Intramolecular Effects in Covalently Connected Units − Ring-Type Oriented Chromophores and their Interactions

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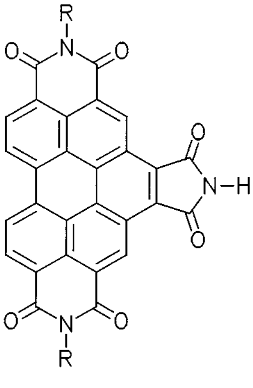
The light harvesting unit **B800** of the bacteria system **LH2** has been simulated by the ring-type arrangement of up to six benzoperylene trisimide chromophores. Exciton coupling has been found in this arrangement.

Introduction

The ring-type arrangement of chromophores is a dominant structural element in the photosynthesis system of bacteria:[1] 18 Identical axially oriented chlorophyll units form the strongly coupled **B850** ring, whereas nine further chlorophyll molecules form equatorially the second weakly coupled ring **B800**. Special interactions of the chromophores are expected for this arrangement.

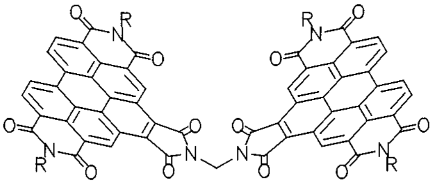
Results and Discussion

We wanted to simulate the **B800** unit and study such interactions with the ring-type arrangement of an increasing number of model chromophores. Highly fluorescent chromophores are therefore especially suitable because the absorbed light can be monitored by fluorescence.



1

We planned to use the recently prepared[2] benzoperylene trisimides (chromophore of **1**) as the chromophores for such structures (see refs.[3,4]).The two six-membered ring imide nitrogen atoms of the trisimide are suitable positions for solutizing long-chain *sec*-alkyl substituents,[5,6] ("swallow-tail" group) and the five-membered ring imide nitrogen atom could be the linker to a base structure by a nucleophilic displacement reaction. However, the necessary unsubstituted **1** is unknown and cannot be prepared by standard procedures because the anhydride **6** doesn't form **1** with ammonia and neither does the perylenetetracarboxylic bisimide with malein imide according to ref.[2] However, amidosulfonic acid in molten imidazole proved to be a suitable reagent for the preparation of unsubstituted five-membered ring imides from anhydrides such as **1** from **6**.



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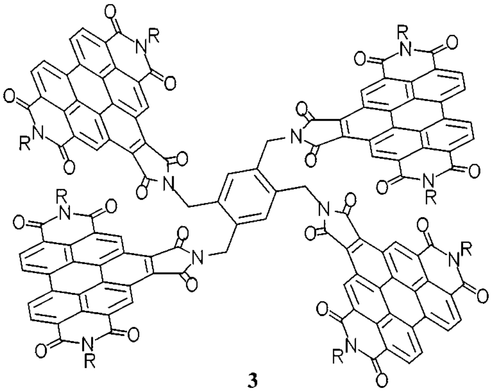

3

The nucleophilic displacement reaction of dibromomethane with **1** gave the bichromophore **2** (Scheme 1; the reported yields in the Exp. Section correspond to isolated, highly purified, analytically pure materials; the chemical yields are between 20 and 60%). Tetrabromopentaerythrite similarly gave the tetrachromophore **5**, although in lower yields because of the steric hindrance. The chromophores in **5** are not ring-type arranged but placed on the surface of a sphere. Better synthetic results were obtained by the use of the more reactive brominated benzyl groups (compare also ref.[4]); these make multiple replacement reactions

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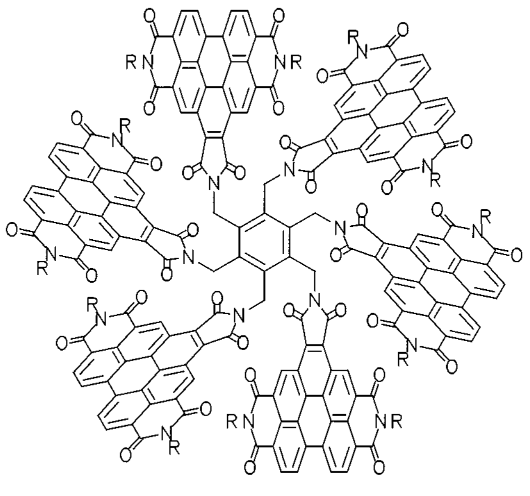

