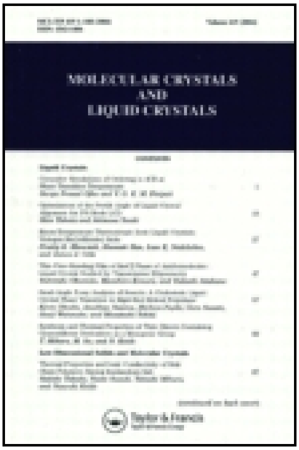

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Octaalkyl Esters of 2,3,9,10,16,17,23,24-(29H,31H)-Phthalocyanineoctacarboxylic Acid: A New Homologous Series of Discotic Liquid Crystals

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Octaalkyl Esters of 2,3,9,10,16,17,23,24-(29H,31H)-Phthalocyanineoctacarboxylic Acid: A New Homologous Series of Discotic Liquid Crystals

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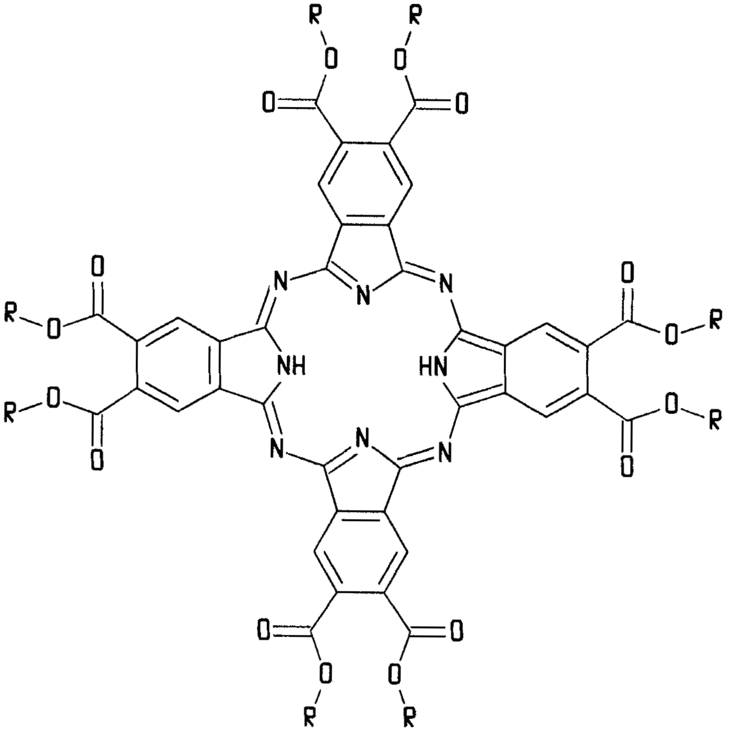
The synthesis of a homologous series of octaalkoxycarbonyl-substituted metal-free phthalocyanines (Pc) is described. The mesomorphic properties of these new materials were studied by differential scanning calorimetry (DSC), optical microscopy and X-ray investigations. All compounds show a discotic mesophase in an extremely large temperature interval including room temperature. X-ray diffraction patterns of the mesophases confirm that all compounds form a hexagonal columnar mesophase of the type D_{ho}.

Keywords: discotic liquid crystals, phthalocyanineoctacarboxylic acid octaalkyl ester

INTRODUCTION

In the field of discotic liquid crystals already some representatives with a phthalocyanine unit as central core are known.[1–22] In most cases the side chains of discotic liquid crystalline phthalocyanines are alkoxy chains or alkoxymethylene chains. As far as we know there is no discotic mesogen of phthalocyanine described in literature with alkoxycarbonyl side chains, so that it seemed interesting to us to synthesize and to investigate such a species. The general formula of the synthesized molecules is



