The Identification of Carbonyl Compounds by Fluorescence: A Novel Carbonyl-Derivatizing Reagent

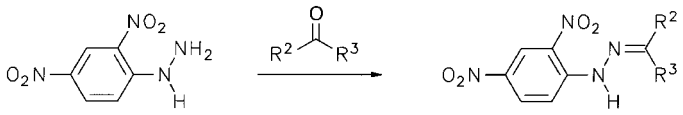
Heinz Langhals* and Wolfgang Jona

Abstract: Fluorescent hydrazones are afforded by the reaction of the nonfluorescent *N*-aminoperylene-3,4:9,10-tetracarboxylic-bisimides with ketones and aldehydes; thus we obtain a fluorescent derivatization for the qualitative and semiquantitative determination of carbonyl compounds.

Keywords: aldehydes · analytical methods · fluorescence spectroscopy · hydrazones · ketones · perylenes

Introduction

The derivatization of aldehydes and ketones with 2,4-dinitrophenylhydrazine (**1**) is a well-established method (Scheme 1).[1] This reaction was originally developed for the characterization of carbonyl compounds by melting points. On the other hand, the strong colour of the 2,4-dinitrophenylhydrazones (**2**) offer the possibility of their visual identification or UV/visible-spectroscopic detection and quantitative determination. This can be carried out simply, but the sensitivity for



1 2

Scheme 1. The reaction of **1** with aldehydes or ketones.

the determination of carbonyl compounds is limited by UV/visible spectroscopy because the concentration of the analyte (c) is proportional to log (I_o/I) according to Beer–Lambert's law. A higher analytic sensitivity would be obtained by the measurement of fluorescence (I_{fl}) instead of absorption, because of the proportionality between c and the intensity of fluorescent light ($c \sim I_{fl}$). The fluorescence detection has also advantages for a visual identification because it can be seen easily, even in strongly coloured solutions. Dansyl hydrazone (RN 33008-06-9) has been used as a fluorescence-derivating reagent[2, 3] of carbonyl compounds. However, it absorbs in the UV region so that there may be an interference by the absorption and fluorescence of biological material. Better results are expected if the absorption is shifted to the visible region.

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Concept

A highly fluorescent, light-stable chromophore with a suitable anchor group is needed for the labelling of carbonyl compounds in order to get a stable and strong fluorescence signal, especially if an intense light source is applied. If the labelling reagent itself were fluorescent, a strong fluorescent background signal would be obtained from the nonconverted reagent. Therefore better results are expected for nonfluorescent labelling reagents that form highly fluorescent carbonyl derivatives; compare with ref. [4]. The reagent can therefore be attached to a quencher that is switched off by the reaction with the carbonyl compound. An efficient fluorescence quenching is obtained by an intramolecular electron transfer (C.T.), which proceeds as long as the n orbital of the quencher (substituent) lies above the HOMO of the chromophore (see Figure 1): the optical excitation leaves a vacant position in the π orbital which is filled by a charge transfer (C.T.) and thus prevents the optical transition back for fluorescence. The quenching may be switched off, for

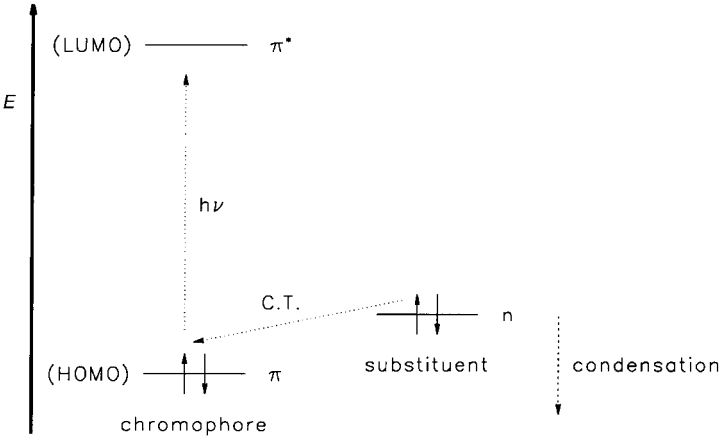

Figure 1. Fluorescence quenching by electron rich substituents. $h\nu$: optical excitation, C.T. charge transfer by intramolecular S.E.T.

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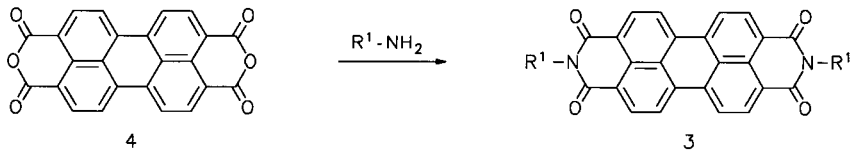
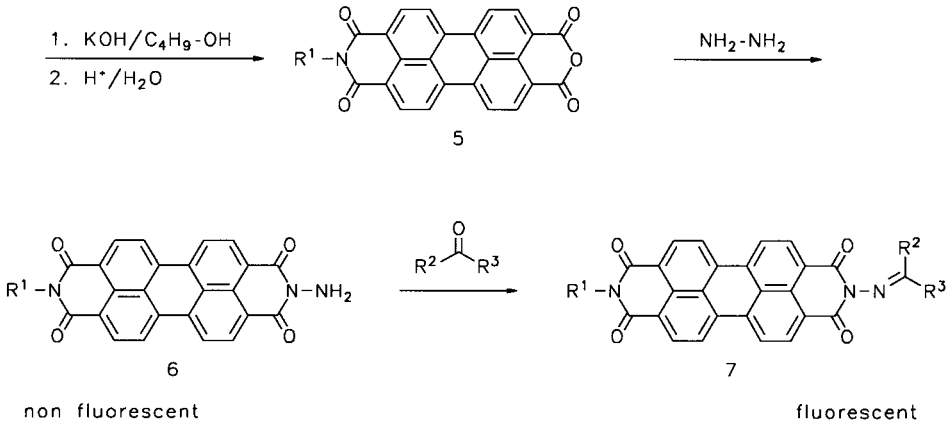
example, by condensation reactions with carbonyl compounds that lower the energy of the *n* orbital beneath the HOMO.



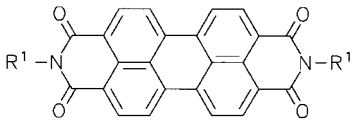
Results and Discussion

The perylene-3,4:9,10-tetracarboxylic-bisimide chromophore (**3**, perylene dyes) is highly fluorescent and extraordinarily photostable,[5] and is therefore useful as a fluorescent-detecting system. Its fluorescence may be quenched by electron-rich substituents such as amino groups (compare ref. [6]) according to the mechanism of Figure 1.



Scheme 2. Reaction scheme for the formation of **6** and **7**. The R groups for 7 are given Table 1.

On the other hand, an attached amino group as a quencher may also serve as a derivatization reagent for carbonyl compounds through the formation of Schiff bases. The nitrogen atom of the resulting Schiff base is less electron rich than in the amino group so that fluorescence quenching will be stopped and the inherent strong fluorescence of the chromophore may be reobtained. The formation of Schiff bases is expected to be most efficient if the amino group is attached to an imide nitrogen atom of **3**, because of the α effect and because of minimal steric hindrance in this position. A further advantage of this position is the fact there are nodes[7] in the HOMO and LUMO of **3**. So the UV/visible spectra are only little affected by the structure of the carbonyl compounds to be derivatized. However, the perylene dye **3g** ($R^1 = NH_2$,



3

3, 5, 6	R^1
a	$(C_4H_9)_2CH-$
b	$(C_6H_{13})_2CH-$
c	$(C_7H_{15})_2CH-$
d	$(C_8H_{17})_2CH-$
e	$(C_9H_{19})_2CH-$
f	$2,5-(C_4H_9)_2C_6H_3-$
g	NH_2-

RN 49546-23-8) exhibits a very low solubility and may be used only as a pigment.[8, 9] The low solubilities of the amino dyes and the corresponding Schiff bases can be overcome if a solubility-increasing long-chain *sec*-alkyl group (swallow-tail substituent[10]) is attached to one nitrogen atom of **3** and the amino group to the other one.

Table 1.

