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Liquid-Crystalline and Electron-Deficient Coronene Oligocarboxylic Esters and Imides By Twofold Benzogenic Diels–Alder Reactions on Perylenes

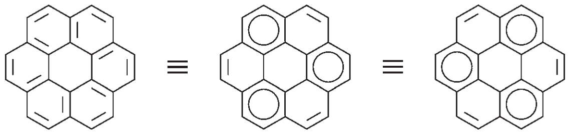
Sonia Alibert-Fouet,[a] Isabelle Seguy,[b] Jean-François Bobo,[c] Pierre Destruel,[b] and Harald Bock*[a]

Abstract: Alkyl esters, imides and imido-esters of coronene-tri-, -tetra- and -octacarboxylic acids are accessible by a twofold oxidative benzogenic Diels–Alder reaction. Alkyl acrylates add to perylene, and maleic alkyl imides react twice with perylene as well as with perylene-tetracarboxylic tetraesters. Coronenes substituted with a greatly variable number of electron-withdrawing substituents are thus accessible, and di- and tetraimide derivatives are shown to be very pronounced electron-acceptor materials. The tri- and tetraalkyl esters and imidoesters self-assemble into columnar liquid-crystalline phases.

Keywords: coronene · Diels–Alder reactions · liquid crystals · organic electronics · self-assembly

Introduction

Amongst benzenoid aromatics, coronene **1** occupies a special place. It is the smallest homologue of benzene with sixfold symmetry, giving it a unique electronic structure due to the perfect delocalisation of aromaticity between the six outer rings. This results in a very high chemical stability compared to other meta-annelated aromatics, such as phenanthrene.[1] In the crystalline state, coronene forms a bidimensional array of parallel columns, in which the molecules are stacked closely and parallel to each other with an exceptionally short distance of 3.43 Å between the aromatic planes.[2] Thus the overlap of π orbitals between neighbouring planes is large and electrons and excitons should travel easily along the columns.[3]



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We have in the last years developed a new class of self-assembling charge-transporting dyes, namely columnar liquid-crystalline esters, imides and imidoesters of arene-oligocarboxylic acids.[4,5] In particular, we have shown, in the case of benzo[ghi]perylene **2** (Scheme 1), that the variation of the number and type (ester/imide) of carboxylic substituents alone permits the access to materials of strongly different electronic character, spanning from fairly strong acceptors to materials with donor-type behaviour. This allowed us to obtain p–n junction light-emitting diodes[5] and solar cells[6] by pairing electron-rich benzo[ghi]perylene-tricarboxylic esters with electron-deficient benzo[ghi]perylene-hexacarboxylic imidoesters and imides.

Coronene is not only a particularly good candidate for obtaining columnar liquid-crystalline self-assembly over wide temperature ranges by substitution with flexible side groups—several liquid crystalline coronene derivatives with various side groups have been reported[7]—but it also allows the introduction of a particularly high number of electron-withdrawing carboxylic substituents, exceeding the hexasubstitution reached with benzo[ghi]perylene.[8] We report here how coronene-tri- to octacarboxylic esters, imides and imidoesters can be obtained by twofold, simultaneous or serial, Diels–Alder reactions, giving access on the one hand to cor-

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[a] Dr. S. Alibert-Fouet, Dr. H. Bock
Centre de Recherche Paul Pascal, CNRS
115, av. Schweitzer, 33600 Pessac (France)
Fax: (+33) 556-845-600
E-mail: bock@crpp-bordeaux.cnrs.fr

[b] Dr. I. Seguy, Prof. P. Destruel
Laboratoire de Génie Electrique de Toulouse
Université Paul Sabatier/CNRS, 118
route de Narbonne, 31062 Toulouse (France)

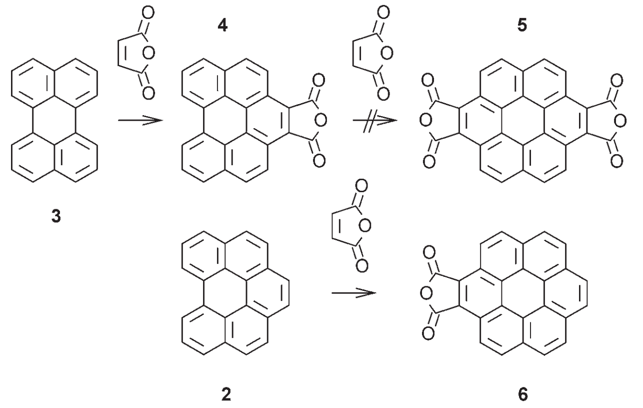
[c] Dr. J.-F. Bobo
Laboratoire de Nano-Magnétisme pour l'Hyperfréquence
CNRS/ONERA, 2 av. Edouard Belin
31055 Toulouse (France)

onenes with electron-withdrawing substituents of variable number and strength, and on the other hand, to columnar liquid-crystalline phases of broad temperature ranges.

To our knowledge, the octasubstituted coronenes described here are the first derivatives of any nonpolymeric aromatic hydrocarbon bearing such a high number of electron-withdrawing carboxylic substituents.

Results and Discussion

The scope of twofold Diels–Alder reactions on perylene and its carboxylic derivatives: The reaction of perylene **3** with maleic anhydride in the presence of an oxidising agent, such as chloranil is known not to proceed beyond the stage of the benzo[ghi]perylene dicarboxylic anhydride **4** (Scheme 1), no coronene tetracarboxylic dianhydride **5** being formed.[9] Unsubstituted benzo[ghi]perylene, on the other hand, is known to react to yield coronene dicarboxylic anhydride **6**.[9]

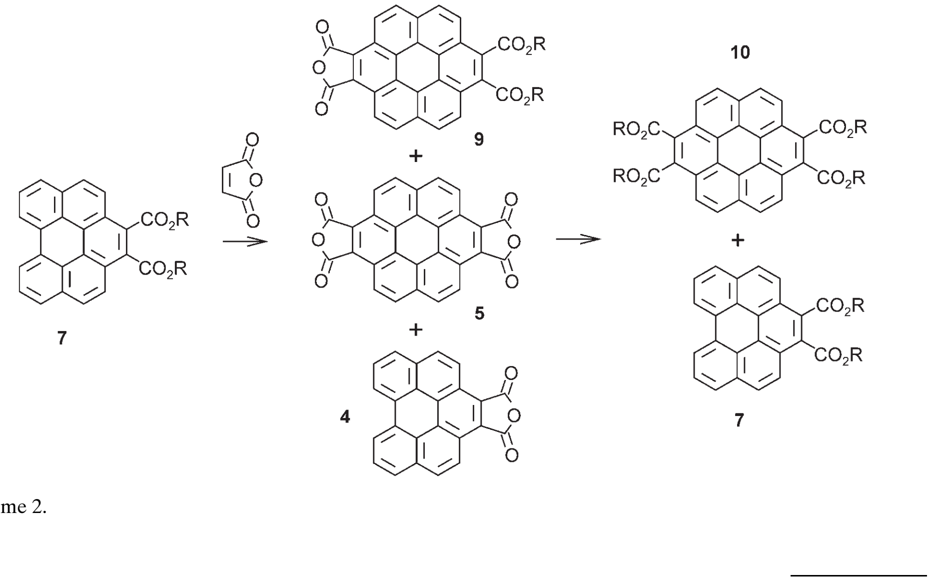


Scheme 1.

