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Substitution of Aromatics by Amines at Room Temperature with Negative Energy of Activation: Amino *peri*-Arylenes as Metal-Free Components for Dye-Sensitized Solar Cells

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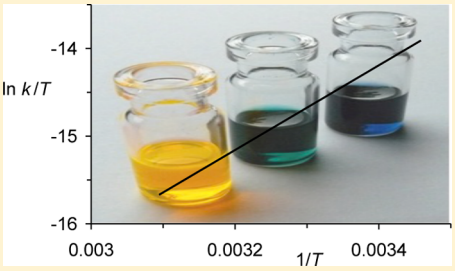
Supporting Information

ABSTRACT: Substitution reactions of the chemically and photochemically unusually stable perylenetetracarboxylic bisimides proceed with neat amines even below room temperature where negative effective energies of activation were found. Analogous reactions proceed with naphthalenecarboximides as the lower homologues and terrylene and quaterrylene carboximides as the higher homologues. Bathochromically absorbing dyes with a novel pattern of substitution were obtained suitable as efficient metal-free light-absorbers for dye-sensitized solar cells.



INTRODUCTION

Organic functional materials are obtaining an increasing interest both in science and technology because of their variability and unproblematic properties. The *peri*-arylene biscarboximides are very promising for such applications where the perylene dyes, perylene-3,4:9,10-tetracarboxylic bisimides, are in the focus of both basic research[1] and industrial applications because of their extraordinarily high chemical and photochemical stability and their high fluorescence quantum yields close to unity. The chemical stability of this class of fluorescent dyes is remarkable because neither concentrated bleach,[2] concentrated sulfuric acid at 100 °C, nor elevated temperatures[3] to 550 °C cause degradation. On the other hand, such high stability interferes with a simple core-substitution being of importance for controlling their photophysical properties. As a consequence, substitutions require comparably rough reaction conditions both for electrophilic and nucleophilic[4] substitution reactions and even for Diels–Alder reactions.[5] These may be problematic for many side groups. A simple and easy reaction for substitution could bring about appreciable progress.

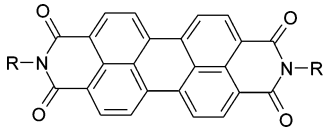
RESULTS AND DISCUSSION

We found, in contrast, to this difficult core-modification, especially in the positions 2 neighbored to the carbonyl groups,[6] an efficient method for the substitution of **1a** by a simple treatment with neat amines such as pyrrolidine in high concentration at room temperature to form stepwise the products **2a** and **3a**; the *N*-1-hexylheptyl swallow-tail substituent[7] renders both the starting material and the reaction products soluble; see Scheme 1.

The reaction proceeds very uniformly as indicated by the two precise isosbestic points at 449 and 545 nm recorded during the whole course of the reaction from **1a** to **2a**; see Figure 1. Precise first-order kinetics were followed both for the degradation of the starting **1a** recorded at 527.0 nm (correlation number $R = 0.9998$ for $n = 15$ measurements at 16 °C) and the formation of the reaction product **2a** recorded at 639.4 nm: see Figure 2.

The temperature dependence of the reaction is even more surprising because it slows with increasing temperature until complete inhibition, whereas cooling accelerates the reaction; this is in contrast to common chemical reactions; for a further example, see ref 8. We investigated a temperature range between 16 and 50 °C for a more extended study and found a slightly better correlation with the Eyring equation ($\ln k/T$ versus $1/T$, $R = 0.980$, $n = 6$; a second-order Eyring-equation, $\ln k/T^2$ versus $1/T$, gives an unimportant further improvement, see the Supporting Information) than with the Arrhenius plot ($\ln k$ versus $1/T$, $R = 0.978$, $n = 6$; $E_a = -38$ kJ·mol^{-1} and intercept 4500). For the former, which we prefer, a strongly negative energy of activation $\Delta H^{\ddagger}$ of −40 kJ·mol^{-1} (−9.6 kcal·mol^{-1}) was found with a strongly negative entropy of activation $\Delta S^{\ddagger} = -450$ J·mol^{-1}·K^{-1} (−110 cal·mol^{-1}·K^{-1}); see Figure 3. These data of activation indicate a complex reaction mechanism for the substitution of **1a**. Small amounts of water catalyze the reaction slightly as well as small amounts of KOH; the latter make the reaction more complex. A complex chain reaction might be the reason for the unusual effective activation data. A radical chain is not very probable because the reaction is not

Chart 1. Perylene Dyes 1



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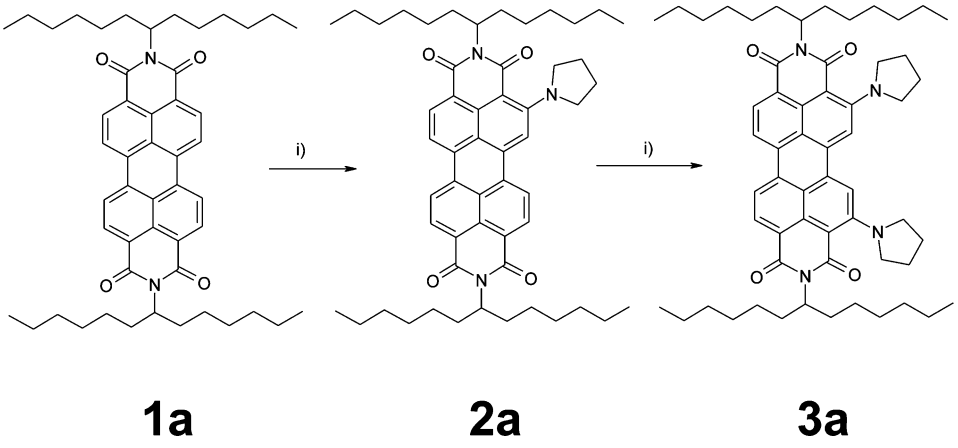
Scheme 1. Synthesis of the Aminoperylenes 2a and 3a[a]



[a]Key: (i) pyrrolidine, neat, room temperature.

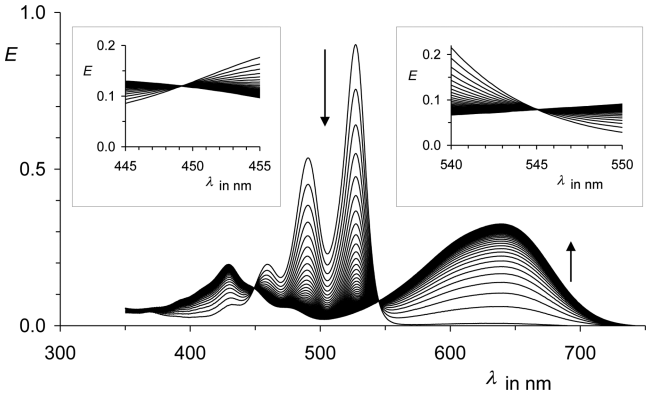


Figure 1. UV/vis spectroscopically followed reaction of **1a** with pyrrolidine at 16 °C in steps of 10 min to form **2a**. Insets: Isosbestic points at 449 and 545 nm.

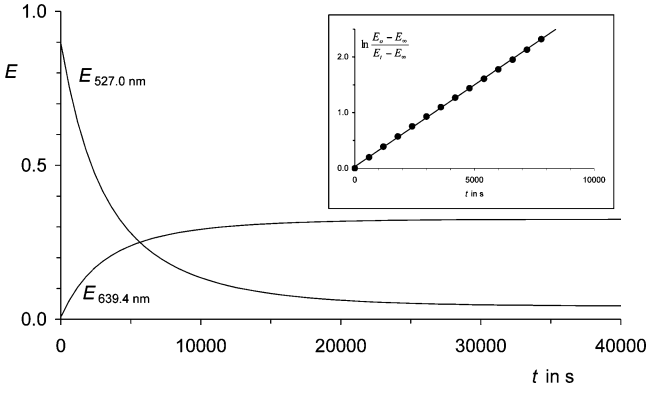


Figure 2. UV/vis spectroscopically recorded reaction kinetics of **1a** with pyrrolidine at 16 °C: degradation of the starting material at 527.0 nm and formation of **2a** at 639.4 nm. Inset: first-order kinetics at 527.0 nm (k_1 = 2.9 × 10^{-4} s^{-1}, R = 0.9998, n = 15 measurements; E_∞ = 0.10).