7	R^1	R^2	R^3
a	$(C_6H_{13})_2CH-$	C_6H_5-	H–
b	$(C_8H_{17})_2CH-$	C_6H_5-	H–
c	$(C_6H_{13})_2CH-$	$4\text{-}CH_3OC_6H_4-$	H–
d	$(C_6H_{13})_2CH-$	$2\text{-}C_4H_3O-$	H–
e	$(C_6H_{13})_2CH-$	$-(CH_2)_5-$	–
f	$(C_6H_{13})_2CH-$	C_4H_9-	H–
g	$(C_6H_{13})_2CH-$	$C_5H_{11}-$	H–
h	$(C_6H_{13})_2CH-$	CH_3-	H–
i	$(C_6H_{13})_2CH-$	$(CH_3)_2C{=}CH-$	CH_3-

The bisanhydride **4** is condensed for the preparation of this type of dye with 7-aminotridecane to **3b**, then partially saponified[11] to the anhydride imide **5b** and condensed with an excess of hydrazine to the reagent **6b** with a free amino group (Scheme 2). A low reaction temperature (100–130 °C), compared with the condensation of other primary amines, is recommended for this reaction. Hydrazine should be applied from a twofold up to tenfold excess. Hydrazine can be applied as the hydrate or its salts like hydraziniumsulphate. The dyes **6** thus obtained are free of fluorescent impurities and should be directly applied as carbonyl reagents after a simple chromatographic purification. The 1-hexylheptyl group in **6b** is a good compromise between solubility-increasing effect and tendency for crystallization. The smaller homologue **6a** and the larger homologues **6c**–**6e** have been prepared in the same way as well as the aromatic derivative **6f**; the *tert*-butyl groups increase the solubility[12] of **6f**. It is of interest that the dyes **6** can also be prepared by the hydrazinolysis of bisimides **3** especially if the substituents R^1 are aromatic. The preferred exchange of the aromatic substituents is demonstrated by the

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hydrazinolysis of the perylene-bisimide, where one substituent at the nitrogen atoms is the aliphatic 1-hexylheptyl and the other one is phenyl: only the phenyl group was exchanged by hydrazine.

The carbonyl derivatives of **6** have been prepared for some frequently used aldehydes and ketones and have been thoroughly purified for comparison. Although the hydrazones **7** are stable in the reaction mixture where they have been prepared, pure derivatives **7** decompose slowly to **6** if they are stored for a long time, certainly caused by the reversibleness of their formation. The decomposition proceeds more quickly in diluted solution; however, the stability of **7** is high enough for their determination even by the use of chromatographic methods. Best results for the isolation of **7** have been obtained if the carbonyl components and **6** have been heated without further additives. A high dilution causes a partial dissociation. The TLC R_f values of **7** for identification of carbonyl compounds and their UV/visible-spectroscopic molar coefficients of extinction for quantitative or semiquantitative determination are reported in Table 2 for frequently used

Table 2. Derivatization of aldehydes an ketones by means of reagent **6a**.

	Carbonyl compound	M.p.	R_f[a]	ε[b]
7a	benzaldehyde		0.87	
7b	benzaldehyde[c,d]	329–332	0.95	87400
7c	anise aldehyde[e]	348–350	0.92	92800
7d	furfural[f]	334–337	0.86	89100
7e	cyclohexanone		0.86	85800
7f	pentanal		0.85	
7g	heptanal		0.88	78600
7h	acetaldehyde		0.70[g]	
7i	mesityloxide		0.82[h]	
7j	secologanin (RN 19351-63-4)		0.16 (0.77[i])	

[a] TLC silica gel, chloroform/ethanol (10:1). [b] $1\,mol^{-1}\,cm^{-1}$ in chloroform, $\lambda_{max} = 525-530$ nm. [c] Reagent **6d**. [d] Fluorescence quantum yield: 59%. [e] Fluorescence quantum yield: 0.03%; fluorescence quenching by the electron-rich substituent. [f] Fluorescence quantum yield: 25%; fluorescence quenching by the electron-rich substituent. [g] Chloroform/ethanol (20:1). [h] Chloroform/acetone (10:1). [i] Byproduct.

types of aldehydes and ketones. The UV/visible spectra of **7** are only little affected by the carbonyl component ($\lambda_{max} =$ 525–530 nm in chloroform) and are similar to **6** (ε about 80000) and **3** (ε about 90000); see Figure 2. Their molar coefficients of extinction are about 87000–92000 and are also only slightly dependent on the substituents.

The nonfluorescent reagent **6b** (or its homologues) can easily be condensed with aldehydes and ketones to the corresponding Schiff bases such as **7a–7i** (see Table 2) in chloroform at 60 °C for analytical purposes. The fluorescence of **7** can easily be seen after a few minutes and the reaction is completed within one hour. The use of a fluorescent lamp and the visual comparison with a blank sample is recommended. The carbonyl compounds may be identified by TLC or HPLC.

Aromatic aldehydes react readily with **6b** and aliphatic aldehydes, aliphatic ketones, or aromatic–aliphatic ketones need a longer reaction time, whereas ketones with two aromatic substituents react very slowly. Best results have been obtained in chloroform solution for the reaction, but the

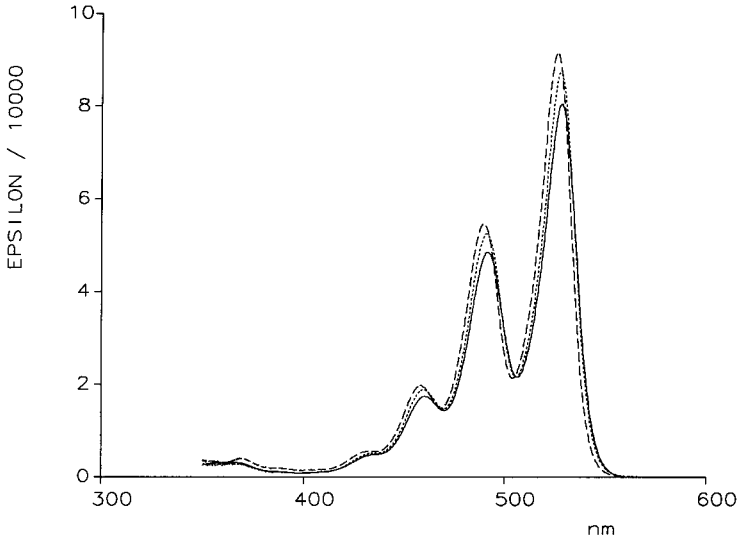

Figure 2. UV/Vis absorption spectra of **6c** (—), **7c** (· · ·) and **3c** (- - -) in chloroform.

condensation is rather insensitive versus solvent effects and the higher boiling 1,1,2,2-tetrachloroethane may be used instead. Finally, more byproducts are obtained in solvents like *pure* THF or ethylacetate. Special care must be taken concerning the absence of carbonyl compounds in the solvents even in trace amounts. On the other hand, esters do not interfere with the detection of aldehydes or ketones because their reaction with the reagent **6** proceeds very slowly. However a neutral to alkaline reaction medium is necessary for the fluorescence detection of carbonyl compounds because the reagent **6** is protonated by acids and thus becomes highly fluorescent; the reagent **6** can also be used as a fluorescent pH indicator for nonaqueous solutions. Strongly acylating substrates like acid halides form fluorescent amides with **6** and must be hydrolyzed before the detection of ketones and aldehydes, or alternatively the reaction products must be separated by chromatographic methods; on the other hand, these compounds can be also determined by the fluorescence of their reaction products with **6**. An identification and semiquantitative determination of carbonyl compounds by fluorescence of **7** can easily be done. There are, however, problems with an exact quantitative determination which may be caused by the reversibility of the condensation reaction and volatileness of the aldehydes and ketones (see above).

The novel analysis method may be of special interest because of its sensitivity for the investigation of complex mixtures which contain some carbonyl compounds. Such problems are frequently encountered with the isolation and identification of natural products; see for example the identification of secologanin[13] (Table 2).

Experimental Section

Preparation of *N*-(alkyl)-*N'*-aminoperylene-3,4:9,10-tetracarboxylic-bisimides and *N*-amino-*N'*-arylperylene-3,4:9,10-tetracarboxylic-bisimides (6) General procedure: N-(alkyl)-perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5**) or *N*-(aryl)-perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (1 mmol) was dissolved in imidazole (2 g) at 130 °C

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(bath), hydrazine hydrate (100% with an excess of 2–10 mmol; the molar ratio is uncritical) was added and allowed to react for 30–60 min. The still warm reaction mixture was dispersed in ethanol, 2N HCl (200 mL) was added, and the suspension was stirred for 1–2 h at room temperature. The solid was collected by vacuum filtration, washed with methanol/water and dried in an oven for 12 h at 100 °C. The solid was further purified by one column separation over alumina (chloroform/ethanol 20:1) and another over silica gel (chloroform/ethanol 20:1). The main fraction was obtained as a dark red, nonfluorescent solution. The chromatography should be carried out rapidly because a slow decomposition of the adsorbed dye may proceed. Only one column separation is necessary if it is done thoroughly. A further purification is obtained by an extractive recrystallization[14] from cyclohexane. However, fluorescent decomposition products are formed therewith in trace amounts which lower the analytical sensitivity of the analysis method so that the simply chromatographed material should be preferred for this application.