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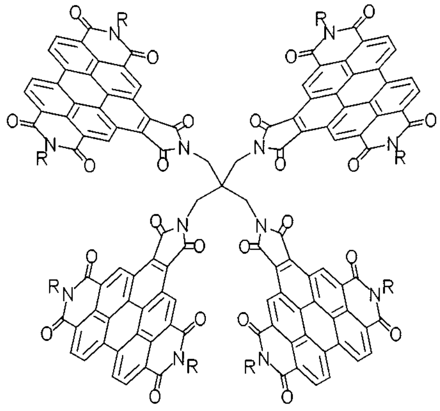
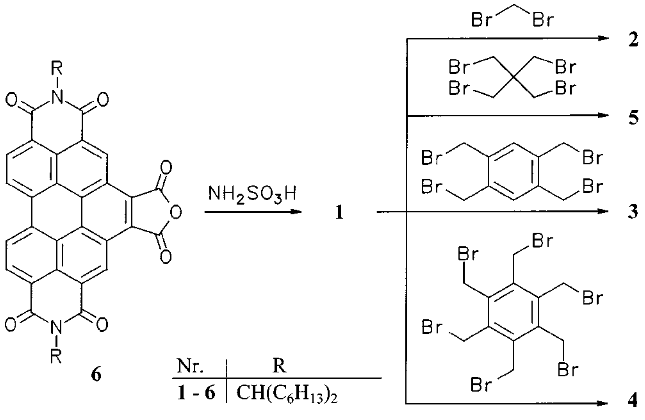


5

possible. Thus, the tetrachromophore **3** could be prepared as well as the hexachromophore **4**.



Scheme 1. Preparation of multichromophoric dyes

The trisimide **1** exhibits a structured UV/vis spectrum (see Figure 1). The absorption maximum at longest wavelength (1) is the vibronic 0−0 transition of the electronic S_0-S_1 transition and the next, more hypsochromic, maxima (2 and 3) are transitions to vibronically excited states (see Table 1). The even more hypsochromic maximum is the S_0-S_2 transition. This higher electronic transition also exhibits a vibronic structure similar to the S_0-S_1. However, the structuration of this transition is not as pronounced as for S_0-S_1. Moreover, the bands at shorter wavelengths are obviously superimposed by further electronic transitions. The multichromophoric dyes **2**, **3** and **4** exhibit a similar structuration of the spectra as **1**. Their molar absorptivities increase roughly with the number of chromophores. However, this increase is not the same for all maxima: it is smaller than expected for the S_0-S_1 transition and larger for the S_0-S_2 transition. As a consequence, maximum no. 4 becomes higher than maximum no. 2 for the hexachromophore.

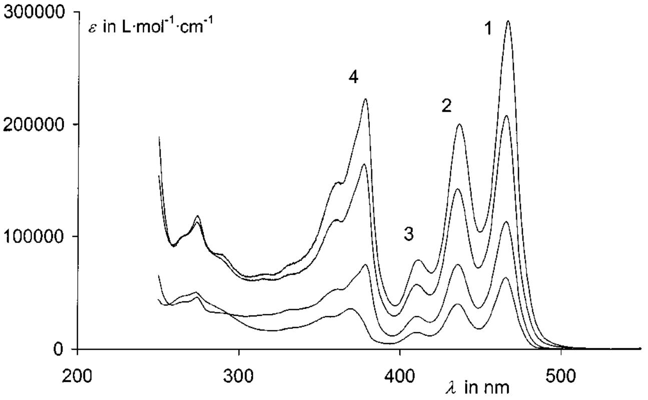


Figure 1. UV/vis absorption spectra of the oligochromophore benzoperylenetrisimides in chloroform; from bottom to top: compounds **1**, **2**, **3** and **4**