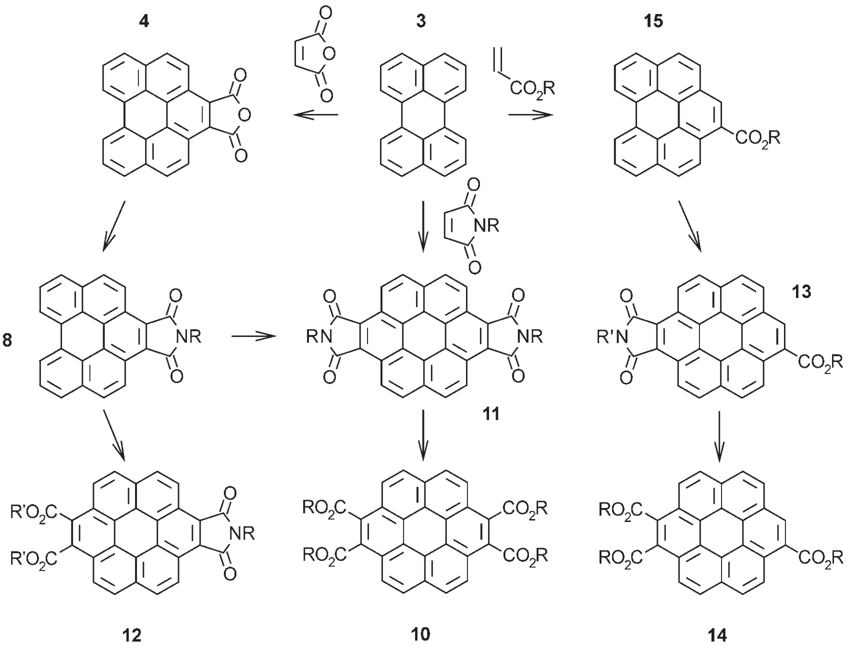
Aiming for coronenecarboxylic esters with more than two ester substituents, we found that benzo[ghi]perylene dicarboxylic alkyl esters **7** or imides **8**, in contrast to the anhydride, are reactive enough to add maleic anhydride or N-alkyl maleimides in the presence of chloranil. This offers a straightforward path to coronene tetracarboxylic acid and its derivatives. The reaction of diesters **7** with maleic anhydride is accompanied by saponification of the ester groups due to the acidic reaction conditions (HCl is formed by degradation of chloranil),[9] yielding the unreactive anhydride **4** (Scheme 2). A mixture of coronene tetracarboxylic diester monoanhydride **9** with **5** and **4** is obtained, which, upon reesterification, yields a mixture of esters **7** and **10** that is practically inseparable.

Benzo[ghi]perylene dicarboxylic imide **8**, on the other hand, does not saponify during the reaction, ensuring complete conversion to the substituted coronene when reacting with either maleic anhydride or an N-alkyl maleimide. Starting from perylene, two efficient pathways to coronene tetracarboxylic diimides **11** and tetraesters **10** emerge thus, one very short and the other cheap and more versatile, additionally allowing access to dissymmetrical diimides and to imido-esters **12** (Scheme 3): 1) Perylene can be reacted directly twice with a maleic N-alkylimide, yielding in a single step and in a few hours the corresponding diimide **11**, which can subsequently be saponified and esterified, or reimidified with a different alkylamine than the one present in the initial maleimide. This approach has the drawback that the maleimide used in the Diels–Alder reaction is used in large excess (as solvent), whilst commercial N-alkyl maleimides are far more expensive than maleic anhydride. The advantage is that coronene tetracarboxylic tetraesters **10** and diimides **11** with various alkyl substituents are accessible from perylene in only three steps (addition of ethylmaleimide, saponification, and esterification or imidification). 2) The use of a maleic imide as a Diels–Alder reagent can be avoided by a) reaction of perylene with maleic anhydride, b) imidification with an alkylamine, c) reaction of the resulting imide **8** with maleic anhydride. The resulting coronene-tetracarboxylic imido-anhydride cannot only be transformed to a symmetrical diimide by reaction with the same alkylamine as in step b or to a tetraester by saponification of the imide group followed by esterification. In contrast to pathway 1, also dissymmetrical diimides **11** may be obtained by using two different amines, and imido-diesters **12** can be obtained by esterification of the resulting imido-anhydride.

We presumed that the partial saponification that occurs when diester **7** is reacted with maleic anhydride or imide may be in part favoured by the vicinity of the two ester



Scheme 2.

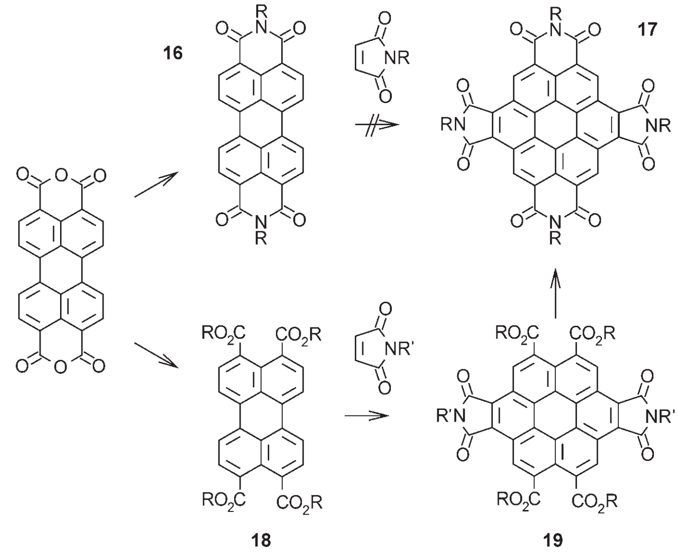


Scheme 3.

groups, which allows ring closure to the anhydride **4**. A benzoperylene monocarboxylic ester should in this case be more resistant to saponification. We therefore considered it possible to obtain coronene-1,2,7-tricarboxylic acid and its derivatives **13** and **14** by reaction of perylene with an alkyl acrylate, followed by addition of maleic anhydride or a maleimide to the resulting monoester **15**.

The first step of this sequence, the oxidative Diels–Alder reaction of perylene with an alkyl acrylate, seemed feasible because of the very high reactivity of perylene towards maleic anhydride (complete reaction occurs within a few minutes at reflux),[9] even though acrylates are known to be far less reactive than maleic anhydride.[10] Indeed, we found that isobutyl acrylate at reflux (132 °C) adds to perylene in the presence of chloranil, but the conversion rate is very slow: a yield of 39 % is isolated after six days, together with 36 % unreacted perylene. Polymerisation of the acrylate is avoided by adding 4-methoxyphenol as radical scavenger. We then resorted to using a higher boiling acrylate, and found that 2-ethylhexyl acrylate at reflux (215 °C) gives the corresponding benzoperylene carboxylic ester overnight in 41 % yield with nearly no perylene recovered and polymerisation of the acrylate still avoided. The imidoester **13**, obtained by addition of *N*-ethyl maleimide to **15**, is efficiently converted into the corresponding triesters **14** by saponification plus esterification.

Given that N-alkyl maleimide converts perylene directly into a substituted coronene, we wondered to what extent this reaction is effective on substituted perylenes with decreased Diels–Alder reactivity. We tried to react *N*,*N'*-di-(3-pentyl)perylene 3:4,9:10-tetracarboxylic diimide (3-pentyl-PTCDI) **16** ($R=CHEt_2$) in refluxing *N*-ethyl maleimide in the presence of an excess of chloranil, but could not detect any trace of twofold addition product **17** (Scheme 4) besides the monoaddition product *N*-ethyl *N'*,*N''*-di-(3-pentyl)benzo[ghi]perylene 1:2,4:5,10:11-hexacarboxylic triimide) after 18 h at reflux. Clearly, the strongly electron-withdrawing imide substituents decrease the Diels–Alder reactivity of the perylene moiety sufficiently to bar the direct access to coronene tetraimides **17** by this route. As perylene tetracarboxylic esters **18** should exhibit an intermediate reactivity between unsubstituted perylene and diimide **16**, we then applied the same reaction conditions to perylene 3,4,9,10-tetracarboxylic tetraisobutyl ester **18** ($R=i$Bu). Two difficulties arise with this reaction: as in the case of the benzoperylene diesters **7**, saponification of the vicinal ester groups occurs as a side reaction, leading to Diels–Alder unreactive anhydrides, and the reaction time is limited to about 18 h by the slow polymerisation of *N*-ethyl maleimide. Still, the tetraester **18** is reactive enough to yield a few percent of coronene tetraester-diimide **19** in this time, and the choice of isobutyl alkyl groups turned out to be fortunate, because it allowed the straightforward separation of the product, which is insoluble in refluxing butanol but easily soluble in chloroform, from the butanol-soluble monoaddition product and the far more polar saponification products. The tetraester-diimide **19** is transformed into a tet-



Scheme 4.

raimide **17** by means of saponification followed by treatment with an alkylamine.