***N*-Amino-*N*′-(1-butylpentyl)perylene-3,4:9,10-tetracarboxylic-bisimide (6a)**: *N*-(1-Butylpentyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5a**, 1.3 g, 2.5 mmol), hydrazine hydrate (200 mg, 4.0 mmol) and imidazole (4 g) were allowed to react, and the reaction mixture was worked up according to the general procedure (reaction time 1 h) to give 820 mg (61%) of **6a**. M.p. > 350 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.70. R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.59; IR (KBr): $\tilde{\nu}$ = 3370 cm^{-1} (w), 3330 (w), 3075 (w), 2957 (m), 2929 (m), 2868 (m), 1698 (s), 1656 (s), 1595 (s), 1577 (m), 1555 (w, sh), 1506 (w), 1465 (w), 1456 (w), 1436 (w), 1404 (s), 1378 (m), 1348 (s), 1302 (m), 1255 (m), 1195 (w), 1173 (m), 1101 (m), 965 (m br), 852 (m), 809 (s), 795 (w), 751 (w), 739 (m); ^{1}H NMR ($CDCl_3$): δ = 0.82 (t, 6H; $2CH_3$), 1.32 (m_c, 8H; $4CH_2$), 1.89 (m_c, 2H; 2α-CH_2), 2.25 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 5.52 (s, 2H; NH_2), 8.47 (d, ^3J = 8.0 Hz, 2H; perylene), 8.52 (d, ^3J = 8.1 Hz, 2H; perylene), 8.57 (d, ^3J = 7.9 Hz, 2H; perylene), 8.63 (br d, ^3J = 7.7 Hz, 2H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.04, 22.63, 29.16, 32.09, 54.83, 122.16, 122.90, 123.35, 126.01, 126.35, 127.90, 129.39, 131.53, 133.89, 135.05, 159.95; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (78700), 491 (48300), 460 (17800); MS (70 eV): *m/z* (%): 532 (14), 531 (40) [M^+], 514 (5) [$M^+ - OH$], 418 (4), 407 (13), 406 (53), 405 (100) [$M^+ - C_9H_{18}$], 390 (6), 388 (4), 377 (7), 376 (25), 84 (5), 82 (8), 55 (4); $C_{33}H_{29}N_3O_4$ (531.6): calcd C 74.56, H 5.50, N 7.90; found C 73.93, H 5.50, N 7.87.

***N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (6b)**: *N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5b**, 2.0 g, 3.5 mmol), hydrazine hydrate (200 mg, 4.0 mmol) and imidazole (4 g) were allowed to react, and the reaction mixture was worked up according to the general procedure (reaction time 1 h) to give 830 mg (40%) of **6b**. M.p. 332–334 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.80; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.61; IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2927 (s), 2857 (m), 1699 (s), 1658 (s), 1595 (s), 1578 (m), 1556 (w), 1510 (w), 1458 (w), 1436 (w), 1404 (s), 1379 (w), 1350 (s), 1303 (w), 1255 (s), 1200 (w), 1174 (w), 1130 (w), 1110 (w), 980 (w), 852 (w), 805 (s), 800 (w), 739 (m); ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.88 (m_c, 2H; 2α-CH_2), 2.24 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 5.48 (s, 2H; NH_2), 8.33 (d, ^3J = 8.2 Hz, 2H; perylene), 8.41 (d, ^3J = 8.2 Hz, 2H; perylene), 8.45 (d, ^3J = 8.0 Hz, 2H; perylene), 8.57 (br d, ^3J = 7.6 Hz, 2H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.03, 22.58, 26.97, 29.23, 31.76, 32.38, 54.91, 122.07, 122.80, 123.26, 125.90, 126.21, 127.78, 129.32, 131.40, 133.74, 134.91, 159.83; UV ($CHCl_3$): λ_{max} (ε) = 527 nm (80000), 491 (48600), 460 (17800); MS (70 eV): *m/z* (%): 588 (10), 587 (25) [M^+], 570 (5) [$M^+ - OH$], 418 (4), 407 (14), 406 (53), 405 (100) [$M^+ - C_{13}H_{26}$], 390 (2), 388 (6), 377 (6), 376 (22), 360 (4); $C_{37}H_{37}N_3O_4$ (587.7): calcd C 75.61, H 6.35, N 7.15; found C 75.32, H 6.24, N 7.01.

***N*-Amino-*N*′-(1-heptyloctyl)perylene-3,4:9,10-tetracarboxylic-bisimide (6c)**: *N*-(1-Heptyloctyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5c**, 1.30 g, 2.16 mmol), hydrazine hydrate (220 mg, 4.40 mmol) and imidazole (5 g) were allowed to react, and the reaction mixture was worked up according to the general procedure (reaction time 1 h) to give 720 mg (55%) of **6c**. M.p. 307–308 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.74; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.56; IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2926 (s), 2855 (m), 1700 (s), 1658 (s), 1616 (w), 1595 (s), 1579 (m), 1508 (w), 1465 (w), 1457 (w), 1438 (w), 1404 (s), 1378 (w), 1349 (br s), 1302 (w), 1255 (s), 1200 (w), 1173 (m), 1125 (w), 1115 (w), 970 (br m), 855 (m), 809 (s), 800 (w), 795 (w), 739 (s); ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.28 (m_c, 20H; $10CH_2$), 1.89 (m_c, 2H; 2α-CH_2), 2.25 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 5.46 (s, 2H; NH_2), 8.27 (d, ^3J = 8.3 Hz, 2H; perylene), 8.35 (d, ^3J = 8.1 Hz, 2H; perylene), 8.38 (d, ^3J = 8.1 Hz, 2H; perylene), 8.55 (br d, ^3J = 7.7 Hz, 2H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.05, 22.60, 27.03, 29.23, 29.53, 31.81, 32.36, 54.92, 121.93, 122.66, 123.14, 125.70, 125.97, 127.57, 129.20, 131.19, 133.50, 134.66, 159.65; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (81500), 492 (49200), 460 (18100); MS (70 eV): *m/z* (%): 616 (11), 615 (26) [M^+], 598 (5) [$M^+ - OH$], 430 (4), 418 (3), 407 (15), 406 (57), 405 (100) [$M^+ - C_{15}H_{30}$], 391 (4), 390 (7), 377 (9), 376 (34), 360 (6), 331 (5), 275 (4), 249 (4), 124 (4), 123 (4), 69 (5), 55 (5); $C_{39}H_{41}N_3O_4$ (615.8): calcd C 76.07, H 6.71, N 6.82; found C 76.48, H 6.74, N 6.89.

***N*-Amino-*N*′-(1-octylnonyl)perylene-3,4:9,10-tetracarboxylic-bisimide (6d)**: *N*-(1-Octylnonyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (1.50 g, 2.38 mmol), hydrazine hydrate (130 mg, 2.60 mmol) and imidazole (6 g) were allowed to react, and the reaction mixture was worked up according to the general procedure (reaction time 1 h) to give 700 mg (46%) of **6d**. M.p. 286–287 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.80; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.55; IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2924 (s), 2854 (s), 1698 (s), 1658 (s), 1595 (s), 1578 (s), 1506 (w), 1485 (w), 1457 (m), 1436 (m), 1404 (s), 1378 (m), 1348 (s), 1302 (m), 1256 (s), 1200 (w), 1173 (m), 1128 (w), 1115 (w), 975 (m), 852 (w), 809 (s), 798 (w), 751 (w), 739 (s); ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.30 (m_c, 24H; $12CH_2$), 1.89 (m_c, 2H; 2α-CH_2), 2.25 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 5.49 (s, 2H; NH_2), 8.35 (d, ^3J = 8.1 Hz, 2H; perylene), 8.42 (d, ^3J = 8.3 Hz, 2H; perylene), 8.46 (d, ^3J = 7.9 Hz, 2H; perylene), 8.57 (br d, 2H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.06, 22.62, 27.02, 29.25, 29.51, 29.57, 31.83, 32.37, 54.92, 122.01, 122.74, 123.20, 125.81, 126.10, 127.69, 129.27, 131.30, 133.62, 134.80, 159.75; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (80600), 492 (48600), 460 (17400); MS (70 eV): *m/z* (%): 644 (13), 643 (27) [M^+], 626 (5) [$M^+ - OH$], 430 (4), 418 (3), 407 (16), 406 (58), 405 (100) [$M^+ - C_{17}H_{34}$], 391 (5), 390 (7), 388 (6), 377 (6), 376 (23), 360 (4), 331 (3); $C_{41}H_{45}N_3O_4$ (643.8): calcd C 76.49, H 7.05, N 6.53; found C 76.51, H 7.08, N 6.60.

