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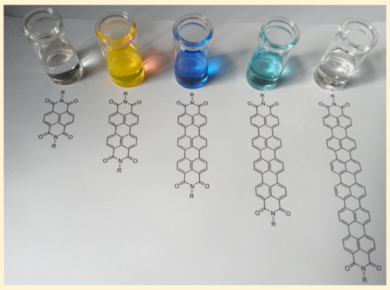
Sexterrylenetetracarboxylic Bisimides: NIR Dyes

Heinz Langhals,* Dominik Zgela, and Robin Lüling

Department of Chemistry, LMU University of Munich, Butenandtstrasse 13, D-81377 Munich, Germany

Ⓢ *Supporting Information*

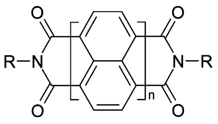
ABSTRACT: Sexterrylenehexacarboxylic bisimides, extended *peri*-arylenes with the alignment of six peri-arranged naphthalene units, were prepared by Suzuki cross coupling and subsequent oxidative ring closure reactions of the perylene units and exhibit NIR absorption at 945 nm. Intermediates are strongly fluorescent with an increased Stokes shift because of dynamic processes.



INTRODUCTION

Dyes absorbing in the near-infrared (NIR) are receiving increasing interest both in research and in technology[1] where the *peri*-arylenes (Chart 1) (also shortened to rylenes in the literature) are attractive candidates[2] for many applications because of their stability and interesting photophysical properties. Chemistry and applications of the lower homologues of **1** are well-established such as for the naphthalene derivatives with $n = 1$ as sun-protecting materials[3] and organic white pigments,[4] the perylenes with $n = 2$ as red pigments[5] and fluorescent dyes,[6] the terrylenes[7] with $n = 3$ for fluorescent applications[8] in the bathochromic visible, and the quaterrylenes[9] reaching the NIR.[10] Chemistry becomes more difficult for the higher homologues. The sexterrylenes with $n = 6$ are unknown; only core-modified derivatives have been reported.[11] (Such derivatives were named hexarylenes; however, we prefer sexterrylenes because of a uniform Latin nomenclature with respect to the lower homologues. Compare the scales in music.)

Chart 1. *peri*-Arylenes



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RESULTS AND DISCUSSION

Here we report the synthesis of sexterrylenetetracarboxylic bisimides where we found that the solubility of intermediates is crucial for a successful synthesis. As a consequence, we attached the highly solubilizing substituent 1-hexylheptyl[6] (S-13 swallow-tail) to the nitrogen atoms of **1**, started synthesis with the bromo perylene carboximide **2a**, and introduced a pinacolato boron group by means of the reaction of **2** with the diborane according to Scheme 1.

The boran **3a**[17] was allowed to react with dibromoperylene in a palladium-catalyzed Suzuki cross coupling to obtain **4a**. A Sakamoto reaction[12] for ring closures[10a] in **4a** was not successful. As an alternative, an oxidative ring closure analogous to that in ref 13 was effective for **5a** where the final product **6a** could be obtained directly from the crude material of **5a** by means of ethanolamine. **6a** was unambiguously identified by means of MALDI with $M^+ = 1250.5$ where the change of mass by the loss of four hydrogen atoms from **4a** to **6a** proves the ring closures. The very bathochromic NIR absorption of **6a** at 941 nm (in warm chlorobenzene at about 70 °C) is a further characteristic indicator for the formation of the final product. However, **6a** could not be efficiently separated from residual starting materials and byproducts where the comparably low solubility presents an obstacle. As a consequence, we attached the much more effectively solubilizing 1-nonyldecyl group[2,6] R (S-19 swallow-tail group) to the starting materials and performed analogous steps from **2b** to **6b**. The latter could be separated from the starting materials and byproducts so that the typical UV/vis/NIR light absorption of the latter could not be detected in the final product. The identity of **6b** is indicated by means of MALDI with $M^+ = 1418.0$ where no other products could be detected, and by the typical carbonyl bands of carboximides at 1631 and 1575 cm^{-1} in the infrared.

