Synthesis and Characterization of Soluble Oligo(9,10-anthrylene)s

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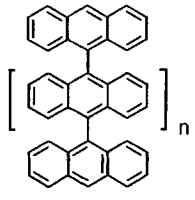
A homologous series of oligo(9,10-anthrylene)s up to the heptamer have been synthesized by reductive coupling of quinones with lithioanthrylenes, followed by reductive aromatization of the intermediate hydroxy species. The method used allows the introduction of different alkyl substituents, which ensure sufficient solubility of the newly synthesized anthrylene systems in common organic solvents. The solid-state conformations of trimers **4** and **5** have been established by X-ray structure analysis; UV/Vis-spectroscopic investigations in solution reveal the anthracene moieties in 9,10-anthrylenes to exist as electronically independent electrophores. The trianthrylenes can be subjected to electrophilic substitution which regioselectively provides e.g. 10-bromo- and 10,10″-dibromo derivatives. These bromides can easily be converted into the corresponding cyano compounds. Under the influence of potassium hydroxide in quinoline the trimer **5** partially cyclizes to helianthrene compounds.

A major challenge to organic synthesis is the design of materials with active physical functions. With respect to optical and electronic applications biaryls, oligoarylenes and polyarylenes serve as important electrophores and chromophores[1,2]. Their properties depend sensitively upon inter-ring conjugation. Sufficient conjugative interaction is expected to create a single extended π-system with drastically lowered HOMO-LUMO energy gap, while interruption of conjugation by strong steric hindrance leads to electronically decoupled π-subunits[3,4]. In dealing with charge-transport purposes, a favorable π-conjugation between monomeric subunits in the neutral or partially charged states is important, which is thought to be connected with decreasing band-gap energies, while for charge storage a conjugation barrier with nearly independent redox-active building blocks is favored[5,6].

On the other hand, "uncoupling" of electrons in π-conjugated compounds also occurs in organic high-spin systems[7], which play a central role in the search for organic ferromagnets[8], and, furthermore, in fluorescence materials with their optical attributes based on photoinduced adiabatic charge-separation mechanisms[9,10].

In this context, oligo(9,10-anthrylene)s **1** seem to be especially promising candidates, because they should combine an almost perpendicular ground-state conformation with good donor and acceptor properties of the individual subunits. In spite of the thoroughly investigated optical and electronic behavior of the well-known prototype 9,9′-bianthryl (**2**)[11,12,13], higher oligo(9,10-anthrylene)s (**1**, $n > 0$) have not been studied, due to their structural irregularity and insolubility in organic solvents.



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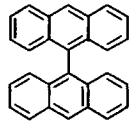

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With respect to these severe shortcomings, we report herein on the synthesis and structural analysis of defined monodisperse oligomers up to the heptamer. Physical investigations of the novel oligo(9,10-anthrylene)s described in this paper are restricted to the structural characterization of the compounds, detailed spectroscopic studies of charged and photoexcited derivatives will be reported elsewhere[14–17]. The introduction of different alkyl substituents is facile and leads to a significant increase in solubility. As a consequence, regioselective derivatization reactions of the new anthrylene systems become possible providing substitution patterns particularly suited for optical and electronic applications.

Results and Discussion

1. Synthesis of Alkyl-Substituted Trimers 3, 4, 5 and Tetramers 12, 13

The anthraquinones **6a** and **6b** (substituted in the 2-, 3- or 2-, 6-positions), which can easily be prepared on a large scale by known procedures[18], serve as starting materials for the synthesis of soluble trianthrylenes **3** and **4**. Thus, treatment of the 9-bromoanthracenes **7a** and **9b** with *n*-butyllithium leads to the corresponding lithioanthracenes **7b** and **9c** which, in turn, are allowed to react with the substituted anthraquinones **6a** and **6b** under inert conditions to yield the coupling products **10a** and **10b**, respectively. These diols are then treated with hydrogen iodide and hypophosphorous acid in glacial acetic acid at 80°C to afford the novel trianthrylenes **3** and **4** after chromatography on silica gel in 60 and 66% yield. The resulting hexa-*tert*-butyl-substituted trianthrylene **4** exists as a mixture of two atropisomers **4a/4b** (Figure 1), due to the sterically hindered rotation of the anthracene subunits about the formal single

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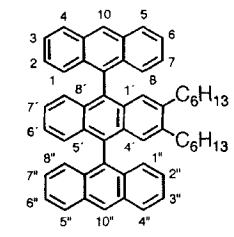

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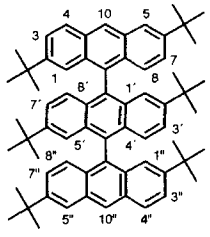

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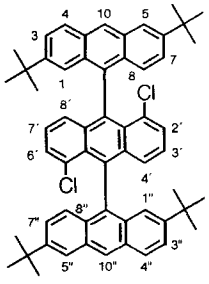

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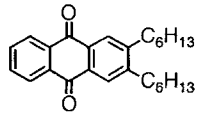
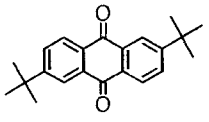
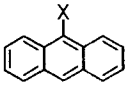


6a

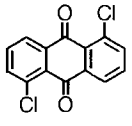


6b

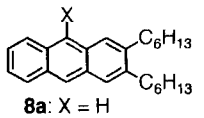


7a: X = Br

7b: X = Li



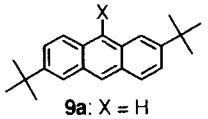
6c



8a: X = H

8b: X = Br

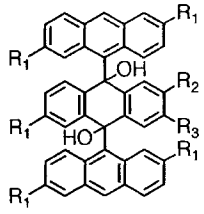
8c: X = Li



9a: X = H

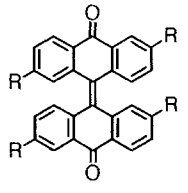
9b: X = Br

9c: X = Li



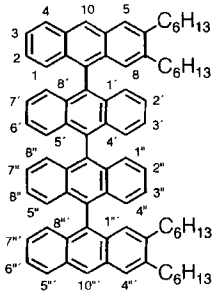
10a: R_1 = H, R_2 = R_3 = C_6H_{13}

10b: R_1 = R_2 = $C(CH_3)_3$, R_3 = H



11a: R = H

11b: R = $C(CH_3)_3$



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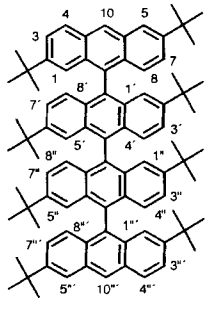


13

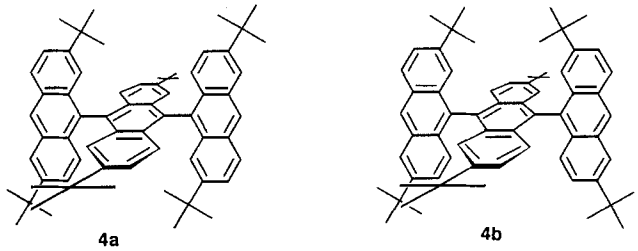
bonds (C9–C9′, C9″–C10′). This is nicely reflected in the ^{1}H- and ^{13}C-NMR spectra of **4**, which show a superposition of NMR signals of the two isomers **4a/4b** in a 3:1 ratio. The formation of the isomers of **4** is also evidenced by two product spots in the TLC (thin-layer chromatography).

