

# Bichromophoric Perylene Derivatives: Energy Transfer from Non-Fluorescent Chromophores

Heinz Langhals\* and Sigrid Saulich<sup>[a]</sup>

**Abstract:** The energy of excitation at non-fluorescent chromophores such as fluorenone and anthraquinone has been trapped by a fast energy transfer to the highly fluorescent perylene bisimides. To this end, anthraquinone, fluorenone and anthracene derivatives have been linked to the perylene bisimides by non-conjugating spacers and fluorescence quantum yield of such assemblies have been determined as a function of the wavelengths of excitation. Energy transfer in such assemblies is strongly influenced by the orientation of the two chromophores. This is of interest for the construction of fluorescence switches.

**Keywords:** dyes/pigments • energy transfer • fluorescence • light-harvesting antennae • perylenes

## Introduction

The investigation of energy transfer processes<sup>[1]</sup> is of general interest (see for example refs. [2–9]) because of their importance for light-harvesting in bacteria and higher plants.<sup>[10, 11]</sup> Usually processes are studied that proceed between highly fluorescent energy donor and acceptor chromophores in order to prevent any loss of energy by fluorescence quenching; see for example ref. [12–14] On the other hand, one may ask if it is possible to use even non-fluorescent energy donors for light harvesting if the energy transfer to the acceptor is fast enough to compete with fluorescence quenching.

## Results and Discussion

We used perylene-3,4:9,10-tetracarboxylic bisimides (**1**)<sup>[15]</sup> as the acceptor for the study of energy transfer according to

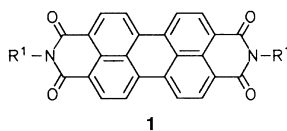


Figure 1 because of their high fluorescence quantum yield<sup>[16]</sup> which guarantees the preservation of the energy of excitation.

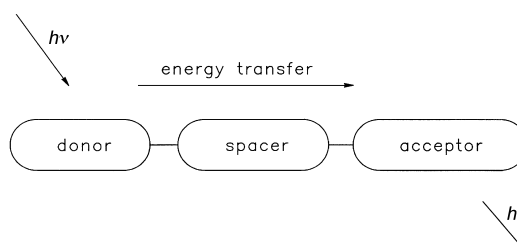


Figure 1. Energy transfer in bichromophoric dyes.

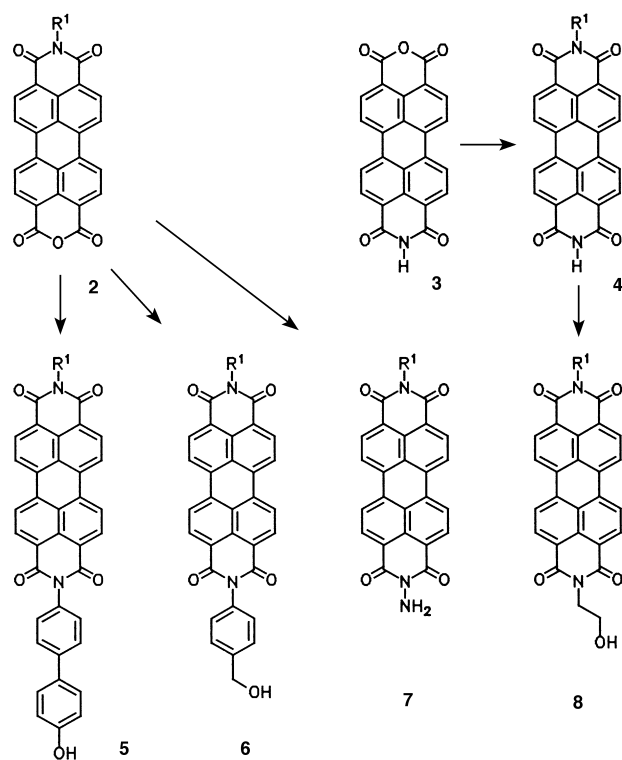
Fluorenone and anthraquinone were applied as energy donors. These chromophores exhibit only a weak fluorescence themselves.<sup>[17]</sup> Pyrene, anthracene and naphthalene derivatives have been used for comparison.

One nitrogen atom of **1** was used for linking energy donors. This is an ideal position for this purpose because there are nodes<sup>[18]</sup> in the orbitals HOMO and LUMO; this causes an efficient electronic decoupling of the attached chromophore and therefore, Förster-type energy transfer through space is preferred instead of the Dexter-type energy transfer<sup>[19, 20]</sup> through bond. A further decoupling was achieved by the introduction of  $sp^3$  hybridized links in spacers and by arranging the two chromophores orthogonal, respectively. The other nitrogen atom of **1** was used for the attachment of solubilizing groups such as long-chain *sec*-alkyl groups (“swallow-tail groups”);<sup>[21, 22]</sup> see for example **1a**) or *tert*-butylphenyl groups.<sup>[23]</sup>

The distances of the donor chromophores and their orientation versus **1** were varied. Therefore, they were both directly linked to the nitrogen atoms and by means of spacers (see Figure 1). Perylenetetracarboxylic bisimides **1** were used as one group of starting materials for synthesis. Their partial

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saponification<sup>[24]</sup> leads to the perylenetetracarboxylic anhydride imides **2**. The condensation of **2** with aromatic amines gave the directly linked bichromophoric dyes **9** (zero spacer) and with aliphatic amines dyes **10**. The condensation of **2** with 4-amino benzylic alcohol led to the dyes **6** with a hydroxybenzylic anchor group and the condensation with 4,4'-amino-hydroxybiphenyl to dyes **5** with hydroxybiphenyl anchor groups. Finally, dye **7** with the amino anchor group was obtained by the reaction of **2** with hydrazine;<sup>[25]</sup> see Scheme 1.



1, 2, 4–8	R <sup>1</sup>
a	1-hexylheptyl
b	1-heptyloctyl
c	1-nonyldecyl
d	2,5-di- <i>tert</i> -butylphenyl

Scheme 1. Preparation of perylene dyes with anchor groups.

The perylene anhydride imide **3** was obtained in a two-step synthesis from the technical perylene-3,4:9,10-tetracarboxylic bisanhydride through the easily accessible perylenetetracarboxylic anhydride monopotassium salt<sup>[24]</sup> and its condensation with ammonia.<sup>[26]</sup> The bisimides **4** were obtained by a condensation of **3** with primary amines. The hydroxyethyl anchor group, dyes **8**, was introduced by nucleophilic displacement reaction with **4**. Dye **4** was also the starting material for dyes with methylene spacers because a nucleophilic displacement reaction with benzylic bromides proceeds easily.

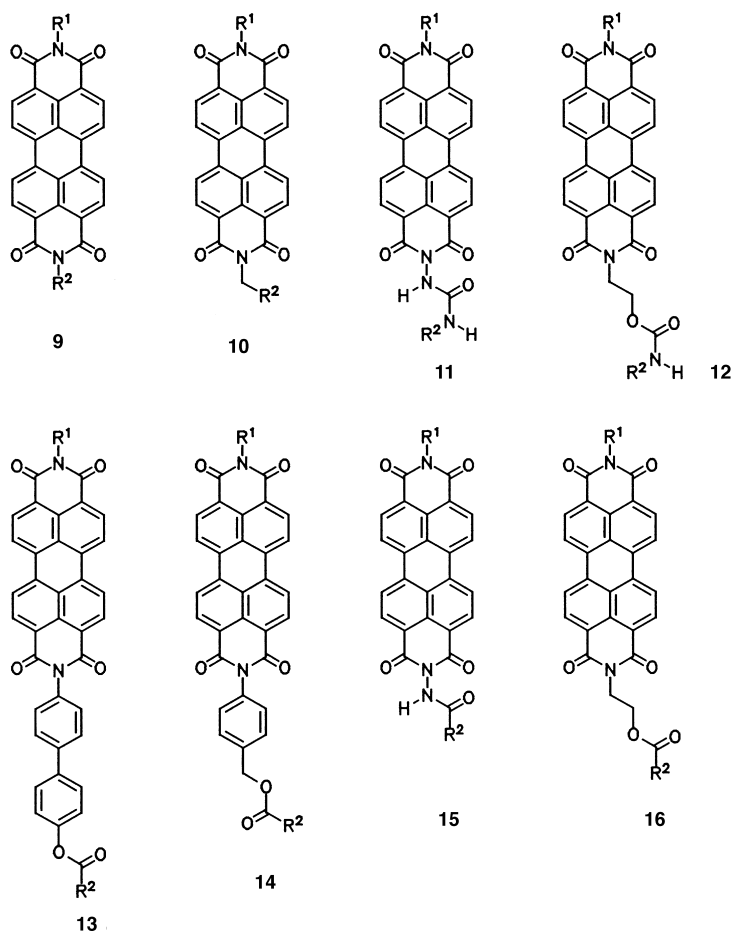
The dyes **5**, **6** and **8** with a hydroxy anchor group were linked to the second chromophore by an esterification using the corresponding carboxylic acid chlorides so that dyes **13**, **14** and **16** were obtained (see Scheme 2). The reaction of the hydroxy derivatives with isocyanates gave the urethanes **12**.

The isocyanates and the amino derivative **7** were also the starting materials for the ureas **11**. Finally, the reaction of the amine **7** with carboxylic chlorides formed the carboxylic amides **15**.

The relative energetic positions of the HOMOs of the perylenebisimide acceptor chromophore (**1**) and the donor chromophore are of central importance for the optical behaviour of the bichromophoric dyes. The position of the HOMO of **1** can be estimated to be about +1.6 V by cyclovoltammetry (oxidation; reduction: –0.54 V).<sup>[27]</sup> The attachment of electron deficient chromophores with low-lying HOMOs to **1** results in a situation according to Figure 2a which shows that the fluorescence behaviour of the acceptor chromophore (**1**) is unaffected by the attached donor chromophore. The excitation of the donor chromophore may cause an energy transfer so that the acceptor chromophore exhibits fluorescence, compare ref. [28]. However, if an electron rich donor chromophore with a high-lying HOMO is attached to **1** the completely different situation of Figure 2b will be obtained. An electronic excitation of the acceptor chromophore or an excitation by an energy transfer causes an unoccupied electronic position in HOMO that can be filled up by an electron transfer from the HOMO of the attached donor chromophore, compare ref. [29]. Thus, the completely filled HOMO of the acceptor prevents a return of the excited electron. As a consequence, a quenching of fluorescence results. Such an electron transfer between the HOMOs competes with fluorescence and the relative rates between the two processes determine the over-all fluorescence quantum yield. The rate of the electron transfer depends on the energetic difference between the two HOMOs and Marcus<sup>[30, 31]</sup> theory may be a useful approach for a quantitative description. This concept can also explain the still unresolved problem<sup>[32]</sup>(Würthner and co-worker) that the fluorescence quantum yield of a perylene bisimide with attached trialkoxyphenyl groups is low whereas a substitution of the perylene nucleus with electron donor groups increases the fluorescence quantum yield stepwise with the number of such groups; these groups increase the HOMO of the perylene dye chromophore so that it is pushed above the HOMO of the substituent.

The comparably electron rich naphthalene, anthracene and pyrene derived bichromophores exhibit low fluorescence quantum yields. This corresponds to the situation of Figure 2b. On the other hand, anthraquinone and fluorenone are sufficiently electron deficient so that the situation of Figure 2a is obtained if they are linked to the perylene bisimides; all of these derivatives exhibit high fluorescence quantum yields if the perylene bisimide chromophore is directly irradiated, for example at 490 nm. This clearly indicates additionally that the two linked chromophores are essentially independent of each other, especially, because no interference by the non-fluorescent attached chromophores is observed.

The additional absorption of the attached chromophores can be calculated from the UV/Vis spectra by subtraction of the spectrum of the basic perylene dye **1a**; the orbital nodes in HOMO and LUMO of **1** are therefore important because they isolate the attached chromophores and render the UV/Vis spectra of the perylene bisimide unit nearly independent from attached groups. We concentrated on the effects of



9-16	R <sup>1</sup>	R <sup>2</sup>
9a	1-hexylheptyl	1-anthraquinoyl
9b	1-hexylheptyl	2-anthraquinoyl
9c	1-hexylheptyl	1-anthracenyl
9d	1-hexylheptyl	2-anthracenyl
9e	1-hexylheptyl	1-naphthyl
9f	1-hexylheptyl	3-pyrenyl
9g	1-hexylheptyl	1-fluorene-9-onyl
9h	1-hexylheptyl	2-fluorene-9-onyl
9i	1-hexylheptyl	3-fluorene-9-onyl
9j	1-hexylheptyl	4-fluorene-9-onyl
10a	1-hexylheptyl	2-anthraquinoyl
10b	1-hexylheptyl	3-pyrenyl
10c	1-hexylheptyl	9-anthracenyl
11a	1-hexylheptyl	2-anthraquinoyl
11b	1-hexylheptyl	2-fluorene-9-onyl
12a	1-hexylheptyl	2-anthraquinoyl
12b	1-heptyloctyl	2-anthraquinoyl
12c	1-hexylheptyl	1-naphthyl
13a	1-hexylheptyl	2-anthraquinoyl
14a	1-hexylheptyl	2-anthraquinoyl
14b	1-hexylheptyl	2-fluorene-9-onyl
15a	1-hexylheptyl	2-anthraquinoyl
15b	1-hexylheptyl	2-fluorene-9-onyl
16a	1-hexylheptyl	2-anthraquinoyl
16b	1-heptyloctyl	2-anthraquinoyl
16c	1-hexylheptyl	1-fluorene-9-onyl
16d	1-hexylheptyl	2-fluorene-9-onyl
16e	1-heptyloctyl	2-fluorene-9-onyl
16f	1-hexylheptyl	4-fluorene-9-onyl
16g	2,5-di- <i>tert</i> -butylphenyl	2-fluorene-9-onyl

Scheme 2. Bichromophoric perylene dyes.

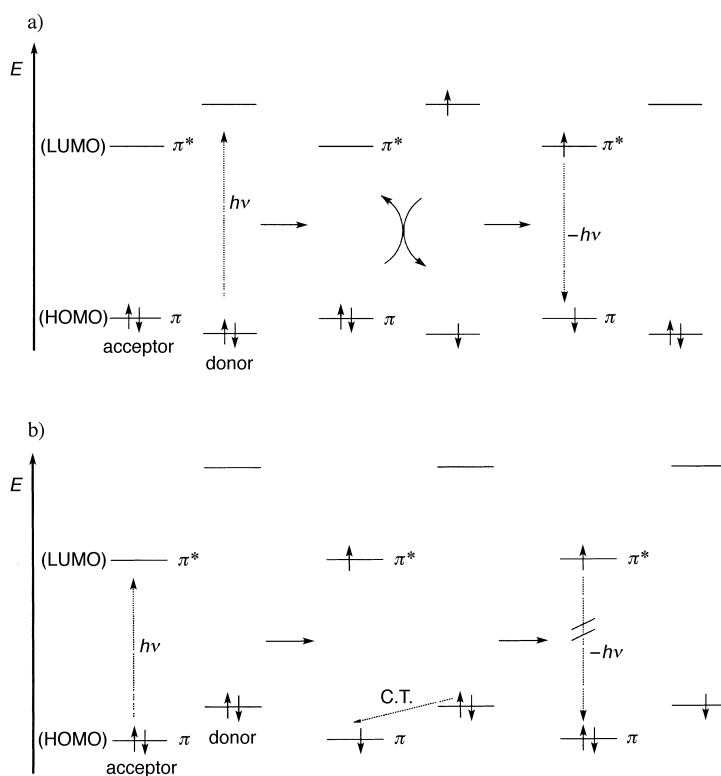


Figure 2. Energy and electron transfer in bichromophoric dyes as discussed in the text.

anthraquinone as a donor chromophore because the absorption of the fluorenone is mainly below 300 nm and thus causes more experimental difficulties. The additional absorption by the anthraquinone chromophore lies between 300 and 350 nm and it is in this spectral region about twice as high as the absorption of the perylene bisimide.

A plot of the fluorescence quantum yield as a function of the wavelengths of excitation is a useful indicator of the efficiency of energy transfer between the two chromophores. One finds high fluorescence quantum yields, nearly unity, for the majority of anthraquinone containing bichromophores (9–16) if the region of long wavelength is irradiated (chromophore of 1) and a sharp drop is found: for the irradiation

tion at about 350 nm; see for example **16a** in Figure 3 and **10a** where the spacer is longer and more flexible in Figure 4 (a rather high level of noise is obtained at about 400 nm because of the low absorptivity of the dye in this spectral region) or in **9b** with a zero spacer; see Figure 5. The constantly high fluorescence quantum yield in the region of long wavelengths is an additional indicator for the independency of the two chromophores. A further proof of this independence is given

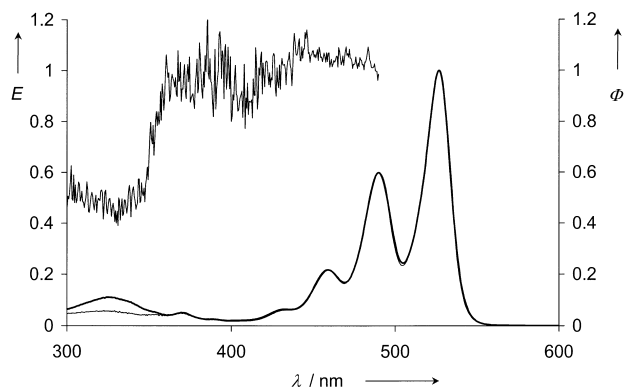


Figure 3. UV/Vis absorption spectra ( $E$ ) of dye **16a** (thick line) compared with **1a** (thin line) in chloroform and fluorescence quantum yield ( $\Phi$ ) of **16a** as a function of the wavelength of excitation (upper noisy line); emission at 577 nm.

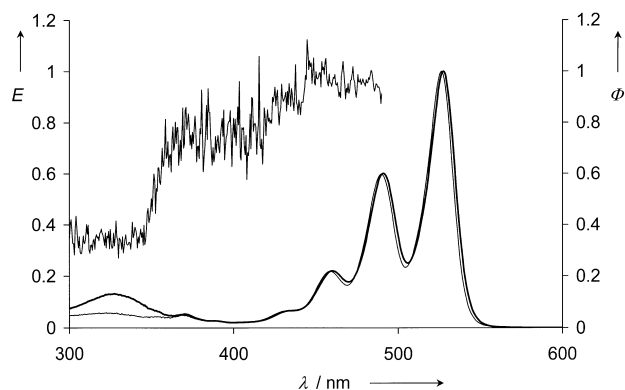


Figure 4. UV/Vis absorption spectra ( $E$ ) of dye **10a** (thick line) compared with **1a** (thin line) in chloroform and fluorescence quantum yield ( $\Phi$ ) of **10a** as a function of the wavelength of excitation (upper noisy line); emission at 577 nm.

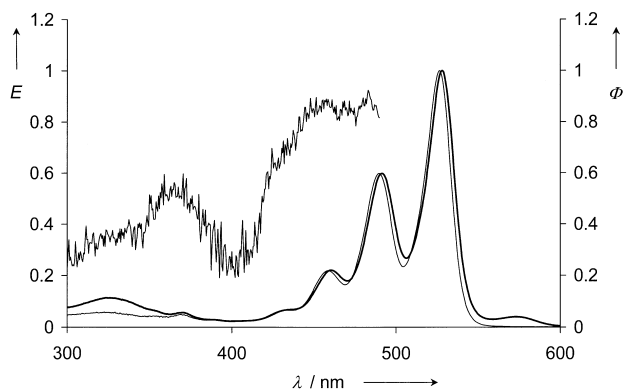


Figure 5. UV/Vis absorption spectra ( $E$ ) of dye **9b** (thick line) compared with **1a** (thin line) in chloroform and fluorescence quantum yield ( $\Phi$ ) of **9b** as a function of the wavelength of excitation (upper noisy line); emission at 577 nm.

by the measurements of fluorescence lifetimes;<sup>[33]</sup> these are independent of the attached chromophore and identical with the monochromophoric dye **1a**; see Table 1. The conclusion is that the influence of the second chromophore on the electronic transitions of the perylene bisimide units (**1**) is negligible.