6b forms a highly electrostatically charged greyish black powder where solutions in chlorobenzene exhibit only weak light absorption in the visible (compare "colorless dyes"[14]), and a structured absorption is found at 945 nm; see Figure 1.

$$\varepsilon_{(\lambda)} = \sum_{i=1}^{n} \varepsilon_{\max(i)} e^{-100\left(\frac{1}{\lambda} - \frac{1}{\lambda_{\max}(i)}\right)^2 / 2\sigma_{(i)}^2} \qquad (1)$$

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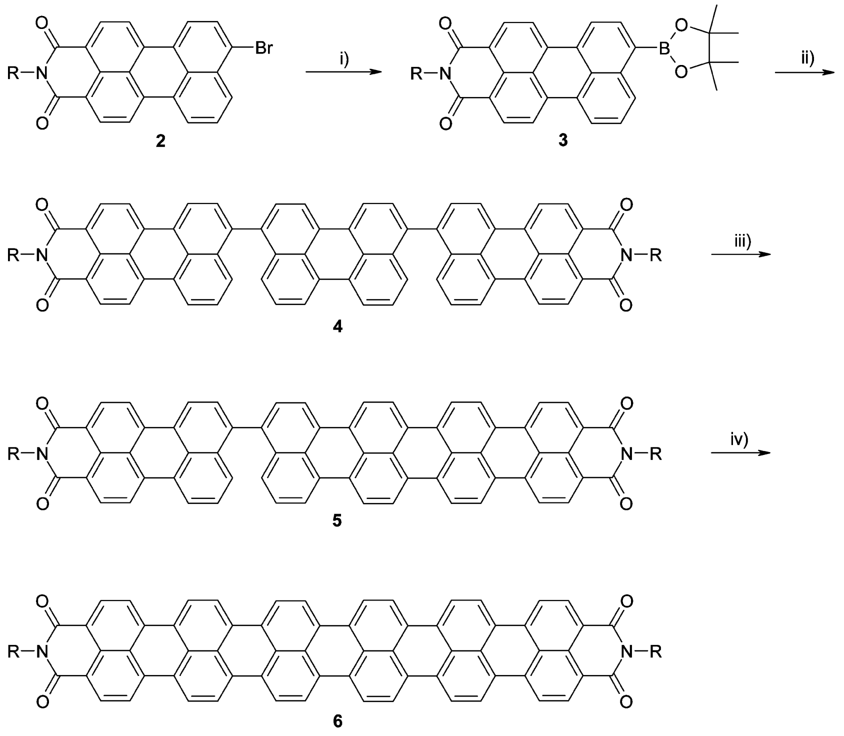
Scheme 1. Synthesis of the Sexterrylenetetracarboxylic Bisimides 6: R = 1-Hexylheptyl for 2a until 6a and R = 1-Nonyldecyl for 2b until 6b[a]



[a](i) Bis-pinacolatodiboran, $PdCl_2(dppf)$, KOAc (ii) 3,9-dibromperylene, $PdCl_2$, triphenylphosphane, (iii) $FeCl_3$, CH_2Cl_2, CH_3NO_2, (iv) K_2CO_3, $HOC_2H_4NH_2$, 130 °C.

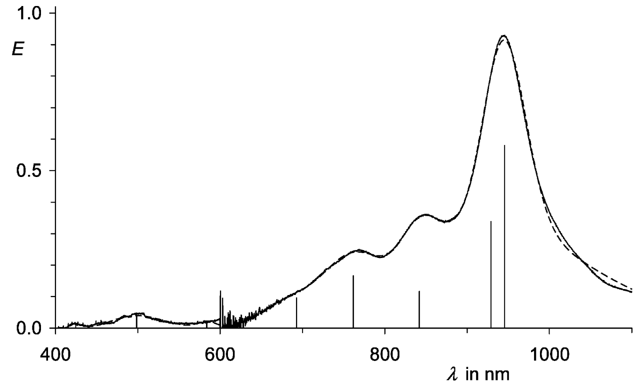


Figure 1. UV/vis/NIR spectrum of highly diluted **6b** in chlorobenzene (solid curve) and simulated spectrum on the basis of a Gaussian analysis (dashed curve, mainly covered by the experimental spectrum). Bars: Intensities and positions of the individual Gaussian bands.