By chromatography on silica gel the preferentially formed atropisomer **4a** can be separated in small quantities for spectroscopic studies, whereby the isomeric purity is confirmed by the simple splitting pattern and the number of resonance signals in the NMR spectra (^{1}H, ^{13}C). Additionally, the structure of isolated **4a** is confirmed by X-ray crystal-structure analysis. In contrast to **4**, trimer **3** does not show the presence of atropisomers, due to its higher symmetry (C_{2v} molecular symmetry) caused by the different substitution pattern.

The preparation of the 1′,5′-dichloro-substituted trimer **5** is achieved by coupling the anthraquinone **6c** with two equivalents of lithioanthracene **9c** followed by reductive aromatization (hydrogen iodide/hypophosphorous acid) and chromatographic purification (yield: 45%). Although considerable amounts of dehalogenated and monocoupled products are isolated from the reaction mixture, it must be mentioned, that the demonstrated synthetic route is a surprisingly simple way to introduce bulky chloro substituents into the inner *peri*-positions of 9,10-anthrylenes. This allows a one-step cyclization of **5** to highly condensed aromatic systems with bathochromically shifted longest wavelength absorptions.

Our synthetic route towards higher oligo(9,10-anthrylene)s requires suitable lithioanthrylene and quinoide compounds for coupling reactions. Thus, for the synthesis of tetramers **12** and **13**, the bianthronylidenes **11a/b** were used instead of anthraquinone derivatives. Consequently, reaction of **11a/b** with lithium compounds **8c** and **9c** in ether under an inert atmosphere, accomplished by treatment of the coupling products with HI/H_3PO_2 provided after column chromatography and recrystallization the pure tetraanthrylenes **12** and **13** in 31 and 55% yield, respectively.

In the case of compound **13** hindered rotation about the inter-ring bonds results in atropisomerism. The existence of diastereomers is firmly established by the appearance of three product spots in the TLC. Additonally, the presence of different atropisomers can be detected in the ^{1}H- and ^{13}C-NMR spectra of **13**, whereby the ^{1}H-NMR signals of the *tert*-butyl groups and the ^{13}C-NMR signals of both aliphatic and aromatic carbon atoms are split. Although hindered rotation of anthracene subunits can be suspected for



4a 4b

Figure 1. Atropisomers of trianthrylene **4**

tetramer **12**, only one isomer is found, due to symmetry arguments caused by the special substitution pattern.

In contrast to the above synthetic route, both Ni(0)- and Pd(0)-induced coupling reactions fail to couple anthrylenes at the 9-, 10-positions, which is obviously due to the strong steric shielding of the reaction centers by the protons in the 1-, 4-, 5-, 8-positions[19]. Thus, for instance, the palladium-catalyzed reaction of (10-bromo-2,6-di-*tert*-butyl-9-anthryl)boronic acid only affords dimeric products at an insufficient rate of conversion[20].

2. X-ray Structure Analysis of 4a and 5

The solid-state structures of the trianthrylenes **4a** and **5** were investigated in order to identify the major atropisomer **4a** formed in the synthesis of **4** and to study the dihedral angle between anthryl groups together with the bond length of the inter-ring C9–C9′, C10′–9″ bonds (for an assignment of carbon centers see **4** and **5**). These two structural features qualitatively describe the extent of the π-conjugation between anthracene units within the molecules **4a** and **5** in the solid state.

The triclinic unit cell of **4a** turned out to consist of one molecule of **4a** located at a center of inversion and two molecules of tetrachloroethane (Figure 2). The anthracene subunits are planar within the limits of error, and the bond length of the central C9–C9′ (C10′–C9″) bond [1.50(1) Å] corresponds to that of a single bond, indicating negligible π–π-inter-ring conjugation between the subunits. The dihedral angle between the central anthracene system and its neighbors (74.5°) also demonstrates an electronic decoupling of the anthracene rings in **4a**. Obviously, due to the four-fold steric hindrance between neighbored anthracene rings caused by the protons in the inner *peri*-positions the molecule is forced into a ground state with non-interacting π-units.

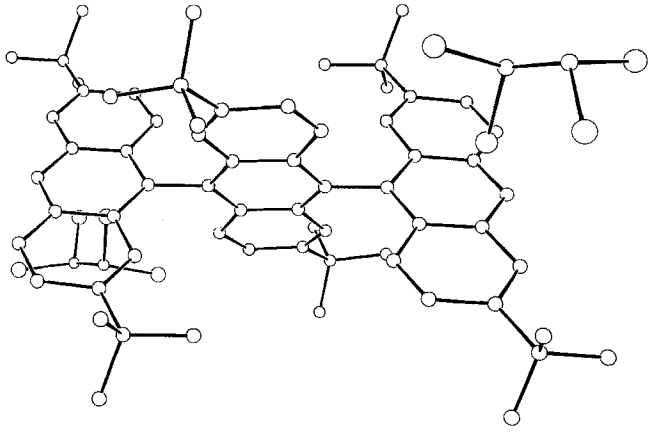


Figure 2. Crystal structure of **4a**

An ORTEP drawing of the structure determined for a yellow-green single crystal of **5** is presented in Figure 3. In contrast to trianthrylene **4a**, the dichloro derivative **5** looses its center of inversion in the solid-state structure. The dihedral angle between the central and terminal anthracene

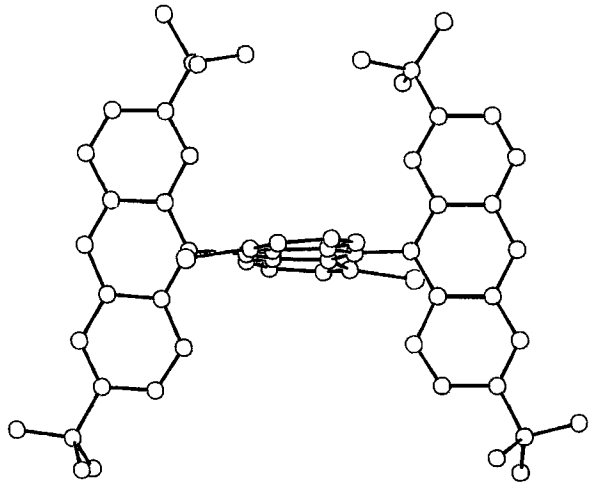


Figure 3. Crystal structure of **5**; for clearity, only one of the two conformations of the disordered *tert*-butyl group is shown

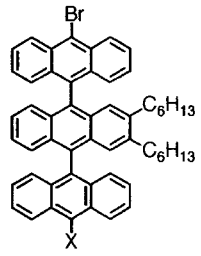
perimeters are 81.5 and 82.7°, respectively. Furthermore, the central anthracene system becomes non-planar, due to the increase in steric hindrance induced by the bulky chloro substituents. The lengths of the bonds connecting the anthracene moieties [C9–C9′: 1.51(1) Å; C10′–C9″: 1.50(1) Å] correspond to that of a typical single bond as in the case of **4a**.

The dihedral angles and bond lengths of central single bonds found in this work are in accordance with those observed for the structure of unsubstituted "dimer" **2**. Becker et al. determined the dihedral angle between the anthracene rings for two crystallographic independent molecules of **2** within the unit cell as 74.65 and 81.5°, respectively[21]. A larger interplanar angle in **2** of 85.5° is reported from a structural analysis of a 9,9′-bianthryl/benzene crystal[22]. Thus, all solid-state structures point to a decoupling of anthracene perimeters in bis- and tris(electrophoric) 9,10-anthrylene systems. The minor difference in the values of inter-ring torsional angles is most probably due to packing effects.

