m, 14 H, 7 × CH$_2$), 1.42 - 1.47 (m, 2 H, CH$_2$), 2.00 - 2.03 (m, 2 H, C$_q$–CH$_2$), 3.42 (s, 3 H, OCH$_3$), 3.78 (t, $^3J(H,H) = 6.8$ Hz, 2 H, N–CH$_2$), 4.61 (t, $^3J(H,H) = 6.8$ Hz, 2 H, N–CH$_2$). $^{13}$C NMR (150 MHz, CDCl$_3$, 25˚C, TMS): $\delta = 14.4$, 23.3, 24.0, 26.0, 35.1, 36.1, 39.0, 40.9, 41.6, 45.9, 114.5, 123.0, 123.1, 123.5, 124.0, 129.4, 131.5, 131.9, 133.4, 135.2, 139.4, 163.5, 164.4 ppm. UV/Vis (CHCl$_3$): $\lambda_{max}$ (E) = 458.8 (0.22), 489.6 (0.60), 526.0 nm (1.00). Fluorescence (CHCl$_3$): $\lambda_{max}$ (I) = 535.0 (1.00), 577.5 (0.53), 68 Green and Sustainable Chemistry
624.5 nm (0.12). Fluorescence quantum yield ($\lambda_{\text{exc}} = 488$ nm, $E_{\text{nm/1 cm}} = 0.0393$; 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+ 70 eV): $m/z$ (%): 660 (62) [$M^+$], 626 (71) [$M^+-\text{CIL}$], 466 (95) [$M^+-\text{C}_{13}\text{H}_{27}$], 432 (100) [$M^+-\text{C}_{14}\text{H}_{27}$], 404 (54) [$M^+-\text{C}_{14}\text{H}_{27}$], 390 (15) [$M^+-\text{C}_{15}\text{H}_{29}$]. HMR (C$_{13}$H$_{27}$ClO$_2$): 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’]diisoquinoline-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 dispersed 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. $R_f$-value (silica gel, CHCl$_3$/EtOH 40:1) = 0.22 (cis-isomer), 0.24 (trans-isomer). IR (KB$r$): $\nu = 2925.1$ (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$^{-1}$ (w). 1H NMR (600 MHz, CDCl$_3$, 25˚C, TMS): cis-isomer: $\delta = 0.83$ (t, $3J(H,H) = 7.0$ Hz, 12 H, 4 × CH$_3$), 1.16 - 1.41 (m, 32 H, 16 × CH$_2$), 1.83 - 1.89 (m, 4 H, 2 × β-CH$_2$), 2.21 - 2.28 (m, 4 H, 2 × β-CH$_2$), 5.15 - 5.21 (m, 2 H, 2 × α-CH), 5.24 - 5.25 (m, 4 H, 2 × N–CH$_2$), 5.86 - 5.88 (m, 2 H, 2 × CH olefin.), 8.57 - 8.74 ppm (m, 16 H, 16 × CH perylene); trans-isomer: $\delta = 0.83$ (t, $3J(H,H) = 7.9$ Hz, 12 H, 4 × CH$_3$), 1.16 - 1.41 (m, 32 H, 16 × CH$_2$), 1.83 - 1.89 (m, 4 H, 2 × β-CH$_2$), 2.21 - 2.28 (m, 4 H, 2 × β-CH$_2$), 4.83 - 4.84 (m, 4 H, 2 × α-CH), 5.15 - 5.21 (m, 2 H, 2 × α-CH), 6.09 - 6.11 (m, 2 H, CH$_2$ olefin), 8.57 - 8.74 ppm (m, 16 H, 16 × CH perylene). UV/Vis (CHCl$_3$): $\lambda_{\text{max}} (E) = 459.8$ (0.23), 490.2 (0.63), 527.2 nm (1.00). Fluorescence quantum yield ($\lambda_{\text{exc}} = 488$ nm, $E_{\text{nm/1 cm}} = 0.0448$; 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+/70 eV): $m/z$ (%): 1197 (51) [$M^+$], 1014 (58) [$M^+-\text{C}_{13}\text{H}_{27}$], 833 (100) [$M^+-2\times\text{C}_{13}\text{H}_{27}$], 815 (33), 624 (22) [$M^+-\text{C}_{13}\text{H}_{27}\text{N}_{2}\text{O}_{4}$], 611 (12) [$M^+-\text{C}_{15}\text{H}_{32}\text{N}_{2}\text{O}_{4}$], 572 (11) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 442 (92) [$M^+-\text{C}_{15}\text{H}_{35}\text{N}_{2}\text{O}_{4}$], 429 (15) [$M^+-\text{C}_{15}\text{H}_{35}\text{N}_{2}\text{O}_{4}$], 417 (56) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 416 (21) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 403 (8) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 390 (92) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 373 (30) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 347 (36) [$M^+-\text{C}_{14}\text{H}_{33}\text{N}_{2}\text{O}_{4}$], 329 (13), 69 (15), 15 (17). HMR (C$_{13}$H$_{27}$N$_2$O$_4$): Calcd. $m/z$: 1196.566; found $m/z$: 1196.561.
1,9-def6,5,10-d’e’f’diisoquinoline-1,3,8,10-tetraone: 2-Allyl-9-(2,5-di-tert-butyphenyl)anthra[2,1,9-def6,5,10-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, treated with further second-generation Hoveyda-Grubbs-catalyst (5 mg, 8 µmol = 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 times with a mixture of chloroform/water 1:1 with the collection of the organic phase and purified by medium pressure chromatography (silica gel, chloroform/ethanol 40:1 at 10 mL·min⁻¹, 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. \( R_f \)-value (silica gel, CHCl₃/EtOH 40:1) = 0.17. UV/Vis (CHCl₃): \( \lambda_{max}(E) = 459.8 \) (0.22), 491.0 (0.58), 529.0 nm (1.00). Fluorescence (CHCl₃): \( \lambda_{max}(I) = 540.5 \) (1.00), 578.0 (0.74), 626.5 nm (0.17). Fluorescence quantum yield (\( \lambda_{exc} = 489 \) nm, \( E_{488 \ nm/cm} = 0.0233 \); reference: 2,9-bis-(1-hexyheptyl)anthra[2,1,9-def6,5,10-d’e’f’]diisoquinoline-1,3,8,10-tetraone (1) with \( \Phi = 1.00 \) [40]): 1.00. MS (DEI+/70 eV): m/z (%): 1151 (24) \[ M+ - C_4H_8 \], 573 (28), 505 (15) \[ M+ - C_{47}H_{47}N_2O_4 \]. HMRS (C₈₀H₆₅N₄O₈): Calcd. m/z: 1209.480 \[ M+ + H \]; found m/z: 1209.479.

