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Tris(tetraceno)triquinacenes: Synthesis and Photophysical Properties of Threefold Linearly Extended Tribenzotriquinacenes

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Dedicated to Professor Dr. Eckehard V. Dehmlow on the occasion of his 80th birthday

Abstract: The linear extension of the rigid, C_{3v}-symmetrical carbon framework of tribenzotriquinacene (TBTQ) along its three wings is reported. The key step of the extension procedure consists of a Diels–Alder reaction of three *ortho*-quinodimethane units generated in situ at the triquinacene core. The use of 1,4-naphthoquinone provides a facile and particularly efficient access to tris(tetraceno)-annellated triquinacenes. The steady-state photophysical properties of these new oligotetracenes bearing three mutually orthogonal chomophores are determined and analyzed by DFT calculations.

Keywords: acenes · photophysics · polycyclic compounds · quinones · UV/Vis spectroscopy

Introduction

Acenes represent one of the most important structural motifs for polycyclic aromatic hydrocarbons,[1] graphene,[2] and carbon nanotubes.[3] Among them, tetracenes and pentacenes have experienced considerable attention because of their excellent performance in the field of organic electronics.[4–10] In particular, charge carrier mobility was found to depend on the ability of acenes to aggregate into highly organized molecular stacks to enable maximum π-orbital overlap within the crystal lattice.[4a,11] However, the poor solubility and low chemical stability of the higher parent acenes have limited their detailed exploration,[1a,12] and methods to circumvent this problem by bending the acene plane have been developed.[13]

In the present work, three acene units have been incorporated into the three-dimensional framework of tribenzotriquinacene (TBTQ, **1**).[14–16] This polycyclic hydrocarbon belonging to the centropolyindane family[17] has a conformationally rigid and highly symmetrical (C_{3v}) carbon framework consisting of three indane wings oriented orthogonally to each other (**A**, Figure 1).[17–19] Owing to this unique spatial arrangement and the bowl-shaped architecture of **1**, we expected increased solubility of threefold aceno-annellated triquinacenes, such as **B**, which would contribute a new facet to the field.[20,21] Different from triptycenes bearing three acene wings oriented perpendicular to a common plane and mutually at 120°,[22] TBTQ-based acenes would stretch out into the three-dimensional space at about 90° to each other, with obvious consequences for the so-called internal free volume (IFV) generated.[22,23]

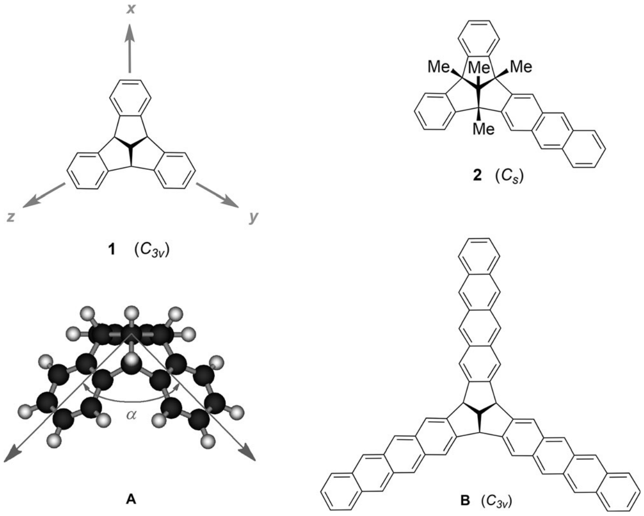

Figure 1. Parent tribenzotriquinacene (TBTQ, **1**), the single-wing-extended TBTQ derivative **2**[28] and the (yet unknown) parent tris(2,3-tetraceno)triquinacene **B**. The insert **A** provides a view along the axis of one indane wing of **1**, illustrating the almost perfect orthogonal orientation of the other two (α = 88°).[18,19]

Whereas various successful directed extensions of the three aromatic wings of the TBTQ system have been reported,[17,18,24–27] threefold ("linear") extension with acene units has not been achieved yet. By contrast, single-wing extension was feasible by Diels–Alder methodology involving in situ-generated TBTQ-based monoaryne and monoisobenzofuran analogues at low temperature for trapping with vari-

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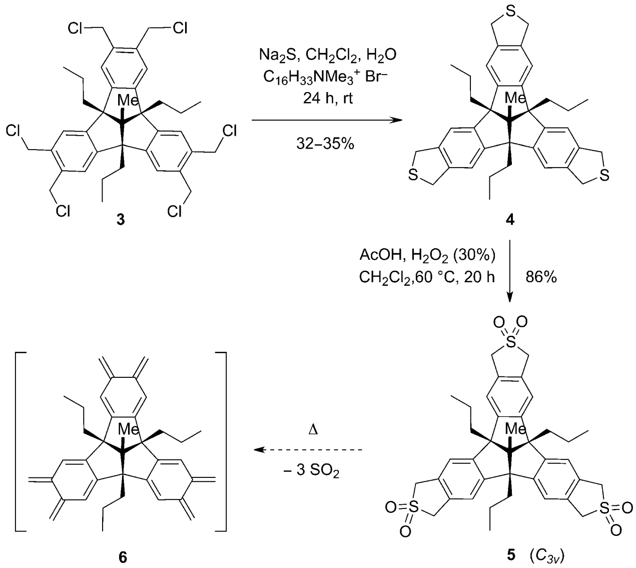
ous dienes and dienophiles, respectively.[28] In this way, the dibenzo[2,3]anthrotriquinacene **2** and several higher single-wing-extended congeners including tetracene and pentacene derivatives were synthesized.[28] Threefold application of this strategy within the same TBTQ framework appears to be impeded by the poor solubility of such extended structures at low temperatures.[17,29] Therefore, we now pursued an alternative, high-temperature strategy involving a threefold Diels–Alder reaction of TBTQ-based *ortho*-quinodimethanes with suitable dienophiles.[30] Under such conditions, the solubility of even threefold-extended intermediates and products was expected to be sufficiently enhanced. In this way, we developed an access to TBTQ analogues bearing three linear acene wings as derivatives of the parent tris(tetraceno)triquinacene **B**. The synthesis and photophysical properties of these new oligoacenes will be reported here.

Results and Discussion

In view of the poor solubility of some extended TBTQ derivatives,[17a] the sixfold chloromethylated 4b,8b,12b-tripropyl-12d-methyl congener **3** was chosen as a starting point (Scheme 1).[25c] According to a procedure reported previously,[25a] treatment of **3** with sodium sulfide under phase-transfer catalysis (PTC) conditions furnished the corresponding threefold thioether **4** in moderate yield. Threefold oxidation to the corresponding tris-sulfone **5** was achieved by use of an excess of acetic acid and hydrogen peroxide in dichloromethane as a co-solvent at elevated temperature (60 °C), producing compound **5** in excellent yield. The structural identity and molecular C_{3v}-symmetry of **4** and **5** was confirmed by using ^{1}H and ^{13}C NMR spectroscopy and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry.