3. Derivatization of Trianthrylene 3

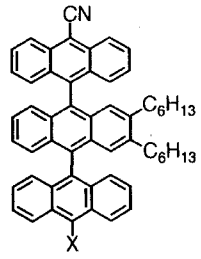
A particularly useful transformation of trianthrylene **3** is bromination, which opens a simple route to the corresponding cyano derivatives and higher homologues of **1**.

Thus, trimer **3** can be regioselectively converted into its 10-mono- and 10,10″-dibromo derivatives **14** and **15** by treating a solution of **3** in CCl_4 at 0°C with one or two equivalents of bromine, respectively (yield after repetitive column chromatography: **14**: 41%; **15**: 59%). The high regioselectivity of the electrophilic reaction must be attributed to the high AO coefficient at centers 9 and 10 of the anthracene frontier orbital[23]. Nevertheless, the use of a large excess of bromine and high reaction temperatures should be avoided, since bromination of the central anthracene moiety to a tribromo derivative of **3** takes place. It should also be mentioned, that the commonly used bromination of anthracene with *N*-bromosuccinimide is less efficient for regioselective mono- and dibromination of **3**.



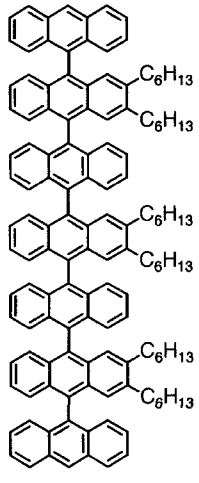
14: X = H

15: X = Br



16: X = H

17: X = CN



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For the synthesis of acceptor-substituted trianthrylenes the mono- and dibromo compounds **14**, **15** were allowed to react with CuCN in dimethylformamide, and the mono- and dicyano derivatives **16**, **17** were isolated by column chromatography in 70 and 40% yield, respectively.

In order to prepare higher oligo(9,10-anthrylene)s, monobromotrianthrylene **14** was quantitatively converted into the corresponding lithio species and then coupled with anthraquinone **6a** to yield compound **18**, in which seven anthracene subunits are connected at their 9-, 10-positions. The reaction sequence is, thus, analogous to one used in trimer synthesis. Remarkably enough, the soluble heptamer **18** can be isolated by size-exclusion chromatography in 18% yield. The ^{1}H-NMR spectrum of **18** is very complex: the signals in the aromatic region at δ = 7.50–7.00 and those in the aliphatic region (δ = 1.30–0.70) appear broad and unstructured, due to the formation of different atropisomers. Nevertheless, according to FD mass-spectroscopic, chromatographic and analytical data the isolated product can reliably be assigned to the pure heptamer **18**.

The results of electron-absorption-spectroscopic measurements on **2**–**4**, **12**, **13**, **18** and **19** in solution reveal only a small bathochromic shift of the longest wavelength band with increasing chain length (Table 1). This finding is consistent with the solid-state investigations of **4a** and **5** and excludes the possibility of significant conjugative interactions between subunits. Thus, the anthracene units in oligo(9,10-anthrylene)s seem to exist as essentially independent electrophors even in solution. The minor differences in λ_{max} values of anthrylenes **2**–**4** and **12**–**19** can be ascribed to the different substitution patterns.

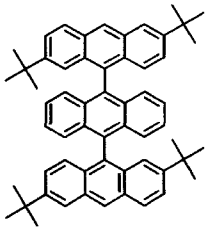
4. Cyclization of 5

Stimulated by Clar's work on benzo[*a*]perylene[24] we treated trimer **5** with KOH in degassed quinoline in order to attain higher fused aromatic systems. In the course of the reaction compound **5** transforms into trianthrylene **19** and soluble helianthrene derivative **20**[25] with elimination of the chloro substituents. Chromatographic purification under inert conditions results in a 30% yield of **19** and in a 60% yield of the new helianthrene **20**. As shown for the first time by Theilacker and Thomas[26] helianthrene and its derivatives cannot be planar in spite of the fact that all their carbon atoms are sp^2-hybridized. The hydrogen atoms at carbon atoms 11 and 12 cause a steric hindrance, which forces the two benzo rings out of the main plane of the aromatic system. Accordingly, helianthrene is dissymmetric and exists in two enantiomeric forms. In the case of derivative **20**, the 2,6-di-*tert*-butyl-9-anthryl substitution in the 7-position of the helianthrene framework offers the possibility of further atropisomerism. Not surprisingly therefore, the NMR spectra (^{1}H, ^{13}C) of **20** are very complex. The results of mass spectrometry, elemental analysis and chromatographic methods (GPC, HPLC, TLC), however, leave no doubt as to the structure and purity of **20**. Consequently, neither the large angle between the anthracene moieties in **5** nor the bulky *tert*-butyl substituents prevent the ring-closure reaction. The cyclization of **5** to yield **20** is further reflected by the helianthrene-type UV/Vis spectrum, which shows a longest wavelength absorption containing four resolved vibronical bands with a maximum of absorption at λ = 583 nm ($CHCl_3$, 293 K)[27]. In addition to the bands of parent helianthrene a weak vibronical band at λ_{max} = 620 nm appears in the longest wavelength transition of **20**, which can be attributed to the influence of the alkyl and anthryl substitution of the helianthrene chromophore in **20**.

Table 1. λ_{max} values [nm] and ε values [10^{-3} l × mol^{-1} × cm^{-1}] from optical absorption spectra of anthrylenes **2**–**4**, **12**–**19**[a]

	2	**3**	**4**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
λ_{max}	391	403	402	406	408	408	409	413	414	406	403
ε	24	27	25	43	42	27	34	28	30	49	26

[a] All spectra measured in dichloromethane solution (T = 293 K).



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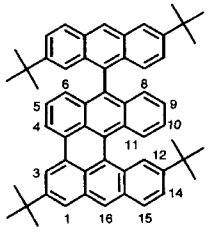

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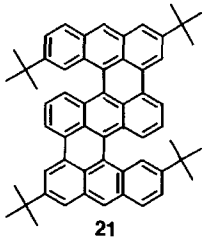

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A twofold ring closure of **5** to the previously unknown compound **21** can also be suspected under the prevailing experimental conditions, since the UV/Vis spectra of the crude product mixture of the cyclization exhibit absorptions at λ = 720–760 nm along with the detection of a peak at *m/z* = 750.2 [M^+] in the FD mass spectra. The isolation of **21**, however, was not possible due to the extremely high affinity of the compound to oxygen and the very poor yield obtained in the reaction. This has led to the conclusion that, in comparison with the second cyclization step of **5** yielding **21**, a dehalogenation resulting in compound **20** is preferred under the present experimental conditions. Nevertheless, the described cyclization reaction is an outstanding one-step route for the preparation of novel helianthrene derivatives in good yields. This route is superior to the known multistep synthesis, which implies drastic conditions[28], and also allows a ready introduction of solubilizing alkyl groups.

