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Synthesis of Soluble Perylenebisamidine Derivatives. Novel Long-Wavelength Absorbing and Fluorescent Dyes

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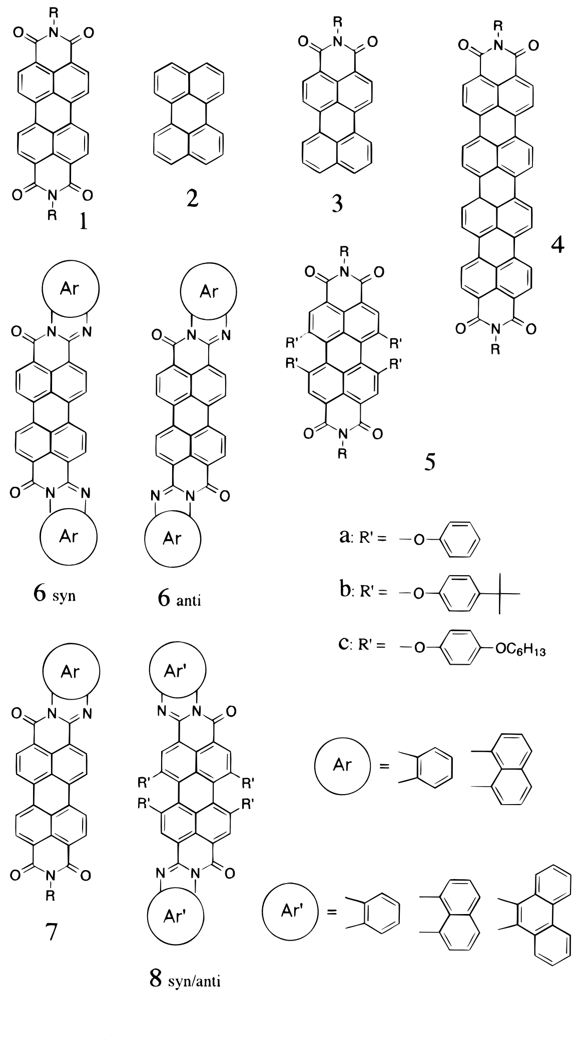
Extension of the π-system of 1,6,7,12-tetrakis(aryloxy)-3,4,9,10-perylenetetracarboxdiimide was achieved by the condensation of 1,6,7,12-tetrakis(aryloxy)-3,4,9,10-perylenetetracarboxylic bisanhydride with 1,2-diaminobenzene, 1,8-diaminonaphthalene, and 9,10-diaminophenanthrene. A full characterization of the resulting novel long-wavelength absorbing dyes by field-desorption mass spectrometry, UV−vis, IR, and ^{1}H and ^{13}C NMR spectroscopies is given. Photostability and thermal stability are reported and discussed.

Introduction

Perylenetetracarboxdiimides **1** are widely used as dyes and pigments since they show outstanding chemical, thermal and photochemical stability.[1−3] In the case of perylenetetracarboxdiimide pigments, color tuning is achieved by variation of the substituent of the imide functions, resulting in modification of the crystal structure.[1,4] Perylene pigments **1**−**3** (Scheme 1) cover the whole range of the visible spectrum and find applications in the fields of paints and lacquers, namely for the car industry. Beside these conventional uses, perylenes are key chromophores for high-tech applications such as reprographic processes,[5] fluorescent solar collectors,[6] photovoltaic cells,[7] optical switches,[8] and lasers.[9] In this context, perylene teracarboxdiimides are generally referred to as functional dyes. However, new developments in the field of perylene tetracarboxdiimide based functional dyes have been limited so far by their insolubility in common organic solvents, hindering a fine-tuning and a shift of their absorption to longer absorption wavelengths.

Dyes which combine absorptions ranging from visible to near-infrared with high photostability and thermal stability are of special interest for the high-tech applications hitherto mentioned. Absorptions in the ranges 530−580 and 760−780 nm are covered by perylenetetracarboxdiimide (**1**)[6a] and quaterrylenetetracarboxdiimide (**4**).[10b,c] Conceptually, two ways to enlarge the π-system of perylene dyes can be envisaged: (i) extension of the perylene core to form higher rylenes such as quaterrylenetetracarboxdiimide (**4**) or (ii) extension of the π-system at the carboxdiimide position leading to perylenebisarylamidine (**6**). The second route generally yields dyes with fairly poor solubility. A noticeable