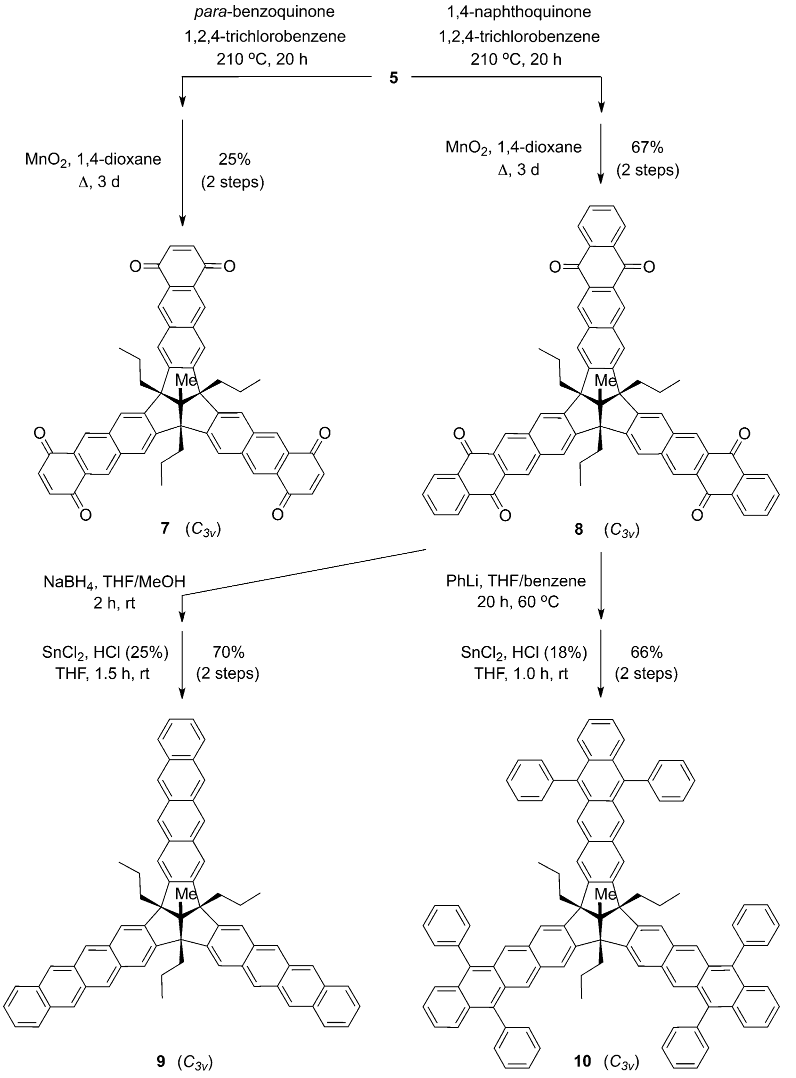


Scheme 1. Synthesis of the TBTQ-based trisulfone **5** as a precursor of TBTQ-based diene intermediates, such as the hypothetical tris(*ortho*-quinodimethano)triquinacene **6**.

2,7-Dihydrobenzo[*c*]thiophene-*S*,*S*-dioxides are known to be valuable precursors for in situ-generation of *ortho*-quinodimethanes for subsequent [4+2] cycloaddition reactions.[30] In this vein, TBTQ-tris-sulfone **5** was found to be a suitable precursor of the triquinacene-based tris-*ortho*-quinodimethane **6**. Although the intermediacy of **6** remains hypothetical, indeed, thermolysis of tris-sulfone **5** gave rise to threefold Diels–Alder reactions with quinones (Scheme 2). Thus, heating compound **5** in 1,2,4-trichlorobenzene in the presence of an excess of *para*-benzoquinone gave a product mixture which, after treatment with activated manganese dioxide in 1,4-dioxane under reflux,[31] furnished the tris-1,4-anthraquinone **7** in moderate yield. Likewise, thermolysis of **5** in the presence of 1,4-naphthoquinone under similar conditions gave a mixture of partially and fully aromatized products, which were subjected to chromatography before aromatization. Careful chromatographic purification afforded tris(tetracene)quinone **8** in good yield. The C_{3v}-symmetrical molecular structure of these first TBTQ derivatives bearing a quinone unit in each of the three wings was confirmed by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. For example, the ^{1}H NMR spectrum of **8** exhibits two distinct 6H singlet resonances for the three inner naphthalene units.

The efficient threefold extension of the TBTQ framework in the case of compound **8** allowed us to synthesize the tris(tetraceno)triquinacene hydrocarbons **9** and **10** (Scheme 2). Quinone **8** was reduced to the corresponding threefold 5,12-dihydrotetracene-5,12-diol by the use of sodium borohydride in THF/methanol.[20d] The hexa-alcohol was not isolated in pure form but reduced further with stannous chloride in aqueous hydrochloric acid[7a] to give tris(2,3-tetraceno)triquinacene **9** as a yellow/orange solid in a remarkably good yield. We were pleased to find that, in line with expectation, this triply wing-extended TBTQ hydrocarbon was readily soluble in various organic solvents and remarkably stable in solution and in the solid state for several weeks in the absence of oxygen.

Sixfold addition of phenyllithium to trisquinone **8** in THF/benzene at 60 °C gave a mixture of stereoisomeric hexa-alcohols that, after purification by column chromatography and subsequent reduction with stannous chloride in HCl/H_2O/THF, gave the corresponding hexaphenyl-substituted tris(2,3-tetraceno)triquinacene **10** as an orange/red solid in good yield. Again in line with expectation, hydrocarbon **10** was found to be well-soluble in usual organic solvents. The identity of hydrocarbons **9** and **10** was confirmed by NMR spectroscopy and MALDI MS. Use of single-electron oxidant matrices {tetracyanoquinodimethane (TCNQ) or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)} gave rise to the molecular radical cations in high relative abundance and the NMR spectra nicely confirmed the expected molecular C_{3v} symmetry of these $C_{68}H_{54}$ and $C_{104}H_{78}$ hydrocarbons.



Scheme 2. Synthesis of the triquinacene-based trisquinones **7** and **8** and of the tris(tetraceno)triquinacenes **9** and **10**.

The fusion of the planar 5,12-diphenyltetracene units to the bowl-shaped triquinacene core in **10** is particularly noteworthy in view of restricted internal rotation. Recently, the barrier towards rotation about the C^{aryl}–C^{aryl} bonds in various 9,10-arylanthracenes was determined to be $\geq$21 kcal mol^{-1}.[32] Actually, the ^{1}H NMR spectrum of **10** exhibits two distinct doublet resonances for the *ortho* protons of the six phenyl groups, which remain separated even at 100 °C (see the Supporting Information). The ^{13}C NMR spectrum of **10** also indicates apparently static phenyl groups. Thus, observation of a strongly hindered rotation in **10** represents a gratifying spin-off of the fact that the bent TBTQ core renders the two otherwise equivalent surfaces of anthracene and higher acene units stereochemically distinct.