Experimental

^{1}H and ^{13}C NMR: Varian Gemini 200, chemical shifts are reported relative to TMS as internal standard (^{13}C NMR: abbreviations used: q = quaternary, t = tertiary, s = secondary, p = primary). – MS (EI): Varian CH7A or VG Trio 2000; (FD): Finnigan MAT 95. – IR: Nicolet 320 FT-IR. – UV/Vis: Perkin-Elmer Lambda 9. – Column chromatography: Glass columns packed with silica gel (Merck Geduran Si 60, 70–230 mesh) or aluminum oxide (Merck Geduran AI 90) with the eluants specified below. – Elemental analyses: Department of Chemistry and Pharmacy at the University of Mainz. – Thin-layer chromatography (TLC): Ready-to-use plates with silica gel 60 F_{254} (Merck). – Melting points (uncorrected): Büchi melting-point apparatus.

1,5-Dichloroanthraquinone (**6c**), *9-bromoanthracene* (**7a**) and *9,9'-bianthronylidene* (**11a**) were purchased from Aldrich and used without further purification. *9,9'-Bianthryl* (**2**)[29], *2,3-dihexylanthraquinone* (**6a**)[18], *2,6-di-tert-butylanthracene* (**9a**)[30], *2,6-di-tert-butylanthraquinone* (**6b**)[18] and *2,2',6,6'-tetra-tert-butyl-9,9'-bianthronylidene* (**11b**)[18] were prepared according to procedures previously described. All new compounds were fully characterized.

2,3-Dihexylanthracene (**8a**): A suspension of aluminum powder (5.1 g, 0.189 mol), mercury chloride (5 mg), CCl_4 (1 ml) in 120 ml of cyclohexanol was refluxed for 3 h. To the heated mixture was then added in small portions anthraquinone **6a** (11.6 g, 0.031 mol), and the suspension was refluxed for further 96 h. After cooling to room temperature, the reaction mixture was treated with 200 ml of 2 N HCl and 500 ml of dichloromethane. The organic phase was washed repeatedly with 2 N HCl and water, dried ($MgSO_4$), and the solvent removed. Column chromatography of the residue on silica gel (mobile phase: CH_2Cl_2) and recrystallization from dichloromethane/methanol (1:1) gave pure **8a**, m.p. 92°C; yield 7.7 g (74%). – ^{1}H NMR ($CDCl_3$): δ = 8.33 (s, 2H; 9-, 10-H), 8.01–7.96 (m, 2H; 5-, 8-H), 7.78 (s, 2H; 1-, 4-H), 7.46–7.41 (m, 2H; 6-, 7-H), 2.83 (t, *J* = 7.7 Hz, 4H; benzylic CH_2), 1.78–1.30 (m, 16H; CH_2), 0.96 (t, *J* = 6.9 Hz, 6H; CH_3). – MS (70 eV): *m/z* (%) = 347 (29) [M^+ + 1], 346 (100) [M^+]. – $C_{26}H_{34}$ (346.6): calcd. C 90.11, H 9.89; found C 89.87, H 9.97.

9-Bromo-2,3-dihexylanthracene (**8b**): A suspension of **8a** (0.77 g, 0.0022 mol), *N*-bromosuccinimide (0.4 g, 0.0022 mol) and anhydrous iron(III) chloride (3 mg) in 150 ml of CCl_4 was refluxed for 4 h. After cooling to room temperature, the succinimide was separated, the filtrate concentrated and the residue poured into 150 ml of methanol. The crude product was filtered and purified by subsequent recrystallization from ethanol; m.p. 128°C; yield 1.3 g (76%). – ^{1}H NMR ($CDCl_3$): δ = 8.53–8.48 (m, 1H; 8-H), 8.53 (s, 1H; 10-H), 8.26 (s, 1H; 1-H), 7.98–7.94 (m, 1H; 5-H), 7.85 (s, 1H; 4-H), 7.59–7.41 (m, 2H; 6-, 7-H), 2.95–2.76 (m, 4H; benzylic CH_2), 1.86–1.65 (m, 4H; CH_2), 1.55–1.34 (m, 12H; CH_2), 1.01–0.87 (m, 6H; CH_3). – MS (70 eV): *m/z* (%) = 425 (90) [M^+ + 1], 424 (33) [M^+], 423 (100) [M^+ – 1]. – $C_{26}H_{33}Br$ (425.5): calcd. C 73.40, H 7.82, Br 18.78; found C 73.61, H 7.93, Br 18.59.

9-Bromo-2,6-di-tertbutylanthracene (**9b**): Compound **9a** (25 g, 0.086 mol) was dissolved in CCl_4 (700 ml). Additionally, a catalytic amount of anhydrous iron(III) was added. To the heated suspension was then added *N*-bromosuccinimide (15.33 g, 0.086 mol) in small portions, and the mixture was refluxed for further 3 h. After cooling to room temperature, the succinimide was filtered off, the solution concentrated and the residue poured into 300 ml of methanol. The precipitate was recrystallized from ethanol to give 25 g (78%) of pure **9b**; m.p. 139°C. – ^{1}H NMR ($CDCl_3$): δ = 1.47 [s, 9H, $C(CH_3)_3$], 1.50 [s, 9H, $C(CH_3)_3$], 7.57 (dd, *J* = 9.09, 1.85 Hz, 1H; 3-H), 7.67 (dd, *J* = 9.41, 1.69 Hz, 1H, 7-H), 7.85 (d, *J* = 1.69 Hz, 1H; 5-H), 7.90 (d, *J* = 9.09 Hz, 1H; 4-H), 8.33 (s, 1H; 10-H), 8.40 (d, *J* = 1.85 Hz, 1H; 1-H), 8.43 (d, *J* = 9.41 Hz, 1H; 8-H). – ^{13}C NMR ($CDCl_3$): δ = 30.9 [p, $C(CH_3)_3$], 34.8 [q, $C(CH_3)_3$], 35.4 [q, $C(CH_3)_3$], 121.8 (t), 122.7 (t), 125.0 (t), 126.2 (t), 126.6 (t), 126.7 (t), 127.3 (t), 128.2 (t), 129.3 (q), 130.1 (q), 130.9 (q), 132.0 (q), 147.6, 149.4 (q; C-2, -6). – MS (70 eV): *m/z* (%) = 370 (99) [M^+ + 1], 369 (29) [M^+], 368 (100) [M^+ – 1], 353 (82) [M^+ – CH_3], 57 (18) [$C(CH_3)_3^+$]. – $C_{22}H_{25}Br$ (369.3): calcd. C 71.54, H 6.82, Br 21.64; found C 71.47, H 6.94, Br 21.51.