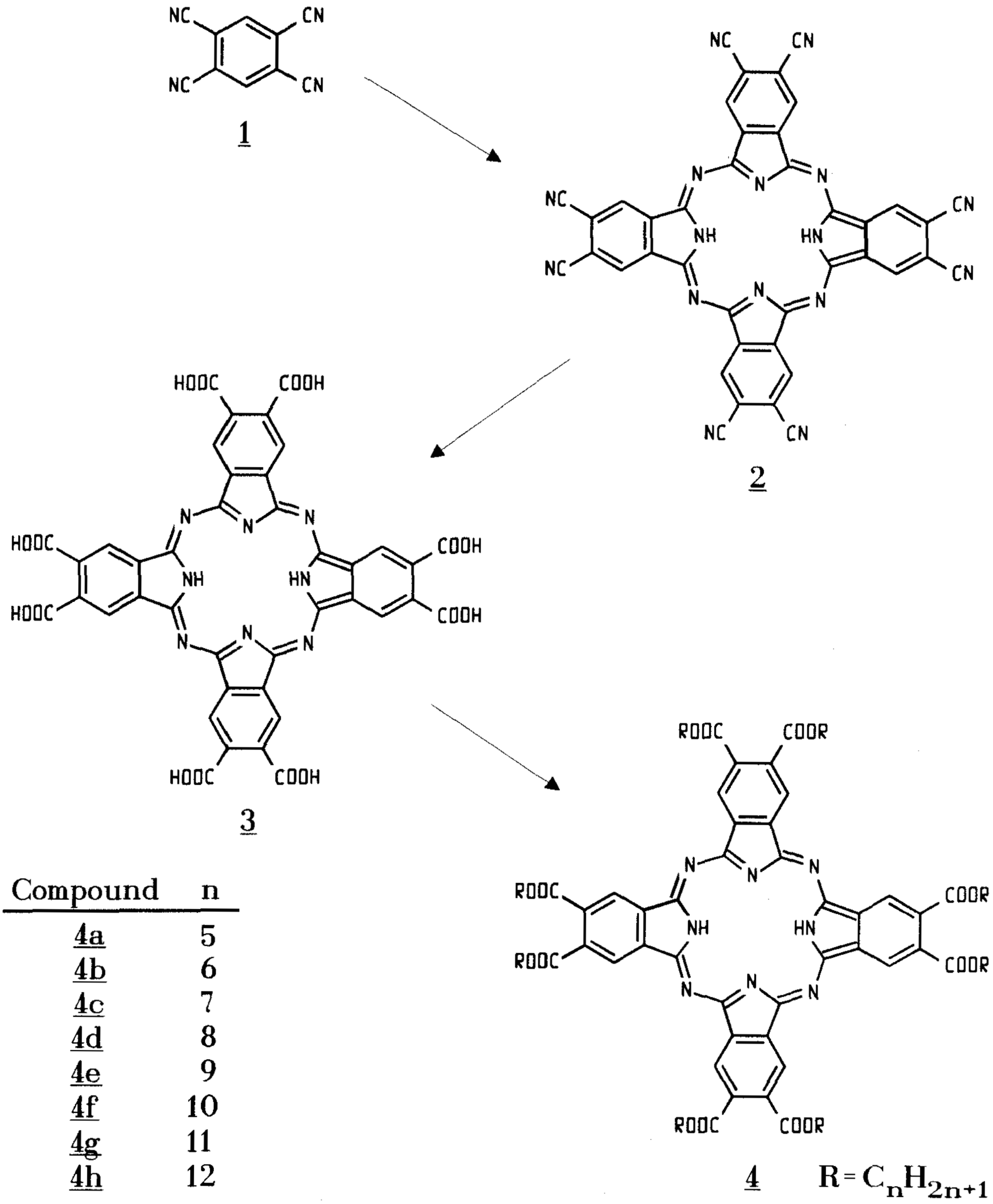
SCHEME I $H_2Pc(COOR)_8$

As expected, these compounds show columnar mesophases which are described in the following.