***N*-Amino-*N*′-(1-nonyldecyl)perylene-3,4:9,10-tetracarboxylic-bisimide (6e)**: *N*-(1-Nonyldecyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5e**, 1.33 g, 2.02 mmol), hydrazine hydrate (320 mg, 6.40 mmol) and imidazole (5 g) were allowed to react, and the reaction mixture was worked up according to the general procedure (reaction time 2 h) to give 800 mg (60%) of **6e**. M.p. 268–271 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.76; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.51; R_f (silica gel; $CHCl_3$/1-butanol 40:1) = 0.28; IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2925 (s), 2854 (m), 1698 (s), 1658 (s), 1617 (w), 1595 (s), 1577 (m), 1507 (w), 1468 (w), 1457 (w), 1437 (w), 1404 (m), 1378 (w), 1349 (s), 1302 (w), 1256 (m), 1202 (w), 1173 (m), 1055 (w), 1040 (w), 975 (br w), 855 (w), 809 (s), 800 (w), 739 (m); ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, 6H; $2CH_3$), 1.28 (m_c, 28H; $14CH_2$), 1.89 (m_c, 2H; 2α-CH_2), 2.23 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 5.49 (s, 2H; NH_2), 8.33 (d, ^3J = 8.1 Hz, 2H; perylene), 8.41 (d, ^3J = 8.1 Hz, 2H; perylene), 8.45 (d, ^3J = 7.7 Hz, 2H; perylene), 8.58 (br s, 2H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.49, 23.05, 27.44, 29.68, 29.98, 32.27, 32.78, 55.34, 122.43, 123.15, 123.62, 126.21, 126.51, 128.10, 129.68, 131.72, 134.03, 135.20, 160.17; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (81000), 492 (49500), 460 (18500); MS (70 eV): *m/z* (%): 673 (3), 672 (13), 671 (29) [M^+], 654 (5), [$M^+ - OH$], 418 (3), 408 (4), 407 (17), 406 (62), 405 (100) [$M^+ - C_{19}H_{38}$], 391 (4), 390 (8), 389 (3), 388 (9), 377 (10), 376 (33), 360 (6), 331 (4), 124 (5), 82 (5), 55 (5); $C_{43}H_{49}N_3O_4$: calcd 671.3723; found 671.3717 (MS); $C_{43}H_{49}N_3O_4$ (671.9): calcd C 76.87, H 7.35, N 6.25; found C 76.80, H 7.25, N 6.32.

***N*-Amino-*N*′-(2,5-di-*tert*-butylphenyl)perylene-3,4:9,10-tetracarboxylic-bisimide (6f)**: *N*-(2,5-Di-*tert*-butylphenyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5f**, 150 mg, 0.26 mmol), hydrazine hydrate (50 mg, 1.00 mmol) and imidazole (2 g) were allowed to react, and the reaction mixture was worked up according to the general procedure (reaction time 30 min) to give 40 mg (26%) of **6f**. M.p. > 350 °C; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.57; R_f (alumina; $CHCl_3$/ethanol 20:1) = 0.35; IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1} (m), 2875 (w), 1701 (br s), 1685 (w), 1666 (br s), 1616 (w), 1594 (s), 1579 (m), 1506 (w), 1434 (w), 1402 (m), 1359 (s), 1255 (m), 1174 (w), 1150 (w), 970 (br w), 855 (w), 828 (w), 809 (m), 804 (w), 741 (m), 735 (w), 651 (w); ^{1}H NMR ($CDCl_3$): δ = 1.27 (s, 9H; $C(CH_3)_3$), 1.34 (s, 9H; $C(CH_3)_3$), 5.55 (s, 2H; NH_2), 7.14 (d, ^4J = 2.2 Hz, 1H; phenyl), 7.46 (dd, ^3J = 8.6 Hz, ^4J = 2.2 Hz, 1H; phenyl), 7.59 (d, ^3J = 8.6 Hz, 1H; phenyl), 8.58 (d, ^3J = 8.1 Hz, 2H; perylene), 8.61 (d, ^3J = 8.2 Hz, 2H; perylene), 8.66 (d, ^3J = 8.0 Hz, 2H; perylene), 8.72 (d, ^3J = 7.9 Hz, 2H; perylene); ^{13}C NMR ($CDCl_3$): δ = 31.22, 31.71, 122.41, 123.16, 123.41, 123.92, 126.36, 127.79,

127.96, 128.75, 129.72, 130.83, 131.60, 131.74, 132.51, 134.52, 135.05, 143.71, 150.22, 160.04, 164.30; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (84650), 491 (50700), 460 (18850); MS (70 eV): *m/z* (%): 593 (3) [M^+], 578 (4) [$M^+ - CH_3$], 576 (3) [$M^+ - OH$], 538 (8), 537 (39), 536 (100) [$M^+ - C_4H_9$], 522 (6), 521 (10), 520 (9) [576 – C_4H_8], 506 (2), 390 (1), 57 (3); $C_{37}H_{28}N_3O_4$: [$M^+ - CH_3$] calcd 578.2080; found 578.2080 (MS); $C_{38}H_{31}N_3O_4$ (593.7): calcd C 76.88, H 5.26, N 7.08; found C 75.93, H 5.39, N 6.83.

Preparation of hydrazones (7)

***N*-(1-Octylnonyl)perylene-3,4:9,10-tetracarboxylic-3,4-(benzylimineimide)-9,10-imide (7b)**: *N*-Amino-*N*′-(1-octylnonyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6d**, 100 mg, 0.16 mmol) was stirred with freshly distilled benzaldehyde (4 mL, 40 mmol) for 4 h at 60 °C. Methanol was added (50 mL). The solid was collected (after 30 min) by vacuum filtration with a glass filter (D 4; *the filters must not contain any acid, even in trace amounts! It is recommended to wash the glass filter with chloroform/triethylamine (10:1) before use.*), washed with methanol and ether, dissolved in a small amount of chloroform, filtered through a glass filter (D 5), methanol was added, the solvents were removed with a rotary evaporator, and the residue was dried at 40 °C for 24 h in vacuo to give 110 mg (96 %) of **7b**. M.p. 329 – 332 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.95; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.88; IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2926 (s), 2854 (m), 1697 (s), 1660 (s), 1616 (w), 1594 (s), 1579 (m), 1506 (w), 1457 (w), 1449 (w), 1435 (w), 1405 (m), 1354 (m), 1338 (s), 1254 (m), 1176 (m), 1000 (w), 965 (w), 851 (m), 809 (s), 800 (m), 755 (m), 739 (m), 690 (m); ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.25 (m_c, 24H; $12CH_2$), 1.89 (m_c, 2H; 2α-CH_2), 2.22 (m_c, 2H; 2α-CH_2), 5.15 (m_c, 1H; NCH), 7.52 (m_c, 3H; phenyl), 7.99 (d, ^3J = 7.1 Hz, 2H; phenyl), 8.29 (d, ^3J = 8.1 Hz, 2H; perylene), 8.37 (d, ^3J = 8.1 Hz, 2H; perylene), 8.44 (d, ^3J = 7.9 Hz, 2H; perylene), 8.56 (brs, 2H; perylene), 8.62 (s, 1H; N=CH); ^{13}C NMR ($CDCl_3$): δ = 14.05, 22.61, 27.04, 29.24, 29.50, 29.56, 31.82, 32.39, 54.93, 122.83, 122.87, 123.02, 125.88, 126.07, 128.42, 128.80, 129.29, 129.36, 130.87, 131.48, 132.49, 132.56, 133.72, 134.57, 159.93, 163.50 (br), 164.20 (br), 171.27; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (87400), 491 (52500), 460 (18900); fluorescence ($CHCl_3$): λ_{max} = 535 nm, 575; fluorescence quantum yield[15] ($c = 7.38 \times 10^{-7}$ mol l^{-1} in $CHCl_3$, reference **3b** with Φ = 100 %, $\lambda_{excit.}$ = 491 nm) = 59 %; MS (70 eV): *m/z* (%): 732 (3), 731 (6) [M^+], 714 (2), 629 (8), 628 (16) [$M^+ - C_7H_5N$], 611 (3), 495 (4), 494 (9), 403 (2), 393 (2), 392 (12), 391 (44), 390 (100) [628 – $C_{17}H_{34}$], 374 (2), 373 (4), 346 (3), 345 (3), 104 (6), 103 (58) [$C_7H_5N^+$], 76 (16), 75 (4), 51 (3), 50 (6); $C_{48}H_{49}N_3O_4$ (731.9): calcd C 78.77, H 6.75, N 5.74; found C 78.82, H 6.99, N 5.77.

