Terrylenimides: New NIR Fluorescent Dyes

Frank O. Holtrup, Gert R. J. Müller, Heribert Quante, Steven De Feyter, Frans C. De Schryver, and Klaus Müllen*

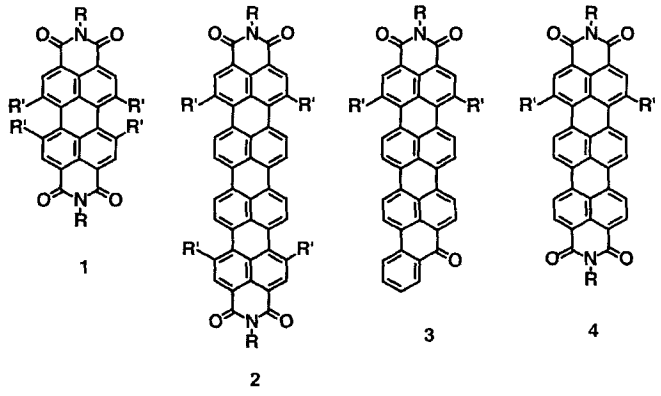
Abstract: Terrylenimides **3** and **4** represent a new class of blue colorants, exhibiting absorption maxima at 650 to 700 nm and fluorescence emissions in the NIR region (673 to 750 nm). The terrylenimides were synthesized by means of various organometallic coupling reactions, catalyzed by transition metal complexes (Ni^0, Pd^0) and starting from the aromatic bromides, boronic acids, or organotin compounds. The terrylenimides have all the properties expected of excellent fluorescent dyes: high extinction coefficients, high fluorescence quantum yields, and very good thermal, chemical, and photochemical stabilities. Owing to its extended π system, **3** can reversibly accept four negative charges. By varying the substituents, **3** and **4** can be modified to serve either as soluble dyes or as insoluble pigments.

Keywords
arenes · C–C coupling · dyes · fluorescence · terrylenes

Introduction

Perylene-3,4:9,10-tetracarboxdiimides **1** (Scheme 1) have been valued for a long time owing to their outstanding chemical and optical properties.[1] They are characterized by a brilliant color, strong fluorescence, and good thermal, chemical, and photochemical stabilities.[2] Perylenediimides **1** absorb in the visible range at 525 nm and show a fluorescence quantum yield of 1 (100%).[3] In addition to their application as commercial dyes and pigments, they are used in reprographical processes,[4] in fluorescence solar collectors,[5] in photovoltaic devices,[6] in dye lasers,[7] and in molecular switches.[8] Recently, we succeeded in synthesizing the quaterrylenetetracarboxdiimides **2** by homocoupling of bromoperylenedicarboximides **5**, followed by oxidative cyclization.[9] Owing to their extended π system, the quaterrylenes **2** exhibit absorption maxima ($\lambda = 764$, R′ = H; 781 nm, R′ = *tert*-butylphenoxy) at much longer wavelengths than the corresponding perylene derivatives (526 nm).[10] Synthesizing the missing link absorbing in the red region would close the gap between the two classes of dyes. The red fluorescent dyes used so far are cyanin,[11] phthalocyanin, xanthene (e.g. rhodamine), and oxazine dyes, some of which have serious disadvantages such as low chemical stability.[12]

We will describe the synthesis of new terrylene derivatives that excel in their long-wavelength absorption and high fluorescence quantum yield, in addition to having high thermal, chemical, and photochemical stabilities. This makes them promising candidates for attractive applications.[13] We have prepared both symmetrical terrylenes with two dicarboximide groups (**4**) and unsymmetrical ones based on benzanthrone (**3**), and we have examined the influence of the structure on the spectroscopic properties.



Scheme 1. R = alkyl, aryl; R′ = H, 4-*tert*-butylphenoxy.

Results and Discussion

The major purpose of our work was to synthesize a new fluorescent dye exhibiting a high fluorescence quantum yield. Our concept was the combination of two well-known fluorescent dyes (perylenimide and benzanthrone) with the aim of obtaining an absorption at longer wavelengths while maintaining the high quantum yield.

In analogy to the synthesis of **2**,[9] we first used Ni^0 complexes to promote the crosscoupling of the bromoperylenimide **5** with

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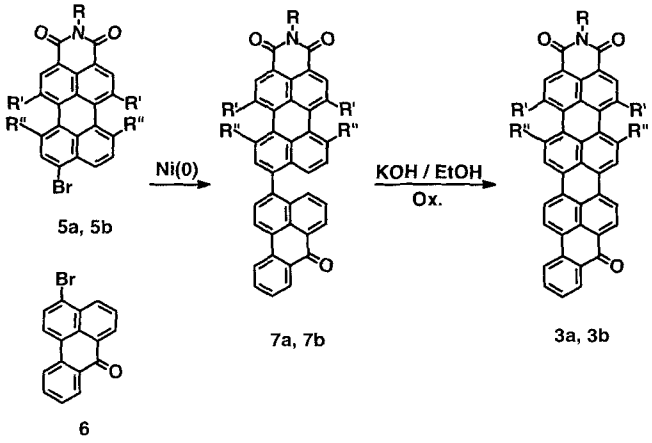
3-bromobenzanthrone (**6**) (Scheme 2). In the case of **5a**, we produced the active species in situ by reducing bis(triphenylphosphine)nickel(II) chloride with zinc and obtained the condensation product **7a** in a 45% yield. To couple **5b** we used [Ni(1,5-cyclooctadiene)$_2$] (Yamamoto conditions,[14] already successful for the synthesis of quaterrylenediimide) and obtained the desired product **7b** in 62% yield. The subsequent cyclization was again achieved in an oxidative alkali melt to give **3a** and **3b** in 34% and 83% yields, respectively. The reason for the low yield of **3a** is the ready saponification of the propylimide; in **3b** the isopropyl groups sterically shield the imide and thus hinder hydrolysis.



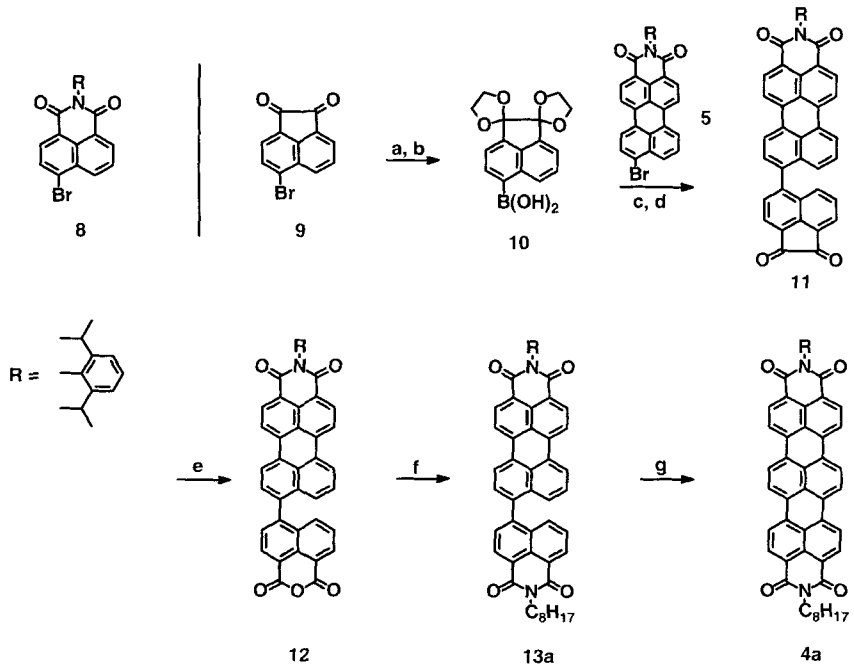
Scheme 2. Syntheses of benzoylterrylenedicarboximide **3a** and **3b** (**a**: R = *n*-propyl, R′ = R″ = 4-*tert*-butylphenoxy; **b**: R = 2,6-diisopropylphenyl, R′ = 4-*tert*-butylphenoxy, R″ = H). Reagents, conditions, and yields: a) **7a**: Ni(PPh$_3$)$_2$Cl$_2$, Zn, NEt$_4$I/THF, 25 °C, 12 h/45%; **7b**: Ni(cod)$_2$, cod, bipy/DMF, 70 °C, 2 d/62%; b) KOH, ox./EtOH, 70 °C, 15 min/80%.

