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Heinz Langhals^a; Ralf Kollfrath^b; Jörg Lindner^a

^a Institut für Organische Chemie der Universität München, München, Germany ^b T.U. München, Lehrstuhl für Makromolekulare Stoffe, Garching, Germany

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THE DETERMINATION OF THE MOLECULAR WEIGHTS OF PERYLENE DYES BY GPC

Heinz Langhals^{1*}, Ralf Kollefrath² and Jörg Lindner¹

Institut für Organische Chemie der Universität München¹,
Karlstrasse 23, D-80333 München, Germany

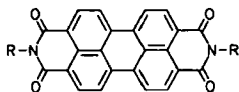
T.U. München², Lehrstuhl für Makromolekulare Stoffe,
Lichtenbergstr. 4, D-85747 Garching, Germany

ABSTRACT

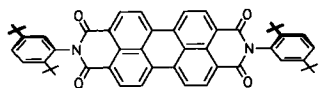
The molecular weights of 6 perylene dyes have been determined by GPC and the structures of bi- and trichromophoric dyes are established by this method. Correlation deviations are interpreted in terms of internal dynamics.

INTRODUCTION

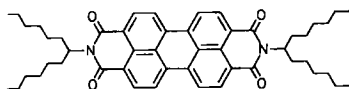
The application of GPC for the determination of molecular weights is a well known domain of macromolecular chemistry. There are, however, only a few examples of the use of this method for lower molecular weights although it may be very helpful for the determination of the structures of complex organic compounds. This is especially of interest for compounds with molecular weights in the order of 1000 or even more because in these cases there are often problems with mass spectroscopy. An example for such complex organic compounds are bi- and trichromophoric dyes because of their large π -systems.



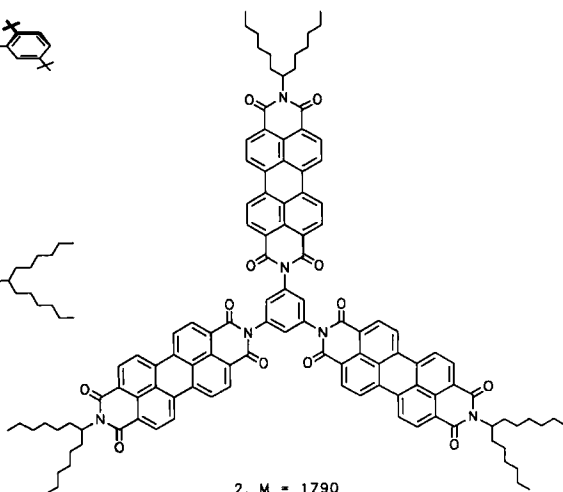
1



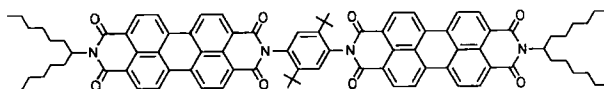
1a, M = 767



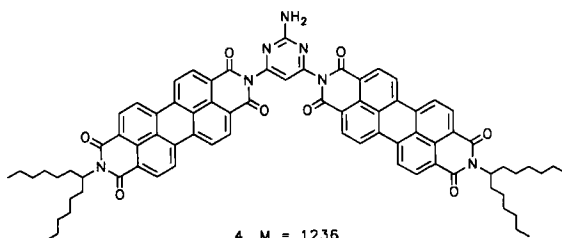
1b, M = 755



2, M = 1790



3, M = 1332

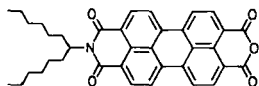


4, M = 1236

RESULTS AND DISCUSSION

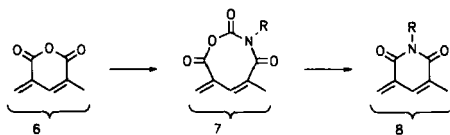
The application of GPC to bi- and trichromophoric compounds is demonstrated for perylene dyes (peryene-3,4:9,10-tetracarboxylic bisimides, **1**). In contrast to the majority of polymers perylene dyes^[1] have large, readily polarizable but rigid π -systems. Because of this special care must be taken in the calibration of GPC.

