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Complementary Synthetic Approaches to Elongated Polycyclic Arenes with Regioisomeric Carboxylic Substitution Patterns

Harald Bock,^{*,[a]} Pauline Carré,^[b] Elizabeth A. Hillard,^[a] and Fabien Durola^{*,[a]}

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The reaction of 1,5-dibromoanthracene with butyllithium and diethyloxalate followed by saponification gives anthrylene-1,5-diglyoxylic acid as a bifunctional reactant. Its double condensation with 2-bromophenylacetic acid, followed by double cyclization, leads to a bright-orange near-linear dinaphtho-anthracene-tetracarboxydiimide with substituents on the naphthalene moieties. An analogous condensation-cyclization sequence of 2,5-dibromophenylene-1,4-diacetic acid with 1-naphthylglyoxylic acid leads to an iso-

meric red diimide substituted on the anthracene nucleus. The striking difference in band gaps shows that diimide substitution on the central moiety of diareno[*a,h*]anthracenes is particularly efficient in inducing long-wavelength absorption. The substitution dependence of the band gap is found to be mainly caused by a variation of the reduction potentials with substituent position, whereas the oxidation potentials are largely substitution-independent.

Introduction

Carboxy-substituted polycyclic aromatic chromophores are attractive both as rather stable dyes and as charge-transport materials in organic electronics,^[1] and their optical and electronic properties have been reported to vary significantly between closely related species such as between planar and helical regioisomers.^[2] Since the advent of novel polymeric forms of sp^2 -hybridized carbon such as single-walled carbon nanotubes^[3] and single-sheet graphene,^[4] they are also of interest as model systems for polymeric graphene nanoribbons^[5] with defined edge geometry and solubilizing and electronically modulating lateral substituents.

We have recently shown^[6] that the glyoxylic Perkin reaction^[7] followed by palladium-catalyzed dehydrobromination^[8] is an efficient tool with which to construct carboxy-functionalized polycyclic arenes, and that 2,5-dibromophenylene-1,4-diacetic acid **1** is an appropriate and easily accessible bifunctional synthon that can be used to build up tetracarboxy-substituted diareno[*a,h*]anthracenes in combination with two molecules of an arylglyoxylic acid.

The derived diimides **2** and **3**, obtained through the reaction of **1** with pyrenyl-1-glyoxylic acid or perylenyl-3-glyox-

ylic acid, showed exceptionally large bathochromic shifts of more than 100 nm of the longest-wavelength absorption maximum compared with the corresponding tetraesters **4** and **5** (Figure 1). Diimide substitution in the 3,4- and 7,8-positions of the central anthracene unit of diareno[*a,h*]anthracenes thus appears to be a particularly efficient means to impart long-wavelength absorption and small electronic band gaps to such polycyclic aromatic chromophores.

Figure 1. Diareno[*a,h*]anthracene-diimides **2** (crystal color: purple) and **3** (green) that exhibit very strong bathochromic absorption band shifts compared with the corresponding tetraesters **4** (orange) and **5** (red).^[6] Undec = *n*-undecyl, Oct = *n*-octyl.

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through the condensation of a central arylene-diglyoxylic acid as a bifunctional synthon with two peripheral *o*-bromoarylacetic acid molecules.

If anthrylene-1,5-diglyoxylic acid **6** is chosen as central building block, diareno[*a,h*]anthracenes similar to those obtained from **1** should be accessible, but with the carboxylic substituents in less central positions.

Results and Discussion

Whereas the synthesis of **6** by Friedel–Crafts-type approaches is not easily envisaged, 1,5-dibromoanthracene **7** is readily available from 1,5-diaminoanthraquinone through reaction with CuBr₂ followed by reduction.^[9] We found that the reaction of dibromoarene **7** with butyllithium at low temperature followed by addition of excess diethyl oxalate yields diglyoxylic ester **8** in 80% yield, which gives **6** upon basic hydrolysis (Figure 2). In principle, this approach, which is based on oxalate quenching of a dilithiated arene-dianion, should be applicable to a variety of polycyclic dibromoarenes to yield the corresponding diglyoxylic acids.