Crosscoupling two different bromides with a Ni^0 complex in this way is a straightforward method of obtaining a new class of fluorescent compounds absorbing at long wavelengths, the benzoylterrylenimides **3**. However, some disadvantages are also apparent: the Ni complex is required in equimolar amounts, the yields are low owing to the homocoupling products that are also formed, and a chromatographic purification is required in the workup. Furthermore, not all bromides can be crosscoupled by this method. Some systems are dehalogenated or undergo exclusive homocoupling under the Yamamoto conditions. More selective reactions were therefore required favoring heterocoupling over mixed homocoupling.

An example where the Yamamoto condensation[14] fails is in the synthesis of symmetrical terrylenetetracarboxdiimides **4**: the coupling reaction of bromoperylenimide **5** and bromonaphthylimide **8** yielded mainly homocoupling products. The synthesis of **4** through heterocoupling would first require the transformation of one of the bromides **5** or **8** into the corresponding boronic acid (or another organometallic compound), which is usually achieved by lithiation or via the Grignard compound. The attempt to metalate **5** or **8** with butyllithium or magnesium, however, resulted solely in the reduction of the imide structure. We therefore chose a synthetic route via the ketal of 5-bromoacenaphthenequinone (**9**) (Scheme 3). The carbonyl groups in **9**[15] were protected against nucleophilic attack by reaction with ethyleneglycol to form ketal groups.[16] The bromide was then transformed into the boronic acid **10** by using standard methods. Compound **10** was used without further purification in a Suzuki coupling[17] with **5**. The resulting condensation product was hydrolyzed quantitatively to **11**. Compound **11** was oxidized by air under basic conditions giving the anhydride **12**, which was transformed into its imide **13** by reaction an amine. In analogy to the preparation of **2**,[9] **13** was cyclized in a KOH melt to give the final compound **4**.

This last route—heterocoupling via a boronic acid—is much more selective than the mixed homocoupling under Yamamoto conditions. Although a little lengthy, it allows intermediates such as **11** and **12** to be condensed with di- or monoamines to yield new useful dyes. One disadvantage is that it is restricted to reactions starting from acenaphthenequinone, because the protection of the carbonyl groups as ketals only works well for this molecule. The carbonyl group in 3-bromobenzanthrone (**6**), for example, cannot be protected by standard procedures (as the ketal with ethyleneglycol, as the dithioketal with propane-1,3-dithiol, or as the silyl ether after reduction to the alcohol), because it is incorporated into the aromatic system.

We therefore continued our search for a short, selective, and widely applicable synthesis of terrylenimides. Using a hexaalkylditin reagent and a palladium catalyst,[18] we succeeded in transforming the bromides **5** into their stannyl derivatives **14**,



Scheme 3. Synthesis of terrylenetetracarboxdiimide **4a**: reagents, conditions, yields: a) ethyleneglycol, conc. H$_2$SO$_4$/*m*-xylene, reflux, 4 d/85%; b) 1. *n*-butyllithium/THF, −78 °C; 2. triisopropylborate/THF, −78 °C; 3. H$_2$O/60%. c) [Pd(PPh$_3$)$_4$], 2M K$_2$CO$_3$/toluene, reflux, 20 h/75%; d) H$_2$SO$_4$, H$_2$O/1-PrOH, reflux, 4 d/>95%; e) KOH, O$_2$/1-PrOH, 60 °C, 4 h/>95%; f) *n*-octylamine/2-PrOH, reflux, 10 h/>95%; g) KOH, ox./EtOH, 70 °C, 15 min/80%.

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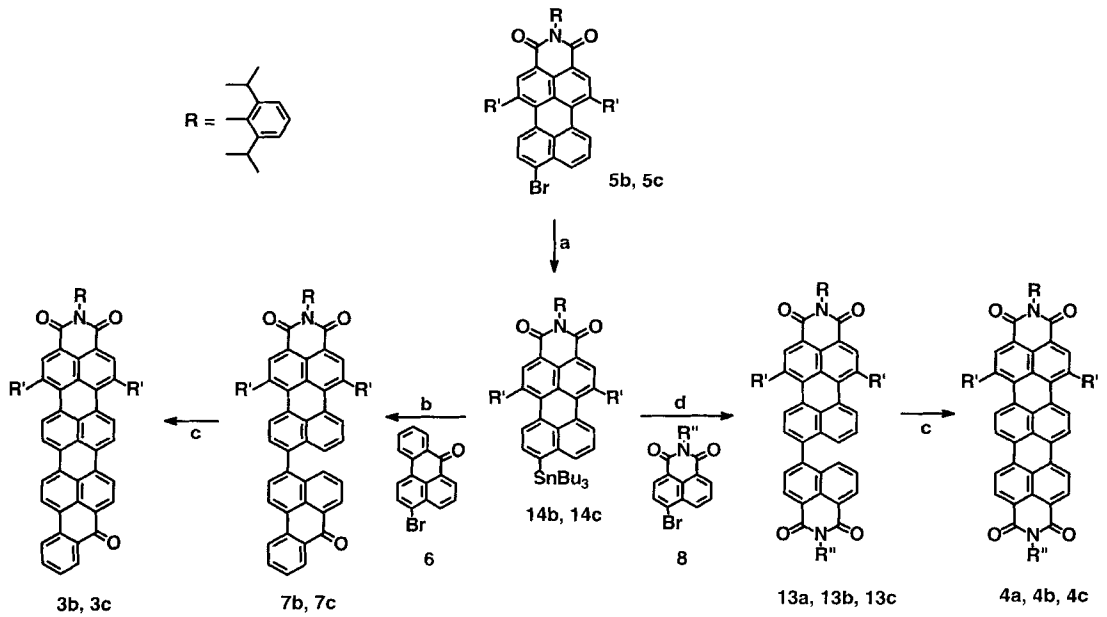

Scheme 4. Syntheses of **3** and **4** (**a**: R′ = H, R″ = *n*-octyl; **b**: R′ = 4-*tert*-butylphenoxy, R″ = 2,6-diisopropylphenyl; **c**: R′ = H, R″ = 2,6-diisopropylphenyl). Reagents, conditions, and yields: a) $Sn_2(Bu)_6$, $[Pd(PPh_3)_4]$/toluene, reflux, 4 d/88%; b) **6**, $[Pd(PPh_3)_4]$/DMF, 90 °C, 4 d/73%; c) KOH, ox./EtOH, 70 °C, 15 min/80%; d) **8**, $[Pd(PPh_3)_4]$/toluene, reflux, 4 d/70%.

which could be condensed with the bromides **6** or **8** (Scheme 4). Since this mild method does not employ nucleophilic organometallic reagents, protection of the imide group is not necessary. Both hexamethylditin and hexabutylditin could be used as stannylating agents, but the latter was preferred, owing to its lower toxicity and price. The tin group could be introduced into all of our bromides (**5**, **6**, and **8**); this demonstrates how tolerant the reaction is to functional and electronic variations. A number of palladium(0) and palladium(II) catalysts can be used, since they are interconvertible in the reaction mixture. The tin compounds can be coupled with a variety of aromatic bromides as described by Stille.[19] Stannane **14** coupled with **6** to yield **7** and with **8** to yield **13**. Minor side reactions were the homocoupling of the stannanes and the bromides, and destannylation. The final cyclizations to the compounds **3** and **4** were again achieved by means of an oxidative alkali melt.

The advantage of the mild stannane route is that protection of the sensitive carbonyl groups and inert conditions are no longer necessary. Both the ketal and the stannane route can be used to prepare terrylenimides **4** with identical or different groups (alkyl, aryl) at the imides. Further reactions such as hydrolysis and decarboxylation can be envisaged. The ready availability of tin compound **14** means that homocoupling reactions with other chromophoric units become accessible.

The dark blue compounds **3** and **4** can be identified unequivocally by ^1H and ^{13}C NMR spectroscopy and FD mass spectrometry. The bay-substituted compounds **3a**, **3b**, and **4b** are especially soluble in all common organic solvents and could thus be completely characterized.