A "calibration" of GPC can be done for example with the monochromophoric perylene dyes **1a**^[2] and **1b**^[3] and **3** which can be easily prepared in a highly pure state. Their structures and molecular weights are well established by conventional methods.



5

A starting material for the preparation of the trichromophoric dye **2** is the anhydride imide **5** which was obtained with standard procedures by the partial alkaline saponification of the corresponding bisimide (**1b**). However a condensation of this anhydride imide with 1,3,5-triaminobenzene does not give **2**, as might be expected, but only monochromophoric perylene derivatives.



The trichromophoric dye **2** is obtained with a new synthetic procedure: instead of the amine the tris formamide of 1,3,5-triaminobenzene is condensed with **5**. Surprisingly, the formamide is more reactive than the amine itself. This might be caused by the formation of the possible intermediate **7** (see also ref.^[4]).

The bichromophoric dyes **3** and **4** are prepared by the condensation of the corresponding amines with **5**. Notice that only two amino groups of triaminopyrimidine react with **5**. Finally, a new synthetic procedure has been developed for the preparation of 1,4-diamino-2,5-di-tert-butylbenzene.

The determination of the molecular mass of **2** was not successful by mass spectroscopy, because of the easy fragmentation of this large molecule not even FAB techniques proved useful.

The molecular mass of **2** is determined without problems by GPC as is shown in Fig. 1: the M_p -value calculated from the measured retention volume fits the calibration line of Fig. 1 within expected experimental error. The trichromophoric structure of **2** is established with this method without doubts.

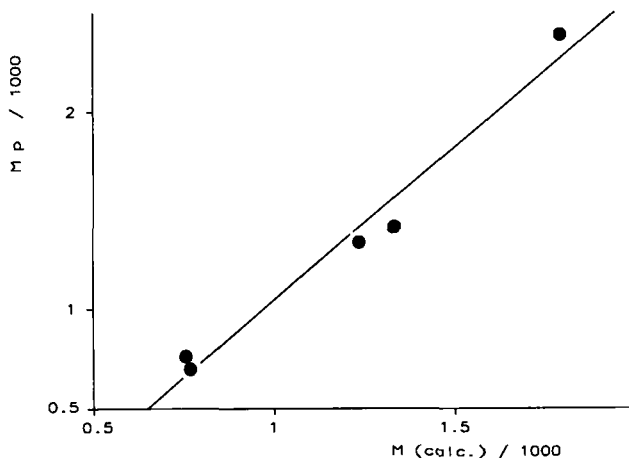


Fig. 1: Calibration line for the determination of the molecular weights of perylene dyes with GPC: equation (1) for calibration; $r = 0.986$, $n = 4$. From left to right: **1b**, **1a**, **4**, **3** and **2**. The molecular weights of the two leftmost points are supported by mass spectroscopy. Calibration line: $M_p = 1.550 \cdot M_{\text{calc.}} - 503.3$ (1).

It is of interest that the dyes **1b**, **3** and **4** which have large flexible structure elements give themselves a better correlation ($M_p = 1.15 \cdot M_{\text{calc.}} - 103.7$; $r = .9989$; $n = 3$) with the calibrating samples of the flexible polystyrene than equation (1). The slope of this correlation is closer to unity than in equation (1) and the offset is smaller. This indicates a similarity of both types of molecules. The essentially rigid, rod-like dye **1a** exhibits a deviation to smaller molecular weight, presumably because of the small diameter of this molecule. On the other hand, the bulky disk-like dye molecule **2** exhibits a deviation to larger molecular weight. These results are interesting concerning the study of conformations and mobility of derivatives of **1** in solution. In spite of this the deviations from the calibrating line of equation (1) are small enough to get an unequivocal result depending of whether the dye under test is monochromophoric, bichromophoric or trichromophoric.

The UV/Vis-spectra of the bi- and trichromophoric dyes **2** ... **4**. resemble very much the spectra of the monochromophoric dyes **1** except that their coefficients of extinction have the twofold or threefold value of that of **1**, respectively. Results concerning intramolecular energy transfer between the chromophores and other physical properties of the bi- and trichromophoric dyes will be reported elsewhere.

EXPERIMENTAL PART

All GPC-measurements were made on WATERS GPC (486 UV-detector, 410 RI-detector) with a series of WATERS Ultrastaygel® columns (7 μ m; 100 Å and 500 Å), and THF as eluent with a flux rate of 0.5 ml per minute. Perylene dye solutions were filtered through 0.2 μ m PTFE-membranes before injection.