Table 1. Fluorescence lifetimes of perylene dyes in chloroform.

Dye	$\lambda_{\text{exc}}^{[a]}$ [nm]	$\lambda_{\text{em}}^{[b]}$ [nm]	$\tau^{[c]}$ [ns]
<b>1a</b>	261	> 520	3.792
	300	> 500	3.958
	497	> 550	3.937
<b>16b</b>	261	> 520	3.858
	300	> 500	3.911
	497	> 550	3.901
<b>16f</b>	261	> 520	3.933
	300	> 500	3.911
	497	> 550	3.930

[a] Wavelengths of excitation. [b] Spectral region of emission. [c] Time constant for fluorescence decay (monoexponential).

The sharp drop of fluorescence quantum yield matches the additional absorption of the attached anthraquinone. Therefore, energy transfer cannot compete with fluorescence deactivation for the majority of anthraquinone derivatives and this is not dependent on whether the anthraquinone is directly connected to the imide nitrogen atom of **1** (dyes **9**) or by different spacers (dyes **10–16**); see for example **9b** in Figure 4. On the other hand, these drops proceed not to zero, but to fluorescence quantum yields of about 40%; this corresponds to the ratio of absorptivities between the linked anthraquinone and the perylenebisimide chromophore at these wavelengths. The conclusion is that the excitation of the two chromophores results in two individual and independent pathways for the fate of the energy of excitation; the energy transmitted to the anthraquinone unit will be lost, however, if energy is transferred to the perylene bisimide it cannot come to the anthraquinone chromophore and will be emitted as fluorescent light. This is remarkable because two energetically similar levels might result in mixing; see the absorption of **12a** in Figure 6 in which the attached chromophore shows an absorption over a broad spectral region.

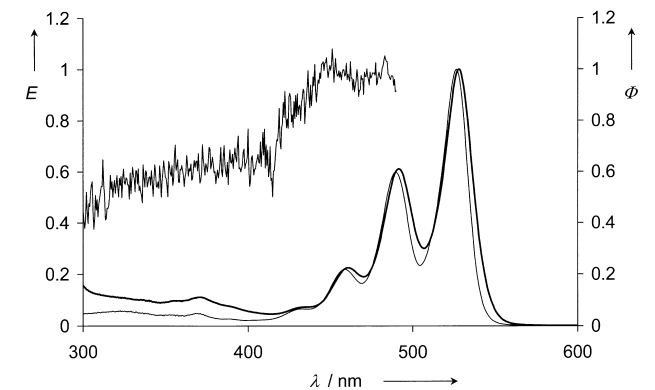


Figure 6. UV/Vis absorption spectra ( $E$ ) of dye **12a** (thick line) compared with **1a** (thin line) in chloroform and fluorescence quantum yield ( $\Phi$ ) of **12a** as a function of the wavelength of excitation (upper noisy line); emission at 577 nm.

The anthraquinone derivative **9a** is an exception to this behaviour because an unaltered high fluorescence quantum yield is observed even for an excitation between 300 and 350 nm where the anthraquinone unit absorbs light; see Figure 7. The conclusion is that in **9a** a very efficient energy transfer proceeds from the anthraquinone chromophore to the perylene bisimide chromophore. This is remarkable because no such energy transfer proceeds in the position isomeric dyes **9b**. This is certainly a consequence of the special and rigid orientation of the two chromophores. Therefore, the orientation of two chromophores is of special importance for the efficiency of energy transfer, especially for transfer from chromophores with low fluorescence quantum yields.

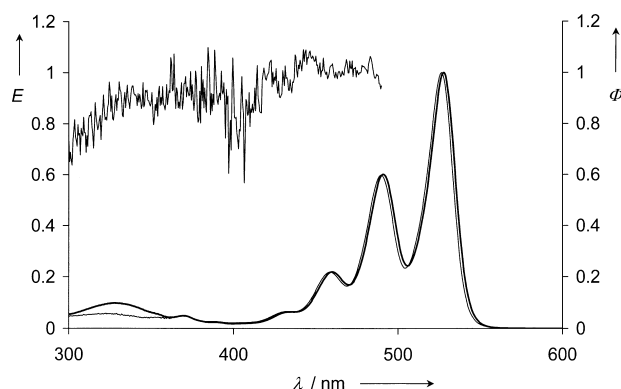


Figure 7. UV/Vis absorption spectra ( $E$ ) of dye **9a** (thick line) compared with **1a** (thin line) in chloroform and fluorescence quantum yield ( $\Phi$ ) of **9a** as a function of the wavelength of excitation (upper noisy line); emission at 577 nm.

where there are maxima in the absorption of the anthracene unit; see Figure 8. This indicates that there is not only a fluorescence quenching by the attached anthracene unit, but also an independent way for energy loss if the anthracene unit is optically excited; this is in as far remarkable as many 9-anthracenyl derivatives exhibit strong fluorescence. A possible explanation for the unusual behaviour of the anthracenyl derivative is given by the fact that it is appreciably less photostable than the other perylene derivatives. Many reaction products are found after irradiation for several days with sunlight. These products could not be separated; however, the UV/Vis spectrum of the mixture clearly indicates that the perylene bisimide chromophore persists, whereas the anthracene unit is destroyed.

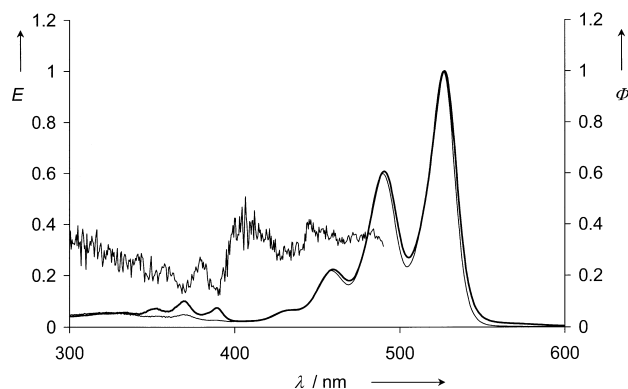


Figure 8. UV/Vis absorption spectra ( $E$ ) of dye **10c** (thick line) compared with **1a** (thin line) in chloroform and fluorescence quantum yield ( $\Phi$ ) of **10c** as a function of the wavelength of excitation (upper noisy line); emission at 577 nm.

Similar effects concerning energy transfer seem to be important for the naphthalene, anthracene and pyrene derivatives. The additional absorption of the second chromophore is more pronounced than for the anthraquinone derivatives, however, the energy transfer processes cannot be as unequivocally determined as for the anthraquinone derivatives because of their lower fluorescence quantum yields. Special effects seem to be important for the anthracene derivatives **10**. There is not only a diminishing of the fluorescence quantum yield in **10c** to less than 40%, but there is a further drop below 400 nm where the anthracene unit absorbs light and minima in fluorescence quantum yield

## Conclusion

Chromophores with low fluorescence quantum yields can be used as light-harvesting systems if their energy of excitation is fast enough transferred to a highly fluorescent acceptor. Not only the distance of the donor to the acceptor needs to be therefore controlled, but also the relative positions of the HOMO of the two chromophores and the orientation of the chromophores versus each other. The control of the energy transfer by the relative orientation of the chromophores is also important for the construction of energy transfer switches, see Figure 9; for fluorescence quenching switches

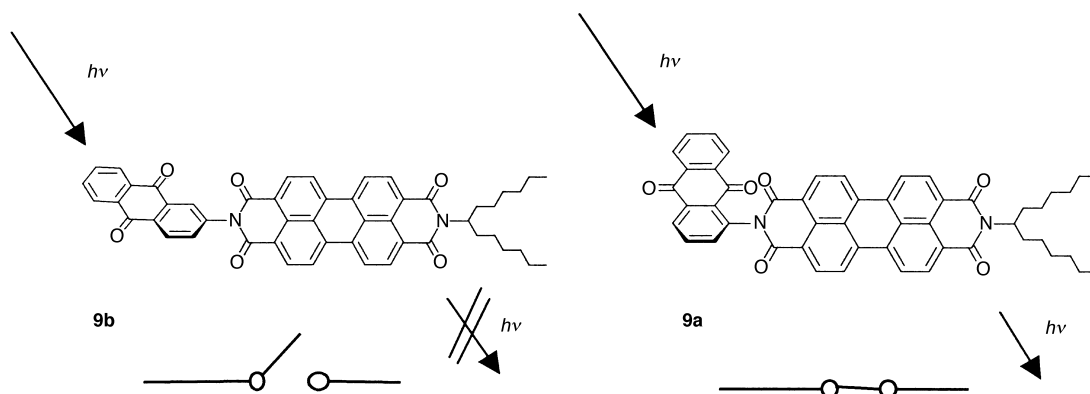


Figure 9. Switch for energy transfer by the orientation of chromophores.

compare<sup>[34, 35]</sup> and molecular switches compare ref. [36]. Such a control can be used for optical computing<sup>[37, 38]</sup> in which the transport of electrical energy by wires in conventional computing is replaced by the oriented transfer of optical energy; for molecular data processing compare ref. [39]. Arrangements of chromophores with switchable energy transfer may be also important for FRET-systems (“Fluorescence Resonance Energy Transfer”) in biochemistry for the analysis of DNA.

## Experimental Section

**Spectra:** UV/Vis absorption spectra: OMEGA 20 from Bruins. Fluorescence spectra and fluorescence quantum yields: Fluorescence Spectrometer 3000 totally corrected according to ref. [28]; the fluorescence quantum yields were obtained by the integration of the emission from 500–800 nm. Fluorescence excitation spectra: LS50B from Perkin Elmer, totally corrected according to ref. [28]; the emission at 490 nm has been used as the reference for fluorescence quantum yields from the integration for the measurements for the wavelengths dependence of fluorescence quantum yields.

**Extractive recrystallization:** The recrystallization of dyes was combined with an extraction according to ref. [40].

**Preparation of N-alkyl-erylene-3,4,9,10-tetracarboxylic bisimides (4)—General procedure:** Perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide (2.0 g, 5.1 mmol), the corresponding alkylamine (8.13 mmol) and imidazole (15 g) were stirred under argon (160 °C, 2 h), having cooled to room temperature and stirred with a mixture of ethanol/2N HCl (100 mL, 30 min). The precipitate was collected by vacuum filtration, treated twice with boiling aqueous potassium carbonate solution (100 mL, 10%, 30 min), washed thoroughly with distilled water, dried under air (120 °C, 16 h), and purified by column separation (silica gel 52X 4 cm) where an orange forerun was removed with chloroform and the main fraction was obtained with chloroform/acetic acid 10:1 as a broad orange red band.

**N-(1-Hexylheptyl)-perylene-3,4,9,10-tetracarboxylic diimide (4a):** Perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (2.0 g, 5.1 mmol) and 7-aminotridecane (1.62 g, 8.13 mmol) were allowed to react and purified according to the general procedure (2.16 g, 74%). M.p. > 300 °C;  $R_f$  (silica gel/CHCl<sub>3</sub>/HOAc 10:1) = 0.85; IR (KBr):  $\tilde{\nu}$  = 3065 w, 2956 m, 2926 m, 2856 m, 1696 s, 1660 s, 1594 s, 1437 m, 1403 m, 1374 w, 1344 s, 1273 m, 1247 w, 1176 w, 811 w, 743 w, 655 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.83 (t, 6H; 2CH<sub>3</sub>), 1.24 (m, 10H; 5CH<sub>2</sub>), 1.33 (m, 6H; 3CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.19 (m, 1H; 1CH), 8.60 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene), 8.62 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.66 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 4H; 4CH perylene), 8.83 (brs, 1H; 1NH).

**N-(1-Heptyloctyl)-perylene-3,4,9,10-tetracarboxylic diimide (4b):** Perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (2.0 g, 5.1 mmol) and 8-aminopentadecane (1.85 g, 8.13 mmol) were allowed to react and purified according to the general procedure (2.36 g, 77%). M.p. > 300 °C;  $R_f$  (silica gel/CHCl<sub>3</sub>/HOAc 10:1) = 0.87; IR (KBr):  $\tilde{\nu}$  = 3179 w br. (NH), 3068 w, 2956 m, 2926 m, 2855 m, 1697 s, 1658 s, 1554 s, 1579 m, 1435 w, 1403 m, 1354 m, 1344 s, 1273 m, 1245 w, 1177 w, 810 m, 742 w, 655 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.82 (t, 6H; 2CH<sub>3</sub>), 1.29 (m, 20H; 10CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.26 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.18 (m, 1H; 1CH), 8.58 (brs, 1H; NH), 8.62 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.62 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.66 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 4H; 4CH perylene).

**N-(1-Nonyldecyl)-perylene-3,4,9,10-tetracarboxylic diimide (4c):** Perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (2.0 g, 5.1 mmol) and 10-aminononadecane (2.30 g, 8.13 mmol) were allowed to react and purified according to the general procedure (1.74 g, 51%). M.p. > 300 °C;  $R_f$  (silica gel/CHCl<sub>3</sub>/HOAc 10:1) = 0.87; IR (KBr):  $\tilde{\nu}$  = 3179 w br. (NH), 3068 w, 2956 m, 2925 s, 2854 s, 1697 s, 1660 s, 1554 s, 1465 w, 1457 w, 1403 m, 1354 m, 1344 s, 1273 m, 811 s, 655 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.82 (t, 6H; 2CH<sub>3</sub>), 1.27 (m, 28H; 14CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.26 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.18 (m, 1H; 1CH), 8.56 (d,

<sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene), 8.58 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.62 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 4H; 4CH perylene), 8.72 (s, 1H; NH).

**Preparation of N-alkyl-N'-hydroxyethyl-erylene-3,4,9,10-tetracarboxylic bisimides (8)—General procedure:** N-alkyl-erylene-3,4,9,10-tetracarboxylic bisimides (4) (1.22 mmol), 2-bromoethanol (5.02 g, 40.2 mmol), anhydrous potassium carbonate (4.67 g, 33.8 mmol) and anhydrous DMF (40 mL) were stirred at 100 °C for 24 h, added to water, acidified with 1N HCl, collected by vacuum filtration, washed three times with distilled water, dried under air, and purified by column separation (silica gel, chloroform/acetone 15:1, broad red band).

**N-(1-Hexylheptyl)-N'-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic diimide (8a):** N-(1-Hexylheptyl)-perylene-3,4,9,10-tetracarboxylic diimide (4a) (700 mg, 1.22 mmol) was allowed to react according to the general procedure to yield the title compound a red dye (510 mg, 68%). M.p. > 300 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.31; IR (KBr)  $\tilde{\nu}$  = 3441 br m (OH), 2955 s, 2928 s, 2857 s, 1697 s, 1658 s, 1595 s, 1579 m, 1439 w, 1405 m, 1342 s, 1251 w, 1173 w, 1055 w, 852 w, 810 s, 746 cm<sup>-1</sup> s; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.83 (t, 6H; 2CH<sub>3</sub>), 1.24 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.81 (t, <sup>3</sup>J(H,H) = 5.2 Hz, 2H; 1CH<sub>2</sub>), 4.04 (brs, 2H; 1CH<sub>2</sub>), 4.50 (t, 2H; 1CH<sub>2</sub>), 5.18 (m, 1H; 1CH), 8.56 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.58 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.66 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 4H; 4CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.05 (2C, CH<sub>3</sub>), 22.60, 26.93, 29.24, 31.78, 32.41 (10C, CH<sub>2</sub>), 42.97 (1C, CH<sub>2</sub>-NR<sub>2</sub>), 54.88 (1C, CH), 61.73 (1C, CH<sub>2</sub>-OH), 122.87, 122.96, 123.27, 126.48, 126.51, 129.51, 131.25, 134.18, 135.04 (20C, CH perylene), 164.24 (4C, C=O); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 261 (31 510), 370 (4120), 435 (4660), 460 (17 040), 491 (47 980), 528 nm (80 200); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 542 (1), 576 nm (0.54); MS (70 eV):  $m/z$  (%): 617 (13) [ $M^+$ +H], 616 (30) [ $M^+$ ], 599 (7), 447 (6), 436 (17), 435 (51) [ $M^+$  - C<sub>13</sub>H<sub>26</sub>], 434 (42) [ $M^+$  - C<sub>13</sub>H<sub>26</sub> - H], 417 (8), 404 (11), 403 (7), 393 (6), 392 (33), 391 (100), 390 (47) [ $M^+$  - C<sub>13</sub>H<sub>26</sub> - C<sub>2</sub>H<sub>5</sub>OH], 373 (17), 347 (6), 346 (13) [ $M^+$  - C<sub>13</sub>H<sub>26</sub> - CH<sub>3</sub>OH - CO<sub>2</sub>], 345 (18); elemental analysis calcd (%) for C<sub>44</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub> (616.8): C 75.95, H 6.54, N 4.54; found: C 75.71, H 6.77, N 4.51.

**N-(1-Heptyloctyl)-N'-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic diimide (8b):** N-(1-Heptyloctyl)-perylene-3,4,9,10-tetracarboxylic diimide (4b, 730 mg, 1.22 mmol) was allowed to react according to the general procedure. Yield 490 mg (62%), m.p. > 300 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.27; IR (KBr):  $\tilde{\nu}$  = 3439 br m (OH), 2926 s, 2855 s, 1694 s, 1658 s, 1595 s, 1439 w, 1404 m, 1342 s, 1251 w, 1173 w, 810 s, 746 cm<sup>-1</sup> s; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.83 (t, 6H; 2CH<sub>3</sub>), 1.28 (m, 20H; 10CH<sub>2</sub>), 1.89 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.44 (brs, 1H; OH), 4.04 (brs, 2H; 1CH<sub>2</sub>), 4.48 (t, <sup>3</sup>J(H,H) = 5.2 Hz, 2H; 1CH<sub>2</sub>), 5.17 (m, 1H; 1CH), 8.44 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.47 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.57 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 4H; 4CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.05 (2C, CH<sub>3</sub>), 22.61, 27.03, 29.23, 29.52, 31.80, 32.37 (12C, CH<sub>2</sub>), 42.95 (1C, CH<sub>2</sub>-NR<sub>2</sub>), 54.90 (1C, CH), 61.60 (1C, CH<sub>2</sub>-OH), 122.76, 122.83, 123.13, 126.13, 126.26, 129.32, 129.38, 131.51, 133.97, 134.81 (20C, CH perylene), 164.09 (4C, C=O); MS (70 eV):  $m/z$  (%): 645 (13) [ $M^+$ +H], 644 (29) [ $M^+$ ], 527 (8), 436 (18), 435 (51), 434 (46), 417 (6), 404 (6), 403 (5), 393 (5), 392 (30), 391 (100), 390 (40) [ $M^+$  - C<sub>15</sub>H<sub>30</sub> - C<sub>2</sub>H<sub>5</sub>OH], 373 (12), 346 (9) [ $M^+$  - C<sub>15</sub>H<sub>30</sub> - C<sub>2</sub>H<sub>5</sub>OH - CO<sub>2</sub>], 345 (11).

