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Synthesis and Aggregation Properties of Water-Soluble Newkome-Dendronized Perylenetetracarboxdiimides

Cordula D. Schmidt,[a] Christoph Böttcher,[b] and Andreas Hirsch*[a]

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The synthesis and characterization of three highly water-soluble perylenetetracarboxdiimide ("perylene bisimide", PBI) dyes **1** and **2b** is presented. The water solubility is provided by peripheral dendronization with 1G- and 2G-Newkome dendrons. The aggregation behaviour of these amphiphiles in water and that of their *tert*-butyl-protected precursor molecules **3** and **4** in organic solvents was investigated by UV/Vis- and fluorescence spectroscopy. The symmetric 1G-dendronized dye **1a** forms aggregates more easily than its 2G-counterpart **1b**. The asymmetric derivatives **2b** reveals pronounced aggregation properties due to the presence of both a 2G-dendron and a flexible and non-bulky dodecyl substituent. The 1G-analogue **2a** is insoluble in water as a result of insufficient overall hydrophilicity caused by only one 1G-Newkome dendron. Within the series of water-soluble perylenes **1** and **2b** the asymmetric derivative **2b** forms the most regularly shaped micelles in water (pH = 7.2) with a mean diameter of 16 nm as demonstrated by transition electron microscopy (TEM). The bola-amphiphiles **1a** and **1b** form a distribution of smaller aggregates on average with less defined shape.

Introduction

We have recently developed several families of functional amphiphiles whose general building principle is depicted in Figure 1.[1] Some of these water-soluble architectures exhibit unprecedented properties such as the formation of shape-persistent micelles whose defined three-dimensional structures could be resolved with molecular precision.[1f,1g,1h,1j] The chromophoric core unit may have various functions. For example, it can enable photo-induced electron transfer[1e] or it may serve as a platform for the binding of polar and apolar building blocks in a stereochemically controlled and tunable fashion. In some cases it can just represent the hydrophobic part (m = 0) contributing to the supramolecular assembly of the amphiphiles.[1b,1c,1i] As polar head groups **P** we have used in most cases Newkome-type dendrons with peripheral carboxylic groups providing excellent water solubility.[8,9] We report here on an extension of this structure principle by introducing the perylene core as chromophoric unit **C**. The incentive was to use the pronounced aggregation properties of perylenes induced by very effective π-π stacking interactions. Aggregation phenomena of perylene dyes have been extensively studied in organic solvents.[2,3,10,11] An excellent review was provided by Würthner[3a] who is one of the pioneers in this field. Typical aggregation motifs include the formation of linear nanobelts,[2] spherical nanoparticles,[2] double-helical[3a] and columnar nanostructures[3b,3c] with linear J-type-[4] or H-type π-π stacking.[5] Although aggregation in aqueous solution is expected to be even more pronounced due to the contribution of hydrophobic interactions only a few perylene dyes who could be transferred into the water phase have been investigated in this regard.[6] Very recently, a systematic study on the formation of micelles, vesicles and rod aggregates based on amphiphilic perylene bisimide (PBI) dyes in water containing 2% THF were published by Würthner and co-workers.[7]

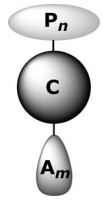


Figure 1. Schematic representation of functional amphiphiles consisting of i) n (n = 1, 2, ...) polar head groups such as Newkome-type oligo-carboxylic acid dendrons, ii) a chromophoric core unit such as a fullerene, calixarene, porphyrin or pyrene moiety and iii) m (m = 0, 1, ...) apolar tail groups such as dodecyl chains.

The amphiphilic PBIs that we used in this study are highly water-soluble, especially when 2G-Newkome dendrons exhibiting a high degree of deprotonation at neutral

[a] Institut für Organische Chemie and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg,
Henkestraße 42, 91054 Erlangen, Germany
Fax: +49-9131-8526864
E-mail: andreas.hirsch@organik.uni-erlangen.de
[b] Forschungszentrum für Elektronenmikroskopie, Institut für Chemie und Biochemie, Freie Universität Berlin,
Fabeckstraße 36a, 14195 Berlin, Germany
Fax: +49-30-838-56589
E-mail: bottcher@chemie.fu-berlin.de

pH are used as head groups **P**. The aggregation to micelles strongly depends on the steric requirement of the head group **P** as determined by optical spectroscopy and transmission-electron-microscopy (TEM).

Results and Discussion

The synthesis of the new water-soluble PBIs **1** and **2** and their *tert*-butyl-protected precursors **3** and **4** (Figure 2) is based on 3,4:9,10-perylenetetracarboxylic dianhydride (PTCDA) **5** as starting material.

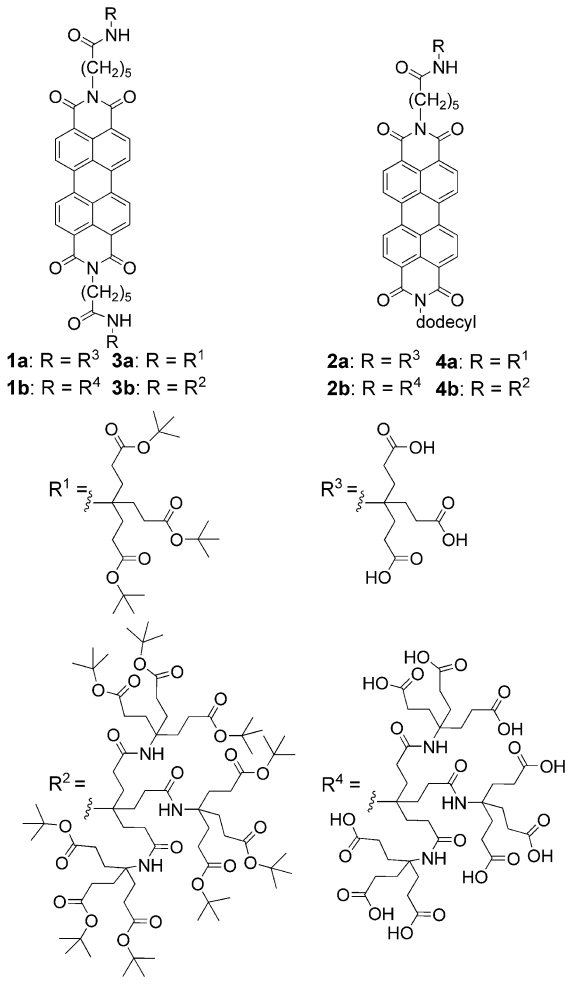
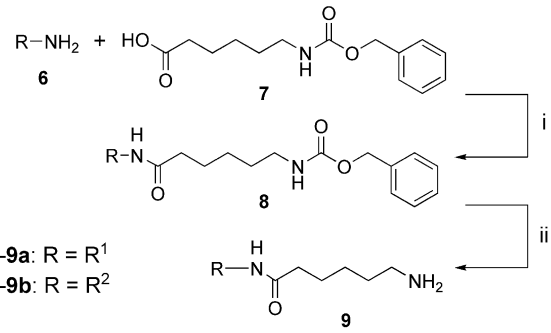