SYNTHESIS AND CHARACTERIZATION

In 1985 Wöhrle and Hündorf[23] described a route to 2,3,9,10,16,17,23,24-(29H,31H)-phthalocyanineoctacarboxylic acid. To esterify this compound we used the well known method of the alkylation of the anion of carboxylic acids with alkyl bromides in a dipolar aprotic solvent under the aid of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).[24,25] The following scheme outlines the complete synthetic route starting from 1,2,4,5-benzenetetracarbonitrile.[26]

Benzenetetracarbonitrile 1 which we obtained following the optimized synthesis decribed by Marose[26] condenses in the presence of lithium-propanolate in 1-propanol to the corresponding phthalocyanineoctacarbonitrile 2. The saponification of the nitrile groups was carried out under base-catalysis (potassium hydroxide in triethylene glycol at 190°C) following the method of Wöhrle and Hündorf[23] with slightly changed reaction conditions. It resulted in the phthalocyanineoctacarboxylic acid 3, which was esterified with a homologous series of alkyl bromides (pentyl bromide to dodecyl bromide) to produce the corresponding homologous series of phthalocyanineoctacarboxylic acid octaalkyl esters 4 using the DBU-method with



1

2

3

4 $R = C_nH_{2n+1}$

Compound	n
4a	5
4b	6
4c	7
4d	8
4e	9
4f	10
4g	11
4h	12

SCHEME II none

acetonitrile as solvent. The purification of the desired products was carried out with medium pressure liquid chromatography (MPLC) over silica gel.

The IR spectra of the phthalocyanineoctacarboxylic acid octaalkyl esters are in agreement with the data published for other metal-free phthalocyanines. Aside from the bands of the alkyl side chains at 2950, 2920, 2850 and 1455 cm^{-1} there are many signals resulting from the aromatic ring.[23] Especially important is the band at 1725 cm^{-1}, which is assigned to the ester group, in addition to the absence of any other signal in the carbonyl region of the IR spectrum, indicating the completeness of the esterification.

The electronic spectra show a doublet in the Q band region at 704 nm and at 667 nm typical for metal-free phthalocyanines.[4] The band position is independent of the side chain length. Furthermore Lambert-Beer's law was found to be valid at concentrations from $3 \cdot 10^{-7}$ to $3 \cdot 10^{-5}$ mol/l indicating no aggregation behaviour in this range, in agreement to what has been reported for octasubstituted silicon-dihydroxophthalocyanines.[15]

In the ^{1}H-NMR-spectra the detected signals were easily assigned to the aromatic protons (singulet), the protons of the $—CH_2—O—$ group (triplet) and the other aliphatic protons resulting in one multiplet. The inner protons show a very broad signal at a chemical shift of −2.6 ppm similar to what has been observed for other metal-free phthalocyanines.[22]

From the dodecyl ester <u>4h</u> the ^{13}C-NMR-spectrum has been recorded. While the assignment of the signals of the aliphatic carbon atoms is straightforward,[27] there is only little information concerning the chemical shifts of the four aromatic carbons.[4,15,28] A gated decoupled spectrum[27] allowed for the assignment of the proton bearing aromatic carbon. The carbon atom of the N=C—N group could be assigned by comparison of the chemical shift measured with the data reported in literature.[15,28] Because of the small difference in the chemical shift of the two remaining signals in the aromatic region of the spectrum, a differentiation between the corresponding carbons was not possible.

A mass spectrum (FABMS) confirmed the structure of the dodecyl ester. The $(M+H)^+$-peak could be detected at 2213 a.u.

DSC MEASUREMENTS

Calorimetric investigations of the octaalkoxycarbonyl-phthalocyanines by DSC showed an endothermic peak in the case of $n = 10$, 11 and 12 (n is the number of carbon atoms in the alkoxy side chain). In the case of $n \leq 9$ no phase transition could be detected in the accessible range from −60°C to +300°C. The transition temperatures and the thermodynamic data derived from the DSC measurements are summarized in Table I. As the investigations by optical microscopy and X-ray diffraction will show, all compounds exhibit a liquid crystalline phase. In the case of the decyl, the undecyl and the dodecyl compound the border of the mesophase to lower temperatures could be detected by DSC, whereas no clearing point could be observed. In the other cases neither the conversion to an isotropic liquid nor the crystallization takes place in the cited temperature range.