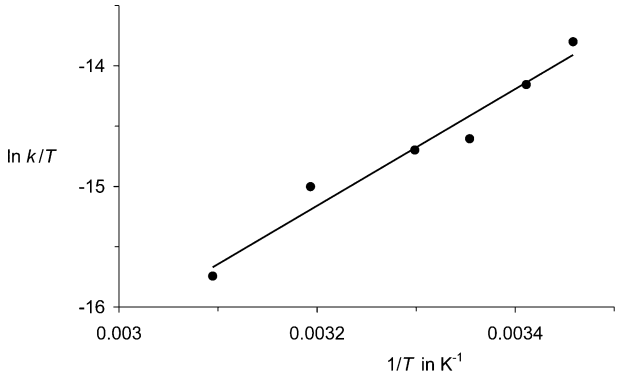


Figure 3. Linear correlation between ln k/T and $1/T$ according to the Eyring theory: $\Delta H^{\ddagger}$ = −40 kJ·mol^{-1} (−9.6 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = −450 J·mol^{-1}·K^{-1} (−110 cal·mol^{-1}·K^{-1}) (R = 0.980, n = 6; **1a** and pyrrolidine 16−50 °C).

influenced by atmospheric oxygen or light. Furthermore, the influence of the concentration of the starting material **1a** ($E_{527\ nm/1\ cm}$ = 0.07−0.5) on the reaction rate is insignificant; this is an indicator against a chain reaction. The application of carefully distilled pyrrolidine did not alter the reaction; residual water seems to be of minor importance. A pre-equilibrium before the rate-determining step can be a further reason for negative energies of activation. However, a postulated intermediate must be energetically favored for overcompensation the energy of activation of the next step and must be entropically disfavored to prevent an accumulation before the reaction. We tested the interaction of **1a** with pyrrolidine for the formation of small amounts of a charge-transfer complex between the electron rich amine and the electron depleted **1a** as a possible intermediate and investigated thoroughly the UV/vis absorption spectra in pure chloroform, in chloroform with 10% pyrrolidine, and in neat pyrrolidine; however, we could not see a significant influence except a slight solvatochromism. We conclude that charge-transfer complexes might be intermediates of a pre-equilibrium but will not be formed in significant stationary concentrations.

We propose for the formation of **2** an initiating nucleophilic attack of pyrrolidine at the group neighbored to a carbonyl group according to Scheme 2. This reaction resembles the Tschitschibabin reaction and is favored by the electronic effect of the carbonyl group and presumably by the formation of a six-membered ring hydrogen-bonded arrangement. A deprotonation of the intermediate would lead to a dihydroaromatic structure where the opposite carbonyl group seems to play a key function. This is supported by the fact that no substitution reaction could be detected for perylene-3,4-dicarboxylic imide where the second carbonyl group is lacking. Finally, the dihydroaromatic product is oxidized to the fully aromatic final

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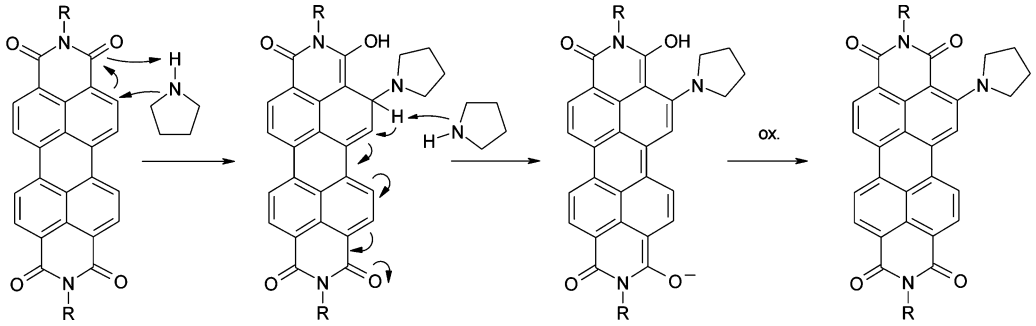
Scheme 2. Proposed Mechanism for the Substitution of 1 with Pyrrolidine To Form 2



product by means of the loss of a hydride ion where atmospheric oxygen, for example, or other residual oxidants may be involved. A pure analogous mechanism to the Tschitschibabin reaction (Chichibabin reaction) with an extrusion of a hydride by protonation and the formation of hydrogen would be an alternative, however could not explain the strong influence of the carboximide structure at the opposite side of the molecule. Detection of the very small amount of hydrogen evolved over a long period remains difficult.

We investigated possible intermediates for the primary attack of amines to **1** by means of quantum chemical calculations (DFT, B3LYP) and found an energetic minimum about 1.4 kJ·mol^{-1} higher than the starting materials for the arrangement of Figure 4 where a tetrahedral pattern is obtained for the

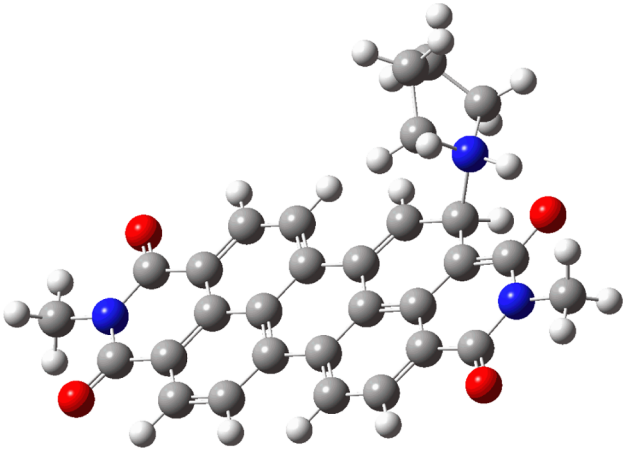
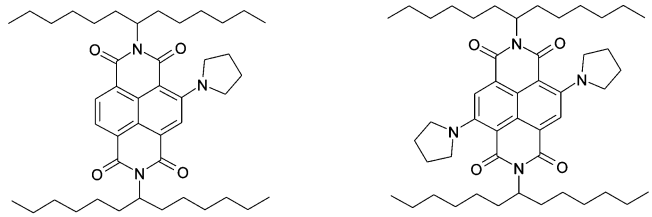


Figure 4. Quantum chemically calculated (DFT, B3LYP) geometry of a complex between the *N*,*N*′-dimethyl derivative of **1** and pyrrolidine.

substituted carbon atom and a hydrogen bond of 1.57 Å from the N−H group to the neighboring carbonyl oxygen atom. The geometry of this arrangement is very restricted because slight variations such as a flip of the hydrogen bond cause strong increases of the energy. This makes a geometrically very restricted, low-activated pathway of the reaction probable as a reason for the unusual parameters of activation where thermal collisions cause disruptions; such conditions resemble enzymatic reactions. A numeric comparison of the calculated energies with the experimental energy of activation is problematic because this would require integrations of the specific heats for all involved species.

The substitution reaction of **1a** can be extended to primary amines such as 1-aminopropane (**2b**) and 1-aminobutane (**2c**)

Chart 2. Aminonaphthalene Dyes 4 and 5



4 **5**

where this reaction proceeds more slowly than with pyrrolidine, presumably as a consequence of lower nucleophilicity. Substitution reactions are even possible with naphthalene-1,8:4,5-tetracaboxylic bisimides[9] as the smaller homologous of **1a** and form the corresponding product **4** where the reaction proceeds appreciably slower than with **1a**. The disubstitution requires a long reaction time. The two pyrrolidine rings are attached to different rings, and **5** is the most probable structure because of electronic effects; however, a secure decision between c2 and cs symmetry was not successful. On the other hand, the molecular mass is unambiguous.

An extension of the reaction to the higher *peri*-arylenes terrylene[10] (**6**) and quaterrylene[11] (**9**) tetracarboxylic bisimide was also successful; see Scheme 3. The substitution of **6** proceeds more quickly than of **1**, whereas the reaction of **9** is slowed again. The monosubstitutions proceed unambiguously neighbored to the carbonyl groups so that the structures of **7** and **10** are clear. The second substitution clearly proceeds also neighbored to carbonyl groups, and we assume the structures **8** and **10**, respectively, for the disubstituted dyes in analogy to **3a**.

The UV/vis absorption spectrum of **2a** exhibits an appreciable bathochromic shift compared with **1a** so that emerald green solutions are obtained; see Figure 5. The spectrum is less structured compared with **1a**, and fluorescence is weak. The introduction of the second amino group in **3a** causes a further bathochromic shift close to the NIR where sapphire blue solutions were formed.

A strong bathochromic shift was induced by the amino substitution of the naphthalene skeleton so that red solutions with maxima at about 480 and 520 nnm of **4** were obtained from the colorless[9] starting material. The second substitution to form **5** causes a further slight bathochromic shift.