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(benzylimineimide)-9,10-imide (7a)**: *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 100 mg, 0.17 mmol) and benzaldehyde (3 mL, 30 mmol) were allowed to react (3 h, 60 °C), and the reaction mixture was worked up as described for **7b** to give **7a**. R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.87; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.78; IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2928 (m), 2857 (m), 1697 (s), 1680 (s), 1616 (w), 1594 (s), 1579 (m), 1449 (m), 1432 (m), 1405 (m), 1355 (m), 1336 (s), 1253 (s), 1176 (m), 852 (w), 809 (s), 755 (m), 739 (w), 683 (w); UV ($CHCl_3$): λ_{max} = 528 nm, 491, 460; fluorescence ($CHCl_3$): λ_{max} = 535 nm, 575; MS (70 eV): *m/z* (%): 675 (8) [M^+], 658 (2), 573 (9), 572 (20) [$M^+ - C_7H_5N$], 555 (4), 494 (8), 406 (5), 405 (9), 392 (11), 391 (41), 390 (100) [572 – $C_{13}H_{26}$], 346 (6), 345 (4), 105 (10), 104 (14), 103 (17) [$C_7H_5N^+$].

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(4-methoxybenzylimineimide)-9,10-imide (7c)**: *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 100 mg, 0.17 mmol) and 4-methoxybenzaldehyde (anisaldehyde, 3 mL, 25 mmol) were allowed to react (1 h, 60 °C), and the reaction mixture was worked up as described for **7b** to give 90 mg (80 %) of **7c**. M.p. 348 – 350 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.92; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.85; R_f (silica gel; $CHCl_3$/1-butanol 40:1) = 0.44; IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1} (w), 2956 (m), 2928 (s), 2857 (m), 1696 (s), 1658 (s), 1594 (s), 1579 (s), 1515 (m), 1457 (m), 1431 (m), 1423 (m), 1405 (s), 1355 (m), 1336 (brs), 1254 (brs), 1205 (w), 1172 (s), 1126 (w), 1110 (w), 1055 (w), 991 (w), 962 (w), 851 (m), 833 (m), 809 (s), 799 (m), 754 (w), 739 (s); ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.90 (m_c, 2H; 2α-CH_2), 2.24 (m_c 2H; 2α-CH_2), 3.91 (s, 3H; OCH_3), 5.18 (m_c, 1H; NCH), 7.02 (d, ^3J = 8.8 Hz, 2H; phenyl), 7.95 (d, ^3J = 8.9 Hz, 2H; phenyl), 8.52 (d, ^3J = 8.2 Hz, 2H; perylene), 8.54 (d, ^3J = 9.1 Hz, 3H; 2H perylene/1H N=CH), 8.63 (d, ^3J = 8.1 Hz, 4H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.02, 22.57, 26.95, 29.21, 31.74, 32.38, 54.86, 114.28, 122.99, 123.16, 125.17, 126.16, 126.40, 128.67, 129.43, 131.23, 131.71, 134.08, 134.83, 160.31, 163.26, 170.63; UV ($CHCl_3$): λ_{max} (ε) = 528 nm (92800), 491 (55900), 460 (20300); fluorescence ($CHCl_3$): λ_{max} = 543 nm, 575; fluorescence quantum yield[15] ($c = 5.61 \times 10^{-7}$ mol l^{-1} in $CHCl_3$, reference **3b** with Φ = 100 %, $\lambda_{excit.}$ = 491 nm) = 0.03 %; MS (70 eV): *m/z* (%): 706 (1), 705 (1) [M^+], 574 (2), 573 (9), 572 (23) [$M^+ - C_8H_7NO$], 555 (5), 524 (4), 403 (2), 392 (13), 391 (45), 390 (100) [$M^+ - C_8H_7NO - C_{13}H_{26}$], 374 (2), 373 (7), 346 (5), 345 (5), 133 (13) [$C_8H_7NO^+$], 103 (5), 90 (4), 55 (2); $C_{45}H_{43}N_3O_5$: calcd 705.3203; found 705.3202 (MS); $C_{45}H_{43}N_3O_5$ (705.9): calcd C 76.57, H 6.14, N 5.95; found C 76.40, H 6.09, N 5.91.

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(2-furfurylimineimide)-9,10-imide (7d)**: *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 100 mg, 0.17 mmol) and furfural (3 mL, 36 mmol) were allowed to react (2 h, 50 °C and then 2 d, 80 °C), and the reaction mixture was worked up as described for **7b** to give 100 mg (91 %) of **7d**. M.p. 334 – 337 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.86; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.79; R_f (silica gel; $CHCl_3$/1-butanol 40:1) = 0.32; IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2928 (m), 2856 (m), 1696 (s), 1660 (brs), 1636 (w), 1623 (w), 1618 (w), 1594 (s), 1578 (m), 1506 (w), 1476 (w), 1457 (w), 1430 (w), 1405 (m), 1331 (brs), 1253 (m), 1176 (m), 1018 (w), 809 (s), 739 (m); ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.22 (m_c, 16H; 8 CH_2), 1.87 (m_c, 2H; 2α-CH_2), 2.22 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 6.62 (dd, J = 1.8 Hz, J = 1.8 Hz, 1H; phenyl), 7.15 (d, J = 3.5 Hz, 1H; phenyl), 7.70 (d, J = 1.7 Hz, 1H; phenyl), 8.52 (d, ^3J = 8.1 Hz, 2H; perylene), 8.52 (s, 1H; N=CH), 8.55 (d, ^3J = 8.2 Hz, 2H; perylene), 8.64 (d, ^3J = 7.9 Hz, 4H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.01, 22.56, 26.94, 29.20, 31.74, 32.37, 54.86, 112.48, 118.67, 122.99, 123.00, 123.26, 123.42 (br), 124.16 (br), 126.19, 126.45, 128.72, 129.44, 131.03 (br), 131.89, 134.07, 135.01, 146.87, 148.03, 158.38, 160.20, 163.43 (br), 164.45 (br); UV ($CHCl_3$): λ_{max} (ε) = 528 nm (89100), 491 (53400), 460 (19000); fluorescence ($CHCl_3$): λ_{max} = 538 nm, 575 (very weak fluorescence); fluorescence quantum yield[15] ($c = 7.36 \times 10^{-7}$ mol l^{-1} in $CHCl_3$, reference **3b** with Φ = 100 %, $\lambda_{excit.}$ = 491 nm) = 25 %; MS (70 eV): *m/z* (%): 666 (2), 665 (4) [M^+], 573 (6) [$M^+ - C_5H_2NO$], 572 (14) [$M^+ - C_5H_3NO$], 555 (3), 485 (3), 484 (6), 405 (3), 392 (10), 391 (43), 390 (100) [572 – $C_{13}H_{26}$], 373 (6), 345 (5); $C_{42}H_{39}N_3O_5$ (665.8): calcd C 75.77, H 5.90, N 6.31; found C 75.66, H 5.69, N 6.40.

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(cyclohexylimineimide)-9,10-imide (7e)**: *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 100 mg, 0.17 mmol) and cyclohexanone (10 mL, 96 mmol) were allowed to react (10 min, 70 °C and then 12 h r.t. until no **6b** could be detected by TLC). The excess of cyclohexanone was removed in vacuo (0.2 Torr) to give **7e**; R_f (silica gel; $CHCl_3$/acetone (10:1) = 0.68; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.86; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.68; IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2928 (m), 2857 (m), 1698 (s), 1660 (s), 1594 (s), 1579 (m), 1506 (w), 1457 (w), 1431 (w), 1405 (m), 1355 (m sh), 1341 (s sh), 1336 (s), 1255 (m), 1208 (w), 1177 (w), 1127 (w), 1110 (w), 980 (w), 965 (w), 852 (w), 809 (m), 741 (w); ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.70 (s, 4H; cyclohexyl), 1.86 (m_c, 2H; 2α-CH_2), 1.96 (s, 2H; cyclohexyl), 2.21 (m_c, 4H; 2α-CH_2/2 cyclohexyl), 2.75 (t, 2H; cyclohexyl), 5.16 (m_c, 1H; NCH), 8.57 (d, ^3J = 8.1 Hz, 2H; perylene), 8.59 (d, ^3J = 8.1 Hz, 2H; perylene), 8.65 (d, ^3J = 8.1 Hz, 4H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.44, 22.98, 25.98, 26.73, 27.34, 27.81, 29.62, 30.84, 32.16, 32.78, 36.22, 54.93, 123.41, 123.65, 126.70, 126.99, 129.93, 131.53, 134.69, 135.33, 160.12, 185.81; UV ($CHCl_3$): λ_{max} (ε) = 527 nm (85800), 491 (51400), 459 (18600); fluorescence ($CHCl_3$): λ_{max} = 539 nm, 575; MS (70 eV): *m/z* (%): 668 (36), 667 (84) [M^+], 651 (6), 650 (12), 626 (7), 624 (55), 585 (11), 557 (6), 556 (10), 487 (17), 486 (56), 485 (62) [$M^+ - C_{13}H_{26}$], 444 (7), 443 (40), 442 (100) [485 – C_3H_7], 429 (6), 404 (9), 403 (19), 392 (16), 391 (60), 390 (65), 389 (6), 376 (10), 375 (34), 373 (28), 363 (5), 362 (15), 361 (21), 347 (10), 346 (31), 345 (22), 333 (9), 305 (10), 302 (7), 275 (6), 274 (7), 69 (12), 65 (7), 55 (20); $C_{43}H_{45}N_3O_4$ (667.8): calcd C 77.33, H 6.79, N 6.29; found C 76.76, H 6.79, N 6.15.