The simplest *o*-bromoarylacetic acid is commercially available 2-bromophenylacetic acid **9**, which should condense with **6** to give bismaleate **10** after esterification, to give the seven-ring all-*kata*-annellated tetraester **11** and diimide **12** after palladium-mediated double dehydrobromination.

The feasibility of the path from **6** to **11** and **12** can be compared with the construction of analogous targets from **1**. To build up the same polycyclic system as in **11** and **12** but with carboxylic substituents in the more central positions that led to very long-wavelength absorption in **2** and **3**, **1** has to be condensed with naphthyl-1-glyoxylic acid **13**^[10] to give bismaleate **14**, which yields doubly cyclized tetraester **15** and diimide **16** after dehydrobromination.

The Perkin condensation of diglyoxylic acid **6** with monoacetic acid **9** (2.4 equiv.) in tetrahydrofuran (THF) heated to reflux over 24 h followed by esterification in situ, gave a significantly lower yield of bismaleate **10** (32%) than the complementary Perkin condensation of diacetic acid **1** with monoglyoxylic acid **13** (2.4 equiv.) to bismaleate **14** (53%), and traces of unreacted diglyoxylic acid could be recovered from the former reaction in the form of **8**. Longer reaction times did not improve the yield of **10**, and higher temperatures (reflux in dioxane) led to substantial darkening during the reaction. The modest yield of 32% appears reasonable if we consider that it is an overall yield of six individual reactions (two Perkin condensations and four esterifications) with an average yield of 83% ($0.827^6 = 0.32$). By analogy, the yield of 53% for **14** corresponds to an average yield of 90% ($0.900^6 = 0.53$) over six individual reactions.

The double intramolecular ring closure by palladium-catalyzed dehydrobromination of **14** to **15** proceeds with notably higher yield (69%) than the analogous reaction of **10** to **11** (46%), even though the reaction sites in **14** are sterically less accessible to the catalyst than those in **10**. We

Figure 2. Synthesis of dinaphtho[1,2-*a*:1',2'-*h*]anthracenes with different carboxylic substitution patterns. Reagents and conditions: (a) THF, −94 °C, BuLi, 4 h, then addition of EtO₂CCO₂Et, 1 h, 80%; (b) NaHCO₃, EtOH/H₂O, reflux, 4 h, 100%; (c) NEt₃, Ac₂O, THF, reflux, 20 h, then addition of EtOH, EtBr, DBU, reflux, 24 h, 32% (**10**) or 53% (**14**); (d) Pd(OAc)₂, PCy₃, K₂CO₃, DMA, 110 °C, 16 h, 46% (**11**) or 69% (**15**); (e) Pent₂CHNH₂, imidazole, *o*-C₆H₄Cl₂, reflux, 6 h, 75% (**12**) or 85% (**16**); Pent = *n*-pentyl.

suspect that in sterically less accessible **14**, ring closure under palladium ejection is more favored than in **10** with respect to unwanted palladium-catalyzed isomerizations.^[11]

The two diimides **12** and **16**, which differ only in the positions of the imide substituents, are easily distinguished by their colors: Whereas the *exo*-isomer **12** is bright-orange in the solid state and yellow in dilute chloroform solution, the *endo*-isomer **16** is red in the solid state and deep-orange in dilute chloroform solution. This translates to absorption spectra (20 μM in chloroform) with respective longest-wavelength absorption peaks at 490 (**12**) and 532 nm (**16**) (Figure 3). The tetraesters show corresponding longest-wavelength peaks at 400 (**11**) and 423 (**15**) nm, with resulting shifts of 90 nm from *exo*-ester **11** to *exo*-imide **12** and 109 nm from *endo*-ester **15** to *endo*-imide **16**. This comparison between otherwise identical systems differing only in their carboxylic substitution positions establishes that the particularly bathochromic absorption of systems such as **2**, **3**, and **16** is caused in substantial part by the localization of

the substituents in the 3,4- and 7,8-positions of the central anthracene moiety of these diareno[*a,h*]anthracenes. The respective absorption edges of 565 (**16**), 525 (**12**), 440 (**15**), and 425 nm (**11**) correspond to optical band gaps of 2.19, 2.36, 2.82, and 2.92 eV, respectively.