2-(1-Octylnonyl)-9-(4’-(2-(1-octylnonyl)anthra[2,1,9-def6,5,10-d’e’f’]diisoquinoline-1,3,8,10-tetraon-9-yl)-stilben-4-yl)anthra[2,1,9-def6,5,10-d’e’f’]diisooquinoline-1,3,8,10-tetraone (7a): 2-(1-Octylnonyl)-9-(4-vinylphenyl)anthra[2,1,9-def6,5,10-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 further 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 starring materials and by-products. Yield 66 mg (17%) red pigment, m.p. > 250°C. IR (KBr): \( \tilde{\nu} = 2952.7 \) (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), 1309.3 (w), 1254.0 (m), 1195.6 (m), 1174.8 (m), 1136.8 (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⁻¹ (w). UV/Vis (H₂SO₄): \( \lambda_{max}(E) = 404.8 \) (0.10), 557.8 (0.58), 602.4 nm (1.00). Fluorescence (H₂SO₄): \( \lambda_{max}(I) = 623.0 \) nm (1.00). MS (FAB+/70 eV): m/z (%): 1433 \[ M' \], 879, 823, 801, 765, 749, 731, 613, 460, 391, 307, 154.

2-(1-Nonyldecy)-9-(4’-(2-(1-nonyldecy)anthra[2,1,9-def6,5,10-d’e’f’]diisoquinoline-1,3,8,10-tetraon-9-yl)stilben-4-yl)anthra[2,1,9-def6,5,10-d’e’f’]diisooquinoline-1,3,8,10-tetraone (6a): 2-(1-Octylnonyl)-9-(4’-(2-(1-octylnonyl)anthra[2,1,9-def6,5,10-d’e’f’]diisoquinoline-1,3,8,10-tetraon-9-yl)-stilben-4-yl)anthra[2,1,9-def6,5,10-d’e’f’]diisooquinoline-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 further 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 starring materials and by-products. Yield 66 mg (17%) red pigment, m.p. > 250°C. IR (KBr): \( \tilde{\nu} = 2952.7 \) (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), 1309.3 (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⁻¹ (w). UV/Vis (H₂SO₄): \( \lambda_{max}(E) = 404.8 \) (0.10), 557.8 (0.58), 602.4 nm (1.00). Fluorescence (H₂SO₄): \( \lambda_{max}(I) = 623.0 \) nm (1.00). MS (FAB+/70 eV): m/z (%): 1433 \[ M' \], 879, 823, 801, 765, 749, 731, 613, 460, 391, 307, 154.
diisoquinoline-1,3,8,10-tetraone (7b): 2-(1-Nonyldecyl)-9-(4-vinylphenyl)anthra[2,1,9-def;6,5,10-d’e’f’]diisoquinoline-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 precipitate of very fine, light red needles 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 starting materials and by-products. Yield 12 mg (4%) dark red pigment, m.p. > 250 °C. IR (KBr): ν = 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⁻¹ (w). UV/Vis (H₂SO₄): λmax (E) = 317.6 (0.30), 402.8 (0.12), 556.8 (0.58), 601.8 nm (1.00). Fluorescence (H₂SO₄): λmax (I) = 631.5 nm (1.00). MS (FAB+ 70 eV): m/z (%): 1490 [M+], 1378, 1225, 1071, 919, 835 [M+ − C₄₃H₄₆N₂O₄], 829, 793, 759 [M+ − C₄₉H₄₉N₂O₄− C₄₃H₄₆N₂O₄], 829, 793, 759 [M+ − C₄₉H₄₉N₂O₄− C₄₃H₄₆N₂O₄].