Table 1. UV/vis absorption maxima of **1** and averaged linear increase of the molar absorptivities ($\Delta\varepsilon$) of the multichromophores **2**, **3** and **4**

No.	Transition	λ_{max} (nm)	ε (L·mol^{-1}·cm^{-1})	$\Delta\varepsilon$ (L·mol^{-1}·cm^{-1})
1	S_0-S_1	466	64000	46000
2	S_0-S_1	435	44000	32000
3	S_0-S_1	410	15000	15000
4	S_0-S_2	369	36000	38000

Exciton interactions of the single chromophores (compare ref.[7] and literature cited therein) are responsible for this different behaviour of the absorption maxima. These exciton interactions are destructive for maximum no. 1, but seem to be constructive for maximum no. 4. A further analysis of the effect was made by means of a linear regression of the increase of the molar absorptivities $\Delta\varepsilon$ as a function of the number of chromophores (n), see Table 1. This increase is about 30% too low for absorption maxima nos. 1 and 2, whereas maximum no. 4 is about 6% too large. Obviously, the increase of the absorption maximum no. 4 is taken from the decrease of maximum nos. 1 and 2.

We made a Gaussian analysis of the UV/vis spectra of **1−5** according to the recently published[8] study using Equation (1). This was successful for both the S_0-S_1 and S_0-S_2 transitions (see Figure 2 for **1**); R values were obtained between 0.019 for **1** and 0.036 for **4** (360−600 nm;

see Table 2 and Figure 3). We found five vibronic transitions for S_0-S_1 with a very similar pattern of intensities to those of the perylenebisimides,[8] and four transitions for S_0-S_2 with $\lambda > 350$ nm. Measurements of the linear dichroism of **1**[9] indicate that there is only one electronic transition for $\lambda > 400$ nm. Therefore, the vibronic structure of S_0-S_1 was further analysed. The integral of the first vibronic band (1), corrected for the number of chromophores, decreases by 15% from dye to dye for the structures **1**−**4**. The same tendency was observed for the vibronic bands 2 and 3, whereas band 4 remains essentially unchanged. These results support the interpretation of changes in spectra by exciton effects. Furthermore, the Ross function[10] was fulfilled for bands nos. 1, 3, 4 and 5. The Ross x parameter is a measure of the nuclear displacement by optical excitation and was found to be 0.781 for **1**; this is appreciably higher than for perylenetetracarboxylic bisimides ($x = 0.745$[8]). The Ross x parameter increases only slightly with the number of chromophores (0.810 for **4**).

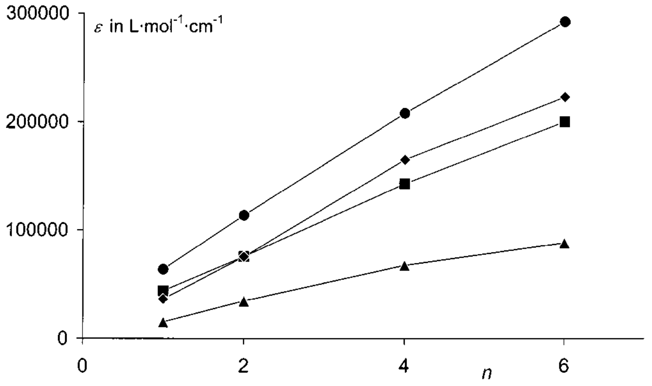


Figure 2. Molar absorptivities (ε) of the absorption maxima no. 1 (●), no. 2 (■), no. 3 (▲) and no. 4 (◆) as a function of the number (n) of chromophores (dyes **1**−**4**)

$$\varepsilon\ (\lambda) = \sum \varepsilon_0 \cdot \exp\left[-\frac{(1/\lambda - 1/\lambda_o)^2}{2\sigma^2}\right] \tag{1}$$

The novel dyes are strongly fluorescent: the fluorescence quantum yields are about 50% and the fluorescence spectra are mirror-type to the absorption spectra. The Stokes shifts of the oligochromophoric dyes are so small and so similar to each other that this can be taken as an additional proof for exciton effects as the origin of the altered intensities of the absorption bands. Dynamic processes could be an alternative, but would increase the Stokes shift and disturb the mirror-type symmetry of the spectra. Whereas a pronounced exciton effect was found in the absorption spectra, the effect is appreciably weaker in fluorescence. Only the most hypsochromic fluorescence band of the hexachromophoric dye exhibits a noticeable but moderate amplification.