**N-(1-Nonyldecyl)-N'-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (8c):** N-(1-Nonyldecyl)-perylene-3,4,9,10-tetracarboxylic bisimide (4c, 800 mg, 1.22 mmol) was allowed to react according to the general procedure (600 mg, 70%). M.p. > 300 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.20; IR (KBr):  $\tilde{\nu}$  = 3450 br m (OH), 2925 s, 2854 s, 1697 s, 1653 s, 1595 s, 1579 m, 1457 w, 1405 m, 1343 s, 1254 w, 1171 w, 1061 w, 810 s, 746 cm<sup>-1</sup> s; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.81 (t, 6H; 2CH<sub>3</sub>), 1.23 (m, 28H; 14CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.24 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.38 (brs, 1H; OH), 4.02 (t, <sup>3</sup>J(H,H) = 5.0 Hz, 2H; 1CH<sub>2</sub>), 4.47 (t, <sup>3</sup>J(H,H) = 4.9 Hz, 2H; 1CH<sub>2</sub>), 5.15 (m, 1H; 1CH), 8.45 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene), 8.48 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene), 8.57 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 4H; 4CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.08 (2C, CH<sub>3</sub>), 22.64, 27.01, 29.27, 29.55, 31.86, 32.36 (16C, CH<sub>2</sub>), 43.23 (1C, CH<sub>2</sub>-NR<sub>2</sub>), 54.88 (1C, CH), 61.63 (1C, CH<sub>2</sub>-OH), 122.77, 122.85, 123.16, 126.48, 126.51, 129.35, 131.54, 134.01, 134.85 (20C, CH Perylen), 164.13 (4C, C=O); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 261 (28 470), 370 (2170), 433 sh (3340), 460 (15 720), 491 (45 970), 528 nm (77 640); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 536 (1.00), 579 (0.53), 626 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490 \text{ nm}}$  = 0.0251/1 cm, CHCl<sub>3</sub>, reference **1a** with

$\Phi = 1.00) = 0.97$ ; MS (70 eV):  $m/z$  (%): 701 (23) [ $M^+ + H$ ], 700 (43) [ $M^+$ ], 683 (10) [ $M^+ - OH$ ], 447 (5), 436 (28), 435 (80) [ $M^+ - C_{10}H_7$ ], 434 (64) [ $M^+ - C_{19}H_{37} - H$ ], 417 (6), 404 (9), 403 (6), 393 (6), 392 (31), 391 (88), 390 (46) [ $M^+ - C_{19}H_{37} - C_2H_5OH$ ], 373 (6), 346 (5) [ $M^+ - C_{15}H_{37} - C_2H_5OH - CO_2$ ], 345 (6); elemental analysis calcd (%) for  $C_{45}H_{52}N_2O_5$  (700.4): C 77.11, H 7.48, N 4.00; found: C 76.67, H 7.37, N 3.82.

***N*-(3,5-Di-*tert*-butylphenyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (8d)**: *N*-(3,5-Di-*tert*-butylphenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8d**, 800 mg, 1.2 mmol) was allowed to react according to the general procedure (600 mg, 70%). M.p. > 300 °C;  $R_f$  (silica gel,  $CHCl_3$ /acetone 15:1) = 0.20; IR (KBr):  $\tilde{\nu} = 3441$  brm (OH), 2963 m, 1700 s, 1663 s, 1595 s, 1579 m, 1506 w, 1437 m, 1404 m, 1358 s, 1345 s, 1252 m, 1174 w, 1064 w, 825 w, 811 m, 748 m, 651  $cm^{-1}$  m; MS (70 eV):  $m/z$  (%): 623 (3) [ $M^+ + H$ ], 622 (6) [ $M^+$ ], 610 (2), 609 (6), 608 (2), 607 (5) [ $M^+ - CH_3$ ], 605 (2) [ $M^+ - OH$ ], 567 (9), 566 (40), 565 (100) [ $M^+ - C(CH_3)_3$ ], 563 (2), 551 (3), 550 (4), 549 (8), 535 (2), 522 (4), 521 (7) [ $M^+ - C(CH_3)_3 - C_2H_5OH$ ], 505 (3).

***N*-(1-Hexylheptyl)-*N'*-(4-hydroxymethyl-phenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (6a)**: *N*-(1-Hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-carboximide-9,10-anhydride (**2a**, 1.03 g, 1.79 mmol), 4-aminobenzylalcohol (300 mg, 2.43 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (10 g) were stirred at 160 °C for 2 h, cooled to room temperature, treated with a small amount of ethanol, acidified with HCl (2N), stirred for 30 min, collected by vacuum filtration, treated two times with boiling potassium carbonate solution (100 mL, 10%, 15 min), collected by vacuum filtration, thoroughly washed with distilled water, dried in air (120 °C, 16 h), purified two times by column separation (silica gel, chloroform/ethanol 20:1 and chloroform/acetone 15:1) to yield a red powder (170 mg, 14%). M.p. > 350 °C;  $R_f$  (silica gel,  $CHCl_3$ /acetone 15:1) = 0.18; IR (KBr):  $\tilde{\nu} = 3448$  brm (OH), 3075 w, 2954 s, 2928 s, 2856 s, 1698 s, 1658 s, 1594 s, 1579 m, 1512 w, 1458 w, 1434 m, 1405 s, 1344 s, 1255 s, 1200 w, 1177 m, 852 w, 811 s, 793 w, 746  $cm^{-1}$  s;  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta = 0.81$  (t, 6H; 2  $CH_3$ ), 1.26 (m, 16H; 8  $CH_2$ ), 1.86 (m, 2H;  $\alpha$ - $CH_2$ ), 2.23 (m, 2H;  $\alpha$ - $CH_2$ ), 4.81 (s, 2H; 1  $CH_2$ ), 5.17 (m, 1H; 1 CH), 7.34 (d,  $^3J(H,H) = 8.2$  Hz, 2H; 2 CH phenyl), 7.58 (d,  $^3J(H,H) = 8.2$  Hz, 2H; 2 CH phenyl), 8.65 (d,  $^3J(H,H) = 8.1$  Hz, 2H; 2 CH perylene), 8.67 (d,  $^3J(H,H) = 8.1$  Hz, 2H; 2 CH perylene), 8.73 (d,  $^3J(H,H) = 8.1$  Hz, 4H; 4 CH perylene);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta = 14.01$  (2 C,  $CH_3$ ), 22.55, 26.91, 29.18, 31.73, 32.36 (10 C,  $CH_2$ ), 54.82 (1 C, CH), 64.94 (1 C,  $CH_2-OH$ ), 123.07, 123.25, 123.34, 124.41, 126.33, 126.75, 127.87, 128.63, 129.57, 129.89, 131.90, 133.91, 134.38, 135.23, 139.11, 141.67, 148.25 (26 C, CH perylene, CH phenyl), 164.2 (4 C, C=O); UV ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = 261$  (36960), 369 (3420), 435 (3780), 459 (17290), 491 (50620), 527 nm (85250); fluorescence ( $CHCl_3$ ):  $\lambda_{max}(I_{rel}) = 535$  (1.00), 577 (0.52), 625 nm (0.12); fluorescence quantum yield ( $\lambda_{exc} = 490$  nm,  $E_{490\text{ nm}} = 0.0311/1$  cm,  $CHCl_3$ , reference **1a** with  $\Phi = 1.00$ ) = 1.01; MS (70 eV):  $m/z$  (%): 679 (10) [ $M^+ + H$ ], 678 (21) [ $M^+$ ], 560 (9), 498 (23), 497 (70), 496 (100) [ $M^+ - C_{13}H_{26}$ ], 495 (19), 467 (14), 390 (18) [ $M^+ - C_{13}H_{26} - C_7H_5OH$ ], 373 (20), 345 (7); elemental analysis calcd (%) for  $C_{44}H_{42}N_2O_5$  (678.8): C 77.85, H 6.24, N 4.13; found: C 77.60, H 6.27, N 4.16.

***N*-(1-Hexylheptyl)-*N'*-(4-(4'-hydroxybiphenyl))-perylene-3,4,9,10-tetracarboxylic bisimide (5a)**: *N*-(1-Hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-carboximide-9,10-anhydride (**2a**, 300 mg, 0.52 mmol), 4-aminobiphenyl-4-ol (100 mg, 0.54 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (3.5 g) were stirred at 140 °C for 2 h, cooled to room temperature, treated with a small amount of ethanol, acidified with HCl (2N), stirred for 30 min, collected by vacuum filtration, treated two times with boiling potassium carbonate solution (100 mL, 10%, 15 min), collected by vacuum filtration, thoroughly washed with distilled water, dried in air (120 °C, 16 h), purified two times by column separation (silica gel, chloroform/ethanol 20:1 and chloroform/acetone 15:1) to yield a red powder (240 mg, 62%). M.p. > 350 °C;  $R_f$  (silica gel,  $CHCl_3$ /acetone 15:1) = 0.45; IR (KBr):  $\tilde{\nu} = 3420$  (brm, OH), 3070 w, 2954 s, 2927 s, 2856 s, 1698 s, 1658 s, 1594 s, 1579 s, 1502 m, 1434 m, 1405 m, 1343 s, 1255 s, 1193 w, 1175 m, 850 m, 825 m, 811 s, 746  $cm^{-1}$  s;  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta = 0.80$  (t, 6H; 2  $CH_3$ ), 1.24 (m 16H; 8  $CH_2$ ), 1.85 (m, 2H;  $\alpha$ - $CH_2$ ), 2.24 (m, 2H;  $\alpha$ - $CH_2$ ), 4.83 (s, 1H; 1 OH), 5.16 (m, 1H; 1 CH), 6.90 (d,  $^3J(H,H) = 8.6$  Hz, 2H; 2 CH biphenyl), 7.36 (d,  $^3J(H,H) = 8.6$  Hz, 2H; 2 CH biphenyl), 7.51 (d,  $^3J(H,H) = 8.6$  Hz, 2H; 2 CH biphenyl), 7.68 (d,  $^3J(H,H) = 8.6$  Hz, 2H; 2 CH biphenyl), 8.68 (d,  $^3J(H,H) = 8.1$  Hz, 4H; 4 CH perylene), 8.76 (d,  $^3J(H,H) = 8.1$  Hz, 4H; 4 CH perylene);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta = 13.98$  (2 C,  $CH_3$ ), 22.54, 26.90, 29.17, 31.72, 32.37 (10 C,  $CH_2$ ),

54.82 (1 C, CH), 115.71, 123.08, 123.25, 123.33, 126.51, 127.78, 128.63, 128.79, 129.60, 129.93, 131.93, 134.37, 135.25, 141.46 (32 C, CH perylene, CH biphenyl), 163.69 (4 C, C=O); UV ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = 261$  (55 520), 279 sh (23 510), 351 (4640), 369 (5190), 431 sh (6350), 459 (20 480), 490 (55 320), 527 nm (91 630); fluorescence ( $CHCl_3$ ):  $\lambda_{max}(I_{rel}) = 535$  (1.00), 575 (0.55), 629 nm (0.14); MS (70 eV):  $m/z$  (%): 741 (13) [ $M^+ + H$ ], 740 (25) [ $M^+$ ], 560 (23), 559 (75), 558 (100) [ $M^+ - C_{13}H_{26}$ ], 557 (10), 373 (21); elemental analysis calcd (%) for  $C_{49}H_{44}N_2O_5$  (740.9): C 79.44, H 5.99, N 3.78; found: C 79.20, H 6.11, N 4.02.

**Fluorene-9-one-1-carboxylic chloride**: Fluorenone-1-carboxylic acid (1.00 g, 4.46 mmol), thionyl chloride (5.0 mL, 69 mmol) and one drop of pyridine were heated under reflux with the exclusion of moisture for 30 min. Subsequently, thionyl chloride was removed in vacuo, anhydrous toluene (1 mL) was added as an entrainer and then removed in vacuo. The residue was recrystallized from anhydrous toluene and dried over phosphorous pentoxide and paraffin to yield the title compound (460 mg, 43%) as a yellow solid. IR (KBr):  $\tilde{\nu} = 1775$  w (COCl), 1715 s, 1675 w, 1607 s, 1468 m, 1415 m, 1297 w, 1139 m, 932 m, 735 s, 687  $cm^{-1}$  w.

**Fluorene-9-one-2-carboxylic chloride**: Fluorenone-2-carboxylic acid (1.00 g, 4.46 mmol) was allowed to react according to fluorene-9-one-1-carboxylic chloride to yield the title compound (690 mg, 64%). M.p. 174–175 °C; IR (KBr):  $\tilde{\nu} = 1749$  s (COCl), 1734 s, 1717 s, 1616 s, 1602 m, 1581 w, 1427 w, 1216 m, 1204 w, 1183 s, 1105 s, 979 m, 882 m, 848 m, 774 s, 768 s, 741 s, 667 s, 647  $cm^{-1}$  s.

**Anthraquinone-2-carboxylic chloride**: Anthraquinone-2-carboxylic acid (1.00 g, 3.96 mmol) was allowed to react according to fluorene-9-one-1-carboxylic chloride to yield the title compound (690 mg, 63%). IR (KBr):  $\tilde{\nu} = 1743$  s (COCl), 1672 s (C=O), 1589 s, 1296 s, 1206 s, 881 m, 712 m, 682  $cm^{-1}$  s.

**Fluorene-9-one-2-isocyanate**: Fluorene-9-one-2-carboxylic chloride (600 mg, 2.48 mmol) was dissolved in anhydrous toluene (20 mL). The solution was added to a suspension of sodium azide (320 mg, 5.00 mmol) in dry toluene, heated under reflux for 20 h, filtrated and evaporated in vacuo to yield the title compound as a yellow solid (440 mg, 81%). IR (nujol):  $\tilde{\nu} = 2279$  s (NCO), 1724 s, 1603 s, 1587 w, 1516 w, 1424 w, 1295 m, 1287 m, 1264 m, 1192 m, 837 s, 763 s, 735 s, 572  $cm^{-1}$  s.

**Anthraquinone-2-isocyanate**: Anthraquinone-2-carboxylic chloride (610 mg, 2.5 mmol) was allowed to react according to fluorene-9-one-2-isocyanate to yield the title compound as a yellow solid (590 mg, 95%). IR (nujol):  $\tilde{\nu} = 2283$  brs (NCO), 1680 s, 1669 w, 1589 m, 1577 w, 1326 m, 1297 m, 1175 w, 718 w, 710  $cm^{-1}$  m.

**9-Bromomethyl-anthracene**: 9-Hydroxymethyl-anthracene (500 mg, 2.4 mmol) was suspended in anhydrous toluene (10 mL), heated to 80 °C for 2 h after having added phosphoric tribromide (0.3 mL, 3.2 mmol), having cooled to room temperature, shaken with aqueous  $NaHCO_3$  (20 mL, 5%), dried ( $CaCl_2$ ) and evaporated to yield the title compound as a (90 mg, 14%). IR (KBr):  $\tilde{\nu} = 3053$  w, 1623 m, 1449 m, 1198 s, 1156 w, 1055 w, 957 w, 883 m, 844 w, 787 m, 730 s, 692 w, 601 w, 550 m, 489  $cm^{-1}$  w; MS (70 eV):  $m/z$  (%): 273 (1) [ $M^+ + H$ ], 272 (8) [ $M^+$ ], 271 (2) [ $M^+ + H$ ], 270 (8) [ $M^+$ ], 192 (9) [ $M^+ + H - Br$ ], 191 (100) [ $M^+ - Br$ ], 190 (15) [ $M^+ + H - Br$ ], 189 (52) [ $M^+ - Br$ ], 165 (7), 163 (2), 163 (5), 96 (13), 95 (16), 83 (9), 82 (3).

**Preparation of bichromophoric dyes by esterification; general procedure**: *N*-(*sec*-Alkyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (0.49 mmol) in anhydrous pyridine (10 mL) and the corresponding carboxylic chloride (0.83 mmol) were stirred (room temperature, drying tube, 24 h). Ice water was added and the solution was briefly treated with 1N HCl, collected by vacuum filtration, washed with distilled water and dried in air (120 °C, 16 h). The reaction product was further purified by column separation.

***N*-(1-Hexylheptyl)-*N'*-(2-ethyloxycarbonyl-2'-anthraquinonyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16a)**: *N*-(1-Hexylheptyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8a**) (200 mg, 0.32 mmol) and anthraquinone-2-carboxylic chloride (180 mg, 0.67 mmol) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/acetone 15:1 and chloroform; broad, red band) to yield a bright red powder (100 mg, 37%). M.p. 280–282 °C;  $R_f$  (silica gel/ $CHCl_3$ ) = 0.07,  $R_f$  (silica gel,  $CHCl_3$ /acetone 15:1) = 0.69; IR (KBr):  $\tilde{\nu} = 3070$  w, 2954 m, 2927 m, 2856 m, 1730 m, 1697 s, 1678 m, 1658 s, 1594 s, 1437 m, 1405 s, 1342 s, 1295 w, 1268 s, 1245 s, 1173 w, 1110 w, 811 s, 746 s, 708  $cm^{-1}$  s;  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C, TMS):

$\delta = 0.83$  (t, 6H; 2CH<sub>3</sub>), 1.31 (m, 16H; 8CH<sub>2</sub>), 1.89 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.23 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.71 (t,  $^3J(\text{H,H}) = 5.0$  Hz, 2H; CH<sub>2</sub>-OR), 4.82 (t,  $^3J(\text{H,H}) = 5.3$  Hz, 2H; CH<sub>2</sub>-NR'<sub>2</sub>), 5.18 (m, 1H; 1CH), 7.77 (m, 2H; 5-H and 8-H anthraquinone), 8.26 (t,  $^3J(\text{H,H}) = 4.9$  Hz, 2H; 6-H and 7-H anthraquinone), 8.31 (d,  $^3J(\text{H,H}) = 7.9$  Hz, 1H; 3-H anthraquinone), 8.39 (dd,  $^3J(\text{H,H}) = 8.0$  Hz,  $^4J(\text{H,H}) = 1.6$  Hz, 1H; 2-H anthraquinone), 8.52 (d,  $^3J(\text{H,H}) = 7.8$  Hz, 2H; 2CH perylene), 8.54 (d,  $^3J(\text{H,H}) = 7.9$  Hz, 2H; 2CH perylene), 8.64 (d,  $^3J(\text{H,H}) = 7.8$  Hz, 4H; 4CH perylene), 8.84 (d,  $^4J(\text{H,H}) = 1.5$  Hz, 1H; 1-H anthraquinone); COSY NMR: cross-peaks at  $\delta = (7.77, 8.26)$ , (8.31, 8.39), (8.39, 8.84); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.08$  (2C, CH<sub>3</sub>), 22.63, 27.05, 29.09, 31.82, 32.41 (10C, CH<sub>2</sub>), 39.36 (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 54.93 (1C, CH), 63.46 (1C, CH<sub>2</sub>-OR), 122.46, 122.83, 122.92, 125.65, 125.79, 127.18, 127.22, 127.42, 128.39, 128.97, 129.14, 131.04, 132.95, 133.17, 133.66, 134.25, 134.39, 134.76, 135.12, 135.72 (32C, CH perylene, CH anthraquinone), 163.22, 164.88 (5C, C=O perylene and ester), 182.00 (1C, C=O fluorenone); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 260 (80850), 275 (20990), 325 (9090), 370 (4160), 433 sh (5020), 459 (18050), 490 (50520), 527 nm (84880); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 535 (1.00), 577 (0.52), 626 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}} = 490$  nm,  $E_{490\text{nm}} = 0.03561$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ;  $m/z$  (%): 851 (4) [ $M^+ + \text{H}$ ], 850 (7) [ $M^+$ ], 669 (12), 668 (24) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 433 (11), 418 (7), 417 (12), 391 (5), 390 (11) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{17}\text{H}_{10}\text{O}_4$ ], 373 (4), 345 (3), 253 (16), 252 (100), 236 (13), 235 (24), 224 (29); elemental analysis calcd (%) for C<sub>53</sub>H<sub>46</sub>N<sub>2</sub>O<sub>8</sub> (850.3): C 76.21, H 5.45, N 3.29; found: C 76.11, H 5.45, N 3.20.