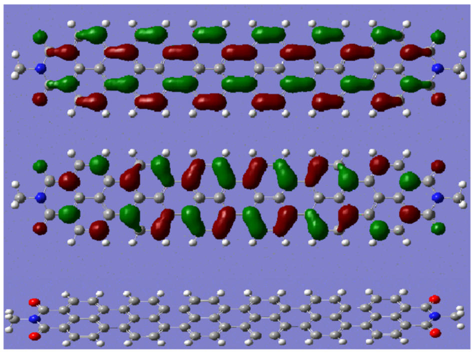


Figure 2. DFT calculations (RB3LYP, basis set 3-21G) of **6c** (R = CH_3). From bottom to top: Side view of the flat structure of **6c**, the orbitals of HOMO and LUMO.

The absorption of **6b** can be resolved into Gaussian bands[15] according to eq 1 where $\varepsilon_{(\lambda)}$ is the absorptivity as a function of the wavelengths λ, and $\varepsilon_{\max(i)}$ are the intensities, $\lambda_{\max(i)}$ the positions, and $\sigma_{(i)}$ the half widths of the individual bands i; the factor of 100 in the exponent simplifies the adaption of the wavelengths in nm to the half widths in kK (10 000 cm^{-1}). The bathochromic absorption of **6b** can be described with $n = 5$ Gaussian bands where the pattern is similar to other *peri*-arylenes **1**. The geometry of **6c** was calculated by means of the DFT method, and a completely flat structure was obtained; see Figure 2.

There are orbital nodes in the HOMO and LUMO of **6c** along the long molecular axis as reported for the lower *peri*-arylenes **1**.[16] As a consequence, a very low electronic influence on the UV/vis spectra is expected from the substituent R. The atomic coefficients at the carbonyl carbon atoms are very small in the HOMO for all *peri*-arylenes, whereas large coefficients were found in the LUMO for the naphthalene derivatives (n = 1) and decrease to become small for **6** (n = 6). The HOMO−LUMO separation decreases with the number n from 363 kJ·mol^{-1} for the naphthalene derivatives with n = 1 to 117 kJ·mol^{-1} for the sexterrylenes with n = 6, where the increase of the energetic position of the HOMO is the most important influence; see Figure 3.

The absorption of **6b** can be further bathochromically shifted by means of protonation such as in concd sulfuric acid. The UV/vis spectra of *peri*-arylenes in lipophilic solvents and in concd sulfuric acid are shown in Figure 4 until n = 6 and reach the very bathochromic 1135 nm for protonated **6b**.

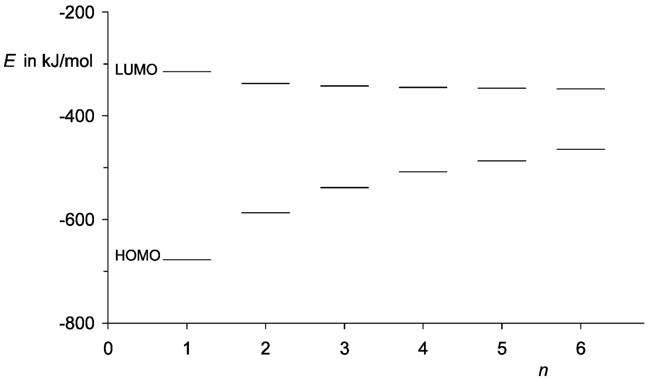


Figure 3. Calculated energies (DFT, B3LYP, basis set 3-21G) of the HOMO (bottom) and the LUMO (top) of the *peri*-arylenes **1** as a function of *n* naphthalene subunits.

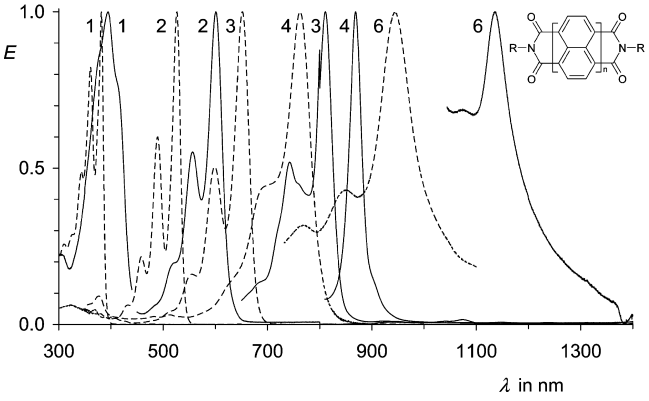


Figure 4. UV/vis/NIR absorption spectra of *peri*-arylenes **1** (R = 1-hexylheptyl) with indicated numbers *n*. Dashed curves: Solutions in the lipophilic chloroform (R = 1-nonyldecyl and chlorobenzene for **6b**). Solid curves: Solutions in 98% H_2SO_4.