Reaction of 2,4,6-triaminopyrimidine with N-(1-hexylheptylperylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide, preparation of 4: 3.70 g (6.45 mmol) N-(1-hexylheptylperylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (5), 10 g imidazole, 200 mg (0.90 mmol) zinc acetate and 270 mg (2.16 mmol) 2,4,6,-triaminopyrimidine are heated for 3 h at 200°C under Ar. The viscous reaction mixture is dispersed in 500 ml ethanol, 100 ml conc. HCl are added and the mixture is then stirred for 8 h. The solid is collected by filtration through a D-4 glass filter, washed with distilled water to neutral and dried (3.2 g). The solid is purified by column separation with CHCl₃/acetic acid 10:1 over silica gel. The initial eluant is discarded. The reddish violet, reddish fluorescing main product is so firmly adsorbed to silica gel that an elution is difficult. It is desorbed by refluxing with a mixture of CHCl₃/acetic acid 70:30. The dye solution is collected by filtration and washing the silica gel with CHCl₃/acetic acid. Most of the solvent mixture is evaporated, water is added and the solid dye collected by filtration through a D-4 glass filter, washed with water to neutral and dried for 8 h at 100°C (2.3 g, 86 %). 100 mg of the product are further purified by column separation with CHCl₃/1-butanol 40:1 over basic Al₂O₃ (activity I). The first fraction is collected. Yield 640 mg (55%). - IR (KBr): ν = 3448 cm⁻¹m, 3230 w, 3100 w, 2954 m, 2927 m, 2856 m, 1715 s, 1700 s, 1675 s, 1660 s, 1636 m, 1594 s, 1579 m, 1550 w, 1505 w, 1470 w, 1455 w, 1430 w, 1405 m, 1354 s, 1339 s, 1255 m, 1225 w, 1205 w, 1175 m, 1125 w, 1110 w, 995 w, 980 w, 965 w, 855 w, 811 s, 747 m, 725 w. - ¹H-NMR (CDCl₃): δ = 0.85 (m,12H,4CH₃), 1.26 (m,32H,16CH₂), 1.89 (m_c,4H,2a-CH₂), 2.2 (m_c,4H,2a-CH₂), 4.24 (m_c,2H,NH₂), 5.20 (m_c,2H,2CH), 7.52 (m_c,1H,CH pyrimidine), 8.47 (m_c,16H,2 x perylene) all signals are broad because of the formation of aggregates. - ¹³C-NMR (CDCl₃) δ = 14.05, 22.70, 27.02, 29.26, 29.71, 31.80, 54.96, 120.74, 121.97, 123.35, 125.18, 125.75, 128.37, 128.85, 130.90, 131.47, 133.19, 133.58, 134.64, 163.23, 163.96. - UV (CHCl₃) λ_{\max} = 529.8 nm, 491.4, 460.0, 423.9. - MS (FAB/CHCl₃, m-NBA): m/z (%) = 1254 (20), 1237 (100), 1236 (45), 596 (26), 414 (100), 358 (30), 275 (18), 237 (8).

C ₇₈ H ₇₃ N ₇ O ₈ ·H ₂ O (1254.4)	calc.	C 74.76	H 6.03	N 7.81
	found	C 74.93	H 6.28	N 7.76

1,3,5-Triaminobenzene-tris-formamide: 1.0 g (4.3 mmol) 1,3,5-triaminobenzene hydrochloride (the hydrochloride is obtained from the amine^[5] by treatment with 2N HCl as yellowish needles, m.p. 300°C. - MS (70 eV): m/z (%) = 231 (0.5) [M⁺], 225 (4), 125 (3), 44 (3), 38 (31), 36 (100) [HCl]) is added to 20 ml anhydrous formic acid and refluxed for 30 min. 250 ml distilled water are added after cooling and the solid collected by vacuum

TABLE 1: Determination of molecular weights M by GPC. $M_{\text{calc.}}$: calculated from chemical formula, M_{found} : determined on the basis of equation (1). Retention times t_p in minutes at peak maximum.