The reactivity of tetracarboxysubstituted perylenes towards oxidative benzogenic Diels–Alder reactions changes dramatically from the dianhydride **20** (PTCDA) via the diimide **16** (PTCDI) to the tetraester **18**, whereas the dianhydride is unreactive even towards onefold addition, the diimide adds one molecule of N-alkyl maleimide or maleic anhydride to form a substituted benzo[ghi]perylene, and the tetraester reacts twice with N-alkyl maleimide, albeit considerably more slowly than unsubstituted perylene.

Columnar liquid-crystalline self-assembly in coronene tetra- and tricarboxylates: We prepared tetraalkyl coronene-1,2,7,8-tetracarboxylates **10a–e** with linear alkyl chains from propyl to octyl, and found in all cases a hexagonal columnar mesophase (by polarising microscopy and powder X-ray diffraction studies) that is stable over large temperature ranges (Table 1). The melting points are in all cases at moderate temperatures, decreasing from 101 °C for the propyl to 47 °C for the octyl homologue, while the clearing temperatures pass from about 280 to 133 °C. Thermal decomposition sets in at about 250 °C, making the clearing temperature of the propyl homologue hard to determine. The butyl homologue exhibits a second columnar liquid-crystalline phase of rectangular symmetry (with main diffraction peaks at 16.1 and 13.7 Å) between the melting point at 88 °C and the transition to the hexagonal mesophase (main diffraction peak at 15.4 Å) at 95 °C. Crystallisation is efficiently suppressed by using branched racemic 2-ethylhexyl chains (**10f**), leading to a hexagonal mesophase at room temperature that clears to the isotropic liquid at 153 °C. In all cases, the diffuse intermolecular spacing between adjacent aromatic planes within the columns is 3.5–3.6 Å in the mesophase.

Decreasing the number of ester side chains from four to three leads to a decrease of both the clearing and the melting temperatures in the trialkyl coronene-1,2,7-tricarboxylates **14a** ($R = nC_3H_7$) and **14b** ($R = nC_4H_9$) (Table 1). The temperature ranges of the mesophases remain large with short chains, illustrating that three short *n*-alkyl ester substituents are fully sufficient on coronene to induce hexagonal columnar liquid-crystalline self-assembly (Figure 1), in contrast to triesters with less disk-shaped aromatic cores, such as triphenylene or 5,6,11,12,17,18-hexaazatrinaphthylene (Scheme 5, **21** and **22**), in which only nematic, plastic crystalline or monotropic (metastable) columnar mesophases are observed.[4]

Table 1. Phase-transition temperatures [°C] of coronene tetra- and tricarboxylic esters **10** and **14**, determined by differential scanning calorimetry

	R	Transitions[a]
10a	*n*-propyl	cr - 101 - col_{hex} - c. 280(dec.) - i
10b	*n*-butyl	cr - 88 - col_{rect} - 95 - col_{hex} - 233 - i
10c	*n*-pentyl	cr - 70 - col_{hex} - 201 - i
10d	*n*-hexyl	cr - 66 - col_{hex} - 182 - i
10e	*n*-octyl	cr - 47 - col_{hex} - 133 - i
10f	*rac*-2-ethylhexyl	cr - 12 - col_{hex} - 153 - i
14a	*n*-propyl	cr - 84 - col_{hex} - 244 - i
14b	*n*-butyl	cr - 71 - col_{hex} - 215 - i

[a] cr = crystalline, col_{rect} = rectangular columnar liquid crystalline, col_{hex} = hexagonal columnar liquid crystalline, i = isotropic liquid, dec. = decomposition.

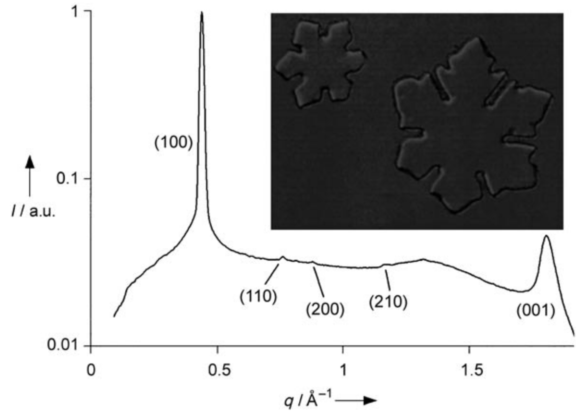
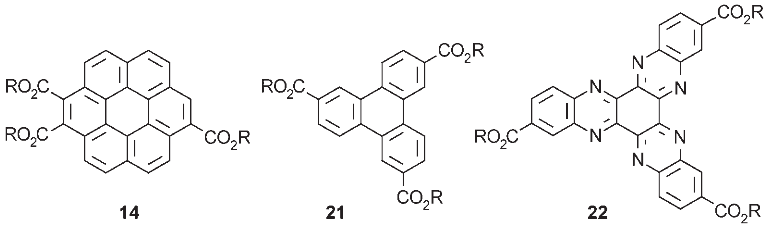


Figure 1. Powder X-ray diffractogram of the hexagonal columnar mesophase of **14b** at 100 °C. Inset: polarising optical microscopy texture of **14b** upon cooling through the liquid-to-mesophase transition. The image was taken with differential interference contrast in reflection mode[11] of a thin film between a silicon wafer and a glass slide.

Whereas the imides **11** and **17** with 4-heptyl side chains (obtained by imidification with 4-aminoheptane, the longest commercially available symmetrical secondary amine) do not melt at accessible temperatures, the imide-diesters **12a** (R = 4-heptyl, R′ = *n*-propyl) and **12b** (R = 4-heptyl, R′ = *rac*-2-ethylhexyl) show a crystal to mesophase transition at 197 and 60 °C, respectively. The X-ray diffractograms reveal, in addition to the broadened disk-to-disk peak at 3.5 Å, only a single lattice peak at 14.6 or 17.0 Å, respectively, indicating the presence of a hexagonal columnar mesophase. No transition from the mesophase to the isotropic liquid could be observed up to 375 °C.



Scheme 5.

Modulation of electronic properties with increasing carboxylic substitution: The carboxylic substitution of coronene leads to a red shift of the absorption spectra in solution, giving the sequence coronene **1** (main absorption peak in chloroform at 304 nm, log $\varepsilon = 5.5$)—triester **14** (316 nm, log $\varepsilon = 5.1$)—diimide **11** (343 nm, log $\varepsilon = 5.0$)—tetraimide **17** (375 nm, log $\varepsilon = 5.1$) (Figure 2). Whilst the red shift from coronene **1** to the triester **14** is small (12 nm; the absorption spectra of the tetraesters **10** and the triesters **14** are nearly identical, all peaks being of similar intensities and at the same wavelengths within ±2 nm) and reflects the only modest influence of the rotationally flexible ester substituents on the central chromophore, the red shift from **1** to the diimide **11** is more than three times as big because the rigid and coplanar imide groups efficiently extend the chromophore. The addition of two further imide groups in **17** results again in a red shift of nearly the same strength. The spectra of **14**, **11** and **17** are broadened with respect to **1**, and the intensity of the α bands is increased. Both of these effects can be attributed to the lower symmetry and to a possible deviation from planarity of the aromatic core. Overall, the ester and imide groups in **14**, **11** and **17** alter the coronene absorption spectrum less dramatically than the two imide groups in coronene-3:4,9:10-tetracarboxylic diimide (for example, **17** without the two lateral pentacyclic imide substituents), which exhibits a more pronounced multiple-peak structure that hints to its structural relation with PTCDI **16**.[7] In parallel to the observed red shift in solution, the colour in the solid state shifts from the pale yellow of coronene to a deep yellow/orange of **17**.