**N-(1-Heptyloctyl)-N'-(2-ethyloxycarbonyl-2'-anthraquinonyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16b):** *N*-(1-Heptyloctyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8b**, 260 mg, 0.40 mmol) and anthraquinone-2-carboxylic chloride (200 mg, 0.74 mmol) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/acetone 15:1 and chloroform; broad, red band) to yield a bright red powder (320 mg, 91%). M.p. 274–277 °C; *R*<sub>f</sub> (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.72, *R*<sub>f</sub> (silica gel/CHCl<sub>3</sub>) = 0.11; IR (KBr):  $\tilde{\nu} = 2926\text{m}, 2855\text{m}, 1728\text{m}, 1697\text{s}, 1678\text{m}, 1658\text{s}, 1595\text{s}, 1579\text{m}, 1437\text{m}, 1405\text{s}, 1343\text{s}, 1295\text{w}, 1268\text{m}, 1246\text{m}, 1173\text{w}, 1110\text{w}, 811\text{s}, 746\text{s}, 707\text{cm}^{-1}\text{s}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.83$  (t, 6H; 2CH<sub>3</sub>), 1.30 (m, 20H; 10CH<sub>2</sub>), 1.91 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.23 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.71 (t,  $^3J(\text{H,H}) = 5.0$  Hz, 2H; CH<sub>2</sub>-OR), 4.83 (t,  $^3J(\text{H,H}) = 4.7$  Hz, 2H; CH<sub>2</sub>-NR'<sub>2</sub>), 5.17 (m, 1H; 1CH), 7.75 (m, 2H; 5-H and 8-H anthraquinone), 8.24 (t,  $^3J(\text{H,H}) = 5.7$  Hz, 2H; 6-H and 7-H anthraquinone), 8.28 (d,  $^3J(\text{H,H}) = 7.9$  Hz, 1H; 3-H anthraquinone), 8.39 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H; 2-H anthraquinone), 8.47 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 2H; 2CH perylene), 8.50 (d,  $^3J(\text{H,H}) = 8.4$  Hz, 2H; 2CH perylene), 8.60 (d,  $^3J(\text{H,H}) = 7.8$  Hz, 4H; 4CH perylene), 8.81 (d,  $^4J(\text{H,H}) = 1.3$  Hz, 1H; 1-H anthraquinone); COSY NMR: cross-peaks at  $\delta = (7.75, 8.24)$ , (8.28, 8.39), (8.39, 8.81); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.04$  (2C, CH<sub>3</sub>), 22.60, 27.04, 29.22, 29.52, 31.80, 32.37 (12C, CH<sub>2</sub>), 39.24, (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 54.86 (1C, CH), 63.36 (1C, CH<sub>2</sub>-OR), 122.67, 122.98, 123.03, 126.00, 126.19, 127.26, 127.28, 127.45, 128.61, 129.28, 129.32, 131.40, 133.15, 133.21, 133.34, 133.97, 134.28, 134.38, 134.65, 134.69, 135.12, 135.88 (32C, CH perylene, CH anthraquinone), 163.39, 164.91 (C=O, 5C perylene and ester), 182.06, 182.25 (C=O, 2C anthraquinone); UV (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 260 (84720), 275 (31020), 325 (9680), 371 (4360), 433 sh (5140), 459 (17970), 490 (49750), 527 nm (83420); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 535 (1.00), 577 (0.52), 625 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}} = 490$  nm,  $E_{490\text{nm}} = 0.03111$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ;  $m/z$  (%): 879 (5) [ $M^+ + \text{H}$ ], 878 (9) [ $M^+$ ], 669 (10), 668 (22) [ $M^+ - \text{C}_{15}\text{H}_{30}$ ], 433 (12), 418 (10), 417 (16), 391 (7), 390 (16) [ $M^+ - \text{C}_{15}\text{H}_{30} - \text{C}_{17}\text{H}_{10}\text{O}_4$ ], 373 (7), 345 (4), 253 (17), 252 (100), 236 (16), 235 (18), 224 (36); elemental analysis calcd (%) for C<sub>56</sub>H<sub>50</sub>N<sub>2</sub>O<sub>8</sub> (879.0): C 76.52, H 5.73, N 3.19; found: C 76.23, H 5.71, N 3.28.

**N-(1-Hexylheptyl)-N'-(2-ethyloxycarbonyl-1-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16c):** *N*-(1-Hexylheptyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8a**) (100 mg, 0.16 mmol) and fluorene-9-one-2-carboxylic chloride (80 mg, 0.33 mmol) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/acetone 15:1 and chloroform; violet band) to yield a red powder (200 mg, 55%). M.p. 276–278 °C; *R*<sub>f</sub> (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.46; IR (KBr):  $\tilde{\nu} = 3070\text{brw}, 2955\text{m}, 2926\text{m}, 2856\text{m}, 1720\text{w}, 1697\text{s}, 1658\text{s}, 1595\text{s}, 1438\text{w}, 1405\text{m}, 1343\text{s}, 1300\text{w},$

1282w, 1253w, 1191w, 1176w, 1139w, 811s, 747cm<sup>-1</sup>s; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.83$  (t, 6H; 2CH<sub>3</sub>), 1.30 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.70 (t,  $^3J(\text{H,H}) = 5.3$  Hz, 2H; CH<sub>2</sub>-OR), 4.80 (t,  $^3J(\text{H,H}) = 5.3$  Hz, 2H; CH<sub>2</sub>-NR'<sub>2</sub>), 5.19 (m, 1H; 1CH), 6.95 (d,  $^3J(\text{H,H}) = 7.3$  Hz, 1H; 5-H fluorenone), 6.98 (t,  $^3J(\text{H,H}) = 7.3$  Hz, 1H; 6-H fluorenone), 7.36 (dt,  $^3J(\text{H,H}) = 7.3$  Hz,  $^4J(\text{H,H}) = 1.6$  Hz, 1H; 7-H fluorenone), 7.44 (d,  $^3J(\text{H,H}) = 7.5$  Hz, 1H; 8-H fluorenone), 7.51 (d,  $^3J(\text{H,H}) = 7.9$  Hz, 1H; 2-H or 4-H fluorenone), 7.52 (d,  $^3J(\text{H,H}) = 7.7$  Hz, 1H; 2-H or 4-H fluorenone), 7.57 (dd,  $^3J(\text{H,H}) = 8.4$  Hz,  $^3J(\text{H,H}) = 8.6$  Hz, 1H; 3-H fluorenone), 8.56 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 2H; 2CH perylene), 8.60 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 4H; 4CH perylene), 8.63 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 2H; 2CH perylene), 8.67 (brs, 2H; 1CH perylene); COSY NMR: cross-peaks at  $\delta = (6.98, 7.36)$ , (7.36, 7.44), (7.52, 7.57); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.01$  (2C, CH<sub>3</sub>), 22.56, 26.93, 29.20, 31.74, 32.37 (10C, CH<sub>2</sub>), 39.00 (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 54.80 (1C, CH), 63.08 (1C, CH<sub>2</sub>-OR), 120.10, 122.28, 122.92, 123.02, 123.30, 124.08, 126.31, 126.45, 128.86, 129.10, 129.52, 129.57, 130.72, 131.21, 131.37, 133.37, 134.21, 134.52, 143.05, 144.82 (32C, Ar), 163.52, 166.73 (5C, C=O perylene and ester), 190.66 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 261 (85160), 370 (4800), 433 sh (5010), 459 (17340), 490 (48130), 527 nm (80410); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 534 (1.00), 577 nm (0.52), 625 (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}} = 490$  nm,  $E_{490\text{nm}} = 0.03111$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ;  $m/z$  (%): 823 (1), 822 (3) [ $M^+$ ], 642 (1), 641 (3), 640 (2) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 391 (1), 390 (2) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{16}\text{H}_{11}\text{O}_3$ ], 224 (28) [ $\text{C}_{14}\text{H}_8\text{O}_3^+$ ], 208 (4), 207 (2) [ $\text{C}_{14}\text{H}_7\text{O}_2^+$ ], 181 (18), 180 (100), 179 (1), 152 (30), 151 (20), 150 (13); elemental analysis calcd (%) for C<sub>53</sub>H<sub>46</sub>N<sub>2</sub>O<sub>7</sub> (823.0): C 77.35, H 5.63, N 3.40; found: C 77.20, H 5.53, N 3.40.

**N-(1-Hexylheptyl)-N'-(2-ethyloxycarbonyl-2-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16d):** *N*-(1-Hexylheptyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8a**) (300 mg, 0.49 mmol) and fluorene-9-one-2-carboxylic chloride (200 mg, 0.83 mmol) were allowed to react according to the general procedure and purified by column separation (silica gel, chloroform/acetone 15:1 to yield a red powder (100 mg, 24%). M.p. 275–277 °C; *R*<sub>f</sub> (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.50; IR (KBr):  $\tilde{\nu} = 3070\text{w}, 2956\text{m}, 2927\text{m}, 2857\text{m}, 1720\text{m}, 1697\text{s}, 1658\text{s}, 1618\text{w}, 1595\text{s}, 1579\text{w}, 1458\text{w}, 1439\text{w}, 1405\text{m}, 1343\text{s}, 1286\text{w}, 1253\text{s}, 1184\text{w}, 1112\text{w}, 811\text{s}, 746\text{s}, 668\text{cm}^{-1}\text{m}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.84$  (t, 6H; 2CH<sub>3</sub>), 1.31 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.66 (s, 2H; CH<sub>2</sub>-OR), 4.77 (s, 2H; CH<sub>2</sub>-NR'<sub>2</sub>), 5.16 (m, 1H; 1CH), 7.36 (t,  $^3J(\text{H,H}) = 7.4$  Hz, 1H; 7-H fluorenone), 7.53 (t,  $^3J(\text{H,H}) = 7.4$  Hz, 1H; 6-H fluorenone), 7.55 (m, 2H; 5-H and 4-H fluorenone), 7.69 (d,  $^3J(\text{H,H}) = 7.4$  Hz, 1H; 8-H fluorenone), 8.17 (dd,  $^3J(\text{H,H}) = 7.6$  Hz,  $^4J(\text{H,H}) = 1.5$  Hz, 1H; 3-H fluorenone), 8.20 (s, 1H; 1-H fluorenone), 8.63 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 2H; 2CH perylene), 8.64 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 4H; 4CH perylene), 8.73 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 2H; 2CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.16$  (2C, CH<sub>3</sub>), 22.70, 27.22, 29.35, 31.89, 32.40 (10C, CH<sub>2</sub>), 39.36 (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 54.88 (1C, CH), 62.82 (1C, CH<sub>2</sub>-OR), 119.59, 120.54, 121.98, 122.40, 122.75, 124.35, 124.90, 128.27, 128.63, 130.04, 130.43, 131.00, 133.01, 133.28, 133.66, 134.11, 134.53, 136.23, 142.76, 147.75 (32C, Ar), 162.84, 165.24 (5C, C=O perylene and ester), 192.28 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 261 (83900), 271 (80840), 299 (9240), 315 (6760), 370 (4910), 434 sh (5200), 456 (18000), 490 (49850), 527 nm (83800); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 535 (1), 577 (0.52), 625 nm (0.12); MS (70 eV):  $m/z$  (%): 823 (8), 822 (14) [ $M^+$ ], 805 (8), 642 (7), 641 (25), 640 (52) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 616 (5), 615 (12) [ $M^+ - \text{C}_{14}\text{H}_7\text{O}_2$ ], 598 (12) [ $M^+ - \text{C}_{14}\text{H}_8\text{O}_3$ ], 435 (8), 434 (10), 433 (28), 418 (16), 417 (33), 416 (12), 415 (10), 391 (15), 390 (32) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{16}\text{H}_{11}\text{O}_3$ ], 373 (15), 345 (10), 224 (29) [ $\text{C}_{14}\text{H}_8\text{O}_3^+$ ], 208 (61), 207 (100) [ $\text{C}_{14}\text{H}_7\text{O}_2^+$ ], 179 (24) [ $\text{C}_{13}\text{H}_7\text{O}^+$ ], 151 (23) [ $\text{C}_{12}\text{H}_7^+$ ]; elemental analysis calcd (%) for C<sub>53</sub>H<sub>46</sub>N<sub>2</sub>O<sub>7</sub> (823.0): C 77.35, H 5.63, N 3.40; found: C 76.87, H 5.89, N 3.50.

**N-(1-Heptyloctyl)-N'-(2-ethyloxycarbonyl-2-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16e):** *N*-(1-Heptyloctyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8b**, 280 mg, 0.43 mmol) and fluorene-9-one-2-carboxylic chloride (210 mg, 0.87 mmol) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/acetone 15:1 and chloroform; violet band) to yield a red powder (200 mg, 55%). M.p. 265–267 °C; *R*<sub>f</sub> (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.61, *R*<sub>f</sub> (silica gel/CHCl<sub>3</sub>) = 0.17; IR (KBr):  $\tilde{\nu} = 3070\text{w}, 2956\text{m}, 2927\text{m}, 2855\text{m}, 1718\text{s}, 1697\text{s}, 1658\text{s}, 1595\text{s}, 1457\text{w}, 1437\text{w}, 1405\text{m}, 1343\text{s}, 1286\text{w}, 1252\text{s}, 1111\text{w}, 810\text{s}, 746\text{cm}^{-1}\text{s}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.82$  (t, 6H; 2CH<sub>3</sub>), 1.27 (m,



20H; 10CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.24 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.71 (t, 2H; CH<sub>2</sub>-OR), 4.73 (brs, 2H; CH<sub>2</sub>-NR'<sub>2</sub>), 5.18 (m, 1H; 1CH), 7.35 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 7-H fluorenone), 7.51 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 1H; 6-H fluorenone), 7.55 (m, 2H; 5-H and 4-H fluorenone), 7.67 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 8-H fluorenone), 8.19 (dd, <sup>3</sup>J(H,H) = 7.5 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H; 3-H fluorenone), 8.20 (s, 1H; 1-H fluorenone), 8.58 (d, <sup>3</sup>J(H,H) = 7.2 Hz, 4H; 4CH perylene), 8.70 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 4H; 4CH perylene); <sup>13</sup>C NMR(CDCl<sub>3</sub>):  $\delta$  = 14.10 (2C, CH<sub>3</sub>), 22.67, 27.17, 29.30, 29.59, 31.88, 32.39 (12C, CH<sub>2</sub>), 39.30 (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 54.87 (1C, CH), 62.84 (1C, CH<sub>2</sub>-OR), 119.80, 120.74, 122.34, 122.71, 122.98, 124.42, 125.12, 125.43, 128.74, 128.96, 130.07, 130.36, 131.04, 133.48, 133.85, 134.35, 134.65, 134.78, 136.33, 142.97, 147.97 (32C, aryl), 163.12, 165.33 (5C, C=O perylene and ester), 192.40 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 261 (83670), 271 (80840), 299 (9150), 369 (4960), 433 sh (5390), 459 (18020), 490 (49200), 527 nm (82080); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 533 (1.00), 577 (0.52), 624 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490\text{nm}} = 0.0311/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.96; MS (70 eV):  $m/z$  (%): 851 (18), 850 (33) [ $M^+$ ], 834 (10), 833 (17), 643 (25) [ $M^+ - C_{14}H_7O_2$ ], 642 (12), 641 (48), 640 (100) [ $M^+ - C_{13}H_6O$ ], 627 (10), 626 (20) [ $M^+ - C_{14}H_8O_3$ ], 435 (11), 434 (12), 433 (35), 418 (20), 417 (40), 416 (15), 415 (11), 391 (14), 390 (34) [ $M^+ - C_{15}H_9O - C_{16}H_{11}O_3$ ], 373 (15), 345 (10), 224 (9) [ $C_{14}H_8O_3^+$ ], 208 (59), 207 (87) [ $C_{14}H_8O_2^+$ ], 180 (17), 179 (16), 151 (14) [ $C_{12}H_7^+$ ]; elemental analysis calcd (%) for C<sub>35</sub>H<sub>50</sub>N<sub>2</sub>O<sub>7</sub> (851.0): C 77.63, H 5.92, N 3.29; found: C 77.68, H 6.03, N 3.20.

**N-(1-Hexylheptyl)-N'-(2-ethyloxycarbonyl-4'-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16f):** *N*-(1-Hexylheptyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8a**) (200 mg, 0.32 mmol) and fluorene-9-one-4-carboxylic chloride (170 mg, 0.71 mmol) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/acetone 15:1 and silica gel, chloroform) to yield a reddish orange powder with solid-state fluorescence (200 mg, 76%). M.p. 239–241 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.67,  $R_f$  (silica gel, CHCl<sub>3</sub>) = 0.12; IR (KBr):  $\tilde{\nu}$  = 2956 w, 2927 m, 2860 w, 1720 w, 1696 s, 1658 s, 1595 s, 1405 m, 1343 s, 1248 m, 810 s, 746 cm<sup>-1</sup> s; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.82 (t, 6H; 2CH<sub>3</sub>), 1.30 (m, 16H; 8CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 4.72 (t, <sup>3</sup>J(H,H) = 5.2 Hz, 2H; CH<sub>2</sub>-OR), 4.82 (t, <sup>3</sup>J(H,H) = 5.3 Hz, 2H; CH<sub>2</sub>-NR'<sub>2</sub>), 5.17 (m, 1H; 1CH), 7.17 (dt, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>4</sup>J(H,H) = 1.0 Hz, 1H; 1CH, 6-H fluorenone), 7.29 (dt, <sup>3</sup>J(H,H) = 7.5 Hz, <sup>4</sup>J = 1.3 Hz, 1H; 1CH 7-H fluorenone), 7.31 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 1H; 1CH, 2-H fluorenone), 7.57 (d, <sup>3</sup>J(H,H) = 7.4 Hz, 1H; 1CH, 5-H fluorenone), 7.77 (dd, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>4</sup>J(H,H) = 1.3 Hz, 1H; 1CH, 1 or 3-H fluorenone), 7.95 (dd, <sup>3</sup>J(H,H) = 7.9 Hz, <sup>4</sup>J(H,H) = 1.3 Hz, 1H; 1CH, 1 or 3-H fluorenone), 8.17 (d, <sup>3</sup>J(H,H) = 7.7 Hz, 1H; CH, 8-H fluorenone), 8.52 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H; 2CH perylene), 8.55 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 4H; 2CH perylene), 8.60 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene), 8.64 (brs, 2H; 2CH perylene); COSY NMR: cross-peaks at  $\delta$  = (7.17, 7.29), (7.17, 7.57), (7.29, 8.17), (7.31, 7.95, 7.77); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.03 (2C, CH<sub>3</sub>), 22.58, 26.94, 29.21, 31.75, 32.37 (10C, CH<sub>2</sub>), 39.26 (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 54.84 (1C, CH), 62.77 (1C, CH<sub>2</sub>-OR), 122.77, 122.93, 123.24, 123.87, 126.17, 126.28, 126.52, 126.65, 127.21, 128.55, 129.48, 131.59, 134.12, 134.25, 134.93, 135.02, 135.45, 136.30, 142.96, 144.14 (32C, aryl), 163.49, 166.41 (5C, C=O perylene and ester), 192.80 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 262 (77900), 272 (48980), 306 (14030), 371 (8330), 435 sh (8500), 460 (22440), 491 (57370), 527 nm (93880); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 535 (1.00), 577 (0.52), 626 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490\text{nm}} = 0.0311/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.95. Solid-state fluorescence:  $\lambda_{\max}$  = 614 nm br.; MS (70 eV):  $m/z$  (%): 823 (6), 822 (9) [ $M^+$ ], 805 (3), 641 (11), 640 (21) [ $M^+ - C_{13}H_{26}$ ], 615 (2) [ $M^+ - C_{14}H_7O_2$ ], 433 (10), 418 (7), 417 (11), 416 (2), 391 (5), 390 (10) [ $M^+ - C_{13}H_{26} - C_{16}H_{11}O_3$ ], 373 (4), 345 (3), 224 (100) [ $C_{14}H_8O_3^+$ ], 208 (7), 207 (33) [ $C_{14}H_7O_2^+$ ], 179 (23) [ $C_{13}H_7O^+$ ], 151 (22) [ $C_{12}H_7^+$ ]; elemental analysis calcd (%) for C<sub>35</sub>H<sub>46</sub>N<sub>2</sub>O<sub>7</sub> (823.0): C 77.35, H 5.63, N 3.40; found: C 77.41, H 5.63, N 3.11.

