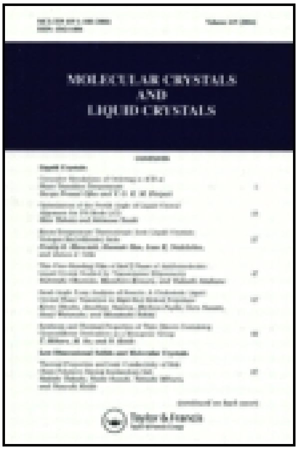

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Synthesis and Liquid-crystalline Behaviour of Tetrakis- and Octakis(13, 17-dioxa nonacosane-15-sulfanyl)Phthalocyanines

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Synthesis and Liquid-crystalline Behaviour of Tetrakis- and Octakis(13,17-dioxa nonacosane-15-sulfanyl)Phthalocyanines*

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Tetra- and octa(13, 17-dioxa nonacosane-15-sulfanyl) substituted metal free- and Ni(II) phthalocyanines have been synthesized from the corresponding phthalonitrile derivatives in the presence the anhydrous metal salt($NiCl_2$) or a strong organic base. The new compounds have been characterised by elemental analyses, IR, NMR and electronic spectroscopy and mass spectra. The mesogenic 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 tetra-substituted compounds(**5a, 5b**) form a hexagonal ordered columnar mesophases(D_{ho}), whereas octa-substituted compounds(**7a, 7b**) lead to centered rectangular disordered columnar mesophases(D_{rd}).

Keywords: phthalocyanine; liquid crystal; metallo mesogen

INTRODUCTION

Phthalocyanines exhibit a number of unique properties that make them of great interest in different scientific and technological areas.[1] There has been renewed interest in the use of phthalocyanines in variety of high-technology fields, includ-

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* Dedicated to Professor Dr. Özer Bekaroğlu on occation of his 65th birthday (May 3, 1998) with our best wishes

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ing use in semiconductor devices, photovoltaics and solar cells, electrophotography, molecular electronics, Langmuir-Blodgett films, electrochromism in display devices, gas sensor, liquid crystals and nonlinear optics and as photosensitizers and electrocatalytic agents.[2] A common requirement in all these applications is enhanced solubility of the phthalocyanine core which is known for its insolubility in most common solvents in case of unsubstituted derivatives. However, in the past few years the introduction of long chain lipophilic substituents on the periphery of the phthalocyanine ring has drastically improved their solubility in nonpolar solvent[1] and in some cases have provided these compound with thermotropic behaviour.[3,4]

The size of the substituent is not the only criterion for the solubility of the substituted phthalocyanines; the symmetry caused by the substituents in periphery is also important. Generally, tetrasubstituted phthalocyanines are more soluble than symmetrically octasubstituted ones (where all the eight substituents are the same), due to the formation of four isomers in the synthesis of tetrasubstituted phthalocyanines.[5]

The recent exploration of phthalocyanines in material science[2a,6,7] e.g. in non-linear optics[8], as liquid crystals[9], in optical data storage[10], as gas sensor[11], demands good solubility of these species LB-film of both tetra- and octasubstituted phthalocyanines have been studied[12–14].

Octaalkyl-[15], octaalkoxy-[16], octaalkoxymethyl-[17], or even "crowned"-phthalocyanines[18] give rise to discotic liquid crystals[4]. Similar behaviour is demonstrated by derivatives with eight alkyl or alkoxymethyl[19] substitution at the non peripheral(1, 4, 8, 11, 15, 18, 22, 25) sites. In addition, a number of unsymmetrically substituted phthalocyanines have been shown to form termotropic liquid crystals.[20] Discotic mesogens are constituted of a central rigid core surround by flexible alkyl chains; such structurally constituted mesogens lead to columnar mesophases where the rigid cores pile up to form columns which are usually arranged along a two-dimensional hexagonal array.[4,21] Discotic mesomorphism makes this kind of compound potentially interesting as one-dimensional conductors[16e,22] in which the conducting chains are formed by the spine of columnar structure, which consist of a central conjugated system surrounded by an insulating region of hydrocarbon chains.

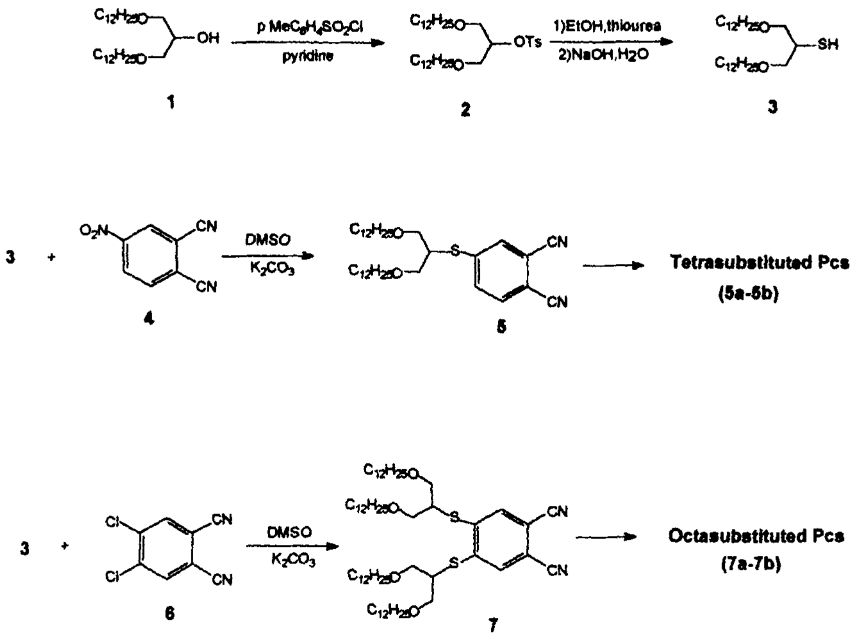
Due to the efficient synthetic methodology developed during the last two decades for symmetrical and unsymmetrical phthalocyanines, novel synthetic modifications on the phthalocyanine core have been accomplished, as described in recent reports of unsymetrically substituted derivatives[22] and symmetrically substituted ones with "active" peripheral substituents: among then crown ethers[23], tetraaza-[24] and tetrathiamacrocycles[25] capable of binding to alkali, transition metal and macrocycle-bridged dimers with alkylthio substituted derivatives.[26]

Phthalocyanines showing mesogenic properties which contain sulfur donors are rather few in number.[27] Thioether groups on the benzene rings of phthalocyanine were also proven to be effective, alkylthio-substituted derivatives to shift the Q-band absorption of the phthalocyanine to a lower-energy region.[28] In the present paper, we describe the synthesis of new sterically hindered tetra- and octa(13,17-dioxa nonacosane-15-sulfanyl)-substituted phthalocyanines. The influence of the presence of the heteroatoms in the side chains on the mesomorphic properties has been determined.