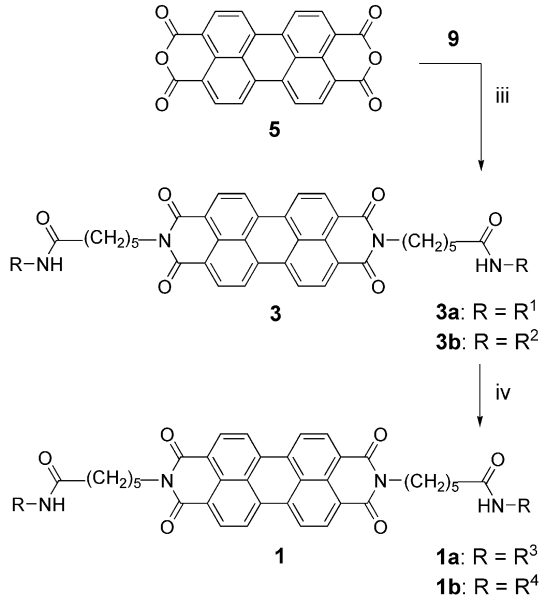
Figure 2. New PBI-amphiphiles **1** and **2** with 1G- and 2G-Newkome dendrons as polar groups **P** and their *tert*-butyl protected precursors **3** and **4**.

In order to avoid steric hindrance which could affect both the coupling of the dendrons itself and the π-π stacking of the perylene chromophores in solution we decided to introduce spacer units between the building blocks **P** and **C**. For this purpose the Newkome dendrons **6** were elongated by DCC-coupling with Cbz-protected caproic acid **7** to give the spacer coupled dendrimers **8** which was subsequently deprotected to afford the amines **9**[14] (Scheme 1).



Scheme 1. Synthesis of the elongated dendritic building blocks **9**. i) DCC, HOBT, DMAP in DMF; ii) Pd/C, H_2 in ethanol.

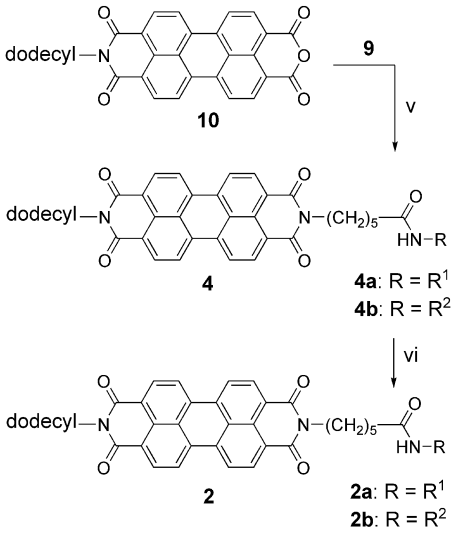
Subsequently, the dumbbell-shaped PBIs **3** were synthesized by treatment of PTCDA (**5**) with two equivalents of the corresponding dendritic amines **9** (Scheme 2). Imidazole was used as basic solvent and zinc acetate served as Lewis acid catalyst following the procedure of Langhals and Wescott.[12] The water-soluble PBIs **1** were then generated by acidic cleavage of the peripheral *tert*-butyl groups of **3** (Scheme 2).



Scheme 2. Synthesis of the water-soluble PBIs **1**. iii) imidazole, zinc acetate, 110 °C, 2 h; iv) formic acid, r. t., 24 h.

For the synthesis of the asymmetric PBI amphiphiles **2** first the *N*-dodecylperylene monoanhydride monoimide **10** was prepared via the perylene monoanhydride monopotassium salt as described previously.[12a,15] Subsequently, **10** was treated with the dendrons **9** to give the protected derivatives **4** (Scheme 3). The final step in the synthesis of the amphiphiles **2** is the acidic deprotection of the *tert*-butyl groups. The deprotected dendritic PBIs **1** and **2b** are highly soluble in buffered water at pH 7.2. Amphiphile **2a**, however, bearing only three acid groups is insoluble in water. It is soluble, for example, in mixtures of chloroform with formic acid or trifluoroacetic acid. The PBIs **1**–**4** form red to

black solids. In solution they exhibit intensive colours and strong fluorescence which varies from red to green depending on the concentration.



Scheme 3. Synthesis of the amphiphilic PBIs **2**. v) imidazole, zinc acetate, 160 °C, 2 h; iv) formic acid, r. t., 24 h.

The electronic absorption spectra of the deprotected amphiphiles **1** and **2b** in water taken at a concentration of 10^{-5} mol/L are depicted in Figure 3. In the case of the dumbbell-shaped amphiphile **1b** carrying two bulky 2G-dendrons three main bands are observed between 450 and 550 nm. The most intensive band appears at λ_{max} = 534 nm. The observed pattern is due to well-resolved vibronic fine structure belonging to the S_0–S_1 transition of the perylene chromophores with a transition dipole moment along the long molecular axis.[13] The overall features of the spectrum is indicative of no or a very low degree of aggregation involving π-π stacking interactions between the perylene moieties. The corresponding 1G-dumbbell **1a** and the amphiphile **2b**, however, whose perylene chromophores are less sterically shielded show absorption spectra with typical bands for aggregated perylene dyes which are in this case hypsochromically shifted (Figure 3).[3a] All over the absorption intensities decrease compared to **1b** and the second band at λ_{max} = 500 nm becomes now the most intensive. Interestingly, for **1a** and **2b** the absorption patterns do not change significantly down to concentrations of 10^{-7} mol/L. Below this concentration the signal to noise ratio is so low, that the expected de-aggregation cannot be observed clearly, at least not by this spectroscopic method.

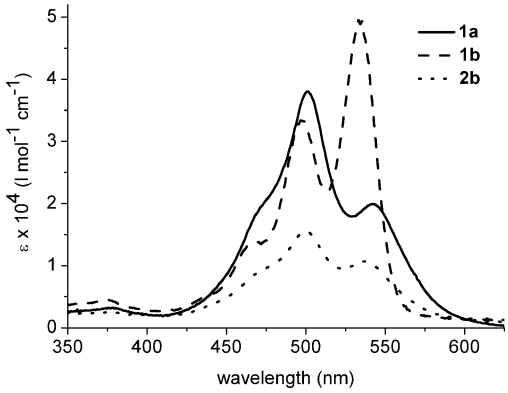


Figure 3. Absorption spectra (room temperature) of **1a**, **1b** and **2b** in water (phosphate buffer, pH 7.2) at a concentration of 10^{-5} mol/L).