**N-(2,5-Di-*tert*-butyl-phenyl)-N'-(2-ethyloxycarbonyl-2'-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (16g):** *N*-(2,5-Di-*tert*-butyl-phenyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8d**, 50 mg, 0.08 mmol) and fluorene-9-one-2-carboxylic acid chloride (0.66 g, 0.16 mmol) were allowed to react according to the general procedure to yield a red solid (40 mg, 60%). M.p. > 350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.25; IR (KBr):  $\tilde{\nu}$  = 3080 w, 2964 m, 2927 m, 1701 (br m), 1697 s, 1664 s, 1617 w, 1594 s, 1457 w, 1437 w, 1404 m, 1356 m, 1346 s, 1285 w, 1252 s,

1183 w, 1112 w, 811 s, 748 cm<sup>-1</sup> s; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 1.27 (s, 9H; 1C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (s, 9H; 1C(CH<sub>3</sub>)<sub>3</sub>), 4.70 (brs, 4H; R<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-OR), 7.08 (d, <sup>4</sup>J(H,H) = 2.1 Hz, 1H; 6-H phenyl), 7.35 (dt, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>4</sup>J(H,H) = 1.2 Hz, 1H; 7-H fluorenone), 7.46 (dd, <sup>3</sup>J(H,H) = 8.6 Hz, <sup>4</sup>J(H,H) = 2.1 Hz, 1H; 4-H phenyl), 7.51 (t, <sup>3</sup>J(H,H) = 7.4 Hz, 1H; 6-H fluorenone), 7.56 (m, 2H; 5-H and 4-H fluorenone), 7.58 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 1H; 3-H phenyl), 7.67 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 8-H fluorenone), 8.18 (dd, <sup>3</sup>J(H,H) = 9.8 Hz, <sup>4</sup>J(H,H) = 1.7 Hz, 1H; 3-H fluorenone), 8.19 (d, <sup>4</sup>J(H,H) = 1.2 Hz, 1H; 1-H fluorenone), 8.62 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H; 2CH perylene), 8.63 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.70 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.72 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 31.23 (3C, CH<sub>3</sub>), 31.74 (3C, CH<sub>3</sub>), 34.29 (1C, C(CH<sub>3</sub>)<sub>3</sub>), 35.53 (1C, C(CH<sub>3</sub>)<sub>3</sub>), 39.20 (1C, CH<sub>2</sub>-NR'<sub>2</sub>), 62.72 (1C, CH<sub>2</sub>-OR), 120.15, 121.15, 123.06, 123.27, 123.32, 123.74, 124.56, 125.49, 126.35, 126.56, 127.79, 128.79, 129.51, 129.84, 130.14, 130.98, 131.72, 131.82, 132.58, 134.17, 134.78, 134.87, 134.91, 136.50, 143.32, 143.76, 148.36, 150.19 (38C, aryl), 163.51, 164.36, 165.41 (5C, C=O perylene and ester), 192.56 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 262 (85990), 271 (80260), 299 (10060), 315 (6150), 369 (5600), 433 sh (6100), 459 (19370), 491 (52590), 527 nm (88100); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 534 (1.00), 576 (0.52), 525 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490\text{nm}} = 0.0374/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.98; MS (70 eV):  $m/z$  (%): 828 (1) [ $M^+$ ], 774 (1), 773 (12), 772 (45), 771 (76) [ $M^+ - C_4H_8$ ], 608 (3), 607 (9), 549 (5), 547 (2), 419 (2), 390 (3), 225 (13), 224 (100) [ $C_{14}H_8O_3^+$ ], 208 (6), 207 (48) [ $C_{14}H_7O_2^+$ ], 179 (16) [ $C_{13}H_7O^+$ ], 151 (33) [ $C_{12}H_7^+$ ]; elemental analysis calcd (%) for C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>7</sub> (828.9): C 78.25, H 4.86, N 3.38; found: C 77.89, H 4.97, N 3.36.

**N-(1-Hexylheptyl)-N'-(4-benzyloxycarbonyl-2'-anthraquinonyl)-perylene-3,4,9,10-tetracarboxylic bisimide (14a):** *N*-(1-Hexylheptyl)-*N'*-(4-hydroxymethyl-phenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**6a**, 100 mg, 0.15 mmol) and anthraquinone-2-carboxyl chloride (80 mg, 0.30 mmol) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/acetone 15:1 and Al<sub>2</sub>O<sub>3</sub> N II, chloroform; broad, orange band) to yield a red powder (50 mg, 37%). M.p. 339–342 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.76; IR (KBr):  $\tilde{\nu}$  = 3070 w, 2928 m, 2856 m, 1710 m, 1698 s, 1660 s, 1594 s, 1434 w, 1405 m, 1343 s, 1268 m, 1247 m, 1174 w, 811 m, 747 m, 708 cm<sup>-1</sup> w; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.81 (t, 6H; 2CH<sub>3</sub>), 1.27 (m, 16H; 8CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.22 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.17 (m, 1H; 1CH), 5.53 (s, 2H; CH<sub>2</sub>-OR), 7.42 (d, <sup>3</sup>J(H,H) = 8.6 Hz, 2H; 2CH phenyl), 7.70 (d, <sup>3</sup>J(H,H) = 8.6 Hz, 2H; 2CH phenyl), 7.81 (m, 2H; 5-H and 8-H anthraquinone), 8.31 (m, 2H; 6-H and 7-H anthraquinone), 8.28 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H; 3-H anthraquinone), 8.44 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H; 2-H anthraquinone), 8.60 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.60 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 2H; 2CH perylene), 8.64 (brs, 2H; 2CH perylene), 8.70 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.96 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H; 1-H anthraquinone); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.03 (2C, CH<sub>3</sub>), 22.57, 26.94, 29.20, 31.75, 32.37 (10C, CH<sub>2</sub>), 54.84 (1C, CH), 66.92 (1C, CH<sub>2</sub>-OR), 123.05, 123.17, 123.34, 126.39, 126.66, 127.38, 127.45, 127.58, 128.76, 129.04, 129.53, 131.88, 133.36, 133.43, 133.56, 134.22, 134.36, 134.46, 134.62, 135.02, 135.20, 136.11, 136.15 (38C, CH perylene, CH anthraquinone, CH phenyl), 163.49, 164.78 (5C, C=O perylene and ester), 182.11, 182.51 (2C, C=O anthraquinone); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 260 (86250), 275 sh (21990), 327 (9090), 368 (4410), 434 sh (5420), 459 (18920), 490 (52450), 527 nm (87450); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 535 (1.00), 578 (0.52), 627 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490\text{nm}} = 0.0311/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.99; MS (70 eV):  $m/z$  (%): 913 (11) [ $M^+ + H$ ], 912 (18) [ $M^+$ ], 895 (6), 732 (14), 731 (37), 730 (48) [ $M^+ - C_{13}H_{26}$ ], 496 (10), 495 (25), 494 (13), 481 (11), 480 (19), 479 (8), 373 (27), 345 (6), 253 (19), 252 (100), 236 (10), 235 (22), 224 (29), 182 (16); elemental analysis calcd (%) for C<sub>39</sub>H<sub>48</sub>N<sub>2</sub>O<sub>8</sub> × H<sub>2</sub>O (931.5): C 76.11, H 5.41, N 3.01; found: C 76.32, H 5.52, N 3.00.

**N-(1-Hexylheptyl)-N'-(4-benzyloxycarbonyl-2'-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (14b):** *N*-(1-Hexylheptyl)-*N'*-(4-hydroxymethyl-phenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**6a**, 100 mg, 0.15 mmol) and fluorene-9-one-2-carboxylic acid chloride (70 mg, 0.30 mmol) were allowed to react according to the general procedure and purified by column separation (silica gel, chloroform/acetone 15:1; broad, orange band) to yield a red powder (120 mg, 90%). M.p. 292–294 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.60; IR (KBr):  $\tilde{\nu}$  = 3070 w, 2954 w, 2976 m, 2856 m, 1711 s, 1698 s, 1658 s, 1617 w, 1594 s, 1579 m, 1433 w, 1405 m,

1343 s, 1285 w, 1254 s, 1177 w, 1123 w, 1110 w, 811 m, 746 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 0.81 (t, 6H; 2CH<sub>3</sub>), 1.26 (m, 16H; 8CH<sub>2</sub>), 1.85 (m, 2H; α-CH<sub>2</sub>), 2.25 (m, 2H; α-CH<sub>2</sub>), 5.17 (m, 1H; 1CH), 5.48 (s, 2H; CH<sub>2</sub>-OR), 7.37 (dt, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>4</sup>J(H,H) = 1.1 Hz, 1H; 7-H fluorenone), 7.39 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 2H; 2CH phenyl), 7.53 (dt, <sup>3</sup>J(H,H) = 7.5 Hz, <sup>4</sup>J(H,H) = 1.2 Hz, 1H; 6-H fluorenone), 7.53 (d, <sup>3</sup>J(H,H) = 7.2 Hz, 1H; 5-H fluorenone), 7.61 (d, <sup>3</sup>J(H,H) = 7.8 Hz, 1H; 4-H fluorenone), 7.67 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 2H; 2CH phenyl), 7.71 (d, <sup>3</sup>J(H,H) = 7.4 Hz, 1H; 8-H fluorenone), 8.26 (dd, <sup>3</sup>J(H,H) = 7.7 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H; 3-H fluorenone), 8.35 (d, <sup>4</sup>J(H,H) = 1.6 Hz, 1H; 1-H fluorenone), 8.64 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H; 2CH perylene), 8.65 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H; 2CH perylene), 8.69 (brs, 2H; 2CH perylene), 8.73 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.04 (2C, CH<sub>3</sub>), 22.58, 26.93, 29.21, 31.76, 32.38 (10C, CH<sub>2</sub>), 66.42 (1C, CH<sub>2</sub>-OR), 120.22, 121.21, 123.09, 123.37, 124.64, 125.46, 128.95, 129.38, 130.19, 130.92, 131.94, 135.26, 136.51 (38C, CH perylene, CH fluorenone, CH phenyl), 163.55 (5C, C=O perylene and ester), 177.02 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) = 261 (85380), 271 (83080), 299 (8140), 315 (5390), 369 (4310), 435 sh (4530), 459 (17160), 490 (48700), 527 nm (82100); fluorescence (CHCl<sub>3</sub>): λ<sub>max</sub> (I<sub>rel</sub>) = 535 (1.00), 577 (0.52), 626 nm (0.12); fluorescence quantum yield (λ<sub>exc</sub> = 490 nm, E<sub>490 nm</sub> = 0.0311/1 cm, CHCl<sub>3</sub>, reference **1a** with Φ = 1.00) = 0.97; MS (70 eV): *m/z* (%): 885 (11) [M<sup>+</sup>+H], 884 (21) [M<sup>+</sup>], 867 (2), 704 (10), 703 (27), 702 (30) [M<sup>+</sup> - C<sub>13</sub>H<sub>26</sub>], 662 (2), 629 (5), 628 (11), 496 (3), 495 (12), 481 (5), 480 (11), 479 (7), 419 (12), 418 (19), 390 (6), 373 (31), 224 (12), 223 (100), 207 (17), 206 (69); elemental analysis calcd (%) for C<sub>58</sub>H<sub>47</sub>N<sub>2</sub>O<sub>7</sub> (884.0): calcd for C 78.80, H 5.36, N 3.17; found: C 78.27, H 5.42, N 3.09; elemental analysis calcd (%) for C<sub>58</sub>H<sub>47</sub>N<sub>2</sub>O<sub>7</sub>: 884.3461; found: 884.3481 (HRMS).

**N-(1-Hexylheptyl)-N'-(2-ethylcarbonyl-N-(1'-naphthyl))-perylene-3,4,9,10-tetracarboxylic bisimide (12c):** 1-Naphthylisocyanate (170 mg, 1.00 mmol), *N*-(1-hexylheptyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8a**, 300 mg, 0.41 mmol) and anhydrous toluene (15 mL) were heated under reflux under Ar for 3 h, evaporated in vacuo, dried (120 °C), purified by column separation (Al<sub>2</sub>O<sub>3</sub> N II, chloroform/ethanol 20:1) and by extractive recrystallization from chloroform to yield a reddish brown powder (210 mg, 65 %). M.p. 232–234 °C; R<sub>f</sub> (Al<sub>2</sub>O<sub>3</sub> N II, CHCl<sub>3</sub>/ethanol 20:1) = 0.43, R<sub>f</sub> (silica gel, CHCl<sub>3</sub>/ethanol 20:1) = 0.29; IR (KBr): ν̄ = 3350 (NH), 3070 w, 2955 s, 2928 s, 2856 s, 1694 brs, 1658 s, 1594 s, 1579 w, 1537 m, 1501 m, 1438 m, 1405 s, 1343 s, 1253 m, 1213 m, 1176 w, 811 s, 794 m, 776 m, 747 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 0.84 (t, 6H; 2CH<sub>3</sub>), 1.29 (m, 16H; 8CH<sub>2</sub>), 1.85 (m, 2H; α-CH<sub>2</sub>), 2.22 (m, 2H; α-CH<sub>2</sub>), 4.58 (t, <sup>3</sup>J(H,H) = 4.2 Hz, 2H; CH<sub>2</sub>-OR), 4.66 (t, <sup>3</sup>J(H,H) = 4.1 Hz, 2H; CH<sub>2</sub>-NR<sub>2</sub>), 5.14 (m, 1H; 1CH), 7.37 (t, <sup>3</sup>J(H,H) = 7.8 Hz, 1H; 1CH naphthalene), 7.47 (t, <sup>3</sup>J(H,H) = 8.5 Hz, 2H; 2CH naphthalene), 7.59 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 1H; 1CH naphthalene), 7.79 (m, 2H; 2CH naphthalene), 8.01 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 1H; 1CH naphthalene), 8.13 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.20 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene), 8.40 (d, <sup>3</sup>J(H,H) = 7.8 Hz, 2H; 2CH perylene), 8.49 (brs, 2H; 2CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.04 (2C, CH<sub>3</sub>), 22.59, 26.97, 29.21, 31.77, 32.32 (10C, CH<sub>2</sub>), 39.84 (1C, CH<sub>2</sub>-NR<sub>2</sub>), 54.87 (1C, CH), 62.88 (1C, CH<sub>2</sub>-OR), 121.16, 122.52, 122.67, 122.81, 125.28, 125.69, 125.86, 125.93, 126.00, 126.11, 128.48, 129.11, 129.17, 131.14, 132.58, 133.73, 134.03, 134.33 (30C, Ar), 154.51, 163.27 (5C, C=O perylene and urethane); UV/Vis (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) = 261 (35050), 293 (10910), 371 (4120), 434 sh (5060), 459 (17710), 490 (49050), 527 nm (81970); fluorescence (CHCl<sub>3</sub>): λ<sub>max</sub> (I<sub>rel</sub>) = 535 (1.00), 578 (0.52), 640 nm (0.13); fluorescence quantum yield (λ<sub>exc</sub> = 490 nm, E<sub>490 nm</sub> = 0.0334/1 cm, CHCl<sub>3</sub>, reference **1a** with Φ = 1.00) = 0.54; MS FAB (3-NBA): *m/z* (%): 787 (1) [M<sup>+</sup>+H], 786 (2) [M<sup>+</sup>], 784 (3), 617 (4), 616 (7) [M<sup>+</sup> - C<sub>11</sub>H<sub>7</sub>NO], 604 (14) [M<sup>+</sup> - C<sub>13</sub>H<sub>26</sub>], 601 (11), 599 (100), 435 [M<sup>+</sup> - C<sub>15</sub>H<sub>7</sub>NO - C<sub>13</sub>H<sub>26</sub>] (6), 419 (11), 418 (36), 417 (57), 391 (9), 390 (6), 373 (10), 345 (6); elemental analysis calcd (%) for C<sub>50</sub>H<sub>47</sub>N<sub>3</sub>O<sub>6</sub> (785.9): C 76.41, H 6.03, N 5.35; found: C 76.17, H 6.15, N 5.23.

**N-(1-Hexylheptyl)-N'-(2-ethylcarbonyl-N-(2'-anthraquinonyl))-perylene-3,4,9,10-tetracarboxylic bisimide (12a):** Anthraquinone-2-isocyanate (90 mg, 0.36 mmol), *N*-(1-hexylheptyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8a**, 140 mg, 0.23 mmol) and anhydrous ligorine (5 mL) were heated under reflux under Ar for 5 h, cooled to room temperature, collected by vacuum filtration (G4), dried (130 °C, 16 h) and purified by column separation (silica gel, chloroform/acetic acid 10:1) and extractive recrystallization from chloroform to yield a bright red powder (30 mg, 15 %). M.p. 283–285 °C; R<sub>f</sub> (silica gel, CHCl<sub>3</sub>/acetic acid 10:1) =

0.73; IR (KBr): ν̄ = 3070 w, 2954 m, 2927 m, 2857 m, 1735 w, 1697 s, 1660 s, 1595 s, 1579 w, 1533 w, 1437 w, 1405 m, 1343 s, 1292 w, 1252 w, 1210 w, 1176 w, 811 m, 747 m, 714 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 0.84 (t, 6H; 2CH<sub>3</sub>), 1.31 (m, 16H; 8CH<sub>2</sub>), 1.91 (m, 2H; α-CH<sub>2</sub>), 2.27 (m, 2H; α-CH<sub>2</sub>), 3.61 (m, 1H; 1NH), 4.65 (s, 2H; CH<sub>2</sub>-OR), 4.73 (s, 2H; CH<sub>2</sub>-NR<sub>2</sub>), 5.21 (m, 1H; 1CH), 7.60 (m, 3H; 3CH anthraquinone), 7.83 (m, 1H; 1CH anthraquinone), 7.94 (m, 1H; 1-H anthraquinone), 8.04 (m, 2H; 2CH anthraquinone), 8.43–8.63 (m, 8H; 8CH perylene); UV/Vis (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) = 261 (51290), 276 (36590), 286 sh (33350), 371 (8590), 434 (5520), 461 (16240), 491 (43890), 528 nm (71590); fluorescence (CHCl<sub>3</sub>): λ<sub>max</sub> (I<sub>rel</sub>) = 538 (1.00), 580 (0.56), 620 nm (0.14); fluorescence quantum yield (λ<sub>exc</sub> = 491 nm, E<sub>491 nm</sub> = 0.0311/1 cm, CHCl<sub>3</sub>, reference **1a** with Φ = 1.00) = 0.96; MS FAB (3-NBA): *m/z* (%): 867 (3) [M<sup>+</sup>+H], 866 (3) [M<sup>+</sup>], 617 (2) [M<sup>+</sup> - C<sub>15</sub>H<sub>7</sub>NO<sub>3</sub>], 615 (5), 601 (7), 600 (31), 599 (70), 598 (7), 597 (7), 513 (4), 419 (15), 418 (52), 417 (100) [M<sup>+</sup> - C<sub>15</sub>H<sub>7</sub>NO<sub>3</sub> - C<sub>13</sub>H<sub>26</sub> - H<sub>2</sub>O], 391 (15), 390 (11), 375 (11), 373 (23), 345 (14); elemental analysis calcd (%) for C<sub>54</sub>H<sub>47</sub>N<sub>3</sub>O<sub>8</sub> (866.0): C 74.90, H 5.47, N 4.85; found: C 74.26, H 5.52, N 5.03.