Figure 3. Absorption spectra of isomeric tetraesters **11** and **15** (dashed) and diimides **12** and **16** (continuous), 20 μM in CHCl_3 . Gray curve: **11** and **12**, black curve: **15** and **16**.

The anodic and cathodic electrochemistry of *endo*-ester **15**, *endo*-imide **16**, *exo*-ester **11**, and *exo*-imide **12** were evaluated by cyclic voltammetry (CV) and by differential pulse voltammetry (DPV) in dichloromethane between +1.7 and -2.0 V vs. Ag/AgNO_3 . Both *endo* compounds **15** and **16** showed a quasireversible to reversible oxidation at approximately $E_{1/2} = 1.18$ V vs. the ferrocenium/ferrocene couple. In the *exo* series, only imide **12** displayed reversible oxidation, at $E_{1/2} = 1.02$ V, whereas an irreversible oxidation of ester **11** occurred at $E_{1/2} = 1.04$ V. Overall, the oxidation behavior is thus only weakly dependent both on the nature of the substituents and on their location. The oxidations are therefore likely centered on the aromatic core.

Scanning cathodically, both *endo* compounds **15** and **16** displayed two reversible reduction processes. The *endo*-ester **15** was more difficult to reduce than the *endo*-imide **16**, with first reduction potentials of -1.85 V for **15** and -1.35 V for **16**, but the separation between the two reduction waves, $\Delta E_{1/2}$, was similar (230 mV for **15** and 260 mV for **16**). On the other hand, the first reduction potentials of the *exo* compounds (-2.03 V for **11** and -1.60 V for **12**) were significantly more negative than those for **15** and **16**, and showed small peak separations of 120 mV (ester **11**) and 60 mV (imide **12**) and the two CV waves were essentially superposed.

The extent of coupling between redox centers in mixed valence species can be estimated by the stability of the mixed-valent state. This thermodynamic parameter can be evaluated by the comproportionation constant $K_C = \exp(\Delta E_{1/2}/25.69)$,^[12] which depends on the peak separation $\Delta E_{1/2}$ of the two reductions in this case. A K_C value of 10^6 or above is generally accepted to imply strong electronic coupling and consequently full electron delocalization in the mixed valent state, corresponding to a Class III compound in the Robin and Day classification.^[13] The larger peak separations $\Delta E_{1/2}$ of around 250 mV in the *endo* com-

pounds **15** and **16** are consistent with previous observations that the distance between redox-active centers in conjugated mixed-valence compounds is inversely related to their redox peak separation.^[14] The comproportionation constants for **15** and **16** are on the order of $K_C = 4 \times 10^4$, which is indicative of weakly coupled Class II systems.^[12]

The nature of the substituents has a much larger role in determining the reduction potentials than the oxidation potentials, indicating that reduction is likely centered on the dicarboxylic substituents. The first reduction is easier in **15** and **16**, in which the substituents are closer to the center of the conjugated system, as compared with **11** and **12**. However, the second reduction is significantly more difficult than the first reduction in **15** and **16** because the proximity and electronic coupling of the substituents make it difficult to generate a second charge. In **11** and **12**, $\Delta E_{1/2}$ is small because the second charge created upon second reduction is located further away from the first charge.