The rise of the melting point with an increasing number of carbon atoms in the alkyl side chain from −16.8°C for the decyl compound to +12.1°C for the dodecyl compound is in good agreement with the observations published for discotic liquid crystalline hexasubstituted triphenylenes[29–31] and scylloinositols,[32] but it contrasts to what has been reported for other octasubstituted phthalocyanines forming col-

TABLE I

Transition temperatures and thermodynamic data for octaalkyl phthalocyanineoctacarboxylates

n	$T_{C \to D}$ °C	$T_{D \to I}$ °C	$\Delta H_{C \to D}$ (kJ/mol)	$\Delta S_{C \to D}$ (J/K·mol)
5	—[a]	>300	—[a]	—[a]
6	—[a]	>300	—[a]	—[a]
7	—[a]	>300	—[a]	—[a]
8	—[a]	>300	—[a]	—[a]
9	—[a]	>300	—[a]	—[a]
10	-16.8	>300	29.2	114
11	- 0.7	>300	44.5	163
12	12.1	>300	57.6	202

[a] no phase transitions could be detected in the range of -60°C to 300°C.

umnar mesophases.[15,20] The values of the transition enthalpies and entropies are in the expected range compared with similar compounds.[2,10,16,20] Except one example[2] the absence of any polymorphism seems to be typical for discotic liquid crystalline octasubstituted phthalocyanines.[15,20] Corresponding to these observations we could not detect any.

Noteworthy is the extraordinary large range of existence of the mesophase of the discotic liquid crystals presented in this study compared to other liquid crystalline phthalocyanines.[1-22] We ascribe this fact to the only difference between the compounds synthesized by us and the liquid crystalline phthalocyanines known before: the nature of the side chains. Obviously the alkoxycarbonyl side chains have a stabilizing effect on the mesophase.

OPTICAL MICROSCOPY

Optical microscopy confirmed the existence of the liquid crystalline phases. Already at room temperature all substances are highly viscous masses, that show birefringence between crossed polarizers. On heating to higher temperatures, the substances become more fluid and optical textures can be observed, which remain stable up to 300°C (see Figure 1). The textures are of a mosaic-like type, which already has been reported in the case of columnar mesophases.[33-35] They do not show any significant difference depending on the chain length.

X-RAY INVESTIGATIONS

Since the structure of the mesophases could not be determined solely on the basis of the optical textures, X-ray diffraction experiments were carried out. Powder