2-(1-Hexylheptyl)-9-{1-(2,2,13-tributyl-13-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d’e’f’]diisoquinoline-1,3,8,10-tetraone)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-Dibutylhex-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-Grubbs-catalyst (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 (10 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⁻¹, red fraction, column 36 × 460 mm and a second medium pressure chromatography. Yield 3.0 mg (3%) red solid. Rf-value (silica gel, CHCl₃/EtOH 40:1) = 0.17. UV/Vis (CHCl₃): λmax (E) = 461.6 (0.29), 491.8 (0.75), 527.4 nm (1.00). Fluorescence (CHCl₃): λmax (I) = 536.8 (1.00), 579.8 nm (0.74). MS (DEI+/70 eV): m/z (%): 1504 (2) [M⁺], 711 (74) [M⁺ − C₂₃H₄₆N₂O₄], 404 (86) [M⁺ − C₂₆H₄₉N₂O₄− C₁₃H₂₇], 390 (100) [404− CH₂].

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-tetraone)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’]diisoquinoline-1,3,8,10-tetraone (10, 100 mg, 0.128 mmol) under argon atmosphere was dissolved in tetrahydrofuran (20 mL), treated with second-generation Hoveyda-Grubbs-catalyst (3, 13 mg, 21 µmol), stirred at room temperature for 18 h, precipitated with...
methanol, collected by vacuum filtration, dried at 110°C in air and purified by column separation (silica gel, chloroform). A pure fraction again forms a spectrum of side products. MS (ESI+/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) anthra[2,1,9-def,5,10-d’é’γ]diisoquinoline-1,3,8,10-tetraone)anthra[2,1,9-def6,5,10-d’e’γ]diisoquinoline-1,3,8,10-tetraone[22]:2,9-Bis-(2,2-dibutyl-hex-5-enyl)anthra[2,1,9-def6,5,10-d’e’γ]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-(2,4,6-trimethylphenyl)-2-imidazolidinyldiene) dichloro(2-isopropoxy-phenylmethyl phenylmethylen) Ruthenium), stirred at 40°C for 5 d, allowed to cool, precipitated with methanol (100 mL), collected by vacuum filtration (D4 glass 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. Rf value (silica gel; CHCl3/EtOH 80:1) = 0.15. IR (KBr): ν = 3502.2 w br., 1953.8 s, 2927.6 s, 2858.7 s, 1697.7 vs, 1656.6 vs, 1593.9 s, 1578.0 s, 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⁻¹ m. 1H NMR (600 MHz, CDCl3, 25°C): δ = 0.84 - 1.75 (m, 84 H, 8 CH3 + 30 CH2), 2.25 - 2.39 (m, 4 H, 2 CH2), 3.85 - 4.42 (m, 12 H, 4 N –CH2R + 4 CHolefin.), 7.08 - 7.20 (m, 4 H, CHarom.), 7.52 - 7.54 (m, 2 H, CH arom.), 7.70 - 7.73 (m, 2 H, CH arom.), 7.82 - 8.65 ppm (m, 8 H, CHarom.). UV CHCl3: λmax (ε) = 468.4 (27300), 494.4 (62800), 530.2 nm (56700). Fluorescence (CHCl3): λmax (Irel) = 533.8 (0.90), 582.8 nm (1.00). Fluorescence quantum yield (λexc = 493 nm, E483nm/1 cm = 0.00997, reference: 2,9-bis-(1-hexylheptyl) anthra[2,1,9-def,6,5,10-d’e’γ]diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 75%. MS (DEI/70 eV): m/z (%):1500 (4) [M+], 778 (31) [M+ − C48H56N2O4], 723 (37) [M+ − C32H36O4], 585 (32) [M+ − C48H56N2O4 − C14H27], 418 (45) [M+ − C8H56N2O4 − 2 × C7H12], 404 (100) [M+ − C6H56N2O4 − C14H27 − C14H27], 391 (57) [M+ − C48H56N2O4 − 2 × C14H27]. HRMS (C100H116N4O8): Calcd. 1500.8794, found 1500.8788.