The optical properties of the tris(aceno)triquinacene derivatives **7**–**10** were investigated by steady-state UV/Vis absorption and fluorescence spectroscopy in dichloromethane solution (see the Supporting Information for explicit data). All compounds were found to exhibit strong and slightly structured absorption bands in the UV region and a second set of absorption bands in the Vis region of the electromagnetic spectrum (Figures 2 and 3). The Vis absorption bands of the TBTQ trisquinones **7** and **8** are broad and almost unstructured. In line with its more extended chromophore, the Vis absorption of **8** is redshifted by $\Delta\tilde{\nu}$= 454 cm^{-1}. In contrast to the trisquinones, the tris(tetraceneno)triquinacenes **9** and **10** show the typical structured band shape of higher acenes in the visible region with lowest-energy transitions at 492 and 512 nm, respectively (Figure 3). The absorption of **9** is close to that of simple 2,3-dialkyltetracenes.[20c] Also, the redshift by $\Delta\tilde{\nu}$= 794 cm^{-1} for **10** compared with **9** is similar to that reported for 5,12-diphenyltetracene and parent tetracene ($\Delta\tilde{\nu}$=770–810 cm^{-1}, solvent-depending values).[33a,34]

The trisquinones **7** and **8** were found to be almost nonfluorescent but to show broad, unstructured emission bands, with the emission of the larger chromophore being strongly redshifted (Figure 2). The emission is independent of the excitation wavelength and the emis-

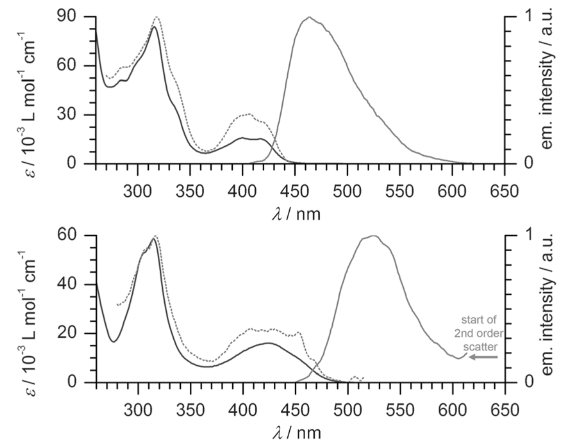


Figure 2. UV/Vis absorption and emission spectra of trisquinones **7** (top) and **8** (bottom) recorded in CH$_2$Cl$_2$. Absorption, solid black lines (left absolute scale); fluorescence, gray lines (right scale); and fluorescence excitation, dashed lines (right scale). Emission spectroscopy: $\lambda_{exc.}$=316 nm, excitation: $\lambda_{monitor}$=465 (**7**) and 525 nm (**8**).

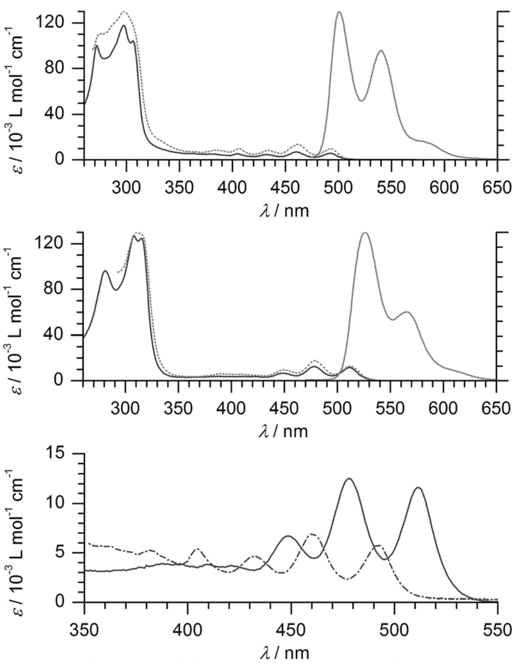


Figure 3. UV/Vis absorption and emission spectra of tristetracenes **9** (top) and **10** (middle) recorded in CH_2Cl_2. Absorption, solid black lines (left absolute scale); fluorescence, gray lines (right scale); and fluorescence excitation, dashed lines (right scale). Emission spectroscopy: $\lambda_{exc.}=461$ nm, excitation: $\lambda_{monitor}=524$ (**9**) and 565 nm (**10**). The magnified Vis part of the absorption spectra of **9** (–•–•) and **10** (——) are shown in the bottom image.

sion excitation spectra match (despite instrumental noise) the absorption spectra. In contrast to the trisquinones, the triquinacene-based tristetracenes **9** and **10** show the typical vibronically structured fluorescence pattern of the higher acenes (Figure 3). Compared with **9**, the hexaphenyl derivate **10** exhibits more strongly redshifted emission bands (500 and 526 nm, respectively; $\Delta\tilde{\nu}=989\,\mathrm{cm^{-1}}$) and also larger $^{0-0}$Stokes shifts ($\Delta\tilde{\nu}=325$ and $520\,\mathrm{cm^{-1}}$, respectively). The quantum yields determined for **9** and **10** differ by an order of magnitude ($\Phi=0.02$ and 0.21, respectively); however, such low values are in line with observations made for alkylated tetracenes.[20] The significantly higher quantum yield of **10** compared with **9** is also in line with the trend found for the single chromophores.[33,37]

DFT calculations on the B3LYP/6-31G** level, as similarly applied by others in related studies,[20e,35a] revealed that the tristetracenes **9** and **10** have their highest occupied molecular orbitals (HOMOs; A_2 symmetry) and lowest occupied molecular orbitals (LUMOs; A_1) spread about the whole C_{3v}-symmetrical molecular framework (see the Supporting Information).[36] Compared with **9**, the energies of the occupied MOs of **10** are slightly increased, whereas the increase of the LUMO energies is negligible. The frontier orbitals remain largely unaffected by the phenyl substitution, but slight differences in electron density distribution were found for HOMO-1 and HOMO-2 when comparing **9** and **10**. The smaller frontier orbital energy gap resulting for **10** is in good agreement with the experimental result.