The substitution of **6** with one pyrrolidine unit induces an appreciable bathochromic shift with a loss of vibronic structure so that deep green solutions of **7** are obtained; see Figure 6. The second substitution with pyrrolidine causes a further

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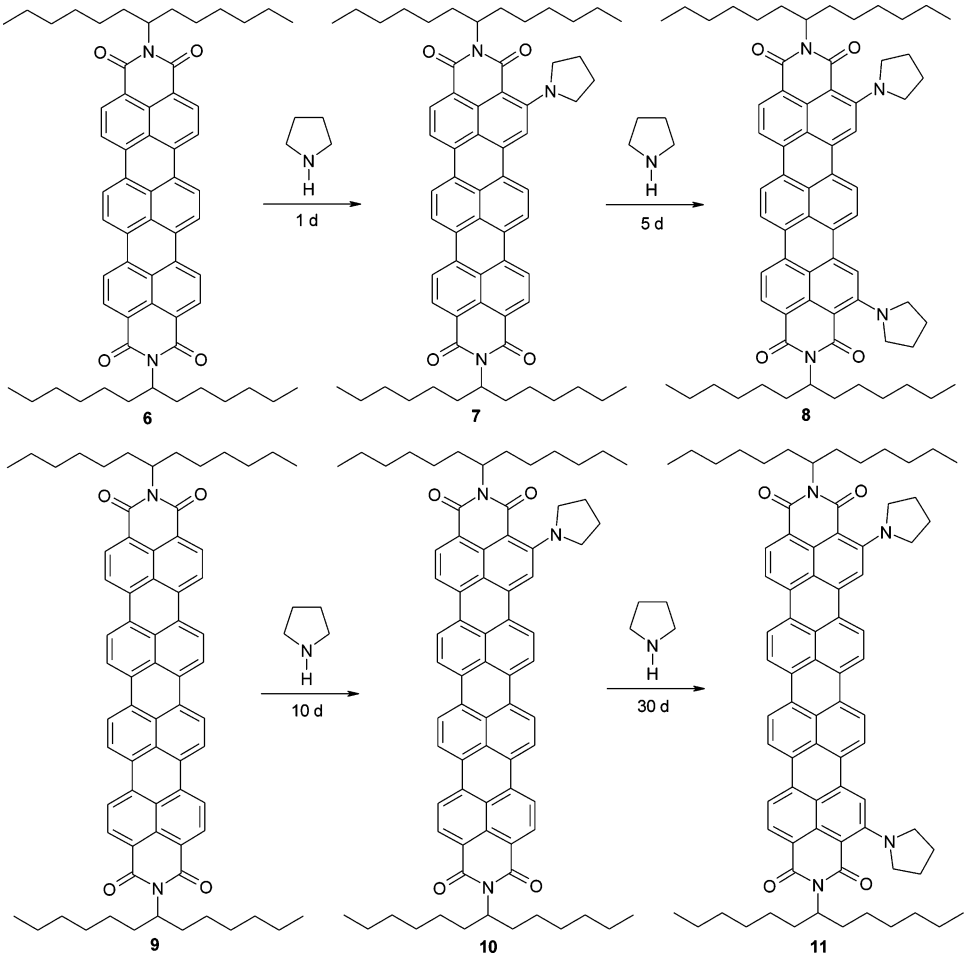
Scheme 3. Substitution of Terrylene- and Quaterrylene Tetracarboxylic Bisimides with Pyrrolidine



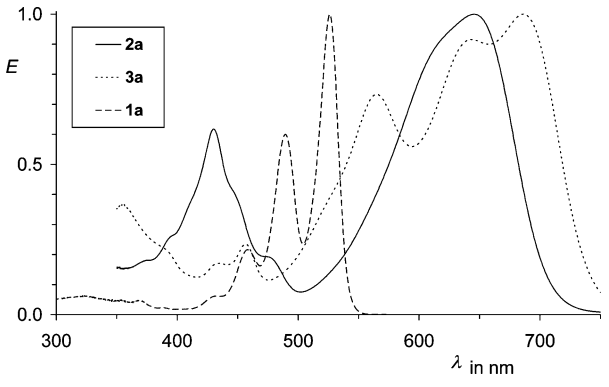


Figure 5. UV/vis spectra of **2a** (solid line) and **3a** (dotted) in chloroform compared with **1a** (dashed).

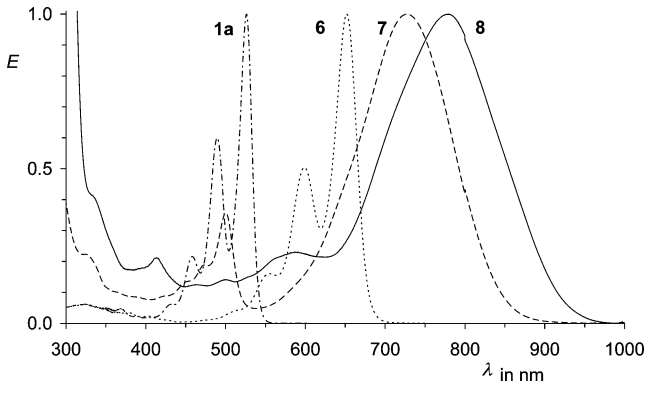


Figure 6. UV/vis spectra of **7** (dashed line) and **8** (solid line) in chloroform compared with **1a** (dotted dashed) and **6** (dotted line).

bathochromic shift to obtain blue solutions of **8** where the absorption extends until the NIR.

The quaterrylene derivative **9** absorbs at long wavelengths in the visible region; see Figure 7 (solid line). The substituent-induced bathochromic shift in **16** (dotted line) is appreciably smaller than for **1a** and **6**, respectively. Even a double substitution in **17** (dashes line) is of minor influence on the position of the absorption maximum; however, the absorption bands are appreciably broadened so that the point of gravity moves bathochromically. There is some residual structuration in the spectrum of **10** and even less in **11**. The fluorescence of all amino substituted derivatives of **1a**, **6**, and **9** is very weak.

The core substitution of **1a**, **6**, and **9** causes not only a bathochromic shift of the light absorption but also increases the electron density of the aromatic core. This makes these substances of interest as working chromophores in solar systems because the absorption spectrum becomes better adapted to the solar radiation and the higher electron density favors the electron injection for charge-separation. We applied Grätzel's cells as dye-sensitized solar cells where titanium dioxide operates as the electron acceptor. The nano structured

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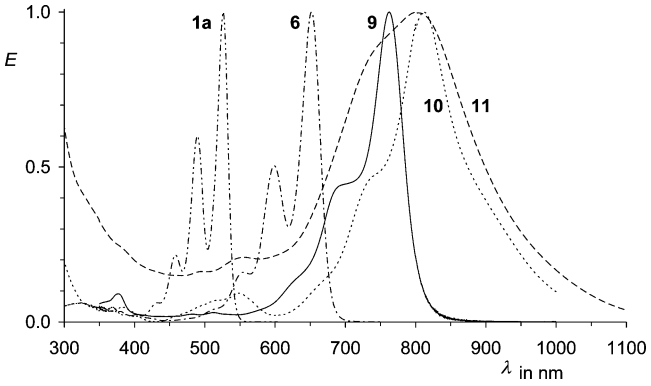
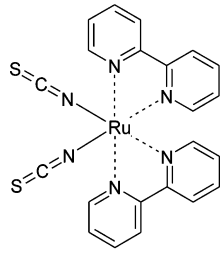


Figure 7. UV/vis spectra of **10** (dotted line) and **11** (dashed line) in chloroform compared with **9** (solid line), **6** (dotted dashed), and **1a** (double dotted line).

Chart 3. Standard Ruthenium Complex for Sensitizing Gätzel's Solar Cells (Dye-Sensitized Solar Cells)



12

titanium dioxide of standard commercial Grätzel cells[12] were doped with various dyes where iodine/iodide was applied as an electrolytic counter electrode. The efficient commercial sensitizer **12** was taken as a reference of efficiency and set to unity for the applied diffuse solar radiation of a clouded sky in Munich; see Figure 8, light column. The unsubstituted *peri*-arylene dyes **1a**, **6**, and **9** exhibit increasing efficiencies with the extension of the chromophoric system caused by the increasing bathochromic absorption and increasing electron density; nos. 1, 2, and 3 in Figure 8. However, their efficiencies do not reach the commercial ruthenuim complex **12** (no. 4). A substitution

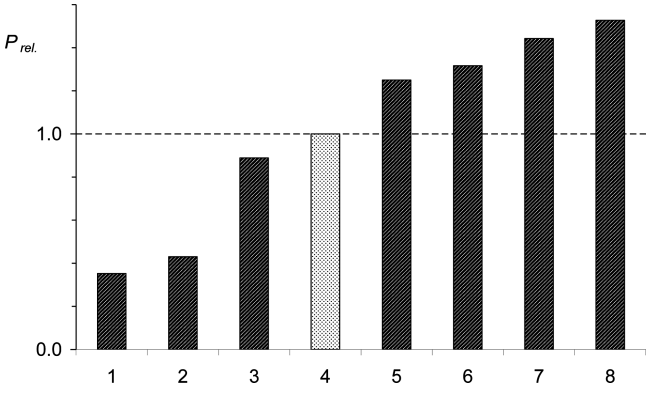


Figure 8. Energy efficiencies (P_{rel}) of dye-sensitized Grätzel solar cells with the technical reference **18** set to unity; light bar no. 4. Key: sensitizing dye **1a**, no. 1; **6**, no. 2; **9**, no. 3; **7**, no. 5; **8**, no. 6; **10**, no. 7; **11**, no. 8.

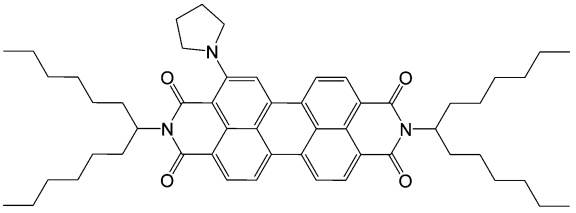
with pyrrolidino groups makes the *peri*-arylenes much more efficient. The monosubstituted terrylene derivative **7** (no. 5) exceeds the commercial complex appreciably. A disubstitution further increases the efficiency slightly (**8**, no. 8). A substitution of the quaterrylene carboximide improved the efficiency appreciably (**7**, no. 7), and finally, a substitution of the quaterrylene derivative (**11**, no. 8) gave the best result for the use in Grätzel cells and exceeds the commercial sensitizer by far.

