DOI: 10.1002/ejoc.200701058

Core-Extended Terrylenetetracarboxdiimides – Novel, Strongly Red Fluorescent Broadband Absorbers

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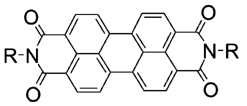
Keywords: Dyes / Pigments / Terrylenes / Fluorescence spectroscopy / Broadband absorbers

Strongly red fluorescent and broadband absorbing benzoterrylenehexacarboxtriimide (**8**) and yellow fluorescent dibenzoterryleneoctacarboxtetraimide (**9**) were prepared by the Diels–Alder reaction of readily soluble terrylenetetracarboxdiimides and subsequent condensation with primary amines. Applications such as for solar energy systems are discussed.

Introduction

Perylenetetracarboxdiimides **1** are of special interest because of their fluorescence quantum yields close to unity and their extraordinarily high light stability.[1–3] However, the light absorption should be more bathochromic for some applications and such a shift can be obtained by the prolongation of the core of **1** to form terrylenetetracarboxdiimides.[4–7] However, this prolongation causes a drop of fluorescence quantum yield to about 60%.[8] It would be of interest to re-establish high quantum yields by an alteration of the structure.



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Results and Discussion

Perylene derivatives **1** can be core-extended by the Clar variant of the Diels–Alder reaction with maleic anhydride[9] where an addition of chloranile causes a re-aromatisation of the primary adduct. Perylenetetracarboxdiimides require rather rough reaction conditions because of the electron depletion of the diene unit by the tetracarboxdiimide structure. We tried an analogous core extension of terrylenetetracarboxdiimides where we expect a more easy reaction because of higher electron density and required readily soluble terrylenetetracarboxdiimide derivatives. This can be achieved by the attachment of long-chain *sec*-alkyl groups (“swallow-tail substituents”)[10,11] to the nitrogen atoms of **5**, where the 1-nonyldecyl substituent proved to be the most efficient.[10]

Thus, we prepared the readily soluble naphthalene-1,8-dicarboximide **3** by the condensation of the anhydride **2** (Scheme 1) with 1-nonyldecylamine according to ref.[12] and allowed **3** to react with the readily soluble **4**[13] according to Sakamoto’s “green route” method[14,15] with the mixed bases potassium *tert*-butoxide/DBN to form **5**. The latter reacts readily in nitrobenzene solution with maleic anhydride. The primary adduct is expected to be a strong reductand, and the possible reduction of nitrobenzene to aniline may cause problems because of condensation with anhydrides. Therefore, an excess of chloranile as a strong oxidant was added in order to suppress such reactions by competition. The solvent nitrobenzene is difficult to remove sufficiently by distillation or chromatography because of strong interaction with the dyes. A surprisingly complete and simple removal was possible by steam distillation. The Diels–Alder reaction proceeded easily under these condition to the mono-adduct **6** and even to the bis-adduct **7**. This indicated the higher reactivity of **5** compared with **1** where only mono-adducts were obtained (compare, however, ref.[16])

The two adducts **6** and **7** were difficult to separate. Therefore, they were directly condensed with 1-nonyldecylamine to form a mixture of **8** and **9**. The attachment of three and four swallow-tail substituents, respectively, renders the materials very soluble, even with respect to the large aromatic systems. A complete chromatographic sepa-

