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From Chrysene to Double [5]Helicenes

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Glyoxylic functionalization of chrysene by Friedel–Crafts acylation with ethyl chloroglyoxylate or by bromination followed by substituent exchange enables the formation of bis[5]helicene-tetracarboxylates and tetracarboxdiimides through Perkin reactions and palladium-catalyzed cyclizations. Tetrasubstituted bishelicenic dichrysenoanthracenes and dinaphthochrysenes are thus obtained from chrysene in four to six steps. In the cyclization to dinaphthochrysenes, a rearrangement of the conjugated carbon skeleton is identified as side reaction. In solution, the diimides form mixtures of *M*,*P*- and *M*,*M*/*P*,*P*-diastereomers, which equilibrate at room temperature when the helices are distant but equilibrate only upon heating when the helices are close and acting in concert. The nonplanar arene geometry allows close π-contacts in two dimensions between neighboring molecules in the crystal.

Introduction

Large, highly condensed arenes with a small number of aromatic sextets offer smaller band gaps and concordantly longer wavelength absorption than their more sextetted isomers, at the expense of reduced chemical stability, for example against air-oxidation. This low stability can be dramatically improved by the incorporation of electron-withdrawing substituents, such as carboxylic ester and especially dicarboximide groups. These substituents not only improve the stability by lowering the LUMO energies, but also reduce the band gap with a further redshift of the absorption edge and can improve solubility through the introduction of alkyl chains of various lengths. The ability of alkylimide groups to render planar arenes soluble is nevertheless limited by the size of the arene for a given number of substituents, as we experienced recently with a diperyleno-anthracene bearing two long α-branched alkylimide groups, which is soluble only on heating in chlorinated solvents.[1] The strong coplanar aggregation of large arenes may be reduced by the introduction of a bend or twist, as is illustrated by the far superior solubilities of helicenes compared with their planar phenacene isomers.[2] Even slight deviations from planarity such as induced by a [4]helicene fragment may give rise to good solubilities and to hindered crystallization even with the shortest alkyl ester substituents, to the extent that crystallization may be suppressed by formation of an anisotropic glass.[3]

An interesting starting material for the construction of nonplanar sextet-poor higher arenes is chrysene **1**, which (a) combines two sextets with three nonsextetted double bonds, (b) contains two bay regions that are suitable for the build-up of sterically crowded structures, and (c) may offer a suitable regioselectivity upon double substitution in positions 6 and 12 to graft arylethylenyl substituents in appropriate positions for the formation of two helicenic fragments in the bay regions. Alternatively, two chrysene-based helicenic fragments in the same molecule could be generated by connecting two chrysenes monofunctionalized in the 6-position by an arylenedivinylene bridge.

Results and Discussion

The Friedel–Crafts acylation of chrysene with ethyl chloroglyoxylate $ClCOCO_2Et$ yields, after hydrolysis of the obtained ethyl ester **2**, chrysenyl-6-glyoxylic acid **3**, which allowed us recently to construct a chrysene-based [7]helicene through glyoxylic Perkin condensation[4] with its own reduction product chrysenyl-6-acetic acid.[5] However, neither **2** nor chrysenyl-6-acetic acid methyl ester could be made to undergo a second acylation with $ClCOCO_2Et$ to yield a 6,12-disubstituted product, with **2** being unreactive and the acetic ester reacting in the 2- or 3-position.

An alternative approach to arylene-diglyoxylic esters that we recently applied to 1,5-dibromoanthracene, which was obtained in 80% yield, is the reaction of an arylene-dianion, obtained from the corresponding dibromoarene, with diethyl oxalate EtO_2CCO_2Et.[6] We therefore attempted to transform the known 6,12-dibromochrysene **4**,[7] which is

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conveniently obtained by bromination of **1** with Br_2 in chloroform, into the corresponding diglyoxylic ester **5** and acid **6** via the chrysene 6,12-dianion and its reaction with diethyl oxalate. In contrast to the anthracenylene-1,5-dianion, which forms in good yield with butyllithium at –94 °C but decomposes partially at room temperature, yields of chrysenylene-6,12-dianion improve (to give **5** in 75% yield) if, after addition of butyllithium, the reaction mixture is warmed to room temperature. This shows that whereas the chrysenylene-dianion is more stable once formed due to the twofold sextet stabilization, its formation requires harsher conditions due to the shorter distance between the two substitution positions.

The mono- and diglyoxylic acids **3** and **6** were subjected to double Perkin condensations with 2,5-dibromophenylene-1,4-diacetic acid **7**[1] and 2-bromophenylacetic acid **8**, respectively, followed by same-pot fourfold esterification with excess alkanol and 1-bromoalkane in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to yield dibromo phenylene-bis(chrysenylmaleic) tetrabutyl ester **9** and chrysenylene-bis(bromophenylmaleic) tetrapropyl ester **10**, respectively, in 69 and 71% yield (Figure 1). These highly congested yet conformationally flexible bismaleates show, as usual,[1,5,6] extremely broadened proton NMR spectra due to slow rotations on the measurement timescale.

The dehydrobromination of **9** in DMA at 110 °C in the presence of catalytic palladium(II) acetate activated with tricyclohexylphosphine[8] yielded dichrysenoanthracene tetraester **11** in 52% yield, which had to be purified by careful column chromatography and multiple recrystallizations to eliminate traces of unidentified aromatic side products of similar polarity. The nonplanarity of **11** is apparent in its proton NMR spectrum: Instead of two triplets for the oxygen-bound methylenes of the two nonequivalent butyl chains, the spectrum shows four double triplets in the region around 4 ppm – the two hydrogen signals of each of the two methylene groups become differentiated by the helical environment, and couple with each other (Figure 2). The aromatic part of the spectrum of **11** shows the expected 11 signals for the 11 aromatic protons per half-molecule; there is no doubling of the signals due to any coexistence of two diastereomers (*M*,*P* and *M*,*M*/*P*,*P*) in solution.