Scheme 1



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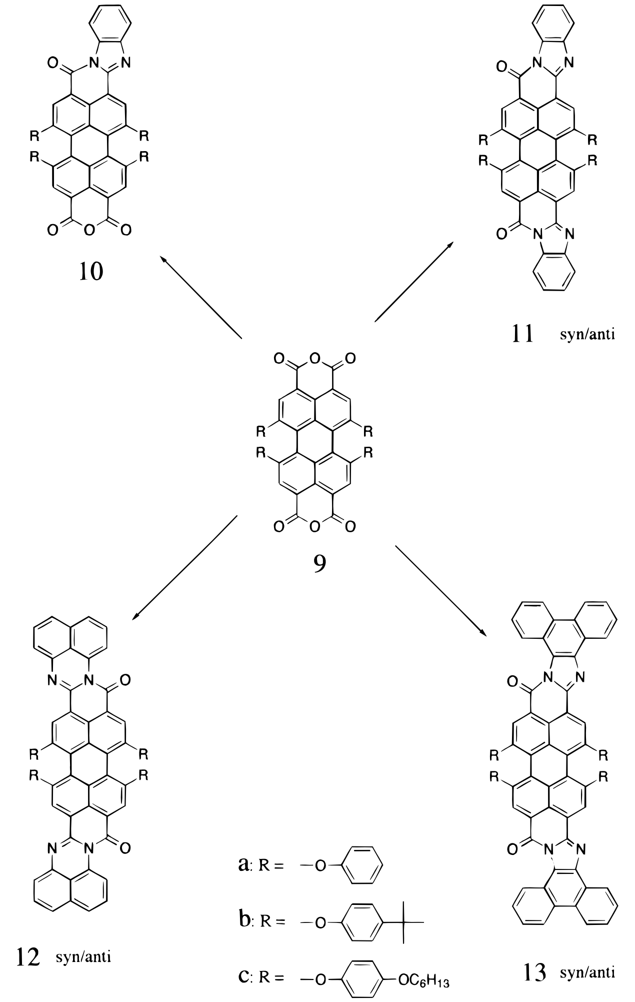
Scheme 2



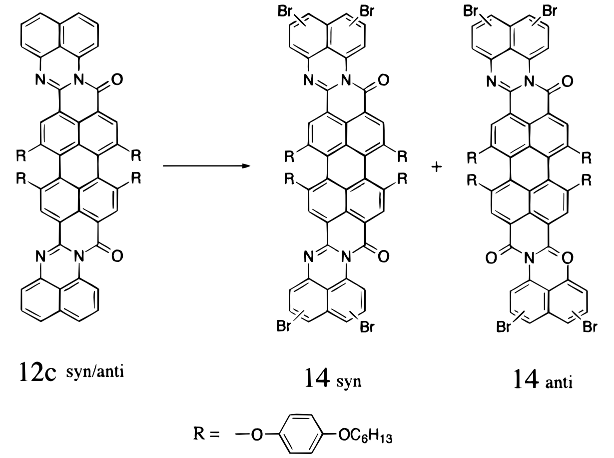
exception to the series of insoluble perylenearylamidine compounds is given by monofunctionalized perylene derivatives **7**, which are reasonably soluble.[12c] Unfortunately, their longer wavelength absorption maxima ($\lambda_{max} = 571-604$ nm, depending on the structure of the aryl group) are only slighty bathochromically shifted as compared to **5**, which displays a typical absorption maximum in the range 570−580 nm.

In this paper, we describe the synthesis and spectroscopic characterization of monoarylamidineperylenes **10** and bisarylamidineperylenes **11**−**14**, substituted in the bay region of the perylene core. Remarkably enough, they combine long-wavelength absorption and emission with fairly high extinction coefficient, good solubility in organic solvents, as well as high thermal stability. Photostability of bisarylamidineperylenes **11b** and **14c** are compared and discussed.

Results and Discussion

The synthesis of compounds **10**−**14**, depicted in Scheme 2, is based on tetrakis(aryloxy)-3,4;9,10-perylenetetracarboxdianhydride (**9**), which were readily available on a gram scale.[10c,13] Condensation of **9** to bisamidine dyes **10**−**13** was carried out in quinoline at 220 °C according to the literature procedure.[12a] With short reaction time (45 min), monoimidazole perylene (**10b**) was obtained as a side product in low yield (16%), from the condensation of dianhydride **9b** with equimolar amount of *o*-phenylenediamine, whereas the main product, **11b**, was obtained in 62% yield. The yield of **11b** was increased to 87% when a 3.3-fold excess of *o*-phenylenediamine and a reaction time of 4 h were employed. Similar reaction conditions were used for the syntheses of **12a**, **12c**, and **13b**, resulting in high yields (72−88%). Purification was easily achieved by silica gel column chromatography and recrystallization. Despite their extended rigid molecular structures, solubilities of condensation products **10**−**13** in common organic solvents were surprisingly good, allowing a full characterization to be performed.