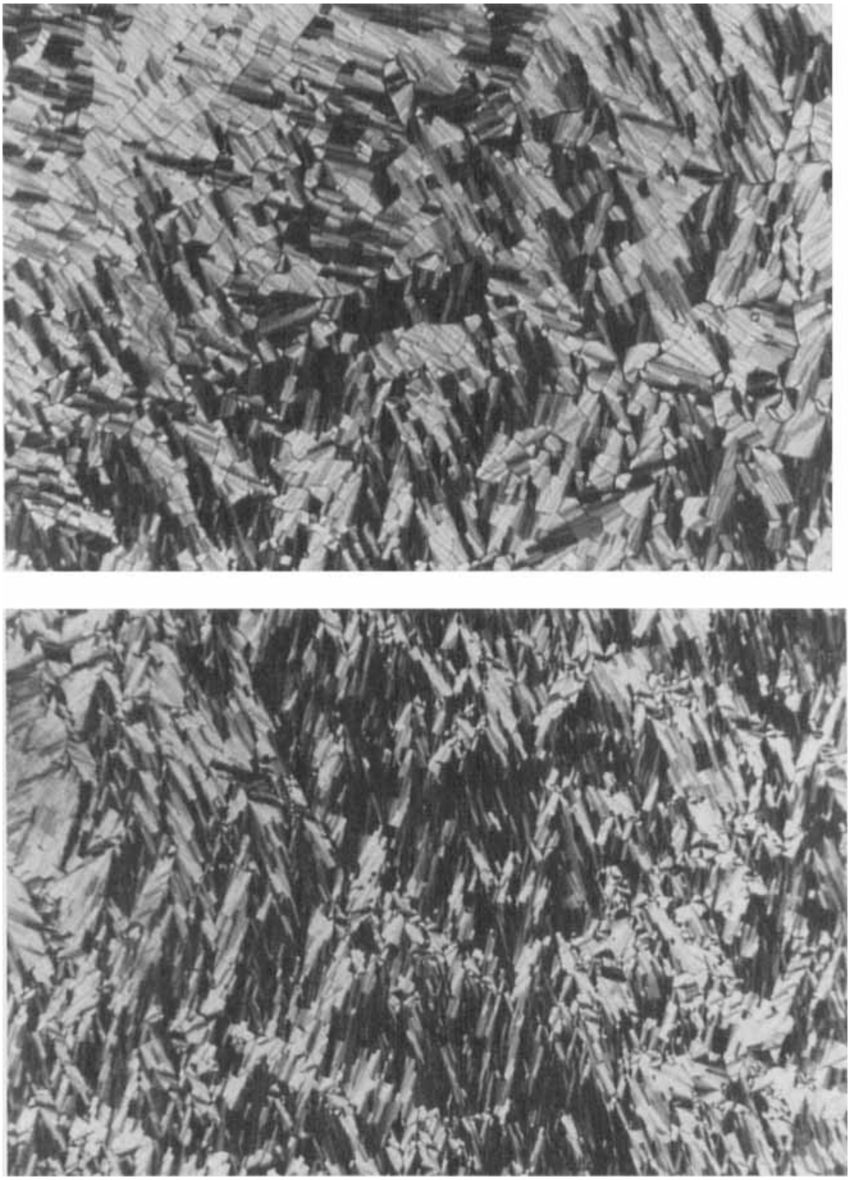


FIGURE 1 Optical textures of liquid crystalline phthalocyanines observed at 200°C (200x, crossed polarizers, top: 4b, bottom: 4e).

diffractogrammes were sufficient to identify the mesophases as D_{ho}-phases according to the nomenclature introduced by Destrade *et al.*[36] as will be shown in the following.

Table II summarizes the Bragg reflections observed in the small angle region and the diameter of the columns calculated from the (1,0)-reflections.

TABLE II

Bragg-spacings (in Å) of liquid crystalline octaalkyl phthalocyanine-octacarboxylates and their assignment in terms of a two-dimensional hexagonal lattice.[a] Column diameters D (in Å) calculated from the (1,0)-reflections

h,k	4a (n=5)	4b (n=6)	4c (n=7)	4d (n=8)
1,0	21.67 s	23.59 s	23.94 s	25.44 s
1,1	12.56 w	-	-	14.73 w
2,0	10.70 m	11.84 m	12.01 m	12.77 w
2,1	8.24 m	8.95 m	9.02 m	9.67 w
3,0	7.31 w	7.87 w	7.96 w	-
2,2	6.13 w	-	-	-
D	25.02	27.24	27.64	29.38
h,k	**4e (n=9)**	**4f (n=10)**	**4g (n=11)**	**4h (n=12)**
1,0	26.55 s	27.08 s	28.25 s	29.40 s
1,1	15.41 m	15.83 m	16.27 m	17.06 m
2,0	13.19 m	13.85 m	14.03 m	14.82 w
2,1	9.82 w	10.28 w	-	-
3,0	8.85 w	-	-	10.28 w
2,2	-	-	-	-
D	30.66	31.27	32.62	33.95

[a] All measurements were performed at room temperature (25°C). Relative intensities are given as follows: s = strong, m = medium, w = weak.