The analogous double cyclization of **10** yielded naphthochrysene tetraester **12**[9] in significantly lower yield of 34%, but, in this case, a relatively large amount (12%) of a slightly more polar side product could be isolated in moderate purity by careful column chromatography. Compared with **12**, this side product has the same molecular mass but shows a doubled set of signals in the ^{1}H NMR spectrum, with the same multiplicities and similar chemical shifts, except for a very pronounced upfield shift for one of the four distinct propyl chains. These data point to the side product being the isomeric dinaphthochrysene **13**, where one of the two bromophenylmaleate substituents in **10** has migrated from the 6-position to the 5-position on the chrysene core, followed by cyclization onto the 6-position, leaving the specific d-t-t-d ^{1}H NMR signal pattern of the four four-hydrogen-bearing benzene nuclei untouched. This naphthalene reversal puts one of the propyloxycarbonyl substituents under significant steric strain and forces it out of the main molecular plane, to experience the shielding influence

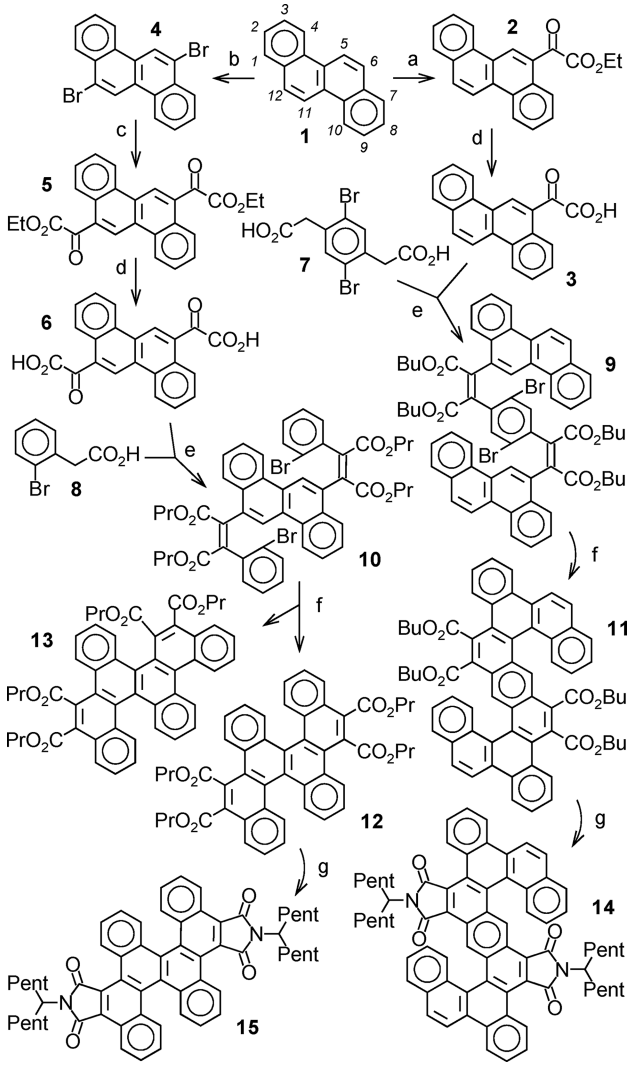

Figure 1. Synthesis of chrysene-based tetracarboxy-substituted bis[5]helicenes. Reagents and conditions: (a) $ClCOCO_2Et$, $ZrCl_4$, CH_2Cl_2, 25 °C, 16 h, 81%;[5] (b) Br_2, $CHCl_3$, reflux, 16 h, 74%; (c) THF, BuLi, –94 °C to 25 °C, 4 h, then addition of EtO_2CCO_2Et, –94 °C to 25 °C, 45 min, 75%; (d) $NaHCO_3$, EtOH/H_2O, reflux, 4 h, 100%; (e) NEt_3, Ac_2O, THF, reflux, 18 h, then addition of ROH, RBr, DBU, reflux, 2 h, 69% (**9**) and 71% (**10**); (f) $Pd(OAc)_2$, PCy_3, K_2CO_3, DMA, 110 °C, 16 h, 52% (**11**) or 34% (**12**) + 12% (**13**); (g) $Pent_2CHNH_2$, imidazole, *o*-$C_6H_4Cl_2$, reflux, 16 h, 74% (**14**) or 61% (**15**); Pent = *n*-pentyl.

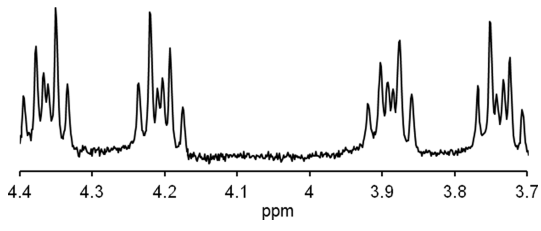

Figure 2. ^{1}H NMR spectrum of **11** in $CDCl_3$: region of the OCH_2 protons showing four double triplets between δ = 4.4 and 3.7 ppm.

of one of the terminal aromatic sextets of the central chrysene moiety; this explains the strong differentiation of one of the chains observed by ^{1}H NMR spectroscopy. A selective relative upfield shift for the signals of one of the four sets of propyl carbon atoms is also notable in the ^{13}C NMR spectrum, together with a selective relative downfield shift of one of the four carbonyl carbon signals. Similar to **11**, the oxygen-bound methylenes of the alkyl chains in **12** and **13** show double triplet ^{1}H NMR signals due to the absence of mirror symmetry on the aromatic plane.