RESULTS AND DISCUSSION

Generally, the substituted phthalocyanines are prepared by cyclotetramerization of substituted 1,2-dicyanobenzenes or 1,3-diimino-1H-isoindoles.[1] If monosubstituted 1,2-dicyano benzenes are employed, tetrasubstituted phthalocyanines with the disadvantage of a mixture of isomers are obtained.[1] 4-Nitro-1,2-dicyanobenzene(**4**) and 1,2-dichloro-4,5-dicyano benzene(**6**) were used recently to prepare 4-monosubstituted and 1,2-disubstituted phthalonitrile derivatives respectively, through base catalysed nucleophilic aromatic displacement[28,29]. The same route was applied to prepare 4-(13,17-dioxa nonacosane-15-sulfanyl)-1,2-dicyano benzene(**4**) from 15-thiol-13,17-dioxa nonacosane(**3**) and 4-nitro-1,2-dicyanobenzene(**4**) (Scheme 1). Similarly, the reaction of compound **3** under the same conditions with 1,2-dichloro-4,5-dicyano benzene(**6**) resulted in the expected compound **7**. The reactions were carried out in dimethyl sulfoxide(DMSO) at 50°C and gave high yields (≈90%). Starting from 15-hydroxy-13,17-dioxa nonacosane(**1**), the synthetic route is outlined in scheme 1. Attempts to prepare the thiol compound from compound **1** according to the common methods were unsuccessful. The compound **1** was converted into thiol compound(**3**) through the tosyl derivative **2** in two steps according to the reported procedure.[30] Tosylation of the hydroxy group was carried out in dry pyridine at 15°C with p-toluenesulfonyl chloride. Conversion of the tosyl compound **2** into the thiol derivative **3** was accomplished by boiling dry ethanol in the presence of thiourea for 48 h. In these reactions, the long reaction times were necessary for good yields.

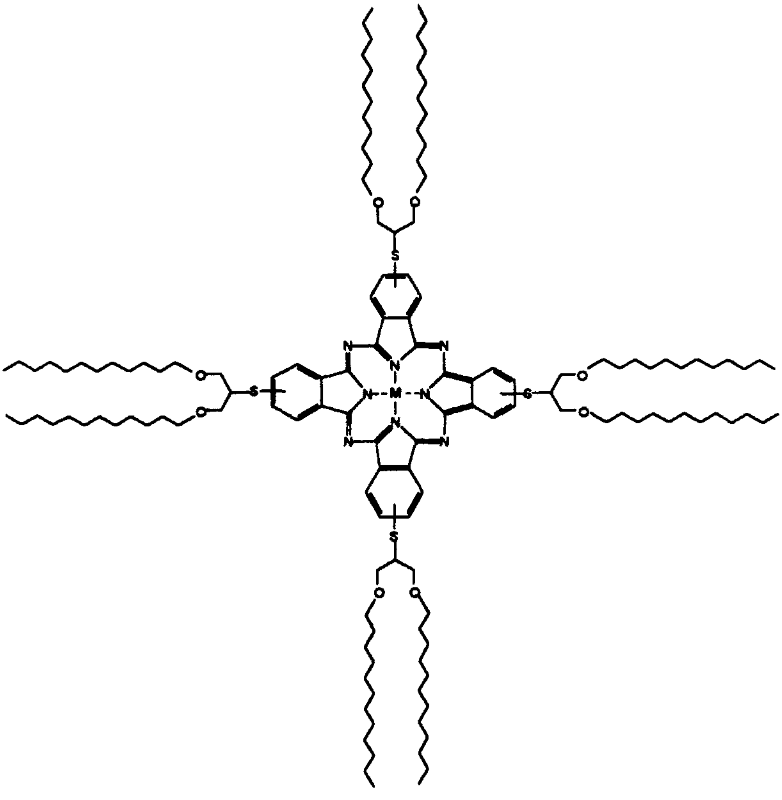
The usual synthetic routes were applied to obtain the tetrasubstituted metal-free phthalocyanine(**5a**) and nickel(II) phthalocyanine(**5b**). Among the many possibilities, preparation of metal-free and nickel(II) phthalocyanines have been especially preferred in order to be able to characterize the structure of these diamagnetic compounds by NMR spectroscopy. The tetrasubstituted metal-free derivative **5a** was synthesized directly by reaction of phthalonitrile **5** in hydro-



SCHEME 1 Chemical pathway used to synthesize the tetra-(**5a**, **5b**) and octasubstituted (**7a**, **7b**) phthalocyanine derivatives : Ts= Tosyl(*p*-$MeC_6H_4SO_2$)

quinone as a uniphase fused melt; here the two electrons required in addition to the 16π electrons of 8 nitriles to yield the 18π electron system of the phthalocyanine core was supplied by the oxidation of hydroquinone.[29a] In the case of nickel(II) phthalocyanine **5b**, cyclotetramerization was carried out in quinoline in presence of a nickel(II) salt (Figure 1).

The preparation of phthalocyanine derivatives from the aromatic nitriles occur under different reaction conditions.[1] A convenient high-yield synthesis requires for the further considerations. For various substituted dinitriles, the reaction in the presence of strong not nucleophilic bases 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) or 1,5-diazabicyclo[4.3.0] non-5-ene(DBN) either in 1-pentanol or in bulk with yields of phthalocyanines up to 90 % is most efficient in comparison to other methods.[31] In addition, these reactions are easy to perform, work under relatively mild conditions and yield pure phthalocyanines. Therefore, octasubstituted metal-free phthalocyanine derivative **7a** was obtained directly from the reaction of dicyano compound **7** in 1-pentanol at reflux temperature in the presence of a strong organic base such as DBU (Figure 2). Also, cyclotetramerization of dinitril derivative **7** in the presence of anhydrous $NiCl_2$



	M
5a	2H
5b	Ni

FIGURE 1 Chemical structure of tetrasubstituted phthalocyanine derivatives

and DBU in 1-pentanol gave the octasubstituted nickel(II) phthalocyanine **7b**. Column chromatography with silica gel was employed to obtain the pure products from the reaction mixtures. The intense green waxy products are very soluble in a number of solvents, except for EtOH, acetone, DMSO, DMF and H_2O. They could thus be thoroughly investigated by ^1H and ^{13}C NMR and UV-VIS spectroscopy in solution. In addition to elemental analysis results (Table I), mass spectra of the new organic intermediates compounds and phthalocyanines obtained by the EI, CI, FAB or FD techniques show relatively intense molecular ion peaks. Another common point in all of these mass spectra is the clear appearance of the fragmentation ion peaks corresponding to the stepwise loss of alkoxy($OC_{12}H_{25}$)groups.

TABLE I Analytical[a] data for the starting materials and phthalocyanines

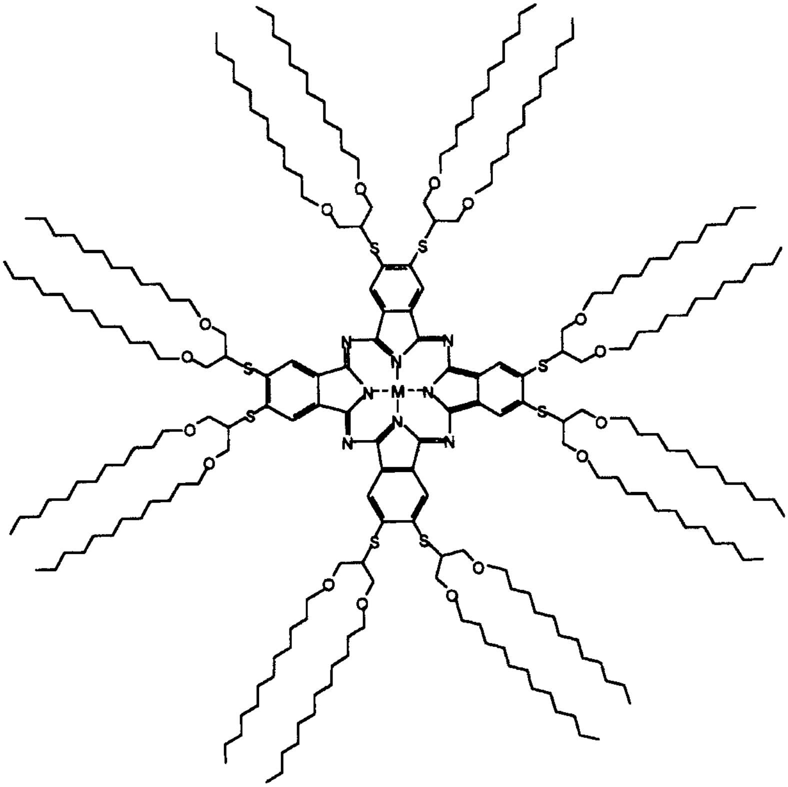
Compound	*Formula*	*Analysis(%)*			
		C	*H*	*N*	*M*
2	$C_{34}H_{63}O_5S$	69.96(69.93)	10.51(10.88)	–	–
3	$C_{27}H_{56}O_2S$	72.16(72.91)	12.56(12.69)	–	–
5	$C_{35}H_{58}N_2O_2S$	73.37(73.76)	10.87(10.08)	4.42(4.92)	–
5a	$C_{140}H_{234}N_8O_8S_4$	73.11(73.57)	10.67(10.32)	4.68(4.90)	–
5b	$C_{140}H_{232}N_8NiO_8S_4$	70.95(71.79)	10.51(9.98)	4.21(4.78)	2.34(2.51)
7	$C_{62}H_{112}N_2O_4S_2$	73.30(73.46)	11.72(11.14)	2.71(2.76)	–
7a	$C_{248}H_{450}N_8O_{16}S_8$	73.11(73.75)	10.68(11.18)	2.28(2.76)	–
7b	$C_{248}H_{448}N_8NiO_{16}S_8$	72.50(72.41)	9.98(10.98)	2.68(2.72)	1.35(1.43)