The thermal stabilities of **3** and **4** are very high—decomposition sets in only above 460 °C, starting at the N-bonded groups, as determined by TGA. Thus the thermal stability corresponds to that of perylenediimide **1** and quaterrylenediimide **2**.[9]

The UV spectra of the terrylenimides show absorption bands at 650 to 700 nm, lying between those of perylenediimide and quaterrylenediimide, as expected (Figure 1). The similarity of the fine structures of the absorption spectra of **1**, **2**, and **4** is most remarkable (Figure 2). The absorption wavelength of terrylenediimide **4** is a little lower (**4a**: $\lambda_{max} = 650$ nm and $\varepsilon = 93000\,M^{-1}cm^{-1}$) than that of benzoylterrylenimide **3**. The absorption wavelength is influenced by the number of phenoxy

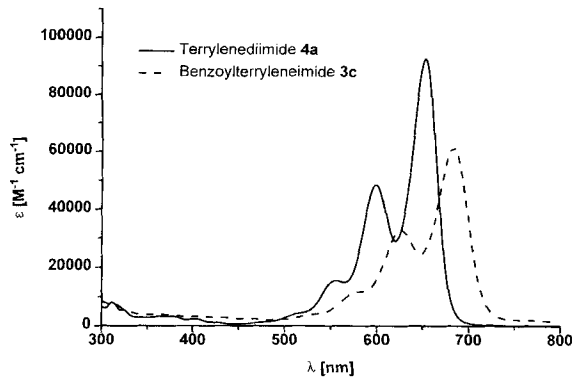

Figure 1. Absorption spectra of **3c** and **4a** ($CHCl_3$).

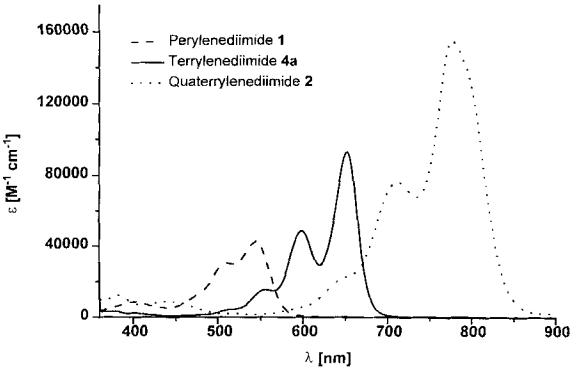

Figure 2. Absorption spectra of **1**, **4a**, and **2** ($CHCl_3$).

substituents in the bay region: The unsubstituted compounds **4a** and **4c** absorb at 650 nm ($\varepsilon = 93000\,M^{-1}cm^{-1}$) and the disubstituted **4b** at 664 nm ($\varepsilon = 120000\,M^{-1}cm^{-1}$). Unsubstituted **3c** absorbs at 676 nm ($\varepsilon = 62000\,M^{-1}cm^{-1}$), disubstituted **3b** at 687 nm ($\varepsilon = 93000\,M^{-1}cm^{-1}$), and tetrasubstituted **3a** at 700 nm ($\varepsilon = 78000\,M^{-1}cm^{-1}$). The high extinction coefficients make the terrylenimides promising candidates for applications as functional dyes.

The absorption spectra of **3** and **4** in sulfuric acid are characterized by narrow bands that are shifted bathochromically by 160 to 200 nm ($\lambda_{max} = 887$ nm (**3c**) and 810 nm (**4a**)) and exhibit extremely high extinction coefficients ($\varepsilon = 182000\,M^{-1}cm^{-1}$ (**3c**) and $508000\,M^{-1}cm^{-1}$ (**4a**)) (Figure 3). This observation

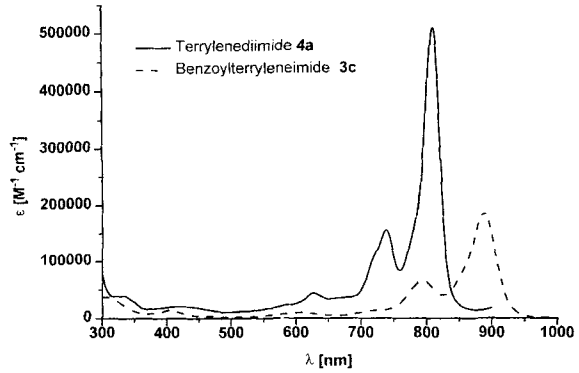

Figure 3. Absorption spectra of **3c** and **4a** in H_2SO_4 (96%).

can be explained by a protonation of the chromophores and the subsequent formation of *J* aggregates.[20] After dilution with water, the terrylenimides can be recovered unchanged; this indicates their high stability to acids and oxidizing agents.

The fluorescence quantum yields of the terrylenimides were determined relative to tetraphenylporphine, which has a known fluorescence quantum yield ($\phi_F = 0.13$)[21] and absorbs at a similar wavelength. The solvent used was methylcyclohexane ($c \approx 1 \times 10^{-6}$ M). The results are outstanding: **4a** exhibits a quantum yield of 90% ($\phi_F = 0.9 \pm 0.1$), and **3c** of 60% ($\phi_F = 0.6 \pm 0.1$). The emission bands are shifted bathochromically by 20 to 50 nm compared to the absorption bands and, in the case of **3a**, already lie in the NIR region at 750 nm (**3b**: 735 nm; **3c**: 701 nm; **4a**: 673 nm; **4b**: 707 nm; **4c**: 668 nm) (Figure 4).

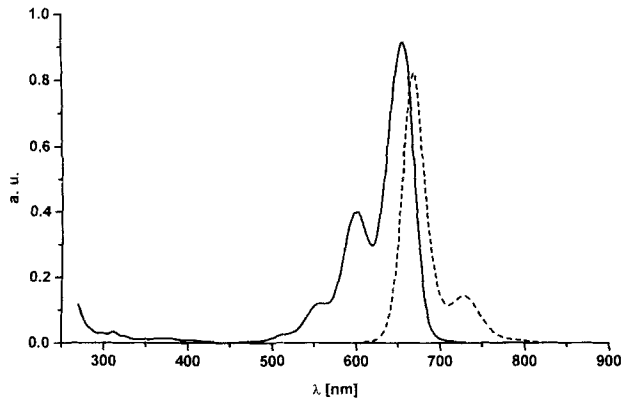

Figure 4. Excitation (—) and emission (- - -) spectra of **4a** ($CHCl_3$).

The photostabilities of **3** and **4** were estimated by exposing non-degassed chloroform solutions of **3** and **4** in quartz cuvettes to UV light ($\lambda = 366$ nm) for a prolonged period of time. After one week no significant changes in the extinction coefficients of the solutions of **3** and **4** could be observed. The samples of **3** and **4** were thus shown to be highly photostable, as stable as a similarly treated sample of perylenetetracarboxdiimide **1**, which is known for its excellent photochemical stability.[3]

Another important aspect for a possible application as optical switches are the redox properties. The reduction potentials of compound **3a** were determined. Four reduction steps can be detected, with potential values of $E = -0.83, -0.92, -2.14$, and -2.52 V. When compared to the corresponding values of tetraphenoxyperylenediimide **1** ($E = -0.85, -1.11, -2.64$ V), the first reduction step shows no significant difference. The second reduction step already occurs at a less negative potential, and for the third step the difference is even greater. The fourth step is impossible for the perylenediimide and can only be observed in the case of terrylenimide. Since the first two reduction steps occur considerably more easily than the third and fourth, it is probable that the first two charges can be stabilized by the dicarboximide groups through a partial delocalization. The third electron gives rise to electrostatic repulsion from the two negative charges already on the molecule and thus requires a higher potential than the first two. The fourth electron can add to the terrylenimide, but not to the perylenediimide, because the former is larger. This explanation is further supported by the fact that 2,5,8,11-tetra-*tert*-butylperylene (a molecule with the perylene core, but without any dicarboximide groups) undergoes only two reduction steps ($E = -1.99$ and -2.55 V).[10] In this case no stabilization of the reduced species is observed owing to the absence of dicarboximide groups, and potentials similar to those of the third step of tetraphenoxyperylenediimide ($E = -2.64$ V) and the third and fourth step of terrylenimide **3** ($E = -2.14$ and -2.52 V) are required for the reduction.

The exceptional electron-acceptor properties of **3** combined with the long-wavelength absorption and emission, and the high stability suggest applications in the field of optoelectronics. Besides the potential applications mentioned earlier, the terrylenimides are promising for uses in the medical (e.g., photochemotherapy) and analytical (e.g., laser fluorometry) fields.

Our future work will include the incorporation of soluble **3** and **4** (substituted by side chains in the bay region) into main-chain polymers in analogy to the perylenediimides **1**.[22] We thus hope to provide new ways of processing and new applications for the terrylenimides.