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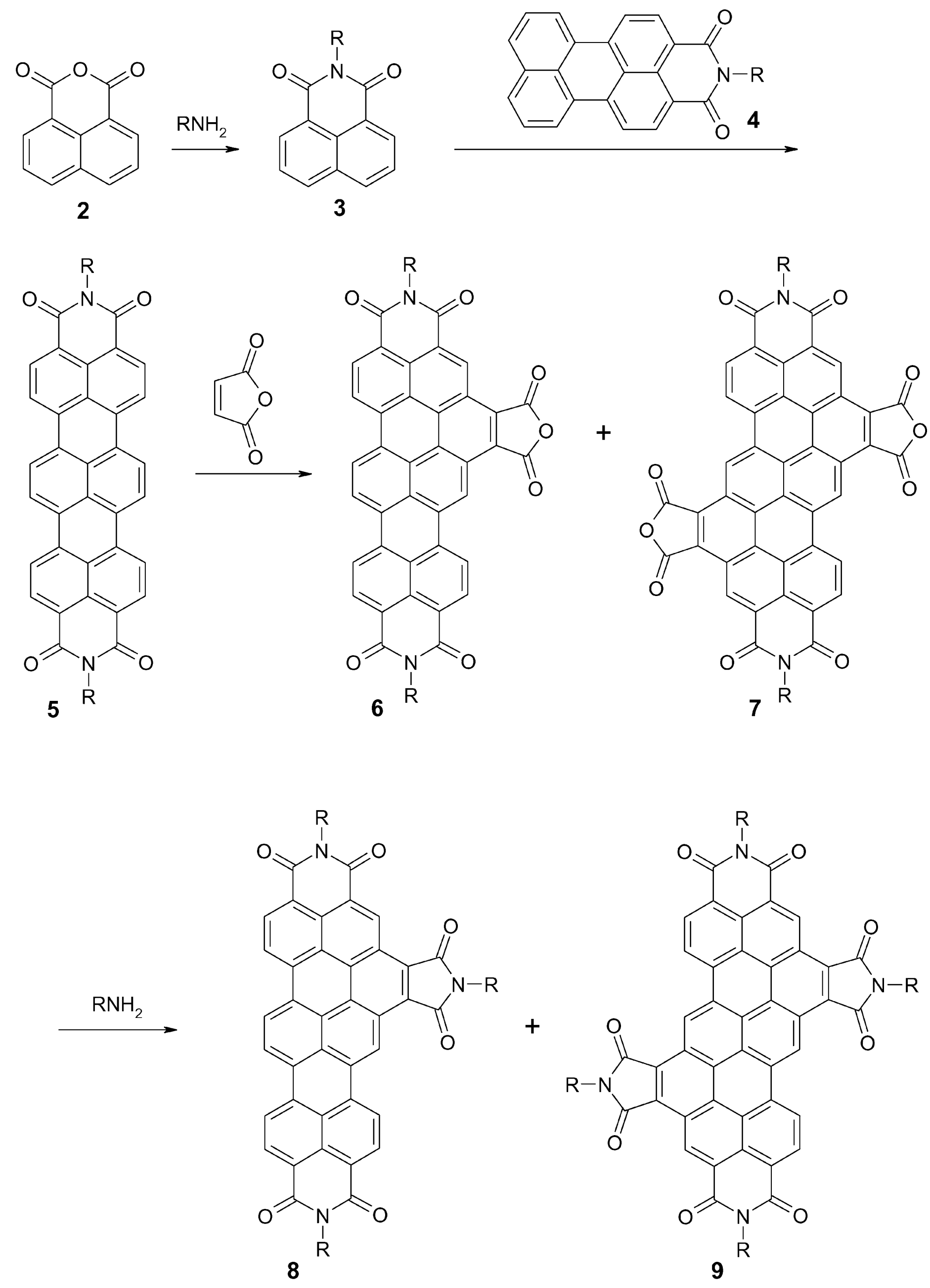

3–9	R
	$(C_9H_{19})_2CH$

Scheme 1. Synthesis of **8** and **9**.

ration of **8** and **9** was successful. Compound **8** is the first benzoterrylenehexacarboxtriimide and **9** not only the first dibenzoperyleneoctacarboxtetraimide but also the first derivative of the aromatic hydrocarbon dibenzoterrylene.

The UV/Vis absorption of **8** is between those of **1** and **5** and corresponds to the hypsochromic shift obtained by the benzannellation of **1** to benzoperylene derivatives; see Figure 1.

There is an additional absorption of **8** in the hypsochromic visible region compared with **5**; see Figure 1. This additional electronic transition is attributed to the five-membered ring imide and is of importance because of broadband absorption of light; this is of interest for applications in solar collectors.[17] The absorption of **9** is even more hypsochromic and is close to the absorption of **1**. However, there is also such an additional absorption in the

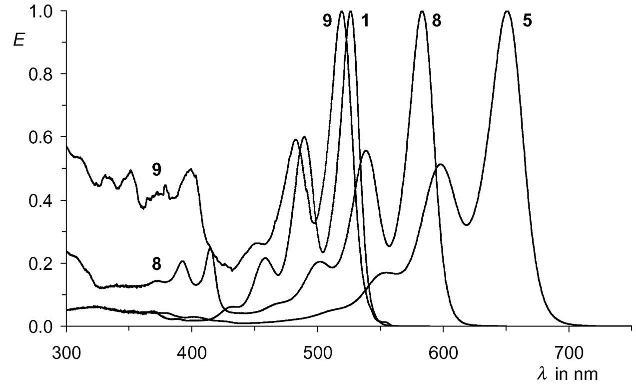

Figure 1. From left to right: UV/Vis absorption spectra of **9**, **1**, **8**, and **5** in chloroform.

hypsochromic region. This makes **9** a broadband absorber when compared with **1**.[11]

Compound **8** exhibits a remarkably strong bright red fluorescence with a quantum yield close to unity; thus, the expected increase of fluorescence quantum yield of **5** by means of structural modifications is verified; see Figure 2.