From the first oxidation and reduction potentials, electrochemical band gaps of 2.54 (**16**), 2.62 (**12**), 3.04 (**15**), and 3.07 (**11**) eV are obtained. These values are respectively 0.35, 0.26, 0.22, and 0.15 eV higher than the optical band gap values estimated above from the absorption edges. The difference corresponds to the exciton binding energy in the neutral excited molecule, which is typically found to be of the order of 0.3 eV.^[15]

With $E_{1/2}(\text{Fc}^+/\text{Fc})$ at 4.80 eV below vacuum, the first reduction and oxidation potentials translate into lowest unoccupied molecular orbital energies E_{LUMO} of -3.45 (**16**), -3.20 (**12**), -2.95 (**15**), and -2.77 (**11**) eV and highest occupied molecular orbital energies E_{HOMO} of -5.98 (**16**), -5.82 (**12**), -5.98 (**15**), and -5.84 (**11**) eV.

Conclusions

As an alternative to the condensation of an aryl-monoglyoxylic acid with a dibromoarylene-diacetic acid, the condensation of a bromoaryl-acetic acid with an arylene-diglyoxylic acid is shown to be a viable new path to arene-tetracarboxylic esters and imides. To provide access to arylene-diglyoxylic acids, a dibromoarene is reacted with butyllithium at low temperature followed by reaction of the resulting arene-dianion with diethyl oxalate. Analogous implementation of the two complementary approaches leads to isomerically substituted tetracarboxy-derivatives of the same elongated *kata*-annellated hydrocarbon, dinaphtho[1,2-*a*;1',2'-*h*]anthracene. This allows us to assert that the positioning of electron-withdrawing substituents on aromatic chromophores has a significant influence on their electronic structure, and that the localization of such substituents on central positions of elongated polycyclic arenes can considerably shift the absorption to longer wavelengths and thus reduce the band gap as well as E_{LUMO} . The reduction potentials are found to be much more dependent on the nature and the positioning of the carboxylic substituents than the oxidation potentials, implying that oxidation is centered largely on the aromatic core, whereas reduction is largely centered on the substituents.

Experimental Section

Diethyl Anthrylene-1,5-diglyoxylate (8): To a stirred suspension of 1,5-dibromoanthracene ^{7[9]} (4.00 g, 336.0 g/mol, 11.9 mmol) in anhydrous THF (400 mL) under argon, a solution of butyllithium (2.5 M in hexane, 19 mL, 47.5 mmol) was added dropwise at −94 °C (acetone–liquid nitrogen cooling bath), and the orange mixture was stirred for 4 h at −94 °C. Diethyl oxalate (15 mL, 1.077 g/mL, 16 g, 146.1 g/mol, 110 mmol) was quickly added at −94 °C. After 30 min at −94 °C, the cooling bath was removed and stirring was continued for 1 h at room temperature. CH₂Cl₂ (200 mL) was added, followed by 1 M hydrochloric acid (100 mL), the phases were separated, the aqueous phase was extracted with CH₂Cl₂ (2 × 100 mL), and the combined organic phases were dried with sodium sulfate and concentrated. Cold methanol (750 mL) was added while stirring, and the precipitated product was filtered off and purified by column chromatography on silica (CH₂Cl₂) and recrystallized from ethanol, yield 3.60 g (378.4 g/mol, 9.5 mmol, 80%); yellow felt-like solid; m.p. 168–171 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.84 (s, 2 H), 8.22 (dd, *J* = 8, 1 Hz, 2 H), 8.13 (dd, *J* = 7, 1 Hz, 2 H), 7.63 (dd, *J* = 8, 7 Hz, 2 H), 4.52 (q, *J* = 7 Hz, 4 H), 1.47 (t, *J* = 7 Hz, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 188.8, 164.7, 138.0, 136.8, 133.9, 128.4, 128.0, 127.2, 124.9, 62.7, 14.4 ppm. FD-HRMS: *m/z* calcd. for C₂₂H₁₈O₆ [M]⁺ 378.1103; found 378.1115.