Scheme 3



Halogenation of aromatic chromophores is a known method in dyestuff chemistry of inducing a bathochromic shift of the absorption maximum at the longest wavelengths. Bromination of **12c** was carried out in dimethylformamide with a 6-fold excess of *N*-bromosuccinimide at 65 °C (Scheme 3). After a few minutes the color of the solution started to change from blue to green, and the reaction time was extended to 4 h. The resulting tetrabromide dye **14** was isolated as a green powder in 61% yield. Despite the four (hexyloxy)phenoxy substituents in the bay region of the perylene core, the solubility of **14** remained only moderate. Therefore, ^{1}H NMR spectra were recorded at high temperatures in deuterated tetrachloroethane. A careful analysis of the spectra indicated that, surprisingly, no bromination occurred on the highly activated (hexyloxy)phenoxy substituents but took place at the naphthalene subunits. Apart from the formation of **14** syn and **14** anti isomers, the existence of different regioisomers was observed so that the exact bromine positions on the naphthalene subunits could not be assigned. However, the existence of a tetrabrominated product was proven beyond any doubt since the expected mass of tetrabrominated product **14**, along with its correct isotopic distribution, was observed as parent ion by FD mass spectroscopy.

UV−vis spectra of bisbenzamidine perylene derivatives **10**−**14** are reported in Table 1. The extension of the π-system induces a dramatic bathochromic shift as

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Table 1. Absorption and Emission Properties in Methylene Chloride at Room Temperature

dyes	absorption max (nm)	extinction coeff (L/cm mol)	emission max (nm)
5	570–580	44 000	580–590
10b	604	52 800	636
11b	629	57 400	661
12a	652	52 000	*a*
12c	643	41 200	*a*
13b	659	44 700	680
14	712	59 000	768

[a] Very weak signal-to-noise ratio; discussed in text.

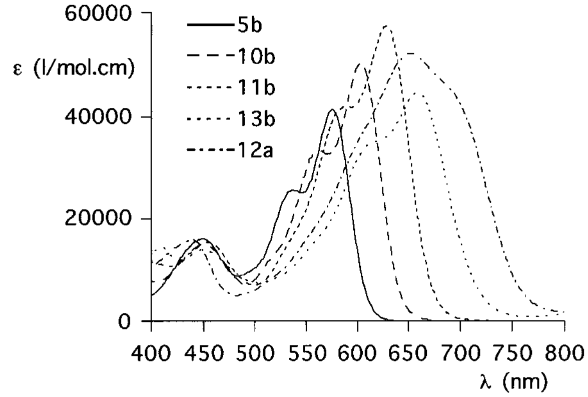

Figure 1. UV–visible absorption spectra of **5b**, **10b**, **11b**, **12a**, and **13b** in methylene chloride at room temperature.

compared to **5**. The maximum of the longest wavelength absorption is shifted to 604 nm in the case of monobenzamidine perylene **10b** (Figure 1). For perylenebisbenzimidazole (**11b**), the maximum of the longest wavelength absorption is shifted to 629 nm. The bisnaphthalene condensation product **12a** and the bisphenanthrene condensation product **13b** exhibit longest wavelength absorption maxima of 652 and 659 nm, respectively.

The condensation products **11**–**13** are very probably generated as a mixture of syn and anti isomers. As the isomers have different absorptions, one could expect a broadening of absorption bands compared to **5b**. The half-height width of the longest absorption band, which is a direct measurement of this broadening, increased from 72 nm (**5b**) to 90 nm (**11b**) to 110 nm (**13b**). Since a broadening of 80 nm is also observed in the case of **10b**, where no syn and anti isomers are present, we believe that it is, at least in part, due to more extended vibration modes and conformational deformations.

In the described series of compounds, absorption spectra are characterized by rather similar vibrational structures. However, the spectra of **12a** and **12c** show only an unstructured broad band (half-height width of 145 nm) with an extinction coefficient of 50 000 (L/mol cm) at 700 nm. One explanation can be seen in the fact that **12a** contains amidine subunits, incorporated in six-membered rings, whereas in the case of **11b**, amidine subunits are incorporated in five-membered rings. The corresponding bisamidine perylene dye **6**, unsubstituted in the bay region, showed a planar structure when amidine subunits were incorporated in five-membered rings. Conversely, **6** containing amidine subunits incorporated in six-membered rings possesses twisted amidine fragments.[5] It is believed that this nonplanarity of the six-membered ring amidine fragments causes the broad absorption observed. UV–vis absorptions of **11b** in a film and in solution are compared in Figure 2. A bathochromic shift is observed in the solid state and is attributed to intermolecular π-interactions. Fluorescence spectra of compounds **11b** (Figure 3) and **13b** (Figure 4) exhibit a typical mirror symmetry between absorption and emission bands, indicating that little structural rearrangement occurs between the ground and the excited state. In the case of compounds **12a** and **12c**, only a very weak signal-to-noise ratio was observed for the emission. It is very likely that the overlap between the very broad absorption and the emission bands causes the reabsorption of the emitted light by the chromophore itself. For these reasons, it was impossible to locate the emission maxima with

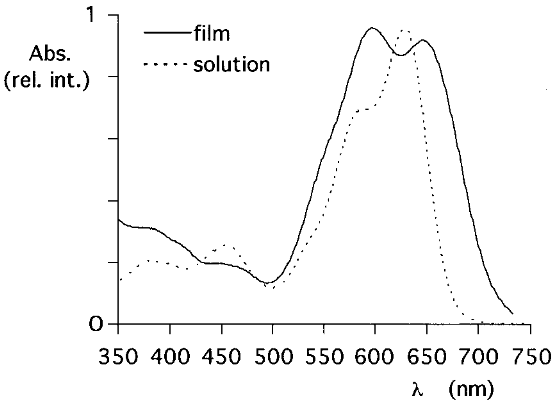

Figure 2. Normalized UV–visible spectra of **11b** at room temperature in a film and in methylene chloride.