Nr.	$M_{\text{calc.}}$	M_{found}	UV: $M_p^a)$ (M_w/M_n)	RI: $M_p^a)$ (M_w/M_n)	UV: t_p	RI: t_p
1a	767	775	698 (1.003)	694 (1.002)	27.90	27.63
1b	755	816	761 (1.003)	754 (1.002)	27.17	27.45
2	1790	1870	2389 (1.070)	2366 (1.030)	23.50	23.78
3	1332	1240	1412 (1.010)	1399 (1.009)	24.80	25.08
4	1236	1190	1335 (1.009)	1322 (1.008)	24.97	25.25

a) according to polystyrene standards (peak maximum).

filtration. It is washed with water to neutral and dried in vacuo for 2 h at 50°C. Yield 50 mg (62%) grey powder - m.p. 265°C. - IR (KBr): $\nu = 3430 \text{ cm}^{-1}$, 3269 m br., 3285 n, 3095 m br., 3000 w, 2879 w, 1677 s br., 1618 s br., 1575 s br., 1514 w, 1453 w, 1435 m, 1406 m, 1287 m br., 1267 m br., 1055 w br., 970 w, 848 m, 829 w, 688 w, 675 w, 556 w, 529 w, 505 m. - $^1\text{H-NMR}$ ($[\text{D}_6]$ -DMSO): $\delta = 3.4$ ($m_c, 3\text{H}, 3\text{NH}$), 6.82, 7.2, 7.70, 8.24, (4 m_c , 3H, aryl), 10.15 ($m_c, 3\text{H}, 3$ aldehyde). - $^{13}\text{C-NMR}$ ($[\text{D}_6]$ -DMSO): $\delta = 104.11, 105.76, 138.74, 138.91, 159.29, 159.43, 161.80, 162.17$. (some weak additional signals from higher formylated products.) - MS (70eV): m/z (%) = 208 (3), 207 (30) [M^+], 179 (21) [$\text{M}^+ - \text{CO}$], 151 (11) [$\text{M}^+ - \text{CO} - \text{CO}$], 123 (13) [$\text{M}^+ - \text{CO} - \text{CO} - \text{CO}$], 111 (14), 105 (22), 97 (23), 96 (15), 95 (26), 91 (17), 85 (35), 84 (13), 83 (27), 82 (12), 81 (23), 71 (58), 69 (37), 60 (100), 43 (68). - The formamide contains a small amount of higher formylated products which do not disturb the subsequent condensation.

$\text{C}_9\text{H}_9\text{N}_3\text{O}_3$ (207.2)	calc.	C 52.17	H 4.38	N 20.23
	found	C 51.14	H 4.43	N 20.04

Reaction of 1,3,5-triaminobenzene with *N*-(1-hexylheptylperylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide, preparation of 2: 3.0 g (5.2 mmol) *N*-(1-hexylheptylperylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide) (5), 12 g imidazole, 359 mg (1.73 mmol) triaminobenzene-tris-formamide are heated for 5 h at 180°C. The reaction