**N-(1-Heptyloctyl)-N'-(2-ethylcarbonyl-N-(2'-anthraquinonyl))-perylene-3,4,9,10-tetracarboxylic bisimide (12b):** Anthraquinone-2-isocyanate (110 mg, 0.44 mmol), *N*-(1-heptyloctyl)-*N'*-(2-hydroxyethyl)-perylene-3,4,9,10-tetracarboxylic bisimide (**8b**, 210 mg, 0.33 mmol) and anhydrous toluene (20 mL) were heated under reflux under Ar for 18 h (change in colour from dark red to light orange after 30 min), cooled to room temperature, collected by vacuum filtration (D4), washed with chloroform/ethanol 20:1 and ethanol, dried at 130 °C for 16 h (bright orange material), and extractively recrystallized from chloroform to yield a bright orange powder with an intense solid-state fluorescence (190 mg, 64 %). M.p. 280–282 °C; R<sub>f</sub> (silica gel, CHCl<sub>3</sub>/ethanol 10:1) = 0.50; IR (KBr): ν̄ = 3320 m (NH), 3070 w, 2954 s, 2926 s, 2855 s, 1742 m, 1697 s, 1659 s, 1594 s, 1579 w, 1535 m, 1438 m, 1405 s, 1343 s, 1293 w, 1251 m, 1209 m, 1176 w, 1060 w, 811 s, 747 m, 721 w, 714 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 0.82 (t, 6H; 2CH<sub>3</sub>), 1.27 (m, 20H; 10CH<sub>2</sub>), 1.90 (m, 2H; α-CH<sub>2</sub>), 2.26 (m, 2H; α-CH<sub>2</sub>), 3.71 (brs, 1H; 1NH), 4.64 (t, <sup>3</sup>J(H,H) = 4.6 Hz, 2H; CH<sub>2</sub>-OR), 4.73 (t, 2H; CH<sub>2</sub>-NR<sub>2</sub>), 5.20 (m, 1H; 1CH), 7.59 (m, 3H; 3CH anthraquinone), 7.82 (m, 1H; 1CH anthraquinone), 7.93 (m, 1H; 1-H anthraquinone), 8.00 (m, 2H; 2CH anthraquinone), 8.40 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 2H; 2CH perylene), 8.43 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 2H; 2CH perylene), 8.53 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 2H; 2CH perylene), 8.61 (brs, 2H; 2CH perylene); UV/Vis (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) = 262 (49620), 276 (34260), 286 (31430), 371 (7030), 434 (4210), 461 (15760), 493 (45220), 529 nm (75190); fluorescence (CHCl<sub>3</sub>): λ<sub>max</sub> (I<sub>rel</sub>) = 538 (1.00), 580 (0.57), 617 nm (0.14); fluorescence quantum yield (λ<sub>exc</sub> = 491 nm, E<sub>491 nm</sub> = 0.0345/1 cm, CHCl<sub>3</sub>, reference **1a** with Φ = 1.00) = 0.86; solid-state fluorescence: λ<sub>max</sub> = 633 nm br; MS FAB (3-NBA): *m/z* (%): 895 (1) [M<sup>+</sup>+H], 894 (2) [M<sup>+</sup>], 893 (1), 628 (8), 627 (17) [M<sup>+</sup> - C<sub>15</sub>H<sub>7</sub>NO<sub>3</sub> - H<sub>2</sub>O], 626 (2), 625 (3), 550 (2), 419 (6), 418 (19), 417 (36) [M<sup>+</sup> - C<sub>15</sub>H<sub>7</sub>NO<sub>3</sub> - C<sub>13</sub>H<sub>30</sub> - H<sub>2</sub>O], 391 (7), 390 (10), 373 (10), 345 (5), 307 (19), 154 (100); elemental analysis calcd (%) for C<sub>56</sub>H<sub>51</sub>N<sub>3</sub>O<sub>8</sub> (894.0): C 75.23, H 5.75, N 4.70; found: C 75.37, H 5.80, N 4.85.

**Condensation of perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboxylic imides with aromatic amines; general procedure:** *N*-(*sec*-Alkyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboxylic imide (**2**) (0.35 mmol), the corresponding aminoaryl compound (0.42 mmol) zinc acetate dihydrate (0.46 mmol) and imidazole (3.5 g) were heated at 150 °C for 2 h. The solution was cooled, but still warm a small amount of ethanol was added, acidified with 2N HCl, stirred for 30 min, collected by vacuum filtration stirred with boiling aqueous potassium carbonate solution (10 %), collected by vacuum filtration, washed with distilled water and dried in air (100 °C, 16 h).

**N-(1-Hexylheptyl)-N'-(1-anthraquinonyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9a):** 1-Amino-anthraquinone (90 mg, 0.42 mmol), *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-carboximide-9,10-anhydride (**2a**, 200 mg, 0.35 mmol) and 1-aminoanthraquinone (90 mg, 0.42 mmol) were allowed to react according to the general procedure, purified by two column separations (Al<sub>2</sub>O<sub>3</sub> N I, chloroform and silica gel, chloroform/acetone 15:1) and an extractive recrystallization from ethanol to yield a red powder (100 mg, 37 %). M.p. 340–343 °C; R<sub>f</sub> (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.80; R<sub>f</sub> (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.55; IR (KBr): ν̄ = 3080 w, 2954 m, 2927 m, 2856 m, 1720 s, 1698 s, 1662 s, 1594 s, 1580 m, 1433 m, 1405 m, 1371 m, 1344 s, 1320 m, 1279 m, 1257 m, 1203 m, 1176 m, 811 m, 747 m, 709 m, 636 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 0.84 (t, 6H; 2CH<sub>3</sub>), 1.31 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H; α-CH<sub>2</sub>), 2.27 (m,

2H;  $\alpha$ -CH<sub>2</sub>), 5.20 (m, 1H; 1CH), 7.68 (dt,  $^3J(\text{H,H}) = 7.5$  Hz,  $J(\text{H,H}) = 1.4$  Hz, 1H; 7-H anthraquinone), 7.74 (dd,  $^3J(\text{H,H}) = 7.7$  Hz,  $^4J(\text{H,H}) = 1.3$  Hz, 1H; 2-H anthraquinone), 7.76 (dt,  $^3J(\text{H,H}) = 7.5$  Hz,  $^4J(\text{H,H}) = 1.3$  Hz, 1H; 6-H anthraquinone), 8.00 (t,  $^3J(\text{H,H}) = 7.8$  Hz, 1H; 3-H anthraquinone), 8.03 (dd,  $^3J(\text{H,H}) = 7.8$  Hz,  $^4J(\text{H,H}) = 1.4$  Hz, 1H; 8-H anthraquinone), 8.29 (dd,  $^3J(\text{H,H}) = 7.8$  Hz,  $^4J(\text{H,H}) = 1.4$  Hz, 1H; 5-H anthraquinone), 8.58 (dd,  $^3J(\text{H,H}) = 7.9$  Hz,  $^4J(\text{H,H}) = 1.4$  Hz, 1H; 4-H anthraquinone), 8.67 (d,  $^3J(\text{H,H}) = 7.6$  Hz, 2H; 2CH perylene), 8.68 (d,  $^3J(\text{H,H}) = 7.9$  Hz, 4H; 4CH perylene), 8.74 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 2H; 2CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.03$  (2C, CH<sub>3</sub>), 22.59, 26.96, 29.22, 31.77, 32.43 (10C, 10CH<sub>2</sub>), 54.85 (1C, CH), 123.07, 123.25, 123.51, 126.50, 127.01, 127.35, 128.99, 129.24, 129.61, 130.29, 131.80, 132.74, 134.03, 134.12, 134.41, 134.63, 135.37, 135.67, 135.84 (32C, CH perylene, CH anthraquinone), 163.85 (4C, C=O), 182.43, 182.60 (2C, C=O anthraquinone); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(\epsilon) = 259$  sh (61380), 273 sh (22020), 326 sh (8520), 431 sh (5270), 460 (19190), 491 (53120), 529 nm (87670); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(I_{\text{rel}}) = 536$  (1.00), 578 (0.53), 626 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}} = 490$  nm,  $E_{490\text{nm}} = 0.0311/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.97; MS (70 eV):  $m/z$  (%): 779 (12) [ $M^+ + \text{H}$ ], 778 (24) [ $M^+$ ], 761 (5), 599 (6), 598 (27), 597 (82), 596 (100) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 569 (5), 568 (20), 567 (41), 540 (12), 523 (9), 522 (8); elemental analysis calcd (%) for C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub>: 778.3043; found: 778.3077 (MS); elemental analysis calcd (%) for C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub> (778.2): C 78.64, H 5.44, N 3.60; found: C 78.35, H 5.50, N 3.53.

**N-(1-Hexylheptyl)-N'-(2-anthraquinonyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9b)**: 2-Amino-anthraquinone (90 mg, 0.42 mmol) and *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-carboximide-9,10-anhydride (**2a**, 200 mg, 0.35 mmol) were allowed to react according to the general procedure and purified by a column separation (Al<sub>2</sub>O<sub>3</sub> N I, chloroform) and an extractive recrystallization from ethanol to yield a red solid (900 mg, 33%). M.p. >350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.79;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.64; IR (KBr):  $\tilde{\nu} = 3070$  w, 2955 m, 2927 m, 2856 m, 1698 s, 1676 s, 1660 s, 1594 s, 1579 m, 1405 m, 1342 s, 1325 w, 1286 m, 1253 m, 1175 m, 811 m, 746 m, 712 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.83$  (t, 6H; 2CH<sub>3</sub>), 1.29 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.27 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.20 (m, 1H; 1CH), 7.83 (m, 3H; 3CH anthraquinone), 8.37 (m, 3H; 3CH anthraquinone), 8.54 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H; 1CH anthraquinone), 8.54 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 6H; 6CH perylene), 8.78 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 2H; 2CH perylene); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(\epsilon) = 256$  (80850), 276 sh (24370), 323 (9790), 436 sh (5590), 461 (18270), 491 (49560), 528 nm (82150); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(I_{\text{rel}}) = 536$  (1.00), 578 (0.54), 628 nm (0.13); fluorescence quantum yield ( $\lambda_{\text{exc}} = 488$  nm,  $E_{488\text{nm}} = 0.0374/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.01; MS (70 eV):  $m/z$  (%): 779 (7) [ $M^+ + \text{H}$ ], 778 (13) [ $M^+$ ], 599 (5), 598 (23), 597 (67), 596 (100) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 595 (11); elemental analysis calcd (%) for C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub>: 778.3043; found: 778.3106 (MS); elemental analysis calcd (%) for C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub> (778.2): C 78.64, H 5.44, N 3.60; found: C 77.94, H 5.69, N 3.66.

**N-(1-Hexylheptyl)-N'-(1-anthracenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9c)**: 1-Aminoanthracene (80 mg, 0.41 mmol) and *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol) were allowed to react according to the general procedure and purified by two column separations (Al<sub>2</sub>O<sub>3</sub> N I, chloroform and silica gel, chloroform/acetone 15:1; orange forerun and broad red main fraction) and an extractive recrystallization from toluene. Yield 110 mg (42%) of **9c**, orange powder, m.p. >350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.70;  $R_f$  (silica gel, CHCl<sub>3</sub>) = 0.23;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.63; IR (KBr):  $\tilde{\nu} = 3050$  w, 2954 m, 2928 m, 2856 m, 1698 s, 1660 s, 1594 s, 1579 m, 1430 w, 1405 m, 1342 s, 1253 m, 1176 m, 811 m, 747 m, 730 w, 637 cm<sup>-1</sup> w; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.84$  (t, 6H; 2CH<sub>3</sub>), 1.29 (m, 16H; 8CH<sub>2</sub>), 1.89 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.28 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.21 (m, 1H; 1CH), 7.40 (dd, 1H; 1CH anthracene), 7.32 (m, 1H; 2CH anthracene), 7.45 (d, 2H; 2CH anthracene), 7.47 (t,  $^3J(\text{H,H}) = 8.3$  Hz, 1H; 1CH anthracene), 7.55 (d,  $^3J(\text{H,H}) = 7.2$  Hz, 1H; 1CH anthracene), 8.72–8.76 (m, 8H; 8CH perylene), 8.81 (s, 1H; 1CH anthracene), 8.84 (s, 1H; 1CH anthracene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.01$  (2C, CH<sub>3</sub>), 22.56, 26.91, 29.18, 31.74, 32.37 (10C, 10CH<sub>2</sub>), 54.84 (1C, CH), 122.85, 123.03, 123.22, 123.53, 124.22, 126.85, 128.06, 128.41, 129.60, 132.07, 132.36, 133.80, 135.46, 135.60, 137.28, 137.57, 139.43 (34C, CH perylene, CH anthracene), 163.05 (4C, C=O); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(\epsilon) = 258$  (97790), 345 (4930), 363 (6770), 384 (5610), 435 sh (2970), 461 (11390), 492 (30440), 529 nm (49700); fluorescence

(CHCl<sub>3</sub>):  $\lambda_{\text{max}}(I_{\text{rel}}) = 536$  (1.00), 577 (0.57), 528 nm (0.17); fluorescence quantum yield ( $\lambda_{\text{exc}} = 490$  nm,  $E_{490\text{nm}} = 0.0311/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.42; MS (70 eV):  $m/z$  (%): 749 (57) [ $M^+ + \text{H}$ ], 748 (100) [ $M^+$ ], 569 (6), 568 (22), 567 (60), 566 (100) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 521 (8), 374 (9), 373 (36), 345 (11), 283 (6); elemental analysis calcd (%) for C<sub>51</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub> (748.9): C 81.79, H 5.92, N 3.74; found: C 81.85, H 5.72, N 3.72.

**N-(1-Hexylheptyl)-N'-(2-anthracenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9d)**: 2-Amino-anthracene (80 mg, 0.41 mmol) and *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol) were allowed to react according to the general procedure and purified by two column separations (Al<sub>2</sub>O<sub>3</sub> N I, chloroform and silica gel, chloroform/acetone 15:1) and extractive recrystallizations from chloroform and toluene to yield a red powder (50 mg, 19%). M.p. >350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.83;  $R_f$  (silica gel, CHCl<sub>3</sub>) = 0.32;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.77; IR (KBr):  $\tilde{\nu} = 2954$  m, 2927 m, 2856 m, 1698 s, 1660 s, 1594 s, 1579 m, 1459 w, 1433 w, 1405 m, 1343 s, 1254 m, 1176 m, 810 m, 746 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.83$  (t, 6H; 2CH<sub>3</sub>), 1.28 (m, 16H; 8CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.19 (m, 1H; 1CH), 6.07 (s, 1H; anthracene), 6.13 (s, 1H; 1CH anthracene), 7.29 (dd,  $^3J(\text{H,H}) = 7.7$  Hz,  $^4J(\text{H,H}) = 1.9$  Hz, 1H; 3-H anthracene), 7.33 (m, 2H; 2CH anthracene), 7.44 (m, 3H; 3CH anthracene), 7.62 (d,  $^3J(\text{H,H}) = 7.6$  Hz, 1H; 4-H anthracene), 8.74 (m, 8H; 8CH perylene); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 14.02$  (2C, CH<sub>3</sub>), 22.57, 26.94, 29.20, 31.75, 32.40 (10C, 10CH<sub>2</sub>), 118.07, 123.10, 128.03, 131.99, 145.44; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(\epsilon) = 258$  (255900), 260 (245650), 343 (8560), 358 (10470), 378 (7800), 460 (19880), 491 (53650), 528 nm (87050); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(I_{\text{rel}}) = 536$  (1.00), 578 (0.57), 631 nm, (0.19); fluorescence quantum yield ( $\lambda_{\text{exc}} = 490$  nm,  $E_{490\text{nm}} = 0.0331/1$  cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi = 1.00$ ) = 0.04; MS (70 eV):  $m/z$  (%): 749 (39) [ $M^+ + \text{H}$ ], 748 (68) [ $M^+$ ], 569 (10), 568 (34), 567 (83), 566 (100) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 565 (9), 522 (7), 521 (16), 374 (11), 373 (41), 346 (7), 345 (21), 328 (5), 284 (6), 283 (10), 182 (5) [ $\text{C}_{13}\text{H}_{26}^+$ ]; elemental analysis calcd (%) for C<sub>51</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub> (748.9): C 81.79, H 5.92, N 3.74; found: C 81.37, H 5.87, N 3.74.

**N-(Hexylheptyl)-N'-(1-naphthyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9e)**: *N*-(1-Hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (100 mg, 0.17 mmol), 1-aminonaphthalene (30 mg, 0.30 mmol), zinc acetate dihydrate (40 mg, 0.18 mmol) and Imidazole (3.5 g) were allowed to react according to the general procedure and purified by two column separations (Al<sub>2</sub>O<sub>3</sub> N I, chloroform and silica gel, chloroform for an orange forerun and chloroform/acetone 15:1 for the broad orange main fraction) to yield a red powder (100 mg, 82%). M.p. >350 °C;  $R_f$  (silica gel/CHCl<sub>3</sub>/acetone 15:1) = 0.65;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.62; IR (KBr):  $\tilde{\nu} = 3070$  w, 2954 m, 2927 m, 2856 m, 1710 s, 1698 s, 1660 s, 1594 s, 1579 m, 1432 w, 1405 m, 1393 w, 1341 s, 1253 s, 1176 w, 811 m, 790 m, 770 w, 746 m, 636 cm<sup>-1</sup> m; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(\epsilon) = 261$  (36840), 281 (11670), 291 (9810), 369 (4240), 433 sh (5400), 459 (18950), 490 (52370), 527 nm (87190); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\text{max}}(I_{\text{rel}}) = 536$  (1.00), 578 (0.53), 627 nm (0.12); MS (70 eV):  $m/z$  (%): 699 (11) [ $M^+ + \text{H}$ ], 698 (20) [ $M^+$ ], 681 (7), 518 (24), 517 (72), 516 (100) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 515 (8), 500 (6), 499 (12), 471 (11), 374 (10), 373 (37), 182 (2); elemental analysis calcd (%) for C<sub>47</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub> (698.9): C 80.78, H 6.06, N 4.01; found: C 81.00, H 6.12, N 4.20.