All reflections could be indexed according to the formula[37]

$$d(h, k) = \left[\frac{4}{3 \cdot D^2}(h_2 + h \cdot k + k^2)\right]^{-1/2}$$

where d are the spacings of the Bragg reflections, h and k are the Miller indices for the two-dimensional hexagonal lattice and D is the distance between adjacent columns. In the wide angle region there is a sharp reflection at 3.5 Å for all derivatives which can be assigned to the intercolumnar distance of the phthalocyanine molecules. This value corresponds to the van-der-Waals distance for aromatic carbon atoms. The structural unit of this liquid crystalline phase is therefore a two-dimensional hexagonal lattice which is formed by columns consisting of cofacially arrayed phthalocyanine molecules with the column axis normal to the aromatic ring plane.

The disordered alkyl side chains give rise to a broad amorphous halo located around 4.7 Å. Additional sharp reflections in the wide angle region appear at 3.8, 3.9 and 4.4 Å which cannot be attributed to high order reflections of the two-dimensional hexagonal lattice because of their high intensity. Presumably they are due to intramolecular scattering within the aromatic phthalocyanine moiety.[15]

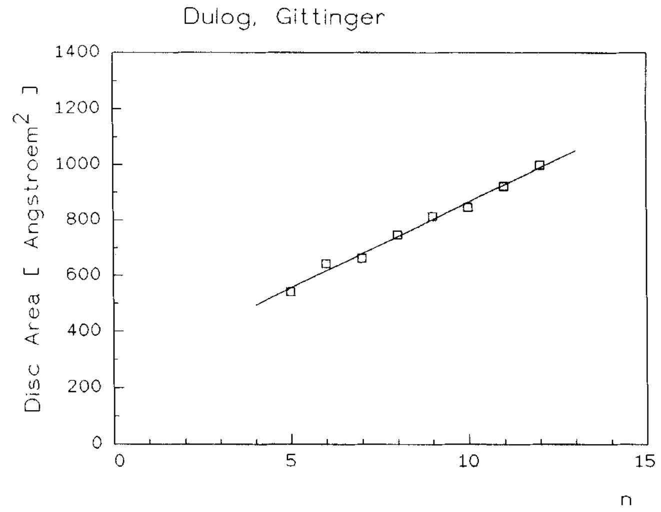


FIGURE 2 Plot of the cross section occupied by a single phthalocyanine molecule in a columnar stack of the mesophase versus the number of carbon atoms per alkyl side chain.

The density derived from the X-ray data is 1.1 g·cm^{-3} for the derivatives bearing long aliphatic chains (calculated from the (1,0)-reflections and the measured intercolumnar distance of the phthalocyanine molecules). This value is in good agreement with experimental data reported by Guillon *et al.*[2]

The cross section of the columns of substituted phthalocyanines is calculated from the (1,0)-reflections. The cross section area is plotted versus the number of carbon atoms per alkyl side chain *n* in Figure 2.

By extrapolating the straight line in Figure 2 to $n = 0$ the area occupied by the phthalocyaninering together with eight surrounding carboxyl groups is seen to be 245 Å^2. This value results in a diameter of 17.7 Å for the central core which is in good agreement with the data reported for similar systems.[2,15,20,39] That implies that in the mesophase the plane of the phthalocyanine core is perpendicular to the column axis.

The slope of the straight line can be used to calculate the volume occupied by a single methylene group in the mesophase. Taking the inter-ring distance of 3.5 Å one gets a value of 27.0 Å^3, which exceeds the volume of a methylene group in crystalline paraffin (24 Å^3)[38] by about 13%. Similar results were found for other liquid crystalline phthalocyanines.[15]

CONCLUSION

As we could demonstrate in the present study, octaalkyl esters of 2,3,9,10,16,17,23,24-(29H,31H)-phthalocyanineoctacarboxylic acid are able to form columnar mesophases of the type D_{ho}. The rather large range of existence of the mesophases from temperatures below 0°C up to temperatures above 300°C seems to be of special interest, as it reveals the stabilizing effect of the alkoxycarbonyl side chains on the mesophases.