Conclusion

Solid-state tetracenes and covalently interconnected bistetracenes with a well-defined spatial alignment of the chromophores are of current interest in photophysical studies,[20,34,35] and the tris(tetraceno)triquinacenes presented here could contribute to the field. Owing to the rigid TBTQ core, the short molecular axis transition dipoles of the tetracene units lie within the same plane at angles of 60° (Figure 4). This peculiar, and possibly unique spatial arrangement corresponds to an orientation factor fixed to $\kappa^2=1.56$.[37]

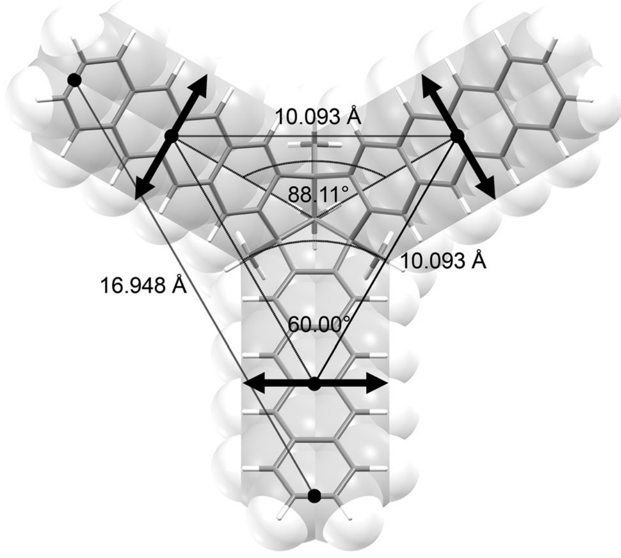


Figure 4. Molecular structure, selected structural parameters, and space-filling model of the tris(2,3-tetraceno)triquinacenes, as calculated by DFT. The short molecular axis transition dipoles are indicated as bold arrows. For simplicity, calculations were performed for the bridgehead tetramethyl derivative.

Experimental Section

Instrumentation and materials: Melting points (uncorrected) were measured with a Büchi B-540 electrothermal melting point apparatus. IR spectra were recorded with a Nicolet-380 FTIR spectrometer equipped with a SmartOrbit diamond ATR cell. UV spectra were recorded with polytetrafluoroethylene (PTFE)-stoppered fused silica 10 mm pathway cuvettes on a Perkin–Elmer Lambda 40 UV/Vis double-beam spectrometer. Fluorescence spectra were acquired on a Perkin–Elmer LS-50B spectrometer with spectral bandwidth (slit widths) set to 5 or 10 nm for low fluorescent compounds. Measurements were performed in a thermostated room at (25 ± 1) °C. NMR spectra were measured with a Bruker DRX 500 instrument (^{1}H: 500.1 MHz, ^{13}C: 125.7 MHz, 25 °C) and referenced on the (residual proton) solvent signal. Electron ionization (EI) mass spectra were recorded with a Fisons VG Autospec X double-focusing mass spectrometer. MALDI measurements were performed with a Voyager-DE MALDI-ToF and DHB, DCTB or TCNQ as matrices. Accurate mass measurements were performed with the Fisons VG sector-field instrument, Autospec X, and a Bruker FT-ICR mass spectrometer, APEX III (7 T). Dichloromethane, cyclohexane and ethyl acetate were distilled before use or used in puriss (p.a.) quality (Fischer, VWR) as received. Reference standards for the relative quantum yield determinations were 9,10-diphenylanthracene (99 %, Acros), rubrene (99 %, Acros), quinine (99 %, puriss., Fluka), and fluorescein (98 %, Merck). All other chemicals were used as delivered. Manganese dioxide was of "activated" grade. 1,2,4-trichlorobenzene (p.a. grade) was dried over molecular sieves (4 Å) and degassed by purging Argon for at least 30 min. Extra-dry tetrahydrofuran was purchased from Acros Organics. Reactions requiring anhydrous conditions were carried out in oven-dried glassware under argon. All reported yields are yields of the isolated product.

Photophysical measurements: All measurements were performed in highly dilute solutions (optical density (O.D.) <0.03, freshly prepared in dim light). The quantum yields were determined by the relative method and cross-checked to the following standards: 9,10-diphenylanthracene in EtOH (aerated), $\Phi_F=0.95$; quinine disulfate in 1 N sulfuric acid (aerated), $\Phi_F=0.55$, fluorescein in 0.1 N aqueous sodium hydroxide (aerated), $\Phi_F=0.92$.[38] These reference values were reproduced within 10% (rel. error); therefore, this error limit is also assigned to the values given above and the validation measurement with rubrene. Excitation was set to (316 ± 1) nm (**7**, **8**) and to (461 ± 1) nm (**9**, **10**; rubrene).

5b-Methyl-4b,9b,14b-tri-*n*-propyl-4b,6,8,9b,11,13,14b,15b-octahydro-1*H*,3*H*-[2]benzothieno[5′,6′:5,6]thieno[3″,4″:5′,6′]indeno-[1′,2′,3′:3,4]pentaleno[1,2-*f*][2]benzothiophene (4): A solution of the sixfold benzyl chloride **3**[25c] (500 mg, 0.710 mmol) and hexadecyltrimethylammonium bromide (193 mg, 0.532 mmol) in anhydrous dichloromethane (50 mL) was stirred under argon while a solution of sodium sulfide nonahydrate (768 mg, 3.20 mmol) in demineralized water (50 mL) was added dropwise through a dropping funnel. The resulting milky mixture was vigorously stirred in the dark at ambient temperature for 24 h. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×25 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by using column chromatography through silica gel (cyclohexane/CH_2Cl_2 6:1 to 3:1) and furnished the product **4** (146 mg, 35%) as a colorless solid. M.p. 176–178 °C.; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta=7.17$ (s, 6H), 4.20 and 4.18 (extremely narrow AB, $J=12.0$ Hz, 2×6H), 2.13 (m, 6H), 1.64 (s, 3H, 12d-CH_3), 1.23–1.17 (m, 6H), 0.96 ppm (t, $J=7.5$ Hz, 9H); ^{13}C NMR (125.7 MHz, CD_2Cl_2): $\delta=147.6$ (C), 140.5 (C), 119.4 (CH), 74.0 (C), 66.4 (C), 41.2 (CH_2), 37.7 (CH_2), 20.8 (CH_2), 15.5 (12d-CH_3), 15.2 ppm (CH_3); IR (neat): $\Delta\tilde{\nu}=2954$, 2909, 2866, 1479, 1432, 1034, 906, 728, 615 cm^{-1}; MS (EI, 70 eV): m/z (%), 594 (9, $[M]^{+\bullet}$), 551 (100), 465 (2), 275.6 (7, $[M-C_3H_7]^{2+}$); MS (ESI+, CH_3CN, $AgBF_4$): m/z: 701 (100, $[M+{}^{107}Ag]^+$), 702 (35), 703 (98), 704 (64), 705 (24); HRMS (ESI+, CH_3CN): m/z calcd for $C_{38}H_{42}S_3{}^{107}Ag$: 701.1494 $[M+{}^{107}Ag]^+$; found: 701.1505. Note: Several attempts carried out under varied conditions did not give higher yields. Tristhioether **4** was found to be highly light- and air-sensitive; therefore, the reaction, work-up, and chromatographic purification were performed by carefully excluding light and oxygen.