■ CONCLUSIONS

One may summarize that a reaction of perylenecarboxylic bisimides proceeds with primary and secondary amines under very mild conditions in a complex reaction and with a negative energy of activation to form bathochromically absorbing aromatic amino derivatives with a novel and unusual substitution pattern. An extension to naphthalene, terrylene, and quaterrylene carboxylic imides indicates a broader application of this novel-type of reaction. The pyrrolidino *peri*-arylenes are efficient sensitizers for Graetzel's solar cells, are more efficient than commercially applied ruthenium complexes, and form a metal-free alternative.

■ EXPERIMENTAL SECTION

General Methods. All FAB spectra were recorded in 3-nitrobenzylalcohol as the matrix. Fluorescence quantum yields were determined analogously to ref 13. The interpretation of NMR signals was verified with carbon−proton (HMBC) and proton−proton (COSY, NOESY)) correlation methods.



***N,N′*-Bis(1-hexylheptyl)-2-(*N*-pyrrolidinyl)perylene-3,4:9,10-tetracarboxybisimide (2a) and *N,N′*-Bis(1-hexylheptyl)-2,11-bis(*N*-pyrrolidinyl)perylene-3,4:9,10-tetracarboxylic Bisimide (3a).** *N,N′*-Bis(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic bisimide (**1a**, 502 mg, 0.665 mmol) was dissolved in pyrrolidine (40.0 mL, 34.6 g, 0.487 mol, quickly darkening deep red solution), stirred at 23 °C for 9 d (further darkening to deep turquoise), evaporated under medium vacuum, and fractionized by column separation (fine silica gel, chloroform, exclusion of daylight) to obtain **2a** and **3a**. Each fraction was purified by a further column separation. First fraction: *N,N′*-bis(1-hexylheptyl)-2-(*N*-pyrrolidinyl)perylene-3,4:9,10-tetracarboxylic bisimide (**2a**). Yield: 288 mg (53%) of dark turquoise, nearly black solid powder. Mp > 250 °C. R_f (silica gel, $CHCl_3$) 0.80. IR (ATR): $\tilde{\nu}$ = 3300 (vw), 2953 (m), 2922 (s), 2854 (s), 1688 (s), 1649 (s), 1611 (w), 1585 (s), 1568 (m), 1557 (m), 1507 (w), 1457 (w), 1419 (m), 1370 (m), 1331 (s), 1277 (w), 1235 (m), 1171 (w), 1118 (w), 1104 (w), 1040 (vw), 950 (w), 844 (w), 807 (m), 749 (w), 723 (w), 696 (vw), 628 cm^{-1} (vw). ^1H NMR (600 MHz, $CDCl_3$, 27 °C): δ = 0.82 (t, ^3J = 7.0 Hz, 12 H, 4 × CH_3), 1.18−1.39 (m, 32 H, 16 × CH_2), 1.82−1.90 (m, 4 H, 4 × β-CH), 2.00 (s (br), 2 H, 2 × β-$CH_{pyrrolidinyl}$), 2.14 (s (br), 2 H, 2 × β-$CH_{pyrrolidinyl}$), 2.22−2.30 (m, 4 H, 4 × β-CH), 2.84 (s (br), 2 H, 2 × α-$CH_{pyrrolidinyl}$), 3.82 (s (br), 2 H, 2 × α-$CH_{pyrrolidinyl}$), 5.16−5.25 (m, 2 H, 2 × α-CH), 7.63 (d, ^3J = 8.0 Hz, 1 H, $CH_{perylene}$), 8.45−8.51 (m, 1 H, $CH_{perylene}$), 8.53−8.59 (m, 3 H, 3 × $CH_{perylene}$), 8.63−8.70 ppm (m, 2 H, 2 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 14.3, 22.8, 22.8, 26.0, 27.1, 27.2, 29.5, 29.5, 32.0, 32.0, 32.7, 32.7, 52.7, 54.7, 54.9, 55.0, 116.4, 120.8, 122.6, 122.7, 123.3, 123.5, 123.7, 124.0, 124.6, 127.6, 129.1, 129.5, 130.8, 131.0, 131.6, 131.8, 133.0, 135.5, 135.8, 148.8, 164.3, 164.4, 165.3, 165.4 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 430 (14050), 475 (4278), 645 nm

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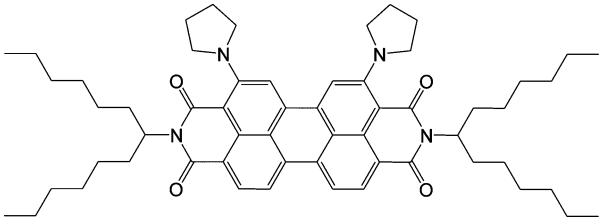
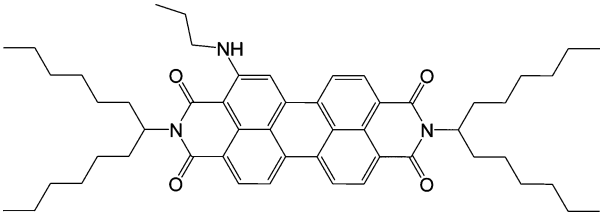
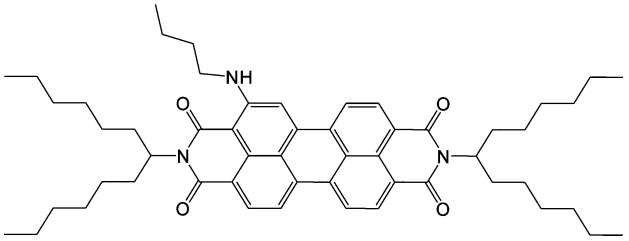
(22960 L mol^{-1} cm^{-1}). Fluorescence ($CHCl_3$, λ_{exc} = 600 nm): λ_{max} = 721 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 600 nm, $E_{600\ nm/1\ cm}$ = 0.0077, reference: **1a** with Φ = 1.00): Φ = 0.03. HRMS/EI ($C_{54}H_{69}N_3O_4$): calcd m/z = 823.5288, found m/z = 823.5280, Δ = −0.8 mmu. Anal. Calcd for $C_{54}H_{69}N_3O_4$ (824.1): C, 78.70; H, 8.44; N, 5.10. Found: C, 78.25; H, 8.10; N, 5.15.



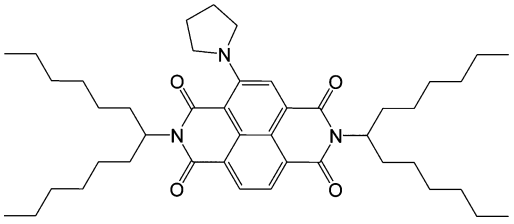
Second Fraction: *N,N′*-Bis(1-hexylheptyl)-2,11-bis(*N*-pyrrolidinyl)-perylene-3,4:9,10-tetracarboxybisimide (**3a**). Yield: 13 mg (2%, extension of the reaction time increases the yield of **3a**) as a dark blue solid powder. Mp > 250 °C. R_f (silica gel, $CHCl_3$): 0.87. IR (ATR): $\tilde{\nu}$ = 3368 (vw), 2953 (m), 2922 (s), 2853 (s), 1684 (s), 1646 (s), 1602 (m), 1580 (s), 1538 (w), 1523 (w), 1512 (w), 1483 (vw), 1456 (m), 1432 (m), 1386 (m), 1350 (m), 1331 (s), 1264 (m), 1241 (m), 1214 (w), 1166 (w), 1109 (w), 1081 (w), 1037 (vw), 973 (vw), 944 (w), 868 (w), 832 (vw), 802 (w), 775 (vw), 752 (w), 722 (w), 698 (vw), 663 (vw), 635 cm^{-1} (vw). ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C): δ = 0.82 (t, ^3J = 6.8 Hz, 12 H, 4 × CH_3), 1.18−1.40 (m, 32 H, 16 × CH_2), 1.81−1.91 (m, 4 H, 4 × β-CH), 1.97 + 2.06 (2*s* (br), 8 H, 2 × 4 × β-$CH_{pyrrolidinyl}$), 2.23−2.32 (m, 4 H, 4 × β-CH), 2.80 (s (br), 4 H, 4 × α-$CH_{pyrrolidinyl}$), 3.73 (s (br), 4 H, 4 × α-$CH_{pyrrolidinyl}$), 5.16−5.21 (m, 1 H, α-CH), 5.24−5.29 (m, 1 H, α-CH), 7.91 (d, ^3J = 8.1 Hz, 2 H, 2 × $CH_{perylene}$), 8.32 + 8.36 (2*s* (br), 2 H, 2 × $CH_{perylene}$), 8.63 (d, ^3J = 8.0 Hz, 1 H, $CH_{perylene}$), 8.68 ppm (d, ^3J = 8.0 Hz, 1 H, $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 14.3, 22.8, 22.9, 25.9, 27.1, 27.3, 29.5, 29.6, 29.9, 30.4, 31.7, 32.0, 32.0, 32.8, 52.3, 54.5, 54.9, 117.3, 117.6, 117.6, 117.9, 118.4, 118.7, 123.6, 128.7, 128.7, 130.1, 130.9, 131.3, 135.7, 135.8, 150.3, 164.7, 164.8, 165.6, 165.9 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 432 (3946), 457 (5789), 565 (19670), 643 (22560), 683 nm (23920 L mol^{-1} cm^{-1}). Fluorescence ($CHCl_3$, λ_{exc} = 564 nm): λ_{max} (I_{rel}) = 746 nm (1.00). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 564 nm, $E_{564\ nm/1\ cm}$ = 0.0088, reference 1a with Φ = 1.00): Φ = 0.10. HRMS/EI ($C_{58}H_{76}N_4O_4$): calcd m/z = 893.5945 [M^+ + H], found m/z = 893.5946 [M^+ + H], Δ = +0.1 mmu. Anal. Calcd for $C_{58}H_{76}N_4O_4$ (893.2): C, 77.99; H, 8.58; N, 6.27. Found: C, 77.48; H, 8.12; N, 6.11.