EXPERIMENTAL PART

IR spectra were recorded on a Philips Pye Unicam SP3-200 infrared spectrophotometer, UV/VIS spectra with a Perkin Elmer Lambda 15 spectrometer. NMR spectra were measured with Bruker AM 200 and AC 250 spectrometers. Calorimetric studies were carried out using a Perkin Elmer DSC 7 and a DuPont DSC 2100. Optical textures were observed using a Zeiss Photomikroskop with a Leitz hotstage 350. X-ray diffraction experiments were performed with a Siemens diffractometer D 500 using Cu-Kα radiation.

Alkyl bromides (Aldrich) and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (Aldrich) were used without purification.

1,2,4,5-Benzenetetracarbonitrile 1 was prepared by the optimized method described by Marose.[26] 109 g (0.5 mol) 1,2,4,5-benzenetetracarboxylic acid dianhydride and 100 g (1.65 mol) urea in 500 ml 1,2-dichlorobenzene were maintained at 140°C for 4 h and at 160°C for additional 2 h. The crude 1,2,4,5-benzenetetracarboxylic acid diimide was filtered with suction, dried in vacuo and stirred in 750 ml concentrated aqueous ammonia for 16 h to give 114 g (0.46 mol) = 91% 1,2,4,5-benzenetetracarboxylic acid tetraamide after drying. The tetraamide was suspended in 700 ml dry DMF. 170 ml (2.36 mol) thionyl chloride was added dropwise at a temperature of 40 to 50°C in two portions of 100 ml first and of 70 ml 2 hrs later. After stirring for additional 16 h at room temperature the reaction mixture was poured on 2 kg of crushed ice. The precipitate was filtered with suction, washed with water and recrystallized from toluene. Yield: 59 g (0.33 mol) = 72%.

^{13}C-NMR (acetone-d_6): δ = 114.4 (CN), 121.2 (C—CN), 139.1 ppm (C—H).

IR (KBr): ν = 3120, 3050 (C—H), 2240 (C≡N), 1485 (C=C), 915 cm^{-1} (C—H δ_{oop}).

2,3,9,10,16,17,23,24-(29H,31H)Phthalocyanineoctacarbonitrile 2[40]: 22.3 g (125 mmol) of 1 was suspended in 1 l *n*-propanol, stirred and refluxed vigorously. With a dilution-apparatus[41] 2.07 g (31.3 mmol) of lithium-*n*-propanolate in 250 ml *n*-propanol was added dropwise (1 drop in 2 s). After completion of the addition the reaction mixture was heated for another 20 minutes. The precipitate was filtered with suction after cooling, washed with propanol and ether and dried in vacuo. Yield: 11.9 g (50%) of a green solid.

^{13}C-NMR (DMSO-d_6): δ = 110.0 (C—H), 115.3 (C≡N), 124.5 (C—CN), 136.5 (HC—C—CNN), 145.8 ppm (N=C—N).

IR (KBr): ν = 2230 (C≡N), 1625, 1560, 1490, 1465, 1315 (C—C), 1155 1130 1090 (C—H, pyrrole ring), 1000, 855, 790, 750 (C—H), 700 cm^{-1} (N—H δ_{oop}).

UV/VIS (H_2SO_4 conc.): λ = 748 (λ_{max}, $\varepsilon = 14 \cdot 10^7$ cm^2/mol), 694, 666, 315 nm.

2,3,9,10,16,17,23,24-(29H,31H)-phthalocyanineoctacarboxylic acid 3[23]: 9.7 g (13.1 mmol) of 2 was heated together with 12.1 g (216 mmol) KOH and 2.5 g (139 mmol) water in 90 ml triethyleneglycol for 7 days at 190°C under inert gas atmosphere and exclusion of light. After that period the ammonia evolution had ceased. The reaction mixture was filtered and acidified with 260 ml 1 molar HCl solution. The blue product was filtered, washed with water, diluted in 200 ml 1 molar NaOH solution and precipitated again with 210 ml 1 molar HCl solution. The precipitate was filtered with suction, washed with water and ether and dried in vacuo. Yield: 8.2 g (72%) of a blue solid.