The nonseparable impurity signals discernible in the ^{1}H NMR spectrum of **13** might stem from the corresponding doubly rearranged symmetric isomer, in which the inversion on chrysene positions 5 and 6 is mirrored by the same inversion on positions 11 and 12. Similar rearrangements might account for the impurities in crude **11**, whereas a greater abundance of rearranged product upon double cyclization of **10** compared with that of **9** may be caused by the smaller size and thus greater mobility of the migrating group in **10**. This observed rearrangement is reminiscent of the migrations between aromatic substitution positions observed in Pd-catalyzed Heck and Suzuki reactions.[10]

To obtain the target diimides, we treated esters **11** and **12** with excess 6-aminoundecane and imidazole in *o*-dichloroethane heated to reflux, and obtained the respectively red and orange diimides **14** and **15** in 74 and 61% yield. Like the esters, these imides bearing four relatively short peripheral pentyl chains are soluble in chlorinated solvents at room temperature and dissolve in hot butanol, which was our solvent of choice for recrystallizations.

In contrast to the esters, the imides show a doubling of the aromatic signals in the ^{1}H NMR spectrum, indicating a coexistence of the *M*,*P* and *M*,*M*/*P*,*P* diastereomers in solution. As the additional imide cycles can be assumed to rigidify the polycyclic cores, it appears that the *M*–*P* helix reversal in the imides is slow compared with the experimental timescale. To verify that the signal doubling can be attributed without ambiguity to reversible helix inversion and not to any other irreversible isomerization, we recorded the spectrum of **14** at various temperatures in high-boiling $Cl_2DC–CDCl_2$, but could not observe any change of the approximate 1.2:1 integral ratio between the two sets of signals. However, when the solvent was changed to $CDCl_3$ or CD_2Cl_2, which, in contrast to 1,1,2,2-tetrachloroethane, possess a permanent dipole moment, the ratio was reversed to approximately 1:1.5 in chloroform and approximately 1:2 in dichloromethane (Figure 3). To ensure that these different ratios are not caused by random variations between samples, we conducted these experiments on a single sample, changing solvents between spectra by evaporation, and we recorded spectra in $Cl_2DC–CDCl_2$ before and after those in the other solvents, which confirmed that the ratio in the same solvent is not history-dependent. This behavior of **14** contrasts with the observation of a history-dependent behavior of **15**: Here again, two complete sets of signals are observed, but the equilibration between the conformers is not instantaneous upon dissolution at room temperature. On one occasion, we collected a small slowly formed second crop of crystals upon recrystallization, which showed only one single set of signals of one conformer in $Cl_2DC–CDCl_2$ at room temperature, but short heating to reflux led to the appearance of a second set of signals with approximately 0.3:1 intensity ratio to the main set, which corresponds to the ratio observed with samples from the main, more quickly precipitated recystallization crop. Changing the solvent to CD_2Cl_2 did not change the ratio.

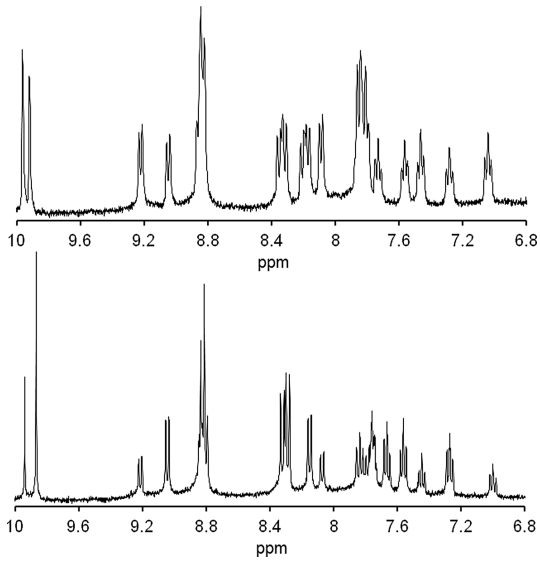

Figure 3. ^{1}H NMR spectrum of **14** in $Cl_2DC–CDCl_2$ (apolar, above) and CD_2Cl_2 (polar, below): region of the aromatic protons between δ = 10.0 and 6.8 ppm, showing distinct sets of signals for two conformers of solvent-dependent relative abundance.

The two diastereomeric forms of **14** thus interconvert in solution at room temperature, whereas the two diastereomeric forms of **15** only do so at elevated temperatures. The two [5]helicene moieties share more carbon atoms in **15** than in **14**. This allows a more independent helix reversal in **14** and requires more cooperativity between the two helices in **15** during the reversal of one of them.

In the ^{13}C NMR spectra of both **14** and **15**, the two linear pentyl moieties of each swallow-tail alkylimide group are differentiated, giving rise to two sets of five signals. This is analogous to the differentiation of the two OCH_2 hydrogen signals of each alkyl chain in the ^{1}H NMR spectra of **11**, **12**, and **13** brought about by the nonplanarity of the polycyclic molecular cores.

Crystals of **14** of sufficient quality for crystallographic structure determination by X-ray diffraction could be obtained by crystallization from *p*-xylene (Figure 4). All molecules are equivalent and in *meso* (*M*,*P*) configuration. They are arranged in loose stacks, with the chrysene units of adjacent stacks interdigitated such that the densely packed chrysene blades lead to close π-orbital contact between molecules along the stacking direction as well as between molecules along a direction perpendicular to the stacks, via the connecting anthracene units that link two chrysene blades that are in contact with different neigh-

boring stacks. In the third dimension, these layers of bi-dimensionally π-connected aromatic moieties are separated by the peripheral alkyl substituents and *p*-xylene lattice solvent molecules.