The optical properties of the intermediates **4** and **5** are of special interest. There are steric interactions between the *peri*-hydrogen atoms of the perylene and perylenedicarboximide in **4b** causing a turning out-of-plane of the two types of chromophores with the consequence of their electronic decoupling; see Figure 5.

As a consequence, both chromophores, the perylendicarboxylic imide and the perylene, are operating essentially independently, causing a broadband absorption; see Figure 6 where the spectra of the perylenedicarboxylic imide (termini of **4**) are compared with those of **4**.

The most bathochromic absorption of the termini dominates in the absorption of **4** with a slight bathochromic shift and some amplification of the vibronic band at the longest wavelength by means of exciton interactions. An additional absorption by the perylene unit is found at shorter wavelengths. This is weaker than the more bathochromic absorption caused by two strongly absorbing carboximides at the termini, whereas there is only one weaker absorbing perylene in between. Light energy absorbed by the perylene can be transferred by means of FRET (Förster resonant energy transfer) to the termini; see Figure 5. The S_1 state of **4** relaxes to an electronically more coupled system S'_1 exhibiting fluorescence at longer wavelengths. As a consequence, the Stokes shift is increased by this dynamic process as described for similar systems;[17] see Figure 5. Finally, the less favorable ground state S'_0 relaxes back to the initial state S_0. The combination of FRET with a dynamic process allows the construction of a broadband absorber with an increased Stokes shift. The same process is expected for **5**; the addition of the absorption spectra of a perylene and a quaterrylene carboximide is found; however, the fluorescence spectra are outside the scale of routine spectrometers because of the very bathochromic spectral region.

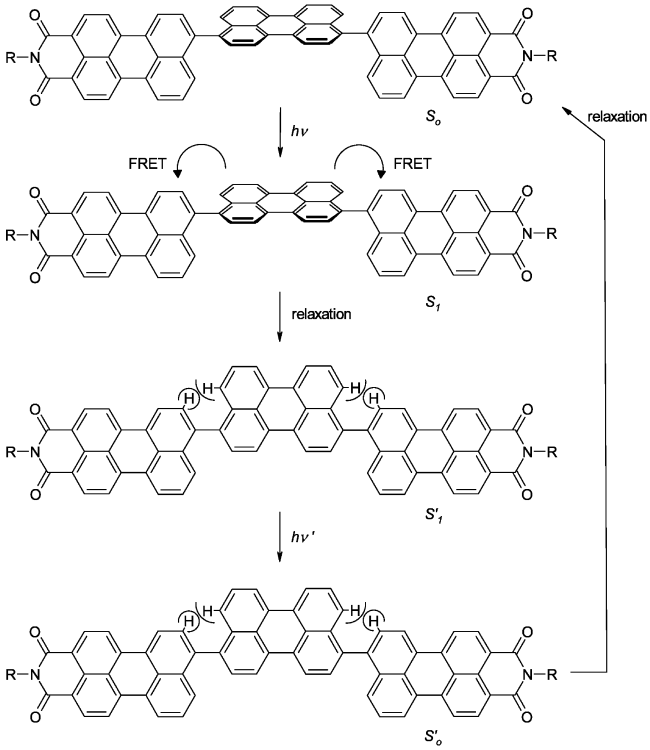


Figure 5. Schematic photophysical dynamic processes of **4**. Starting at the S_0 state with decoupled chromophores. The S_1 state is photochemically generated ($h\nu$) where FRET (Förster resonant energy transfer) may transfer energy to the terminal chromophores. A relaxation to the S'_1 state proceeds and causes bathochromically shifted fluorescence to the S'_0 state where the circle is closed by means of relaxation to the S_0 state.

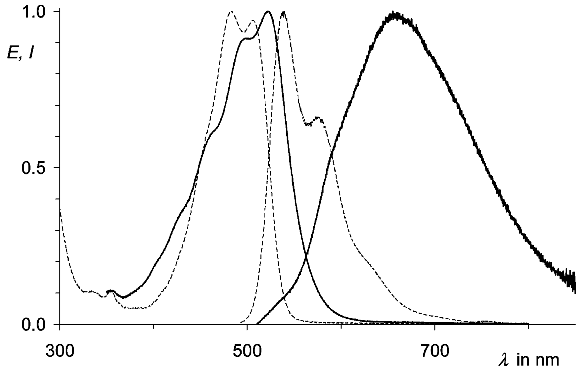


Figure 6. Absorption (left) and fluorescence (right) spectra in chloroform. **4b**: solid curves (λ_{exc} = 501 nm) compared with the spectra of perylene-3,4-dicarboximide (dashed curves, λ_{exc} = 490 nm).