***N*-(1-Hexylheptyl)perylen-3,4:9,10-tetracarboxylic-3,4-(1-butylimineimide)-9,10-imide (7f)**: *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 100 mg, 0.17 mmol) and pentanal (valeraldehyde, 5 mL, 47 mmol) were allowed to react (24 h, r.t.), and the reaction mixture was worked up as described for **7e**. The product could not be purified by chromatography with silica gel because a slow decomposition of the adsorbed material took place. Yield 90 mg (90 %) of **7f**. R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.85; R_f (silica gel; $CHCl_3$/ethanol 20:1) = 0.88; IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2928 (m), 2857 (w), 1698 (s), 1660 (s), 1616 (w), 1594 (s), 1579 (m), 1510 (w), 1457 (w), 1432 (w), 1405 (m), 1354 (m), 1336

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(s), 1254 (m), 1207 (w), 1177 (m), 851 (w), 809 (m), 800 (w), 739 (m); ^{1}H NMR ($CDCl_3$): $\delta = 0.81$ (t, 6H; $2CH_3$), 1.03 (t, 3H; CH_3), 1.26 (m_c, 16H; $8CH_2$), 1.60 (m_c, 2H; CH_2), 1.76 (m_c, 2H; CH_2), 1.88 (m_c, 2H; 2α-CH_2), 2.22 (m_c 2H; 2α-CH_2), 2.70 (q, 2H; CH_2), 5.16 (m_c, 1H; NCH), 8.02 (t, 1H; N=CH), 8.50 (m_c, 8H; perylene); ^{13}C NMR ($CDCl_3$): $\delta = 13.86$, 14.03, 22.30, 22.58, 26.97, 27.88, 29.22, 31.76, 32.37, 33.28, 54.86, 122.89, 123.00, 123.13, 126.06, 131.56, 133.96, 134.78, 160.04, 177.76; UV ($CHCl_3$): $\lambda_{max} =$ 528 nm, 491, 460; fluorescence ($CHCl_3$): $\lambda_{max} = 535$ nm, 575; MS (70 eV): *m/z* (%): 655 (4) [M^+], 614 (4), 613 (9), 599 (4), 598 (9), 587 (9), 586 (20), 573 (6), 572 (13) [$M^+ - C_5H_9N$], 557 (4), 556 (4), 474 (8), 431 (8), 416 (9), 406 (5), 405 (13), 404 (17), 403 (5), 392 (13), 391 (53), 390 (100) [$572 - C_{13}H_{26}$], 376 (5), 375 (7), 374 (7), 373 (9), 346 (9), 345 (8); $C_{42}H_{45}N_3O_4$: calcd 655.3410; found 655.3405 (MS).

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(1-hexylimineimide)-9,10-imide** (**7g**): *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 160 mg, 0.28 mmol) and heptanal (enanthaldehyde, 2 mL, 14.3 mmol) were allowed to react (4 h, 50 °C), and the reaction mixture was worked up as described for **7e**. The product was further purified by column separation (silica gel/ethyl acetate), which should be quickly carried out, to give 90 mg (48%) of **7g**; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.88; R_f (silica gel/ethyl acetate) = 0.81; IR (KBr): $\tilde{\nu} =$ 2955 cm^{-1} (m), 2928 (m), 2857 (m), 1700 (s), 1660 (s), 1595 (s), 1579 (m), 1506 (w), 1465 (w), 1457 (w), 1430 (w), 1405 (m), 1352 (m sh), 1337 (s), 1254 (m), 1177 (m), 850 (w), 809 (m), 798 (w), 739 (m); ^{1}H NMR ($CDCl_3$): $\delta =$ 0.81 (t, 6H; $2CH_3$), 0.91 (t; 3H; CH_3), 1.28 (m_c, 20H; $8CH_2/2CH_2$), 1.56 (m_c, 2H; CH_2), 1.85 (m_c, 2H; 2α-CH_2), 2.24 (m_c, 2H; 2α-CH_2), 2.40 (t, $^3J =$ 8.3 Hz, 2H; CH_2), 2.70 (dd, $^3J = 7.5$ Hz, $^4J = 1.3$ Hz, 2H; CH_2), 5.18 (m_c, 1H; NCH), 8.02 (t, $^3J = 6.5$ Hz, 1H; N=CH), 8.45 (d, $^3J = 8.1$ Hz, 2H; phenyl), 8.48 (d, $^3J = 8.1$ Hz, 2H; perylene), 8.57 (d, $^3J = 8.0$ Hz, 2H; perylene), 8.63 (br s, 2H; perylene); ^{13}C NMR ($CDCl_3$): $\delta = 14.02$, 22.04, 22.57, 25.77, 26.96, 28.81, 29.21, 31.54, 31.75, 32.37, 33.59, 43.89, 54.85, 122.07, 122.78, 122.91, 123.04, 123.14, 123.23, 123.28, 126.10, 126.34, 128.64, 129.38, 131.60, 133.99, 134.81, 134.90, 160.06, 163.38 (br), 164.39 (br), 177.70 (**7g** decomposes in solution to the starting materials so that additional signals of the latter have been obtained, for example ^{1}H NMR: $\delta = 9.75$; ^{13}C NMR: $\delta = 202.86$); UV ($CHCl_3$): λ_{max} (ε) = 527 nm (78600), 491 (44600), 460 (11200); fluorescence ($CHCl_3$): $\lambda_{max} = 535$ nm, 576; MS (70 eV): *m/z* (%): 684 (3), 683 (5) [M^+], 614 (4), 613 (10), 598 (8), 587 (8), 586 (16), 574 (5), 573 (16), 572 (18) [$M^+ - C_7H_{13}N$], 502 (6), 431 (5), 416 (6), 405 (8), 404 (10), 403 (5), 392 (16), 391 (58), 390 (100) [$572 - C_{13}H_{26}$], 375 (6), 374 (7), 373 (8), 346 (9), 345 (8), 83 (20), 82 (25), 69 (5), 55 (13), 54 (9); $C_{44}H_{49}N_3O_4$ (683.9): calcd C 77.28, H 7.22, N 6.14; found C 77.86, H 7.23, N 6.27.

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(methylimineimide)-9,10-imide** (**7h**): *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 50 mg, 0.09 mmol) and acetaldehyde (3 mL, 53 mmol) were allowed to react (3 d, 30 °C bath temperature), and the reaction mixture was worked up as described for **7b** to give a mixture of 40% **7h** and 60% **6b** (^{1}H NMR: $\delta = 7.95$ (**7h**) and $\delta = 5.48$ (**6b**)); R_f of **7h** (silica gel; $CHCl_3$/ethanol 20:1) = 0.70; ^{1}H NMR ($CDCl_3$): $\delta = 0.81$ (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.88 (m_c, 2H; 2α-CH_2), 2.24 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 5.48 (s, 2H; NH_2), 7.95 (t, 1H; N=CH), 8.50 (m_c, 8H; perylene); UV ($CHCl_3$): $\lambda_{max} = 528$ nm, 490, 460; fluorescence ($CHCl_3$): $\lambda_{max} = 535$ nm, 575; MS (70 eV): *m/z* (%): 614 (3), 613 (7) [M^+], 596 (2), 587 (3), 573 (4), 572 (9) [$M^+ - CH_3CN$], 432 (8), 431 (4) [$M^+ - C_{13}H_{26}$], 406 (8), 405 (14), 392 (10), 391 (45), 390 (100) [$572 - C_{13}H_{26}$], 376 (5), 346 (5), 345 (5), 55 (5).