**N-(Hexylheptyl)-N'-(3-pyrenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9f)**: 3-Amino-pyrene (90 mg, 0.42 mmol), *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (3.5 g) were allowed to react according to the general procedure and purified by column separation (Al<sub>2</sub>O<sub>3</sub> N I, chloroform) to yield a red powder (220 mg, 68%). M.p. >350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.85;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.76; IR (KBr):  $\tilde{\nu} = 3050$  w, 2954 m, 2926 m, 2856 m, 1720 w, 1696 s, 1660 s, 1616 w, 1594 s, 1579 m, 1437 w, 1405 m, 1343 s, 1254 m, 1175 w, 844 w, 811 m, 749 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 0.84$  (t, 6H; 2CH<sub>3</sub>), 1.32 (m, 16H; 8CH<sub>2</sub>), 1.87 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.24 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.21 (m, 1H; CH), 7.84 (d,  $^3J(\text{H,H}) = 9.2$  Hz, 1H; 10-H pyrene), 7.93 (t,  $^3J(\text{H,H}) = 7.7$  Hz, 1H; 7-H pyrene), 7.98 (d,  $^3J(\text{H,H}) = 9.3$  Hz, 1H; 9-H pyrene), 8.02 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H; 2-H pyrene), 8.05 (s, 4-H pyrene, 2H; 5-H pyrene), 8.06 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H; 8-H pyrene), 8.13 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H; 6-H pyrene), 8.32 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H; 3-H pyrene), 8.54 (d,  $^3J(\text{H,H}) = 8.3$  Hz, 2H; 2CH perylene), 8.58 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 2H; 2CH perylene), 8.63 (brs, 2H; 2CH perylene), 8.75 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 2H; 2CH perylene); <sup>13</sup>C NMR

(CDCl<sub>3</sub>):  $\delta$  = 14.03 (2C, CH<sub>3</sub>), 22.58, 26.98, 29.22, 31.77, 32.40 (10C, 10CH<sub>2</sub>), 54.82 (1C, CH), 121.16, 123.05, 123.16, 123.30, 124.48, 125.33, 125.45, 125.53, 125.80, 126.12, 126.22, 126.51, 126.64, 127.11, 127.97, 128.09, 128.94, 129.06, 129.37, 130.06, 130.65, 130.87, 131.84, 131.99, 134.11 (36C, CH perylene, CH pyrene), 163.97 (4C, C=O); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 261 (52560), 277 (52530), 312 (16610), 326 (30800), 342 (43170), 366 (5650), 435 sh (6690), 460 (21180), 491 (56650), 528 nm (92840); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 534 (1.00), 579 (0.60), 635 nm (0.19); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 491 nm,  $E_{491\text{nm}}$  = 0.0296/1 cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi$  = 1.00) = 0.01; MS (70 eV):  $m/z$  (%): 773 (41), 772 (70) [ $M^+$ ], 593 (8), 592 (33), 591 (86), 590 (100) [ $M^+ - C_{13}H_{26}$ ], 545 (14), 374 (17), 373 (64), 346 (12), 345 (24), 328 (8), 296 (9), 202 (12); elemental analysis calcd (%) for C<sub>53</sub>H<sub>44</sub>N<sub>2</sub>O<sub>5</sub> (772.9): C 82.36, H 5.74, N 3.62; found: C 82.19, H 5.75, N 3.88.

**N-(1-Hexylheptyl)-N'-(1-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9g)**: 1-Amino-fluorene-9-one (80 mg, 0.41 mmol), *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (3.5 g) were allowed to react according to the general procedure and purified by column separation (Al<sub>2</sub>O<sub>3</sub> N I, chloroform) to yield a red powder (150 mg, 57%). M.p. 327–329 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.67;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.61; IR (KBr):  $\tilde{\nu}$  = 3080 w, 2954 m, 2927 m, 2856 m, 1713 s, 1698 s, 1658 s, 1610 m, 1594 s, 1579 m, 1452 w, 1434 w, 1405 m, 1343 s, 1255 m, 1200 w, 1176 w, 811 m, 755 m, 747 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.82 (t, 6H; 2CH<sub>3</sub>), 1.27 (m, 16H; 8CH<sub>2</sub>), 1.86 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.24 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.18 (m, 1H; 1CH), 7.23 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 1H; 7-H fluorenone), 7.27 (dd, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>4</sup>J(H,H) = 1.3 Hz, 1H; 2-H fluorenone), 7.47 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 6-H fluorenone), 7.48 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 8-H fluorenone), 7.56 (d, <sup>3</sup>J(H,H) = 7.3 Hz, 1H; 5-H fluorenone), 7.64 (dd, <sup>3</sup>J(H,H) = 7.6 Hz, <sup>4</sup>J(H,H) = 1.4 Hz, 1H; 4-H fluorenone), 7.67 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 3-H fluorenone), 8.59 (d, <sup>3</sup>J = 8.1 Hz, 4H; 4CH perylene), 8.65 (brs, 2H; 2CH perylene), 8.68 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene); COSY NMR (CDCl<sub>3</sub>): cross-peaks at  $\delta$  = (7.23, 7.47, 7.48, 7.56), (7.27, 7.63, 7.67); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.01 (2C, CH<sub>3</sub>), 22.56, 26.93, 29.20, 31.74, 32.38 (10C, 10CH<sub>2</sub>), 54.78 (1C, CH), 120.52, 120.97, 122.99, 123.22, 123.28, 124.39, 129.38, 130.23, 131.74, 134.83, 135.10, 135.57, 143.77, 146.00 (32C, CH perylene, CH fluorenone), 163.18 (4C, C=O), 191.55 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 252 (77490), 261 (94380), 369 (4560), 432 sh (5490), 459 (19320), 490 (53700), 527 nm (89850); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 535 (1.00), 578 (0.52), 626 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490\text{nm}}$  = 0.0368/1 cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi$  = 1.00) = 1.01; MS (70 eV):  $m/z$  (%): 752 (18), 751 (33) [ $M^+$ ], 733 (7), 571 (8), 570 (35), 569 (100) [ $M^+ - C_{13}H_{26}$ ], 568 (84), 542 (7), 541 (35), 540 (77), 539 (14), 513 (5), 512 (17), 511 (12), 496 (8), 495 (11); elemental analysis calcd (%) for C<sub>50</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub> (750.9): C 79.98, H 5.64, N 3.73; found: C 80.00, H 5.75, N 3.78.

**N-(1-Hexylheptyl)-N'-(2-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9h)**: 2-Amino-fluorene-9-one (80 mg, 0.41 mmol), *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (3.5 g) were allowed to react according to the general procedure and purified by column separation (Al<sub>2</sub>O<sub>3</sub> N I, chloroform) to yield a violet powder (50 mg, 19%). M.p. > 350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.85;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.88; IR (KBr):  $\tilde{\nu}$  = 3070 w, 2954 m, 2927 m, 2856 m, 1698 (brs), 1658 s, 1616 w, 1594 s, 1579 m, 1457 m, 1430 w, 1405 m, 1342 s, 1254 m, 1191 w, 1176 m, 1100 w, 811 s, 746 m, 738 cm<sup>-1</sup> w; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.83 (t, 6H; 2CH<sub>3</sub>), 1.29 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.27 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.19 (m, 1H; 1CH), 7.36 (t, <sup>3</sup>J(H,H) = 7.4 Hz, 1H; 7-H fluorenone), 7.49 (dd, <sup>3</sup>J(H,H) = 7.6 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H; 5-H fluorenone), 7.55 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 6-H fluorenone), 7.62 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 8-H fluorenone), 7.64 (d, <sup>4</sup>J(H,H) = 1.9 Hz, 1H; 1H; fluorenone), 7.72 (d, <sup>3</sup>J(H,H) = 7.6 Hz, 1H; 3-H fluorenone), 7.73 (d, <sup>3</sup>J(H,H) = 7.6 Hz, 1H; 4-H fluorenone), 8.71 (d, <sup>3</sup>J(H,H) = 7.9 Hz, 6H; 6CH perylene), 8.77 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 252 88310), 261 (122500), 368 (5080), 433 sh (6060), 459 (19990), 490 (54520), 527 nm (90640); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 536 (1.00), 579 (0.52), 626 nm (0.12); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 490 nm,  $E_{490\text{nm}}$  = 0.0311/1 cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi$  = 1.00) = 1.01; MS (70 eV):  $m/z$  (%): 751 (11), 750 (20) [ $M^+$ ], 733 (5), 570 (24), 569 (72), 568 (100) [ $M^+ - C_{13}H_{26}$ ], 567 (9), 523 (4), 374 (5), 373

(20), 345 (4); elemental analysis calcd (%) for C<sub>50</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub> (750.9): C 79.98, H 5.64, N 3.73; found: C 77.58, H 5.50, N 3.64; analysis calcd for C<sub>50</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub>: 750.3093; found: 750.3094 (HRMS).

**N-(1-Hexylheptyl)-N'-(3-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9i)**: 3-Amino-fluorene-9-one (80 mg, 0.41 mmol), *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (3.5 g) were allowed to react according to the general procedure and purified by column separation (Al<sub>2</sub>O<sub>3</sub> N I, chloroform) to yield a red powder (150 mg, 57%). M.p. > 350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.48;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.50; IR (KBr):  $\tilde{\nu}$  = 3080 w, 2954 m, 2927 m, 2856 m, 1713 s, 1700 s, 1660 s, 1614 w, 1594 s, 1579 m, 1448 w, 1432 w, 1405 m, 1342 s, 1254 m, 1176 w, 810 m, 746 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.83 (t, 6H; 2CH<sub>3</sub>), 1.31 (m, 16H; 8CH<sub>2</sub>), 1.90 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.27 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.12 (m, 1H; 1CH), 7.30 (dd, <sup>3</sup>J(H,H) = 7.6 Hz, <sup>4</sup>J(H,H) = 1.6 Hz, 1H; 2-H fluorenone), 7.33 (dt, <sup>3</sup>J(H,H) = 7.9 Hz, <sup>4</sup>J(H,H) = 1.6 Hz, 1H; 7-H fluorenone), 7.45 (d, <sup>3</sup>J(H,H) = 7.3 Hz, 1H; 5-H fluorenone), 7.48 (t, <sup>3</sup>J(H,H) = 7.8 Hz, 1H; 6-H fluorenone), 7.57 (d, <sup>4</sup>J(H,H) = 1.7 Hz, 1H; 4-H fluorenone), 7.68 (d, <sup>3</sup>J(H,H) = 7.4 Hz, 1H; 8-H fluorenone), 7.85 (d, <sup>3</sup>J(H,H) = 7.7 Hz, 1H; 1-H fluorenone), 8.60 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2H; 2CH perylene), 8.66 (brs, 2H; 2CH perylene), 8.72 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H; 2CH perylene); COSY NMR: cross-peaks at  $\delta$  = (7.30, 7.57, 7.85), (7.33, 7.45, 7.48, 7.68); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.01 (2C, CH<sub>3</sub>), 22.56, 26.97, 29.19, 31.74, 32.37 (10C, 10CH<sub>2</sub>), 54.91 (1C, CH), 120.73, 121.37, 122.86, 123.02, 123.39, 124.44, 125.08, 126.28, 126.62, 129.43, 129.49, 129.55, 129.76, 131.88, 134.00, 134.25, 134.30, 134.78, 135.34, 140.87, 143.65, 145.86 (32C, CH perylene, CH fluorenone), 163.24 (4C, C=O), 192.74 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 252 (89280), 261 (127320), 369 (4580), 434 sh (5560), 460 (19280), 491 (53420), 528 nm (89190); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 537 (1.00), 581 (0.53), 630 nm (0.13); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 491 nm,  $E_{491\text{nm}}$  = 0.0266/1 cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi$  = 1.00) = 0.94; MS (70 eV):  $m/z$  (%): 751 (8), 750 (14) [ $M^+$ ], 571 (6), 570 (30), 569 (78), 568 (100) [ $M^+ - C_{13}H_{26}$ ], 567 (28), 523 (9), 442 (9), 373 (15), 182 (6) [ $C_{13}H_{26}^+$ ]; elemental analysis calcd (%) for C<sub>50</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub> (750.9): C 79.98, H 5.64, N 3.73; found: C 80.26, H 5.97, N 3.77.

**N-(1-Hexylheptyl)-N'-(4-fluorene-9-onyl)-perylene-3,4,9,10-tetracarboxylic bisimide (9j)**: 4-Amino-fluorene-9-one (80 mg, 0.41 mmol), *N*-(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (3.5 g) were allowed to react according to the general procedure and purified by column separation (Al<sub>2</sub>O<sub>3</sub> N I, chloroform) to yield a red powder (120 mg, 46%). M.p. > 350 °C;  $R_f$  (silica gel, CHCl<sub>3</sub>/acetone 15:1) = 0.55;  $R_f$  (Al<sub>2</sub>O<sub>3</sub> N I, CHCl<sub>3</sub>) = 0.56; IR (KBr):  $\tilde{\nu}$  = 3080 w, 2954 m, 2927 m, 2855 m, 1713 s, 1698 s, 1660 s, 1611 w, 1594 s, 1579 m, 1468 w, 1432 w, 1405 m, 1342 s, 1302 w, 1253 m, 1176 w, 811 m, 747 m, 734 cm<sup>-1</sup> m; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 0.83 (t, 6H; 2CH<sub>3</sub>), 1.31 (m, 16H; 8CH<sub>2</sub>), 1.88 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 2.25 (m, 2H;  $\alpha$ -CH<sub>2</sub>), 5.17 (m, 1H; 1CH), 7.01 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H; 5-H fluorenone), 7.16 (dt, <sup>3</sup>J(H,H) = 7.6 Hz, <sup>4</sup>J(H,H) = 1.3 Hz, 1H; 7-H fluorenone), 7.22 (dt, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>4</sup>J(H,H) = 1.1 Hz, 1H; 6-H fluorenone), 7.43 (dd, <sup>3</sup>J(H,H) = 7.9 Hz, <sup>4</sup>J(H,H) = 1.1 Hz, 1H; 3-H fluorenone), 7.52 (t, <sup>3</sup>J(H,H) = 7.7 Hz, 1H; 2-H fluorenone), 7.67 (dd, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>4</sup>J(H,H) = 1.3 Hz, 1H; 8-H fluorenone), 7.84 (dd, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>4</sup>J(H,H) = 1.4 Hz, 1H; 1-H fluorenone), 8.73 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 6H; 6CH perylene), 8.80 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H; 2CH perylene); COSY NMR: cross-peaks at  $\delta$  = (7.01, 7.22), (7.16, 7.22), (7.43, 7.52), (7.52, 7.84); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.02 (2C, CH<sub>3</sub>), 22.58, 26.95, 29.20, 31.75, 32.39 (10C, 10CH<sub>2</sub>), 54.91 (1C, CH), 121.73, 122.72, 123.19, 123.63, 124.62, 129.47, 130.15, 130.28, 132.37, 135.79, 135.87, 136.10, 141.45, 142.39 (32C, CH perylene, CH fluorenone), 163.06 (4C, C=O), 192.60 (1C, C=O fluorenone); UV (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) = 251 (79330), 259 (85660), 370 (4780), 435 sh (5520), 460 (18750), 491 (51570), 528 nm (85900); fluorescence (CHCl<sub>3</sub>):  $\lambda_{\max}$  ( $I_{\text{rel}}$ ) = 536 (1.00), 581 (0.54), 529 nm (0.13); fluorescence quantum yield ( $\lambda_{\text{exc}}$  = 491 nm,  $E_{491\text{nm}}$  = 0.0311/1 cm, CHCl<sub>3</sub>, reference **1a** with  $\Phi$  = 1.00) = 0.98; MS (70 eV):  $m/z$  (%): 751 (19), 750 (34) [ $M^+$ ], 733 (7), 571 (7), 570 (28), 569 (77), 568 (100) [ $M^+ - C_{13}H_{26}$ ], 552 (10), 551 (20), 523 (14), 373 (11); elemental analysis calcd (%) for C<sub>50</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub> (750.9): C 79.98, H 5.64, N 3.73; found: C 80.49, H 5.74, N 3.75; analysis calcd for C<sub>50</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub>: 750.3094; found: 750.3042 (HRMS).

**N-(1-Hexylheptyl)-N'-(3-methylpyrenyl)-perylene-3,4,9,10-tetracarboxylic bisimide (10b)**: 3-Ainomethylpyrene hydrochloride (110 mg, 0.41 mmol),

*N*-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-carboximide (**2a**, 200 mg, 0.35 mmol) and imidazole (3.5 g) were allowed to react according to the general procedure and purified by column separation ( $\text{Al}_2\text{O}_3$  N I, chloroform) to yield light red powder (200 mg, 73%). M.p.  $>350^\circ\text{C}$ ;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.80;  $R_f$  ( $\text{Al}_2\text{O}_3$  N I,  $\text{CHCl}_3$ ) = 0.71; IR (KBr):  $\tilde{\nu}$  = 3050 w, 2954 m, 2927 m, 2856 m, 1695 s, 1658 s, 1594 s, 1579 m, 1437 w, 1404 m, 1355 m, 1338 s, 1253 m, 1173 w, 847 w, 810 m,  $750\text{ cm}^{-1}$  m;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 0.82 (t, 6H; 2  $\text{CH}_3$ ), 1.27 (m, 16H; 8  $\text{CH}_2$ ), 1.88 (m, 2H;  $\alpha\text{-CH}_2$ ), 2.26 (m, 2H;  $\alpha\text{-CH}_2$ ), 5.19 (m, 1H; CH), 6.13 (s, 2H; 1  $\text{CH}_2$ ), 7.91 (d,  $^3J(\text{H,H})$  = 8.9 Hz, 1H; 10-H pyrene), 7.94 (t,  $^3J(\text{H,H})$  = 7.4 Hz, 1H; 7-H pyrene), 7.95 (d,  $^3J(\text{H,H})$  = 9.0 Hz, 1H; 9-H pyrene), 8.03 (d,  $^3J(\text{H,H})$  = 8.2 Hz, 1H; 4-H pyrene), 8.06 (d,  $^3J(\text{H,H})$  = 7.9 Hz, 1H; 5-H pyrene), 8.09 (d,  $^3J(\text{H,H})$  = 7.7 Hz, 1H; 6-H pyrene), 8.14 (d,  $^3J(\text{H,H})$  = 7.8 Hz, 1H; 8-H pyrene), 8.17 (d, 1H;  $^3J(\text{H,H})$  = 9.3 Hz, 3-H pyrene), 8.50 (d,  $J(\text{H,H})$  = 8.2 Hz, 2H; 2 CH perylene), 8.52 (d,  $^3J(\text{H,H})$  = 9.0 Hz, 2H; 2 CH perylene), 8.64 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 4H; 4 CH perylene), 8.66 (d,  $^3J(\text{H,H})$  = 9.6 Hz, 2H; 2-H pyrene); COSY NMR: cross-peaks at  $\delta$  = (7.91, 7.93), (7.94, 8.06, 8.09), (8.03, 8.06), (8.17, 8.66);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 13.97 (2 C,  $\text{CH}_3$ ), 22.54, 26.93, 29.18, 31.73, 32.38 (10 C,  $\text{CH}_2$ ), 41.49 (1 C,  $\text{CH}_2$ ), 54.80 (1 C, CH), 122.89, 123.03, 123.12, 124.69, 124.84, 125.05, 125.13, 125.83, 126.08, 126.27, 126.42, 127.22, 127.26, 127.81, 128.86, 129.45, 130.16, 130.69, 130.76, 131.22, 131.70, 132.08, 132.99, 134.19, 134.86, 139.30 (36 C, CH perylene, CH pyrene), 162.65, 163.67 (4 C, C=O); UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 261 (45250), 278 (46850), 302 sh (8070), 315 (15790), 328 (32510), 344 (46060), 370 (4320), 434 sh (5160), 460 (19030), 491 (52840), 528 nm (87020); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 534 (1.0), 571 nm (0.6); MS (70 eV):  $m/z$  (%): 788 (4) [ $M^+ + \text{H}$ ], 787 (70) [ $M^+$ ], 605 (6) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 604 (6), 416 (4), 391 (5), 390 (8) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{17}\text{H}_{11}$ ], 217 (17), 216 (100), 215 (73), 182 (18); elemental analysis calcd (%) for  $\text{C}_{54}\text{H}_{46}\text{N}_2\text{O}_4$  (787.0): C 82.42, H 5.89, N 3.56; found: C 82.99, H 5.91, N 3.73.

**Coupling of chromophores by the formation of carboxylic amides; general procedure:** *N*-(*sec*-Alkyl)-*N'*-(amino)-perylene-3,4:9,10-tetracarboxylic bisimide (0.26 mmol) and a carboxylic chloride (0.52 mmol) in anhydrous toluene (20 mL) were stirred under Ar at room temperature for 20 h. The reaction product was collected by vacuum filtration (D4) and dried at  $130^\circ\text{C}$  for 16 h.