■ CONCLUSIONS

Sexterrylenetetracarboxylic bisimides (**1**, *n* = 6) were prepared by Suzuki cross coupling of dibromoperylene with boronoperylenedicarboxylic imides, and stepwise subsequent oxidative ring closure reactions formed greyish black powders with an absorption maximum in the NIR at 945 nm and only a weak light absorption in the visible region. Highly solubilizing substituents at the nitrogen atoms, swallow-tail substituents, particularly the 1-nonyldecyl group, are important both for synthesis and purification. A protonation by means of concentrated sulfuric acid shifts the absorption further bathochromically to 1135 nm.

Synthetic intermediates with single bonds between the aromatics are strongly fluorescent and exhibit increased Stokes shifts by photoinduced dynamic processes resembling previously described sequences in bichromophoric perylene dicarboximides; these optical properties are of interest both for laser and light-collecting applications such as for fluorescent solar collectors.

EXPERIMENTAL SECTION

General. All FAB spectra were recorded in 3-nitrobenzyl alcohol as the matrix. Fluorescence quantum yields were determined analogous to that in ref 8.

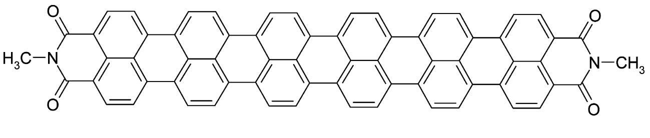
***N*-(1-Nonyldecyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylenedicarboximide (3b).** *N*-(1-Nonyldecyl)-9-bromoperylene-3,4-dicarboximide[18] (**2b**, 8.00 g, 12.0 mmol) was treated with the exclusion of moisture and air with bis(pinacolato)diboron (3.96 g, 15.6 mmol) and potassium acetate (3.52 g, 36.0 mmol) in dry 1,4-dioxane (120 mL) with stirring, treated with $PdCl_2$(dppf) (dppf =1,1′-bis(diphenylphosphino)ferrocene) (440 mg, 0.601 mmol), refluxed for 19 h (bath 70 °C), evaporated in vacuo, purified by column separation (silica gel 40−63 μm, dichloromethane/isohexane 3:1), dissolved in a minimal amount of chloroform, precipitated with methanol, and dried at 110 °C. Yield 4.40 g (52%) red solid, mp 165 °C. R_f (silica gel, chloroform): 0.80. R_f (silica gel, chloroform/isohexane): 0.77. IR (ATR): $\tilde{\nu}$ = 2921 (m), 2852 (m), 1687 (s), 1650 (s), 1615 (w), 1590 (s), 1576 (m), 1507 (w), 1481 (w), 1459 (w), 1419 (w), 1411 (w), 1376 (w), 1350 (s), 1328 (vs), 1271 (w), 1246 (m), 1206 (w), 1166 (w), 1137 (m), 1114 (m), 1068 (w), 1048 (w), 965 (w), 858 (m), 839 (w), 821 (vw), 808 (m), 775 (vw), 763 (w), 750 (m), 721 (w), 699 (m), 681 (w), 619 (w), 581 cm^{-1} (w). ^1H NMR ($CDCl_3$/TMS, 600 MHz): δ = 0.83 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 × CH_3), 1.13−1.39 (m, 28 H, 10 × CH_2), 1.46 (s, 12 H, 4 × CH_3), 1.79−1.90 (m, 2 H, CH_2), 2.21−2.30 (m, 2 H, CH_2), 5.15−5.23 (m, 1H, NC*H*), 7.64−7.69 (m, 1 H, CH_{pery}), 8.18 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH_{pery}), 8.40−8.47 (m, 4 H, CH_{pery}), 8.51−8.63 (m, 2 H, CH_{pery}), 8.86 ppm (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, CH_{pery}). ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 165.4, 164.4, 138.2, 137.5, 137.4, 137.0, 136.9, 136.4, 132.2, 132.0, 131.9, 131.7, 131.4, 131.2, 130.0, 129.3, 127.9, 127.4, 126.8, 123.6, 122.6, 120.9, 120.4, 84.4, 54.5, 32.6, 32.0, 29.7, 29.4, 27.1, 25.1, 22.8, 14.3 ppm. UV/vis ($CHCl_3$): λ_{max} (E_{rel}) = 265 (1.0), 485 (0.93), 506 nm (0.94). Fluorescence ($CHCl_3$, λ_{exc} = 489 nm): λ_{max} (I_{rel}) = 541 (1.00), 579 nm (0.92). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 489 nm; $E_{489\ nm/1\ cm}$ = 0.0145; reference S-13 with Φ = 1.00): Φ = 0.88. MS (DEP/EI): *m*/*z* (%) = 713.5 (55) [M^+], 587.4 (11) [$M^+ - C_{41}H_{49}N_1O_2$], 447.2 (100) [$M^+ - C_{28}H_{22}N_1O_2B$], 321.1 (52) [$M^+ - C_{22}H_{11}N_1O_2$]. HRMS ($C_{47}H_{60}NO_4{}^{11}B$): Calcd *m*/*z*: 713.4615, found *m*/*z*: 713.4617, Δ = 0.0002 mmu.