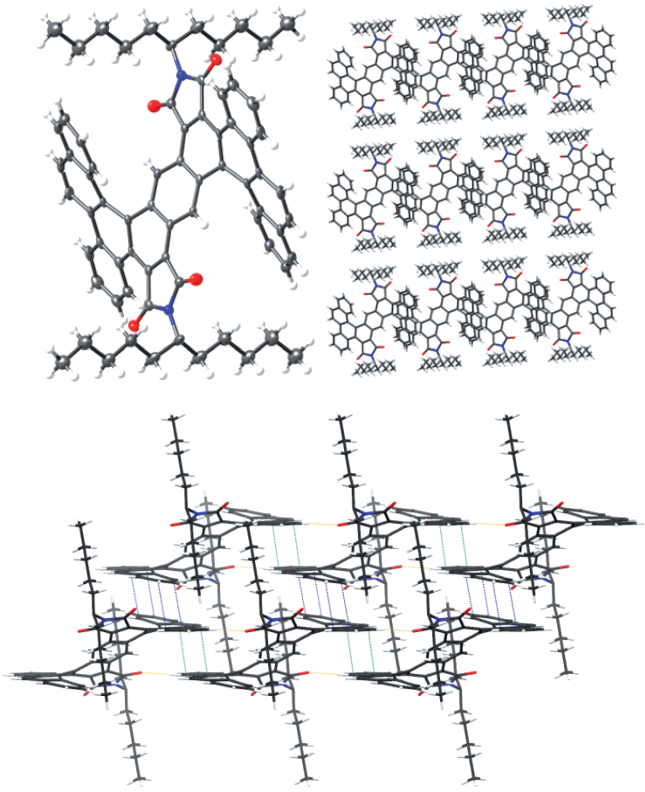

Figure 4. Crystallographic structure of **14**. Top, left: Single molecule of **14**, thermal ellipsoids are depicted at the 50% level. Top, right: View along the stacking direction showing the arrangement in π-connected layers separated by alkyl regions. Lattice *p*-xylene molecules are omitted for clarity. Bottom: Portion of the crystal structure showing the packing of the diimide, forming layers by π-stacking; close carbon–carbon contacts are depicted by green and blue dashed lines, with C–C distances as short as ca. 3.286(4) and 3.387(4) Å (blue) and 3.399(4) Å (green); weak C–H···O hydrogen bonds are also present with d_{C-O} = 3.392(4) Å (orange dashed lines). C black, H white, N blue, O red.

The absorption spectra of tetraesters **11** (yellow) and **12** (pale-yellow) and the diimides **14** (red) and **15** (orange) testify to the usual decrease in optical band gap from ester to corresponding imide. The shifts of absorption edge (**11**: 500 nm/2.48 eV, **12**: 440 nm/2.82 eV, **14**: 620 nm/2.00 eV, **15**: 530 nm/2.34 eV in dilute chloroform solution, Figure 5) from **11** to **14** and from **12** to **15** are notably of identical absolute energy value (–0.48 eV), corresponding to relative reductions of the band gap energy by about one fifth and one sixth, respectively. The proportionally greater band gap reduction from **11** to **14** is in line with our previously reported findings that changes of the electron-withdrawing substitution at central *a*,*h*-diannellated anthracene bridges are particularly influential on the band gap of polycyclic arenes.[1,6]

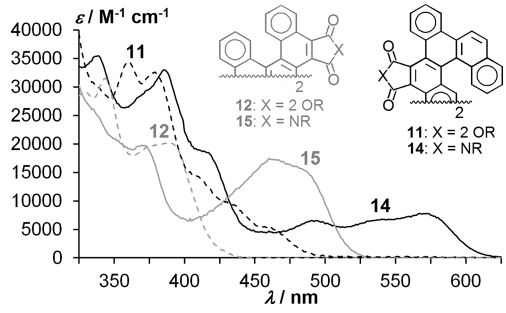

Figure 5. Absorption spectra (20 μM in $CHCl_3$) of tetraesters **11** and **12** (dashed) and diimides **14** and **15** (continuous). Black curves: **11** and **14**, gray curves: **12** and **15**.

The anodic and cathodic electrochemistry of **11**, **12**, **14**, and **15** was evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dichloromethane between +1.7 and –2.0 V vs. $Ag/AgNO_3$. Both dinaphthochrysenes **12** and **15** displayed reversible oxidation waves at $E_{1/2}$ = +1.11 V vs. the ferrocenium/ferrocene couple, with no discernible influence of the nature of the substituents on the oxidation potential. The dichrysenoanthracenes **11** and **14** show two oxidation waves, with little variation of the potentials from **11** to **14** induced by the substituents. Ester **11** underwent a reversible oxidation with $E_{1/2}$ = +0.92 V, followed by a second irreversible oxidation with $E_{1/2}$ = +1.26 V. Both oxidation processes for the corresponding imide **14** were irreversible ($E_{1/2}$ = +0.97 and +1.21 V).

Scanning cathodically, both imides show two apparently reversible reduction waves. In dinaphthochrysene **15**, the reductions are very close to one another, with $E_{1/2}$ = –1.57 and –1.67 V, whereas the separation is better for dichrysenoanthracene **14** at $E_{1/2}$ = –1.37 and –1.64 V. The larger peak separation, $\Delta E_{1/2}$, for **14** (240 mV from DPV) than in **15** ($\Delta E_{1/2}$ = 110 mV) suggests a better delocalization of the radical in the one-electron reduced compound over the aromatic core in **14** than in **15**. Reduction of the esters is considerably more difficult than of the imides, with $E_{1/2}$ = –1.82 for **11** and $E_{1/2}$ = –2.04 for **12** (from DPV).

From the first reduction and oxidation potentials and $E_{1/2}(Fc^+/Fc)$ = –4.80 eV, lowest unoccupied molecular orbital energies E_{LUMO} of –2.98 (**11**), –2.76 (**12**), –3.43 (**14**), and –3.23 (**15**) eV and highest occupied molecular orbital energies E_{HOMO} of –5.72 (**11**), –5.91 (**12**), –5.77 (**14**), and –5.91 (**15**) eV are obtained, which yield electrochemical band gaps of 2.74 (**11**), 3.15 (**12**), 2.34 (**14**), and 2.68 (**15**) eV. These band gaps are slightly larger than the optical band gaps inferred from the absorption spectra, implying exciton binding energies of 0.26 to 0.34 eV.