[a] calculated values are given in parenthesis

In the IR spectra characteristic vibrations corresponding to ether groups(C-O-C) at 1120–1100 cm^{-1} and CH_2 stretching at ca. 2950–2850 cm^{-1} are common for the starting compounds(**1–3**) as well as for the phthalocyanines (**5a, 5b, 7a, 7b**). Conversion of the tosyl compound **2** into the thiol derivative **3** was confirmed by the disappearance of the sharp SO_2 stretching vibrations at 1370 and ca 1180 cm^{-1} and the appearance of the very weak SH vibration at 2580 cm^{-1}. The sharp peak for the C≡N vibrations 2220 cm^{-1} in **5** and **7** disappears after phthalocyanine formation. The NH groups in the inner core of the metal-free phthalocyanines **5a** and **7a** give a weak absorption at 3300 cm^{-1}.

NMR investigation of the compounds **2**, **3**, **5**, and **7** have provided the characteristic chemical shifts for the structures as expected. In the ^1H NMR analysis of all these compounds in deuteriated chloroform, methyl protons appear as triplet at ca 0.88 ppm, the aliphatic protons as multiplets at ca 1.26 ppm and aliphatic CH protons as a multiplet between 3.10 and 4.65 ppm according to the functional groups. When the ^1H NMR spectra of the tosyl(**2**) and thiol(**3**) compounds were examined, conversion of the tosyl derivative **2** into the thiol compound **3** was confirmed by the disappearance of the chemical shift of the aromatic protons as two pairs of doublet at 7.32 and 7.84 ppm and the appearance of characteristic of the deuterium-exchangeable SH protons as a doublet at 1.84 ppm. The ^1H NMR spectrum of dinitril compound **3** showed the singlet-doublet-doublet signals at 7.77, 7.68 and 7.63 ppm for the aromatic hydrogens. On the other hand, in the ^1H NMR spectrum of the other dinitril compound **5** is observed only one singlet signal at 7.76 ppm for the aromatic protons.

The ^{13}C NMR spectra of compound **3**, **5** and **7** show eight different signals for the aliphatic carbon atoms between ca. 12 and ca. 72 ppm. The aromatic carbon



	M
7a	2H
7b	Ni

FIGURE 2 Chemical structure of octasubstituted phthalocyanine derivatives

atoms of the tosyl group for compound **2** were observed as four different signals between 124.82 and 145.30 ppm. The ^{13}C NMR spectra of **5** and **7** were quite similar, but the spectra indicated the presence of the nitrile carbon atoms at 115.15 and 15.52 ppm as two signals in **5** and at 115.44 ppm, as only one signal in **7**, as expected. The mass spectra of **5** and **7** exhibit the molecular ion peaks at 570.4 and 1012.9 by the EI and FAB techniques, respectively.

^{1}H NMR spectra of the tetra- and octasubstituted phthalocyanines(**5a, 5b, 7a, 7b**) clearly indicate that the bulky substituents have prevented aggregation, so that sharp peaks can be observed even at the high concentrations used in these techniques.[32] Metal-free phthalocyanines **5a** and **7a** show characteristic chemical shift at 7.97–8.13 and 8.68–9.03 ppm as two different multiplets, at 9.54 ppm as a singlet respectively, corresponding to the deshielded aromatic protons. The strongly shielded cavity protons occur at –3.30 and –3.50 ppm for **5a** and **7a** respectively and the signals disappear by deuterium exchange.

The high solubility of the phthalocyanines has enabled us to obtain ^{13}C NMR spectra. The chemical shift values in these spectra closely follow the empirically calculated ones, and D_{4h} symmetry of the metallophthalocyanines and D_{2h} symmetry of the metal-free phthalocyanines prevails.[33] The attached proton test(APT) indicates the presence of three monoprotonated carbons in the aromatic region; these are at 121.99, 123.52 and 131.25 ppm for **5b** corresponding to one protonated carbon in the phthalocyanine core. The ^{13}C NMR spectra of the octasubstituted phthalocyanines **7a** and **7b** are in excellent agreement with the proposed structures. The carbon atom of the N=C-N group in the phthalocyanine core for octasubstituted phthalocyanines **7a** and **7b** could be assigned by comparison of the chemical shift measured with the data reported in literature.[17c,34] In the ^{13}C NMR spectra of **7a** and **7b** show signals for four aromatic carbon atoms between ca.124 and ca. 155 ppm and eight aliphatic carbon atoms between ca. 14 and ca.71 ppm, as expected.

A close investigation of the mass spectra of the tetra- and octasubstituted phthalocyanines(**5a, 5b**, **7a, 7b**) confirmed the proposed structures. The mass spectra of **5a** and **7a** were obtained by FAB technique using a *m*-nitro benzyl alcohol(MNBA) as matrix; the region of the molecular ions and of the other bigger fragment ions is shown in Figure 3 and 4, respectively, together with the corresponding leaving groups. Field desorption(FD) mass spectrometry permitted us to characterize **7b** unambiguously. In addition to the $[M]^+$ peak at 4113, fragment ions corresponding to the loss of $OC_{12}H_{25}$ ($[M\text{-}185]^+$), $CH(CH_2OC_{12}H_{25})_2$ ($[M\text{-}411]^+$), $5(CH(CH_2OC_{12}H_{25})_2)$ ($[M\text{-}2058]^+$) were easily identified.