8,8′-(Perylene-3,10-diyl)bis(2-(1-nonyldecyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinolin-1,3(2*H*)-dione) (4b). *N*-(1-Nonyldecyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-perylenedicarboximide (**3b**) (2.00 g, 2.80 mmol), 3,10-dibromoperylene (580 mg, 1.40 mmol), and potassium carbonate (1.16 g, 8.41 mmol) were dispersed in a mixture of toluene (115 mL), distilled water (57 mL), and ethanol (6 mL), treated with $Pd(PPh_3)_4$ (160 mg, 0.14 mmol, catalyst), refluxed for 24 h (bath 80 °C, evaporated in vacuo, purified by column separation (silica gel, toluene), evaporated, and dried at 110 °C. Yield 400 mg (33%) red solid, mp >300 °C. R_f (silica gel, chloroform): 0.62. IR (ATR): $\tilde{\nu}$ = 2920 (m), 2850 (m), 1691 (s), 1650 (s), 1590 (m), 1571 (m), 1502 (w), 1455 (w), 1407 (w), 1388 (w), 1348 (s), 1291 (w), 1243 (m), 1189 (w), 1169 (w), 1108 (w), 1045 (w), 898 (w), 840 (w), 824 (w), 810 (s), 752 (s), 720 (w), 669 (w), 655 (w), 618 cm^{-1} (w). ^1H NMR ($CDCl_3$/TMS, 600 MHz): δ = 0.84 (t, $^3J_{H,H}$ = 7.0 Hz, 12 H, 4 × CH_3), 1.15−1.37 (m, 56 H, 28 × CH_2), 1.82−1.93 (m, 4 H, 2 × CH_2), 2.22−2.33 (m, 4 H, 2 × CH_2), 5.15−5.25 (m, 2H, 2 × NC*H*), 7.29−7.85 (m, 12 H, CH_{pery}), 8.21−8.74 ppm (m, 16 H, CH_{pery}). ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 165.28, 165.27, 141.5, 140.5, 138.0, 137.7, 136.9, 134.1, 133.9, 133.8, 132.1, 131.6, 131.5, 131.3, 130.12, 130.08, 129.8, 129.7, 129.7, 129.30, 129.28, 129.2, 128.99, 128.94, 128.92, 128.41, 128.39, 128.37, 127.5, 127.3, 127.2, 126.74, 126.72, 125.4, 123.9, 123.4, 123.2, 121.0, 120.6, 120.5, 120.3, 120.2, 54.6, 32.6, 32.0, 29.9, 29.7, 29.4, 27.2, 22.8, 21.6, 14.3 ppm. UV/vis ($CHCl_3$): λ_{max} (E_{rel}) = 501 (0.82), 524 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 501 nm): 660 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 501 nm; $E_{501\ nm/1\ cm}$ = 0.0963; reference S-13 with Φ = 1.00): Φ = 0.57. MS (FAB^+): *m*/*z* (%):1423.95 (5) [MH^+], 1173.6 (5) [$M^+ - C_{84}H_{72}N_2O_4$], 891.3 (3) [$M^+ - C_{64}H_{30}N_2O_4$]. MS (FAB^-): *m*/*z* (%):1423.9 (10) [MH^+], 1172.8 (16) [$M^+ - C_{84}H_{72}N_2O_4$]. HRMS ($C_{102}H_{107}N_2O_4$): Calcd *m*/*z*: [MH^+] 1423.8231, found *m*/*z*: 1423.8212, Δ = 0.0019 mmu.