***N*-(1-Hexylheptyl)-*N'*-(aminocarbonyl-2'-anthraquinonyl)-perylene-3,4:9,10-tetracarboxylic bisimide (15a):** *N*-(1-Hexylheptyl)-*N'*-(amino)-perylene-3,4:9,10-tetracarboxylic bisimide (150 mg, 0.26 mmol) and anthraquinone-2-carboxylic chloride (140 mg, 0.52 mmol) were allowed to react according to the general procedure and purified by two extractive recrystallizations (toluene and chloroform) to yield a reddish brown powder (160 mg, 73%). M.p.  $>360^\circ\text{C}$ ;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.46;  $R_f$  ( $\text{Al}_2\text{O}_3$  N II,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.47; IR (KBr):  $\tilde{\nu}$  = 3350 w (NH), 3080 w, 2927 m, 2856 m, 1724 w, 1697 s, 1658 s, 1594 s, 1404 m, 1347 s, 1253 s, 1173 m, 810 s, 740 s, 709  $\text{cm}^{-1}$  s;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 0.82 (t, 6H; 2  $\text{CH}_3$ ), 1.27 (m, 16H; 8  $\text{CH}_2$ ), 1.89 (m, 2H;  $\alpha\text{-CH}_2$ ), 2.27 (m, 2H;  $\alpha\text{-CH}_2$ ), 3.66 (s, 1H; 1 NH), 5.20 (m, 1H; 1 CH), 7.84 (m, 2H; 2 CH anthraquinone), 8.38 (m, 2H; 2 CH anthraquinone), 8.50 (brs, 2H; 2 CH anthraquinone), 8.63 (d,  $^3J(\text{H,H})$  = 8.4 Hz, 2H; 2 CH perylene), 8.67 (d,  $^3J(\text{H,H})$  = 8.6 Hz, 2H; 2 CH perylene), 8.75 (d,  $^3J(\text{H,H})$  = 8.0 Hz, 4H; 4 CH perylene), 8.96 (s, 1H; 1-H anthraquinone); UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 259 (76660), 276 sh (18390), 331 br. (9410), 367 (6820), 434 sh (7430), 460 (22530), 491 (59700), 528 nm (97860); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 535 (1.00), 577 (0.54), 627 nm (0.13); MS (70 eV):  $m/z$  (%): 822 (5) [ $M^+ + \text{H}$ ], 821 (9) [ $M^+$ ], 641 (9), 640 (24), 639 (30) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 588 (6), 587 (15), 407 (16), 406 (60), 405 (100) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{15}\text{H}_6\text{O}_3$ ], 391 (6), 390 (10), 377 (11), 376 (31), 251 (11), 250 (7), 249 (40), 236 (12), 235 (70), 221 (13), 207 (13); elemental analysis calcd (%) for  $\text{C}_{52}\text{H}_{43}\text{N}_3\text{O}_7$  (821.9): C 75.99, H 5.27, N 5.11; found: C 76.29, H 5.67, N 5.34.

***N*-(1-Hexylheptyl)-*N'*-(aminocarbonyl-2'-fluorene-9-onyl)-perylene-3,4:9,10-tetracarboxylic bisimide (15b):** *N*-(1-Hexylheptyl)-*N'*-(amino)-perylene-3,4:9,10-tetracarboxylic bisimide (100 mg, 0.17 mmol) and fluorene-9-on-2-carboxylic chloride (120 mg, 0.49 mmol) were allowed to react according to the general procedure and purified by an extractive recrystallization from chloroform to yield a reddish orange powder (50 mg, 37%). M.p.  $>360^\circ\text{C}$ ;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.28; IR (KBr):  $\tilde{\nu}$  = 3070 w, 2927 m, 2856 m, 1722 s, 1697 s, 1660 s, 1616 w, 1594 s, 1579 w, 1458 w, 1404 m, 1347 m, 1306 w, 1255 m, 1176 w, 810 m,  $740\text{ cm}^{-1}$  m; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 261 (93070), 270 (85790), 298 sh (10990), 314 sh

(7640), 370 (5060), 434 sh (5930), 459 (19580), 490 (53100), 527 nm (87580); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 537 (1.00), 579 (0.54), 629 nm (0.13); MS (70 eV):  $m/z$  (%): 794 (19) [ $M^+ + \text{H}$ ], 793 (34) [ $M^+$ ], 776 (8), 613 (17), 612 (39), 611 (34) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 406 (3), 405 (3), 391 (4), 390 [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{14}\text{H}_7\text{NO}_2$ ] (5), 377 (4), 376 (7), 221 (50) [ $M^+ - \text{C}_{14}\text{H}_7\text{NO}_2$ ], 208 (16), 207 (100); elemental analysis calcd (%) for  $\text{C}_{53}\text{H}_{43}\text{N}_3\text{O}_8$  (793.9): C 77.16, H 5.46, N 5.29; found: C 77.01, H 5.49, N 5.31.

***N*-(1-Hexylheptyl)-*N'*-(aminocarbonyl-2'-fluorene-9-onyl)-perylene-3,4:9,10-tetracarboxylic bisimide (11b):** *N*-(1-Hexylheptyl)-*N'*-(amino)-perylene-3,4:9,10-tetracarboxylic bisimide (100 mg, 0.17 mmol) and fluorene-9-one-2-isocyanate (120 mg, 0.54 mmol) in anhydrous toluene (10 mL) were stirred under Ar at room temperature for 24 h, evaporated in vacuo (12 mbar) and purified by column separation (silica gel, chloroform/acetone 15:1 for a light red forerun and chloroform/ethanol 20:1 for the broad red main fraction) to yield a violet solid (110 mg, 80%). M.p. 296–299  $^\circ\text{C}$  decomp;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.02;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{ethanol}$  20:1) = 0.57; IR (KBr):  $\tilde{\nu}$  = 3380 w (NH), 3070 w, 2927 m, 2856 m, 1730 w, 1698 s, 1660 m, 1595 s, 1579 w, 1549 w, 1493 w, 1458 m, 1430 w, 1404 w, 1346 m, 1301 m, 1253 m, 1177 m, 1109 w, 810 m, 765 w, 738  $\text{cm}^{-1}$  m; UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 262 (75190), 272 (80030), 315 sh (16770), 331 sh (11120), 436 sh (5110), 461 (13070), 492 (33390), 528 nm (54510); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 536 (1.00), 577 (0.63), 528 nm (0.18); MS FAB (3-NBA):  $m/z$  (%): 809 (1) [ $M^+$ ], 589 (6), 588 (13) [ $M^+ - \text{C}_{14}\text{H}_7\text{O}_2\text{N}$ ], 587 (3), 407 (3), 406 (7) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{14}\text{H}_7\text{O}_2\text{N}$ ], 405 (4), 392 (3), 391 (7) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{14}\text{H}_7\text{O}_2\text{N-NH}$ ], 390 (4), 376 (2), 362 (2), 361 (2); elemental analysis calcd (%) for  $\text{C}_{51}\text{H}_{44}\text{N}_4\text{O}_6$  (808.9): C 75.72, H 5.48, N 6.93; found: C 74.45, H 5.15, N 6.59.

**Coupling of two chromophores by methylene spacers; general procedure:** *N*-(*sec*-Alkyl)-perylene-3,4:9,10-tetracarboxylic bisimide, the corresponding alkyl bromide and potassium carbonate in anhydrous DMF were stirred under Ar at  $100^\circ\text{C}$  for 24 h. 10% KOH was added and the mixture was stirred at room temperature for 1 h, acidified with conc. HCl and stirred for further 30 min. The precipitate was collected by vacuum filtration, dried at  $130^\circ\text{C}$  for 16 h and purified by column separation.

***N*<sup>2</sup>,*N*<sup>2'</sup>-Bis-(1-hexylheptyl)-*N*<sup>1</sup>,*N*<sup>1'</sup>-(1,2-ethandiyl)-bis-perylene-3,4:9,10-tetracarboxylic bisimide:** *N*-(1-Hexylheptyl)-perylene-3,4:9,10-tetracarboxylic bisimide (200 mg, 0.35 mmol), dibromomethane (0.70 mL, 10 mmol) and potassium carbonate (1.3 g, 9.4 mmol) in anhydrous DMF (20 mL) and 10% KOH (5 mL) were allowed to react according to the general procedure and purified by two column separations (silica gel, chloroform/*n*-butanol 40:1 and chloroform/acetone 15:1), evaporated and extracted with cyclohexane. The extract was discarded and the remaining solid extractively recrystallized from chloroform to yield a red solid (100 mg, 49%). M.p.  $>350^\circ\text{C}$ ;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{n-butanol}$  40:1) = 0.16;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.59; IR (KBr):  $\tilde{\nu}$  = 3070 w, 2954 m, 2927 s, 2856 m, 1698 s, 1660 s, 1594 s, 1435 m, 1405 s, 1356 m, 1344 m, 1325 s, 1265 m, 1212 w, 1175 w, 852 w, 811 s, 751 m,  $745\text{ cm}^{-1}$  m;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 0.78 (t, 12H; 4  $\text{CH}_3$ ), 1.21 (m, 32H; 16  $\text{CH}_2$ ), 1.77 (m, 4H;  $\alpha\text{-CH}_2$ ), 2.13 (m, 4H; 2H;  $\alpha\text{-CH}_2$ ), 5.07 (m, 2H; 2CH), 6.72 (s, 2H;  $\text{R}_2\text{N-CH}_2\text{-NR}_2$ ), 8.48 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 2H; 2 CH perylene), 8.50 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 4H; 4 CH perylene), 8.57 (brs, 2H; 2 CH perylene), 8.67 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 2H; 2 CH perylene);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 14.01 (4 C,  $\text{CH}_3$ ), 22.55, 26.94, 29.18, 31.75, 32.29 (20 C,  $\text{CH}_2$ ), 38.73 (1 C,  $\text{CH}_2$ ), 54.80 (1 C, CH), 122.81, 123.01, 123.08, 126.17, 126.38, 128.80, 129.35, 130.86, 131.68, 134.07, 134.78 (40 C, CH perylene), 162.99 (8 C, C=O perylene); UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 370 (6160), 434 sh (8170), 460 (32390), 492 (94330), 532 nm (174560); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 538 (1.00), 580 (0.40), 631 nm (0.08); MS (70 eV):  $m/z$  (%): 1157 (0.6) [ $M^+$ ], 974 (1) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 793 (3) [ $M^+ - \text{C}_{26}\text{H}_{42}$ ], 404 (2) [ $\text{C}_{25}\text{H}_{12}\text{N}_2\text{O}_4^+$ ], 391 (6), 390 (8) [ $\text{C}_{24}\text{H}_{10}\text{N}_2\text{O}_4^+$ ], 374 (1), 182 (46) [ $\text{C}_{13}\text{H}_{26}^+$ ]; elemental analysis calcd (%) for  $\text{C}_{75}\text{H}_{72}\text{N}_4\text{O}_8$  (1157.4): C 77.83, H 6.27, N 4.84; found: C 77.62, H 6.29, N 4.78.

***N*-(1-Hexylheptyl)-*N'*-(methyl-9'-anthracenyl)-perylene-3,4:9,10-tetracarboxylic bisimide (10c):** *N*-(1-Hexylheptyl)-perylene-3,4:9,10-tetracarboxylic bisimide (100 mg, 0.17 mmol), 9-(bromomethyl)-anthracene (80 mg, 0.30 mmol) and potassium carbonate (650 mg, 4.70 mmol) in anhydrous DMF (10 mL) was allowed to react according to the general procedure (10% KOH was replaced by 20 mL of distilled water) and purified by column separation (silica gel, chloroform; separation of a violet forerun from the broad red main fraction) and an extractive recrystallization from cyclohexane to yield a violet powder (30 mg, 23%). M.p. 209–211  $^\circ\text{C}$ ;  $R_f$

(silica gel,  $\text{CHCl}_3$ ) = 0.19; IR (KBr):  $\tilde{\nu}$  = 3050 w, 2954 m, 2926 m, 2856 m, 1698 s, 1658 s, 1594 s, 1579 m, 1447 w, 1434 w, 1405 m, 1378 w, 1334 m, 1250 w, 1171 w, 810 s, 749 m, 731  $\text{cm}^{-1}$  w;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta$  = 0.81 (t, 6H; 2  $\text{CH}_3$ ), 1.26 (m, 16H; 8  $\text{CH}_2$ ), 1.86 (m, 2H;  $\alpha$ - $\text{CH}_2$ ), 2.24 (m, 2H;  $\alpha$ - $\text{CH}_2$ ), 5.17 (m, 1H; 1 CH), 6.39 (s, 2H; 1  $\text{CH}_2$ ), 7.44 (t,  $^3J(\text{H,H})$  = 8.0 Hz, 2H; 2 CH anthracene), 7.53 (dt,  $^3J(\text{H,H})$  = 9.0 Hz,  $^4J(\text{H,H})$  = 1.3 Hz, 2H; 2 CH anthracene), 8.00 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 2H; 2 CH anthracene), 8.45 (s, 1H; 5-H anthracene), 8.50 (d,  $^3J(\text{H,H})$  = 8.2 Hz, 2H; 2 CH perylene), 8.54 (d,  $^3J(\text{H,H})$  = 8.8 Hz, 2H; 2 CH perylene), 8.58 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 2H; 2 CH perylene), 8.61 (d,  $^3J(\text{H,H})$  = 9.0 Hz, 2H; CH anthracene), 8.63 (m, 2H; 2 CH perylene);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 13.99 (2C,  $\text{CH}_3$ ), 22.54, 26.90, 29.18, 31.72, 32.36 (10C,  $\text{CH}_2$ ), 38.18 (1C,  $\text{CH}_2$ -NR $_2$ ), 54.77 (1C, CH), 122.89, 123.12, 123.19, 124.73, 124.77, 126.04, 126.33, 126.35, 128.06, 128.48, 129.24, 129.51, 131.08, 131.37, 131.75, 134.27, 134.74 (34C, Ar), 163.88 (4C, C=O perylene); UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 260 (122 100), 351 (8286), 369 (11 930), 390 (10 120), 433 sh (5380), 460 (18 130), 492 (49 170), 528 nm (80 760); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 534 (1.00), 578 (0.53), 626 nm (0.13); MS (70 eV):  $m/z$  (%): 763 (51) [ $M^+ + \text{H}$ ], 762 (90) [ $M^+$ ], 582 (9), 581 (21), 580 (19) [ $M^+ - \text{C}_{13}\text{H}_{26}$ ], 572 (9), 392 (5), 391 (18), 390 (31) [ $M^+ - \text{C}_{13}\text{H}_{26} - \text{C}_{15}\text{H}_{10}$ ], 373 (4), 346 (4), 345 (3), 192 (36), 191 (100), 190 (18) [ $\text{C}_{15}\text{H}_{10}^+$ ], 189 (24); elemental analysis calcd (%) for  $\text{C}_{52}\text{H}_{46}\text{N}_2\text{O}_6$  (763.0): C 81.86, H 6.08, N 3.67; found: C 81.81, H 6.12, N 3.67.

**N-(1-Hexylheptyl)-N'-(methyl-2-anthraquinoyl)-perylene-3,4,9,10-tetracarboxylic bisimide (10a):** N-(1-Hexylheptyl)-perylene-3,4,9,10-tetracarboxylic bisimide (200 mg, 0.35 mmol), 2-(bromomethyl)-anthraquinone (200 mg, 0.66 mmol) and potassium carbonate (1.3 g, 9.4 mmol) in anhydrous DMF (20 mL) were allowed to react according to the general procedure (10% KOH was replaced by 20 mL of distilled water) and purified by column separation (silica gel, chloroform; separation of a red forerun) to yield a red powder (40 mg, 14%). M.p. 342–345 °C;  $R_f$  (silica gel,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.86;  $R_f$  ( $\text{Al}_2\text{O}_3$  N I,  $\text{CHCl}_3/\text{acetone}$  15:1) = 0.47; IR (KBr):  $\tilde{\nu}$  = 3070 w, 2954 m, 2927 m, 2856 m, 1697 s, 1660 s, 1594 s, 1580 m, 1437 m, 1405 m, 1378 w, 1339 s, 1294 m, 1172 m, 811 m, 743 w, 712  $\text{cm}^{-1}$  m;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta$  = 0.79 (t, 6H; 2  $\text{CH}_3$ ), 1.34 (m, 16H; 8  $\text{CH}_2$ ), 1.85 (m, 2H;  $\alpha$ - $\text{CH}_2$ ), 2.23 (m, 2H;  $\alpha$ - $\text{CH}_2$ ), 5.16 (m, 1H; 1 CH), 5.54 (s, 2H; 1  $\text{CH}_2$ ), 7.73 (t,  $^3J(\text{H,H})$  = 6.4 Hz, 1H; 6-H or 7-H anthraquinone), 7.90 (dd,  $^3J(\text{H,H})$  = 8.1 Hz,  $^4J(\text{H,H})$  = 1.8 Hz, 1H; 3-H anthraquinone), 8.23 (d,  $^3J(\text{H,H})$  = 7.3 Hz, 1H; 5-H or 8-H anthraquinone), 8.25 (d,  $^3J(\text{H,H})$  = 7.8 Hz, 1H; 5-H or 8-H anthraquinone), 8.25 (d,  $^3J(\text{H,H})$  = 8.0 Hz, 1H; 4-H anthraquinone), 8.36 (d,  $^4J(\text{H,H})$  = 1.4 Hz, 1H; 1-H anthraquinone), 8.59 (d,  $^3J(\text{H,H})$  = 8.2 Hz, 2H; 2 CH perylene), 8.60 (d,  $^3J(\text{H,H})$  = 8.1 Hz, 2H; 2 CH perylene), 8.67 (d,  $^3J(\text{H,H})$  = 7.9 Hz, 4H; 4 CH perylene); COSY NMR: cross-peaks at  $\delta$  = (7.73, 8.23, 8.25), (7.90, 8.25), (7.90, 8.36);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 14.01 (2C,  $\text{CH}_3$ ), 22.57, 26.94, 29.21, 31.76, 32.40 (10C,  $\text{CH}_2$ ), 43.54 (1C,  $\text{CH}_2$ -NR $_2$ ), 54.85 (1C, CH), 122.77, 123.01, 123.36, 126.86, 127.16, 127.18, 127.51, 127.75, 128.19, 129.50, 129.53, 129.62, 131.92, 132.74, 133.04, 133.46, 133.53, 133.73, 134.02, 134.04, 134.19, 134.57, 134.61, 135.23, 143.80 (32C, CH anthraquinone, CH perylene), 163.37 (4C, C=O perylene), 182.73, 182.88 (2C, C=O anthraquinone); UV ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 258 (87 740), 277 (24 430), 327 br. (10 810), 436 sh (5260), 460 (17 310), 491 (47 230), 528 nm (78 960); fluorescence ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $I_{\text{rel}}$ ) = 537 (1.00), 579 (0.52), 625 nm (0.12); solid-state fluorescence:  $\lambda_{\text{max}}$  = 654 nm; MS (70 eV):  $m/z$  (%): 793 (14) [ $M^+ + \text{H}$ ], 792 (23) [ $M^+$ ], 775 (5), 613 (7), 612 (28), 611 (78), 610 (100) [ $M^+ - \text{C}_{15}\text{H}_{26}$ ], 593 (6), 375 (5), 373 (15), 372 (18), 346 (18), 345 (4); elemental analysis calcd (%) for  $\text{C}_{52}\text{H}_{44}\text{N}_2\text{O}_6$  (792.9): C 78.77, H 5.59, N 3.53; found: C 78.60, H 5.30, N 3.13; analysis calcd for  $\text{C}_{52}\text{H}_{44}\text{N}_2\text{O}_6$ : 792.3199; found: 792.3233 (HRMS).

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