On the other hand aggregation of the G2 dumbbell **1b** cannot be observed up to a concentration of 1×10^{-4} M. Higher concentrated solutions cannot be analyzed quantitatively, since the absorptions are getting too concentrated. Obviously, the dumbbell **1b** carrying two bulky G2 dendrons exhibits a considerably less pronounced tendency to form π-stacking arrangements than **1a** and **2b**, whose perylene moieties can be approached by an adjacent molecule much easier.

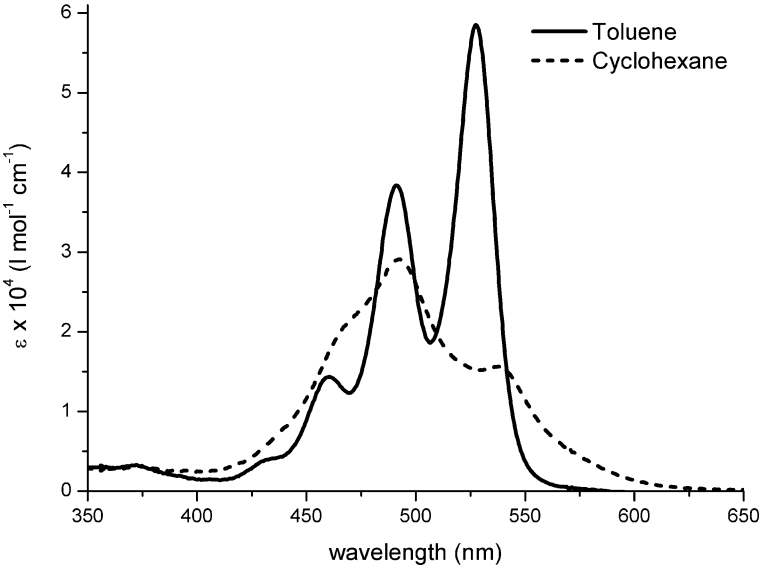


Figure 4. Absorption spectra (room temperature) of **3b** in toluene and cyclohexane at a concentration of 10^{-5} mol/L.

Similar investigations of the protected counterparts **3** and **4** in toluene as solvent reveal a significantly different behaviour. At a concentration of 10^{-5} mol/L in all cases the typical feature of de-aggregated PBIs are found independent of the nature of the peripheral substituent (Figure 5). Increasing the concentration to more than 10^{-4} mol/L still did not lead to any indication for aggregation. Beyond this concentration the absorptions are getting so intensive that UV/Vis spectroscopy with 4 mm cuvettes cannot be used for a proper characterization of the aggregation properties. Similar results were obtained when using chloroform or methanol as solvents. In contrast, when using cyclohexane as solvent aggregation of the protected 2nd-generation PBIs **3b** and **4b** is promoted even at comparatively low concentrations (10^{-5} mol/L) (Figure 4). However, the 1st-generation analogues **3a** and **4a** are not soluble in cyclohexane.

Since the transition between the monomeric and the aggregated states cannot be investigated with UV/Vis spectroscopy, fluorescence spectra of the compounds in the concentration range of 10^{-3} to 10^{-7} M were recorded. As shown in Figure 5 the fluorescence spectra of **3** and **4** in toluene look like mirror images of the corresponding absorption spectra at low concentrations.

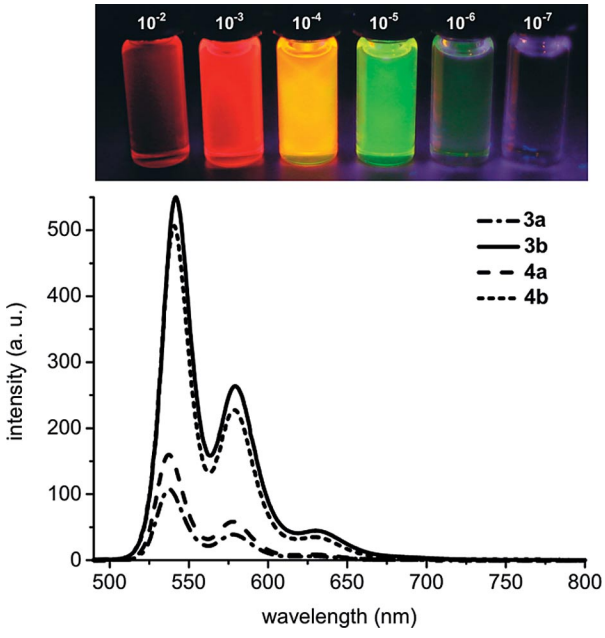


Figure 5. Fluorescence spectra of the protected PBIs **3** and **4** at 10^{-6} M concentrations in toluene (bottom) and fluorescence of **3b** at different concentrations in toluene, excited at 366 nm (top).

Figure 5 shows the influence of the steric requirement of the dendrons. At the same concentration the smaller 1st-generation PBIs **3a** and **4a** are more tightly stacked than the 2nd-generation derivatives **3b** and **4b** and therefore the fluorescence quenching is more pronounced.

The fluorescence spectra of the water-soluble perylene dyes **1** and **2b** display qualitatively the same features as those found for the corresponding protected precursors **3** and **4**, but the intensities of the absorption bands are much lower (Figure 6). As it was also shown for **3** and **4**, the overall steric requirement of the dendrons in **1** and **2b** influences the aggregation of the perylene dyes. The less hindered symmetrical 1G-dendronized **1a** and the amphiphilic 2G-dendronized **2b** aggregate more strongly resulting in more reduced fluorescence intensity than the **1b** carrying two bulky 2G dendrons.

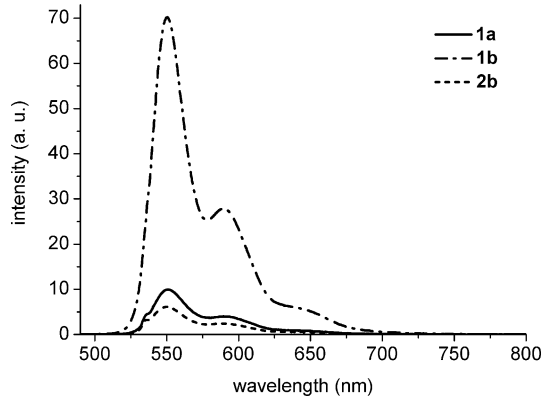


Figure 6. Fluorescence spectra of the water-soluble symmetric and amphiphilic PBIs **1** and **2b** at 10^{-6} M concentrations in water (phosphate buffer, pH = 7.2).