Experimental Procedure

All commercially available reagents and solvents were used without further purification unless otherwise stated. THF was distilled from potassium, and DMF from calcium hydride. Column chromatography was performed on silica gel (Merck, Geduran Si 60), mesh size 70–230. IR spectra (KBr method) were recorded on a Nicolet FT-IR 320 spectrometer, UV/Vis spectra were taken on a Perkin-Elmer Lambda 9 spectrometer and fluorescence spectra were measured on a Spex Fluorolog 2 Type F212 spectrometer. NMR spectra were recorded on AMX500, Bruker AC300, and Varian Gemini 200 spectrometers (at room temperature, unless otherwise noted); the operating frequencies are given with the data. FD mass spectra were recorded on a Finnigan MAT312 spectrometer (resolution $M/\Delta M = 1000$; accuracy

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$\Delta M = \pm 0.5$ u). Thermogravimetric analyses were performed on a Mettler TG 50. For the cyclovoltammetric experiments on **3a** (in THF, with Bu_4NPF_6 added) a Potentiostat/Galvanostat PAR Model 173 was used. The photostability of **3** and **4** was estimated with a UV lamp (Camag, 0.25 A, 220 V), placing the cuvettes 12 cm away from the lamp. Elemental analyses were performed by the Department of Chemistry and Pharmacy of the University of Mainz.

***N*-Propyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-9-(3-benzanthronyl)perylene-3,4-dicarboximide (7a)**: $Ni(PPh_3)_2Cl_2$ (326 mg, 0.50 mmol), activated zinc (120 mg, 1.84 mmol), and Et_4NI (129 mg, 0.50 mmol) were placed in a Schlenk flask and dried in vacuo at 100 °C for 4 h. Dry THF (120 mL) was added under argon, and the mixture stirred at room temperature for 4 h to form the active nickel(0) complex. *N*-Propyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-9-bromoperylene-3,4-dicarboximide (**5a**) (279 mg, 0.27 mmol) and 3-bromobenzanthrone (**6**) (0.43 g, 1.40 mmol) were added and the mixture stirred at room temperature for 12 h. The solvent was evaporated, and the residue purified by column chromatography on silica gel (80 × 10 cm, CH_2Cl_2). The product was recrystallized from CH_2Cl_2/MeOH to give **7a** as a red solid (145 mg, 45%). m.p. 252 °C. IR (KBr): $\tilde{\nu}$ = 2961, 1699 (C=O), 1660 (C=O), 1592, 1580, 1505, 1405, 1320, 1277, 1217, 1173, 888, 835, 781 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 278 (4.81), 408 (4.37), 543 (4.48) nm. ^1H NMR (500 MHz, CD_2Cl_2): δ = 8.69 (d, J = 8 Hz, 1H), 8.50 (d, J = 8 Hz, 1H), 8.44 (d, J = 8 Hz, 1H), 8.36 (d, J = 8 Hz, 1H), 8.15 (s, 2H), 7.98 (brs, 1H), 7.76 (t, J = 8 Hz, 1H), 7.60–7.70 (brs, 2H), 7.57 (t, J = 8 Hz, 1H), 7.32 (d, J = 8 Hz, 1H), 7.27 (m, 5H), 7.18 (m, 4H), 6.98 (d, J = 9 Hz, 1H), 6.90 (d, J = 9 Hz, 2H), 6.84 (m, 4H), 6.77 (d, J = 9 Hz, 2H), 4.08 (t, J = 7 Hz, 2H, N-CH_2-C) 1.71 (m, 2H, C-CH_2-C), 1.31 (s, 9H), 1.30 (s, 9H), 1.23 (s, 9H), 1.20 (s, 9H), 0.97 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 183.7 (C=O), 163.9 (C=O), 156.8, 155.5, 154.2, 154.1, 154.0, 153.9, 147.1, 147.0, 139.8, 136.2, 134.8, 134.2, 134.0, 132.8, 131.5, 130.0, 129.1, 129.0, 128.1, 128.0, 127.1, 127.0, 126.9, 124.9, 124.0, 123.9, 123.2, 122.9, 121.8, 121.0, 120.7, 120.1, 119.9, 119.8, 117.8, 115.8, 115.1, 42.1, 34.5, 31.9, 31.8, 11.8. FD-MS (8 kV): m/z: 1184.0 (100%) [M^+] (calcd. 1183.54). $C_{82}H_{73}NO_7$ (1183.84): calcd. C 83.22, H 6.13, N 1.18; found C 83.07, H 5.99, N 1.30.

***N*-(2,6-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-9-(3-benzanthronyl)-perylene-3,4-dicarboximide (7b)**: A solution of Ni(1,5-cyclooctadiene)$_2$ (1.038 g, 3.70 mmol), 2,2′-bipyridyl (605 mg, 3.70 mmol), and 1,5-cyclooctadiene (364 mg, 3.37 mmol) in dry DMF (70 mL) were stirred for 1 h at room temperature under argon. *N*-(2,6-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-9-bromoperylene-3,4-dicarboximide (**5b**) (1.500 g, 1,75 mmol) and 3-bromobenzanthrone (**6**) (1.350 g, 4.40 mmol) were added and the mixture stirred at 70 °C for 2 d. The reaction mixture was poured onto 1 L of HCl/water (1:1), and the precipitate was filtered off, dried, and purified by column chromatography on silica gel (100 × 10 cm, CH_2Cl_2). The product was recrystallized from CH_2Cl_2/MeOH to give **7b** as a red solid (1.092 g, 62%). m.p. 247–249 °C. IR (KBr): $\tilde{\nu}$ = 2961, 1708 (C=O), 1671 (C=O), 1598, 1505, 1412, 1332, 1272, 1208, 1173, 877, 843, 811, 780 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 275 (4.67), 409 (4.20), 521 (4.68) nm. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.48 (d, J = 8 Hz, 1H), 9.37 (d, J = 7 Hz, 1H), 8.80 (d, J = 7 Hz, 1H), 8.59 (d, J = 8 Hz, 1H), 8.56 (d, J = 7 Hz, 1H), 8.41 (m, 3H), 7.94 (d, J = 8 Hz, 1H), 7.83–7.07 (m, 18H), 2.76 (h, J = 7 Hz, 2H), 1.35 (s, 18H), 1.17 (d, J = 7 Hz, 12H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 184.3 (C=O), 163.7 (C=O), 154.3, 154.2, 153.8, 147.9, 147.8, 146.2, 141.0, 139.9, 136.5, 134.3, 134.0, 133.4, 132.9, 132.4, 131.6, 131.3, 131.2, 130.5, 130.1, 129.9, 129.6, 129.5, 129.3, 129.2, 129.1, 129.0, 128.7, 128.6, 128.4, 127.7, 127.5, 127.3, 124.8, 124.7, 124.4, 124.2, 123.6, 122.2, 119.0, 118.9, 34.9, 31.9, 29.6, 24.5. FD-MS (8 kV): m/z: 1005.4 (100%) [M^+] (calcd. 1005.44). $C_{71}H_{59}NO_5$ (1006.26): calcd. C 84.75, H 5.91, N 1.39; found C 84.39, H 5.62, N 1.45.