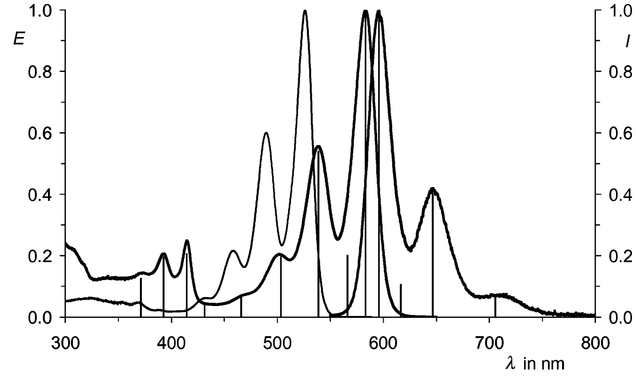

Figure 2. Absorption (thick line, center) and fluorescence spectra (thick line, right) of **8** in chloroform, compared with the absorption of **1** (thin line, left). Bars: Gaussian analysis of the spectra of **8**, with positions and intensities of the Gaussian bands.

A Gaussian analysis[18,19] of the spectra according to Equation (1) was successful and exhibits a similar, however, bathochromically shifted pattern as was observed for **1**; see Table 1 and Figure 2. An additional, structured absorption is observed at about 400 nm, making this dye useful as a broadband absorber.

$$\varepsilon(\lambda) = \sum \varepsilon_o \cdot \exp\left[-\frac{(1/\lambda - 1/\lambda_o)^2}{2\sigma^2}\right] \qquad (1)$$

Table 1. Gaussian analysis of UV/Vis spectra of **8** in chloroform (380–820 nm) according to Equation (1).

Gaussian bands	Absorption of **8**	Fluorescence of **8**
$\lambda_{max}(1)$[a]	583.2	595.7
$2\ \sigma^2(1)$[b]	0.148	0.171
$E_{max}(1)$[c]	0.987	0.985
$\lambda_{max}(2)$[a]	566.1	616.7
$2\ \sigma^2(2)$[b]	0.090	0.066
$E_{max}(2)$[c]	0.200	0.105
$\lambda_{max}(3)$[a]	538.7	646.4
$2\ \sigma^2(3)$[b]	0.305	0.263
$E_{max}(3)$[c]	0.539	0.408
$\lambda_{max}(4)$[a]	503.3	705.5
$2\ \sigma^2(4)$[b]	0.646	0.466
$E_{max}(4)$[c]	0.197	0.071
$\lambda_{max}(5)$[a]	466.0	810.0
$2\ \sigma^2(5)$[b]	0.917	0.831
$E_{max}(5)$[c]	0.065	0.007
$\lambda_{max}(6)$[a]	431.2	
$2\ \sigma^2(6)$[b]	0.628	
$E_{max}(6)$[c]	0.041	
$\lambda_{max}(7)$[a]	414.5	
$2\ \sigma^2(7)$[b]	0.149	
$E_{max}(7)$[c]	0.206	
$\lambda_{max}(8)$[a]	392.5	
$2\ \sigma^2(8)$[b]	0.882	
$E_{max}(8)$[c]	0.195	
R[d]	0.015	0.030

[a] Calculated wavelength in nm. [b] Linewidth in $10^6\ \mathrm{cm}^{-2}$ [kK^2]. [c] Calculated absorptivity for $E_{max} = 1.00$. [d] Residual; $R = \sqrt{\int[\varepsilon(\lambda)_{calcd.} - \varepsilon(\lambda)_{exp.}]^2 d\lambda / \int[\varepsilon(\lambda)_{exp.}]^2 d\lambda}$.