Conclusions

Polycyclic aromatic tetraalkyl esters and dialkylimides incorporating two [5]helicene fragments are accessible from chrysene in five or six steps through double Perkin reactions of chrysenylglyoxylic or chrysenylenediglyoxylic acids with dibromophenylenediacetic or bromophenylacetic acids fol-

lowed by Pd-catalyzed dehydrobrominations. From the Pd-catalyzed cyclization of doubly bromophenylmaleate-substituted chrysene, a rearranged side product could be isolated in which one of the substituents has migrated to an adjacent position on the chrysene core before cyclizing. The helicenic aromatic environment leads to a remarkable diastereotopic differentiation of the alkyl substituents in the NMR spectra both in the esters and in the imides, and to the formation of an equilibrium between *M*,*P* and *M*,*M*/*P*,*P* helix diastereomers of the imides in solution. The relative abundances of the diastereomers as detected by NMR spectroscopic analysis shift dynamically with solvent polarity at room temperature in dichrysenoanthracene-diimide **14**, where the two helical moieties are more distant and inversion of one helix can be assumed to only weakly effect the other, whereas equilibration necessitates heating in dinaphthochrysene-diimide **15**, where the two helices are more closely intertwined and helix inversion can be supposed to be more concerted and thus less free. The nonplanarity of the bishelicenic esters and imides renders them soluble in chlorinated solvents at room temperature even with rather short alkyl substituents, and the combination of imide substituents with an extended, rather sextet-poor π-electron system leads in **14** to a particularly broad absorption spectrum covering the visible wavelength region up to 620 nm, associated with a small optical band gap of 2.00 eV. The crystal packing of **14** is remarkable by its bidimensional distribution of π-contacts, which is made possible by the twisted aromatic core; in contrast to many planar alkyl-decorated large arenes that tend to form unidimensional π-stacks surrounded by alkyl peripheries, **14** forms 2D layers of closely packed arene moieties separated by layers of alkyl chains. The combination of this exceptional bidimensional electronic contact with acceptor-type behavior and moderate band gap could be of interest for application in organic electronics.

Experimental Section

6,12-Dibromochrysene (4):[7] Chrysene (**1**, 12.3 g, 228.3 g/mol, 54 mmol) was suspended in chloroform (300 mL), bromine (5.8 mL, 3.1 g/mL, 18.0 g, 159.8 g/mol, 113 mmol) in chloroform (100 mL) was added dropwise, and the heterogeneous mixture was heated to reflux for 16 h. After cooling to room temperature, methanol (300 mL) was added to complete the precipitation, the product was filtered off, rinsed with methanol and recrystallized from toluene (1.5 L), yield 15.3 g (386.1 g/mol, 40 mmol, 74%); white needles; m.p. 275–282 °C (with simultaneous sublimation) [ref.[7] 260 °C (dec.)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 2 H), 8.71 (d, 7.5 Hz, 2 H), 8.43 (d, 7.5 Hz, 2 H), 7.78 (t, 7.5 Hz, 2 H), 7.75 (t, 7.5 Hz, 2 H) ppm.

Diethyl Chrysenylene-6,12-diglyoxylate (5): To a stirred suspension of finely powdered 6,12-dibromochrysene **4** (3.00 g, 386.1 g/mol, 7.8 mmol) in anhydrous THF (250 mL) under argon, a solution of butyllithium (2.5 M in hexane, 12.5 mL, 31.3 mmol) was added dropwise at –94 °C (acetone–liquid nitrogen cooling bath), and the mixture was stirred for 3 h under slow warming to room temperature. After 1 h more at room temperature, the mixture was cooled again to –94 °C, and diethyl oxalate (10.6 mL, 1.077 g/mL, 11.4 g, 146.1 g/mol, 78 mmol) was quickly added. After 15 min more at –94 °C, the cooling bath was removed and stirring was continued for 30 min at room temperature. CH_2Cl_2 (100 mL) was added, followed by 1 M hydrochloric acid (50 mL), the phases were separated, the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic phases were dried with sodium sulfate and concentrated. Cold methanol (500 mL) was added while stirring, and the precipitated product was filtered off and purified by column chromatography on silica (CH_2Cl_2) and recrystallized from ethanol, yield 2.40 g (428.4 g/mol, 5.6 mmol, 75%); thin, yellow needles; m.p. 187–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (s, 2 H), 8.92 (dd, *J* = 8, 1 Hz, 2 H), 8.68 (dd, *J* = 8, 1 Hz, 2 H), 7.82 (dt, *J* = 1, 8 Hz, 2 H), 7.77 (dt, *J* = 1, 8 Hz, 2 H), 4.59 (q, *J* = 7 Hz, 4 H), 1.51 (t, *J* = 7 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.7, 164.1, 131.4, 131.1, 129.6, 129.1, 128.9, 128.8, 128.7, 126.5, 123.2, 63.1, 14.5 ppm. FD-HRMS: *m*/*z* calcd. for $C_{26}H_{20}O_6$ $[M]^+$ 428.1260; found 428.1272.

Chrysenylene-6,12-diglyoxylic Acid (6): Diethyl chrysenylene-6,12-diglyoxylate **5** (4.28 g, 428.4 g/mol, 10 mmol) was suspended in ethanol (200 mL), a solution of sodium hydrogen carbonate (20 g) in water (400 mL) was added, and the mixture was stirred and heated to reflux for 4 h. The resulting mostly homogeneous solution was freed from a small quantity of insolubles by filtration and poured into 2% aqueous hydrochloric acid (1 L). The gelatinous precipitate was filtered off, washed with a small quantity of water and allowed to dry in air. The orange solid product (4.17 g, quantitative yield) was used without further purification, m.p. > 300 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.35 (s, 2 H), 8.96 (d, *J* = 8 Hz, 2 H), 8.71 (d, *J* = 8 Hz, 2 H), 7.95 (t, *J* = 8 Hz, 2 H), 7.89 (t, *J* = 8 Hz, 2 H) ppm (no discrete acid proton detected). ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 191.5, 166.7, 131.5, 130.4, 128.7, 128.6, 128.3, 128.1, 127.1, 125.6, 123.5 ppm. FD-HRMS: *m*/*z* calcd. for $C_{22}H_{12}O_6$ $[M]^+$ 372.0634; found 372.0644.