N,N′-Bis(1-hexylheptyl)-2-(*N*-propylamino)perylene-3,4:9,10-tetracarboxylic Bisimide (2b). *N,N′*-Bis(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic bisimide (**1a**, 206 mg, 0.273 mmol) was dissolved in 1-aminopropane (20.0 mL, 14.4 g, 0.244 mol), treated slowly dropwise with distilled water (3.0 mL, 3.0 g, 0.17 mol, red solution), stirred at 23 °C for 10 d (color change to brown and finally to olive green), evaporated in vacuo, and purified by column separation (fine silica gel, chloroform; with the exclusion of daylight). Yield: 26 mg (12%) as a dark blackish turquoise slightly oily solid. R_f (silica gel, $CHCl_3$): 0.89. IR (ATR): $\tilde{\nu}$ = 3357 (vw), 2956 (m), 2924 (s), 2855 (m), 1694 (m), 1654 (m), 1612 (w), 1589 (m), 1570 (w), 1560 (w), 1540 (vw), 1512 (vw), 1458 (w), 1428 (w), 1397 (vw), 1378 (vw), 1340 (m), 1329 (m), 1271 (w), 1250 (w), 1177 (vw), 1106 (vw), 842 (vw), 806 (w), 748 (vw), 725 cm^{-1} (vw). ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C): δ = 0.82 + 0.83 (2*t*, ^3J = 7.0 Hz, 12 H, 4 × CH_3), 1.14 (t, ^3J = 7.4 Hz, 3 H, $CH_{3/n\text{-propylamino}}$), 1.18−1.37 (m, 32 H, 16 × CH_2), 1.82−1.90 (m, 6 H, 4 × β-CH + β-$CH_{2/n\text{-propylamino}}$), 2.21−2.29 (m, 4 H, 4 × β-CH), 3.49 (t, ^3J = 7.1 Hz, 2 H, α-$CH_{2/n\text{-propylamino}}$), 5.14−5.23 (m, 2 H, 2 × α-CH), 6.05 (s (br), 1 H, $NH_{n\text{-propylamino}}$), 8.25−8.28 (m, 1 H, $CH_{perylene}$), 8.41−8.46 (m, 1 H, $CH_{perylene}$), 8.50 (d, ^3J = 8.2 Hz, 1 H, $CH_{perylene}$) 8.54 (d, ^3J = 8.1 Hz, 1 H, $CH_{perylene}$), 8.58−8.69 (m, 2 H, 2 × $CH_{perylene}$), 8.89 ppm (d, ^3J = 8.2 Hz, 1 H, $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 12.0, 14.3, 22.8, 22.8, 23.1, 27.1, 27.2, 29.4, 29.5, 32.0, 32.0, 32.6, 32.7, 46.9, 54.8, 121.3, 121.4, 123.1, 124.3, 128.0, 128.6, 130.2, 147.9, 163.9, 164.2, 164.9, 165.3 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 429 (7516), 473 (1813), 611 nm (12830 L mol^{-1} cm^{-1}). Fluorescence ($CHCl_3$, λ_{exc} = 622 nm): λ_{max} = 746 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 622 nm, $E_{622\ nm/1\ cm}$ = 0.0089, reference: **1a** with Φ = 1.00): Φ = 0.04. HRMS/EI ($C_{53}H_{69}N_3O_4$): calcd m/z = 811.5288, found m/z = 811.5263; Δ = −2.5 mmu. Anal. Calcd for $C_{53}H_{69}N_3O_4$ (812.1): C, 78.38; H, 8.56; N, 5.17. Found: C, 77.97; H, 8.87; N, 5.10.



N,N′-Bis(1-hexylheptyl)-2-(*N*-butylamino)perylene-3,4:9,10-tetracarboxylic Bisimide (2c). *N,N′*-Bis(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic bisimide (**1a**, 300 mg, 0.397 mmol), 1-aminobutane (40.0 mL, 29.6 g, 0.405 mol), and distilled water (9.0 mL, 9.0 g, 0.50 mol) were allowed to react as was described for **2b** (stirred at 23 °C for 15 d, color changed to brown and grayish violet) and purified by column separation (fine silica gel, chloroform, and a second column with chloroform/*n*-pentane 2:1). Yield: 35 mg (11%) as a dark blackish turquoise slightly oily solid. R_f (silica gel, $CHCl_3$): 0.89. IR (ATR): $\tilde{\nu}$ = 3320 (w), 2955 (m), 2924 (s), 2855 (m), 1693 (m), 1653 (m), 1612 (w), 1589 (m), 1571 (w), 1560 (w), 1511 (vw), 1457 (w), 1428 (w), 1396 (vw), 1377 (vw), 1338 (m), 1270 (w), 1248 (w), 1180 (w), 1122 (vw), 1099 (vw), 974 (vw), 876 (vw), 842 (vw), 806 (w), 748 (w), 725 cm^{-1} (vw). ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C): δ = 0.82 + 0.83 (2*t*, ^3J = 7.0 Hz, 12 H, 4 × CH_3), 1.06 (t, ^3J = 7.4 Hz, 3 H, $CH_{3/n\text{-butylamino}}$), 1.18−1.37 (m, 32 H, 16 × CH_2), 1.54−1.60 (m, 2 H, γ-$CH_{2/n\text{-butylamino}}$), 1.80−1.88 (m, 6 H, 4 × β-CH + β-$CH_{2/n\text{-butylamino}}$), 2.21−2.29 (m, 4 H, 4 × β-CH), 3.52 (t, ^3J = 7.1 Hz, 2 H, α-$CH_{2/n\text{-butylamino}}$), 5.13−5.22 (m, 2 H, 2 × α-CH), 6.01 (s (br), 1 H, $NH_{n\text{-butylamino}}$), 8.25−8.28 (m, 1 H, $CH_{perylene}$), 8.40−8.44 (m, 1 H, $CH_{perylene}$), 8.46 (d, ^3J = 8.0 Hz, 1 H, $CH_{perylene}$) 8.51 (d, ^3J = 8.0 Hz, 1 H, $CH_{perylene}$), 8.58−8.65 (m, 2 H, 2 × $CH_{perylene}$), 8.87 ppm (d, ^3J = 8.1 Hz, 1 H, $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 14.1, 14.3, 14.3, 20.7, 22.8, 22.8, 22.9, 27.2, 29.4, 29.5, 29.6, 29.9, 29.9, 30.4, 30.5, 31.6, 31.8, 32.0, 32.0, 32.1, 32.6, 32.6, 44.9, 54.7, 121.2, 121.3, 123.0, 124.2, 127.9, 128.5, 130.2, 147.9, 163.8, 164.2, 164.9, 165.2 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 429 (13830), 622 nm (22550 L mol^{-1} cm^{-1}). Fluorescence ($CHCl_3$, λ_{exc} = 620 nm): λ_{max} (I_{rel}) = 730 nm (1.00). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 620 nm, $E_{620\ nm/1\ cm}$ = 0.0099, reference: **1a** with Φ = 1.00): Φ = 0.11. HRMS/EI ($C_{54}H_{71}N_3O_4$): calcd m/z = 825.5445, found m/z = 825.5431, Δ = −1.4 mmu.



2,7-Bis(1-hexylheptyl)-4-pyrrolidin-1-yl-benzo[*lmn*][3,8]-phenanthroline-1,3,6,8-tetraone (4) and the Product of Disubstitution with Pyrrolidine (5). 2,7-Bis(1-hexylheptyl)benzo-[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone (0.500 g, 0.793 mmol) and pyrrolidine (200.0 mL, 173.0 g, 2.44 mol) were allowed to react as

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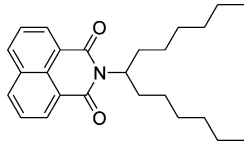
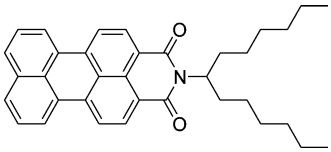
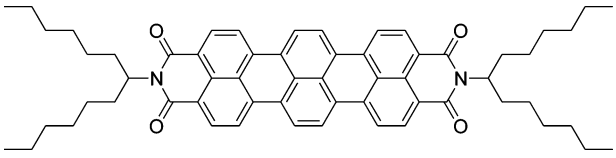
described for **2a** (exclusion of daylight, 23 °C, 13 d, color change to orange, red and then dark brown). Yield: 4 mg (reddish orange, very tough solid, mixture, mainly consisting of **4** with smaller amounts of **5**). ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C) (30): δ = 0.80−0.83 (m, 12 H, 4 × CH_3), 1.13−1.37 (m, 32 H, 16 × CH_2), 1.77−1.87 (m, 4 H, 4 × β-CH), 2.05 (s (br), 4 H, 4 × β-$CH_{pyrrolidinyl}$), 2.16−2.24 (m, 4 H, 4 × β-CH), 3.51 (s (br), 4 H, 4 × α-$CH_{pyrrolidinyl}$), 5.08−5.18 (m, 2 H, 2 × α-CH), 7.97−8.01 (m, 1 H, CH_{aryl}), 8.71−8.74 ppm (m, 2 H, CH_{aryl}). HRMS/EI ($C_{44}H_{65}N_3O_4$) (4): calcd m/z = 699.4975, found m/z = 699.4970, Δ = −0.5 mmu. HRMS/EI ($C_{48}H_{72}N_4O_4$) (5): calcd m/z = 768.5554, found m/z = 768.5553, Δ = −0.1 mmu.