Except for differences in the absolute intensity and slight shifts of the fluorescence maxima, the concentration-dependent fluorescence spectra show the same trends for all synthesized symmetric, asymmetric, protected and free-acid PBIs **1**–**4**. As an example, the quantitative spectra of the amphiphilic 2G-dendronized perylene **2b** is shown in Figure 7. In all cases the fluorescence maximum is batho-

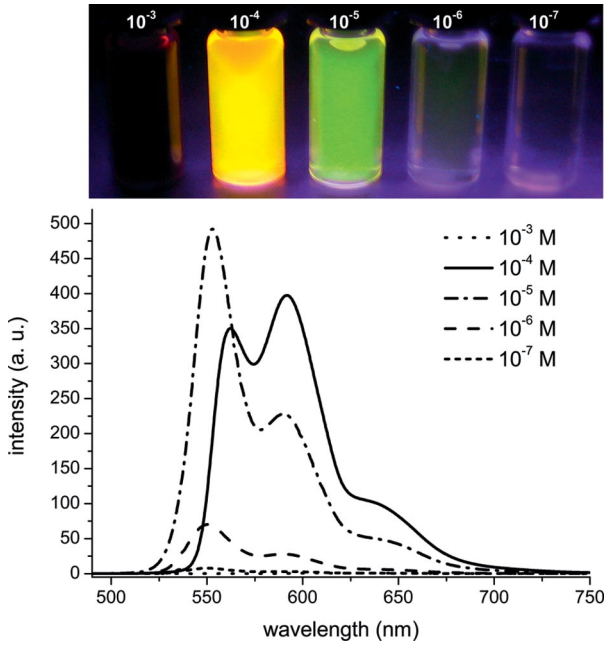


Figure 7. Bottom: quantitative fluorescence spectra of **1b** in phosphate buffered water (pH 7.2) from 10^{-3} to 10^{-7} M. Top: fluorescence of PBI **1b** at different concentrations in phosphate buffer solution (pH 7.2), excited at 366 nm.

chromically shifted from 537/550 (10^{-7}–10^{-5} M) to 630–700 nm (10^{-4}–10^{-3} M). The intensity first increases and then is drastically quenched at higher concentrations (see Figures 7, 8 and 9).

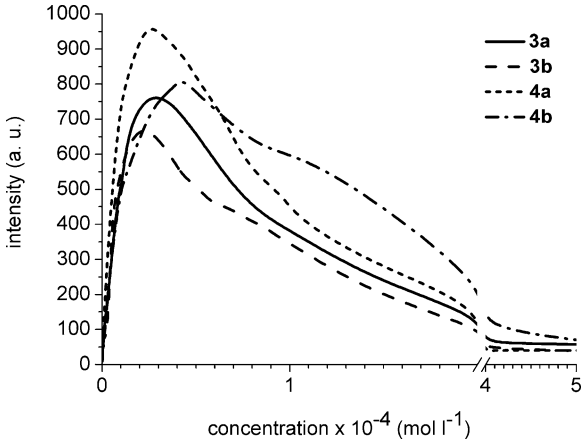


Figure 8. Fluorescence intensity as function of the concentration of **3** and **4** in toluene.

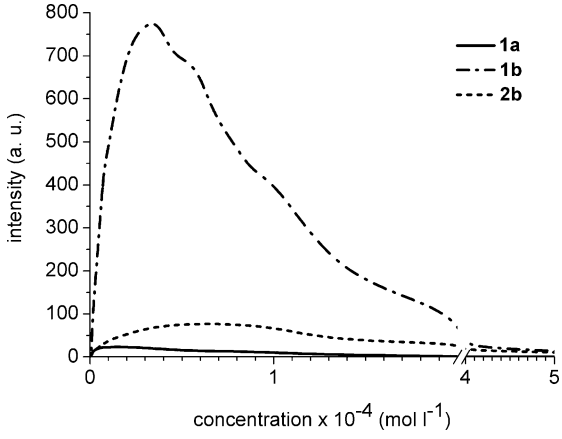


Figure 9. Fluorescence intensity as function of the concentration of **1** and **2b** in phosphate-buffered water at pH 7.2.

For further comparison of the influence of the steric hindrance on the aggregation behaviour, the fluorescence intensities as a function of the concentration are displayed in Figures 8 and 9. Increasing the concentration of **3** and **4** in toluene from 10^{-7} M to about 10^{-5} M causes more intense fluorescence intensity. Further an increase of concentration causes the fluorescence to be successively quenched due to aggregation. In general the fluorescence intensity of the 1G-compounds **3a** and **4a** are lower than those of the corresponding 2G-derivatives **3b** and **4b**.

Figure 9 shows that the least hindered water-soluble 1G-derivatives **1a** exhibit the lowest fluorescence intensity in the whole concentration range. Also in the case of the amphiphilic 2G-system **2b** pronounced fluorescence quenching in the entire concentration regime is observed. However, in the case of sterically most hindered symmetrically 2G-den-

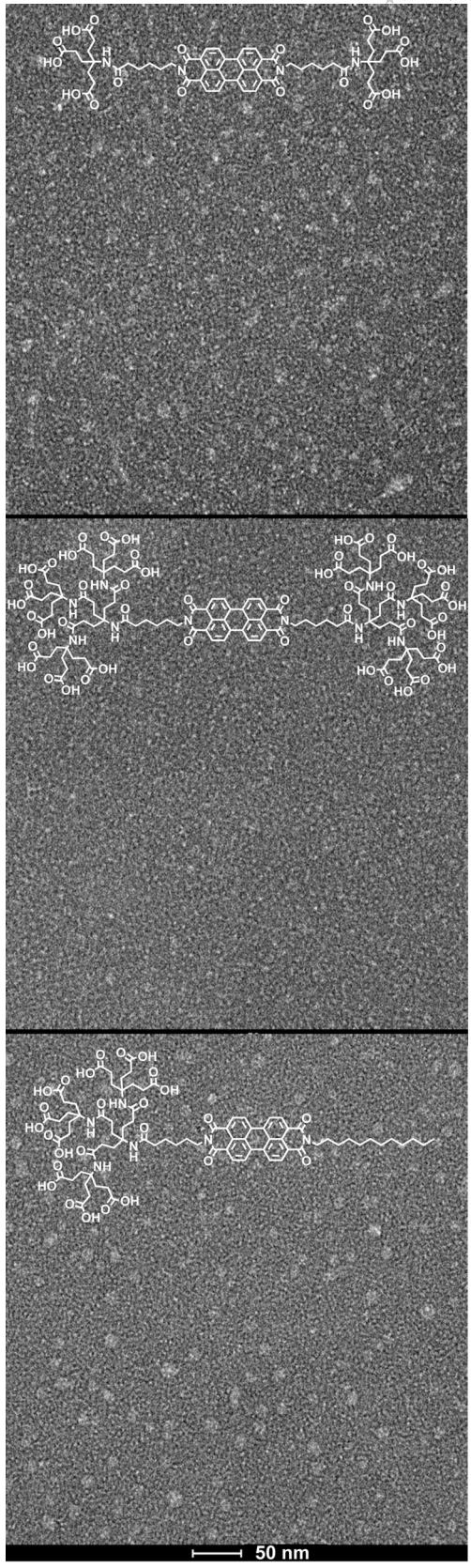


Figure 10. TEM images of compounds **1a** (top), **1b** (middle) and **2b** (bottom) each prepared from 10^{-3} M solutions in phosphate-buffered water at pH 7.2 and stained with 2% phosphotungstic acid in 1% trehalose.

dronized **1b** a fluorescence quenching behaviour is found that is similar to those of all protected precursors **3** and **4**.