Tetrabutyl 2,5-Dibromo-1,4-phenylenebis[(6-chrysenyl)maleate] (9): Chrysenyl-6-glyoxylic acid **3**[5] (4.80 g, 300.3 g/mol, 16 mmol), 2,5-dibromophenylene-1,4-diacetic acid **7**[1] (2.64 g, 352.0 g/mol, 7.5 mmol), triethylamine (7.5 g, 101.2 g/mol, 74 mmol), and acetic anhydride (10 g, 102.1 g/mol, 0.1 mol) were stirred in THF (150 mL) and heated to reflux under exclusion of moisture for 18 h. Then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 25 g, 152.2 g/mol, 0.16 mol), butanol (50 g, 74.1 g/mol, 0.67 mol), and 1-bromobutane (50 g, 137.0 g/mol, 0.36 mol) were added and heating to reflux was continued for 2 h. Chloroform (500 mL) and 10% aqueous HCl (300 mL) were added, the phases were separated, and the organic phase was dried with sodium sulfate and concentrated. The residue was purified by recrystallization from butanol, purified by column chromatography on silica ($CHCl_3$), and again recrystallized from butanol, yield 5.93 g (1141.0 g/mol, 5.2 mmol, 69%); pale-yellow solid; m.p. 173–177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80–6.60 (several broad overlapping peaks, 24 H), 4.40–3.15 (3 broad overlapping peaks, 8 H), 1.90–0.30 (several broad overlapping peaks, 28 H) ppm. The strong signal broadening due to slow rotations, evident from the ^{1}H NMR spectrum, did not allow the recording of a meaningful ^{13}C NMR spectrum. FD-HRMS: *m*/*z* calcd. for $C_{66}H_{60}Br_2O_8$ $[M]^+$ 1140.2634; found 1140.2725.

Tetrapropyl 6,12-Chrysenylenebis[(2-bromophenyl)maleate] (10): Crude diacid **6** (4.17 g, 10 mmol), 2-bromophenylacetic acid **8** (5.38 g, 215.0 g/mol, 25 mmol), triethylamine (10 g, 101.2 g/mol, 0.10 mol), and acetic anhydride (13 g, 102.1 g/mol, 0.13 mol) were stirred in THF (150 mL) and heated to reflux under exclusion of moisture for 18 h. Then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 40 g, 152.2 g/mol, 0.26 mol), propanol (60 g, 60.1 g/mol, 1.0 mol),

and 1-bromopropane (60 g, 123.0 g/mol, 0.5 mol) were added and heating to reflux was continued for 2 h. $CHCl_3$ (700 mL) and 10% aqueous HCl (400 mL) were added, the phases were separated, and the organic phase was dried with sodium sulfate and concentrated. The viscous liquid residue crystallized slowly upon addition of methanol while stirring. The solid product was filtered off and purified by column chromatography on silica ($CHCl_3$) and another crystallization was conducted by adding methanol while stirring to the liquid, yield 6.61 g (934.7 g/mol, 7.1 mmol, 71%); off-white solid; m.p. 225–229 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65–8.47 (broad, 4 H), 8.24 (d, J = 8 Hz, 2 H), 7.80–7.50 (broad, 4 H), 7.45–7.28 (broad, 2 H), 7.05–6.87 (broad, 2 H), 6.87–6.72 (m, 4 H), 4.21 (t, J = 7 Hz, 4 H), 4.25–4.07 (broad, 4 H), 1.68 (sext, J = 7 Hz, 4 H), 1.70–1.50 (2 broad overlapping peaks, 4 H), 0.88 (t, J = 7 Hz, 6 H), 0.87–0.67 (2 broad overlapping peaks) ppm. The strong signal broadening due to slow rotations, evident from the ^{1}H NMR spectrum, did not allow the recording of a meaningful ^{13}C NMR spectrum. FD-HRMS: m/z calcd. for $C_{50}H_{46}Br_2O_8$ $[M]^+$ 934.1539; found 934.1537.

Tetrabutyl Dichryseno[7,6-*a*;7,6-*h*]anthracene-7,8,20,21-tetracarboxylate (11): Tetrabutyl 2,5-dibromo-1,4-phenylenebis[(6-chrysenyl)-maleate] **9** (1.14 g, 1141.0 g/mol, 1 mmol), palladium(II) acetate (0.09 g, 224.5 g/mol, 0.4 mmol), tricyclohexylphosphine (0.20 g, 280.4 g/mol, 0.7 mmol), and potassium carbonate (1.38 g, 138.2 g/mol, 10 mmol) were stirred in dimethylacetamide (DMA, 20 mL) under argon at 110 °C for 16 h. $CHCl_3$ (100 mL) was added, the solids were filtered off, the solvents were evaporated (rotary evaporator with boiling water bath, 12 mbar), and the residue was purified by column chromatography on silica ($CHCl_3$) and threefold recrystallization from butanol, yield 0.51 g (979.2 g/mol, 0.52 mmol, 52%); yellow, semiamorphous solid without clear melting-point. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (s, 2 H), 8.77 (d, J = 9 Hz, 2 H), 8.76 (d, J = 8 Hz, 2 H), 8.43 (d, J = 8 Hz, 2 H), 8.19 (d, J = 9 Hz, 2 H), 8.05 (d, J = 8 Hz, 2 H), 8.04 (d, J = 8 Hz, 2 H), 7.65 (t, J = 8 Hz, 2 H), 7.59 (t, J = 8 Hz, 2 H), 7.53 (t, J = 8 Hz, 2 H), 7.36 (t, J = 8 Hz, 2 H), 4.36 (dt, J = 11, 7 Hz, 2 H), 4.21 (dt, J = 11, 7 Hz, 2 H), 3.89 (dt, J = 11, 7 Hz, 2 H), 3.74 (dt, J = 11, 7 Hz, 2 H), 1.62–1.52 (m, 4 H), 1.47–1.37 (m, 4 H), 1.36–1.14 (m, 8 H), 0.89 (t, J = 7 Hz, 6 H), 0.79 (t, J = 7 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 169.6, 167.8, 133.1, 132.0, 131.2, 130.7, 129.94, 129.90, 129.8, 129.6, 129.4, 128.3, 128.0, 127.6, 127.24, 127.19, 126.8, 126.7, 126.3, 125.7, 125.0, 124.7, 123.9, 120.9, 66.5, 66.3, 30.4, 30.3, 19.3, 19.2, 14.0, 13.8 ppm. FD-HRMS: m/z calcd. for $C_{66}H_{58}O_8$ $[M]^+$ 978.4132; found 978.4137.