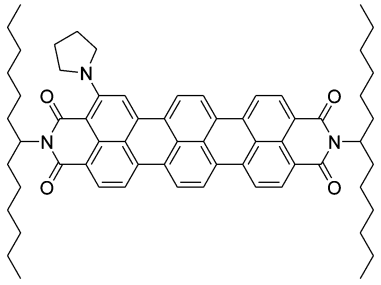
2-(1-Hexylheptyl)benzo[*de*]isoquinolin-1,3-dione (6 Precipitate 1). 1-Hexylheptylamine (5.04 g, 25.1 mmol) and 1,8-naphthalenedicarboxcylicanhydride (5.00 g, 25.2 mmol) in imidazole (12 g) under argon atmosphere were heated at 130 °C for 3 h, allowed to cool, treated with 2 M aqueous HCl (500 mL), extracted two times with $CHCl_3$ dries with $MgSO_4$, evaporated in vacuo, and purified by column separation (silica gel 40−63 μm, $CHCl_3$/isohexane 1:1). Yield: 6.2 g (65%) as a yellowish oil. R_f (silica gel, chloroform): 0.85. IR (ATR): $\tilde{\nu}$ = 3068.0 (w), 2953.5 (s), 2921.6 (s), 2852.6 (s), 1700.8 (s), 1659.7 (s), 1628.1 (m),1588.5 (s), 1515.4 (w), 1463.7 (m), 1435.6 (w), 1397.5 (m), 1372.5 (m), 1339.3 (s), 1236.0 (s), 1176.1 (w, br), 1093.4 (w), 1071.9 (w), 1027.7 (w), 879.7 (w), 844.8 (w), 779.9 (s), 720.9 (w), 696.1 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.81 (t, ^3J(H,H) = 7.1 Hz, 6 H, 2 × CH_3), 1.16−1.35 (m, 16 H, 8 × CH_2), 1.79−1.86 (m, 2 H, β-CH_2), 2.18−2.26 (m, 2 H, β-CH_2), 5.13−5.20 (m, 1 H, NCH), 0.7.74 (t, ^3J(H,H) = 7.7 Hz, 2 H, 2 × $CH_{aromat.}$), 8.18 ppm (d, ^3J(H,H) = 8.1 Hz, 2 H, 2 × $CH_{aromat.}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS): δ = 14.0, 22.6, 26.9, 29.2, 31.7, 32.4, 54.4, 122.7, 123.4, 126.9, 128.3, 130.8, 131.5, 133.5, 164.3, 165.4 ppm. MS (DEI$^+$/70 eV): m/z: 379.3 (6) [M$^+$], 199.1 (13), 198.1 (100), 180.0 (12), 84.9 (14), 82.9 (23). HRMS ($C_{25}H_{33}NO_2$): calcd m/z 379.2511, found m/z 379.2507, Δ = +0.0004. Anal. Calcd for $C_{25}H_{33}NO_2$ (379.3): C, 79.11; H, 8.76; N, 3.69. Found: C, 78.73; H, 8.87; N, 3.70.



2-(1-Hexylheptyl)benzo[*de*]isoquinolin-1,3-dione (6 Precipitate 2). Perylene-3,4-dicarboxylic Anhydride (1.00 g, 3.10 mmol) and 1-hexylheptylamine (680 mg, 3.41 mmol) in imidazole (5 g) were reacted at 140 °C for 2 h, allowed to cool, precipitated while warm with 2 M aqueous HCl (200 mL), collected by vacuum filtration (D4 glasfilter), dried in air at 110 °C, and used for the next steps without further purification. Yield: 1.54 g (99%) as a red solid. Mp: 167 °C. R_f (silica gel/chloroform): 0.85. IR (ATR): $\tilde{\nu}$ = 3319 (w), 3069 (w), 2954 (s), 2854 (s), 1769 (s), 1732 (m) 1697 (s), 1657 (s), 1592 (s), 1577 (m), 1538 (m), 1506 (w), 1455 (w), 1404 (m), 1352 (m), 1314 (s), 1266 (m), 1246 (m), 1200 (w), 1175 (w), 1140 (w), 1123 (m), 1014 (m), 852 (w), 807 (w), 750 (w), 735 (m) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.83 (t, ^3J(H,H) = 7.0 Hz, 6 H, 2 × CH_3), 1.19−1.39 (m, 16 H, 8 × CH_2), 1.84−1.91 (m, 2 H, β-CH_2), 2.22−2.30 (m, 2 H, β-CH_2), 5.16−5.24 (m, 1 H, NCH), 7.58 (t, ^3J(H,H) = 7.8 Hz, 2 H, 2 × $CH_{perylene.}$), 7.85 (d, ^3J(H,H) = 8.0 Hz, 2 H, 2 × $CH_{perylene.}$), 8.32 (d, ^3J(H,H) = 8.1 Hz, 2 H, 2 × $CH_{perylene}$), 8.35 (d, ^3J(H,H) = 7.4 Hz, 2 H, $CH_{perylene}$), 8.50 ppm (br, 2H, $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS): δ = 14.0, 22.6, 27.0, 29.3, 31.8, 32.4, 54.3, 119.8, 123.2, 126.7, 127.6, 128.9, 129.6 130.5, 130.8, 131.6, 134.0, 136.5, 164.1, 165.0 ppm. UV/vis ($CHCl_3$): λ_{max} (E_{rel}) = 483 (1.00), 506 nm (0.98). Fluorescence ($CHCl_3$, λ_{max} = 483 nm): λ_{max} (I_{rel}) = 540 (1.00), 568 nm (0.52). MS (DEP/EI): m/z = 505 (2) [M + 2H]$^+$, 504 (9) [M + H]$^+$, 503 (23) [M]$^+$, 487 (2), 486 (6), 333 (2), 323 (1), 322 (6), 321 (33), 320 (100), 304 (3), 303 (2), 277 (5), 275 (1), 251 (2), 250 (2). HRMS ($C_{35}H_{37}O_2N$): calcd m/z 503.2824, found m/z 503.2827, Δ = −0.0003.



2,11-Bis(1-hexylheptyl)benzo[13,14]pentapheno[3,4,5-*def*:10,9,8-*d′e′f′*]diisoquinolin-1,3,10,12(2*H*,11*H*)-tetraone (6). Potassium *tert*-butanolate (634 mg, 5.65 mmol) and diazabicyclo[4.3.0]non-5-ene (DBN, 946 mg, 7.62 mmol) in dry toluene (10 mL) with very thorough exclusion of moisture and air (argon atmosphere) were stirred at 120 °C for 15 min and treated dropwise within 10 min with 2-(1-hexylheptyl)benzo[*de*]isoquinolin-1,3-dione (850 mg, 2.24 mmol) and 2-(1-hexylheptyl)-1*H*-benzo-[5,10]anthra[2,1,9-*def*]isoquinolin-1,3(2*H*)-dione (640 mg, 1.27 mmol) in degassed, dry toluene (8 mL) (spontaneous color change to dark blue), stirred at 120 °C for 2 h, allowed to cool, precipitated while warm with 2 M aqueous HCl (50 mL), collected by vacuum filtration (D4 glas filter), washed with 2 M aqueous HCl and distilled water, dried in air at 110 °C for 16 h, and purified by column separation (silica gel 40−63 μm, chloroform). Yield: 598 mg (54%) as a blue solid. Mp > 250 °C. R_f (silica gel, chloroform): 0.35. IR (ATR): $\tilde{\nu}$ = 2952 (m), 2919 (s), 2850 (m), 2361 (w), 1691 (s), 1649 (s), 1583 (s), 1572 (s), 1505 (w), 1456 (m), 1418 (w), 1350 (s), 1323 (s), 1302 (m), 1248 (m), 1205 (m), 1172 (w), 1144 (w), 1104 (w), 1022 (w), 954 (w), 852 (w), 840 (w), 806 (s), 790 (m), 748 (m), 723 (w), 693 (w), 680 (m), 667 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.84 (t, ^3J(H,H) = 7.0 Hz, 12 H, 4 × CH_3), 1.20−1.42 (m, 32 H, 16 × CH_2), 1.88−1.94 (m, 4 H, β-CH_2), 2.24−2.32 (m, 4 H, β-CH_2), 5.18−5.25 (m, 2 H, NCH), 8.38−8.46 (m, 8 H, $CH_{terrylene}$), 8.54−8.63 (m, 4 H, $CH_{terrylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS): δ = 14.1, 22.6, 27.0, 29.3, 31.8, 32.4, 54.6, 121.3, 121.7, 122.5, 124.1, 125.9, 128.5, 129.7, 130.8, 131.0, 131.8, 135.3, 163.8, 164.8 ppm. UV/vis ($CHCl_3$): λ_{max}(E_{rel}) = 555.2 (0.16), 598.9 (0.51), 651.8 (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 599 nm): λ_{max} (I_{rel}) = 666.2 (1.00), 731.7 (0.47). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 599 nm, $E_{599\ nm/1\ cm}$ = 0.0136, reference S-13 with Φ = 1.00): 0.93. MS (DEP/EI) m/z: 880 (20) [M$^+$ + 2H], 879 (35) [M$^+$ + H], 878 (72) [M$^+$], 701 (32), 698 (64), 696 (100), 85 (46), 83 (59), 67 (26), 57 (32), 55 (48), 44 (73), 43 (30), 41 (51). HRMS ($C_{60}H_{66}N_2O_4$): calcd m/z 878.5023, found m/z 878.5012, Δ = +0.0011. Anal. Calcd for $C_{60}H_{66}N_2O_4$ (878.5): C, 81.97; H, 7.57; N, 3.19. Found: C, 81.68; H, 7.50; N, 3.14.