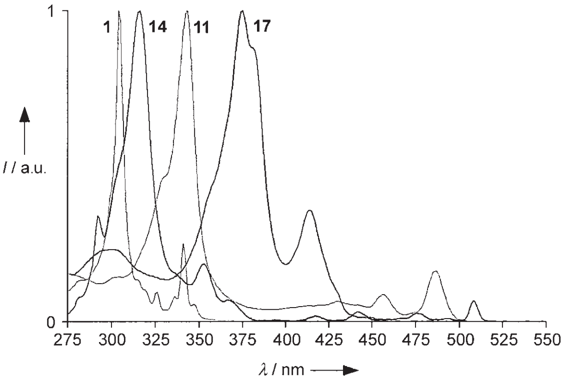


Figure 2. Normalised absorption spectra of coronene **1**, triester **14**, diimide **11** and tetraimide **17** in chloroform (10^{-2} mol L^{-1}).

The long-wavelength limits of the absorption spectra of **1**, **14**, **11** and **17** in chloroform are at about 420, 450, 500 and 520 nm, corresponding to 2.95, 2.75, 2.50 and 2.40 eV, respectively.

Helium I ultraviolet photoemission spectroscopy (UPS) was performed on 200 Å thick films of coronene diimide **11** and tetraimide **17** evaporated on silicon substrates to determine the highest occupied molecular orbital energies E_{HOMO} (Figure 3). The HOMO position ($\mathrm{HOMO}_{\text{cut-off}}$) is conventionally taken as the intercept between the tangent to the leading edge of the lowest binding energy feature of the spectrum and the zero-intensity background line.[12]

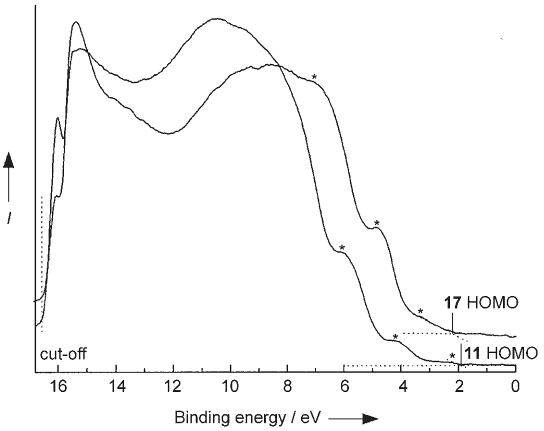


Figure 3. HeI (21.2 eV) UPS spectra of 200 Å coronene diimide **11** and tetraimide **17** films on silicon. Each spectrum is recorded with a −3 V bias on the sample.

E_{HOMO} was determined by adding the $\mathrm{HOMO}_{\text{cut-off}}$ (1.9 eV for **11** and 2.2 eV for **17**) with respect to the experimentally measured value of the Fermi energy level E_F (=zero binding energy) to the work function of each film. The work function is determined in the same UPS run by measuring the photoemission spectrum of a fresh gold film evaporated on the sample, yielding a value of 4.6 eV in both cases.[12] E_{HOMO} is thus found to be $4.6+1.9=6.5$ eV for the diimide and $4.6+2.2=6.8$ eV for the tetraimide.

From these E_{HOMO} values, the lowest unoccupied molecular orbital values E_{LUMO} can be estimated from the optical band gap of 2.5 and 2.4 eV, respectively, as obtained from the absorption spectra. The optical band gap is slightly smaller than the "real" or transport band gap, the difference between the two being the excitonic binding energy. By analogy with perylene tetracarboxylic *N,N′*-dimethylimide (Me-PTCDI, **16** ($R = CH_3$)), this difference between the optical band gap and the transport band gap can be estimated to be 0.3 eV,[13] leading to transport band gaps of 2.8 and 2.7 eV, and E_{LUMO} values of 3.7 and 4.1 eV for **11** and **17**.

For comparison, unsubstituted coronene has reported E_{HOMO} and E_{LUMO} values of 5.9 and 2.6 eV.[14]

Thus, diimide **11** and tetraimide **17**, in spite of their larger band gaps, are good electron acceptors whose E_{LUMO} values approach or attain, respectively, those of widely used C_{60} (with an E_{LUMO} of 3.96 eV),[15] and of PTCDIs (well-established electron-acceptor materials with an E_{LUMO} of 4.1 eV).[13]

Conclusion

In summary, tri- to octacarboxysubstituted coronenes are readily accessible by twofold benzogenic Diels–Alder addition of N-alkyl maleimides, maleic anhydride and alkyl acrylates on unsubstituted or carboxysubstituted perylene.

Whilst many of the ester derivatives self-assemble into columnar liquid-crystalline mesophases over large temperature ranges and room temperature mesomorphism is found with branched side chains, the di- and tetraimides are shown to be strong electron acceptors, even though the large band gap of the coronene chromophore disfavours good acceptor-type E_{LUMO} values. This indicates that multiple carboxylic substitution by benzogenic Diels–Alder additions might lead to even more efficient electron acceptors if applied to chromophores with a smaller band gap than perylene.

Experimental Section

General methods: NMR spectra were recorded on a Bruker Avance 400 spectrometer. IR spectra were recorded on a Nicolet 750 Magna FTIR spectrometer. UV/Vis spectra were recorded on a Unicam UV4 spectrometer. Petroleum ether of b.p. range 40–65°C was used where stated.