Tetra- and octa(13,17-dioxa nonacosane-15-sulfanyl) substituted phthalocyanines **(5a, 5b, 7a, 7b)** show intense Q absorption bands above 700 nm (Table II). The metal-free phthalocyanines **5a** and **7a** give doublet Q band as a result of the D_{2h} symmetry. The nickel(II) phthalocyanines **5b** and **7b** exhibit intense Q bands around 700 nm with a relatively sharp absorption peak and almost no shoulder on the higher energy side, which would correspond to aggregated species. For all the phthalocyanines the effect of thia-substitution was a shift of these intense Q-bands to higher wavelenghts when compared with unsubstituted, alkyl- or alkoxy-substituted derivatives. The relative intensity of these peaks are concentration dependent at higher concentrations, but show no appreciable change in the range 10^{-5}-10^{-6} mol l^{-1} in different solvents(chloroform, dichloromethane, CCl_4, benzene). Moreover aggregation is not detectable in metha-

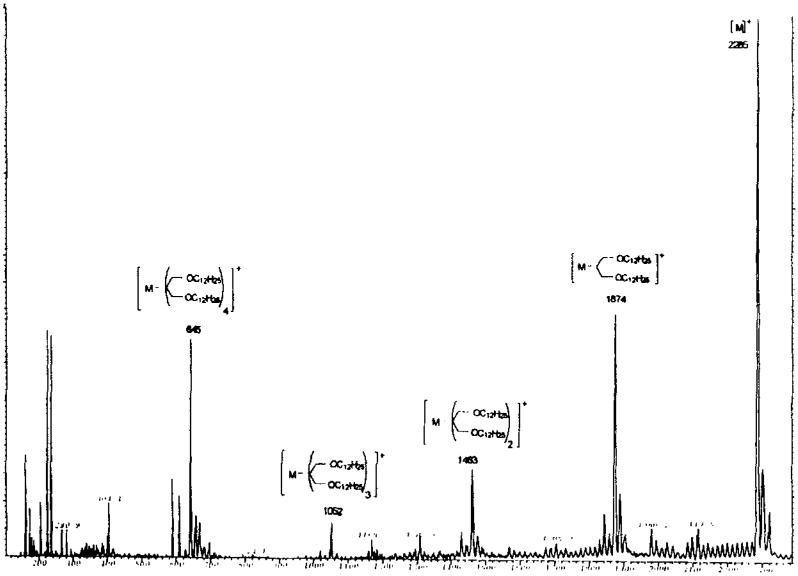


FIGURE 3 Mass spectrum of tetrasubstituted phthalocyanine (**5a**)

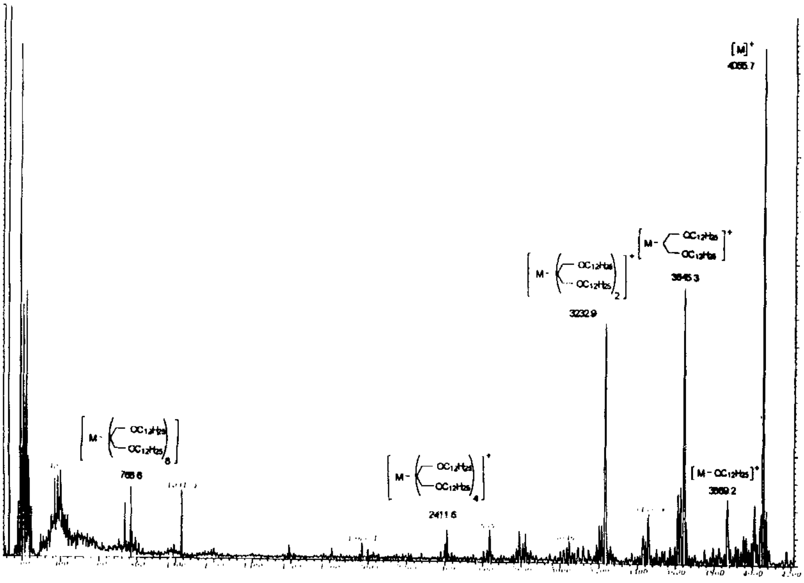


FIGURE 4 Mass spectrum of octasubstituted phthalocyanine (**7a**)

nol/chloroform(1:1) mixture. Consequently, tetra- and octa(13,17-dioxa nonacosane-15-sulfanyl) substituted phthalocyanines can be considered as one of the few examples of the phthalocyanines that are extremely soluble in apolar solvents but which do not aggregate in solution.

TABLE II Electronic spectra of the phthalocyanines in chloroform

Compound	λ_{max}*(nm) (*$10^{-4}\varepsilon/l\ mol^{-1}cm^{-1}$*)*
5a	710(16.30), 680(13.00), 660(4.20)^a, 620(3.40), 420(3.08)^b, 343 (7.60)
5b	702(13.80), 674(2.90)^a, 630(2.60), 426(1.80)^b, 321(6.12)
7a	733(18.00), 700(15.50), 660(4.58)^a, 632(3.50), 420(3.50)^b, 358(7.00)
7b	703(20.40), 675(4.20)^a, 628(3.70), 435(2.80)^b, 320(8.90)

CHARACTERIZATION OF THE MESOPHASES

Thermotropic Phase-Bahaviour

The DSC-measurements (DSC-7, Perkin Elmer) of all four compounds show a significant sharp peak in the vicinity of 10 degrees (second heating, heating rate 5 °C/min) which relates to the melting transition. In addition the DSC diagram of the tetra-substituted compounds **5a** and **5b** depicts a weak peak at about 135 °C (**5a**) and 171 °C (**5b**) in the second heating cycle that belongs to the clearing point (Table III). These investigations indicate that the compounds exhibit a thermotropic liquid crystalline phase between the melting and clearing point.[15b,17a,35,36] No such additional peaks are observed for the octa-substituted compounds **7a** and **7b** which exclude further phase transitions. Only the melting to the isotropic liquid is present (Table III).

TABLE III Phase transition temperature from DSC-measurements, melting- and clearing-points with a heating rate of 5 °C/min

Compound	*Phase transition temperature (°C)*					
	1. Heating		*Cooling*		*2. Heating*	
5a	13	141	132	4	11	135
5b	9	171	171	5	11	171
7a	37			0	2	
7b	38			2	10	

Optical Microscopy of Thermotropic Mesophases

The textures received for **5a** and **5b** are similar to those described in literature.[15a,17a,20b,37] Excellent textures of samples, preferably fan- or flower-like textures (Figure 5 and 7), of the mesophases were obtained by slowly cooling from the isotropic melt. Figure 6 shows an example of a crystallisation in microscope upon further cooling producing a uniform fine texture. Under different conditions, if compounds **7a** and **7b** are quickly cooled with a cooling rate of about 5 °C/min from the isotropic phase, both compounds form a spherolitic-like-liquid-crystalline texture if the samples are kept at room temperature for a long time (about one day) (Figure 8).

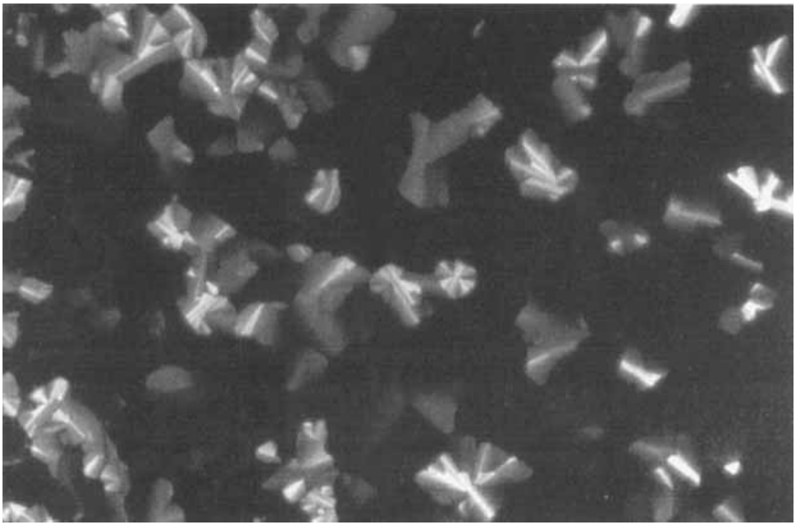


FIGURE 5 Fan- or flower-like texture at 128 °C of compound **5a** (See Color Plate XI at the back of this issue)

X-Ray Diffraction

X-ray investigations of the thermotropic phases were carried out with a flat film and a Debye-Scherrer camera (Philips) at room temperature with samples filled in 0.7 mm capillaries. The samples of compound **7a** and **7b** are cooled slowly from isotropic liquid and kept in the refrigerator at about 8 °C for some hours before they were used. All samples are in the liquid crystalline state as discussed above.