The exciton interaction described here shall be further studied with other large multichromophoric systems; this will be reported elsewhere.

Table 2. Gaussian analysis of UV/vis spectra in chloroform (30−600 nm)

Dye	**1**	**2**	**5**	**3**	**4**
$n_{\text{chrom.}}$ [a]	1	2	4	4	6
$\lambda_{\max}(1)$ [b]	465.3	465.2	465.5	464.9	465.9
$2\sigma^2(1)$ [c]	0.173	0.185	0.177	0.204	0.206
$\varepsilon_{\max}(1)$ [d]	61800	111700	218800	204500	288700
$\lambda_{\max}(2)$ [b]	452.3	452.2	452.4	451.0	451.7
$2\sigma^2(2)$ [c]	0.089	0.095	0.090	0.074	0.075
$\varepsilon_{\max}(2)$ [d]	10200	18400	37200	33200	43800
$\lambda_{\max}(3)$ [b]	435.6	435.8	435.8	435.8	436.8
$2\sigma^2(3)$ [c]	0.303	0.321	0.308	0.308	0.317
$\varepsilon_{\max}(3)$ [d]	39200	73600	140400	138600	195200
$\lambda_{\max}(4)$ [b]	410.4	410.8	410.7	410.5	411.3
$2\sigma^2(4)$ [c]	0.547	0.545	0.596	0.710	0.683
$\varepsilon_{\max}(4)$ [d]	14500	28300	54000	56200	77700
$\lambda_{\max}(5)$ [b]	390.5	387.7	390.2	391.6	392.3
$2\sigma^2(5)$ [c]	0.126	0.288	0.159	0.101	0.101
$\varepsilon_{\max}(5)$ [d]	3310	7200	15010	18450	24680
$\lambda_{\max}(6)$ [b]	372.2	379.8	375.7	377.4	377.8
$2\sigma^2(6)$ [c]	0.482	0.095	0.312	0.317	0.324
$\varepsilon_{\max}(6)$ [d]	26400	33900	69000	133100	181200
$\lambda_{\max}(7)$ [b]	365.2	374.2	367.7	368.7	367.8
$2\sigma^2(7)$ [c]	0.625	0.230	0.228	0.096	0.096
$\varepsilon_{\max}(7)$ [d]	7400	26900	35600	7500	10800
$\lambda_{\max}(8)$ [b]	354.3	362.3	358.0	361.1	361.5
$2\sigma^2(8)$ [c]	0.844	1.996	1.471	1.068	1.068
$\varepsilon_{\max}(8)$ [d]	18100	49200	77700	91100	118400
$\lambda_{\max}(9)$ [b]	333.3	331.2	330.1	335.1	335.8
$2\sigma^2(9)$ [c]	3.480	2.671	4.554	4.091	4.091
$\varepsilon_{\max}(9)$ [d]	18600	33300	64300	67400	77000
R [e]	0.0187	0.0195	0.0208	0.0324	0.0359

[a] Number of chromophores. − [b] Calculated wavelength in nm. − [c] Linewidth in 10^6 cm^{-2} (kK^2). − [d] Calculated absorptivity in L·mol^{-1}·cm^{-1}. − [e] Residual;

$$R = \sqrt{\int[\varepsilon(\lambda)_{calcd} - \varepsilon(\lambda)_{\exp}]^2 d\lambda \ / \ \int[\varepsilon(\lambda)_{\exp}]^2 d\lambda}\ .$$