Benzo[*ghi*]perylene-1-carboxylic (2-ethylhexyl)ester (15, R = 2-ethylhexyl): Chloranil (15.0 g, 61 mmol) and perylene (5.0 g, 20 mmol) were added to a solution of *p*-hydroxyanisole (1.0 g, 8 mmol) in 2-ethylhexyl acrylate (45 g, 350 mmol), and the mixture was heated to reflux with stirring. The mixture rapidly turned darkish green and partially solidified. Reflux was continued with vigorous stirring for 24 h. After cooling to room temperature, the mixture was separated on a large silica column with a petroleum ether/dichloromethane 2:1 mixture to yield **15** (R = 2-ethylhexyl), which was recrystallised from butanol. Chromatograpy and recristallisation are both repeated once. Yellow crystalline gum; yield: 3.5 g (41 %); m.p. 61 °C;. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 9.06$ (d, J = 9 Hz, 1H; ArH), 8.78 (s, 1H; ArH), 8.74 (d, J = 8 Hz, 1H; ArH), 8.71 (d, J = 8 Hz, 1H; ArH), 8.04 (d, J = 8 Hz, 1H; ArH), 8.01 (d, J = 9 Hz, 1H; ArH), 7.97 (d, J = 8 Hz, 1H; ArH), 7.93–7.84 (m, 4H; ArH), 4.50 (d, J = 6 Hz, 2H; $\mathrm{CH_2O}$), 1.93 (hept, J = 6 Hz, 1H; CH), 1.70–1.54 (m, 4H; $\mathrm{CH_2}$), 1.52–1.38 (m, 4H; $\mathrm{CH_2}$), 1.09 (t, J = 7 Hz, 3H; $\mathrm{CH_3}$), 0.99 ppm (t, J = 7 Hz, 3H; $\mathrm{CH_3}$); ^{13}C NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 168.4$ ($\mathrm{CO_2}$), 132.7 ($\mathrm{C_{Ar}}$), 131.5 ($\mathrm{C_{Ar}}$), 130.5 ($\mathrm{C_{Ar}}$), 130.0 ($\mathrm{C_{Ar}}$), 129.1 ($\mathrm{C_{Ar}H}$), 128.5 ($\mathrm{C_{Ar}H}$), 127.8 ($\mathrm{C_{Ar}H}$), 127.6 ($2\times\mathrm{C_{Ar}}$), 127.5 ($\mathrm{C_{Ar}H}$), 127.0 ($\mathrm{C_{Ar}H}$), 126.8 ($\mathrm{C_{Ar}H}$), 126.5 ($\mathrm{C_{Ar}H}$), 126.4 ($\mathrm{C_{Ar}H}$), 126.0 ($\mathrm{C_{Ar}}$), 125.1 ($\mathrm{C_{Ar}}$), 124.9 ($2\times\mathrm{C_{Ar}}$), 124.8 ($\mathrm{C_{Ar}H}$), 124.3 ($\mathrm{C_{Ar}}$), 121.0 ($\mathrm{C_{Ar}H}$), 120.7 ($\mathrm{C_{Ar}H}$), 67.9 ($\mathrm{CH_2O}$), 39.2 (CH), 30.9 ($\mathrm{CH_2}$), 29.3 ($\mathrm{CH_2}$), 24.3 ($\mathrm{CH_2}$), 23.2 ($\mathrm{CH_2}$), 14.3 ($\mathrm{CH_3}$), 11.4 ppm ($\mathrm{CH_3}$); elemental analysis calcd (%) for $\mathrm{C_{31}H_{28}O_2}$: C 86.08, H 6.52; found: C 85.86, H 6.63.

Coronene 1,2,7-tricarboxylic 1:2-ethylimide 7-(2-ethylhexyl)ester (13, R = 2-ethylhexyl, R′ = ethyl): Compound **15** (R = 2-ethylhexyl) (2.0 g, 4.6 mmol), *N*-ethyl-maleimide (10 g, 80 mmol), *p*-hydroxyanisole (0.35 g, 2.8 mmol) and chloranil (5 g, 20 mmol) were thoroughly mixed and heated with stirring to reflux (oil bath at 240 °C) for 8 h. After cooling to room temperature (whereupon the mixture solidified), chloroform (30 mL) was added and reflux was continued until dissolution. The mixture was poured onto a silica column. Impurities and reactants were eluted first with dichloromethane/petroleum ether 1:1, followed by dichloromethane/ethyl acetate 10:1 to elute the product, which was recrystallised from butanol. Golden yellow crystalline gum; yield: 1.8 g (70 %); m.p. >250 °C; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 9.93$ (d, J = 9 Hz, 1H; ArH), 9.66 (d, J = 8 Hz, 1H; ArH), 9.64 (d, J = 8 Hz, 1H; ArH), 9.48 (s, 1H; ArH), 8.86 (d, J = 8 Hz, 1H; ArH), 8.80 (d, J = 8 Hz, 1H; ArH), 8.73 (br d, J = 8–9 Hz, 3H; ArH), 4.50 (d, J = 6 Hz, 2H; $\mathrm{CH_2O}$), 3.61 (q, J = 7 Hz, 2H; $\mathrm{CH_2N}$), 2.00 (hept, J = 6 Hz, 1H; CH), 1.74–1.36 (m, 11H), 1.18 (t, J = 7 Hz, 3H; $\mathrm{CH_3}$), 1.09 ppm (t, J = 7 Hz, 3H; $\mathrm{CH_3}$); ^{13}C NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 168.3$ ($2\times$CO), 167.3 ($\mathrm{CO_2}$), 129.1 ($\mathrm{C_{Ar}H}$), 127.4 ($2\times\mathrm{C_{Ar}}$), 126.2 ($\mathrm{C_{Ar}H}$), 126.0 ($\mathrm{C_{Ar}}$), 125.8 ($\mathrm{C_{Ar}H}$), 125.6 ($3\times\mathrm{C_{Ar}H}$), 124.7 ($\mathrm{C_{Ar}}$), 124.1 ($\mathrm{C_{Ar}}$), 123.9 ($\mathrm{C_{Ar}H}$), 121.7 ($\mathrm{C_{Ar}}$), 121.6 ($\mathrm{C_{Ar}}$), 120.7 ($\mathrm{C_{Ar}H}$), 119.9 ($\mathrm{C_{Ar}H}$), 119.8 ($\mathrm{C_{Ar}}$), 119.4 ($\mathrm{C_{Ar}}$), 119.1 ($\mathrm{C_{Ar}}$), 118.6 ($\mathrm{C_{Ar}}$), 118.3 ($\mathrm{C_{Ar}}$), 116.9 ($\mathrm{C_{Ar}}$), 116.8 ($\mathrm{C_{Ar}}$), 116.5 ($\mathrm{C_{Ar}}$), 68.0 ($\mathrm{CH_2O}$), 39.2 (CH), 32.5 ($\mathrm{CH_2N}$), 31.0 ($\mathrm{CH_2}$), 29.3 ($\mathrm{CH_2}$), 24.4 ($\mathrm{CH_2}$), 23.3 ($\mathrm{CH_2}$), 14.7 ($2\times\mathrm{CH_3}$), 11.4 ppm ($\mathrm{CH_3}$); elemental analysis calcd (%) for $\mathrm{C_{37}H_{31}NO_4}$: C 80.27, H 5.64, N 2.53; found: C 79.81, H 5.64, N 2.53.