The low angle of the X-ray diffraction diagrams of the compounds **5a** and **5b** show up to seven sharp Bragg reflections with d-spacing ratio 1: $1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$

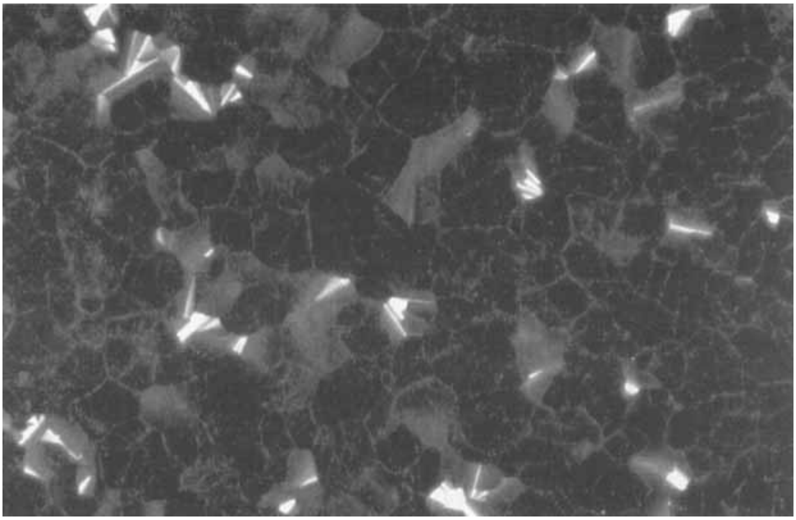


FIGURE 6 Crystallisation at 5 °C of compound **5a** (See Color Plate XII at the back of this issue)

(Table IV).[15b,17a,35,37] This result suggests a two-dimensional hexagonal lattice with disk-like molecules stacked in columns in a hexagonal arrangement. The X-ray data may be indexed with a two-dimensional hexagonal unit cell and the cell parameters (Table VI) determined with the data of Table IV.

The unit cell dimension represents the distance between the axes of two neighbouring cylindrical piles of molecules in such an arrangement and can be estimated as follows. The diameter of the aromatic core is about 15 Å. the length of the side-chains in the extended all-trans conformation is about 20 Å. The X-ray results agree with these estimated geometrical parameters of the piles of molecules, if the structure consists of close packed cores with interlocked side-chains filling the space between them. The intercolumnar distance then corresponds to the expansion of a core and one all-trans-side chain as obtained from X-ray investigations.

Compared with the two tera-substituted sulphur-linked phthalocyanine-centered poly(oxyethylene)'s[38], in **5a** and **5b**, the distance between the cylindrically packed phthalocyanine cores is somewhat larger despite taken into account the different length of the side-chains. All four compounds contain four side-chains connected to the linking atom at the core. In contrast to Ref.[38] the side-chains of **5a** and **5b** are swallow-tailed and comparable with double side-groups which require more space.

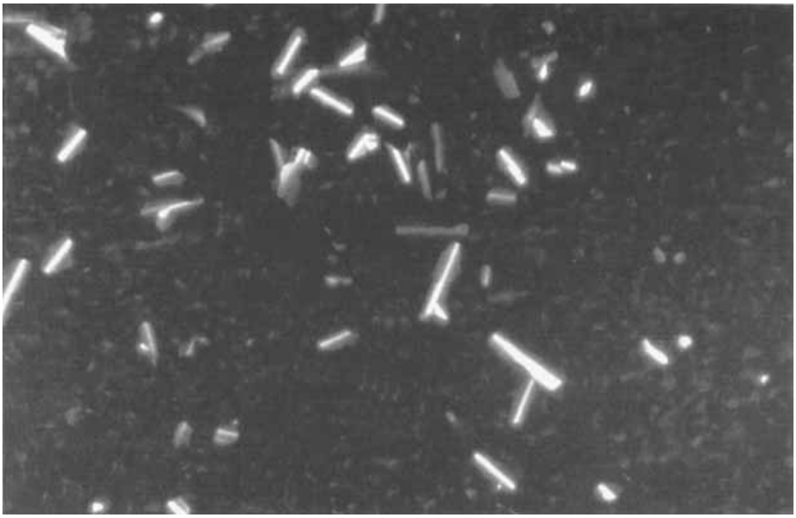


FIGURE 7 Fan-like texture at 165 °C of compound **5b** (See Color Plate XIII at the back of this issue)

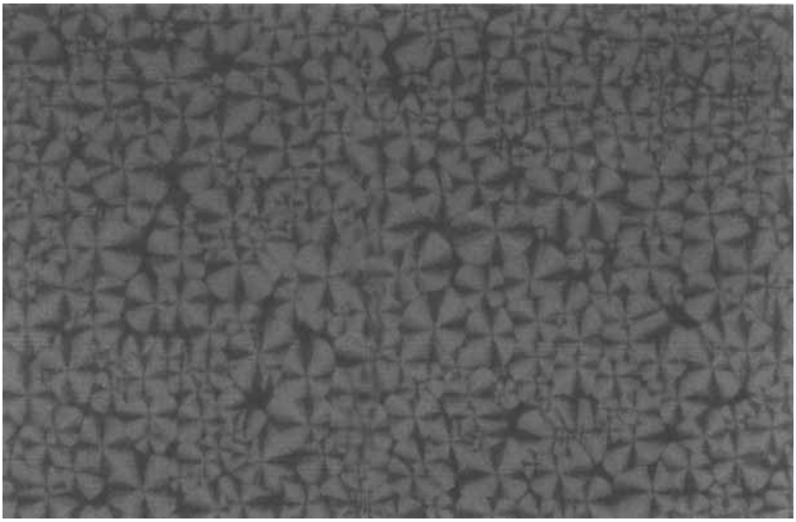


FIGURE 8 Spherolitic-like texture at room temperature of compound **7b** (annealing one day from isotropic liquid) (See Color Plate XIV at the back of this issue)

The distance between adjacent columns is independent on central metal or hydrogens of the phthalocyanine molecules. There exists no difference in spacing between the nickel-complexed compound **5b** and metal-free **5a** with the same number of side-chains.

TABLE IV X-ray powder diffraction data of compound **5a** and **5b**

Compound	*5a*	*5b*	*ratio*	*hkl*
	d-spacing[Å]			
	31.9 s[a]	32.3 s	1	100
	18.5m	18.5m	$\sqrt{3}$	110
	16.1 w	16.0 m	$\sqrt{4}$	200
	11.9 w	12.1 m	$\sqrt{7}$	210
		10.6 w	$\sqrt{9}$	300
	9.3 wd	9.2 w	$\sqrt{12}$	220
	8.9 w	8.9 w	$\sqrt{13}$	310
	4.5 md	4.6 md		
	3.3 m	3.3 m		

a. s: sharp; m: middle; w: weak; d: diffuse

In the wide angle regions the compounds show a diffuse halo at about 4.5 Å which is compatible with the disorder of the paraffinic tails in the side-chain. An additional reflection at about 3.3 Å is observed which may be assigned to the packing of macrocyclic subunits in the columns. The sharpness of this reflection of compounds **5a** and **5b** suggests good order within the columns and is consistent with the strong intramolecular periodicity associated with the discotic hexagonal ordered D_{ho}-mesophase.