Tetrapropyl Dinaphtho[1,2-*g*;1,2-*p*]chrysene-9,10,19,20-tetracarboxylate (12) and Tetrapropyl Dinaphtho[2,1-*g*;1,2-*p*]chrysene-5,6,11,12-tetracarboxylate (13): Tetrapropyl 6,12-chrysenylenebis[(2-bromophenyl)maleate] **10** (1.87 g, 934.7 g/mol, 2 mmol), palladium(II) acetate (0.18 g, 224.5 g/mol, 0.8 mmol), tricyclohexylphosphine (0.40 g, 280.4 g/mol, 1.4 mmol), and potassium carbonate (2.76 g, 138.2 g/mol, 20 mmol) were stirred in dimethylacetamide (DMA, 40 mL) under argon at 110 °C for 16 h. $CHCl_3$ (200 mL) was added, the solids were filtered off, the solvents were evaporated (rotary evaporator with boiling water bath, 12 mbar), and the residue was purified by column chromatography on silica ($CHCl_3$). The main product **12** was recrystallized from butanol, yield 524 mg (772.9 g/mol, 0.68 mmol, 34%) as a pale-yellow solid. The slightly more polar secondary product **13** formed a gel when a hot butanol solution of the compound was cooled to room temperature or below, but could nevertheless be separated from the butanol by vacuum filtration followed by drying in vacuo, yield 182 mg (772.9 g/mol, 0.24 mmol, 12%); pale-yellow solid that contains small inseparable amounts of presumably the doubly rearranged isomer.

Compound 12: Semiamorphous solid without a clear melting point. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.58 (d, J = 8 Hz, 2 H), 8.17 (d, J = 8 Hz, 2 H), 8.08 (d, J = 8 Hz, 2 H), 7.87 (d, J = 8 Hz, 2 H), 7.63 (t, J = 8 Hz, 2 H),7.42 (t, J = 8 Hz, 2 H), 7.39 (t, J = 8 Hz, 2 H), 7.25 (t, J = 8 Hz, 2 H), 4.57 (dt, J = 11, 7 Hz, 2 H), 4.51 (dt, J = 11, 7 Hz, 2 H), 3.39 (dt, J = 11, 7 Hz, 2 H), 3.25 (dt, J = 11, 7 Hz, 2 H), 1.87 (sext, J = 7 Hz, 4 H), 1.78 (sext, J = 7 Hz, 4 H), 1.06 (t, J = 7 Hz, 6 H), 0.92 (t, J = 7 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 170.6, 168.9, 133.5, 133.2, 131.2, 130.8, 130.7, 129.2, 128.7, 128.4, 128.1, 127.7, 127.54, 127.52, 127.45, 127.3, 126.5, 126.3, 68.60, 68.58, 22.6, 22.2, 10.9, 10.7 ppm. FD-HRMS: m/z calcd. for $C_{50}H_{44}O_8$ $[M]^+$ 772.3036; found 772.3029.

Compound 13: Semiamorphous solid without a clear melting point. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.24 (d, J = 8 Hz, 1 H), 8.76 (d, J = 8 Hz, 1 H), 8.65 (d, J = 8 Hz, 1 H), 8.21 (d, J = 8 Hz, 1 H), 8.14 (d, J = 8 Hz, 2 H), 8.07 (d, J = 8 Hz, 1 H), 7.91 (d, J = 8 Hz, 1 H), 7.88 (t, J = 8 Hz, 1 H), 7.79 (t, J = 8 Hz, 1 H), 7.63 (t, J = 8 Hz, 1 H), 7.51 (t, J = 8 Hz, 1 H), 7.49 (t, J = 8 Hz, 1 H), 7.46 (t, J = 8 Hz, 1 H), 7.43 (t, J = 8 Hz, 1 H), 7.31 (t, J = 8 Hz, 1 H), 4.54 (dt, J = 11, 7 Hz, 1 H), 4.49–4.35 (m, 3 H), 4.31 (dt, J = 11, 7 Hz, 1 H), 4.25 (dt, J = 11, 7 Hz, 1 H), 3.70 (dt, J = 11, 7 Hz, 1 H), 3.21 (dt, J = 11, 7 Hz, 1 H), 1.87 (sext, J = 7 Hz, 2 H), 1.77 (sext, J = 7 Hz, 2 H), 1.70 (sext, J = 7 Hz, 2 H), 1.12 (sext, J = 7 Hz, 2 H), 1.06 (t, J = 7 Hz, 3 H), 0.96 (t, J = 7 Hz, 3 H), 0.89 (t, J = 7 Hz, 3 H), 0.44 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 170.9, 169.2, 169.0, 168.8, 134.8, 134.0, 133.3, 133.0, 132.8, 131.3, 131.0, 130.9, 130.8, 130.1, 129.6, 129.3, 129.2, 129.1, 128.5, 128.3, 128.24, 128.19, 128.02, 127.99, 127.95, 127.86, 127.7, 127.6, 127.51, 127.45, 127.39, 127.0, 126.7, 126.3, 126.2, 123.6, 68.57, 68.53, 68.46, 67.8, 22.6, 22.4, 22.2, 21.8, 10.91, 10.89, 10.83, 10.2 ppm. FD-HRMS: m/z calcd. for $C_{50}H_{44}O_8$ $[M]^+$ 772.3036; found 772.3040.