Coronene 1,2,7-tricarboxylic tripropylester (14a): Compound **13** (R = 2-ethylhexyl, R′ = ethyl) (1.0 g, 1.8 mmol) was stirred at reflux with potassium carbonate (15 g) in methanol (30 mL) overnight. The mixture was then poured into water (200 mL) and the coronene tricarboxylic acid formed was precipitated by adding an excess of concentrated hydrochloric acid, filtered off and dried under vacuum. The resulting solid (0.7 g) was powdered and stirred at reflux overnight with 1-bromopropane (5 g), propanol (5 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4 g) in acetonitrile (30 mL). The solvent was evaporated and the residue was purified by column chromatography (silica, dichloromethane/ethyl acetate 20:1) and recrystallised from propanol. Yellow crystalline gum; yield: 0.71 g (70 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 9.32$ (d, J = 9 Hz, 1H; ArH), 8.78 (d, J = 9 Hz, 2H; ArH), 8.74 (s, 1H; ArH), 8.44 (d, J = 9 Hz, 1H; ArH), 8.35 (d, J = 9 Hz, 1H; ArH), 8.31 (d, J = 9 Hz, 1H; ArH), 8.16 (d, J = 8 Hz, 1H; ArH), 8.11 (d, J = 8 Hz, 1H; ArH), 4.71 (t, J = 7 Hz, 2H; $\mathrm{CH_2O}$), 4.70 (t, J = 7 Hz, 2H; $\mathrm{CH_2O}$), 4.66 (t, J = 7 Hz, 2H; $\mathrm{CH_2O}$), 2.15 (sext, J = 7 Hz, 2H; $\mathrm{CH_2}$), 2.091 (sext, J = 7 Hz, 2H; $\mathrm{CH_2}$), 2.089 (sext, J = 7 Hz, 2H; $\mathrm{CH_2}$), 1.34 (t, J = 7 Hz, 3H; $\mathrm{CH_3}$), 1.258 (t, J = 7 Hz, 3H; $\mathrm{CH_3}$), 1.255 ppm (t, J = 7 Hz, 3H; $\mathrm{CH_3}$); ^{13}C NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 168.9$ ($\mathrm{CO_2}$), 168.8 ($\mathrm{CO_2}$), 167.8 ($\mathrm{CO_2}$), 129.9 ($\mathrm{C_{Ar}H}$), 129.3 ($\mathrm{C_{Ar}}$), 128.7 ($\mathrm{C_{Ar}}$), 128.2 ($\mathrm{C_{Ar}}$), 127.9 ($\mathrm{C_{Ar}}$), 127.2 ($2\times\mathrm{C_{Ar}H}$), 126.9 ($\mathrm{C_{Ar}H}$), 126.6 ($\mathrm{C_{Ar}H}$), 125.8 ($\mathrm{C_{Ar}H}$), 125.7 ($2\times\mathrm{C_{Ar}}$), 124.7 ($\mathrm{C_{Ar}H}$), 124.4 ($\mathrm{C_{Ar}H}$), 124.3 ($\mathrm{C_{Ar}}$), 124.0 ($\mathrm{C_{Ar}}$), 123.8 ($\mathrm{C_{Ar}H}$), 123.6 ($\mathrm{C_{Ar}}$), 122.1 ($\mathrm{C_{Ar}}$), 121.8 ($\mathrm{C_{Ar}}$), 121.5 ($\mathrm{C_{Ar}}$), 120.9 ($\mathrm{C_{Ar}}$), 119.8 ($\mathrm{C_{Ar}}$), 119.6 ($\mathrm{C_{Ar}}$), 68.1 ($2\times\mathrm{CH_2O}$), 67.1 ($\mathrm{CH_2O}$), 22.6 ($\mathrm{CH_2}$), 22.4 ($2\times\mathrm{CH_2}$), 11.1 ($\mathrm{CH_3}$), 11.0 ppm ($2\times\mathrm{CH_3}$); elemental analysis calcd (%) for $\mathrm{C_{36}H_{30}O_6}$: C 77.40, H 5.41; found: C 77.58, H 5.18.

Coronene 1,2,7,8-tetracarboxylic tetrapropylester (10a): Perylene (6.0 g, 24 mmol), *N*-ethyl-maleimide (37.5 g, 300 mmol), *p*-hydroxyanisole (1.5 g, 12 mmol) and chloranil (22.5 g, 91 mmol) were thoroughly mixed and heated with stirring to reflux (oil bath at 240 °C) for 6 h. The mixture became highly viscous at the end of this time. Without reducing the bath temperature, DMF (50 mL) was added cautiously through the reflux condenser, and reflux was continued until the mixture became fluid again. The mixture was vacuum-filtered hot though a glass filter to separate the insoluble diimide **11** (R = ethyl) which was boiled out with DMF (300 mL), filtered hot, washed on the glass filter with ethanol and dried, yielding 5.9 g (50 %) of a yellow powder, which was insoluble in all common solvents and which did not melt below 375 °C. The powder was transferred to a 100 mL flask, methanol (60 mL) and potassium hydroxide (40 g) were added and the mixture was heated with stirring to boiling temperature. The methanol was left to boil off until about 60 mL of a transparent brownish solution remain. Reflux was continued overnight at about 130 °C (oil bath at 150 °C). The solution was diluted with water (500 mL) and the tetraacid was precipitated by adding an excess of concentrated hydrochloric acid to the stirred solution. The orange gelatinous acid was vacuum-filtered off on a glass filter, washed with water on the filter and dried under vacuum at 100 °C overnight, yielding 11.7 g of impure dianhydride **5**, which was powdered and refluxed with 1-bromopropane (50 g), 1-propanol (50 g) and DBU (40 g) in acetonitrile (200 mL) overnight. The dianhydride dissolves quickly, giving a yellow solution, from which a yellow precipitate separates. The mixture was poured into methanol (500 mL) and the precipitate was filtered off. Compound **10a** was separated from the insoluble part of the precipitate by being dissolved with stirring in dichloromethane and was purified by column chromatography (silica, dichloromethane/ethyl acetate 100:1) and recrystallisation from propanol. Yellow powder; yield: 4.1 g (27 % with respect to perylene, 54 % with respect to **11** (R = ethyl)); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 9.13$ (d, J = 9 Hz, 4H; ArH), 8.89 (d, J = 9 Hz, 4H; ArH), 4.67 (t, J = 7 Hz, 8H; $\mathrm{CH_2O}$), 2.02 (sext, J = 7 Hz, 8H; $\mathrm{CH_2}$), 1.18 ppm (t, J = 7 Hz, 12H; $\mathrm{CH_3}$); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 168.6$ ($\mathrm{CO_2}$), 128.9 ($\mathrm{C_{Ar}}$), 128.6 ($\mathrm{C_{Ar}}$), 127.6 ($\mathrm{C_{Ar}H}$), 124.7 ($\mathrm{C_{Ar}H}$), 124.0 ($\mathrm{C_{Ar}}$), 121.8 ($\mathrm{C_{Ar}}$), 120.0 ($\mathrm{C_{Ar}}$), 68.1 ($\mathrm{CH_2O}$), 22.3 ($\mathrm{CH_2}$), 10.9 ppm ($\mathrm{CH_3}$); elemental analysis calcd (%) for $\mathrm{C_{40}H_{36}O_8}$: C 74.52, H 5.63; found: C 74.60, H 5.67.

Benzo[*ghi*]perylene 1,2-dicarboxylic (4-heptyl)imide (8, R = 4-heptyl): Perylene (10 g, 40 mmol), chloranil (21 g, 85 mmol) and maleic anhydride (150 g, 1.5 mol) were thoroughly mixed and heated with stirring to reflux (oil bath at 240 °C) for 10 min. Hot xylene (200 mL) was added with stirring and the precipitated anhydride **4** was filtered off and purified by boiling out in ethyl acetate/chloroform 2:1 (600 mL), followed by hot filtration. The anhydride (13.7 g, 100 %) was added to a solution of 4-heptylamine (7.5 g, 65 mmol) in DMF (300 mL) and refluxed overnight. On cooling, the imide precipitates. Methanol (700 mL) was added with stirring to complete the crystallisation. The product was dissolved in hot chloroform and purified by column chromatography (silica, chloroform), and finally boiled out in butanol (800 mL), in which it does not dissolve. Orange powder; yield: 15.5 g (88 %); m.p. 262 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 9.15$ (d, $J = 9$ Hz, 2H; ArH), 8.87 (d, $J = 8$ Hz, 2H; ArH), 8.13 (d, $J = 8$ Hz, 2H; ArH), 8.11 (d, $J = 9$ Hz, 2H; ArH), 8.01 (t, $J = 8$ Hz, 2H; ArH), 4.48 (tt, $J = 10$, $J = 5$ Hz, 1H; CH), 2.40–2.20, 1.90–1.80 (2 × m, 4H; CH$_2$), 1.49 (sext, $J = 7$ Hz, 4H; CH$_2$), 1.02 ppm (t, $J = 7$ Hz, 6H; CH$_3$); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 170.6$ (C=O), 132.2 (2 × C$_{\mathrm{Ar}}$), 130.1 (C$_{\mathrm{Ar}}$H), 127.4 (C$_{\mathrm{Ar}}$H), 127.3 (C$_{\mathrm{Ar}}$H), 127.2 (C$_{\mathrm{Ar}}$), 124.6 (C$_{\mathrm{Ar}}$), 124.3 (C$_{\mathrm{Ar}}$), 123.5 (C$_{\mathrm{Ar}}$), 122.9 (C$_{\mathrm{Ar}}$H), 121.5 (C$_{\mathrm{Ar}}$H), 51.7 (CHN), 35.1 (CH$_2$), 20.2 (CH$_2$), 14.0 ppm (CH$_3$); elemental analysis calcd (%) for $C_{31}H_{25}NO_2$: C 83.95, H 5.68, N 3.16; found: C 83.94, H 5.79, N 3.18.