***N*-Propyl-1,6,7,16-tetra(4-*tert*-butylphenoxy)-11(CO),12-benzoylterrylene-3,4-dicarboximide (3a)**: Compound **7a** (145 mg, 0.12 mmol), KOH (20 g), and ethanol (20 mL) were heated to 120 °C for 2.5 h. The mixture was dissolved in water and acidified with 2 M HCl, and the residue was removed by filtration, dried, and purified by column chromatography on silica gel (CH_2Cl_2) to separate any remaining starting material. The crude product (some of it was partially dephenoxylated) was purified by GPC ($CHCl_3$) and recrystallization from CH_2Cl_2/MeOH to give **3a** (98 mg, 34%). m.p. > 360 °C. IR (KBr): $\tilde{\nu}$ = 2961, 1699 (C=O), 1659 (C=O), 1586, 1505, 1402, 1335, 1280, 1225, 1176, 834, 552 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 251 (4.94), 265 (4.94), 398 (3.88), 455 (4.05), 700 (4.89) nm. ^1H NMR (500 MHz, [D$_8$]THF): δ = 8.40 (d, J = 8 Hz, 1H), 8.25 (d, J = 8 Hz, 1H), 8.18 (d, J = 8 Hz, 1H), 8.10 (s, 1H), 8.06 (s, 1H), 8.06 (d, J = 6 Hz, 1H), 7.87 (s, 1H), 7.84 (s, 1H), 7.80 (d, J = 8 Hz, 1H), 7.73 (d, J = 8 Hz, 1H), 7.67 (t, J = 7 Hz, 1H), 7.49 (t, J = 7 Hz, 1H), 7.32 (d, J = 9 Hz, 2H), 7.31 (d, J = 9 Hz, 2H), 7.28 (d, J = 9 Hz, 2H),7.21 (d, J = 9 Hz, 2H), 6.95 (d, J = 9 Hz, 2H), 6.86 (d, J = 9 Hz, 2H), 6.77 (d, J = 9 Hz, 2H), 6.72 (d, J = 9 Hz, 2H), 4.08 (t, J = 7 Hz, 2H, N-CH_2-C) 1.71 (m, 2H, C-CH_2-C), 1.33 (s, 9H), 1.28 (s, 18H), 1.27 (s, 9H), 0.96 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 182.1 (C=O), 163.4 (C=O), 157.1, 156.8, 155.5, 155.0, 154.8, 154.7, 154.6, 147.5, 147.2, 147.1, 147.0, 136.0, 135.6, 135.4, 133.3, 132.1, 131.8, 131.4, 131.3, 129.0, 128.6, 128.1, 127.7, 127.5, 127.4, 127.3, 127.1, 122.9, 122.7, 122.3, 121.0, 119.9, 119.6, 119.4, 119.3, 118.6, 117.5, 114.2, 113.2, 42.3, 31.8, 31.7, 31.6, 25.4, 25.2, 25.0, 22.1, 11.7. FD-MS (8 kV): m/z: 1181.8 (100%) [M^+] (calcd. 1181.52). $C_{82}H_{71}NO_7$ (1181.46): calcd. C 83.36, H 6.14, N 1.19; found C 82.99, H 6.01, N 1.27.

***N*-(2,6-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-11(CO),12-benzoylterrylene-3,4-dicarboximide (3b)**: Compound **7b** (500 mg, 0.5 mmol), KOH (60 g), and ethanol (60 mL) were heated to 120 °C for 2.5 h. The mixture was dissolved in water and acidified with 2 M HCl, and the residue was removed by filtration, dried, and purified by column chromatography on silica gel (60 × 10 cm, CH_2Cl_2). The product was recrystallized from CH_2Cl_2/MeOH to give **3b** (412 mg, 83%). m.p. > 360 °C. IR (KBr): $\tilde{\nu}$ = 2960, 1705 (C=O), 1668 (C=O), 1643, 1584, 1505, 1343, 1278, 1209, 1174, 1013, 842, 808 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 251 (4.81), 262 (4.81), 434 (3.78), 632 (4.71), 687 (4.97) nm. Fluorescence emission (exc.: 675 nm): 735 nm. ^1H NMR (500 MHz, [D$_8$]THF): δ = 9.26 (d, J = 9 Hz, 1H), 9.22 (d, J = 9 Hz, 1H), 9.16 (m, 1H), 9.09 (d, J = 9 Hz, 1H), 8.43 (t, J = 8 Hz, 1H), 8.35 (t, J = 9 Hz, 1H), 8.30 (m, 2H), 8.16 (m, 5H), 8.04 (d, J = 8 Hz, 1H), 7.59 (d, J = 9 Hz, 1H), 7.54 (dd, J = 9 Hz, J = 3 Hz, 2H), 7.50 (m, 1H), 7.30 (d, J = 8 Hz, 2H), 7.24 (m, 3H), 2.85 (h, J = 7 Hz, 2H, CH), 1.41 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 1.18 (d, J = 7 Hz, 12H, *i*Pr). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.9 (C=O), 163.3 (C=O), 163.2 (C=O), 153.9, 153.8, 153.3, 147.4, 147.3, 145.7, 145.6, 140.5, 139.4, 136.1, 133.8, 133.5, 133.0, 132.5, 131.9, 131.1, 130.7, 130.0, 129.7, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1 (2 signals), 128.0, 127.2 (2 signals), 127.1, 127.0, 126.9, 126.8, 124.3, 124.2, 123.9, 123.7, 123.1, 121.8, 121.7, 118.5, 118.4, 34.4 (*t*Bu, Cq), 34.3 (*t*Bu, Cq), 31.5 (*t*Bu, CH_3), 29.1 (*i*Pr, CH), 24.0 (*i*Pr, CH_3). FD-MS (8 kV): m/z: 1003.7 (100%) [M^+] (calcd. 1003.42). $C_{71}H_{57}NO_5$ (1004.24): calcd. C 84.92, H 5.72, N 1.39; found C 84.53, H 5.84, N 1.27.

***N*-(2,6-Diisopropylphenyl)-9-(4-acenaphthenequinonyl)perylene-3,4-dicarboximide (11)**: A solution of 4-bromoacenaphthenequinone (**9**) (15.0 g, 57 mmol), ethyleneglycol (30.0 g, 480 mmol), and *p*-toluenesulfonic acid (200 mg, 1 mmol) in *m*-xylene (700 mL) were refluxed for 4 d. The resulting water was removed from the reaction by means of molecular sieve (4 Å). Every 12 h more ethyleneglycol (20 g, 322 mmol) and *p*-toluenesulfonic acid (200 mg, 1 mmol) were added to the mixture. After it had cooled down, the solution was washed three times with aqueous $NaHCO_3$ (1 M). The solvent was evaporated, and the residue recrystallized from petroleum ether (800 mL) to give white ketal (16.4 g, 85%) (the resulting ketal is a mixture of two isomers that can both be used in the subsequent reaction; for clarity only one form is shown). To a solution of the ketal (3.0 g, 8.6 mmol) in THF (80 mL) at −78 °C, butyllithium (6.5 mL, 10.4 mmol, 1.6 M in hexane) was added. After 2 h of stirring, the solution was transferred to a solution of triisopropylborate (8.1 g, 43.0 mmol) in THF (200 mL) at −78 °C. After 3 h at this temperature, the reaction was allowed to warm to room temperature, the solvent evaporated, and the residue dissolved in CH_2Cl_2 and washed with water. The solvent was evaporated again and the residue recrystallized from toluene (20 mL) to give the boronic acid **10** (1.6 g, 60%). Due to the ease of hydrolysis of the ketal function, the product was not purified further and used in the following coupling.

9-Bromoperylene-3,4-dicarboximide (**5c**) (1.0 g, 1.8 mmol), the boronic acid **10**, and $Pd(PPh_3)_4$ (55 mg, 3 mol%) were refluxed in a mixture of toluene (70 mL) and an aqueous K_2CO_3 solution (2 N, 20 mL) for 15 h. The organic phase was seperated, the toluene evaporated, and the residue purified by column chromatography (silica gel, CH_2Cl_2) to give the coupled ketal (960 mg, 80%). The ketal was hydrolyzed by refluxing it (1.0 g, 1.3 mmol) in a mixture of 1-propanol (500 mL), water (20 mL), and sulfuric acid (1 mL) for 3 d. The solution was poured onto 2 L of water containing $NaHCO_3$

(5.0 g), and the precipitate removed by filtration to give **11** (95% purity). It was further purified by column chromatography (silica gel, 40 × 5 cm, CH_2Cl_2) to give pure **11** (880 mg, 99%). m.p. 220 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2960, 2926, 1730 (C=O), 1701 (C=O), 1662, 1606, 1592, 1577, 1359, 1246, 812 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 537 nm (4.67), 485 (4.65), 320 (4.15). ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.65–8.59 (m, 3H), 8.55–8.48 (m, 3H), 8.25 (d, J = 7 Hz, 1H), 8.12 (d, J = 7 Hz, 1H), 7.94 (d, J = 7 Hz, 1H), 7.89 (d, J = 9 Hz, 1H), 7.74–7.69 (m, 2H), 7.51 (m, 2H), 7.42 (t, J = 8 Hz, 1H), 7.27 (d, J = 8 Hz, 2H), 2.69 (h, J = 7 Hz, 2H), 1.12 (d, J = 7 Hz, 12H). ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 120 °C): δ = 188.3 (C=O), 188.0 (C=O), 163.8 (C=O), 146.1, 145.6, 144.0, 138.3, 137.3, 137.0 132.9, 132.0, 131.7, 131.1, 130.5, 130.4, 130.3, 130.1, 129.7, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3, 127.9, 126.9, 124.3, 124.0, 123.4, 122.6, 122.1, 121.4, 121.2, 120.9,120.8, 29.1, 24.1. FD-MS (8 kV): m/z: 660.6 (100%) [M^+] (calcd. 661.23). $C_{46}H_{31}NO_4$ (661.77): calcd. C 83.49, H 4.72, N 2.12; found C 83.88, H 5.12, N 2.27.