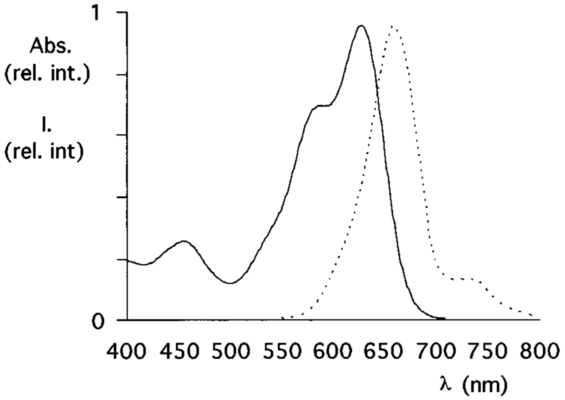

Figure 3. Normalized UV–visible absorption (solid line) and uncorrected fluorescence (dashed line) spectra of **11b** in methylene chloride at room temperature.

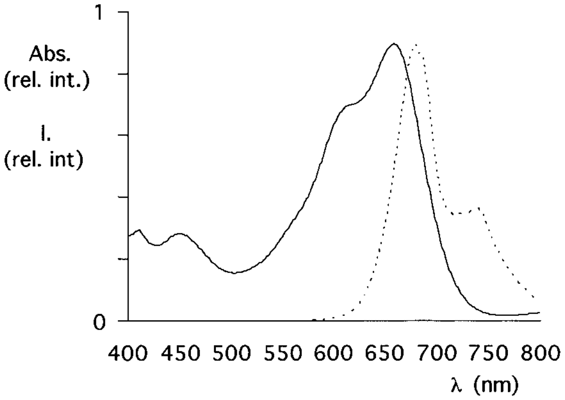

Figure 4. Normalized UV–visible absorption (solid line) and uncorrected fluorescence (dashed line) spectra of **13b** in methylene chloride at room temperature.

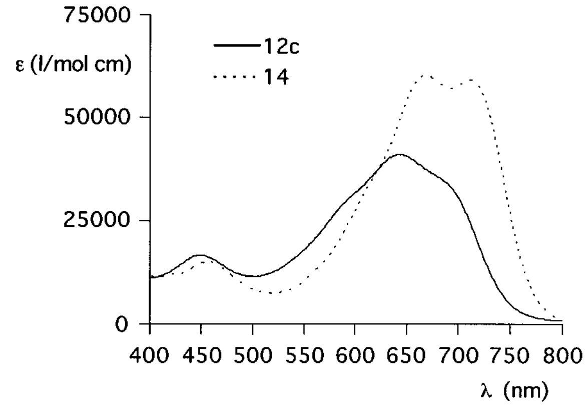

Figure 5. UV−visible absorption spectra of **12c** and **14** in methylene chloride at room temperature.

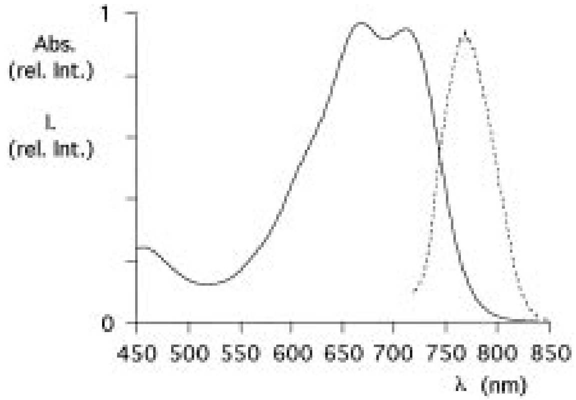

Figure 6. Normalized UV−visible absorption (solid line) and uncorrected fluorescence (dashed line) spectra of **14** in methylene chloride at room temperature.

accuracy. Bromination of **12** to the tetrabromo compound **14** shifts the longest wavelength absorption maximum to 712 nm and raises the extinction coefficient to 60 000 (L/mol cm) (Figure 5). Despite its extended π-structure and the presence of four bromine atoms, **14** exhibits a fluorescence peak with an emission maximum at 768 nm (Figure 6). Note that the tail of the emission spectrum of **14** above 800 nm is probably perturbed by the nonlinear spectral response of the photomultiplier in the 800−850 nm range. Therefore, it is likely that the emission spectrum of **14** appears narrower than it is in reality.