Coronene 1,2,7,8-tetracarboxylic di-(4-heptyl)imide (11, R = 4-heptyl): Compound **8** (R = 4-heptyl) (6.5 g, 15 mmol), chloranil (20 g, 81 mmol) and maleic anhydride (150 g) were thoroughly mixed and heated with stirring to reflux (oil bath at 240 °C) for 4 d. Chloroform (150 mL) was added, the mixture was refluxed for a few minutes and filtered to yield 8.6 g of crude, brownish yellow imide-anhydride, which was refluxed overnight with 4-heptylamine (9.0 g, 78 mmol) in DMF (300 mL). The mixture was added to ethanol (1 L) with stirring. The diimide precipitated and was filtered off, dissolved in hot chloroform, purified by column chromatography (silica, chloroform) and finally boiled out in butanol (800 mL) in which it does not dissolve. Deep yellow powder (only sparingly soluble in chloroform); yield: 6.4 g (69 %); m.p. > 375 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 9.87$ (d, $J = 9$ Hz, 4H; ArH), 8.81 (d, $J = 9$ Hz, 4H; ArH), 4.60 (tt, $J = 10$, $J = 5$ Hz, 2H; CHN), 2.47–2.37 (m, 4H; CH$_2$), 2.01–1.91 (m, 4H; CH$_2$), 1.59 (sext, $J = 7$ Hz, 8H; CH$_2$), 1.08 ppm (t, $J = 7$ Hz, 12H; CH$_3$); ^{13}C NMR (300 MHz, APT, CDCl$_3$): $\delta = 170.2$ (C=O), 129.8 (C$_{\mathrm{Ar}}$), 128.1 (C$_{\mathrm{Ar}}$H), 124.6 (C$_{\mathrm{Ar}}$), 123.7 (C$_{\mathrm{Ar}}$H), 123.1 (C$_{\mathrm{Ar}}$), 122.1 (C$_{\mathrm{Ar}}$), 120.2 (C$_{\mathrm{Ar}}$), 52.1 (CHN), 35.1 (CH$_2$), 20.3 (CH$_2$), 14.0 ppm (CH$_3$); elemental analysis calcd (%) for $C_{42}H_{38}N_2O_4$: C 79.47, H 6.03, N 4.41; found: C 79.37, H 6.04, N 4.45.

Coronene 1,2,7,8-tetracarboxylic 1:2-(4-heptyl)imide 7,8-di-propylester (12a): Compound **8** (R = 4-heptyl) (6.5 g, 15 mmol), chloranil (20 g, 81 mmol) and maleic anhydride (150 g) were thoroughly mixed and heated with stirring to reflux (oil bath at 240 °C) for 4 d. Chloroform (150 mL) was added, the mixture was refluxed for a few minutes and was then filtered to yield 8.6 g of crude, brownish yellow imide-anhydride, which was refluxed overnight with 1-bromopropane (50 g), 1-propanol (50 g) and DBU (40 g) in acetonitrile (200 mL) overnight. The mixture was poured into methanol (500 mL) and the precipitate was filtered off. The imide-diester was separated from the insoluble part of the precipitate by being dissolved in dichloromethane with stirring and was purified by column chromatography (silica, dichloromethane followed by dichloromethane/ethyl acetate 50:1) and recrystallisation from boiling butanol. Yellow powder; yield: 6.2 g (66 %); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 9.03$ (d, $J = 9$ Hz, 2H; ArH), 8.60 (d, $J = 9$ Hz, 2H; ArH), 8.22 (d, $J = 9$ Hz, 2H; ArH), 8.09 (d, $J = 9$ Hz, 2H; ArH), 4.71 (t, $J = 7$ Hz, 4H; CH$_2$O), 4.53 (tt, $J = 9$, $J = 6$ Hz, 1H; CHN), 2.45–2.35 (m, 2H; CH$_2$), 2.13 (sext, $J = 7$ Hz, 4H; CH$_2$), 2.09–1.99 (m, 2H; CH$_2$), 1.65 (sext, $J = 7$ Hz, 4H; CH$_2$), 1.29 (t, $J = 7$ Hz, 6H; CH$_3$), 1.16 ppm (t, $J = 7$ Hz, 6H; CH$_3$); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 170.2$ (C=O), 168.3 (C=O), 128.7 (C$_{\mathrm{Ar}}$), 128.6 (C$_{\mathrm{Ar}}$), 127.7 (C$_{\mathrm{Ar}}$H), 127.1 (C$_{\mathrm{Ar}}$H), 124.9 (C$_{\mathrm{Ar}}$H), 123.9 (C$_{\mathrm{Ar}}$), 123.8 (C$_{\mathrm{Ar}}$), 122.9 (C$_{\mathrm{Ar}}$H), 122.8 (C$_{\mathrm{Ar}}$), 121.3 (C$_{\mathrm{Ar}}$), 120.6 (C$_{\mathrm{Ar}}$), 119.0 (C$_{\mathrm{Ar}}$), 68.1 (CH$_2$O), 51.7 (CHN), 35.1 (CH$_2$), 22.3 (CH$_2$), 20.3 (CH$_2$), 14.0 (CH$_3$), 10.8 ppm (CH$_3$); elemental analysis calcd (%) for $C_{41}H_{37}NO_6$: C 76.98, H 5.83, N 2.19; found: C 76.68, H 6.04, N 2.16.

Perylene 3,4,9,10-tetracarboxylic di-(4-heptyl)imide (16, R = 4-heptyl): PTCDA **20** (16 g, 41 mmol) was refluxed with 4-heptylamine (17.5 g, 152 mmol) in DMF (400 mL) overnight. Methanol (600 mL) was added to precipitate the diimide, which was filtered off, purified by column chromatography (silica, dichloromethane) and boiled out overnight in butanol (800 mL), in which it dissolves only partially at reflux. Deep-red powder; yield: 21.3 g (89 %); m.p. 365 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.65$ (d, $J = 8$ Hz, 4H; ArH), 8.60 (d, $J = 8$ Hz, 4H; ArH), 5.24 (tt, $J = 9.0$, $J = 6.0$ Hz, 2H; CHN), 2.32–2.22 (m, 4H; CH$_2$), 1.88–1.79 (m, 4H; CH$_2$), 1.42–1.25 (m, 8H; CH$_2$), 0.93 ppm (t, $J = 7$ Hz, 12H; CH$_3$); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 164.2$ (CO), 134.6 (C$_{\mathrm{Ar}}$), 131.6 (C$_{\mathrm{Ar}}$H), 129.7 (C$_{\mathrm{Ar}}$), 126.5 (C$_{\mathrm{Ar}}$), 123.7 (C$_{\mathrm{Ar}}$), 123.1 (C$_{\mathrm{Ar}}$H), 54.3 (CHN), 34.6 (CH$_2$), 20.2 (CH$_2$), 14.1 ppm (CH$_3$); elemental analysis calcd (%) for $C_{38}H_{38}N_2O_4$: C 77.79, H 6.53, N 4.77; found: C 77.69, H 6.65, N 4.79.