***N*-(2,6-Diisopropylphenyl)-9-(4-*N*-octyl-naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (13a)**: A solution of **11** (600 mg, 0.9 mmol) and KOH (5.0 g) in 1-propanol (300 mL) was heated in the presence of air to 60 °C for 2 h. The solution was poured onto HCl (2 L, 1 N) and the precipitate removed by filtration to give **12** (600 mg, 98%). A solution of **12** (500 mg, 0.74 mmol) and *n*-octylamine (1.0 g) in isopropanol (300 mL) was refluxed for 8 h. The solution was poured onto 1 L of 1 M HCl, and the precipitate removed by filtration and recrystallized from ethanol (300 mL) to give **13a** (570 mg, 97%). m.p. 293 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2958, 2922, 1699 (C=O), 1660 (C=O), 1590, 1577, 1356, 1245, 1234, 812, 787, 757 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 536 nm (4.60), 483 (4.60), 340 (4.17). ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.69 (d, J = 7 Hz, 1H), 8.64–8.57 (m, 4H), 8.54 (d, J = 9 Hz, 1H), 8.50–8.47 (m, 2H), 7.83 (m, 1H), 7.81 (m, 1H), 7.64 (d, J = 8 Hz, 1H), 7.59 (m, 1H), 7.48 (t, J = 8 Hz, 1H), 7.44–7.38 (m, 2H), 7.28 (d, J = 8 Hz, 2H), 4.15 (m, 2H), 2.68 (m, 2H), 1.72 (m, 2H), 1.41 (m, 2H), 1.32 (m, 2H), 1.28–1.18 (m, 6H), 1.12 (d, J = 7 Hz, 12H), 0.84 (m, 3H). ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 120 °C): δ = 164.4 (C=O), 164.2 (C=O), 164.1 (2 C, C=O), 146.0 (q), 144.5 (q), 139.5 (q), 137.7 (q), 137.4 (q), 133.6 (q), 132.4 (t), 132.3 (t), 131.7 (t), 131.5 (q), 131.3 (q), 131.0 (t), 130.7 (q), 130.2 (q), 129.9 (q), 129.5 (2 C, t), 129.3 (t), 129.2 (t), 128.8 (q), 128.5 (q), 128.0 (t), 127.6 (t), 127.3 (q), 124.5 (t), 124.2 (t), 123.5 (t), 123.4 (q), 123.1 (q), 121.8 (q), 121.6 (q), 121.1 (t), 121.0 (t), 41.0 (CH_2), 32.1 (CH_2), 30.0 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.5 (CH_2), 27.5 (CH_2), 24.3 (CH_3), 22.9 (CH_2), 14.4 (CH_3). FD-MS (8 kV): m/z: 787.9 (100%) [M^+] (calcd. 788.36), 393.8 (9%) [M^{2+}]. $C_{54}H_{48}N_2O_4$ (788.99): calcd. C 82.20, H 6.13, N 3.55; found C 82.07, H 5.99, N 3.30.

***N*-(2,6-diisopropylphenyl)-*N'*-octylterrylene-3,4,11,12-tetracarboxdiimide (4a)**: Compound **13a** (460 mg, 0.58 mmol), KOH (30.0 g) and ethanol (60 mL) were heated to 70 °C for 20 min. The dark blue melt was poured onto 2 M HCl (400 mL), the precipitate removed by filtration, washed twice with water, and extracted twice with boiling ethanol to dissolve the impurities to give **4a** (370 mg, 80%). m.p. > 360 °C. TGA: 463 °C. IR (KBr): $\tilde{\nu}$ = 2959, 2925, 1694 (C=O), 1656 (C=O), 1585, 1378, 1357, 1330, 1304, 1248, 841, 809, 751 cm^{-1}. UV/Vis (2.41×10^{-5} M in $CHCl_3$): λ_{max} (logε) = 650 nm (4.97), 598 (4.68), 553 (4.20). Fluorescence emission (exc.: 590 nm): 673 nm. ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.67 (d, J = 8.0 Hz, 2H), 8.56 (m, 8H), 8.47 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.0 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 4.15 (t, J = 7.0 Hz, 2H), 2.77 (h, J = 7.0 Hz, 2H), 1.75 (m, 2H), 1.44–1.27 (m, 10H), 1.18 (d, J = 6.8 Hz, 12H), 0.89 (t, 3H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 163.5 (C=O), 163.4 (C=O), 145.8, 135.9, 135.5, 131.7, 131.2 (2 C), 131.0, 130.9, 129.2, 128.6, 128.5, 126.3, 126.0, 124.4, 124.3, 123.9, 122.1, 122.0 (2 C), 121.5, 121.4, 40.6, 31.7, 29.3, 29.2, 29.1, 28.2, 27.2, 24.0, 22.5, 14.0. FD-MS (8 kV): m/z: 786.5 (100%) [M^+] (calcd. 786.35). $C_{54}H_{46}N_2O_4$ (786.98): calcd. C 82.42, H 5.89, N 3.56; found C 82.57, H 5.55, N 3.20.

***N*-(2,6-Diisopropylphenyl)-9-(tributyltin)perylene-3,4-dicarboximide (14c)**: A solution of **5c** (13.5 g, 24.1 mmol), hexabutylditin (26.3 g, 45.3 mmol), and $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol, 0.3 mol%) in toluene (700 mL) was refluxed for 3 d. The solvent was evaporated and the residue purified by column chromatography (silica gel, 31 × 9 cm, CH_2Cl_2) to give **14c** as a red solid (16.4 g, 88%). m.p. 158–159 °C. IR (KBr): $\tilde{\nu}$ = 2958, 1699 (C=O), 1663 (C=O), 1590, 1463, 1355, 1292, 1245, 838, 814, 804, 750 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 521 nm (4.54), 496 (4.56), 267 (4.45). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 8 Hz, 1H), 8.65 (d, J = 8 Hz, 1H), 8.50 (d, J = 8 Hz, 1H), 8.47 (d, J = 8 Hz, 1H), 8.46 (d, J = 8 Hz, 1H), 8.40 (d, J = 7 Hz, 1H), 7.88 (d, J = 8 Hz, 1H), 7.84 (d, J = 7 Hz, 1H), 7.69 (t, J = 8 Hz, 1H), 7.49 (t, J = 8 Hz, 1H, H-4'), 7.35 (d, J = 8 Hz, 2H, H-3', H-5'), 2.79 (h, J = 7 Hz, 2H, CH), 1.69–1.56 (m, 6H, Sn–CH_2), 1.44–1.33 (m, 6H, CH_2), 1.31–1.27 (m, 6H, CH_2), 1.20 (d, J = 7 Hz, 12H, CH–CH_3), 0.92 (t, J = 7 Hz, 9H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ = 164.0 (C=O), 149.7, 145.7, 140.1, 138.0, 137.7, 136.3, 133.4, 132.0, 131.1, 130.5, 129.8, 129.4, 129.2, 127.0, 126.8, 124.0, 123.7, 122.7, 120.8, 120.0, 119.9, 29.3, 29.2, 27.3, 24.0 (CH–CH_3), 13.6, 10.8. FD-MS (8 kV): m/z: 770.5 (100%) [M^+] (calcd. 771.31). $C_{46}H_{53}NO_2Sn$ (770.63): calcd. C 71.70, H 6.93, N 1.82; found C 72.05, H 6.68, N 2.20.