mixture is dispersed after cooling in 1 l ethanol, 100 ml conc. HCl are added and the suspension is stirred for 2 h. The solid precipitate is collected by vacuum filtration through a D-4 glass filter, washed with distilled water to neutral and dried for 2 h at 100°C (2.8 g). It is dissolved in 30 ml CHCl₃/1-butanol and purified by column separation over Al₂O₃ (activity I) with this solvent mixture. A yellowish green fluorescing initial eluant is discarded and the orange to red fluorescing main fraction is filtered through a D-4 glass filter, evaporated, washed with distilled water and dried for 5 h at 50°C in vacuo. Yield 800 mg (26%) - m.p. 285-300°C (dec.) - R_f (silica gel; CHCl₃/acetic acid 10:1) = 0.85 - R_f (Al₂O₃; CHCl₃/n-BuOH 40:1) = 0.52. - IR (KBr): $\nu = 3090 \text{ cm}^{-1}$ w, 2953 m, 2926 m, 2856 m, 1713 m, 1698 s br., 1675 m, 1660 s br., 1616 w, 1594 s, 1579 m, 1506 w, 1457 w br., 1431 w br., 1405 m, 1339 s, 1252 m, 1195 w, 1174 w, 1130 w, 1125 w, 1110 w, 985 w, 965 w, 852 w, 811 m, 795 w, 746 m, 647 m. - UV (CHCl₃): λ_{max} (ϵ) = 433 nm (17140), 461 (53200), 492,5 (155100), 530 (298700). - Fluorescence (CHCl₃): λ_{max} = 538 nm, 578. - ¹H-NMR (CDCl₃): $\delta = 0.82$ (m,18H,6CH₃), 1.24 (m,48H,24CH₂), 1.86 (m,6H,3a-CH₂), 2.17 (m,6H,3a-CH₂), 5.20 (m,3H,3CH), 8.61 (m,27H,aryl) (broad lines because of the formation of aggregates). - ¹³C-NMR (CDCl₃): $\delta = 14.04, 22.59, 26.96, 29.22, 31.78, 32.38, 54.77, (7\text{-tridecyl}), 122.98, 126.34, 129.30, 129.51, 131.33, 134.39$ (6C perylene), 162.74, 163.02 (2C=O), 163.62 (1C benzene). The signals of the aromatic C-atoms and of the C=O-groups form intense, unresolved groups of peaks. - MS (70eV) m/z (%) = 756 (18), 755 (30), 574 (10), 573 (31), 572 (24) [C₃₇H₃₆N₂O₄], 392 (31), 391 (84), 390 (100) [C₂₄H₁₀N₂O₄], 321 (30), 181 (7), 149 (16), 124 (12), 122 (11), 111 (10), 109 (10), 105 (12), 97 (19), 93 (12), 91 (18), 85 (14), 83 (25), 81 (28), 78 (37), 77 (28), 71 (28), 70 (16), 62 (56), 56 (62), 56 (28), 55 (77). - MS (FAB, CHCl₃/m NBA): m/z = 1809 (0.2) [M⁺+H₂O], 1726, 1378, 1240 (0.4), 1099, 963, 853 (0.4), 754 (0.5), 622, 572 (1.7), 554, 390, 288, 165.

C ₁₁₇ H ₁₀₈ N ₆ O ₁₂ ·H ₂ O (1808.1)	calc.	C 77.72	H 6.13	N 4.64
	found	C 77.99	H 6.27	N 4.84

The water of the stable hydrate of **2** is removed by drying in medium vacuo for 8 h at 100°C.

C ₁₁₇ H ₁₀₈ N ₆ O ₁₂ (1790.1)	calc.	C 78.49	H 6.08	N 4.69
	found	C 78.25	H 6.08	N 4.84

1,4-Di-tert-butyl-2,5-dinitrobenzene: 144 ml red, fuming nitric acid, 544 ml 98% sulfuric acid and 316 ml 1,2-dichloroethane are cooled to -5°C and a solution of 190 g (1.00 mol) 1,4-di-tert-butylbenzene^[6] in 198 ml 1,2-dichloroethane are added dropwise with intense stirring and cooling according to ref.^[7]; the reaction temperature must not exceed -5°C! The reaction mixture is then poured onto 3 l crushed ice. The organic phase is separated, washed once with 400 ml 2N NaOH and twice with 400 ml water, dried with MgSO₄ and recrystallized four times from ethanol. It is important that the mother liquor of the first crystallisation is not too concentrated because of crystallisation of byproducts which can be removed only with difficulty by the further crystallisations. Yield 53.8 g (19%) (ref.^[7])

24%) - m.p. 192-193 °C (ref.^[7] 193-193.5°C). - IR (KBr) : $\nu = 3015 \text{ cm}^{-1}$ w, 3003 w, 2963 m, 2874 w, 1541 vs, 1502 w, 1486 m, 1449 w, 1402 w, 1380 s, 1369 s, 1357 s, 1271 m, 1249 m, 1106 w, 895 s, 860 w, 828 s, 750 w, 532 w. - ¹H-NMR (CDCl₃) : $\delta = 1.40$ (s, 18 H, C(CH₃)₃), 7.45 (s, 2 H, aryl). - ¹³C-NMR (CDCl₃) : $\delta = 151.54$ (2 C, C-2 / C-5), 140.96 (2 C, C-1 / C-4), 124.41 (2 C, C-3 / C-6), 35.62 (2 C, -C(CH₃)₃), 30.27 (6 C, -C(CH₃)₃).