***N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-(2-(4-methyl-pent-3-ene)imineimide)-9,10-imide** (**7i**): *N*-Amino-*N*′-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 300 mg, 0.50 mmol) and freshly distilled mesityloxide (80 mg, 0.80 mmol) were dissolved in hot benzene (80 mL), allowed to react (24 h, reflux), and the reaction mixture was worked up as described for **7e**. It was further purified by column separation (dried silica gel; dried chloroform/acetone 10:1) to give 90 mg (90%) of **7i**. R_f (silica gel; $CHCl_3$/acetone 10:1) = 0.82; ^{1}H NMR ($CDCl_3$): $\delta = 0.83$ (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.90 (m_c, 2H; 2α-CH_2), 2.24 (m_c 2H; 2α-CH_2), 5.18 (m_c, 1H; NCH), 6.01 (s, 1H; C=CH), 8.50 (m_c, 8H; perylene); ^{13}C NMR ($CDCl_3$): $\delta = 14.02$, 20.04, 21.26, 22.56, 26.93, 27.47, 29.20, 31.74, 32.36, 54.57, 122.57, 122.98, 123.10, 123.32, 126.10, 126.90, 129.20, 129.60, 131.59, 134.20, 134.86, 148.10, 159.52, 170.70; UV ($CHCl_3$): $\lambda_{max} = 527$ nm, 491, 460; fluorescence ($CHCl_3$): $\lambda_{max} = 534$ nm, 576; MS (70 eV): *m/z* (%): 667 (4) [M^+], 628 (4), 627 (9), 613 (4), 612 (13), 573 (6), 572 (12), 555 (4), 446 (9), 445 (10), 431 (10), 430 (33), 404 (5), 403 (5), 392 (18), 391 (57), 390 (100), 389 (5), 376 (5), 375 (6), 374 (7), 373 (10), 362 (5), 361 (5), 347 (4), 346 (9), 345 (8), 302 (4), 95 (16), 55 (6).

Fluorescence derivatizing by means of 6 for trace analysis: reaction of 6a with benzaldehyde: A stock solution of **6a** (0.390 mg in 50 mL chloroform) with a content of 1.47×10^{-5} mol l^{-1} was prepared. 99 mg of benzaldehyde were diluted with chloroform to 50 mL and 2.00 mL of this solution were further diluted to 1 l giving a reference solution with a content of 3.73×10^{-8} mol l^{-1}. For the determination of benzaldehyde several 2.00 mL (2.94×10^{-8} mol) lots of the stock solution of **6a** were each mixed with an increasing amount of the reference solution of benzaldehyde, refluxed for 30 min, and the intensity of their fluorescent light was determined by means of a fluorimeter. The following volumes of the reference solution have been used; the found fluorescence intensity is reported in brackets: 0 mL (5.0), 0.1 (6.0), 0.2 (6.0), 0.4 (6.6), 0.8 (6.2), 1.6 (11). Generally, better results have been obtained with higher concentrations of benzaldehyde and furthermore this the fluorescence becomes visible.

Fluorescence-derivatizing of complex natural products by means of 6; the reaction of secologanin (RN 19351-63-4) with 6b: Several micrograms of secologanin and of **6b** were heated in chloroform (3 mL, 3 h, 60 °C, the reagents must be free of acids), which resulted in a visible fluorescence by the application of a standard fluorescence lamp (365 nm). The fluorescent derivatization can be followed by TLC: R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.74 (nonfluorescent **6b**), R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.16 (fluorescent main product), R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.77 (fluorescent byproduct).

***N*-(1-Octylnonyl)-*N*′-(*N*″-ethoxycarbamidyl)perylene-3,4:9,10-bis(dicarboximide)**: Triethylamine (40 mg, 0.40 mmol) was added to *N*-amino-*N*′-(1-octylnonyl)perylene-3,4:9,10-tetracarboxylic-bisimide (**6d**, 220 mg, 0.34 mmol) and ethylchloroformate (40 mg, 0.36 mmol), and was stirred at 60 °C for 3 h. The mixture was cautiously added to ethanol/water (1:1, 150 mL) and vigorously stirred for 2 h. The precipitate was collected by vacuum filtration (glass filter D 4) washed with water three times, dried in an oven at 100 °C and further purified by column separation (silica gel; chloroform/ethanol 10:1). Methanol (100 mL) was added to the main fraction, the solvent was evaporated, and the residue dried in medium vacuum at 60 °C to give 150 mg (68%). M.p. 277–278 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.66; R_f (silica gel; $CHCl_3$/1-butanol 40:1) = 0.27; R_f (silica gel; $CHCl_3$/triethylamine 40:1) = 0.17; IR (KBr): $\tilde{\nu} = 2954$ cm^{-1} (m), 2926 (m), 2855 (m), 1718 (s), 1700 (s), 1660 (s), 1636 (m), 1616 (m), 1595 (s), 1580 (m), 1506 (w), 1465 (w), 1457 (w), 1404 (m), 1348 (m), 1305 (m), 1254 (m), 1175 (m), 810 (m), 750 (m), 668 (m); ^{1}H NMR ($CDCl_3$): $\delta = 0.80$ (t, 6H; $2CH_3$), 1.28 (m_c, 27H; $12CH_2/CH_3$), 1.92 (m_c, 2H; 2α-CH_2), 2.25 (m_c, 2H; 2α-CH_2), 4.31 (br d, 2H; OCH_2), 5.15 (m_c, 1H; NCH), 7.17 (br s, 1H; NH), 8.21 (br d, 2H; perylene), 8.31 (br d, 4H; perylene), 8.53 (br d, 2H; perylene); ^{13}C NMR ($CDCl_3$): $\delta = 14.06$, 14.42, 22.62, 27.10, 29.26, 29.53, 31.82, 55.09, 62.92, 122.36, 122.72, 123.26, 125.85, 126.04, 128.92, 129.00, 129.10, 130.86, 131.69, 133.47, 134.87, 155.18, 161.40; UV ($CHCl_3$): λ_{max} (ε) = 526 nm (82900), 490 (49900), 459 (18100); fluorescence ($CHCl_3$): $\lambda_{max} = 535$ nm, 574; MS (70 eV): *m/z* (%): 716 (21), 715 (46) [M^+], 698 (12) [$M^+ - OH$], 669 (5), 480 (6), 479 (31), 478 (77), 477 (100) [$M^+ - C_{17}H_{34}$], 433 (11), 432 (22), 431 (24), 414 (5), 407 (6), 406 (35), 405 (75), 391 (22), 390 (37), 388 (6), 377 (12), 376 (43), 347 (10), 320 (8), 319 (5); $C_{44}H_{49}N_3O_6$ (715.8): calcd C 73.82, H 6.90, N 5.87; found C 73.81, H 6.94, N 5.80.

***N*-(1-Hexylheptyl)-*N*′-(*N*″-ethoxycarbamidyl)perylene-3,4:9,10-bis(dicarboximide)**: Triethylamine (20 mg, 0.20 mmol) was added to *N*-amino-*N*′-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-bisimide (**6b**, 100 mg, 0.17 mmol) and ethylchloroformate (20 mg, 0.18 mmol), and was stirred at 60 °C for 3 h. The mixture was cautiously added to ethanol/water (1:1, 50 mL) and vigorously stirred for 2 h. The precipitate was collected by vacuum filtration (glass filter D 4), washed with water three times and dried in an oven at 100 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.66; R_f (silica gel; $CHCl_3$/1-butanol 40:1) = 0.19; R_f (alumina; $CHCl_3$/ethanol 10:1) = 0.68; R_f (alumina; $CHCl_3$/1-butanol 40:1) = 0.34; IR (KBr): $\tilde{\nu} = 2927$ cm^{-1} (m), 2857 (w), 1718 (m), 1700 (s), 1653 (m), 1636 (m), 1595 (s), 1577 (m), 1505 (w), 1457 (w), 1437 (w), 1420 (m), 1254 (m), 1176 (w), 1109 (w), 1043 (w), 809 (m); ^{1}H NMR ($CDCl_3$): $\delta = 0.82$ (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.33 (s, 3H; O-CH_2CH_3), 1.90 (m_c, 2H; 2α-CH_2), 2.25 (m_c, 2H; 2α-CH_2), 4.32 (q, 2H; OCH_2), 5.16 (m_c, 1H; NCH), 8.51 (m_c, 8H; perylene); ^{13}C NMR ($CDCl_3$): $\delta = 14.04$, 14.41, 22.59, 27.01, 29.23, 31.77, 32.41, 55.03,

62.96, 122.47, 122.84, 123.37, 126.31, 129.20, 131.90, 133.68, 135.44, 155.17, 166.51.