15b-Methyl-4b,9b,14b-tri-*n*-propyl-4b,6,8,9b,11,13,14b,15b-octahydro-1*H*,3*H*-[2]benzothieno[5′,6′:5,6]thieno[3″,4″:5″,6′]indeno-[1′,2′,3′:3,4]pentaleno[1,2-*f*][2]benzothiophene-*S*,*S*,*S*′,*S*′,*S*″,*S*″-hexoxide (5): A solution of compound **4** (110 mg, 0.185 mmol) in dichloromethane (2–3 mL) was added to glacial acetic acid (6 mL) followed by slow addition of hydrogen peroxide (30%; 2 mL) at ambient temperature. The resulting mixture was stirred at 60 °C for 20 h. After cooling to room temperature, the mixture was carefully added to a saturated solution of sodium bicarbonate to neutralize the excess acid. The aqueous suspension was then extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford the product **5** (110 mg, 86%) as a colorless solid (note that subsequent precipitation with chloroform/*n*-pentane could be helpful to remove associated solvents). M.p. > 340 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.19$ (s, 6H), 4.35 and 4.30 (AB, $J=16.0$ Hz, 2×6H), 2.12 (m, 6H), 1.63 (s, 3H, 12d-CH_3), 1.20–1.13 (m, 6H), 0.95 ppm (t, $J=7.5$ Hz, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=148.5$ (C), 130.7 (C), 121.0 (CH), 72.0 (C), 67.2 (C), 56.9 (CH_2), 40.8 (CH_2), 20.4 (CH_2), 15.1 (12d-CH_3), 15.0 ppm (CH_3); IR (neat): $\Delta\tilde{\nu}=2955$, 2928, 2869, 1480, 1310, 1225, 1156, 1125, 751, 576 cm^{-1}; MS (MALDI+, DHB, CH_2Cl_2/MeOH): m/z: 713 (100, $[M+Na]^+$), 729 (70, $[M+K]^+$); HRMS (MALDI+, DHB, CH_2Cl_2/MeOH): m/z calcd for $C_{38}H_{42}O_6S_3Na$: 713.2035 $[M+Na]^+$; found 713.2033; m/z calcd for $C_{76}H_{84}O_{12}S_6Na$: 1403.4179 $[2M+Na]^+$; found 1403.4178. Note: Treatment with of **4** with *meta*-chloroperbenzoic acid in dichloromethane at ambient temperature produced only mixtures of partially oxidized products.

23b-Methyl-1,4,9,12,17,20-hexaoxo-6b,14b,22b-tri-*n*-propyl-1,4,6b,9,12,14b,17,20,22b,23b-decahydro-naphtho[2,3:*f*]di(2,3-anthro)-[2,3:4,5]pentaleno[1,6:*ab*]indene (7): A suspension of compound **5** (240 mg, 0.348 mmol) and *para*-benzoquinone (1.128 g, 10.44 mmol) in 1,2,4-trichlorobenzene (8.0 mL) was placed in a Schlenk tube and heated at 210 °C (metal bath temperature) under argon for 20 h. After cooling to room temperature, a part of the solvent was removed by Kugelrohr distillation (70 °C, 1.0×10^{-2} mbar). The residue was diluted with a small amount of chloroform and purified by column chromatography through silica gel (cyclohexane/EtOAc 9:1 to 2:1) to afford a yellow-colored solid. This material was re-dissolved in anhydrous 1,4-dioxane (30 mL) and then manganese dioxide (2–3 g) was added. The mixture was stirred and heated at reflux for 3 d. After the mixture had cooled to ambient temperature, it was passed through a pad of silica gel and washed several times with ethyl acetate. After removing the solvents under reduced pressure, the residue was purified once again by column chromatography through silica gel (cyclohexane/EtOAc 6:1 to 2:1) to furnish the product **7** (70 mg, 25%) as a yellow solid. M.p. > 350 °C.; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=8.63$ (s, 6H), 8.16 (s, 6H), 7.02 (s, 6H), 2.50 (m, 6H), 1.84 (s, 3H, 12d-CH_3), 1.28–1.32 (m, 6H), 1.03 ppm (t, $J=7.5$ Hz, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=184.4$ (CO), 151.4 (C), 140.0 (CH), 135.0 (C), 128.8 (CH), 128.0 (C), 124.6 (CH) 72.8 (C), 67.4 (C), 42.1 (CH_2), 20.5 (CH_2), 15.5 (12d-CH_3), 15.1 ppm (CH_3); IR (neat): $\Delta\tilde{\nu}=2955$, 2915, 2847, 1667, 1472, 1462, 1449, 1289, 1134, 1049, 755, 728 cm^{-1}; MS (MALDI+, DCTB, CH_2Cl_2): m/z: 810 (100, $[M]^{-\bullet}$); HRMS (MALDI+, DCTB, CH_2Cl_2/MeOH): m/z calcd for $C_{56}H_{42}O_6$: 810.2986 $[M]^{-\bullet}$; found: 810.2992. Note: It is obvious that a major part of the actual yield of **7** was lost by formation of follow-up addition (probably triptycene-type) products, as indicated by the MALDI MS of the crude product mixtures.

30b-Methyl-5,10,15,20,25,30-hexaoxo-7b,17b,27b-tri-*n*-propyl-5,7b,10,15,17b,20,25,27b,30,30b-decahydro-anthro[2,3:*f*]di(2,3-tetraceno)-[2,3:4,5]pentaleno[1,6:*ab*]indene (8): In analogy to the procedure given above for compound **7**, tris-sulfone **5** (220 mg, 0.320 mmol) and 1,4-naphthoquinone (252 mg, 1.60 mmol) were reacted in 1,2,4-trichlorobenzene (7.0 mL) and the mixture of adducts thus obtained was subjected to oxidation with activated manganese dioxide (4–5 g) in 1,4-dioxane (30 mL) heated at reflux for 3 d. The trisquinone **8** (205 mg, 67%) was obtained as a yellow solid. M.p. > 350 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=8.89$ (s, 6H), 8.39 and 7.81 (AA′BB′, 2×6H), 8.24 (s, 6H), 2.50 (m, 6H), 1.87 (s, 3H, 12d-CH_3), 1.37–1.31 (m, 6H), 1.06 ppm (t, $J=7.5$ Hz, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=182.8$ (CO), 151.5 (C), 135.4 (C), 134.5 (C), 134.1 (CH), 129.5 (CH), 129.4 (C), 127.5 (CH), 124.6 (CH), 72.9 (C), 67.4 (C), 42.2 (CH_2), 20.6 (CH_2), 15.6 (12d-CH_3), 15.2 ppm (CH_3); IR (neat): $\Delta\tilde{\nu}=3064$, 2951, 2866, 1673, 1586, 1447, 1276, 968, 956, 941, 714 cm^{-1}; MS (MALDI+, DCTB, CH_2Cl_2): m/z: 960 (30) $[M]^{+\bullet}$, 961 (47) $[M+H]^+$, 917 (100) $[M-C_3H_7]^+$; HRMS (MALDI(−), DCTB, CH_2Cl_2/MeOH): m/z calcd for $C_{68}H_{48}O_6$: 960.3456 $[M]^{-\bullet}$; found: 960.3481; HRMS calcd for $C_{65}H_{41}O_6$: 917.2908 $[M-C_3H_7]^{-\bullet}$; found: 917.2915.