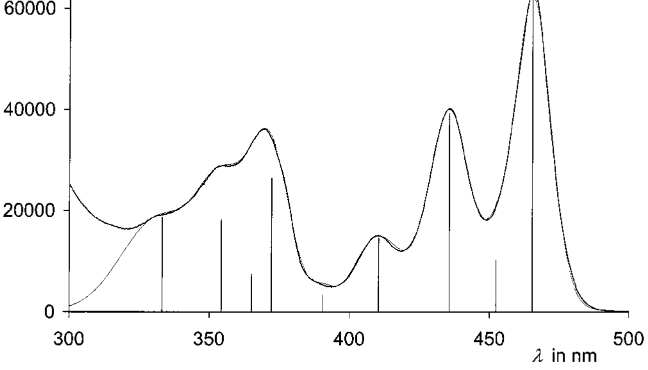


Figure 3. UV/vis absorption spectrum of **1** in chloroform (thick line), simulated spectrum from the Gaussian analysis (thin line) and calculated absorptivities and line positions (bars)

Experimental Section

1: *N,N'*-Bis(1-hexylheptyl)benzo[*ghi*]perylene-2,3,8,9,11,12-hexacarboxylic-2,3;8,9-bis(dicarboximide)-11,12-anhydride[2] (1.00 g, 1.17 mmol, **6**), imidazole (6 g) and amidosulfuric acid (4.57 g, 47.16 mmol, finely pulverized) were heated (160 °C, 4 h, Ar), cooled down, treated with hydrochloric acid (400 mL, 2 N), stirred (1 h), collected by vacuum filtration, washed with bidistilled water (200 mL), dried (120 °C in air, 16 h), dispersed in small amounts of chloroform, purified by column separation (silica gel, chloroform/acetone 15:1, to remove a yellowish green fluorescent forerun), further purified by a second column separation (neutral Al_2O_3, chloroform/acetone, 15:1), precipitated with methanol from the concentrated eluent and dried under medium vacuum at 80 °C. Yield: 830 mg (84%) of **1** as a bright yellow shining powder, m.p. > 260 °C (dec.). − R_f (chloroform/acetone, 15:1): 0.64. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} s, 2927 s, 2857 m, 1773 w, 1733 m, 1706 s, 1664 s, 1625 m, 1595 w, 1522 w, 1458 w, 1415 m, 1346 m, 1365 m, 1319 s, 1267 w, 1237 w, 1174 w, 958 w, 944 w, 812 m, 766 m, 659 w. − UV/vis ($CHCl_3$): λ_{max} (ε) = 332 nm (20560), 369 (36180), 410 (15030), 435 (43800), 466 (63600). − Fluorescence ($CHCl_3$, quantum corrected): λ_{max} (I_{rel}) = 474 nm (1.00), 507 (0.50), 544 (0.12). − Fluorescence quantum yield ($c = 6.06 \times 10^{-7}$ mol·L^{-1} in chloroform, reference: tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100% ,[11] $\lambda_{excit.}$ = 440 nm): 49%. − ^1H NMR ($CDCl_3$): δ = 0.80 (t, 12 H, 4 CH_3), 1.10−1.42 (m, 32 H, 16 CH_2), 1.88−2.00 (m, 4 H, CH_2-CH_2), 2.23−2.42 (m, 4 H, CH_2-CH_2), 5.28 (m_c, 2 H, N−CH), 8.64 (s, 1 H, N−H), 9.22 (br. S, 2 H, perylene), 9.42 (d, 2 H, perylene), 10.21 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.0, 29.2, 31.7, 32.4, 55.3, 123.5, 124.1, 125.1, 127.8, 128.0, 128.3, 133.4, 167.5. − MS (70 eV): *m/z* (%) = 847 (31) [M^+], 830 (3), 762 (4), 666 (84) [$M^+ - C_{13}H_{26}$], 581 (2), 510 (1), 496 (7), 484 (100) [$M^+ - 2\ C_{13}H_{26}$], 466 (15), 438 (4), 413 (3) [$M^+ - 2\ C_{13}H_{26} - NC_2O_2$], 382 (1). − $C_{54}H_{61}N_3O_6$ (848.1): calcd. C 76.47, H 7.25, N 4.95; found C 76.54, H 7.37, N 4.79.