Anthrylene-1,5-diglyoxylic Acid (6): Diethyl anthrylene-1,5-diglyoxylate **8** (3.78 g, 378.4 g/mol, 10 mmol) was suspended in ethanol (125 mL). A solution of sodium hydrogen carbonate (8.4 g, 84.0 g/mol, 100 mmol) in water (250 mL) was added and the mixture was stirred and heated to reflux for 4 h. The resulting homogeneous solution was poured into 5% aqueous hydrochloric acid (500 mL). The precipitate was filtered off, washed with 5% aqueous hydrochloric acid, and allowed dry in air. The yellow solid product (3.22 g, 322.3 g/mol, 10 mmol, quantitative yield) was used without further purification. m.p. >250 °C (dec.). ¹H NMR (400 MHz, [D₆]DMSO): δ = 9.78 (s, 2 H), 8.62 (d, *J* = 8.5 Hz, 2 H), 8.24 (d, *J* = 7 Hz, 2 H), 7.80 (t, *J* = 8 Hz, 2 H) ppm (no discrete acid proton detected). ¹³C NMR [100 MHz, [D₆]DMSO]: δ = 191.0, 166.4, 137.4, 136.7, 133.1, 127.4, 127.1, 126.2, 125.6 ppm. FD-HRMS: *m/z* calcd. for C₁₈H₁₀O₆ [M]⁺ 322.0477; found 322.04775.

Tetraethyl 1,5-Anthrylenebis[(2-bromophenyl)maleate] (10): Anthrylene-1,5-diglyoxylic acid **6** (1.61 g, 322.3 g/mol, 5 mmol), 2-bromophenylacetic acid **9** (2.58 g, 215.0 g/mol, 12 mmol), triethylamine (5 g, 101.2 g/mol, 0.05 mol), and acetic anhydride (7 g, 102.1 g/mol, 0.07 mol) were stirred and heated to reflux in anhydrous THF (60 mL) under argon for 20 h. A solution of DBU (15 g, 152.2 mmol, 0.1 mol), ethanol (20 g, 46.1 g/mol, 0.4 mol), and bromoethane (20 g, 109.0 g/mol, 0.2 mmol) in anhydrous THF (50 mL) was then added and the mixture was stirred and heated to reflux under exclusion of moisture for 24 h. Chloroform and 5% aqueous hydrochloric acid were added, the phases were separated, the aqueous phase was extracted with chloroform, the combined chloroform extracts were dried with sodium sulfate, the solvent was evaporated, and the resulting crude product was purified by column chromatography (CH₂Cl₂ containing 1% ethanol) on silica and recrystallized from ethanol, yield 1.33 g (828.5 g/mol, 1.61 mmol, 32%); yellow solid; m.p. 210–213 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.80–8.45 (broad, 2 H), 7.97 (d, *J* = 8.5 Hz, 2 H), 7.70–7.15 (2 broad overlapping peaks, 6 H), 7.10–6.65 (2 broad overlapping peaks, 6 H), 4.30 (q, *J* = 7 Hz, 4 H), 4.40–4.10 (broad, 4 H), 1.30 (t, *J* = 7 Hz, 6 H), 1.35–1.15 (broad, 6 H) ppm. The strong signal broadening due to slow rotations, evident from the ¹H NMR spectrum, did not allow the recording of

a meaningful ¹³C NMR spectrum. FD-HRMS: *m/z* calcd. for C₄₂H₃₆Br₂O₈ [M]⁺ 826.0777; found 826.0777.