***N*-1-(Hexylheptyl)-*N'*-(phenyl)perylene-3,4:9,10-bis(dicarboximide)**:[16] *N*-(1-Hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5b**, 600 mg, 1.04 mmol), freshly distilled aniline (280 mg, 3.0 mmol), zincacetate dihydrate (100 mg, 0.46 mmol) and imidazole (3 g) were stirred for 3 h at 150 °C. The still warm mixture was diluted with ethanol (10 mL) and added with stirring to 2 N HCl (100 mL) and further stirred for 2 h. The precipitate was collected by vacuum filtration (D 4 glass filter), thoroughly washed with methanol/water, dried in an oven at 100 °C and purified by column separation (silica gel/chloroform) to give 510 mg (75 %). R_F (silica gel/$CHCl_{3)}$ = 0.53; IR (KBr): $\tilde{\nu}$ = 2955 (m) cm^{-1}, 2927 (m), 2857 (m), 1699 (s), 1660 (s), 1594 (s), 1579 (m), 1505 (w), 1490 (w), 1455 (w), 1433(w), 1405 (w), 1334 (s), 1255 (m), 1199 (w), 1177 (m), 1124 (w), 1110 (w), 1075 (w), 965 (w), 852 (w), 840 (w), 810 (w), 745 (w), 700 (w), 637 (w); UV ($CHCl_3$): λ_{max} (ε) = 492 (18750), 492 (52270), 528 (86730); fluorescence ($CHCl_3$): λ_{max} = 538 nm, 578; ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.88 (m_c, 2H; 2α-CH_2), 2.24 (m_c, 2H; 2α-CH_2), 5.16 (m_c, 1H; NCH), 7.35 (m_c, 2H; phenyl), 7.53 (m_c, 3H; phenyl), 8.50 (m_c, 8H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.03, 22.58, 26.95, 29.21, 31.76, 32.38, 54.85, 123.03, 123,31, 123.36, 126.39, 126.65, 128.60, 128.88, 129.45, 129.53, 129.82, 131.77, 134.26, 135.08, 135.09, 163.53; MS (70 eV): *m/z* (%): 649 (14), 648 (30) [M^+], 631 (7), 479 (4), 469 (3), 468 (18), 467 (69), 466 (100) [$M^+ - C_{13}H_{26}$], 465 (20), 449 (5), 422 (5), 421 (8); $C_{43}H_{40}N_2O_4$ (648.8): calcd C 79.60, H 6.21, N 4.31; found C 79.61, H 6.28, N 4.49.

Hydrazinolysis of *N*-1-(hexylheptyl)-*N'*-(phenyl)perylene-3,4:9,10-bis(dicarboximide): *N*-1-(Hexylheptyl)-*N'*-(phenyl)perylene-3,4:9,10-bis(dicarboximide) (500 mg, 0.77 mmol), hydrazine hydrate (100 %, 1.0 mL, 20.0 mmol) and *tert*-butyl alcohol (10 mL) were refluxed with stirring for 20 h, then added to water (200 mL) and stirred for 1 h. The precipitate was collected by vacuum filtration (D 4 glass filter), dried at 120 °C in an oven and purified by column separation (silica gel/chloroform 10:1). The product was identical to **6b** according to its spectroscopic data.

***N*-(1-Hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-3,4-((2-hydrazopyridine)-*N*^{2}ylimide)-9,10-imide**: *N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**5b**, 250 mg, 0.44 mmol), 2-hydrazopyridine (200 mg, 1.80 mmol) and 2-methoxyethanol (20 mL) were stirred for 20 h at room temperature (neither the addition of additional 2-hydrazopyridine nor increasing the reaction temperature to 70 °C completed the reaction). The solvent was evaporated in vacuo and the residue purified by column separation (alumina; chloroform/ethanol 10:1) and by flash chromatography (silica gel; chloroform/acetic acid 10:1). The solvent was evaporated and the residue thoroughly washed with water/methanol and dried in vacuo at 60 °C to give 70 mg (24 %). M.p. > 350 °C; R_f (silica gel; $CHCl_3$/ethanol 10:1) = 0.57; R_f (silica gel; $CHCl_3$/acetic acid 10:1) = 0.48; IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} (br m), 2956 (m), 2927 (m), 2856 (m), 1718 (m), 1700 (s), 1685 (br m), 1658 (s), 1594 (s), 1579 (m), 1506 (w), 1476 (w), 1459 (w), 1437 (m), 1404 (m), 1355 (m), 1346 (s), 1319 (w), 1253 (br m), 1175 (m), 1110 (w), 1090 (w), 1035 (w), 966 (w), 855 (w), 810 (s), 746(m); ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6H; $2CH_3$), 1.28 (m_c, 16H; $8CH_2$), 1.87 (m_c, 2H; 2α-CH_2), 2.26 (m_c, 2H; 2α-CH_2), 5.17 (m_c, 1H; NCH), 6.85 (m_c, 2H; phenyl), 7.57 (t, ^3J = 7.8 Hz, ^4J = 1 Hz, 1H; phenyl), 8.14 (d, ^3J = 5.0 Hz, 1H; phenyl), 8.58 (d, ^3J = 8.1 Hz, 2H; perylene), 8.59 (d, ^3J = 8.0 Hz, 2H; perylene), 8.67 (d, ^3J = 8.0 Hz, 4H; perylene); ^{13}C NMR ($CDCl_3$): δ = 14.02, 22.57, 26.94, 29.20, 31.75, 32.37, 54.90, 108.82, 117.65, 122.93, 123.44, 126.30, 126.71, 129.49, 132.20, 134.10, 135.36, 137.99, 148.21, 157.02, 162.45; UV ($CHCl_3$): λ_{max} (ε) = 527 nm (79100), 490 (48100), 459 (17700); fluorescence ($CHCl_3$): λ_{max} = 542 nm, 577; MS (70 eV): *m/z* (%): 666 (5), 665 (20), 664 (41) [M^+], 648 (4), 647 (9) [$M^+ - OH$], 619 (6), 495 (4), 484 (17), 483 (41), 482 (39) [$M^+ - C_{13}H_{26}$], 465 (7), 439 (11), 438 (45), 437 (100) [$M^+ - C_{13}H_{26} - CO$], 392 (4), 390 (5), 319 (5), 94 (5), 55 (5); $C_{42}H_{40}N_4O_4$ (664.8): calcd C 75.88, H 6.06, N 8.43; found C 75.94, H 5.99, N 8.22.

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[1] J. Buckingham, *Quart. Rev. Chem.* **1969**, *23*, 37 – 56.
[2] R. Chayen, R. Dvir, S. Gould, A. Harell, *Anal. Biochem.* **1971**, *42*, 283 – 286.
[3] R. Wintersteiger, *GIT Supplement Chromatograhie* **1988**, *3/88*, 5 – 11.
[4] J. M. Anderson, *Anal. Biochem.* **1986**, *152*, 146 – 153.
[5] H. Langhals, *Heterocycles* **1995**, *40*, 477 – 500.
[6] A. Rademacher, S. Märkle, H. Langhals, *Chem. Ber.* **1982**, *115*, 2927 – 2934.
[7] H. Langhals, S. Demmig, H. Huber, *Spectrochim. Acta* **1988**, *44A*, 1189 – 1193.
[8] E. Honold (Cassella AG), DOS 1147702, **1960**; *Chem. Abstr.* **1963**, *59*, 15416f.
[9] P. Gangneux, E. Marechal, *Bull. Soc. Chim. Fr.* **1973**, 1466 – 1483.
[10] H. Langhals, S. Demmig, T. Potrawa, *J. Prakt. Chem.* **1991**, *333*, 733 – 748.
[11] H. Kaiser, J. Lindner, H. Langhals, *Chem. Ber.* **1991**, *124*, 529 – 535.
[12] H. Langhals, Increasing the solubility of aromatic compounds, DOS 3016764, **1980**; *Chem. Abstr.* **1982**, *96*, P70417x.
[13] L.-F. Tietze, *Angew. Chem.* **1983**, *95*, 840 – 853; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 828 – 841.
[14] H. Langhals, *Chem. Ber.* **1985**, *118*, 4641 – 4645.
[15] H. Langhals, J. Karolin, L. B.-Å. Johansson, *J. Chem. Soc. Faraday Trans.*, in press.
[16] J. Lindner, Thesis, University of Munich, **1992**, p. 120.

  0947-6539/98/0411-2116 $ 17.50+.50/0