C ₁₄ H ₂₀ N ₂ O ₄ (280.3)	calc.	C 59.99	H 7.19	N 9.99
	found	C 60.11	H 7.32	N 9.68

1,4-Diamino-2,5-di-tert-butylbenzene: 1.50 g (5.35 mmol) 1,4-Di-tert-butyl-2,5-dinitrobenzene and 1.3 ml (27 mmol) hydrazine hydrate are dissolved in 15 ml ethanol with warming up. A little Raney-nickel which has been washed with ethanol is added. An exothermic reaction with the evolution of gas takes place. A second portion of Raney-nickel is added after this reaction has slowed down and the mixture is then refluxed for 20 min. The hot mixture is filtered through a D-4 glass filter and immediately poured onto 200 ml cold water. The precipitate is collected after 20 min. by vacuum filtration and then quickly dried. Yield 1.13 g (96%) - m.p. 167-169 °C (ref.^[8] 170.5-172°C). - IR (KBr) : $\nu = 3432 \text{ cm}^{-1}$ m, 3311 m, 3215 w, 2964 s, 2868 m, 1632 br. m, 1512 s, 1477 w, 1409 s, 1389 m, 1362 m, 1301 m, 1261 m, 1230 m, 1127 m, 876 m, 715 br. m, 666 br. m, 610 m, 488 m. - ¹H-NMR (CDCl₃) : $\delta = 1.38$ (s, 18 H, C(CH₃)₃), 3.46 (s br., 4 H, NH₂), 6.57 (s br., 2 H, aryl). - ¹³C-NMR (CDCl₃) : $\delta = 29.72, 31.28, 117.43, 133.30, 136.36$.

C ₁₄ H ₂₄ N ₂ (220.4)	calc.	C 76.31	H 10.98	N 12.71
	found	C 76.34	H 11.05	N 12.60

1,4-Bis-[N-(1-hexylheptyl),N'-yl-perylene-3,4:9,10-tetracarboxylicbisimide]-2,5-di-tert-butylbenzene (3): 100 mg (0.45 mmol) 1,4-Diamino-2,5-di-tert-butylbenzene, 520 mg (0.91 mmol) N-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (5)^[9] and 120 mg zinc acetate dihydrate are layered under Ar with 1.50 g imidazole. The mixture is molten with stirring by means of an oil bath of 160°C and kept for 4 h at this temperature. 25 ml ethanol are added to the still warm and liquid mixture followed by 50 ml 2N HCl. The mixture is then stirred for 1 h and the solid is collected by vacuum filtration through a D-4 glass filter. It is then dried over night and further purified by column separation with CHCl₃/acetic acid 10:1 over silica gel and by a second column separation with CHCl₃/diethyl ether 20:1. The solvent is evaporated and the solid dried in vacuo. Yield 531 mg (89%) - m.p. > 300°C - *R_f* (silica gel/CHCl₃) = 0.18 - *R_f* (silica gel; CHCl₃/acetic acid 10:1) = 0.79 - *R_f* (silica gel; CHCl₃/ether 10:1) = 0.73. - IR (KBr) : $\nu = 3442 \text{ cm}^{-1}$ br. m, 2955 m, 2927 m, 2857 m, 1698 s, 1659 br. s, 1594 s, 1579 m, 1507 w, 1467 w, 1433 w, 1405 m, 1376 m, 1339 s, 1253 m, 1200 w, 1175 w, 1025 w, 967 w, 852 w, 812 m, 749 w. - UV (CHCl₃) : λ_{max} (ϵ) = 459 nm (36250), 492 (105030), 529 (193000). - Fluorescence (CHCl₃) : λ_{max} = 535 nm, 575. - ¹H-NMR (CDCl₃) : $\delta =$

0.84 (t, 6 H, CH_3), 1.25 (m_c , 10 H, CH_2), 1.31 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 1.88 (m_c , 2 H, CH_2), 2.26 (m_c , 2 H, CH_2), 5.19 (m_c , 1 H, CH), 7.31 (s, 2 H, aryl), 8.76 (m_c , 8 H, perylene).

$\text{C}_{88}\text{H}_{90}\text{N}_4\text{O}_8$ (1331.7)	calc.	C 79.37	H 6.81	N 4.21
	found	C 79.54	H 6.90	N 4.19

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