2,9-Bis-(2,9-bis-(2,2,7,7-tetraethylct-4-en-8-yl)anthra[2,1,9-def,6,5,1 0-d’e’γ]diisoquinoline-1,3,8,10-tetraone)anthra[2,1,9-def6,5,10-d’e’γ]diisoq uinoline-1,3,8,10-tetraone[20]:2,9-Bis-(2-allyl-2-butylhexyl)anthra[2,1,9-def6,5,10-d’e’γ]diisoquinoline-1,3,8,10-tetraone (19, 100 mg, 133 µmol) under argon atmosphere was dissolved with warming in dry THF (125 mL), treated with second-generation Hoveyda-Grubbs catalyst (3, 13 mg, 20 µmol; 15 mol%), stirred at 60°C for 18 h (orange fluorescent mixture); stirred at room temperature for 31 h, concentrated in vacuum, precipitated with methanol, collected by vacuum filtration (D4 glass 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. Rf-value (silica gel; CHCl₃/EtOH 60:1) = 0.24. IR (ATR): ν = 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 (m), 1436.4 (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⁻¹ (w). UV/Vis (CHCl₃): λmax (E) = 467.4 (0.52) (sh.), 490.6 (1.00), 527.4 nm (0.78). Fluorescence (CHCl₃): λmax (I) = 529.8 (0.21), 637.0 nm (1.00). MS: (DEI +/70 eV): m/z (%): 1444 (9) [M+], 1265 (3) [M+ − C₁₃H₂₄], 1252 (3) [M+ − C₁₄H₂₆].

2,9-Bis-(2,2-dibutylhept-6-enyl)anthra[2,1,9-def;6,5,10-de’f’]diisoquinoline-1,3,8,10-tetraone (100 mg, 124 µmol) under argon atmosphere was dissolved in dry THF (150 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, 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, chloroform/ethanol 60:1) and purified by preparative TLC (silica gel, chloroform). Yield 67 mg (69%) dark red pigment, m.p. > 250˚C. Rf-value (silica gel; CHCl₃/EtOH 60:1) = 0.24. IR (ATR): ν = 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), 850.4 (w), 809.1 (m), 795.6 (w), 747.4 (m), 671.9 (w), 638.0 cm⁻¹ (w). UV/Vis (CHCl₃): λmax (E) = 467.4 (0.52) (sh.), 490.6 (1.00), 527.4 nm (0.78). Fluorescence (CHCl₃): λmax (I) = 529.8 (0.21), 637.0 nm (1.00). Fluorescence quantum yield (λexc = 493 nm, E₄⁹₃m/1 cm = 0.0100, reference: 2,9-Bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-de’f’]diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 0.75. MS: (DEI’/70 eV): m/z (%): 1557 (5) [M+], 543 (5) [M’ − C₇H₄N₂O₂], 529 (6) [M’ − C₇H₄N₂O₂].