For further investigations of the aggregation behaviour of compounds **1a**,**b** and **2b** in water, TEM images were recorded (Figure 10).

For the symmetrical 1G-PBI **1a**, irregularly shaped aggregates are observed in the TEM micrograph (Figure 10, top). The size of the corresponding micelles varies from 5.7 nm to 38.5 nm. The TEM image of the symmetric 2G-PBI **1b** display only very small aggregates with a maximum diameter of 4 nm diameter (Figure 10, middle). In Figure 10 at the bottom the comparatively regularly shaped globular micelles of the 2G-amphiphile **2b** are shown. Most of the micelles have a diameter of 16.0 nm.

Conclusions

We have presented the synthesis and characterization of three very water-soluble perylene bisimides **1** and **2b**. The water solubility is provided by peripheral dendronization with 1G- and 2G-Newkome dendrons. Their aggregation behaviour in water depends strongly on the overall steric requirement of the attached dendrons. Compared to the precursor molecules **3** and **4**, which are soluble in organic solvents the aggregation of **1** and **2b** is further facilitated by hydrophobic interactions between the perylene core and the water subphase. The symmetric 1G-dendronized **1a** aggregates more strongly than its 2G-counterpart **1b**, which is demonstrated by optical spectroscopy and transmission electron microscopy (TEM). The asymmetric derivative **2b**, although containing a bulky 2G-dendron, reveals pronounced aggregation properties due to the presence of the flexible and non-bulky dodecyl substituent. Within this series of amphiphiles it forms the most regularly shaped micelles in water (pH 7.2) with a mean diameter of 16 nm as demonstrated by TEM. Its 1G-analogue is not soluble in water, because the presence of just one 1G-Newkome dendron does not provide sufficient overall hydrophilicity. These new amphiphilic perylenes have potential as membrane labels both in artificial and biological systems.

Experimental Section

Materials and Methods: The precursor molecules **6** and **7** were synthesized according to literature procedures.[8,17] *N*-Dodecyl-3,4,9,10-perylenetetracarboxylic 3,4-anhydride 9,10-imide was synthesized via the method described of Nagao et al.[15] ^{1}H and ^{13}C NMR spectra were recorded with a Jeol JNM EX 400, Jeol JNM GX (each 400 MHz for ^{1}H and 100 MHz for ^{13}C) and a Jeol Bruker Avance 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer. Chemical shifts are reported in ppm at room temperature (r. t.) using $CDCl_3$ as solvent and internal standard unless otherwise indicated. Abbreviations used for splitting patterns are s = singlet, d = doublet, t = triplet, m = multiplet. IR spectra were recorded with an ASI React IR™ 1000 spectrometer. For UV/Vis spectra a Specord S 600 was used. Fluorescence was measured with a Shimadzu RF-5301 PC spectrometer. FAB-Mass spectrometry was carried out on a Micromass Zabspec (Cs+) spectrometer with 3-nitrobenzyl alcohol as matrix. For elemental analyses a CE instrument EA 1110 CHNS was used.

Transmission Electron Microscopy: Droplets of the sample solution (5 μL) were applied on hydrophilised [60 s glow discharging in a BALTEC MED 020 (BALTEC, Liechtenstein) at 8 W] Formvar®-supported carbon-coated copper grids (400 mesh) for 30 s. The supernatant fluid was removed by blotting with a filter paper; then a droplet of 2% (w/v) phosphotungstic acid (PTA) in 1% (w/v) trehalose (pH 7.2) was applied for another 60 s. The contrasting material was removed by means of filter paper and the sample was allowed to dry in the air. Trehalose is knowingly beneficial for the preservation of irradiation-sensitive materials upon drying as it is thought to replace or retain structural water.[16] The contrast of the small objects, especially in the case of compound **1b**, was found to be significantly improved by the trehalose if compared with conventional staining with PTA alone.

The dried samples were inserted into a Tecnai F20 TEM (FEI company, Oregon, USA) equipped with a Schottky field emission gun illumination. Images were taken at an accelerating voltage of 160 kV using a FEI Eagle 2k CCD camera (binning: 1x; integration time: 1 s) at a calibrated pixel size of 0.2268 nm/pixel, which is equivalent to a magnification of 100000-fold.

General Procedure for the Preparation of 8–9: 6-[(Benzyloxycarbonyl)amino]caproic acid (**7**) was stirred for 14 d in DMF at r. t. with 1.5 equiv. of DCC, HOBT, DMAP and di-*tert*-butyl 4-amino-4-(2-*tert*-butoxycarbonylethyl)heptanedioate (**6a**) for the formation of **8a** or with **6b** for the formation of **8b**. The products **8** where then deprotected via hydrogenation with Pd/C in ethanol for 5 h to give the free amines **9**.

General Procedure for the Preparation of 1–4: The amines **9a** and **9b** were condensed with 3,4:9,10-perylenetetracarboxylic dianhydride (**5**) or *N*-dodecyl-3,4,9,10-perylenetetracarboxylic 3,4-anhydride 9,10-imide (**10**), respectively in the presence of 20 equiv. of imidazole and 0.3 equiv. of zinc acetate.[12] For the symmetric compounds **3** and the asymmetric systems **4** reaction temperatures of 110 °C and 160 °C, respectively, were applied. The corresponding free acids **1a/b** and **2a/b** were obtained by stirring **3a/b** and **4a/b** with formic acid for 24 h at room temperature.

6-[(Benzyloxycarbonyl)amino]capronamide Derivative 8a: Yield 1.729 g (55.7%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.26 (m, 2 H, CH_2), 1.32 (s, 27 H, CH_3), 1.40, 1.55 (m, 4 H, CH_2), 1.84 (m, 6 H, CH_2), 1.98 (m, 2 H, CH_2), 2.10 (m, 6 H, CH_2), 3.08 (m, 2 H, CH_2), 4.78 (br. s, 1 H, NH), 5.00 (s, 2 H, Ar-CH_2-O), 5.75 (br. s, 1 H, NH), 7.24 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.04, 26.12 (2 C, CH_2), 27.85 (9 C, CH_3), 29.40 (1 C, CH_2), 29.62 (3 C, CH_2), 29.72 (3 C, CH_2), 36.93 (1 C, CH_2), 40.63 (1 C, CH_2), 57.10 (1 C, quat. C-N), 66.23 (1 C, benzyl-CH_2), 80.40 (3 C, quat. C *t*Bu), 127.74, 127.82, 128.24 (5 C, Ar-CH), 136.54 (1 C, Ar-C), 156.25 (1 C, NHCOOR), 172.13 (1 C, CONH), 172.64 (3 C, COOR) ppm. IR: $\tilde{\nu}$ = 3381, 3347, 2980, 2945, 1722, 1698, 1671, 1532, 1459, 1417, 1393, 1366, 1324, 1305, 1254, 1216, 1197, 1150, 1108, 1038, 1000, 969, 946, 845, 779, 753, 699, 634 cm^{-1}. $C_{36}H_{58}N_2O_9$ (664): calcd. C 65.25, H 8.82, N 4.23; found C 65.18, H 8.95, N 4.36.