The octa-substituted compounds **7a** and **7b** also exhibit up to seven Bragg reflections, which cannot be described by a hexagonal lattice (Table V). The X-ray data may indexed with a two-dimensional rectangular lattice like other compounds reported in the literature.[39] With the data of Table V the two-dimensional unit cell with the a- and b-dimensions shown in Table VI is obtained. The arrangement of the neighbouring piles of molecules is pseudohexagonal. The distance between the axes of these piles corresponds to the b-dimension and is independent on the filling of the phthalocyanine centre but somewhat larger than the distance in **5a** and **5b**. This is not surprising since eight swallow-tailed side-chains require more space between the phthalocyanine rings than four.

In the wide angle regions the compounds show two diffuse halos at about 5.0 and 4.3 Å (**7a**) and 4.8 and 4.2 Å (**7b**), respectively. The diffuse appearance of smaller reflection suggests that the mesophase may belong to the D_{rd}-type with a discotic rectangular disordered packing of columns. In comparison with the tetra-substituted compounds **5a** and **5b**, the extension of the two-dimensional lattice is not the only consequence of the large number of side-chains in **7a** and **7b**. It has been noticed that the stacking distance along the axis of the columns also increases.

TABLE V X-ray powder diffraction data of compound **7a** and **7b**

Compound 7a		*Compound 7b*	
d-spacing [Å]	*hkl*	*d-spacing [Å]*	*hkl*
35.7 s[a]	110	35.7 s	110
28.6 m	200	28.1 s	200
17.6 m	220	17.8 w	220
14.3 wd	400	14.3 w	320
11.6 wd	330	12.0 w	420
9.3 wd	600	8.9 w	440
5.0 md		4.8 md	
4.3 md		4.2 md	

a. s: sharp; m: middle; w: weak; d: diffuse

TABLE VI Two-dimensional hexagonal (**5a**, **5b**) and rectangular (**7a**, **7b**) cell dimensions

Compound	*a[Å]*	*b[Å]*
5a	37.0	
5b	37.0	
7a	57.2	45.7
7b	56.2	46.2

EXPERIMENTAL PART

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Multiplicities are given as s(singlet), d(doublet), t(triplet) and m(multiplet). Infrared spectra in sodium chloride cell or KBr pellets were recorded on a Perkin- Elmer 983 spectrophotometer. Optical spectra in UV-visible region were recorded with a Varian DMS spectrophotometer using 1 cm pathlength cuvettes at room temperature. Elemental analysis were carried out by the Instrumental Analysis Laboratory of TÜBİTAK, Marmara Research Center. Mass spectra were recorded on a VG Zab-Spec spectrometer. Transition temperatures were determined at scan rates of 10°C min^{-1}using a Perkin Elmer 7 System differential scanning calorimeter calibrated with indium. Optical textures were observed with the polarising microscope Olympus BH-2 equipped with the hot stage and temperature-controller Linkam PR 600, and pictures were taken with the camera Olympus OM-2n of thin samples.

4-Nitrophthalonitrile(**4**)[40], 1,2-dichloro-4,5-dicyano benzene(**6**)[29b] and 15-hydroxy-13,17-dioxa nonacosane(**1**)[17c] were prepared according to literature procedures. All other reagents and solvents were reagent-grade quality, were obtained from commercial suppliers and were dried as described in Perrin and Armarego[41] before use. Optical characterisation was performed using a polarisation microscope with a Mettler hot stage.

15-Tosyloxy-13, 17-Dioxa Nonacosane (2)

A solution of 15- hydroxy- 13,17-dioxa nonacosane(**1**) (7 g, 16.3 mmol) in dry pyridine(18 ml) was cooled to 5°C and a solution of p-toluenesulfonyl chloride (3.42 g, 17.9 mmol) in dry pyridine(7 ml) was added with stirring under argon at a rate so that the temperature of the reaction mixture never exceeded 15°C. After stirring for 48 h at room temperature, the reaction mixture was poured into crushed ice, and the resulting aqueous solution was extracted with CH_2Cl_2. The organic layer was washed at 0°C with 6 N HCl solution,with H_2O, dried with Na_2SO_4, and evaporated to give a viscous oil which was chromatographed on silica gel (CH_2Cl_2: n-hexane/ 1:1). This compound is a colorless viscous oil. Yield: 8 g (84%).

IR v_{max}/cm^{-1}(KBr cell)= 2950–2850 (CH_2), 1600, 1460, 1370, 1190–1180 (SO_2), 1120–1100 (C-O-C), 940, 820, 780, 670, 550.

^1H NMR ($CDCl_3$): δ ppm= 0.88 (t, 6H, CH_3), 1.25 (m, 36H, CH_2), 1.43 (m, 4H, OC-CH_2), 2.43 (s, 3H, Ar-CH_3), 3.33 (t, 4H, OCH_2), 3.56 (d, 4H, OCH_2), 4.65 (m, 1H, CH), 7.32 (d, 2H, ArH), 7.84 (d, 2H, ArH).

^{13}C NMR (APT) ($CDCl_3$): δ ppm= 14.10 (CH_3), 21.61 (CH_2), 22.69 (CH_2), 26.01 (CH_2), 29.65–29.38 (CH_2), 31.93 (CH_2), 69.29 (OCH_2), 71.74 ($O\underline{C}H_2CH$-OTos), 79.87 (CH), 124.82 (ArC-CH_3), 128.04 (Ar CH), 129.52 (Ar CH), 145.30 (ArC-SO_2)

MS (electron impact) (EI) m/z (%)= 583.7 (6) $[M]^+$, 416.4 (15) $[M\text{-}C_{12}H_{25}]^+$, 410.5 (30) $[M\text{-OTos}]^+$, 357.3 (5), 243.3 (36) $[M\text{-}2(C_{12}H_{25})]^+$, 226.3 (78), 197.2 (91), 173.1 (54), 155.1 (98), 140.2 (14), 125.1 (27), 111.1 (47), 99.1 (53), 83.1 (72), 71.1 (96).

15- Thiol-13,17- Dioxa Nonacosane (3)

15-Tosyloxy-13,17-dioxa nonacosane (**2**) (8.97 g, 15.37 mmol) was dissolved in anhydrous ethanol (55 ml), and thiourea (1.5 g, 19.70 mmol) was added and then, the mixture was refluxed for 48 h under stirring, after which was time the solvent was removed by distillation until the total volume was 25 ml. To the resulting solution, a solution of sodium hydroxide (1.24 g, 31 mmol) in 28 ml H_2O (degassed with argon) was added under argon atmosphere. This mixture was refluxed and stirred for an additional 6 h, under argon. The two-phase system which resulted was cooled and separated, and the upper aqueous phase was acidified with dilute HCl and extracted with diethylether(3 × 50 ml). The ether layer was combined with the oily organic layer from the reaction mixture, and this solution was dried over Na_2SO_4. The dried ether solution was filtered and evaporated to remain a thick liquid which was purified by column chromatography on silica gel using n-hexane: CH_2Cl_2/ 5:1 as eluent. Yield: 4.5 g (66%).

IR ν_{max}/cm^{-1}(KBr cell)= 2950–2850 (CH_2), 2580 (SH),1560, 1380, 1120–1100 (C-O-C), 720.

^1H NMR ($CDCl_3$): δ ppm= 0.88 (t, 6H, CH_3), 1.27 (m, 36H, CH_2), 1.56 (m, 4H, OC-CH_2), 1.84 (d 1H, SH), 3.10 (m, 1H, CH), 3.44 (t, 4H, OCH_2), 3.54 (d, 4H, OCH_2).

^{13}C NMR (APT) ($CDCl_3$) δ ppm= 14.14 (CH_3), 22.73 (CH_2), 26.20 (CH_2), 29.41–29.68 (CH_2), 31.97 (CH_2), 39.60 (CH), 71.38 (OCH_2), 72.38 ($O\underline{C}H_2$-CHS).