2-But-3-enyl-2-hexyloctyl-9-(2-but-3-enyl-2-hexyloctyl-9-(2,2,9,9-tetabutyl-dedec-6-en-10-yl)anthra[2,1,9-def;6,5,10-de’f’]diisoquinoline-1,3,8,10-tetraone(2): 9-Bis-(2-but-3-enyl-2-hexyloctyl)anthra[2,1,9-def;6,5,10-de’f’]diisoquinoline-1,3,8,10-tetraone (1, 80 mg, 100 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). Yield: 28 mg (26%) dark red pigment, m.p. > 250°C. Rf-value (silica gel; CHCl₃/EtOH 60:1) = 0.25. IR (ATR): ν = 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), 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⁻¹ (w). UV/Vis (CHCl₃): λmax (E) = 467.4 (0.52) (sh.), 490.6 (1.00), 527.4 nm (0.78). Fluorescence (CHCl₃): λmax (I) = 529.8 (0.21), 637.0 nm (1.00). Fluorescence quantum yield (λexc = 493 nm, E₄⁹₃m/1 cm = 0.0100, reference: 2,9-Bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-de’f’]diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [40]): 0.75. MS: (DEI’/70 eV): m/z (%): 1557 (5) [M+], 543 (5) [M’ − C₇H₄N₂O₂], 529 (6) [M’ − C₇H₄N₂O₂].
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uinoline-1,3,8,10-tetraone\}-9-(2,2-dibutylhept-6-enyl)anthra[2,1,9-def6,5,10-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-tetrabutyldodec-6-en-12-yl]yl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone]anthra[2,1,9-def6,5,10-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 × 44 mm) and further by medium pressure chromatography (silica gel, chloroform, column 36 × 460 mm, 25 mL·min\(^{-1}\)). Yield 10 mg (10%) dark red pigment, m.p. > 250 ˚C. Rf-value (silica gel; CHCl\(_3\)/EtOH 10:1) = 0.54. IR (ATR): \(\nu = 3479.4\) (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\(^{-1}\) (w). UV/Vis (CHCl\(_3\)): \(\lambda_{\text{max}}\) (E) = 466.6 (0.44), 493.8 (1.00), 529.8 nm (0.84). Fluorescence (CHCl\(_3\)): \(\lambda_{\text{max}}\) (I) = 537.5 (0.70), 584.5 (0.77), 628.5 nm (1.00). MS: (DEI +/70 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\(_2\)O\(_5\)], 432 (58) [C\(_{26}\)H\(_{12}\)N\(_2\)O\(_5\)], 404 (100) [C\(_{25}\)H\(_{10}\)N\(_2\)O\(_4\)], 390 (88) [C\(_{24}\)H\(_{8}\)N\(_2\)O\(_4\)].

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-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (15) and 2-(1,4-but-2-en-diyl)-9-(1,12-(2,2,11,11-tetrabutyldodec-6-en-diyl)bis-anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (16): 2-Allyl-9-(2,2-dibutyl-hept-6-enyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraione (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-tetrabutyldodec-6-en-12-yl]yl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone]anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-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. R\(_f\)-value (silica gel; CHCl\(_3\)/EtOH 20:1) = 0.46. UV/Vis (CHCl\(_3\)): \(\lambda_{\text{max}}\) (E) = 492.2 (1.00), 528.8 nm (0.80). Fluorescence (CHCl\(_3\)): \(\lambda_{\text{max}}\) (I) = 534.5 (0.31), 628.0 nm (1.00). Fluorescence quantum yield (\(\lambda_{\text{exc}}\) = 491 nm, \(E_{\text{abs}}/\text{cm}\) = 0.0126 cm\(^{-1}\), reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def6,5,10-d'e'f']diisoquinoline-1,3,8,10-
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tetraone (1) with Φ = 1.00 [40]): 0.69. MS: (DEI+/70 eV): m/z (%): 1220 (<1) [M'], 1182 (<1) [M' − C6H6], 1138 (<1) [M' − 2 x C6H5], 443 (18) [C29H16N2O4], 404 (85) [M' − C25H12N2O4], 391 (100) [C24H10N2O4]. 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-def'de'f']diisoquinoline-1,3,8,10-tetraone): Yield 5 mg (5%) dark red powder.

\[ R_f \text{-value (silica gel; CHCl}_3/EtOH \ 20:1) = 0.29. \]

UV/Vis (CHCl3): \( \lambda_{max} (E) = 492.0 \) (1.00), 528.8 nm (0.78). Fluorescence (CHCl3): \( \lambda_{max} (I) = 535.0 \) (0.36), 630.5 nm (1.00). Fluorescence quantum yield (\( \lambda_{exc} = 491 \) nm, \( E_{491nm/1cm} = 0.0154 \) cm\(^{-1}\)), reference: 2,9-bis-(1-hexylheptyl)anthra-[2,1,9-def,5,10-\( d'e'f' \)]diisoquinoline-1,3,8,10-tetraone (1) with Φ = 1.00 [13]): 0.88. MS: (DEI+/70 eV): m/z (%): 1220 (1) [M'], 1138 (1) [M' − 2 x C6H5], 443 (20) [C29H16N2O4], 404 (82) [M' − C25H12N2O4], 391 (100) [C24H10N2O4].

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**Conflicts of Interest**

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

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