Besides the chromophoric properties, thermal and photostability are important criteria for practical applications of long-wavelength absorbing dyes. Conventional perylene bisimide derivatives are stable up to 480 °C. Despite their more extended π-system, compounds **11**−**13** exhibit a fairly good thermal stability up to 430 °C, as observed by thermogravimetric analysis. The tetrabrominated chromophore **14** showed a lower thermal stability of up to 315 °C. However, it should be pointed out that these thermal stabilities are sufficient for high-temperature applications, since compounds **11**−**13** are potential candidates for use as laser dyes.[9] Incorporation of **11**−**14** in many thermoplastics during processing is also possible since it is generally carried out between 150 and 300 °C.

Photostability is not in itself an inherent property of dyestuffs but is also a function of the nature of the dispersion medium, i.e., solid or liquid matrix, the light spectrum, in particular in the UV range, as well as the ambient atmosphere.[6a] We have studied the photostability of compounds **11b** and **12c** in nondegassed chloroform solutions exposed to the radiation of a UV lamp with a wavelength centered around 366 nm. Similarly to various perylenes dyes dispersed in poly(methyl methacrylate) and exposed to solar radiation,[6a] we observe in Figures 7 and 8 a bleaching of the absorption maxima of chromophores **11b** and **12c**, respectively, but also the appearance of longer wavelength absorptions. Moreover, a hypsochromic shift of the absorption maxima is observed for both chromophores. Plotting the change of the absorption maxima (in percent) as a function of time (Figure 9) indicates that the photodegradation of compound **12c** is significantly faster than for compound **11c**. Note as well that both compounds exhibit a self-accelerated photodegradation suggesting that photodegradation products catalyze the degradation of genuine chromophores.

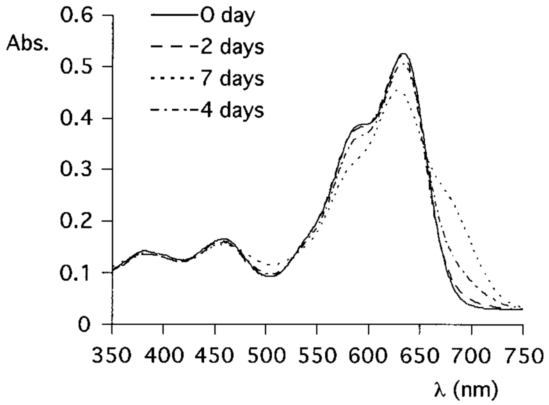

Figure 7. UV−visible absorption spectra of **11** in chloroform at room temperature, after various exposure time to a UV lamp with an emission centered around 366 nm.

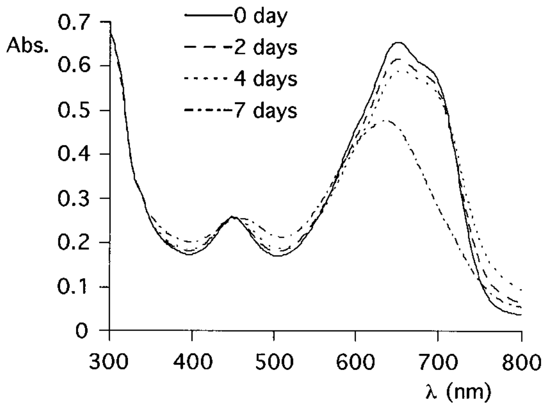

Figure 8. UV−visible absorption spectra of **12** in chloroform at room temperature, after various exposure time to a UV lamp with an emission centered around 366 nm.

Concluding Remarks

We have reported the synthesis of new, soluble perylene chromophores **10**−**14** in high yields via a short and convenient synthetic scheme. The absorptions of these new dyes insert in the gap between absorptions centered around 580 nm and centered around 740 nm for already existing perylenes and quaterrylenes, respectively. Moreover, a fine-tuning of long-wavelength absorption from 580 to 712 nm was demonstrated by subtle variation of the nature and the functionalization of the aromatic groups at the amidine position. Remarkably, these dyes also exhibit fluorescence and good

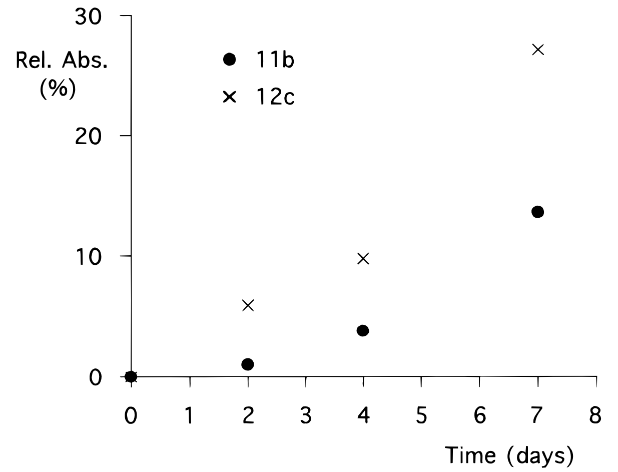

Figure 9. Evolution of the absorbance variation (percent) at the longest absorbtion wavelength of **11b** and **12c** as a function of exposure time (in days).

thermal stability. Therefore, high-tech applications requiring dyes with tailor-made absorption and emission in a specific region of the visible spectra can be envisaged.