30b-Methyl-7b,17b,27b-tri-*n*-propyl-7b,17b,27b,30b-tetrahydroanthro-[2,3:*f*]di(2,3-tetraceno)[2,3:4,5]pentaleno[1,6:*ab*]indene (9): A solution of compound **8** (100 mg, 0.105 mmol) in tetrahydrofuran/methanol (5:1, 12 mL) was stirred at ambient temperature while sodium borohydride (120 mg, 3.15 mmol) was added in small portions. The mixture was further stirred under argon at this temperature for 2 h and then diluted with ice/water. The resulting mixture was concentrated and the residue was dissolved in ethyl acetate (25 mL) and washed with brine (2×15 mL). The organic layers were dried over sodium sulfate, filtered, and then concentrated under reduced pressure to furnish a colorless residue, which was re-dissolved in tetrahydrofuran (20 mL) and degassed by purging with argon for 20 min. A saturated solution of tin(II) chloride (4 mL) in 25% aqueous hydrochloric acid solution was then added to this solution at room temperature. The solution was stirred for an additional 1.5 h under argon. After completion (checked by TLC), the mixture was extracted with diethyl ether (3×15 mL). The combined organic layers were washed with brine (2×15 mL), dried over anhydrous sodium sulfate, filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography through silica gel (cyclohexane/CH_2Cl_2 9:1) to furnish the product **9** (64 mg, 70%) as a yellow-orange solid. M.p. decomposes >250°C; ^1H NMR (500 MHz, CD_2Cl_2): $\delta=8.75$ (s, 6H), 8.66 (s, 6H), 8.24 (s, 6H), 7.99 and 7.38 (AA′BB′, 2×6H), 2.62 (m, 6H), 1.90 (s, 3H, 12d-CH_3), 1.42–1.47 (m, 6H), 1.08 ppm (t, $J=7.5$ Hz, 9H); ^{13}C NMR (125.7 MHz, CD_2Cl_2): $\delta=149.1$ (C), 132.1 (C), 131.3 (C), 130.0 (C), 128.1 (CH), 125.9 (CH), 125.7 (CH), 124.9 (CH), 121.5 (CH), 72.7 (C), 66.6 (C), 42.7 (CH_2), 20.5 (CH_2), 15.7 (12d-CH_3), 15.0 ppm (CH_3); IR (neat): $\Delta\tilde{\nu}==2953$, 2917, 2848, 1454, 1280, 1260, 1156, 1070, 884, 748 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{abs} (ε)=297 (118), 306 (104), 432 (4.64), 460 (6.94), 492 nm (5.81 10^{-3} $L\,mol^{-1}\,cm^{-1}$); MS (MALDI+, TCNQ, MeCN/THF): m/z: 870 (80, $[M]^{+\bullet}$), 871 (100, $[M+H]^+$), 827 (60) $[M-C_3H_7]^+$, 828 (65) $[M+H-C_3H_7]^{+\bullet}$; HRMS (MALDI+, DCTB, CH_2Cl_2/MeOH): m/z calcd for $C_{68}H_{54}$: 870.4220 $[M]^{+\bullet}$; found: 870.4218.

30b-Methyl-5,10,15,20,25,30-hexaphenyl-7b,17b,27b-tri-*n*-propyl-7b,17b,27b,30b-tetrahydroanthro[2,3:*f*]di(2,3-tetraceno)-[2,3:4,5]pentaleno[1,6:*ab*]indene (10): A solution of compound **8** (75 mg, 0.078 mmol) in anhydrous tetrahydrofuran/benzene (1:1, 10 mL) was stirred while a solution of phenyllithium in di-*n*-butyl ether (1.9 M) (4.21 mL, 8.00 mmol) was added dropwise at 0°C under argon. The reaction mixture was heated to 60°C (oil bath temperature) for 20 h. After careful hydrolysis, the resulting mixture was extracted with diethyl ether (3×15 mL). The combined organic layers were washed with brine and dried over sodium sulfate, filtered, and then concentrated under reduced pressure. The residue was subjected to column chromatography through silica gel (cyclohexane/EtOAc 9:1 to 3:1) to furnish a solid material, which was re-dissolved in tetrahydrofuran (12 mL). This solution was degassed by purging with argon for 15 min. Then, a saturated solution of tin(II) chloride (4.0 mL) in 18% aqueous hydrochloric acid was added at room temperature. The resulting solution was stirred for 1 h under argon and in the absence of light. After completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with diethyl ether (3×15 mL). The combined organic layers were washed with brine (2×15 mL), dried over anhydrous sodium sulfate, filtered, and then concentrated under reduced pressure. The residue was purified by column chromatography through silica gel (cyclohexane/CH_2Cl_2 9:1) to furnish the product **10** (69 mg, 66%) as an orange/red solid. M.p. >250°C (decomp.); ^1H NMR (500 MHz, CD_2Cl_2): $\delta=8.30$ (s, 6H), 7.88 (s, 6H), 7.72–7.80 (m, 18), 7.63 and 7.24 (AA′BB′, 2×6H), 7.60 (m, 6H), 7.53 (m, 6H), 2.35 (bs, 6H), 1.70 (s, 3H, 12d-CH_3), 1.15–1.25 (m, 6H), 0.90 ppm (t, $J=7.5$ Hz, 9H); ^1H NMR (500 MHz, $C_2D_2Cl_4$): $\delta=8.22$ (s, 6H), 7.80 (s, 6H), 7.61–7.64 (m, 18), 7.55 and 7.16 (AA′BB′, 2×6H), 7.48–7.50 (m, 6H), 7.39–7.41 (m, 6H), 2.28 (bs, 6H), 1.61 (s, 3H, 12d-CH_3), 1.15–1.20 (m, 6H), 0.84 ppm (t, $J=7.5$ Hz, 9H); ^{13}C NMR (125.7 MHz, CD_2Cl_2): $\delta=149.0$ (C), 139.4 (C), 136.7 (C), 131.7 (C), 131.5 (CH), 131.4 (CH), 129.1 (C), 128.7 (C), 128.6 (CH), 128.5 (CH), 127.4 (CH), 126.8 (CH), 125.1 (CH), 124.5 (CH), 121.6 (CH), 72.3 (C), 66.4 (C), 42.7 (CH_2), 20.2 (CH_2), 15.2 (12d-CH_3), 14.9 ppm (CH_3); IR (neat): $\Delta\tilde{\nu}=2955$, 2924, 2867, 1455, 1440, 1392, 1261, 1072, 900, 746, 701, 669 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{abs} (ε)=308 (127), 315 (125), 449 (6.70), 478 (12.5), 512 nm (11.6 10^{-3} $L\,mol^{-1}\,cm^{-1}$); MS (MALDI+, DCTB, CH_2Cl_2): m/z: 1327 (95; merged peaks of $[M]^{+\bullet}$ and $^{13}C_1-[M]^{+\bullet}$), 1359 (100; merged peaks of $[M]^{+\bullet}$ and $^{13}C_1-[M]^{+\bullet}$ of O_2 adduct), 1391 (60; merged peaks of $[M]^{+\bullet}$ and $^{13}C_1-[M]^{+\bullet}$ of twofold O_2 adduct);[39] HRMS (MALDI+, DCTB, CH_2Cl_2/MeOH): m/z calcd for $C_{104}H_{78}$: 1326.6098 $[M]^{+\bullet}$; found: 1326.6140.