2: Compound **1** (800 mg, 0. 94 mmol) was homogenized with anhydrous K_2CO_3 (3.37 g 24.44 mmol). Dry dibromomethane (810 mg, 4.70 mmol) and anhydrous DMF (40 mL) were then added under argon. The mixture was heated with stirring (100 °C, 24 h, argon) and dispersed in doubly distilled water (100 mL) after cooling. The solid was collected by vacuum filtration, dried (120 °C, in air, yellowish brown powder), purified by column separation (silica gel, chloroform/acetone, 15:1), further purified by a second column separation (silica gel, chloroform/*n*-butyl alcohol, 40:1, to remove a yellowish forerun), precipitated from the concentrated eluent with methanol, collected by vacuum filtration and dried (in air, 120 °C). Yield: 260 mg of **2** (15.3%) as an orange to yellow powder, m.p. > 250 °C. − R_f (chloroform/acetone, 15:1): 0.95. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} s, 2927 s, 2857 m, 1771 w, 1731 m, 1705 s, 1663 s, 1625 m, 1596 w, 1524w, 1458 w, 1415 m, 1365 m, 1319 s, 1275 w, 1240 w, 1175 w, 942 w, 847 w, 813 m, 766 m, 659 w. − ^1H NMR ($CDCl_3$): δ = 0.80 (t, 24 H, 8 CH_3), 1.10−1.42 (m, 64 H, 32 CH_2), 1.88−2.00 (m, 8 H, 2 CH_2-CH_2), 2.23−2.42 (m, 8 H, 2 CH_2-CH_2), 5.28 (m_c, 4 H, 4 N−CH), 6.70 (s, 2 H, RN−CH_2−NR), 9.22 (br. s, 4 H, perylene), 9.42 (d, 4 H, perylene), 10.21 (s, 4 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 23.6, 27.0, 27.2, 31.7, 33.4, 58.1, 123.5, 124.1, 125.3, 128.6, 129.0, 132.4, 167.5. − UV/vis (chloroform): λ_{max} (ε) = 274 nm (46200), sh 361 (53420), 379 (75070), 410 (29350), 435 (75250), 466 (113500). − Fluorescence (chloroform, quantum corrected): λ_{max} ($I_{rel.}$) = 475 nm (1.00), 508 (0.59), 552 (0.14). − Fluorescence quantum yield ($c = 3.90 \times 10^{-7}$ mol·L^{-1} in chloroform, reference: trametheyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%,[11] $\lambda_{exit.}$ = 440 nm): 44%. − MS (FAB+, *Cs* 20 kV): *m/z* (%) = 1706 (5) [M^+], 1432 (2), 1008 (4), 680 (1), 496 (18). − $C_{109}H_{122}O_{12}N_6$ (1706.20): calcd. C 76.64, H 7.19, N 4.91, found C 76.64, H 7.20, N 4.84.

3: Compound **1** (800 mg, 0.94 mmol), anhydrous K_2CO_3 (3.37 g, 24.4 mmol), 1,2,4,5-tetrakis(bromomethyl)benzene (90 mg, 0.21 mmol) and anhydrous DMF (40 mL) were allowed to react and purified analogously to **2**. Yield: 240 mg of **3** (7.2%) shiny yellow powder, m.p. > 250 °C. − R_f (chloroform/acetone, 15:1): 0.92. − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} s, 2927 s, 2857 m, 1774 w, 1713 m, 1664 s, 1596 w, 1522w, 1458 w, 1414 m, 1365 m, 1319 s, 1278 w, 1240 w, 1172 w, 940 w, 847 w, 813 m, 756 m, 660 w. − UV/vis (chloroform): λ_{max} (ε) = 275 nm (112400), sh 359 (114600), 377 (165000), 410 (67160), 435 (142700), 466 (208000). − Fluorescence (chloroform, quantum corrected): λ_{max} ($I_{rel.}$) = 476 nm (1.00), 508 (0.62), 547 (0.17). − Fluorescence quantum yield ($c = 1.84 \times 10^{-7}$ mol·L^{-1} in chloroform, reference: tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%,[11] $\lambda_{excit.}$ = 440 nm): 42%. − ^1H NMR ($CDCl_3$): δ = 0.73−2.64 (br. m, CH_3 and CH_2), 5.33 (m_c, N−CH), 5.68 (m, benzyl-CH_2), 9.13 (br. m, aromatic H), 9.43 (br. m, aromatic H), 10.40 (br. m, aromatic H). − $C_{226}H_{250}N_{12}O_{24}$ (3518.5): calcd. C 77.14, H 7.16, N 4.77; found C 77.19, H 7.21, N 4.71.