2',3'-Dihexyl-9,10-trianthrylene (**3**): To a suspension of **7a** (15.42 g, 0.06 mol) in absolute diethyl ether (400 ml) at 0°C was added 41.6 ml of *n*-butyllithium (1.6 M in hexane). After stirring the mixture for 15 min at 0°C, a solution of **6a** (7.56 g, 0.02 mol) in absolute diethyl ether (100 ml) was added dropwise. The mixture was stirred for 72 h, then the reaction was quenched with 10 ml of acetic acid and the ether removed. The residue was dissolved in acetic acid (300 ml) under argon. Finally, 40 ml of H_3PO_2 (aqueous solution, 50%) and 5 ml of HI (aqueous solution, 57%) were added. The reaction mixture was kept at 80°C for 2 h. After cooling to room temperature, the yellow precipitate was filtered off and purified by column chromatography [petroleum ether/dichloromethane (5:1)] to afford 8.3 g (60%) of **3**; m.p. 248°C. – ^{1}H NMR ($C_2D_2Cl_4$): δ = 8.74 (s, 2H; 10'-, 10''-H), 8.26–8.18 (m, 4H; 4-, 5-, 4''-, 5''-H), 7.56–7.50 (m, 4H; 3-, 6-, 3''-, 6''-H), 7.46–7.24 (m, 8H, 1-, 2-, 7-, 8-, 1''-, 2''-, 7''-, 8''-H), 7.22–7.00 (m, 4H; 5'-, 6'-, 7'-, 8'-H), 6.95 (s, 2H; 1'-, 4'-H), 2.35 (t, *J* = 7.8 Hz, 4H; benzylic CH_2), 1.25–0.80 (m, 16H; CH_2), 0.71 (t, *J* = 6.3 Hz, 6H; CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.3 (C-2', 3'), 134.4 (q), 133.0 (q), 132.3 (q), 132.2 (q), 131.6 (q), 131.2 (q), 129.1 (t), 127.7 (t), 127.6 (t), 126.3 (t), 126.2 (t), 125.8 (t), 125.6 (t), 33.0 (CH_2), 31.9 (CH_2), 30.7 (CH_2), 29.2 (CH_2), 22.9 (CH_2), 14.5 (CH_3). – MS (70 eV): *m/z* (%) = 698 (100) [M^+], 329 (87) [M^+ – 2 anthryl – CH_3], 177 (43) [anthryl$^+$]. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3053, 2961, 2935, 2926, 2918, 1457, 1441, 1310, 1012, 922, 884, 846, 786, 742, 720, 608, 546. – UV/Vis (CH_2Cl_2): λ_{max} = 403 nm. – $C_{54}H_{50}$ (699.0): calcd. C 92.79, H 7.21; found C 92.67, H 7.30.

2,2',2'',6,6',6''-Hexa-tert-butyl-9,10-trianthrylene (**4**): A solution of **6b** (4.2 g, 0.0132 mol) in absolute diethyl ether (200 ml), a suspension of **9b** (10 g, 0.026 mol) in absolute diethyl ether (100 ml), 16.5 ml (0.026 mol) of *n*-butyllithium (1.6 M in hexane), 10 ml of acetic acid and a mixture of 30 ml of H_3PO_2 (aqueous solution,

50%), 2 ml of HI (aqueous solution, 57%) and acetic acid (250 ml) were allowed to react as described for **3**. The crude product was then purified by recrystallization from ethanol and column chromatography on silica gel [petroleum ether/dichloromethane (10:1)] to give 3.9 g (66%) of **4** (two atropisomers); m.p. 280°C (dec.). By further chromatography on silica gel [petroleum ether/dichloromethane (20:1)] one atropisomer of **4** (**4a**) could be separated in small quantities for spectroscopic studies. – ^{1}H NMR ($CDCl_3$, atropisomer **4a**): δ = 0.96 [s, 18H; $C(CH_3)_3$], 1.15 [s, 18H; $C(CH_3)_3$], 1.49 [s, 18H; $C(CH_3)_3$], 7.17–7.32 (m, 12H; aromatic), 7.61 (dd, *J* = 8.9 Hz, 1.4 Hz, 2H; 3-, 3″-H), 8.08 (d, *J* = 1.4 Hz, 2H; 5-, 5″-H), 8.13 (d, *J* = 8.9 Hz, 2H; 4-, 4″-H), 8.64 (s, 2H; 10-, 10″-H). – ^{13}C NMR ($CDCl_3$, mixture of 2 atropisomers): δ = 30.5 [p; $C(CH_3)_3$], 30.6 [p; $C(CH_3)_3$], 30.8 [p; $C(CH_3)_3$], 30.9 [p; $C(CH_3)_3$], 34.5 [q; $C(CH_3)_3$], 34.7 [q; $C(CH_3)_3$], 34.8 [q; $C(CH_3)_3$], 121.6 (t), 122.4 (t), 122.6 (t), 124.3 (t), 124.4 (t), 124.9 (t), 125.1 (t), 126.1 (t), 126.2 (t), 126.9 (t), 127.1 (t), 128.0 (t), 128.1 (t), 130.0 (q), 130.2 (q), 130.3 (q), 130.4 (q), 130.6 (q), 130.8 (q), 130.9 (q), 131.2 (q), 131.4 (q), 132.8 (q), 133.0 (q), 146.7, 146.8, 146.9, 147.1, 147.2 (q; C-2, -2′, -2″, -6, -6′, -6″). – FD MS: *m/z* (%) = 870 (11) [M^+ + 2], 869 (41) [M^+ + 1], 868 (79) [M^+], 867 (100) [M^+ – 1]. – IR (KBr): ṽ = 3045–2868 cm^{-1}, 1631, 1480, 1459, 1363, 1253, 894, 819, 813, 582. – UV/Vis (CH_2Cl_2): λ_{max} = 402 nm. – $C_{66}H_{74}$ (867.3): calcd. C 91.40, H 8.60; found C 91.51, H 8.67.

1′,5′-Dichloro-2,2″,6,6″-tetra-tert-butyl-9,10-trianthrylene (**5**): A solution of **9b** (1 g, 0.0026 mol) in absolute diethyl ether, 1.66 ml of *n*-butyllithium (1.6 M in hexane) and a suspension of **6c** (386 mg, 0.0013 mol) in 50 ml of absolute diethyl ether were allowed to react as described for compound **3**. After a 48-h reaction time, the reaction was quenched with 20 ml of acetic acid, and the ether was removed from the reaction mixture. The residue was dissolved in 100 ml of acetic acid, the solution treated with 10 ml of H_3PO_2 (aqueous solution, 50%) and 1 ml of HI (aqueous solution, 57%), kept for 3 h at 80°C and finally cooled to 5°C. The yellow precipitate was purified by column chromatography on silica gel [mobile phase: petroleum ether/dichloromethane (5:1)] to afford 480 mg (45%) of **5**; m.p. 290°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 8.64 (s, 2H; 10-, 10′-H), 8.13 (d, *J* = 9.1 Hz, 2H; 4-, 4″-H), 8.06 (d, *J* = 1.5 Hz, 2H; 5-, 5″-H), 7.62 (dd, *J* = 9.1 Hz, 1.5 Hz, 2H; 3-, 3″-H), 7.41 (dd, *J* = 9.1 Hz, 1.5 Hz, 2H; 7-, 7″-H), 7.36–7.27, 7.01–6.90 (2 × m, 8H; 1-, 1″-, 2′-, 3′-, 4′-, 6′-, 7′-, 8′-H), 7.14 (d, *J* = 9.1 Hz, 2H; 8-, 8″-H), 1.13 [s, 18H; $C(CH_3)_3$], 0.96 [s, 18H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 148.3, 147.5, 135.1, 134.9, 134.8, 132.9, 131.8, 131.7, 131.6, 130.6, 130.2, 129.1, 128.8, 128.6, 127.0, 126.7, 125.9, 125.6, 124.9, 123.2, 121.5, 35.3 [$C(CH_3)_3$], 35.2 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$], 31.4 [$C(CH_3)_3$]. – FD MS: *m/z* (%) = 822 (100) [M^+], 823 (65) [M^+ + 1], 824 (85) [M^+ + 2], 825 (46), [M^+ + 3]. – $C_{58}H_{56}Cl_2$ (824.0): calcd. C 84.54, H 6.85, Cl 8.61; found C 84.67, H 6.96, Cl 8.42.