MS (EI), m/z (%): 447.4 (3) $[M]^{+3}$, 410.40 (16) $[M\text{-}SH]^+$, 276.2 (12) $[M\text{-}C_{12}H_{25}]^+$, 245.2 (15), 225.2 (97), 199.2 (94), 183.2 (20), 169.2 (57), 140.1 (13), 127.1 (27), 113.1 (57), 91.0 (82), 74.0 (98) $[M\text{-}2(OC_{12}H_{25})]^+$.

4-(13,17-Dioxa Nonacosane-15-Sulfanyl) Phthalonitrile (5)

4- Nitrophthalonitrile (**4**) (0.670 g, 3.9 mmol) was dissolved in anhydrous dimethyl sulfoxide (8 ml) under argon and 15-thiol-13,17-dioxa nonacosane (**3**) (1.792 g, 4.03 mmol) was added. After stirring for 15 min at 50°C, dry and finely powdered potassium carbonate (0.835 g, 6.05 mmol) was added portion wise over 0.5 h with efficient stirring. The reaction mixture was stirred under argon at 50°C for 48 h. After cooling, the mixture was poured into crushed ice (60 g). The dinitrile compound **5** was extracted with CH_2Cl_2 (4 × 25 ml). The organic layer was dried with Na_2SO_4 and evaporated to give an oily product. The pure product was obtained by recrystallization from methanol/ petroleum ether (40/60) (1:1). The product was soluble in CH_2Cl_2, $CHCl_3$, CCl_4, diethylether, and n-hexane, insoluble in ethanol, methanol, acetone, DMF, DMSO and H_2O. Yield: 2.1 g (95%). mp.38°C.

IR ν_{max}/cm^{-1}(KBr cell)= 2980–2850 (CH_2), 2220 (C≡N), 1580, 1470, 1380, 1120–1100 (C-O-C), 830, 720, 525.

^{1}H NMR ($CDCl_3$): δ ppm= 0.88 (t, 6H, CH_3), 1.26 (m, 36H, CH_2), 1.55 (m, 4H, OC-CH_2), 3.45 (t, 4H, OCH_2), 3.62 (d, 4H, OCH_2), 3.70 (m, 1H, CH), 7.63 (d, 1H, ArH), 7.68 (d, 1H, ArH), 7.77 (s, 1H, ArH).

^{13}C NMR (APT) ($CDCl_3$): δ ppm= 14.13 (CH_3), 22.71 (CH_2), 26.11 (CH_2), 29.11–29.66 (CH_2), 31.94 (CH_2), 47.73 (CH), 70.56 (OCH_2), 71.61 ($O\underline{C}H_2$-CHS), 113.33 (ArC), 113.45 (ArC), 115.15 (C≡N), 115.52 (C≡N), 131.48 (Ar CH), 131.83 (Ar CH), 133.04 (Ar CH), 146.66 (Ar CS).

MS (EI), m/z (%): 570.4 (33) $[M]^+$, 402.2 (11) $[M\text{-}C_{12}H_{25}]^+$, 383.3 (6) $[M\text{-}OC_{12}H_{25}]^+$, 339.1 (5) $[M\text{-}2(C_{12}H_{25})]^+$, 327.1 (5), 225.1 (97), 199.0 (68) $[M\text{-}2(OC_{12}H_{25})]^+$, 186.1 (78), 172.0 (69), 155.0 (66), 145.0 (26), 107.0 (45), 91.0 (85), 71.0 (88).

1,2-Di (13, 17-Dioxa Nonacosane-15-Sulfanyl) Phthalonitrile (7)

7 was prepared according to the same procedure as described for preparation **5** by starting with 1,2-dichloro-4,5-dicyano benzene (**6**) (0.475g, 2.42 mmol), 15-thiol-13,17-dioxa nonacosane (**3**) (2.151 g, 4.84 mmol) and potassium carbonate (1.2 g, 8.71 mmol). The resulting light yellow oily product was recrystallized from dichloromethane/ methanol mixture(2:1). This compound was soluble in CH_2Cl_2, $CHCl_3$, CCl_4, diethylether, and n-hexane, insoluble ethanol, methanol, acetone, DMF, DMSO and H_2O. Yield: 2.3 g (93%), mp. 30°C.

IR ν_{max}/cm^{-1} (KBr cell)= 2980–2850 (CH_2), 2220 (C≡N), 1570, 1460, 1370, 1270, 1220, 1120–1100 (C-O-C), 720, 530.

^{1}H NMR ($CDCl_3$): δ ppm= 0.88 (t, 12H, CH_3), 1.26 (m, 72H, CH_2), 1.56 (m, 8H, OC-CH_2), 3.44 (t, 8H, OCH_2), 3.65 (d, 8H, OCH_2), 3.69 (m, 2H, CH), 7.76 (s, 2H, ArH).

^{13}C NMR (APT) ($CDCl_3$): δ ppm= 14.01 (CH_3), 22.69 (CH_2), 26.12 (CH_2), 29.37–29.65 (CH_2), 31.92 (CH_2), 47.95 (CH), 70.49 (OCH_2), 71.77 ($O\underline{C}H_2$-CHS), 111.65 (CN-Ar$\underline{C}$), 115.44 (C≡N), 131.41 (Ar CH), 144.55 (Ar C-S).

MS (fast atom bombardment) (FAB), m/z (%): 1012.9 (7) $[M]^+$, 827.7 (15) $[M\text{-}OC_{12}H_{25}]^+$, 644.5 (5) $[M\text{-}2(OC_{12}H_{25})]^+$, 601.4 (15), 473.2 (5), 409.4 (14), 357.1 (10), 225.2 (98), 169.2 (20).

Tetrakis(13, 17-Dioxa Nonacosane-15-Sulfanyl) Phthalocyanine (5a)

A Schlenk tube was charged with 4-(13,17-dioxa nonacosane-15-sulfanyl) phthalonitrile (**5**) (0.285 g, 0.5 mmol) and hydroquinone (0.066 g, 0.6 mmol) (purified by sublimation) under argon and sealed.The reaction was stirred at

195–200°C for 20 h. After cooling to room temperature, it was treated with ethanol (5 ml) and the product filtered off and washed with the same solvent. The dark green waxy product was purified by column chromatography with silica gel (eluent:chloroform). The product was soluble in common organic solvents, except for ethanol, methanol, acetone, DMSO, DMF and H_2O. Yield: 0.065g (23%).

IR ν_{max}/cm^{-1}(KBr cell)= 3300 (NH), 2950–2850 (CH_2), 1600, 1470, 1380, 1310,1260, 1120–1100 (C-O-C), 1020, 900, 870, 820, 750.

^1H NMR ($CDCl_3$): δ ppm = -3.30 (br, NH), 0.81 (t, 24H, CH_3), 1.14 (m, 144H, CH_2), 1.71 (m, 16H, OC-CH_2), 3.64 (t, 16H, OCH_2), 4.03 (br, 20H, CH OCH_2), 7.97–8.13(m, 4H, ArH), 8.68–9.03 (m, 8H, ArH).

^{13}C NMR (APT) ($CDCl_3$): δ ppm= 14.03 (CH_3), 22.62 (CH_2), 26.29 (CH_2), 29.29–29.82 (CH_2), 31.85 (CH_2), 48.79 (CH), 70.51 (OCH_2), 71.74 ($O\underline{C}H_2$-CHS), 122.75 (Ar CH), 123.67 (Ar CH), 124.01 (Ar CH), 131.57 (Ar CH), 133.68 (Ar C), 136.35 (Ar C), 138.83 (Ar C), 148.55 (Ar C).