Experimental Part

^{1}H and ^{13}C NMR spectroscopy: Varian Gemini 200 MHz and Brucker AC 300 MHz. Mass spectrometry, field desorption (FD): Finnigan MAT 312. Infrared spectroscopy: Nicolet FT-IR 320. UV−vis absorption spectroscopy: Perkin-Elmer Lambda 9. UV−vis emission spectroscopy: (i) Spectrometer: double monochromator Fluorolog 2, type F212, Spex USA; focus length: 0.22 m, resolution; 0.2 nm, spectral range: 200−900 nm. (ii) Photomultiplier Hamamatsu R298, cooled at 30 °C; spectral range: 185−850 nm. (iii) Geometry of the spectrofluorometer: photomultiplier perpendicular to the excitation beam. (iv) Spectra are reported uncorrected. (v) The concentrations of the solution were tailored to have an absorbance of 0.1 or lower to minimize the reabsorption of emission by the sample. Thermogravimetric analysis: Mettler TG 50. Melting point (uncorrected): Büchi melting point apparatus. Elemental analyses were performed at the Department of Chemistry and Pharmacy at the Mainz University. Column chromatography: glass columns packed with silica gel (Merck Geduran Si 60, 70−230 mesh). Photostability tests were carried out with a Camag laboratory lamp having an emission centered around 366 nm. Quartz cuvettes containing the dye solutions were placed at a distance of 10 cm of the lamp and photostability was monitored by UV−vis absorption spectroscopy.

Solvents used were commercial p.a. quality except for quinoline and dimethylformamide (distilled over CaH_2, under reduced pressure). All other reagents were purchased from Aldrich and used without purification. The syntheses of 1,6,7,12-tetrakis(aryloxy)-3,4:9,10-perylenetetracarboxdianhydride (**9a-c**) have previously been described in the literature.[10c,13]

3,4:9,10-Bis(1,2-benzimidazole)-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene (Syn and Anti Isomers) (11b). 1,6,7,12-Tetra(aryloxy)-3,4:9,10-perylenetetracarboxdianhydride (**9b**, 3.0 g, 3 mmol), 1.1 g (10 mmol) of *o*-phenylenediamine, and 500 mg of zinc acetate were added to 150 mL of dry quinoline. The reaction mixture was stirred at 220 °C for 4 h. The reaction mixture was concentrated under reduced pressure, chilled to room temperature, and poured into 1 L of a 10 vol % HCl solution. A precipitate appeared, was removed by filtration, washed thoroughly with water, and dried under vacuum. Purification was carried out by chromatography (SiO_2, toluene). **11b** was eluted first and further purified by recrystallization from methanol with methylene chloride affording 2.98 g of a blue powder with a yield of 87%.

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 135 °C), δ 8.60/8.59 (s/s, 2H, H-2,11/H-2′,8′), 8.50/8.49 (s/s, 2H, H-5,8/H-5′,11′), 8.55 (m, 2H, H-15/15′), 7.85 (m, 2H, H-18/18′), 7.45 (m, 4H, H-16,16′/17,17′), 7.35 (d, 8H, Ph-H-3,3′), 6.99 (dd, 8H, Ph-H-2,2′), 1.39 (s, 36H, *tert*-butyl). ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 135 °C), δ 159.97, 156.19, 156.06, 155.79, 153.23, 152.87, 148.58, 147.56, 147.37, 147.12, 147.01, 143.37, 131.85, 126.74, 125.94, 122.55, 121.26, 119.99, 119.46, 119.17, 116.27, 115.77. FD-MS: *m*/*z* = 1129.1 (M^+, 100%) required M^+ = 1129.4. UV−vis: (CH_2Cl_2) λ_{max} (ϵ) = 292 (69 400), 384 (12 400), 455 (15 500), 591 (41 800), 629 (57 400) nm. IR (KBr) ν = 2957, 2905, 2867, 1698, 1587, 1548, 1508, 1497, 1465, 1448, 1410, 1395, 1361, 1338, 1309, 1279, 1213, 1172, 1107, 1089, 1014, 879, 830, 820, 752, 554 cm^{-1}. $C_{76}H_{64}N_4O_6$: found C 79.85, H 5.60, N 4.97; calcd C 80.83, H 5.71, N 4.96. mp > 300 °C.

3,4-(1,2-Benzimidazole)-1,6,7,12-tetraphenoxy-9,10-perylenedicarboxianhydride (10b). Reaction conditions and workup were similar to those of **11b**, but less *o*-phenylenediamine, 660 mg (6 mmol), was added, and reaction time was shortened to 45 min. Purification was carried out by chromatography (SiO_2, toluene). **10b** as its zinc salt was eluted first and further purified by recrystallization from methanol with methylene chloride affording 642 mg of a blue powder with a yield of 19%. The second blue fraction eluted was **11b**. Recrystallization under conditions described above afforded 2.13 g of a blue powder with a yield of 62%. **10b** as its zinc salt was converted into the anhydride by treatment with 2 N KOH and neutralization.