2,2‴,3,3‴-Tetrahexyl-9,10-tetraanthrylene (**12**): To a solution of **8b** (0.75 g, 2.0 × 10^{-3} mol) in absolute diethyl ether (100 ml) at 0°C under argon was added 1.15 ml of *n*-butyllithium (1.6 M in hexane). The mixture was stirred for 15 min, and then a suspension of **11a** (353 mg, 9.2 × 10^{-4} mol) in absolute diethyl ether (100 ml) was added dropwise. After stirring for 24 h, the reaction was quenched with 10 ml of glacial acetic acid and the ether removed. The residue was dissolved in acetic acid (100 ml), the solution treated with 10 ml of H_3PO_2 (aqueous solution, 50%) and 1.5 ml of HI (aqueous solution, 57%), kept for 2 h at 80°C and finally cooled to room temperature. The yellow precipitate was purified by recrystallization from dichloromethane/hexane (1:1) and chromatography on silica gel [petroleum ether/dichloromethane (5:1)]; yield 260 mg (31%) of **12**. – ^{1}H NMR ($C_2D_2Cl_4$): δ = 8.67 (s, 2H; 10-, 10‴-H), 8.21 (m, 2H; 5-, 5‴-H), 7.99 (s, 2H; 4-, 4‴-H), 7.60–7.15 (m, 22H; aromatic), 7.03 (s, 2H, 1-, 1‴-H), 2.83 (t, *J* = 7.2 Hz, 4H; benzylic CH_2), 2.61 (t, *J* = 7.02 Hz, 4H; benzylic CH_2), 1.80–0.94 (m, 38H; CH_2, CH_3), 0.67 (t, *J* = 5.8 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.3, 140.2 (q; C-2, -3), 135.0 (q), 134.4 (q), 132.6 (q), 132.2 (q), 132.1 (q), 132.0 (q), 131.9 (q), 131.8 (q), 131.5 (q), 129.1 (t), 128.0 (t), 127.9 (t), 127.8 (t), 127.5 (t), 127.4 (t), 127.3 (t), 126.6 (t), 126.4 (t), 126.3 (t), 126.2 (t), 126.1 (t), 126.0 (t), 125.7 (t), 125.4 (t), 33.4 (CH_2), 33.1 (CH_2), 32.4 (CH_2), 32.0 (CH_2), 31.2 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.1 (CH_2), 23.2 (CH_2), 22.9 (CH_2), 14.6 (CH_3), 14.4 (CH_3). – FD MS: *m/z* (%) = 1043 (100) [M^+], 1044 (82) [M^+ + 1], 1045 (36) [M^+ + 2]. – IR (KBr): ṽ = 3059 cm^{-1}, 2954, 2926, 2855, 1455, 1438, 1023, 901, 761, 742. – UV/Vis (CH_2Cl_2): λ_{max} = 406 nm. – $C_{80}H_{82}$ (1043.5): calcd. C 92.08, H 7.92; found C 92.29, H 7.81.

2,2′,2″,2‴,6,6′,6″,6‴-Octa-tert-butyl-9,10-tetraanthrylene (**13**): A solution of **9b** (2.44 g, 0.0066 mol) in absolute *tert*-butyl methyl ether, 14.1 ml of *n*-butyllithium (1.6 M in hexane), a solution of **11b** (2 g, 0.0033 mol) in absolute *tert*-butyl methyl ether, 10 ml of acetic acid and a mixture of acetic acid (200 ml), H_3PO_2 (10 ml, aqueous solution, 50%) and HI (0.5 ml, aqueous solution, 57%) were allowed to react as described for compound **12**. The yellow precipitate was purified by recrystallization from acetic anhydride; yield: 2.1 g (55%) of **13** (3 atropisomers); m.p. 290°C. – ^{1}H NMR ($CDCl_3$): δ = 1.09 [s, 12H; $C(CH_3)_3$], 1.13 [s, 12H; $C(CH_3)_3$], 1.18 [s, 12H; $C(CH_3)_3$], 1.21 [s, 12H; $C(CH_3)_3$], 1.26 [s, 12H; $C(CH_3)_3$, 1.57 [s, 12H; $C(CH_3)_3$], 7.32–7.58 (m, 18H; aromatic); 7.68 (d, *J* = 9.08 Hz, 2H; 3-, 3″-H), 8.16 (s, 2H; 5-, 5″-H), 8.21 (d, *J* = 9.08 Hz, 2H; 4-, 4″-H), 8.71 (s, 2H; 10-, 10‴-H). – ^{13}C NMR ($CDCl_3$): δ = 31.2 [p; $C(CH_3)_3$], 31.4 [p; $C(CH_3)_3$], 31.5 [p; $C(CH_3)_3$], 35.1 [q; $C(CH_3)_3$], 35.2 [q; $C(CH_3)_3$], 35.3 [q; $C(CH_3)_3$], 35.3 [q; $C(CH_3)_3$], 35.4 [q; $C(CH_3)_3$], 35.5 [q; $C(CH_3)_3$], 122.3 (t), 122.4 (t), 123.1 (t), 123.2 (t), 124.9 (t), 125.0 (t), 125.1 (t), 125.2 (t), 125.5 (t), 125.7 (t), 126.8 (t), 126.9 (t), 127.5 (t), 127.6 (t), 127.7 (t), 128.6 (t), 128.7 (t), 130.7 (q), 130.8 (q), 130.9 (q), 131.1 (q), 131.2 (q), 131.5 (q), 131.6 (q), 131.7 (q), 131.9 (q), 132.0 (q), 132.1 (q), 133.4 (q), 133.5 (q), 133.6 (q), 133.9 (q), 134.1 (q), 147.4, 147.5, 147.6, 147.8, 147.9 (q; C-2, -2′, -2″, -2‴, -6, -6′, -6″, -6‴). – IR (KBr): ṽ = 3080–2868 cm^{-1}, 1629, 1480, 1459, 1362, 1254, 896, 813, 596. – FD MS: *m/z* (%) = 1156 (49) [M^+ + 1], 1155 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} = 408 nm. – $C_{88}H_{98}$ (1155.7): calcd. C 91.45, H 8.55; found C 91.35, H 8.45.

10-Bromo-2′,3′-dihexyl-9,10-trianthrylene (**14**): A solution of bromine (0.32 g, 0.002 mol) in 50 ml of CCl_4 was added dropwise during 6 h at 0°C to a solution of **3** (1.4 g, 0.002 mol) in CCl_4 (250 ml). The mixture was allowed to react for another 6 h at room temperature. After concentration of the combined solutions, the reaction mixture was poured into 100 ml of methanol. The precipitate was chromatographed twice on silica gel [mobile phases: petroleum ether/dichloromethane (i) (10:1), (ii) (3:1)] and recrystallized from hexane/dichloromethane chloride (4:1) to give 0.62 g (41%) of **14**; m.p. 280°C (dec.). – ^{1}H NMR ($C_2D_2Cl_4$): δ = 8.78–8.74 (m, 3H; 4-, 5-, 10″-H), 8.28–8.18 (m, 2H; 4″-, 5″-H), 7.71–7.65 (m, 2H; 3-, 6-H), 7.60–7.55 (m, 2H; 3″-, 6″-H), 7.50–7.25 (m, 8H; 1-, 2-, 7-, 8-, 1″-, 2″-, 7″-, 8″-H), 7.20–7.11 (m, 4H; 5′-, 6′-, 7′-, 8′-H), 6.96 (s, 1H; 1′-H), 6.93 (s, 1H, 4′-H), 2.36–2.32 (m, 4H; benzylic CH_2), 1.57–0.80 (m, 16H, CH_2), 0.75–0.69 (m, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 140.8, 140.5 (q; C-2′, -3′), 135.4 (q), 134.2 (q), 133.5 (q), 133.1 (q), 132.3 (q), 132.2 (q), 131.6 (q), 131.2 (q), 129.1 (t), 128.6 (t), 128.2 (t), 127.8 (t), 127.6 (t), 127.4 (t), 126.7 (t), 126.4 (t), 126.3 (t), 126.1 (t), 125.9 (t), 125.7 (t), 124.0 (q; C-10), 33.1 (CH_2), 33.0 (CH_2), 32.0 (CH_2), 30.9 (CH_2), 30.7 (CH_2), 29.3 (CH_2), 23.0 (CH_2), 14.5 (CH_3). – MS