***N,N′*-Bis(1-hexylheptyl)-2-pyrrolidinoterrylene-3,4:11,12-tetracarboxylic Bisimide (7).** 2,11-Bis(1-hexylheptyl)benzo[13,14]-pentapheno[3,4,5-*def*:10,9,8-*d′e′f′*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (**6**, 100 mg, 0.114 mmol) was dissolved in pyrrolidine (40 mL), stirred at room temperature for 24 h, evaporated, and purified by column separation (silica gel, chloroform). Yield: 73 mg (68%) as a green solid. Mp > 250 °C. R_f (silica gel, chloroform): 0.75. IR (ATR): $\tilde{\nu}$ = 2952 (m), 2919 (s), 2850 (m), 2361 (w), 1691 (s), 1649 (s), 1583 (s), 1572 (s), 1505 (w), 1456 (m), 1418 (w), 1350 (s), 1323 (s), 1302 (m), 1248 (m), 1205 (m), 1172 (w), 1144 (w), 1104 (w), 1022 (w), 954 (w), 852 (w), 840 (w), 806 (s), 790 (m), 748 (m), 723 (w), 693 (w), 680 (m), 667 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C,

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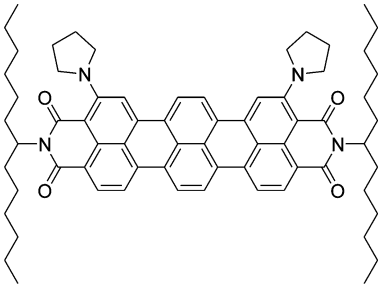
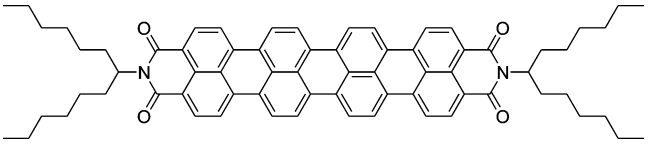
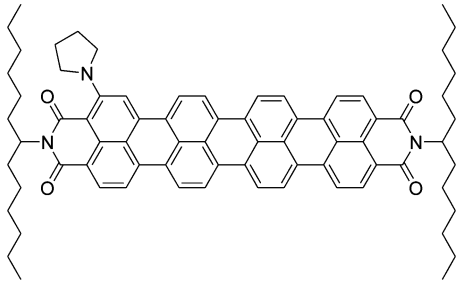
TMS): δ = 0.82 (t, ^3J(H,H) = 7.0 Hz, 12H, 4 × CH_3), 1.13−1.39 (m, 32 H, 16 × CH_2), 1.82−1.91 (m, 4 H,2 × β-CH_2), 1.95−2.11 (m, 4H, 2 × 2 × β-$CH_{pyrrolidinyl}$), 2.21−2.32 (m, 4 H, 2 × β-CH_2), 2.85 (s (br), 2 H, 2 × α-$CH_{pyrrolidinyl}$), 3.77 (s (br), 2 H, 2 × α-$CH_{pyrrolidinyl}$), 5.19−5.25 (m, 2 H, 2 × NCH), 7.82−7.88 (m, 1 H, $CH_{terrylene}$), 8.37−8.60 ppm (m, 10 H, 10 × $CH_{terrylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.0, 22.6, 25.7, 27.0, 29.3, 29.7, 31.8, 31.9, 32.4, 32.5, 52.0, 54.4, 118.5, 120.0, 120.3, 122.1, 122.2, 123.7, 123.8, 124.0, 126.0, 126.2, 127.0, 127.9, 128.2, 129.5, 130.1, 131.8, 132.1, 136.2, 147.6 ppm. UV/vis ($CHCl_3$): λ_{max}(ε) = 421.3 (4130), 452.7 (7010), 472.6 (10100), 499.7 (19700), 727.2 nm (56800). MS (DEP/EI) m/z: 949.6 (31.8) [M^+ + 2H], 948.6 (76.5) [M^+ + H], 947.6 (100) [M^+], 766.4 (11.4), 584.2 (19.8), 583.2 (30.2), 69.1 (13.0), 55.1 (14.9), 41.0 (12.0). HRMS ($C_{64}H_{73}N_3O_4$): calcd 947.5601, found m/z 947.5588, Δ = +0.0013. Anal. Calcd for $C_{64}H_{73}N_3O_4$ (947.6): C, 81.06; H, 7.76; N, 4.43. Found: C, 80.65; H, 7.97; N, 4.18.



_N,N′_-Bis(1-hexylheptyl)-2,13-dipyrrolidinoterrylene-3,4:11,12-tetracarboxylic Bisimide (8). 2,11-Bis(1-hexylheptyl)-benzo[13,14]pentapheno[3,4,5-*def*:10,9,8-*d′e′f′*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (**6**, 100 mg, 0.114 mmol) was dissolved in pyrrolidine (40 mL), stirred at room temperature for 9 d, evaporated, and purified by column separation (silica gel, chloroform). Yield: 96 mg (83%) as a blue solid. Mp > 250 °C. R_f (silica gel, chloroform): 0.83. IR (ATR): $\tilde{\nu}$ = 2952 (m), 2919 (s), 2850 (m), 2361 (w), 1691 (s), 1649 (s), 1583 (s), 1572 (s), 1505 (w), 1456 (m), 1418 (w), 1350 (s), 1323 (s), 1302 (m), 1248 (m), 1205 (m), 1172 (w), 1144 (w), 1104 (w), 1022 (w), 954 (w), 852 (w), 840 (w), 806 (s), 790 (m), 748 (m), 723 (w), 693 (w), 680 (m), 667 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.82 (td, ^3J(H,H) = 7.0 Hz, ^2J(H,H) = 1.8 Hz 12 H, 4 × CH_3), 1.13−1.42 (m, 32 H, 16 × CH_2), 1.81−1.91 (m, 4 H, 2 × β-CH_2), 1.91−2.19 (m, 8 H, 2 × 4 × β-$CH_{pyrrolidinyl}$), 2.19−2.35 (m, 4 H, 2 × β-CH_2), 2.86 (s (br), 4 H, 4 × α-$CH_{pyrrolidinyl}$), 3.76 (s (br), 4 H, 4 × α-$CH_{pyrrolidinyl}$), 5.13−5.30 (m, 2 H, 2 × NCH), 8.15−8.46 (m, 4 H, 4 × $CH_{terrylene}$), 8.45−8.68 ppm (m, 6 H, 6 × $CH_{terrylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.0, 22.6, 25.6, 26.9, 27.0, 29.3, 31.8, 32.4, 32.5, 52.1, 54.4, 54.6, 117.8, 118.0, 118.6, 119.2, 119.4, 123.5, 125.3, 126.1, 130.6, 131.1, 131.9, 132.3, 148.8 ppm. UV/vis ($CHCl_3$): λ_{max}(ε) = 413.8 (8780), 468.7 (4610), 499.9 (5800), 562.2 (9800), 589.0 (10900), 777.2 nm (52120). MS (DEP/EI) m/z: 1019.6 (25) [M^+ + 3 H], 1018.6 (51) [M^+ + 2 H], 1017.6 (77) [M^+ + H], 1016.6 (100) [M^+], 947.6 (21), 652.2 (21), 391.0 (19), 182.2 (17), 97.1 (28), 85.1 (30), 84.1 (27), 83.1 (54), 81.1 (19), 71.1 (40), 70.1 (39), 69.1 (84), 67.1 (23), 57.1 (68), 56.1 (50), 55.1 (84), 43.0 (57), 43.0 (23), 42.0 (20), 41.0 (59). HRMS ($C_{68}H_{80}N_4O_4$): calcd 1016.6180, found 1016.6154 Δ = +0.0026. Anal. Calcd for $C_{68}H_{80}N_4O_4$ (1016.6): C, 80.28; H, 7.93; N, 5.51. Found: C, 80.20; H, 7.90; N, 5.32.