Final remark: Further attempts to treat sulfone **5** with other dienophiles, including dimethyl acetylenedicarboxylate, dimethylfumarate, 1,4-anthraquinone and even C_{60}-fullerene, largely failed; very complex mixtures of products were obtained in these cases. In the case of 1,4-anthraquinone and dimethylfumarate, the MALDI MS of the crude product mixtures indicated the formation of threefold cycloaddition products in minor amounts (<5%).

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[1] a) R. Mondal, R. M. Adhikari, B. K. Shah, D. C. Neckers, *Org. Lett.* **2007**, *9*, 2505–2508; b) E. Clar, *Polycyclic Hydrocarbons, Vol. 1, 2*, Academic Press, London, New York, **1964**; c) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, New York, **1997**.

[2] a) R. Rieger, K. Müllen, *J. Phys. Org. Chem.* **2010**, *23*, 315–325; b) D. D. L. Chung, *J. Mater. Sci.* **2002**, *37*, 1475–1489.

[3] S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603–605.

[4] a) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028–5048; b) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945; c) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460–492; *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483.

[5] a) G. K. R. Senadeera, P. V. V. Jayaweera, V. P. S. Perera, K. Tennakone, *Solar Energy* **2002**, *73*, 103–108; b) C. Videlot, D. Fichou, F. Garnier, *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1335–1338; c) S. C. Dahlberg, M. E. Musser, *J. Chem. Phys.* **1979**, *71*, 2806–2810.

[6] a) J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, *4*, 15–18; b) H. E. Katz, Z. Bao, S. L. Gilat, *Acc. Chem. Res.* **2001**, *34*, 359–369; c) M. L. Tang, T. Okamoto, Z. Bao, *J. Am. Chem. Soc.* **2006**, *128*, 16002–16003.

[7] a) S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2003**, *5*, 4245–4248; b) L. C. Picciolo, H. Murata, Z. H. Kafafi, *Appl. Phys. Lett.* **2001**, *78*, 2378–2380; c) M. A. Wolak, B. Jang, L. C. Palilis, Z. H. Kafafi, *J. Phys. Chem. B* **2004**, *108*, 5492–5499.

[8] a) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99–117; b) A. R. Murphy, J. M. J. Fréchet, P. Chang, J. Lee, V. Subramanian, *J. Am. Chem. Soc.* **2004**, *126*, 1596–1597.

[9] R. Schmidt, S. Göttling, D. Leusser, D. Stalke, A. M. Krause, F. Würthner, *J. Mater. Chem.* **2006**, *16*, 3708–3714.

[10] F. Valiyev, W. S. Hu, H. Y. Chen, M. Y. Kuo, I. Chao, Y. T. Tao, *Chem. Mater.* **2007**, *19*, 3018–3026.

[11] a) C. D. Sheraw, T. N. Jackson, D. L. Eaton, J. E. Anthony, *Adv. Mater.* **2003**, *15*, 2009–2011; b) M. D. Curtis, J. Cao, J. W. Kampf, *J. Am. Chem. Soc.* **2004**, *126*, 4318–4328.

[12] a) E. Clar, *Chem. Ber.* **1939**, *72B*, 2137–2139; b) H. Angliker, E. Rommel, J. Wirz, *Chem. Phys. Lett.* **1982**, *87*, 208–212.

[13] M. Watanabe, K. Y. Chen, Y. J. Chang, T. J. Chow, *Acc. Chem. Res.* **2013**, *46*, 1606–1615.

[14] a) D. Kuck, *Angew. Chem.* **1984**, *96*, 515–516; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 508–509; b) D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449–1460; c) D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **1989**, *101*, 626–628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 595–597; d) D. Kuck, E. Neumann, A. Schuster, *Chem. Ber.* **1994**, *127*, 151–164; e) T. X. Zhang, L. Zhou, X. P. Cao, D. Kuck, *Chin. J. Org. Chem.* **2007**, *27*, 946–957.

[15] G. Markopoulos, L. Henneicke, J. Shen, Y. Okamoto, P. G. Jones, H. Hopf, *Angew. Chem.* **2012**, *124*, 13057–13060; *Angew. Chem. Int. Ed.* **2012**, *51*, 12884–12887.

[16] D. Kuck, *Naturwiss. Rundsch.* **2013**, *66*, 138–139.

[17] a) D. Kuck, *Chem. Rev.* **2006**, *106*, 4885–4925; b) D. Kuck, *Pure Appl. Chem.* **2006**, *78*, 749–775.

[18] D. Kuck, A. Schuster, R. A. Krause, J. Tellenbröker, C. P. Exner, M. Penk, H. Bögge, A. Müller, *Tetrahedron* **2001**, *57*, 3587–3613.

[19] J. G. Brandenburg, S. Grimme, P. G. Jones, G. Markopoulos, H. Hopf, M. K. Cyranski, D. Kuck, *Chem. Eur. J.* **2013**, *19*, 9930–9938.

[20] a) C. Kitamura, *Chem. Rec.* **2012**, *12*, 506–514, and references therein; b) C. Kitamura, A. Takenaka, T. Kawase, T. Kobayashi, H. Naito, *Chem. Commun.* **2011**, *47*, 6653–6655, and references therein; c) C. Kitamura, T. Ohara, A. Yoneda, T. Kawase, T. Kobayashi, H. Naito, *Chem. Lett.* **2011**, *40*, 58–59; d) C. Kitamura, C. Matsumo-

to, A. Yoneda, T. Kobayashi, H. Naito, T. Komatsu, *Eur. J. Org. Chem.* **2010**, 2571–2575; e) C. Kitamura, Y. Abe, T. Ohara, A. Yoneda, T. Kawase, T. Kobayashi, H. Naito, T. Komatsu, *Chem. Eur. J.* **2010**, *16*, 890–898.