6-Aminocapronamide Derivative 9a: Yield 1.411 g (92.4%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.38 (s, 27 H, CH_3 + m, 2 H, CH_2), 1.45 (m, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 1.93 (m, 6 H, CH_2), 2.08 (t, ^3J = 7.35 Hz, 2 H, CH2), 2.16 (m, 6 H, CH_2), 2.69 (t, ^3J = 6.97 Hz, 2 H, CH_2), 2.98 (br. s, 2 H, NH_2), 6.00 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.29, 26.20 (2 C, CH_2), 27.99 (9 C, CH_3), 29.68, (3 C, CH_2), 29.78 (3 C, CH_2),

31.98 (1 C, CH_2), 37.10 (1 C, CH_2), 41.36 (1 C, CH_2), 57.23 (1 C, quat. C-N), 80.62 (3 C, quat. C *t*Bu), 172.49 (1 C, CONH), 172.89 (3 C, COOR) ppm. IR: $\tilde{\nu}$ = 3304, 2980, 2937, 2872, 1725, 1644, 1548, 1459, 1420, 1393, 1366, 1316, 1251, 1216, 1146, 1100, 1038, 950, 849, 760, 679 cm^{-1}. $C_{28}H_{52}N_2O_7$ (530) × 0.17 $CHCl_3$: calcd. C 61.74, H 9.66, N 5.09; found C 61.66, H 9.58, N 5.11.

Compound 8b: Yield 5.677 g (86.9%).^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.41 (s, 81 H, CH_3), 1.55 (m, 6 H, CH_2), 1.94 (m, 24 H, CH_2), 2.16 (m, 26 H, CH_2), 3.19 (m, 2 H, 18), 5.07 (s, 2 H, Ar-CH_2-O), 5.26 (m, 1 H, NH), 6.09 (br. s, 3 H, NH), 7.31 (m, 5 H, Ar-CH), 7.68 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.30, 25.24, 26.17 (3 C, CH_2), 28.04 (27 C, CH_3), 29.49, 29.76 (18 C, CH_2), 31.69 (3 C, CH_2), 31.90 (3 C, CH_2), 36.93 (1 C, CH_2-CO), 40.81 (1 C, CH_2-NH), 57.46 (3 C, quat. C-N), 57.63 (1 C, quat. C-N), 66.43 (1 C, Ar-CH_2-O), 80.57 (9 C, quat. C *t*Bu), 127.91, 128.04, 128.40 (5 C, Ar-CH), 136.76 (1 C, Ar-C), 156.47 (1 C, NHCOOBz), 172.67 (9 C, COOR), 172.88 (3 C, CONH), 173.31 (1 C, CONH) ppm. IR: $\tilde{\nu}$ = 3308, 2976, 2934, 1725, 1652, 1536, 1455, 1420, 1393, 1366, 1316, 1251, 1216, 1150, 1104, 1031, 953, 849, 757, 699 cm^{-1}. $C_{90}H_{151}N_5O_{24}$ (1688): calcd. C 64.07, H 9.02, N 4.15; found C 63.83, H 8.92, N 4.25.