Perylene 3,4,9,10-tetracarboxylic tetraisobutylester (18, R = isobutyl): PTCDA **20** (20 g, 51 mmol), 1-bromo-2-methylpropane (100 g), isobutanol (65 g) and DBU (75 g) were refluxed in acetonitrile (800 mL) overnight. The stirred suspension quickly turned orange even prior to heating, and an orange precipitate was formed. After cooling to room temperature, the precipitation of tetraester was completed by adding methanol (1 L). The precipitate was filtered off, purified by column chromatography (silica gel, dichloromethane) and recrystallised from boiling butanol. Orange needles; yield: 26 g (78 %) (cr - 188 °C - col$_{\mathrm{hex}}$ - 320 °C - i); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.14$ (d, $J = 8$ Hz, 4H; ArH), 7.96 (d, $J = 8$ Hz, 4H; ArH), 4.12 (d, $J = 7.0$ Hz, 8H; CH$_2$O), 2.12 (m, 4H; CH), 1.04 ppm (d, $J = 7.0$ Hz, 24H; CH$_3$); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 168.5$ (CO$_2$), 133.0 (C$_{\mathrm{Ar}}$), 130.5 (C$_{\mathrm{Ar}}$), 130.3 (C$_{\mathrm{Ar}}$H), 129.0 (C$_{\mathrm{Ar}}$), 128.8 (C$_{\mathrm{Ar}}$), 121.4 (C$_{\mathrm{Ar}}$H), 71.5 (CH$_2$), 27.9 (CH), 19.4 ppm (CH$_3$); IR (KBr film): $\tilde{\nu} = 2960$, 2875, 1724, 1705, 1589, 1477, 1395, 1308, 1298, 1275, 1186, 1172, 1139, 1099, 1007, 941, 844, 805, 749 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ ($\log \varepsilon$) = 266 (4.3), 354 (3.4), 444 (4.5), 472 nm (4.6 mol^{-1} dm^3 cm^{-1}); MS (DCI, NH$_3$): m/z (%): 671 (100) $[M+NH_4]^+$; elemental analysis calcd (%) for $C_{40}H_{44}O_8$: C 73.60, H 6.79; found: C 73.59, H 6.83.

Coronene 1,2,4,5,7,8,10,11-octacarboxylic 4:5,10:11-di-ethylimide 1,2,7,8-tetraisobutylester (19, R = isobutyl, R′ = ethyl): Compound **18** (R = isobutyl) (7.8 g, 12 mmol) *N*-ethyl-maleimide (25 g, 200 mmol), *p*-hydroxyanisole (1.2 g, 10 mmol) and chloranil (15 g, 61 mmol) were thoroughly mixed and heated in a 100 mL flask with initial stirring to reflux (oil bath at 240 °C) for 18 h. (The mixture became highly viscous after about 6 h and stirring was no longer possible). Chloroform (50 mL) was added and the mixture was heated to reflux again for three hours with vigorous stirring to partially dissolve the gum. The suspension was washed out of the reaction flask with more chloroform (500 mL) and filtered through a large glass filter. The filtrate was concentrated and separated on a wide silica column. First, the reactants and brownish impurities were eluted with chloroform, and then the product fraction was eluted with chloroform/ethyl acetate 10:1. Refluxing in butanol (50 mL) followed by hot filtration through a preheated large glass filter efficiently removed the more soluble benzo[ghi]perylene side product, and the product was further purified by column chromatography (silica, chloroform/ethyl acetate 20:1). Yellow powder; yield: varying between 0.25 and 1.1 g (2 to 10 %, depending on extent of concurrent saponification); m.p. > 375 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 10.36$ (s, 4H; ArH), 4.36 (d, $J = 7$ Hz, 8H; CH$_2$O), 4.11 (q, $J = 7$ Hz, 4H; CH$_2$N), 2.12 (m, 4H; CH), 1.55 (t, $J = 7$ Hz, 6H; CH$_3$), 1.04 ppm (d, $J = 7$ Hz, 24H; CH$_3$); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 168.9$ (C=O), 168.2 (C=O), 131.7 (C$_{\mathrm{Ar}}$), 127.4 (C$_{\mathrm{Ar}}$), 127.1 (C$_{\mathrm{Ar}}$H), 125.2 (C$_{\mathrm{Ar}}$), 124.4 (C$_{\mathrm{Ar}}$), 123.0 (C$_{\mathrm{Ar}}$), 122.8 (C$_{\mathrm{Ar}}$), 72.4 (CH$_2$O), 33.6 (CH$_2$N), 28.1 (CH), 19.5 (CH$_3$), 14.3 ppm (CH$_3$); IR (KBr film): $\tilde{\nu} = 3448$, 2963, 2875, 1760, 1723, 1705, 1472, 1441, 1397, 1378, 1350, 1259, 1196, 1159, 1065, 1014, 994, 923, 768 cm^{-1}; UV/Vis (CHCl$_3$): $\lambda_{\max}$ ($\log \varepsilon$) = 357 (5.1), 405 (4.0), 428 (3.8), 453 (3.5), 483 nm (3.4 mol^{-1} dm^3 cm^{-1}); MS (DCI, NH$_3$): m/z (%): 913 (87) $[M+NH_4]^+$, 914 (100) $[M+H+NH_4]^+$; elemental analysis calcd (%) for $C_{52}H_{50}N_2O_{12}$: C 69.79, H 5.63, N 3.13; found: C 69.55, H 5.76, N 3.17.

Coronene 1,2,4,5,7,8,10,11-octacarboxylic 1:2,4:5,7:8,10:11-tetra-(4-heptyl)imide (17, R = 4-heptyl): Compound **19** (R = isobutyl, R′ = ethyl) (0.5 g, 0.56 mmol) and potassium carbonate (15 g) were heated with stirring to reflux in methanol (30 mL). 10 mL of methanol were allowed to boil off, and heating was continued at 150 °C (bath temperature) overnight. After cooling to room temperature, the solidified mixture was dissolved in water (200 mL). Concentrated hydrochloric acid was added to precipitate the octaacid formed, and the mixture was cooled to 0 °C to complete the precipitation. The solid (0.3 g) was filtered off and dried under vacuum. It was stirred at reflux with 4-heptylamine (3 g, 26 mmol) in DMF (50 mL) overnight. The mixture was poured into methanol (500 mL) to precipitate the product, which was filtered off and purified by column chromatography (silica, chloroform/ethyl acetate 20:1) and recrystallised from boiling butanol (500 mL). Orange/yellow powder; yield: 0.24 g (44 %); m.p. >375 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.17$ (s, 4H; ArH), 5.52 (tt, $J = 10.0$, $J = 6.0$ Hz, 2H; CHN), 4.63 (tt, $J = 10.0$, $J = 5.0$ Hz, 2H; CHN), 2.55–2.34 (m, 8H; CH_2), 2.04–1.85 (m, 8H; CH_2), 1.49 (sext, $J = 7.0$ Hz, 16H; CH_2), 1.01 (t, $J = 7.0$ Hz, 12H; CH_3), 0.99 ppm (t, $J = 7.0$ Hz, 12H; CH_3); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta =$ 169.0 (CO), 163.9 (CO), 129.2 ($C_{Ar}H$), 128.2 (C_{Ar}), 125.9 (C_{Ar}), 125.2 (C_{Ar}), 124.5 (C_{Ar}), 124.2 (C_{Ar}), 120.5 (C_{Ar}), 55.1 (CHN), 52.6 (CHN), 34.8 (CH_2), 34.6 (CH_2), 20.3 (CH_2), 20.1 (CH_2), 14.1 (CH_3), 13.9 ppm (CH_3); elemental analysis calcd (%) for $C_{60}H_{64}N_4O_8$: C 74.36, H 6.66, N 5.78; found: C 74.40, H 6.70, N 5.62.

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[6] Bilayer solar cells made of a 30 to 70 nm thick layer of benzoperylene triethylester and a 50 nm layer of benzoperylene hexacarboxylic trialkylimide or dialkylimide-dialkylester[5] between ITO and Al electrodes yield open circuit voltages in excess of 1 V.

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