(70 eV): *m/z* (%) = 777 (100) [M^+], 698 (69) [M^+ − Br], 178 (42) [anthryl$^+$]. − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3054, 2953, 2926, 2855, 1455, 1439, 1306, 920, 884, 756, 734, 633, 603. − UV/Vis (CH_2Cl_2): λ_{max} = 408 nm. − $C_{54}H_{49}Br$ (777.9): calcd. C 83.38, H 6.35, Br 10.27; found C 83.49, H 6.41, Br 10.12.

10,10″-Dibromo-2′,3′-dihexyl-9,10-trianthrylene (**15**): Compound **3** (2 g, 0.0028 mol) was dissolved in 200 ml of CCl_4, and a solution of bromine (0.448 g, 0.003 mol) in CCl_4 (30 ml) was added dropwise during 2 h at 0°C. After a further reaction time of 20 h, the mixture was concentrated and the crude precipitated with methanol. Column chromatography on silica gel [mobile phase: petroleum ether/dichloromethane (3:1)] and recrystallization from dichloromethane/methanol (3:2) afforded 1.4 g (59%) of **15**; m.p. 285°C (dec.). − ^{1}H NMR ($C_2D_2Cl_4$): δ = 8.78−8.72 (m, 4H, 4-, 5-, 4″-, 5″-H), 7.71−7.63 (m, 4H; 3-, 6-, 3″-, 6″-H), 7.41−7.35 (m, 8H; 1-, 1″-, 2-, 2″-, 7-, 7″-, 8-, 8″-H), 7.10−7.07 (m, 4H; 5′-, 6′-, 7′-, 8′-H), 6.94 (s, 2H; 1′-, 4′-H), 2.36 (t, *J* = 6.6 Hz, 4H; benzylic CH_2), 1.26−0.84 (m, 16H; CH_2), 0.72 (t, *J* = 6.1 Hz, 6H; CH_3). − ^{13}C NMR ($CDCl_3$): δ = 140.9 (q; C-2′, -3′), 135.0 (q), 132.7 (q), 131.5 (q), 131.2 (q), 128.7 (t), 128.1 (t), 127.8 (t), 127.5 (t), 126.7 (t), 126.2 (t), 125.9 (t), 124.1 (q; C-10, -10″), 33.1 (CH_2), 32.0 (CH_2), 30.9 (CH_2), 29.3 (CH_2), 23.0 (CH_2), 14.52 (CH_3). − MS (70 eV): *m/z* (%) = 857 (100) [M^+], 776 (52) [M^+ − Br]. − IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1}, 3064, 2954, 2926, 2855, 1622, 1438, 1303, 1026, 921. − UV/Vis (CH_2Cl_2): λ_{max} = 409 nm. − $C_{54}H_{48}Br_2$ (856.8): calcd. C 75.70, H 5.65, Br 18.65; found C 75.58, H 5.71, Br 18.79.

10-Cyano-2′,3′-dihexyl-9,10-trianthrylene (**16**): A suspension of **14** (250 mg, 0.32 × 10^{-3} mol) and CuCN (250 mg) in freshly distilled dimethylformamide (150 ml) was refluxed for 4 h under an inert atmosphere. After cooling to room temperature, the mixture was poured into a dilute iron(II) sulfate solution (600 ml, 1 M in water), repeatedly extracted with dichloromethane and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed twice on silica gel [mobile phases: (i) dichloromethane methylene chloride, (ii) dichloromethane/petroleum ether (1:1)] to afford 160 mg (70%) of **16**. − ^{1}H NMR ($C_2D_2Cl_4$): δ = 8.77 (s, 1H; 10″-H), 8.70 (d, *J* = 8.8 Hz, 2H; 4-, 5-H), 8.23 (d, *J* = 8.4 Hz, 2H; 4″-, 5″-H), 7.79 (t, *J* = 8.8 Hz, 2H; 3-, 6-H), 7.70−7.61 (m, 2H; 3″-, 6″-H), 7.56 (m, 12H; aromatic), 7.01, 6.85 (2 × s, 2H; 1′-, 4′-H), 2.38 (t, *J* = 6.8 Hz, 4H; benzylic CH_2), 1.29−1.19 (m, 4H; CH_2), 1.16−0.99 (m, 12H; CH_2), 0.75 (t, *J* = 5.5 Hz, 6H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 142.1, 141.1, 140.6, 134.1, 133.8, 132.2, 132.1, 131.7, 131.5, 131.2, 131.1, 130.9, 130.8, 129.5, 129.2, 128.6, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.9, 126.6, 126.5, 126.4, 126.3, 126.2, 125.9, 125.8, 125.6, 118.2 (C-10), 106.8 (CN), 33.0 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 29.2 (CH_2), 22.9 (CH_2), 14.5 (CH_3). − MS (70 eV): *m/z* (%) = 724 (56) [M^+ + 1], 723 (100) [M^+], 722 (18) [M^+ − 1]. − UV/Vis (CH_2Cl_2): λ_{max} = 413 nm. − $C_{55}H_{49}N$ (724.0): calcd. C 91.24, H 6.82; found C 91.13, H 6.89.

10,10″-Dicyano-2′,3′-dihexyl-9,10-trianthrylene (**17**): A mixture of **15** (300 mg, 0.35 × 10^{-3}), CuCN (500 mg) and freshly distilled dimethylformamide (150 ml) was refluxed for 5 h under an inert atmosphere. After cooling to room temperature, the reaction mixture was poured into a dilute iron(II) sulfate solution (600 ml, 1 M in water), extracted with dichloromethane, the extract was dried ($MgSO_4$), and then the solvent was removed. The crude product was purified by column chromatography on silica gel (mobile phase: dichloromethane) to yield 105 mg (40%) of **17**. − ^{1}H NMR ($CDCl_3$): δ = 8.69 (d, *J* = 8.63 Hz, 4H; 4-, 4″-, 5-, 5″-H), 7.83−7.75 (m, 4H; 3-, 3″-, 6-, 6″-H), 7.48−7.40 (m, 8H; 1-, 1″-, 2-, 2″-, 7-, 7″-, 8-, 8″-H), 7.11−7.05 (m, 4H; 5′-, 6′-, 7′-, 8′-H), 6.86 (s, 2H; 1′-, 4′-H), 2.39 (t, *J* = 6.9 Hz, 4H; benzylic CH_2), 1.31−1.20 (m, 4H; CH_2), 1.15−0.86 (m, 12H; CH_2), 0.76 (t, *J* = 5.5 Hz, 6H; CH_3). − ^{13}C NMR ($CDCl_3$): δ = 141.4 (C-2′, -3′), 133.7, 131.8, 131.6, 131.0, 130.7, 129.6, 128.4, 127.5, 127.1, 126.4, 125.7, 118.0 (C-10, C-10″), 107.1 (CN), 33.0 (CH_2), 31.9 (CH_2), 30.6 (CH_2), 29.2 (CH_2), 22.9 (CH_2), 14.5 (CH_3). − FD MS: *m/z* (%) = 750 (20) [M^+ + 2], 749 (64) [M^+ + 1], 748 (100) [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} = 414 nm. − $C_{56}H_{48}N_2$ (749.0): calcd. C 89.80, H 6.46; found C 89.67, H 6.38.