Compound 9b: Yield 0.245 g (96.04%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.42 (s, 81 H, CH_3), 1.67, 1.85 (m, 6 H, CH_2), 1.96 (m, 24 H, CH_2), 2.19 (m, 26 H, CH_2), 2.75 (t, ^3J = 6.69 Hz, 2 H, CH_2), 3.28 (br. s, 2 H, NH_2), 6.40 (br. s, 3 H, NH), 7.30 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 25.56, 26.24 (2 C, CH_2), 28.05 (27 C, CH_3), 29.70, 29.80 (18 C, CH_2), 30.66 (1 C, CH_2), 31.72, 31.92 (6 C, CH_2), 36.67 (1 C, CH_2), 40.94 (1 C, CH_2-NH_2), 57.52 (3 C, quat. C-N), 58.18 (1 C, quat. C-N), 80.55 (9 C, quat. C *t*Bu), 172.80 (9 C, COOR), 173.19 (3 C, NHCO), 173.60 (1 C, NHCO) ppm. IR: $\tilde{\nu}$ = 3277, 2980, 2934, 1725, 1652, 1544, 1455, 1420, 1396, 1366, 1316, 1254, 1216, 1146, 1104, 1038, 953, 849, 757, 687 cm^{-1}. $C_{82}H_{145}N_5O_{22}$ (1553) × 0.5 $CHCl_3$: C 61.44, H 9.09, N 4.34; found C 61.63, H 8.86, N 4.54.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 3a:** Prepared from **9a** (1.00 g, 1.89 mmol) and PTCDA (0.376 g, 0.95 mmol). Purified by column chromatography in $CHCl_3$. Yield 1.03 g (78.5%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.41 (s, 54 H, CH_3), 1.48 (m, 4 H, CH_2), 1.75 (m, 12 H, CH_2), 1.96 (m, 12 H, CH_2), 2.20 (m, 16 H, CH_2), 4.15 (t, ^3J = 7.16 Hz, 4 H, CH_2-N), 5.94 (br. s, 2 H, NH), 8.19 (m, 4 H, Ar-CH), 8.39 (m, 4 H, Ar-CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 25.32, 26.61, 27.47 (6 C, CH_2), 28.01 (18 C, CH_3), 29.73 (6 C, CH_2), 29.81 (6 C, CH_2), 37.13 (2 C, CH_2), 40.28 (2 C, CH_2), 57.21 (2 C, quat. C-N), 80.53 (6 C, quat. C *t*Bu), 122.67, 122.91, 125.64, 128.77, 130.85, 133.83 (20 C, Ar-C), 162.88 (4 C, CON), 172.40 (2 C, CONH), 172.83 (6 C, COOR) ppm. IR: $\tilde{\nu}$ = 3323, 2976, 2934, 2868, 1729, 1698, 1656, 1594, 1540, 1455, 1405, 1366, 1316, 1251, 1216, 1150, 1104, 1038, 953, 849, 811, 745 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 458 nm, 489, 526; fluorescence: λ_{max} = 533 nm, 575, 622. $C_{80}H_{108}N_4O_{18}$ (1413) × 0.25 $CHCl_3$: C 66.77, H 7.56, N 3.88; found C 66.70, H 7.24, N 3.97.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 3b:** Prepared from **9b** (0.403 g, 0.259 mmol) and PTCDA (0.051 g, 0.131 mmol). Purified by column chromatography with ethyl acetate. Yield 0.293 g (65.25%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.35 (s, 162 H, CH_3 + m. 4 H, CH_2), 1.64 (m, 4 H, CH_2), 1.74 (m, 4 H, CH_2), 1.95 (m, 48 H, CH_2), 2.13 (m, 52 H, CH_2), 4.16 (t, ^3J = 6.47 Hz, 4 H, CH_2-N), 6.15 (br. s, 6 H, NH), 7.22 (br. s, 2 H, NH), 8.58 (m, 8 H, Ar-CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 25.01, 26.45, 27.58 (6 C, CH_2), 27.91 (54 C, CH_3), 29.63 (18 C, CH_2), 29.66 (18 C, CH_2), 31.54 (6 C, CH_2), 31.63 (6 C, CH_2), 36.73 (2 C, CH_2CO), 40.35 (6 C, CH_2), 57.30 (6 C, quat. C-N), 60.26 (2 C, quat. C-N), 80.42 (18 C, quat. C *t*Bu), 123.18, 126.35, 129.29, 131.47, 134.60 (20 C, Ar-C), 163.42 (4 C, CON), 172.70 (18 C, COOR), 172.91 (6 C, CONH), 173.13 (2 C, CONH) ppm. IR: $\tilde{\nu}$ = 2976, 1729, 1656, 1594, 1544, 1455, 1393, 1366, 1316, 1254, 1216, 1150, 1100, 1031, 957, 849, 811 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 458 nm, 489, 526; fluorescence: λ_{max} = 533 nm, 576, 621. $C_{188}H_{294}N_{10}O_{48}$ (3461) × 1 $CHCl_3$: C 63.38, H 8.30, N 3.91; found C 63.63, H 8.60, N 3.73.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 1a:** Yield 0.386 g (99.04%). ^{1}H NMR (300 MHz, $CDCl_3$:TFA, 3:1, 25 °C): δ = 1.55 (m, 4 H, CH_2), 1.82 (m, 8 H, CH_2), 2.20 (m, 12 H, CH_2), 2.43 (m, 4 H, CH_2), 2.52 (m, 12 H, CH_2), 4.30 (t, ^3J = 7.35 Hz, 4 H, CH_2-N), 6.70 (br. s, 2 H, NH) 8.06 (s, 3 H, COOH), 8.74 (m, 8 H, Ar-CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 25.29, 26.12, 26.88 (6 C, CH_2), 28.23 (6 C, CH_2), 29.06 (6 C, CH_2), 36.17 (2 C, CH_2), 41.86 (2 C, CH_2-N), 59.35 (2 C, quat. C-N), 122.28, 124.39, 126.42, 129.34, 133.06, 135.82 (20 C, Ar-C), 167.58 (4 C, CON), 178.26 (2 C, CONH), 180.41 (6 C, COOH) ppm. IR: $\tilde{\nu}$ = 2930, 2856, 2706–2559, 1691, 1644, 1594, 1575, 1544, 1444, 1420, 1401, 1382, 1343, 1289, 1254, 1181, 1131, 811, 754, 721, 668 cm^{-1}. UV/Vis (phosphate buffer pH 7.2): λ_{max} = 501 nm, 537; fluorescence: λ_{max} = 549 nm, 589. $C_{56}H_{60}N_4O_{18}$ (1078) × 2 HCOOH: C 59.58, H 5.52, N 4.79; found C 59.35, H 5.69, N 4.97.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 1b:** Yield 0.082 g (98.7%). ^{1}H NMR (400 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 1.54, 1.76, 1.83 (m, 12 H, CH_2), 2.19 (m, 48 H, CH_2), 2.32 (m, 4 H, CH_2), 2.48 (m, 48 H, CH2), 4.30 (m, 4 H, CH_2), 7.10 (br. s, 6 H, NH), 7.17 (2 H, NH), 8.84 (m, 8 H, Ar-CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 25.91, 26. 57, 27.26 (3 C, CH_2), 28.32 (18 C, CH_2), 29.14 (18 C, CH_2), 31.30 (6 C, CH_2), 31.96 (6 C, CH_2), 36.47 (2 C, CH_2), 41.59 (2 C, CH_2), 59.53 (2 C, quat. C-N), 59.79 (6 C, quat. C-N), 122.62, 124.84, 126.98, 129.85, 133.66, 136.58 (20 C, Ar-C), 166.29 (2 C, CONRCO), 177, 20 (6 C, CONH), 179.72 (2 C, CONH), 181.02 (18 C, COOH) ppm. IR: $\tilde{\nu}$ = 2930, 2856, 2706–2559, 1691, 1644, 1594, 1544, 1444, 1405, 1343, 1293, 1185, 1139, 1104, 834, 799, 745, 722 cm^{-1}. UV/Vis (phosphate buffer solution, pH 7.2): λ_{max} = 497 nm, 533; fluorescence: λ_{max} = 547 nm, 588. $C_{116}H_{150}N_{10}O_{48}$ (2452) × 7 HCOOH: C 53.24, H 5.96, N 5.05; found C 53.08, H 6.28, N 5.07.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 4a:** Prepared from **9a** (0.110 g, 0.208 mmol) and *N*-dodecyl-3,4,9,10-perylenetetracarboxylic 3,4-anhydride 9,10-imide (0.122 g, 0.218 mmol). Purified by column chromatography with $CHCl_3$. Yield 0.066 g (56.18%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.86 (t, ^3J = 6.84 Hz, 3 H, CH_3), 1.27 (br. m, 14 H, CH_2), 1.39 (br. m, 2 H, CH_2), 1.42 (s, 27 H, CH_3), 1.49 (m, 2 H, CH_2), 1.76 (m, 8 H, CH_2), 1.97 (m, 6 H, CH_2), 2.20 (m, 8 H, CH_2), 4.15 (m, 4 H, CH_2), 5.92 (s, 1 H, NH), 8.20 (m, 4 H, Ar-H), 8.40 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.09 (1 C, CH_3), 22.66, 25.32, 26.61, 27.17, 27.49 (5 C, CH_2), 28.04 (3 C, CH_3), 29.33, 29.78, 29.57 (3 C, CH_2), 29.62 (3 C, CH_2), 29.64 (broad, 2 C, CH_2), 29.78 (3 C, CH_2), 29.88 (broad, 2 C, CH_2), 31.90 (1 C, CH_2), 37.17 (1 C, CH_2), 40.29, 40.70 (2 C, CH_2), 57.26 (1 C, quat. C-N), 80.57 (3 C, quart- C *t*Bu), 122.65, 122.94, 123.01, 125.69, 128.80, 128.81, 130.81, 130.87, 133.82, 133.87 (20 C, CH_2), 162.90, 162.91 (4 C, CON), 172.39 (1 C, CONH), 172.85 (3 C, COOR) ppm. IR: $\tilde{\nu}$ = 2922, 2853, 1725, 1695, 1652, 1594, 1540, 1440, 1405, 1343, 1247, 1150, 1100, 1038, 1015, 953, 849, 811, 745, 676 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 458 nm, 489, 526; fluorescence: λ_{max} = 533 nm, 575, 622. $C_{64}H_{83}N_3O_{11}$ (1070) × 0.5 $CHCl_3$: C 68.55, H 7.45, N 3.72; found C 68.44, H 7.47, N 3.85.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 4b:** Prepared from **9b** (0.575 g, 0.037 mmol) and *N*-dodecyl-3,4,9,10-perylenete-