***N*-(2,6-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-9-(tributyltin)perylene-3,4-dicarboximide (14b)** can be synthesized analogously: A solution of **5b** (5.0 g, 5.8 mmol), hexabutylditin (6.8 g, 11.7 mmol), and $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol, 1.6 mol%) in toluene (300 mL) was refluxed for 3 d. The solvent was evaporated, and the residue purified by column chromatography on silica gel (30 × 5 cm, CH_2Cl_2) to give **14b** as a red solid (5.3 g, 85%). m.p. 263 °C. IR (KBr): $\tilde{\nu}$ = 2958, 2925, 1708 (C=O), 1671 (C=O), 1597, 1506, 1334, 1282, 1210 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 524 nm (4.53), 488 (4.38), 290 (4.42). ^1H NMR (500 MHz, $C_2D_2Cl_4$): δ = 9.29 (d, J = 8 Hz, 1H), 9.19 (d, J = 8 Hz, 1H), 8.19 (s, 1H), 8.18 (s, 1H), 7.80 (d, J = 8 Hz, 1H), 7.76 (d, J = 8 Hz, 1H), 7.60 (t, J = 8 Hz, 1H), 7.40 (m, 4H), 7.34 (m, 1H), 7.20 (d, J = 8 Hz, 2H), 7.09 (m, 4H), 2.53 (h, J = 7 Hz, 2H, *i*Pr), 1.53 (m, 6H, α-CH_2), 1.29 (m, 24H, β-CH_2; *t*Bu), 1.19 (m, 6H, γ-CH_2), 1.05 (d, J = 7 Hz, 12H, *i*Pr), 0.83 (t, J = 7 Hz, 9H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ = 163.5 (C=O), 154.1, 153.7, 153.2, 153.1, 149.2, 147.9, 147.7, 145.7, 139.3, 133.7, 132.1, 131.0, 129.8, 128.4, 128.1, 127.4, 127.2, 126.8, 122.9, 121.3, 121.2, 119.7, 34.6, 31.8, 29.4, 29.3, 27.7, 24.3, 14.0, 11.0. FD-MS (8 kV): m/z: 1067.0 (100%) [M^+] (calcd. 1067.49). $C_{66}H_{77}NO_4Sn$ (1067.04): calcd. C 74.29, H 7.27, N 1.31; found C 74.40, H 7.62, N 1.20.

***N*-(2,6-Diisopropylphenyl)-9-(3-benzanthronyl)perylene-3,4-dicarboximide (7c)**: A solution of **14c** (1.245 g, 1.6 mmol), 3-bromobenzanthrone (**6**) (0.501 g, 1.6 mmol), and $Pd(PPh_3)_4$ (56 mg, 0.05 mmol, 3 mol%) in DMF (100 mL) was heated to 100 °C for 2 d. After 1 d, more $Pd(PPh_3)_4$ (56 mg, 0.05 mmol) was added. The solvent was evaporated, the residue taken up in CH_2Cl_2, washed with 2 M HCl, and purified by column chromatography on silica gel (30 × 5 cm, CH_2Cl_2) to give **7c** as an orange solid (0.827 g, 73%). m.p. 255 °C. IR (KBr): $\tilde{\nu}$ = 2962, 1698 (C=O), 1655 (C=O), 1592, 1575, 1358 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 517 nm (4.63), 491 (4.62). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.80 (dd, J = 7 Hz, J = 1 Hz, 1H), 8.70 (d, J = 8 Hz, 1H), 8.68 (d, J = 8 Hz, 1H), 8.62 (dd, J = 8 Hz, J = 1 Hz, 2H), 8.55 (d, J = 8 Hz, 2H), 8.50 (d, J = 8 Hz, 2H), 8.44 (d, J = 8 Hz, 1H), 7.92 (dd, J = 8 Hz, J = 1 Hz, 1H), 7.81 (dt, J = 8 Hz, J = 2 Hz, 1H), 7.78 (d, J = 8 Hz, 1H), 7.72 (d, J = 8 Hz, 1H), 7.65 (t, J = 8 Hz, 1H), 7.61 (t, J = 8 Hz, 1H), 7.52 (d, J = 8 Hz, 1H), 7.49 (d, J = 7 Hz, 1H), 7.47 (d, J = 8 Hz, 1H), 7.34 (d, J = 8 Hz, 2H), 2.74 (h, J = 7 Hz, 2H), 1.15 (d, J = 6.8 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.9 (C=O), 164.0 (C=O), 145.8 (q), 145.7 (q), 140.4 (q), 140.0 (q), 137.5 (q), 137.3 (q), 136.0 (q), 133.9 (q), 133.6 (t), 133.5 (t), 132.4 (q), 132.1 (t), 131.1 (q), 131.0 (q), 130.6 (q), 130.1 (t), 129.6 (q), 129.5 (q), 129.4 (t), 128.9 (q), 128.7 (t), 128.6 (t), 128.3 (t), 128.2 (q), 128.1 (q), 127.4 (t), 127.3 (t), 127.0 (q), 124.0 (t), 123.7 (t), 123.3 (t), 123.2 (t), 121.3 (q), 121.2 (q), 120.6 (t), 120.5 (t), 29.2 (CH), 24.0 (CH_3). FD-MS (8 kV): m/z: 708.8 (100%) [M^+] (calcd. 709.26). $C_{51}H_{35}NO_3$ (709.85): calcd. C 86.30, H 4.97, N 1.97; found C 86.59, H 5.20, N 2.31.

***N*-(2,6-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-9-(3-benzanthronyl)perylene-3,4-dicarboximide (7b)**: A solution of **14b** (1.627 g, 1.6 mmol), 3-bromobenzanthrone (**6**) (0.528 g, 1.6 mmol), and $Pd(PPh_3)_4$ (56 mg, 0.05 mmol, 3 mol%) in DMF (100 mL) was heated at 100 °C for 2 d. After 1 d, more $Pd(PPh_3)_4$ (56 mg, 0.05 mmol) was added. The solution was poured onto 2 M HCl (500 mL), the precipitate removed by filtration, washed with water and purified by column chromatography on silica gel (30 × 5 cm, CH_2Cl_2) to give **7b** as a red solid (1.172 g, 73%). The analytical data are given above.

***N*-(2,6-Diisopropylphenyl)-11(CO),12-benzoylterrylene-3,4-dicarboximide (3c)**: Compound **7c** (427 mg, 0.6 mmol), KOH (7.5 g), and ethanol (15 mL) were heated to 70 °C for 15 min. The dark blue melt was poured onto water,

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acidified with 2M HCl, extracted with CH_2Cl_2, and purified by column chromatography on silica gel (12 × 2.7 cm). The starting material eluted with CH_2Cl_2, and then switching to THF to elute **3c** (341 mg, 80%). m.p. > 360 °C. TGA: 475 °C. IR (KBr): $\tilde{\nu}$ = 2962, 1702 (C=O), 1666 (C=O), 1579, 1505, 1358, 1329, 1302, 1284, 1247, 839, 811, 751 cm^{-1}. UV/Vis (1.40×10^{-5} M in $CHCl_3$): λ_{max} (logε) = 684 nm (4.79), 626 (4.52). Fluorescence emission (exc.: 630 nm): 701 nm. ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.84 (d, J = 8.0 Hz, 1H), 8.67–8.49 (m, 12H), 8.37 (d, J = 7.9 Hz, 1H), 7.76 (t, J = 7.3 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H),7.27 (d, J = 8.0 Hz, 2H) 2.74 (h, J = 6.9 Hz, 2H), 1.15 (d, J = 6.8 Hz, 12H). Owing to the low solubility of **3c** no ^{13}C NMR spectrum was recorded. FD-MS (8 kV): m/z: 706.8 (100%) [M^+] (calcd. 707.25). $C_{51}H_{33}NO_3$ (707.83): calcd. C 86.54, H 4.70, N 1.98; found C 86.27, H 4.35, N 2.36.

***N*-(2,6-Diisopropylphenyl)-9-(4-*N*-octyl-naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (13a)**: A solution of **14c** (3.30 g, 4.40 mmol), *N*-octyl-4-bromonaphthalene-1,8-dicarboximide (**8a**) (2.60 g, 6.70 mmol), and Pd(PPh_3)$_4$ (30 mg, 0.03 mmol) in toluene (100 mL) was refluxed for 4 d. The solvent was evaporated and the residue purified by column chromatography on silica gel (40 × 5 cm, CH_2Cl_2) and recrystallization from ethanol to give **13a** as a red solid (2.43 g, 70%). The analytical data are given above.