2′,2‴,2⁗,3′,3‴,3⁗-Hexahexyl-9,10-heptaanthrylene (**18**): 0.35 ml of *n*-butyllithium (1.6 M in hexane) was injected by a syringe into a solution of **14** (400 mg, 5.2 × 10^{-4} mol) in absolute THF (100 ml) under argon at −50°C. After a reaction time of 30 min, a solution of **6a** (80 mg, 2.6 × 10^{-4} mol) in 30 ml of absolute THF was added dropwise. The mixture was then stirred for 24 h. After heating to room temperature, the reaction was quenched with 20 ml of acetic acid and the ether removed. The yellow residue was dissolved in 70 ml of acetic acid the solution was treated with H_3PO_2 (10 ml, aqueous solution, 50%) and HI (0.5 ml, aqueous solution, 57%), kept for 3 h at 80°C and finally cooled to 5°C. The yellow precipitate was purified by recrystallization from chloroform/methanol and by preparative gel-permeation chromatography (mobile phase: $CHCl_3$) to yield 72 mg (18%) of **18**. − ^{1}H NMR ($CDCl_3$): δ = 8.72 (s, 2H; 10-, 10⁗⁗-H), 8.30−8.15 (m, 4H; 4-, 5-, 4⁗⁗-, 5⁗⁗-H), 7.50−7.00 (m, 46H; aromatic), 2.45−2.20 (m, 12H; benzylic CH_2), 1.30−0.70 (m, 66H; CH_2, CH_3). − FD MS: *m/z* (%) = 1741 (11) [M^+ + 2], 1740 (42) [M^+ + 1], 1739 (100) [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} = 406 nm. − $C_{134}H_{130}$ (1740.5): calcd. C 92.47, H 7.53; found C 92.16, H 7.62.

2,2″,6,6″-Tetra-tert-butyl-9,10-trianthrylene (**19**) *and 2,13-Di-tert-butyl-7-(2,6-di-tert-butyl-9-anthryl)helianthrene* (**20**): A suspension of **5** (500 mg, 0.487 × 10^{-3} mol) and 1 g of KOH in 30 ml of freshly distilled and degassed quinoline was kept for 2 h at 160−180°C under an inert atmosphere. After cooling to room temperature, the quinoline was removed in vacuo, and the residue extracted with degassed dichloromethane under argon. The violet solution was concentrated and the residue chromatographed on aluminum oxide (mobile phase: dichloromethane) under inert conditions. Then the products were further purified by preparative size-exclusion chromatography (mobile phase: $CHCl_3$); yield: 220 mg (60%) of **20** and 109 mg (30%) of **19**. − **19**: M.p. 275°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 8.65 (s, 2H; 10-, 10″-H), 8.15 (d, *J* = 8.9 Hz, 2H; 4-, 4″-H), 8.06 (d, *J* = 1.6 Hz, 2H; 5-, 5″-H), 7.62 (dd, *J* = 1.8 Hz, 8.9 Hz, 2H; 3-, 3″-H), 7.38 (d, *J* = 1.8 Hz, 2H; 1-, 1″-H), 7.35 (dd, *J* = 1.6 Hz, 8.8 Hz, 2H; 7-, 7″-H), 7.30−7.04 (m, 10H; 1′-, 2′-, 3′-, 4′-, 5′-, 6′-, 7′-, 8-, 8′-, 8″-H), 1.45 [s, 18H; $C(CH_3)_3$], 1.13 [s, 18H; $C(CH_3)_3$]. − FD MS: *m/z* (%) = 754 (100) [M^+], 755 (40) [M^+ + 1], 756 (14) [M^+ + 2]. − UV/Vis (CH_2Cl_2): λ_{max} = 403 nm. − $C_{58}H_{58}$ (755.1): calcd. C 92.26, H 7.74; found C 91.93, H 7.87. − **20**: ^{1}H NMR ($CDCl_3$, mixture of isomers): δ = 9.05 (m, 1H; aromatic); 8.84 (m, 1H; aromatic); 8.68 (m, 2H, aromatic), 8.40−8.00 (m, 4H; aromatic); 7.61−6.90 (m, 12H; aromatic), 1.68, 1.57, 1.52, 1.49, 1.34, 1.27, 1.22 [8 × s, 36H; $C(CH_3)_3$]. − FD MS: *m/z* (%) = 753 (100) [M^+], 754 (36) [M^+ + 1], 755 (8) [M^+ + 2]. − UV/Vis ($CHCl_3$): λ_{max} = 583, 620 nm. − $C_{58}H_{56}$ (753.1): calcd. C 92.51, H 7.50; found C 92.64, H 7.62.

Crystal-Structure Analyses[31]: Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu-K_α radiation (λ = 1.5405 Å). The structures were solved by direct methods (SIR). − **4a**: Yellow single crystal (0.37 × 0.20 × 0.32 mm); triclinic; space group $P\bar{1}$; *a* = 13.5425(6), *b* = 14.3222(7), *c* = 9.878(1) Å; α = 107.826(6), β = 105.068(7), γ = 74.608(3)°; *V* = 1714(2) $Å^3$; *Z* = 1; ρ(calcd.) =

1.165 g cm^{-3}; μ = 33.47 cm^{-1}; 5437 reflexions were measured {observed: 2741[$I > 6\sigma(I)$]; 5089 unique}. The unit cell consists of one molecule of **4a** located at an inversion center and two molecules of tetrachloroethane. Hydrogen atoms were placed into their computed positions by using known bond geometries and were refined in the riding mode with isotropic temperature coefficients. During the last full-matrix least-squares refinement anisotropic temperature coefficients were calculated for all non-hydrogen atoms. The R factors were R = 0.093 and R_w = 0.091 (w = 1). – **5**: Yellow-green single crystal (0.42 × 0.37 × 0.32 mm); monoclinic; space group $P\,2_1/c$; a = 14.488(1), b = 25.933(4), c = 12.580(1) Å; β = 91.285(6)°; V = 4725(2) $Å^3$; Z = 4; ρ(calcd.) = 1.158 g cm^{-3}; μ = 15.05 cm^{-1}; 5017 reflexions measured (all unique) of which 2277 with $I > 3\sigma(I)$ were considered. The unit cell consists of one molecule for which one of the *tert*-butyl groups is placed in two conformations in a 3:2 distribution. Hydrogen atoms were located on their computed positions by using known bond geometries and were refined in two blocks in the riding mode with isotropic temperature coefficients. The population parameters of the disordered *tert* butyl group were not refined. The refinement of carbon and chloro atoms was made in two sets with anisotropic temperature factors. The final R factors were R = 0.063 and R_w = 0.063 (w = 1).

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