Conclusions

The broad absorption in the visible region and the bright red fluorescence of **8** are of special interest for solar energy applications such as in fluorescent solar collectors.[17] The dibenzo analogue **9** exhibits a bright yellow fluorescence similar to that of **1** with a quantum yield also close to unity; see Figure 2. Compounds **1** and **9** may be interchanged for the majority of applications; however, there is an additional hypsochromic absorption of **9**, making this dye interesting for broadband applications such as for fluorescent solar collectors.[17]

Experimental Section

***N*-(1-Nonyldecyl)-1,8-naphthalenedicarboximide (3):** 1-Nonyldecylamine (673 mg, 2.38 mmol), 1,8-naphthalenedicarboxylic anhydride (**2**, 500 mg, 2.52 mmol) and imidazole (2 g) were heated under argon at 130 °C for 3 h, cooled, and treated still warm with a mixture of 2 M HCl/acetic acid (1:1); the mixture was extracted two times with chloroform. The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and purified by column chromatography (silica gel 60; $CHCl_3$/isohexane, 1:1). Yield 650 mg (59 %) light yellow, honey-like substance, R_f (silica gel; $CHCl_3$/isohexane, 1:1) = 0.8. ^1H NMR ($CDCl_3$, 200 MHz, 23 °C): δ = 8.64–8.50 (m, 2 H), 8.25–8.14 (m, 2 H), 8.80–8.69 (m, 2 H), 5.26–5.06 (m, 1 H), 2.35–2.10 (m, 2 H), 1.90–1.70 (m, 2 H), 1.40–1.02 (m, 28 H), 0.95–0.75 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz, 25.0 °C): δ = 165.4, 164.3, 133.4, 131.5, 131.5, 130.8, 128.3, 126.9, 123.4, 123.7, 54.4, 32.4, 31.8, 29.5, 29.5, 29.2, 26.9, 22.6, 14.1 ppm. MS (GC/EI): *m/z* (%) = 463 (10) [M^+], 336 (5) [$M^+ - C_9H_{19}$], 198 (100) [$M^+ - C_{19}H_{38}$]. $C_{31}H_{45}NO_2$ (463.7): calcd. C 80.30, H 9.78, N 3.02; found C 80.19, H 9.98, N 3.05.

***N*,*N′*-Bis(1-nonyldecyl)-3,4:11,12-terrylenetetracarboxdiimide (5):** *N*-(1-Nonyldecyl)-3,4-perylenedicarboximide[13] (**4**, 1.00 g, 1.70 mmol), potassium *tert*-butoxide (3.64 g, 32.4 mmol), DBN (4.86 mL, 40.7 mmol) and diglyme (4.00 mL) were heated under argon at 130 °C, treated continuously by means of a syringe with

N-(1-nonyldecyl)-1,8-naphthalenedicarboximide (**3**, 1.50 g, 3.23 mmol) within 6 h, stirred at 130 °C for 3 h, cooled, poured onto water (200 mL), stirred for 1 h, collected by vacuum filtration, dried in air (100 °C) and purified by column chromatography (silica gel; chloroform/isohexane, 3:1). Yield 270 mg (15%), R_f ($CHCl_3$) = 0.7. ^{1}H NMR ($CDCl_3$, 600 MHz, 25.0 °C): δ = 8.61 (d, ^3J = 17.8 Hz, 4 H), 8.50 (s, 4 H), 8.46 (d, ^3J = 7.9 Hz, 4 H), 5.25–5.18 (m, 2 H), 2.32–2.24 (m, 4 H), 1.93–1.86 (m, 4 H), 1.40–1.16 (m, 56 H), 0.83 (t, ^3J = 8.0 Hz, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz, 25.0 °C): δ = 164.9, 163.9, 135.4, 131.8, 131.0, 130.9, 129.8, 128.6, 125.9, 124.1, 122.5, 121.8, 121.3, 104.8, 54.6, 32.4, 31.9, 29.7, 29.6, 29.6, 29.3, 27.0, 22.7, 14.1 ppm. UV/Vis (chloroform): λ_{max} (E_{rel}) = 651 (100), 598 (51), 555 (17) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 668 (100), 730 (26) nm. MS (DEP/EI): *m*/*z* (%) = 1047 (100) [M^+], 781 (36) [$M^+ - C_{19}H_{38}$], 514 (45) [$M^+ - 2\ C_{19}H_{38}$].