***N*-(2,6-Diisopropylphenyl)-9-(4-*N*-(2,6-diisopropylphenyl)-naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (13c)**: A solution of **14c** (1.50 g, 1.95 mmol), *N*-(2,6-diisopropylphenyl)-4-bromonaphthalene-1,8-dicarboximide (**8c**) (1.30 g, 2.90 mmol), and Pd(PPh_3)$_4$ (30 mg, 0.03 mmol) in toluene (100 mL) was refluxed for 4 d. The solvent was evaporated and the residue purified by column chromatography on silica gel (30 × 4 cm, CH_2Cl_2) to give **13c** as a red solid (1.02 g, 70%). m.p. 290 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2960, 1703 (C=O), 1666 (C=O), 1590, 1578, 1354, 1238 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 513 nm (4.56), 484 (4.55), 264 (4.41). ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.76 (d, J = 7 Hz, 1H), 8.67 (m, 3H), 8.61 (d, J = 8 Hz, 1H), 8.56 (d, J = 8 Hz, 1H), 8.51 (m, 2H), 7.93 (dd, J = 9 Hz, J = 1 Hz, 1H), 7.88 (d, J = 7 Hz, 1H), 7.70 (d, J = 8 Hz, 1H), 7.66 (m, 1H), 7.53 (m, 2H), 7.43 (m, 2H), 7.30 (m, 4H), 2.78 (m, 4H), 1.19 (m, 24H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 164.2 (C=O), 164.1 (C=O), 164.0 (2 C, C=O), 146.2, 144.7, 139.4, 137.5, 137.2, 133.8, 132.8, 132.2, 132.1, 131.9, 131.7, 131.5, 131.2, 130.8, 130.5, 129.5, 129.4, 129.1, 128.7, 128.0, 127.6, 127.4, 124.4, 124.1, 123.7, 123.4, 122.2, 122.0, 121.1, 121.1, 29.5, 24.2. FD-MS (8 kV): m/z: 836.4 (100%) [M^+] (calcd. 836.36). $C_{58}H_{48}N_2O_4$ (837.03): calcd. C 83.23, H 5.78, N 3.35; found C 83.07, H 6.01, N 3.55.

***N*-(2,6-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-9-(4-*N*-(2,6-diisopropylphenyl)naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (13b)**: A solution of **14b** (1.40 g, 1.31 mmol), *N*-(2,6-diisopropylphenyl)-4-bromonaphthalene-1,8-dicarboximide (**8c**) (0.86 g, 1.97 mmol), and Pd(PPh_3)$_4$ (30 mg, 0.03 mmol) in toluene (150 mL) was refluxed for 4 d. The solvent was evaporated and the residue purified by column chromatography on silica gel (40 × 5 cm, toluene) to give **13b** as a red solid (1.16 g, 78%). m.p. 151–152 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2962, 1708 (C=O), 1671 (C=O), 1589, 1505, 1361, 1353, 1272, 1239, 1208 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 517 nm (4.55), 487 (4.38, sh), 340 (4.43), 274 (4.45). ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 9.51 (d, J = 8 Hz, 1H), 9.41 (d, J = 8 Hz, 1H), 8.74 (d, J = 8 Hz, 1H), 8.61 (m, 2H), 8.32 (d, J = 8 Hz, 2H), 7.94 (d, J = 8 Hz, 1H), 7.88 (d, J = 8 Hz, 1H), 7.66 (m, 2H), 7.53 (m, 2H), 7.43 (m, 6H), 7.30 (m, 4H), 7.12 (m, 5H), 2.75 (m, 4H), 1.34 (m, 18H), 1.19 (m, 24H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 164.0 (C=O), 163.9 (C=O), 163.0 (C=O), 154.2, 152.9, 147.8, 145.8, 145.7, 145.6, 145.5, 145.0, 138.1, 133.8, 132.7, 132.5, 131.9, 131.5, 131.3, 131.2, 131.1, 130.9, 130.8, 130.7, 129.8, 129.1, 128.9, 128.6, 128.2, 127.9, 127.1, 127.0, 126.3, 126.1, 123.7, 123.3, 122.8, 122.7, 122.0, 118.8, 118.7, 34.3, 31.3, 29.1, 29.0, 23.8. FD-MS (8 kV): m/z: 1132.2 (100%) [M^+] (calcd. 1132.54). $C_{78}H_{72}N_2O_6$ (1133.45): calcd. C 82.66, H 6.40, N 2.47; found C 83.05, H 6.01, N 2.35.

***N,N'*-bis(2,6-diisopropylphenyl)terrylene-3,4,11,12-tetracarboxdiimide (4c)**: Compound **13c** (500 mg, 0.6 mmol), KOH (30.0 g) and ethanol (60 mL) were heated to 70 °C for 20 min. The dark blue melt was poured onto 2M HCl (400 mL). The precipitate was removed by filtration, washed twice with water, and extracted twice with boiling ethanol to dissolve the impurities to give **4c** (400 mg, 80%). m.p. > 360 °C. IR (KBr): $\tilde{\nu}$ = 2965, 2925, 1703 (C=O), 1660 (C=O), 1585, 1378, 1359 cm^{-1}. UV/Vis (2.41×10^{-5} M in $CHCl_3$): λ_{max} (logε) = 650 nm (4.97), 598 (4.68), 553 (4.20). Fluorescence emission (exc.: 575 nm): 668 nm. ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.70 (m, 8H), 8.61 (d, J = 8 Hz, 4H), 7.43 (t, J = 8 Hz, 2H), 7.29 (d, J = 8 Hz, 4H), 2.74 (h, J = 7 Hz, 4H), 1.17 (d, J = 7 Hz, 24H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 163.5 (C=O), 146.0 (q), 136.1 (q), 131.7 (t), 131.5 (q), 131.4 (q), 130.5 (q), 129.2 (t), 129.0 (q), 126.6 (q), 124.6 (t), 123.9 (t), 122.4 (q), 121.7 (t), 29.3 (*C*H), 23.8 (*C*H$_3$). FD-MS (8 kV): m/z: 834.7 (100%) [M^+] (calcd. 834.35), 417.9 (10%) [M^{2+}]. $C_{58}H_{46}N_2O_4$ (835.02): calcd. C 83.43, H 5.55, N 3.35; found C 83.77, H 5.89, N 3.28.

***N,N'*-bis(2,6-diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)terrylene-3,4,11,12-tetracarboxdiimide (4b)**: Compound **13b** (500 mg, 0.44 mmol), KOH (30.0 g), and ethanol (60 mL) were heated to 70 °C for 20 min. The dark blue melt was poured onto 2M HCl (400 mL), the precipitate removed by filtration, washed twice with water, and extracted twice with boiling ethanol to dissolve the impurities to give **4b** (401 mg, 80%). m.p. > 360 °C. IR (KBr): $\tilde{\nu}$ = 2962, 1704 (C=O), 1667 (C=O), 1589, 1579, 1505, 1357, 1327 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 664 nm (5.08), 615 (4.82). Fluorescence emission (exc.: 575 nm): 707 nm. ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 9.59 (d, J = 9 Hz, 2H), 8.66 (m, 4H), 8.56 (d, J = 8 Hz, 2H), 8.32 (s, 2H), 7.46 (d, J = 9 Hz, 4H), 7.40 (m, 2H), 7.28 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 7.17 (d, J = 9 Hz, 4H), 2.73 (h, J = 7 Hz, 2H), 2.68 (h, J = 7 Hz, 2H), 1.36 (s, 18H), 1.15 (d, J = 7 Hz, 12H), 1.12 (d, J = 7 Hz, 12H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 163.7 (C=O), 163.0 (C=O), 155.3 (q), 152.9 (q), 148.3 (q), 146.0 (q), 145.8 (q), 136.6 (q), 131.8 (t), 130.9 (q), 130.5 (q), 130.3 (q), 130.0 (q), 129.4 (t), 129.2 (t), 128.0 (q), 127.3 (t), 126.6 (q), 125.5 (q), 124.6 (t), 123.9 (t), 123.8 (t), 122.9 (t), 122.6 (q), 122.5 (q), 121.7 (q), 121.3 (t), 119.0 (t), 108.4 (q), 34.5 (*t*Bu, C_q), 31.5 (*t*Bu, *C*H$_3$), 29.2 (*i*Pr, *C*H), 23.9 (*i*Pr, *C*H$_3$). FD-MS (8 kV): m/z: 1130.9 (100%) [M^+] (calcd. 1130.52). $C_{78}H_{70}N_2O_6$ (1131.44): calcd. C 82.80, H 6.24, N 2.48; found C 82.51, H 6.58, N 2.22.

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