^{1}H NMR (200 MHz, $CDCl_3$, 30 °C), δ 8.54 (s, 1H, H-2), 8.45 (m, 1H, H-15), 8.43 (s, 1H, H-5), 8.19 (s, 1H, H-11), 8.18 (s, 1H, H-8), 7.75 (m, 1H, H-18), 7.45 (m, 2H, H-16,17), 7.2 (m, 8H, Ph-H-3,3′,3″,3‴), 6.8 (m, 8H, Ph-H-2,2′,2″,2‴), 1.31/1.30 (s/s, 36H, *tert*-butyl). FD-MS: *m*/*z* = 1157.9 (M^+, 100%) required M^+ = 1157.3. UV−vis: (CH_2Cl_2) λ_{max} (ϵ) = 289 (59 277), 379 (8535), 451 (15 772), 563 (34 335), 604 (52 797) nm. IR (KBr) ν = 2962, 2936, 2908, 2869, 1700, 1663, 1590, 1550, 1507, 1411, 1363, 1350, 1311, 1304, 1282, 1216, 1174 cm^{-1}. $C_{70}H_{60}N_2O_8$: found C 78.74, H 5.81, N 2.44; calcd C 79.52, H 5.72, N 2.65. mp > 300 °C.

3,4:9,10-Bis(1,8-naphthapyrimidine)-1,6,7,12-tetraphenoxyperylene (Syn and Anti Isomers) (12a). Reaction conditions and workup were similar to those of **11b**, but amounts of reagents and solvent were different. 1,6,7,12-Tetraphenoxy-3,4:9,10-perylenetetracarboxdianhydride (**9a**, 1.0 g, 1.3 mmol), 624 mg (1.9 mmol) of 1,8-diaminonaphthalene, and 100 mg of zinc acetate were added to 100 mL of dry quinoline. Purification was carried out by chromatography (SiO_2, toluene), affording 1.16 g as a blue powder with a yield of 88%.

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 135 °C), δ 8.68 (d, 2H, H-14,14′), 8.46 (s, 2H, H-2,11), 8.16 (s, 2H, H-5,8), 7.5 (m, 8H, H-naphthyl), 7.35 (m, 8H, Ph-H-3,3′), 7.15 (m, 6H, Ph-4, H-naphthyl), 7.05 (m, 8H, H−Ph-2,2′). FD-MS: *m*/*z* = 1004.0 (M^+, 100%) required M^+ = 1005.0. UV−vis: (CH_2Cl_2) λ_{max} (ϵ) = 301 (41 427), 439 (15 924), 652 (52 039) nm. IR (KBr) ν = 1680, 1625, 1586, 1553, 1506, 1488, 1457, 1404, 1370, 1335, 1290, 1270, 1216, 1209, 1193, 1174, 1160, 1024, 877, 8.25, 7.66, 692 cm^{-1}. $C_{68}H_{36}N_4O_6$: found C 79.98, H 3.70, N 5.54; calcd C 81.26, H 3.61, N 5.57. mp > 300 °C.

3,4:9,10-Bis(1,8-naphthapyrimidine)-1,6,7,12-tetrakis-(4-hexyloxyphenoxy)perylene (Syn and Anti Isomers) (12c). Reaction conditions and workup were similar to those of **11b**, but amounts of reagents and solvent were different. 1,6,7,12-Tetrakis(4-hexyloxyphenoxy)-3,4:9,10-perylenetetracarboxdianhydride (**9c**, 1.0 g, 0.86 mmol), 475 mg (3 mmol) of 1,8-diaminonaphthalene, and 200 mg of zinc acetate were added to 100 mL of dry quinoline. Purification was carried out by chromatography (SiO_2, toluene), affording 1.05 g as a blue powder with a yield of 87%.

^{1}H NMR (200 MHz, $CDCl_3$, 30 °C), δ 8.39 (m, 2H, H-naphthyl), 8.04/7.99 (s/s, 2H, H-2,11,2′,8′), 7.81/7.76 (s,s, 2H, H-5,8,5′,11′), 7.1−7.4 (m, 8H, H-naphthyl), 6.99 (m, 2H, H-naphthyl), 6.7−6.9 (m, 16H, Ph-H), 4.02 (m, 8H, a-CH_2), 1.84 (m, 8H, b-CH_2), 1.2−1.8 (m, 24H, $(CH_2)_3$), 0.97 (m, 12H, CH_3). FD-MS: *m*/*z* = 1405.1 (M^+, 100%) required M^+ = 1405.7. UV−vis: (CH_2Cl_2) λ_{max} (ϵ) = 449 (16 702) 643 (41 203) nm. IR (KBr) ν = 2953, 2929, 2868, 2858, 1682, 1656, 1625, 1588, 1555, 1500, 1473, 1470, 1405, 1371, 1336, 1291, 1272, 1246, 1201, 1175, 1161, 825, 767 cm^{-1}. $C_{92}H_{84}N_4O_{10}$: found C 77.62, H 5.74, N 3.69; calcd C 78.61, H 6.02, N 3.99. mp = 274 °C.