***N*,*N*′,*N*′′-Tris(1-nonyldecyl)benzo[*ghi*]terrylene-3,4:6,7:11,12-hexacarboxtriimide (8) and *N*,*N*′,*N*′′,*N*′′′-Tetrakis(1-nonyldecyl)dibenzo[*ghi*,*tuv*]terrylene-3,4:6,7:11,12:14,15-octacarboxtetraimide (9):** *N*,*N*′-Bis(1-nonyldecyl)-3,4:11,12-terrylenetetracarboxdiimide (35 mg, 33 µmol), maleic anhydride (80 mg, 0.82 mmol), chloranile (16 mg, 66 µmol) and nitrobenzene (10 mL) were stirred at 210 °C (bath temperature, colour change from blue to violet) for 2 h, cooled and poured onto 2 M HCl (50 mL). The nitrobenzene was removed by steam distillation and the residue collected by vacuum filtration, dried at 110 °C, condensed without further purification under argon with 1-nonyldecylamine (15 mg, 53 µmol) in imidazole (1.3 g) at 140 °C for 4 h, cooled, treated with a mixture of 2 M HCl and acetic acid (1:1, 20 mL), collected by vacuum filtration and purified by column chromatography (silica gel 60; $CHCl_3$). The first fraction contained an orange mixture of **8**, **9** and aliphatic by-products (R_f = 0.9; silica gel; chloroform) and was further purified by column chromatography (silica gel; isohexane). After the separation of an orange forerun, the eluent was changed to chloroform/isohexane (2:1), and orange **9** as the next fraction and then violet **8** were collected. Yield 10 mg (22%) of **8** as violet powder, R_f ($CHCl_3$) = 0.5. ^{1}H NMR ($CDCl_3$, 600 MHz, 25.0 °C): δ = 10.51 (s, 1 H), 10.46 (d, ^3J = 16.5 Hz, 1 H), 9.41 (d, ^3J = 8.7 Hz, 1 H), 9.34 (d, ^3J = 8.6 Hz, 1 H), 9.15 (d, ^3J = 8.6 Hz, 1 H), 9.12 (d, ^3J = 8.6 Hz, 1 H), 9.02 (d, ^3J = 8.1 Hz, 1 H), 8.75 (m, 3 H), 5.32 (m, 2 H), 5.23 (m, 1 H), 2.32 (m, 6 H), 1.91 (m, 6 H), 1.27 (m, 84 H), 0.87 (m, 18 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 584 (100), 539 (54), 503 (19), 415 (24), 393 (20) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 595 (100), 647 (29) nm. Fluorescence quantum yield [$CHCl_3$; E_{495nm} = 0.0211, λ_{ex} = 495 nm; reference: *N*,*N*′-bis(1-hexyheptyl)perylene-3,4:9,10-tetracarboxdiimide with Φ = 100%]: Φ = 100%. MS (DEP/EI): *m*/*z* (%) = 1408 (60) [M^+ (2 ^{13}C)], 1140 (40) [$M^+ - C_{19}H_{38}$], 873 (100) [$M^+ - 2\ C_{19}H_{38}$], 607 (52) [$M^+ - 3\ C_{19}H_{38}$]. MS (FIA/ESI): calcd. for $C_{95}H_{127}N_3O_6$ 1405.9693, found 1405.9667, Δ = –2.6 mmu. **9**: Yield ca. 2 mg (4%) of an orange powder, R_f ($CHCl_3$) = 0.6. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 519 (100), 483 (59), 452 (26), 399 (49) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 530 (100), 574 (32) nm. Fluorescence quantum yield [$CHCl_3$; E_{483nm} = 0.0306, λ_{ex} = 483 nm; reference: *N*,*N*′-bis(1-hexyheptyl) perylene-3,4:9,10-tetracarboxdiimide with Φ = 100%]: Φ = 100%. MS (DEP/EI): *m*/*z* (%) = 1766 (100) [M^+ (2 ^{13}C)], 1500 (90) [$M^+ - C_{19}H_{38}$], 1233 (65) [$M^+ - 2\ C_{19}H_{38}$], 967 (18) [$M^+ - 3\ C_{19}H_{38}$], 701 (15) [$M^+ - 4\ C_{19}H_{38}$]. HRMS (FIA/ESI): calcd. for $C_{118}H_{165}N_4O_8$ 1766.2617, found 1766.2612, Δ = –0.5 mmu.

Acknowledgments

We thank General Electric and the Fonds der Chemischen Industrie for financial support.

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Received: November 8, 2007