MS (FAB), m/z (%): 2285 (96) $[M]^+$, 1874 (47) $[M\text{-}CH(CH_2OC_{12}H_{25})_2]^+$, 1712 (38), 1526 (25), 1463 (17)$[M\text{-}2(CH(CH_2OC_{12}H_{25})_2)]^+$, 1052 (10) $[M\text{-}3(CH(CH_2OC_{12}\ H_{25})_2)]^+$, 891 (6), 645 (41) $[M\text{-}4(CH(CH_2OC_{12}H_{25})_2)]^+$, 593 (30), 480 (21).

Tetrakis(13, 1 7-Dioxa Nonacosane-15-Sulfanyl) Phthalocyaninato Nickel (II) (5b)

A mixture of 5 (0.793 g, 1.37 mmol), anhydrous $NiCl_2$ (0.054 g, 0.42 mmol) and quinoline (0.75 ml) was heated and stirred at 200°C for 20 h, under argon. After cooling to room temperature, the reaction mixture was diluted with ethanol (10 ml) and the waxy precipitate was separated. It was heated with ethanol and filtered off to remove impurities. The crude green product was purified by column chromatography (Silica gel, CH_2Cl_2: n-hexane/ 1:1). This compound was soluble in common solvents. Yield: 0.100 g (12%).

IR ν_{max}/cm^{-1}(KBr cell)= 2950–2850 (CH_2), 1610, 1460, 1380, 1320,1270, 1120–1100 (C-O-C), 940, 820, 750.

^1H NMR ($CDCl_3$): δ ppm= 0.80 (t, 24H, CH_3), 1.13 (m, 144H, CH_2), 1.67 (m, 16H, OC-CH_2), 3.63 (t, 16H, OCH_2), 4.01 (br, 20H, CH and OCH_2), 7.83–8.02(m, 4H, ArH), 8.43–8.81 (m, 8H, ArH)

^{13}C NMR (APT) ($CDCl_3$): δ ppm= 14.08 (CH_3), 22.65 (CH_2), 26.31 (CH_2), 29.34–29.85 (CH_2), 31.90 (CH_2), 48.52 (CH), 70.47 (OCH_2), 71.74 ($O\underline{C}H_2$-CHS), 121.99 (Ar CH), 122.41 (Ar CH), 123.52 (Ar CH), 131.25 (Ar CH), 133.88 (Ar C), 136.45 (Ar C), 138.04 (Ar C), 144.11 (Ar C).

MS (FAB), m/z (%): 2342.2 (50) $[M]^+$, 1930.3 (22) $[M\text{-}CH(CH_2OC_{12}H_{25})_2]^+$, 1518.9 (14) $[M\text{-}2(CH(CH_2OC_{12}H_{25})_2]^+$, 1108.4 (12), $[M\text{-}3(CH(CH_2OC_{12}H_{25})_2)]^+$, 957.7 (18), 696.9 (66) $[M\text{-}4(CH(CH_2OC_{12}H_{25})_2)]^+$, 639.4 (81), 583.4 (90), 391.3 (80), 307.1 (95), 227.2 (75), 154.1 (95).

2,3,9,10,16,17,23, 24-Octakis(13, 1 7-Dioxa Nonacosane-15-Sulfanyl) Phthalocyanine (7a)

A mixture of 1,2-di(13,17-dioxa nonacosane-15-sulfanyl)phthalonitril (7) (0.245 g, 0.24 mmol) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (0.054 ml, 0.36 mmol) in n-pentanol (4 ml) was refluxed under argon atmosphere for 60 h. After the reaction mixture had been cooled to room temperature, ethanol was added and the resulting precipitate was collected by filtration, washed with ethanol and then dried. The crude product was purified by column chromatography over silica gel with CH_2Cl_2. The dark green waxy compound was soluble in CH_2Cl_2, $CHCl_3$, CCl_4, benzene, n-hexane, diethylether, insoluble in ethanol, DMSO, DMF and H_2O. Yield: 0.065 g (26%).

IR ν_{max}/cm^{-1} (KBr cell): 3300 (NH), 2950–2850 (CH_2), 1600, 1460, 1400, 1370, 1280, 1120–1100 (C-O-C), 1020, 940, 760, 720, 680.

^1H NMR ($CDCl_3$): δ ppm = -3.50 (br, 2H, NH), 0.82 (t, 48H, CH_3), 1.09 (m, 288H, CH_2), 1.67 (m, 32H, OC-CH_2), 3.60 (t, 32H, OCH_2), 4.00 (d, 32H, OCH_2), 4.15 (m, 8H, CH), 9.54(s, 8H, ArH).

^{13}C NMR (APT) ($CDCl_3$) δ ppm= 14.09 (CH_3), 22.65 (CH_2), 26.28 (CH_2), 29.31–29.81 (CH_2), 31.88 (CH_2), 48.22 (CH), 70.46 (OCH_2), 71.69 ($O\underline{C}H_2$-CHS), 125.29 (Ar CH), 135.00 (Ar C), 141.03 (Ar C-S), 155.75 (N-C=N).

MS (FAB), m/z (%): 4055.7 (95) $[M]^+$, 3869.2 (14) $[M\text{-}OC_{12}H_{25}]^+$, 3645.3 (32) $[M\text{-}CH(CH_2OC_{12}H_{25})_2]^+$, 3457.9 (9), 3232.9 (44) $[M\text{-}2(CH(CH_2OC_{12}H_{25})_2)]^+$, 3046.7 (5), 2635.7 (7), 2411.6 (8) $[M\text{-}4(CH(CH_2OC_{12}H_{25})_2)]^+$, 1031.3 (14), 768.6 (13) $[M\text{-}8(CH(CH_2OC_{12}H_{25})_2]^+$, 402.0 (17).

2,3,9,10,16,17,23,24-Octakis(13, 17-Dioxa Nonacosane- 15-Sulfanyl) Phthalocyaninato Nickel (II) (7b)

A mixture of dinitrile derivative 7 (0.253 g, 0.25 mmol), DBU (0.057 ml, 0.386 mmol) and anhydrous $NiCl_2$ (0.066 g, 0.51 mmol) in n-pentanol (4.4 ml) was refluxed under argon atmosphere for 65 h. After the reaction mixture had been cooled to room temperature, ethanol (5 ml) was added to it and the waxy precipitate was separated. The crude product was purified by column chromatography over silica gel with dichloromethane. Yield: 0.110 g (43%).

IR ν_{max}/cm^{-1} (KBr cell): 2950 (CH_2), 1600, 1460, 1400, 1370, 1280, 1120–1100 (C-O-C), 1020, 940, 760, 720, 680.

^1H NMR ($CDCl_3$): δ ppm= 0.81 (t, 48H, CH_3), 1.09 (m, 288H, CH_2), 1.62 (m, 32H, OC-CH_2), 3.59 (t, 32H, OCH_2), 3.97 (d, 32H, OCH_2), 4.04 (m, 8H, CH), 9.43 (s, 8H, ArH).

^{13}C NMR (APT) ($CDCl_3$): δ ppm= 14.03 (CH_3), 22.61 (CH_2), 26.26 (CH_2), 29.28–29.63 (CH_2), 31.85 (CH_2), 48.22 (CH), 70.44 (OCH_2), 71.64 ($O\underline{C}H_2$-CHS), 124.53 (Ar CH), 135.55 (Ar C), 140.91 (Ar C-S), 151.98 (N-C=N).

MS (field desorption) (FD), m/z (%): 4113 (98) $[M]^+$, 3928.1 (6) $[M\text{-}OC_{12}H_{25}]^+$, 3702.4 (8) $[M\text{-}CH(CH_2OC_{12}H_{25})_2]^+$, 2058.0 (15) $[M\text{-}5(CH(CH_2OC_{12}H_{25})_2)]^+$, 1873.1 (3).

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