***N*,*N*′-Bis(1-pentylhexyl) Dichryseno[7,6-*a*;7,6-*h*]anthracene-7,8:20,21-tetracarboxdiimide (14):** Tetraester **11** (143 mg, 979.2 g/mol, 0.15 mmol), 6-aminoundecane (0.3 g, 171.3 g/mol, 1.75 mmol), imidazole (4 g), and *o*-dichlorobenzene (6 g) were stirred and heated to reflux under argon for 16 h. The mixture was dissolved in $CHCl_3$, washed with 5% aqueous hydrochloric acid, and concentrated. The product was precipitated by adding methanol, filtered off, and purified by column chromatography on silica ($CHCl_3$) and recrystallized from *p*-xylene, whereby crystals suitable for X-ray crystallographic structure determination were obtained, yield 111 mg (1025.3 g/mol, 0.11 mmol, 74%); red crystals; m.p. > 300 °C. ^{1}H NMR [400 MHz, $(CDCl_2)_2$, mixture of two conformers of approximately equal abundance, 1 H = one H in one of the conformers]: δ = 9.97 (s, 2 H), 9.92 (s, 2 H), 9.22 (d, J = 8 Hz, 2 H), 9.05 (d, J = 8 Hz, 2 H), 8.88–8.80 (m, 8 H), 8.36 (d, J = 9 Hz, 2 H), 8.32 (d, J = 9 Hz, 2 H), 8.21 (d, J = 9 Hz, 2 H), 8.17 (d, J = 8 Hz, 2 H), 8.09 (d, J = 8 Hz, 2 H), 7.88–7.78 (m, 8 H), 7.73 (t, J = 8 Hz, 2 H), 7.57 (t, J = 8 Hz, 2 H), 7.46 (t, J = 8 Hz, 2 H), 7.28 (t, J = 8 Hz, 2 H), 7.04 (t, J = 8 Hz, 2 H), 4.19 (broad, 4 H), 2.04 (broad, 8 H), 1.70 (broad, 8 H), 1.30 (broad, 48 H), 0.88 (m, 24 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two conformers): δ = 169.94, 169.90, 168.8, 168.7, 134.0, 133.7, 133.3, 133.1, 132.7, 132.1, 131.5, 131.42, 131.36, 131.25, 131.0, 130.9, 130.8, 130.3, 130.2, 129.7, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 128.0, 127.4, 127.3, 127.2, 126.8, 126.5, 126.3, 125.73, 125.68, 125.57, 125.4, 123.7, 123.5, 123.4, 123.1, 120.6, 120.5, 52.8, 52.7, 32.9, 32.8, 32.7, 32.5, 31.9, 31.8, 31.72, 31.68, 26.7, 26.6, 26.5, 22.84, 22.78,

22.72, 14.3 ppm. FD-HRMS: *m*/*z* calcd. for $C_{72}H_{68}N_2O_4$ $[M]^+$ 1024.5179; found 1024.5195.

***N*,*N*′-Bis(1-pentylhexyl) Dinaphtho[1,2-*g*;1,2-*p*]chrysene-9,10:19,20-tetracarboxdiimide (15):** Tetraester **12** (428 mg, 772.9 g/mol, 0.55 mmol), 6-aminoundecane (0.65 g, 171.3 g/mol, 3.8 mmol), imidazole (6 g), and *o*-dichlorobenzene (9 g) were stirred and heated to reflux under argon for 16 h. The mixture was dissolved in $CHCl_3$, washed with 5% aqueous hydrochloric acid, and concentrated. The product was precipitated by adding methanol, filtered off, and purified by column chromatography on silica ($CHCl_3$) and recrystallized from a 1:3 mixture of butanol and ethanol, yield 295 mg (875.1 g/mol, 0.34 mmol, 61%); orange semiamorphous solid without a clear melting point. ^{1}H NMR [400 MHz, $(CDCl_2)_2$, main conformer]: δ = 9.39 (d, J = 8 Hz, 2 H), 9.05 (d, J = 8 Hz, 2 H), 8.68 (d, J = 8 Hz, 2 H), 7.82 (d, J = 8 Hz, 2 H), 7.77 (t, J = 8 Hz, 2 H), 7.55 (t, J = 8 Hz, 2 H), 7.53 (t, J = 8 Hz, 2 H), 7.38 (t, J = 8 Hz, 2 H), 4.39 (tt, J = 10, 5 Hz, 2 H), 2.21 (broad, 4 H), 1.85 (broad, 4 H), 1.34 (broad, 24 h), 0.89 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, main conformer): δ = 170.0, 169.8, 133.8, 133.3, 131.3, 130.81, 130.77, 130.6, 129.7, 129.1, 128.5, 128.3, 127.8, 127.5, 127.0, 126.8, 126.4, 126.1, 125.6, 53.0, 33.0, 32.8, 31.9, 31.8, 26.83, 26.77, 22.82, 22.76, 14.28, 14.25 ppm. FD-HRMS: *m*/*z* calcd. for $C_{60}H_{62}N_2O_4$ $[M]^+$ 874.4710; found 874.4721.

Supporting Information (see footnote on the first page of this article): Crystallographic data of **14**, electrochemical data, ^{1}H and ^{13}C NMR spectra.

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