4: Compound **1** (800 mg, 0.94 mmol), anhydrous K_2CO_3 (3.37 g, 24.4 mmol), 1,2,3,4,5,6-hexakis(bromomethyl)benzene (88 mg, 0.14 mmol) and anhydrous DMF (40 mL) were allowed to react analogously to **2**. Yield: 52 mg of **4** (1.0%) as a brownish yellow powder, m.p. > 250 C. − R_f (chloroform/acetone, 15:1): 0.98. − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} s, 2927 s, 2857 m, 17752 w, 1712 m, 1665 s, 1578 w, 1522w, 1456 w, 1415 m, 1364 m, 1318 s, 1278 w, 1242 w, 1133 w, 940 w, 823 m, 755 m, 660 w. − UV/vis (chloroform): λ_{max} (ε) = 274 nm (112900), sh 361 (144400), 378 (222800), 411 (87930), 436 (200300), 466 (292200). − Fluorescence (chloroform, quantum corrected): λ_{max} ($I_{rel.}$) = 475 nm (1.00), 508 (0.62), 542 (0.26). − Fluorescence quantum yield ($c = 1.05 \times 10^{-7}$ mol·L^{-1} in chloroform, reference: tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%,[11] $\lambda_{excit.}$ = 440 nm): 41%. − ^1H NMR ($CDCl_3$): δ = 0.70−2.20 (br. m, CH_3 and CH_2), 5.11 (m_c, N−CH), 5.33 (m, benzyl-CH_2), 9.16 (br. m, aromatic H), 9.48 (br. m, aromatic H). − $C_{336}H_{372}N_{18}O_{36}$ (5238.75): calcd. C 77.03, H 7.15, N 4.81; found C 77.15, H 7.21, N 4.68.

5: Compound **1** (800 mg, 0.94 mmol), anhydrous K_2CO_3 (3.37 g, 24.4 mmol), pentaerythrityltetrabromide (85 mg, 0.22 mmol) and anhydrous DMPU (40 mL) were allowed to react analogously to **2**. Yield: 72 mg of **5** (2.2%) as an ochre colored powder, m.p. > 250 °C. − R_f (chloroform/acetone, 15:1): 0.96. − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} s, 2927 s, 2857 m, 1772 w, 1713 m, 1665 s, 1598 w, 1522w, 1458 w, 1412 m, 1364 m, 1318 s, 1278 w, 1242 w, 1172 w, 940 w, 813 m, 755 m, 660 w. − UV/vis (chloroform): λ_{max} (ε) = 263 nm (91390), 273 (100300), sh 355 (100300), 370 (124400), 410 (56070), 436 (144500), 466 (223900). − Fluorescence (chloroform, quantum corrected): λ_{max} ($I_{rel.}$) = 475 nm (1.00), 507 (0.50), 544 (0.11). − Fluorescence quantum yield ($c = 1.26 \times 10^{-7}$ mol·L^{-1} in chloroform, reference: tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%,[11] $\lambda_{excit.}$ = 440 nm): 65%. − ^1H NMR ($CDCl_3$): δ = 0.85 (t, CH_3), 1.26−1.57 (m, CH_2), 1.99−2.20 (m, α-CH_2-CH_2), 2.38−2.64 (m, α-CH_2-CH_2), 5.33 (m_c, N−CH), 9.24−9.48 (br. m, aromatic H), 10.47 (br. m, aromatic H). − $C_{221}H_{248}N_{12}O_{24}$ (3456.5): calcd. C 76.79, H 7.23, N 4.86; found C 76.57, H 7.54, N 4.93.

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