^{13}C-NMR (D_2O/NaOD): δ = 179 (COOH), 159, 141, 122 ppm (C arom.).

IR (KBr): ν = 3400 (O—H), 1705 (C=O), 1450, 1365, 1275 (C—C), 1080 (pyrrole ring), 1010, 795, 745, 715 (C—H), 620 cm^{-1} (C—C). UV/VIS (DMSO): λ = 705 (λ_{max}, ε = $17 \cdot 10^7$ cm^2/mol), 681, 345 nm.

2,3,9,10,16,17,23,24-(29H,31H)-phthalocyanineoctacarboxylic acid octaalkyl ester 4: In a 100 ml round bottomed flask equipped with a reflux condensor and a magnetic stirrer 100 mg (0.116 mmol) of 3, 1.86 mmol of alkyl bromide and 283 mg (1.86 mmol) of DBU in 20 ml acetonitrile were refluxed for 16 h under inert gas atmosphere and exclusion of light. After cooling at room temperature the reaction mixture was diluted with 80 ml water and extracted with chloroform. From the organic phase the solvent was removed in vacuo. The product was purified by MPLC (silica gel 15 μm, chloroform). Yield: 26–38%. Data from elemental analysis are collected in Table III.

^{1}H-NMR ($CDCl_3$): δ = −2.6 (N—H), 0.8–2.0 (m, alkyl), 4.6 (—O—CH_2—), 9.4 ppm (arom.).

IR (KBr): ν = 2950, 2920, 2850 (C—H), 1725 (C=O), 1455 (—CH_2—), 1280, 1180 (C—C), 1085 (pyrrole ring), 1015 (C—H), 745 (—CH_2—), 665 cm^{-1} (C—C).

UV/VIS (DMSO): λ = 704 (λ_{max}, ε = $18 \cdot 10^7$ cm^2/mol), 667, 347 nm.

Spectral data for the dodecyl compound: FABMS: 2213 $(M+H)^+$, ^{13}C-NMR

TABLE III

Elemental analysis of octasubstituted phthalocyanines 4

	%C		%H		%N	
n	found	calc.	found	calc.	found	calc.
5	67.74	67.30	6.76	6.92	8.15	7.85
6	69.44	68.64	7.55	7.46	7.09	7.28
7	70.59	69.79	7.88	7.93	7.20	6.78
8	71.46	70.80	8.37	8.34	6.72	6.35
9	71.93	71.68	8.58	8.70	6.38	5.97
10	72.99	72.47	8.92	9.02	5.92	5.63
11	73.13	73.18	9.15	9.31	5.77	5.33
12	73.79	73.81	9.45	9.56	5.32	5.06

n	formula	molecular weight
5	$C_{80}H_{98}N_8O_{16}$	1427.7
6	$C_{88}H_{114}N_8O_{16}$	1539.9
7	$C_{96}H_{130}N_8O_{16}$	1652.1
8	$C_{104}H_{146}N_8O_{16}$	1764.3
9	$C_{112}H_{162}N_8O_{16}$	1876.6
10	$C_{120}H_{178}N_8O_{16}$	1988.9
11	$C_{128}H_{194}N_8O_{16}$	2101.0
12	$C_{136}H_{210}N_8O_{16}$	2213.2

($CDCl_3$): δ = 14.1 ($—CH_3$, $^1J_{C—H}$ = 125 Hz), 22.7 ($—\underline{C}H_2—CH_3$), 26.2 ($—O—CH_2—\underline{C}H_2—$), 28.8–29.8 (7 inner alkyl carbons), 31.9 ($—\underline{C}H_2—CH_2—CH_3$), 66.7 ($—O—CH_2—$, $^1J_{C—H}$ = 147 Hz), 124.5 (C—H arom., $^1J_{C—H}$ = 171 Hz), 134.6, 137.4 (arom.), 150.2 (N—C=N), 167.6 ppm (—CCO—).

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