3,4:9,10-Bis(9.10-phenanthreneimidazole)-1,6,7,12-tetrakis(4-*tert*-butylphenoxy)perylene (Syn and Anti Isomers) (13b). Reaction conditions and workup were similar to those of **11b**, but amounts of reagents and solvent were different. 1,6,7,12-Tetra(4-*tert*-butylphenoxy)-3,4:9,10-perylenetetracarboxdianhydride (**9b**, 1.0 g, 1 mmol), 500 mg (2.4 mmol) of 1,8-diaminophenanthrene, and 100 mg of zinc acetate were added to 100 mL of dry quinoline. Purification was carried out by chromatography (SiO_2, toluene) affording 974 mg as a blue-violet powder with a yield of 72%.

^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 135 °C), δ 9.51 (m, 2H, H-15,15′), 8.72 (m, 4H, H-18,18′,21,21′), 8.64 (m, 2H, H-24,24′), 8.59/8.58 (s/s, 2H, H-2,11/H-2′,8′), 8.54/8.53 (s/s, 2H, H-5,8/H-5′,11′), 7.6−7.7 (m, 8H, H-16,16′,17,17′,22,22′,23,23′), 7.2−7.4 (m, 8H, Ph-H-3,3′), 6.9−7.1 (m, 8H, Ph-H-2,2′), 1.34 (s, 18H, *tert*-butyl), 1.28 (s, 18H, *tert*-butyl). FD-MS: m/z = 1329.2 (M^+, 100%) required M^+ = 1329.6. UV−vis: (CH_2Cl_2) λ_{max} (ϵ) = 254 (110 985), 299 (61 084), 349 (30 293), 410 (14 589), 450 (14 035), 659 (44 705) nm. IR (KBr) ν = 2961, 2925, 2906, 2868, 2855, 1703, 1591, 1580, 1555, 1506, 1496, 1442, 1423, 1409, 1361, 1342, 1313, 1273, 1216, 1191, 1174, 1158, 1102, 1088, 1056, 1015, 880, 817, 755, 723 cm^{-1}. $C_{92}H_{72}N_4O_6$: found C 82.50, H 5.28, N 4.03; calcd C 83.11, H 5.46, N 4.20. mp > 300 °C.

3,4:9,10-Bis(tetrabromo-1,8-naphthapyrimidine-1,6,7,12-tetrakis(4-hexyloxyphenoxy)perylene (Syn and Anti Isomers) (14). Bis(1,8-naphthapyrimidine)-1,6,7,12-tetrakis(4-hexyloxyphenoxy)-3,4:9,10-perylenetetracarboxdiimide (**12c**, 5.0 g, 3.6 mmol) was dissolved in 500 mL of dry dimethylformamide. The temperature was raised to 65 °C, and 4.45 g (25 mmol) of *N*-bromosuccinimide was added. The reaction mixture was stirred at this temperature for 4 h. After this time the reaction mixture was cooled to room temperature and poured into 2 L of 10 vol % HCl solution. The formed precipitate was removed by filtration, washed with plenty of water, and dried under vacuum. Purification was carried out by chromatography (SiO_2, toluene) and precipitation in methanol affording 3.74 g as a green powder with a yield of 61%.

Since **14** is a mixture of several regioisomers, integration of the ^{1}H NMR spectrum does not correspond to the number of protons, and hence only chemical shifts are given in the aromatic region from 8.3 to 6.8 ppm. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 135 °C), δ 8.84 (d, arom), 8.60 (d, arom), 8.58 (d, arom), 7.5−7.6 (m, arom), 8.11 (s, arom), 8.10 (s, arom), 7.94 (s, arom), 7.93 (s, arom), 7.88 (d, arom), 7.85 (d, arom), 7.57 (t, arom), 6.9−7.2 (m, Ph-H), 4.04 (m, 8H, α-CH_2), 1.86 (m, 8H, β-CH_2), 1.5 (m, 24H, $(CH_2)_3$), 1.02 (m, 12H, CH_3). FD-MS: m/z = 1720.2 (M^+, 100%) required M^+ = 1721.2. UV−vis: (CH_2Cl_2) λ_{max} (ϵ) = 456 (15 184), 667 (60 339), 712 (59 070) nm. IR (KBr) ν = 2952, 2927, 2856, 1686, 1611, 1580, 1553, 1498, 1474, 1404, 1374, 1337, 1311, 1284, 1245, 1197, 1161, 1124, 1101, 1091, 1076, 1060, 1037, 1007, 881, 827, 807 cm^{-1}. $C_{92}H_{80}N_4O_{10}Br_2$: found C 63.09, H 4.72, N 3.02, Br 17.98; calcd C 64.20, H 4.68, N 3.26, Br 18.57. mp > 300 °C.

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