Tetraethyl 2,5-Dibromo-1,4-phenylenebis[(1-naphthyl)maleate] (14): Prepared from 2,5-dibromophenylene-1,4-diacetic acid **1[6]** (1.76 g, 352.0 g/mol, 5 mmol) and naphthylglyoxylic acid **13[10]** (2.40 g, 200.2 g/mol, 12 mmol) by following the preceding procedure for the preparation of **10** from **6** and **9**, yield 2.18 g (828.5 g/mol, 2.63 mmol, 53%); off-white solid; m.p. 206–209 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.20–6.40 (5 broad overlapping peaks, 16 H), 4.40–3.90 (broad, 8 H), 1.20 (t, *J* = 7 Hz, 6 H), 1.25–0.90 (broad, 6 H) ppm. The strong signal broadening due to slow rotations, evident from the ¹H NMR spectrum, did not allow the recording of a meaningful ¹³C NMR spectrum. FD-HRMS: *m/z* calcd. for C₄₂H₃₆Br₂O₈ [M]⁺ 826.0777; found 826.0779.

Tetraethyl Dinaphtho[1,2-*a*:1',2'-*h*]anthracene-8,9,17,18-tetracarboxylate (11): Tetraethyl 1,5-anthrylenebis[(2-bromophenyl)maleate] **10** (1.66 g, 828.5 g/mol, 2 mmol), palladium diacetate (0.09 g, 225.5 g/mol, 0.4 mmol), tricyclohexylphosphine (0.24 g, 280.4 g/mol, 0.9 mmol), and potassium carbonate (2.76 g, 138.2 g/mol, 20 mmol) were stirred at 110 °C in anhydrous dimethylacetamide (DMA, 30 mL) under argon for 16 h. After cooling to room temperature, hot chloroform was added, the solids were filtered off, the filtrate was washed with 5% aqueous hydrochloric acid, dried with sodium sulfate, and concentrated. The crude product was precipitated by adding ethanol, and the precipitate was filtered off and purified by column chromatography on silica in chloroform and recrystallized from butanol, yield 0.61 g (666.7 g/mol, 0.91 mmol, 46%); pale-yellow solid; m.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.85 (s, 2 H), 8.78 (d, *J* = 8 Hz, 2 H), 8.67 (d, *J* = 9 Hz, 2 H), 8.17 (d, *J* = 8 Hz, 2 H), 8.12 (d, *J* = 9 Hz, 2 H), 7.80 (t, *J* = 7.5 Hz, 2 H), 7.70 (t, *J* = 7.5 Hz, 2 H), 4.60 (q, *J* = 7 Hz, 4 H), 4.50 (q, *J* = 7 Hz, 4 H), 1.50 (t, *J* = 7 Hz, 4 H), 1.27 (t, *J* = 7 Hz, 4 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 168.6, 131.4, 130.71, 130.68, 130.6, 130.2, 128.7, 128.4, 128.3, 128.1, 127.8, 126.3 (×2), 123.9, 123.8, 121.5, 62.6, 62.5, 14.4, 14.1 ppm. FD-HRMS: *m/z* calcd. for C₄₂H₃₄O₈ [M]⁺ 666.2254; found 666.2251.

Tetraethyl Dinaphtho[1,2-*a*:1',2'-*h*]anthracene-5,6,14,15-tetracarboxylate (15): Prepared from **14** by following the procedure for the preparation of **11** from **10**, yield 0.92 g (666.7 g/mol, 1.38 mmol, 69%); pale-yellow felt-like solid; m.p. 269–272 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.65 (s, 2 H), 8.87 (d, *J* = 9 Hz, 2 H), 8.33 (d, *J* = 7.5 Hz, 2 H), 8.24 (d, *J* = 9 Hz, 2 H), 8.09 (d, *J* = 7.5 Hz, 2 H), 7.70 (t, *J* = 7.5 Hz, 2 H), 7.66 (t, *J* = 7.5 Hz, 2 H), 4.68 (q, *J* = 7 Hz, 4 H), 4.50 (q, *J* = 7 Hz, 4 H), 1.55 (t, *J* = 7 Hz, 4 H), 1.35 (t, *J* = 7 Hz, 4 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 170.6, 168.5, 133.4, 131.4, 130.6, 130.5, 130.1, 129.8, 129.6, 128.9, 127.1, 126.8, 126.6, 126.4, 124.4, 121.5, 120.9, 62.7, 62.6, 14.5, 14.0 ppm. FD-HRMS: *m/z* calcd. for C₄₂H₃₄O₈ [M]⁺ 666.2254; found 666.2256.