***N*,*N*′-(1-Hexylheptyl)sexterrylene-3,4:17,18-tetracarboximide (6a).** 8,8′-(Perylene-3,10-diyl)bis(2-(1-hexylheptyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinolin-1,3(2*H*)-dione)[17] (**4a**, 20 mg, 0.016 mmol) was dissolved with the exclusion of moisture and air in dichloromethane (3.5 mL), treated dropwise with anhydrous iron(III)chloride (18 mg, 0.11 mmol) in nitromethane (0.5 mL), stirred at 40 °C for 18 h, evaporated in vacuo, washed with 2 M aqueous HCl and distilled water, dried at 110 °C (**5a**), instantly refluxed (bath 130 °C) with the exclusion of moisture and air with potassium carbonate (11 mg, 0.080 mmol) in 0.1 mL of ethanolamine for 16 h (black, viscous material), thoroughly washed 2 M aqueous HCl and distilled water (D4 glass filter), washed with acetone and chloroform, extracted by means of a Soxhlet apparatus with chloroform for 16 h, and dried. Yield: 7 mg (35%); greyish black solid. UV/vis ($CHCl_3$): λ_{max} (E_{rel}) = 548 (0.37), 728 (1.00), 939 nm (0.49). MS (MALDI-TOF) *m*/*z*: [M^+] Calcd for $C_{90}H_{78}N_2O_4$: 1250.6; found: 1250.5 (100).

***N*,*N*′-(1-Nonyldecyl)sexterrylene-3,4:17,18-tetracarboximide (6b).** With the exclusion of air and moisture (argon atmosphere), 8,8′-(perylene-3,10-diyl)bis(2-(1-nonyldecyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinolin-1,3(2*H*)-dione) (**4b**, 340 mg, 0.24 mmol) were dissolved in dichloromethane (6.5 mL), treated dropwise with a solution of iron(III)chloride (270 mg, 1.67 mmol) in nitromethane (1.3 mL), stirred at room temperature for 24 h, evaporated in vacuo, washed with 2 M aqueous HCl and distilled water, dried at 110 °C in air (**5b**, MS, MALDI TOF: *m*/*z* = 1420.3, M^+), instantly treated with the exclusion of air and moisture for the second ring closure with anhydrous potassium carbonate (260 mg, 1.92 mmol) and ethanolamine (6.8 mL), refluxed at 130 °C for 18 h (black, viscous mixture), collected by vacuum filtration (D4 glass filter), repeatedly washed with 2 M aqueous HCl and distilled water and then with acetone and chloroform and continuously extracted with chloroform by means of a Soxhlet apparatus for 16 h (bath 90 °C). Yield 120 mg (32%) fine grayish black, strongly electrostatically charging solid, mp >300 °C. R_f (silica gel, chloroform): 0.00, no side or other products detectable. IR (KBr): $\tilde{\nu}$ = 2918 (s), 2850 (s), 2376 (m), 1631 (w), 1575 (w), 1385 (w), 1095 (m), 801 (m). UV/vis (chlorobenzene): λ_{max} (E_{rel}) = 768 (0.32), 852 (0.43), 945 nm (1.00). MS (MALDI-TOF) *m*/*z*: [M^+] Calcd for $C_{90}H_{78}N_2O_4$: 1418.8; found: 1418.0 (100). ^1H NMR (C_6D_5Cl, 600 MHz) and ^{13}C NMR (C_6D_5Cl, 600 MHz) incapable of measurement.

Results of Calculations: Atomic Coordinates of 6c According to Figure 2. Calculation type = FOPT. Calculation method = RB3LYP. Basis set = 3-21G. Charge = 0. Spin = singlet. Total energy = −2927.55895789 au.



6c

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02092.

> Spectroscopic data of **2b**–**6b**, Gaussian analysis of the spectrum of **6b**, calculated atomic coordinates of **6c**, and synthesis of **6a** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Langhals@lrz.uni-muenchen.de.

Notes

The authors declare no competing financial interest.

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