tracarboxylic 3,4-anhydride 9,10-imide (0.021 g, 0.037 mmol). Purified by column chromatography using EtOAc/$CHCl_3$ (1:1) as eluent. Yield 0.041 g (52.23%);^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.86 (m, 3 H, CH_3), 1.24 (m, 14 H, CH_2), 1.40 (m, 81 H, CH_3 and 8 H, CH_2), 1.72 (m, 6 H, CH_2), 1.95 (m, 24 H, CH_2), 2.17 (m, 26 H, CH_2), 4.20 (m, 4 H, CH_2-N), 6.13 (br. s, 3 H, NH), 7.20 (br. s, 1 H, NH), 8.58 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.08 (1 C, CH_3), 22.64 (1 C, CH_2), 24.83, 25.07, 26.48, 27.07, 27.61 (5 C, CH_2), 28.04 (27 C, CH_3), 29.31, 29.35, 29.53, 29.59, 29.62 (5 C, CH_2), 29.77, 29.82 (18 C, CH_2), 31.66, 31.67, 31.79, 31.88 (8 C, CH_2), 33.90 (1 C, CH_2), 40.42, 40.45 (2 C, CH_2-N), 57.41 (1 C, quat. C-N), 57.39 (3 C, quat. C-N), 80.42 (9 C, quat. C *t*Bu), 122.88, 123.01, 123.13, 129.09, 131.11, 131.26, 134.31, 134.36 (20 C, Ar-C), 163.29, 163.23 (4 C, CON), 172.65 (9 C, COOR), 172.87 (3 C, CONH), 173.12 (1 C, CONH) ppm. IR: $\tilde{\nu}$ = 3354, 3320, 2976, 2930, 2856, 1725, 1695, 1656, 1594, 1536, 1455, 1366, 1343, 1316, 1289, 1251, 1216, 1146, 1100, 1034, 953, 849, 811, 754, 691 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 458 nm, 489, 526; fluorescence: λ_{max} = 534 nm, 575, 620. $C_{118}H_{176}N_6O_{26}$ (2095) × 1 $CHCl_3$: C 64.55, H 8.06, N 3.80; found C 64.22, H 8.52, N 3.84.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 2a:** Yield 0.030 g (98.58%). ^{1}H NMR (300 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 0.87 (m, 3 H, CH_3), 1.28 (br. s, 18 H, CH_2), 1.58 (m, 2 H, CH_2), 1.81 (m, 6 H, CH_2), 2.21 (m, 6 H, CH_2), 2.52 (m, 8 H, CH_2), 4.27 (m, 4 H, CH_2-N), 6.85 (br. s, 1 H, NH), 8.79 (m, 8 H, Ar-CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 13.83 (1 C, CH_3), 22.77, 25.37, 26.25, 27.13, 28.20, 29.13, 29.41, 29.50, 29.64, 29.71, 29.78, 32.07 (20 C, CH_2), 36.33 (1 C, CH_2), 40.49, 42.08 (2 C, CH_2-N), 59.24 (1 C, quat. C-N), 122.27, 122.70, 124.41, 124.61, 124.57, 126.59, 126.66, 129.50, 129.55, 133.27, 135.83, 136.25 (20 C, Ar-C), 165.65, 165.73 (4 C, CON), 171.96 (1 C, CONH), 180.25 (3 C, COOH) ppm. IR: $\tilde{\nu}$ = 2953, 2922, 2853, 1695, 1652, 1594, 1556, 1509, 1440, 1405, 1378, 1343, 1305, 1254, 1185, 1158, 1089, 1015, 965, 911, 853, 811, 749, 722, 672 cm^{-1}. UV/Vis (HCOOH/$CHCl_3$ 1:1): λ_{max} = 533 nm, 496, 465; fluorescence: λ_{max} = 539 nm, 582. $C_{52}H_{59}N_3O_{11}$ (903) × 3.3 HCOOH: C 62.97, H 6.27, N 3.98; found C 63.00, H 6.30, N 3.99.

***N,N′*-Substituted Perylene-3,4:9,10-tetracarboxdiimide 2b:** Yield 0.059 g (92.86%). ^{1}H NMR (400 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 0.89 (m, 3 H, CH_3), 1.32 (m, 18 H, CH_2), 1.84 (m, 8 H, CH_2), 2.22 (m, 24 H, CH_2), 2.37 (m, 2 H, CH_2), 2.52 (m, 24 H, CH_2), 4.32 (m, 4 H, CH_2-N), 8.86 (m, 8 H, Ar-CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TFA, 1:1, 25 °C): δ = 13.62 (1 C, CH_3), 22.84 (1 C, CH_2), 24.34, 25.74, 27.22 (3 C, CH_2), 28.24, 29.11, 29.49, 29.58, 29.72, 29.79, 29.85, 29.97, 31.29, 31.82, 32.16 (33 C, CH_2), 34.47 (1 C, CH_2), 41.4, 42.19 (2 C, CH_2), 59.50 (1 C, quart- C-N), 59.76 (3 C, quat. C-N), 122.51, 122.84, 124.76, 124.90, 126.90, 129.81, 133.64, 133.71, 136.35, 136.66, 138.67 (20 C, Ar-C), 166.27, 166.29 (4 C, CONCO), 177.04 (3 C, CONH), 178.99 (1 C, CONH), 181.01 (9 C, COOH) ppm. IR: $\tilde{\nu}$ = 3331, 2922, 2849, 2768–2501, 1691, 1644, 1590, 1544, 1440, 1401, 1378, 1339, 1309, 1243, 1181, 1100, 972, 903, 853, 807, 754, 718, 672 cm^{-1}. UV/Vis (phosphate buffer solution, pH 7.2): λ_{max} = 376 nm, 500, 542; fluorescence: λ_{max} = 548 nm, 588. $C_{82}H_{104}N_6O_{26}$ (1589) × 7 HCOOH: C 55.91, H 6.22, N 4.40; found C 55.81, H 6.41, N 4.63.

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