[21] a) J. Reichwagen, H. Hopf, A. Del Guerzo, C. Belin, H. Bouas-Laurent, J. P. Desvergne, *Org. Lett.* **2005**, *7*, 971–974; b) J. Reichwagen, H. Hopf, J. P. Desvergne, A. Del Guerzo, H. Bouas-Laurent, *Synthesis* **2005**, *20*, 3505–3507; c) C. Giansante, G. Raffy, C. Schäfer, H. Rahma, M. T. Kao, A. G. L. Olive, A. Del Guerzo, *J. Am. Chem. Soc.* **2011**, *133*, 316–325.

[22] T. M. Long, T. M. Swager, *Adv. Mater.* **2001**, *13*, 601–604.

[23] Y. Jiang, C. F. Chen, *Eur. J. Org. Chem.* **2011**, 6377–6403.

[24] a) J. Tellenbröker, D. Kuck, *Angew. Chem.* **1999**, *111*, 1000–1004; *Angew. Chem. Int. Ed.* **1999**, *38*, 919–922; b) X. P. Cao, D. Barth, D. Kuck, *Eur. J. Org. Chem.* **2005**, 3482–3488; c) L. Zhou, X. P. Cao, G. B. Neumann, H. G. Stammler, D. Kuck, *Synlett* **2005**, 2771–2775; d) B. Bredenkötter, S. Henne, D. Volkmer, *Chem. Eur. J.* **2007**, *13*, 9931–9938; e) P. E. Georghiou, L. Dawe, H. A. Tran, J. Stübe, B. Neumann, H. G. Stammler, D. Kuck, *J. Org. Chem.* **2008**, *73*, 9040–9047; f) T. Wang, Z. Y. Li, A. L. Xie, X. J. Yao, X. P. Cao, D. Kuck, *J. Org. Chem.* **2011**, *76*, 3231–3238; g) S. Henne, B. Bredenkötter, A. A. Dehghan Baghi, R. Schmid, D. Volkmer, *Dalton Trans.* **2012**, *41*, 5995–6002.

[25] a) L. Zhou, T. X. Zhang, B. R. Li, X. P. Cao, D. Kuck, *J. Org. Chem.* **2007**, *72*, 6382–6389; b) E. U. Mughal, D. Kuck, *Org. Biomol. Chem.* **2010**, *8*, 5383–5389; c) E. U. Mughal, D. Kuck, *Eur. J. Org. Chem.* **2012**, 3416–3423.

[26] a) M. Harig, B. Neumann, H. G. Stammler, D. Kuck, *Eur. J. Org. Chem.* **2004**, 2381–2397; b) Y. Kirchwehm, A. Damme, T. Kupfer, H. Braunschweig, A. Krüger, *Chem. Commun.* **2012**, *48*, 1502–1504; c) J. Vile, M. Carta, C. G. Bezzu, N. B. McKeown, *Polym. Chem.* **2011**, *2*, 2257–2260; d) R. Saravanakumar, G. Markopoulos, L. G. Bahrin, P. G. Jones, H. Hopf, *Synlett* **2013**, *24*, 453–456.

[27] H. Langhals, M. Rauscher, J. Strübe, D. Kuck, *J. Org. Chem.* **2008**, *73*, 1113–1116.

[28] W. X. Niu, E. Q. Yang, Z. F. Shi, X. P. Cao, D. Kuck, *J. Org. Chem.* **2012**, *77*, 1422–1434.

[29] J. Tellenbröker, Doctoral Thesis, Bielefeld University, **1999**.

[30] a) J. L. Segura, N. Martín, *Chem. Rev.* **1999**, *99*, 3199–3246; b) R. L. Funk, K. P. C. Vollhardt, *Chem. Soc. Rev.* **1980**, *9*, 41–61; c) S. Kotha, D. Kashinath, P. Khedkar, *Synthesis* **2007**, *21*, 3357–3360.

[31] a) S. Kotha, P. Khedkhar, *J. Org. Chem.* **2009**, *74*, 5667–5670; b) S. Kotha, P. Khedkhar, *Chem. Rev.* **2012**, *112*, 1650–1680.

[32] K. Nikitin, H. Müller-Bunz, Y. Ortin, J. Muldoon, M. J. McGlinchey, *Org. Lett.* **2011**, *13*, 256–259.

[33] a) C. Burgdorff, T. Kircher, H. G. Löhmannsröben, *Spectrochim. Acta Part A* **1988**, *44*, 1137–1141; b) C. Burgdorff, H. G. Löhmannsröben, *J. Lumin.* **1994**, *59*, 201–208.

[34] S. T. Roberts, R. E. McAnally, J. N. Mastron, D. H. Webber, M. T. Whited, R. L. Brutchey, M. E. Thompson, S. E. Bradforth, *J. Am. Chem. Soc.* **2012**, *134*, 6388–6400.

[35] a) A. M. Müller, Y. S. Avlasevich, W. W. Schoeller, K. Müllen, C. J. Bardeen, *J. Am. Chem. Soc.* **2007**, *129*, 14240–14250; b) J. J. Burdett, C. J. Bardeen, *Acc. Chem. Res.* **2013**, *46*, 1312–1320; c) H. Yamagata, J. Norton, E. Hontz, Y. Olivier, D. Beljonne, J. L. Brédas, R. J. Silbey, F. C. Spano, *J. Chem. Phys.* **2011**, *134*, 204703–204711; d) S. H. Lim, T. G. Bjorklund, F. C. Spano, C. J. Bardeen, *Phys. Rev. Lett.* **2004**, *92*, 107402–107404.

[36] This is intriguing, because the parent tribenzotriquinacenes, for example, the bridgehead tetramethyl derivative of **1**, were calculated to have a nonsymmetrical electron-density distribution in the HOMOs and LUMOs (see the Supporting Information).

[37] a) R. E. Dale, J. Eisinger, W. E. Blumberg, *Biophys. J.* **1979**, *26*, 161–193; b) B. W. van der Meer, *Rev. Mol. Biotechnol.* **2002**, *82*, 181–196; c) G. D. Scholes, *Annu. Rev. Phys. Chem.* **2003**, *54*, 57–87.

[38] a) S. Fery-Forgues, D. Lavabre, *J. Chem. Educ.* **1999**, *76*, 1260–1264; b) A. M. Brouwer, *Pure Appl. Chem.* **2011**, *83*, 2213–2228.

[39] The measurement is accompanied by the addition of dioxygen to compound **11** to produce endoperoxides, the molecular ions of which appeared at *m*/*z* 1359 and *m*/*z* 1391, respectively.

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