Quaterrylene-3,4:13,14-tetracarboxy-3,4:13,14-bis(1-hexylheptylimide) (9). Potassium *tert*-butanolate (290 mg, 2.03 mmol) and diazabicyclo[4.3.0]non-5-ene (DBU, 0.340 mL, 2.70 mmol) under very thorough exclusion of air and moisture (argon atmosphere) were stirred in dry toluene (10 mL) at 130 °C for 0.5 h, treated with 9,9′-bis[perylene-3,4-dicarboxy-3,4-(1-hexylheptylimide)] (670 mg, 0.680 mmol) in degassed, dry toluene (15 mL) dropwise within 1 h (color change to dark), stirred at 130 °C for 2.5 h, allowed to cool, treated with 2 M aqueous HCl (150 mL), extracted with chloroform (3 × 40 mL), dried with $MgSO_4$, evaporated in vacuo, and purified by column separation (silica gel 40−63 μm, chloroform, second, turquoise fraction). Yield: 573 mg (84%) as a turquoise solid. Mp > 250 °C. R_f (silica gel, chloroform): 0.20. ^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.89 (t, ^3J(H,H) = 6.6 Hz, 12 H, 6 × CH_3), 1.20−1.40 (m, 32 H, 16 × CH_2), 1.99 (m, 4 H, β-CH_2), 2.31(m, 4 H, β-CH_2), 5.18 (m, 2 H, NCH), 7.59 (m, 4 H 4 × $CH_{quaterrylene}$), 7.95 (m, 8 H, 8 × $CH_{quaterrylene}$), 8.27 ppm (m, 4 H, 4 × $CH_{quaterrylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS): δ = 14.1, 22.7, 27.2, 29.4, 31.9, 32.5, 54.6, 120.1, 122.2, 123.5, 127.0, 127.6, 128.9, 129.6, 131.0, 135.1 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 628.2 (18360), 691.4 (62900), 762.2 nm (151800). MS (DEP/EI): m/z:1004.5 (9) [M^+ + 2H], 1003.5 (22) [M^+ + H], 1002.5 (28) [M^+], 640.0 (11), 639.0 (27), 638.0 (42), 182.0 (23), 111.0 (12), 97.0 (30), 84.0 (25), 83.0 (51), 82.0 (12), 71.1 (17), 70.1 (55), 69.1 (99) 68.1 (10), 67.1 (22), 57.1 (38), 56.1 (55), 55.1 (100), 54.0 (21), 43.0 (47), 42.0 (17), 41.0 (67). HRMS ($C_{70}H_{70}N_2O_4$): calcd m/z: 1002.5336, found m/z 1002.5349, Δ = −0.0013. Anal. Calcd for $C_{70}H_{70}N_2O_4$ (1002.5): C, 83.80; H, 7.03; N, 2.79. Found: C, 83.75; H, 7.02; N, 2.67.



_N,N′_-Bis(1-hexylheptyl)-2-pyrrolidinoquaterrylene-3,4:13,14-tetracarboxylic Bisimide (10). Quaterrylene-3,4:13,14-tetracarboxy-3,4:13,14-bis(1-hexylheptylimide) (**9**, 100 mg, 0.100 mmol) was dissolved in pyrrolidine (40 mL), stirred at room temperature for 10 d, evaporated, and purified by column separation (silica gel, chloroform). Yield: 96 mg (83%) as a violet solid. Mp > 250 °C. R_f (silica gel, chloroform): 0.73. IR (ATR): $\tilde{\nu}$ = 2954.8 (m), 2924.9 (s), 2855.0 (m), 1688.7 (vs), 1650.3 (s), 1594.9 (m), 1568.6 (vs), 1542.3 (w), 1500.3 (w), 1484.0 (w), 1457.4 (w), 1414.5 (w), 1391.1 (w), 1346.2 (vs), 1322.1 (m), 1287.6 (s), 1248.1 (w), 1230.1 (m), 1174.2 (w), 1126.3 (w), 1105.6 (w), 1077.9 (w), 1052.0 (w), 946.4 (w), 908.5 (w), 840.0 (w), 807.8 (m), 751.9 (w), 732.0 (w), 668.6 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.78−0.89 (m, 12 H, 4 × CH_3), 1.21−1.41 (m, 32 H, 16 × CH_2), 1.86−1.94 (m, 4 H, 2 × β-CH_2), 1.99−2.10 (m, 4 H, 2 × 2 × β-$CH_{pyrrolidinyl}$), 2.23−2.35 (m, 4 H, 2 × β-CH_2), 2.84 (s (br), 2 H, 2 × α-$CH_{pyrrolidinyl}$), 3.75 (s (br), 2 H, 2 × α-$CH_{pyrrolidinyl}$), 5.19−5.25 (m, 2 H, 2 × NCH), 7.95−8.61 ppm (m, 15 H, 15 × $CH_{quaterrylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.0, 22.6, 25.5, 25.6, 27.1, 29.3, 29.5, 29.7, 31.9, 32.5, 32.6, 54.4, 54.5, 114.3, 121.4, 123.8, 123.9, 124.2, 126.0, 128.1, 130.0, 130.9, 131.9, 134.4, 135.7, 146.8, 147.8, 164.1, 164.8, 165.1 ppm. UV/vis ($CHCl_3$): λ_{max}(ε) = 381.2 (9630), 470.2 (6270), 515.5 (9300), 546.7 (11200), 671.3 (14960), 811.8 nm (86600). MS (FAB$^+$) m/z: 1072 (1) [M^+ + H], 1071 (1) [M^+]. HRMS ($C_{74}H_{77}N_3O_4$): calcd 1071.5914, found 1071.5911, Δ = −0.0003. Anal. Calcd for $C_{74}H_{77}N_3O_4$ (1071.6): C, 82.88; H, 7.24; N, 3.92. Found: C, 82.47; H, 7.60; N, 3.81.

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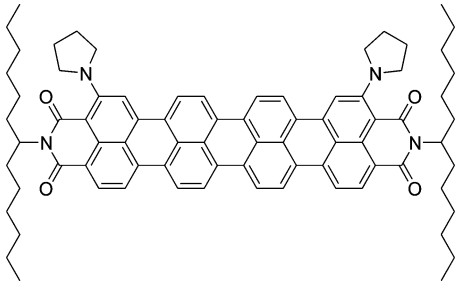

***N,N′*-Bis(1-hexylheptyl)-2,15-dipyrrolidinoquaterrylene-3,4:13,14-tetracarboxylic Bisimide (11).** Quaterrylene-3,4:13,14-tetracarboxy-3,4:13,14-bis(1-hexylheptylimide) (**9**, 100 mg, 0.100 mmol) was dissolved in pyrrolidine (40 mL), stirred at room temperature for 14 d, evaporated, and purified by column separation (silica gel, chloroform). Yield: 96 mg (83%) as a violet solid. Mp > 250 °C. R_f (silica gel, chloroform): 0.81. IR (ATR): $\tilde{\nu}$ = 2954.8 (m), 2924.9 (s), 2855.0 (m), 1688.7 (vs), 1650.3 (s), 1594.9 (m), 1568.6 (vs), 1542.3 (w), 1500.3 (w), 1484.0 (w), 1457.4 (w), 1414.5 (w), 1391.1 (w), 1346.2 (vs), 1322.1 (m), 1287.6 (s), 1248.1 (w), 1230.1 (m), 1174.2 (w), 1126.3 (w), 1105.6 (w), 1077.9 (w), 1052.0 (w), 946.4 (w), 908.5 (w), 840.0 (w), 807.8 (m), 751.9 (w), 732.0 (w), 668.6 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.78−0.89 (m, 12 H, 4 × CH_3), 1.21−1.41 (m, 32 H, 16 × CH_2), 1.86−1.94 (m, 4 H, 2 × β-CH_2), 1.99−2.10 (m, 4 H, 2 × 2 × β-$CH_{pyrrolidinyl}$), 2.23−2.35 (m, 4 H, 2 × β-CH_2), 3.40−3.77 (m, 2 H, 2 × α-$CH_{pyrrolidinyl}$), 3.94−4.31 (m, 2 H, 2 × α-$CH_{pyrrolidinyl}$), 5.19−5.25 (m, 2 H, 2 × NCH), 7.95−8.61 ppm (m, 14H, 14 × $CH_{quaterrylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): not recorded because of low solubility and high tendency for aggregation. UV/vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 463.5 (7350), 490.3 (9350), 555.6 (7610), 589.7 (8210), 851.0 nm (73390). MS (FAB$^+$): *m*/*z* 1140.7 (100) [M$^+$]. HRMS ($C_{78}H_{84}N_4O_4$): calcd *m*/*z* 1140.6493, found *m*/*z* 1140.6497, Δ = +0.0004.

Reaction Kinetic Measurements. Measurements were carried out in distilled, neat pyrroldine in 1 cm cuvettes in contact to atmospheric oxygen and recorded UV/vis spectroscopically (for the optical density see the Supporting Information). No influence was found by the exclusion of air by means of an argon atmosphere.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data of **2**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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