***N,N'*-Bis(1-pentylhexyl) Dinaphtho[1,2-*a*:1',2'-*h*]anthracene-8,9,17,18-tetracarboxydiimide (12):** Tetraethyl dinaphtho[1,2-*a*:1',2'-*h*]anthracene-8,9,17,18-tetracarboxylate **11** (0.20 g, 666.7 g/mol, 0.30 mmol), 6-aminoundecane^{11[6]} (0.34 g, 171.3 g/mol, 2 mmol), and imidazole (5 g) were stirred and heated to reflux in *o*-dichlorobenzene (10 g) under argon for 6 h. After cooling to room temperature, the solidified mixture was dissolved in hot chloroform, the solution was washed with 5% aqueous hydrochloric acid, and the chloroform was evaporated. The product was precipitated by adding methanol and purified by column chromatography (chloroform) on silica and recrystallized from xylenes, yield 0.185 g (825.1 g/mol, 0.30 mmol, 75%); orange solid; m.p. >300 °C. ¹H

NMR (400 MHz, CD₂Cl₂): δ = 10.28 (s, 2 H), 9.41 (d, J = 8 Hz, 2 H), 8.88 (d, J = 8 Hz, 2 H), 8.82 (d, J = 9.5 Hz, 2 H), 8.45 (d, J = 9.5 Hz, 2 H), 7.92 (t, J = 7.5 Hz, 2 H), 7.86 (t, J = 7.5 Hz, 2 H), 4.43 (tt, J = 10, 5 Hz, 2 H), 2.32–2.20 (m, 4 H), 1.90–1.79 (m, 4 H), 1.48–1.25 (m, 24 H), 0.87 (t, J = 7 Hz, 12 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 170.03, 169.97, 134.2, 133.3, 132.4, 130.6, 129.8, 129.5, 128.8, 127.9, 127.8, 127.3, 126.5, 126.2, 124.8, 123.8, 121.1, 52.7, 32.7, 31.8, 26.8, 22.9, 14.3 ppm. FD-HRMS: m/z calcd. for C₅₆H₆₀N₂O₄ [M]⁺ 824.4553; found 824.4558.

***N,N'*-Bis(1-pentylhexyl) Dinaphtho[1,2-*a*;1',2'-*h*]anthracene-5,6:14,15-tetracarboxdiimide (16):** Prepared from **15** by following the procedure used for the preparation of **12** from **11**, yield 0.21 g (825.1 g/mol, 0.30 mmol, 85%); red solid; m.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 10.90 (s, 2 H), 9.49 (d, J = 8 Hz, 2 H), 9.09 (d, J = 9 Hz, 2 H), 8.26 (d, J = 9 Hz, 2 H), 8.04 (d, J = 7.5 Hz, 2 H), 7.77 (t, J = 7.5 Hz, 2 H), 7.72 (t, J = 7 Hz, 2 H), 4.44 (tt, J = 9.5, 5 Hz, 2 H), 2.33–2.21 (m, 4 H), 1.93–1.82 (m, 4 H), 1.46–1.23 (m, 24 H), 0.86 (t, J = 7 Hz, 12 H) ppm. ¹³C NMR (100 MHz, CDCl₃, 55 °C): δ = 170.5, 169.9, 134.5, 133.9, 132.6, 132.0, 130.7, 130.3, 129.6, 129.0, 128.2, 128.1, 126.8, 125.9, 124.8, 122.3, 122.0, 53.3, 33.0, 31.9, 26.9, 22.8, 14.2 ppm. FD-HRMS: m/z calcd. for C₅₆H₆₀N₂O₄ [M]⁺ 824.4553; found 824.4556.

Supporting Information (see footnote on the first page of this article): Electrochemical data, ¹H and ¹³C NMR spectra.

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