Separation and mesogenic properties of tetraalkoxy-substituted phthalocyanine isomers†

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The main aim of this paper is to describe the separation and properties of four possible structural isomers of non-peripherally substituted nickel(II) phthalocyanine. Two isomers (C_{4h} and D_{2h}) of this compound were separated by preparative thin layer chromatography; however the other two isomers (C_{2v} and C_s) were separated by HPLC only with an analytical chiral column. The individual isomers and symmetry were assigned on the basis of the ^{1}H NMR signals of the aromatic protons of the phthalocyanine ring system. The pure C_{4h} isomer exhibited liquid crystalline properties at room temperature while the isomeric mixture containing four structural isomers was liquid. The other three isomers were liquid under the same conditions. The mesogenic properties of pure C_{4h} isomer were determined by differential scanning calorimetry, optical polarizing microscopy and X-ray diffractometry. This is the first report of the separation of a liquid crystalline pure isomer in the field of phthalocyanine chemistry.

Introduction

Phthalocyanines, which were first developed as industrial pigments, have been actively exploited in various technological applications such as optical recording photovoltaics, photocopying, gas sensing, liquid crystals and photodynamic therapy.[1] The performance of these materials depends not only on the molecular composition including the metal center and the number, position and nature of the substituents, but also on the molecular architecture. The molecular arrangement in the condensed phase is a determining factor controlling many of the physical properties of the macrocycles including the electrical and photo-conductivity, magnetic susceptibility and optical non-linearity. A decisive disadvantage of phthalocyanine and metal phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework.[2] Because of their lower degree of order in the solid state, tetrasubstituted phthalocyanines are more soluble than the corresponding octasubstituted ones.

There are a couple of studies regarding the separation of the four different isomers of a tetrasubstituted metallophthalocyanine using chromatographic methods;[3,4] however there is only one study about the properties of the separated pure isomers which showed the separation and characterization of two structural isomers (C_{2v} and C_s) of zinc tetranitrophthalocyanine.[5] These isolated isomers were evaluated in terms of their photophysical and photobiological properties. To the best of our knowledge, our study is the first report about the liquid crystalline properties of a single separated isomer (C_{4h}).

Clearly, highly ordered crystals and films of phthalocyanine materials will be more favored if pure single isomers are used rather than a mixture of different isomers in the detailed study of electrical and optical properties of soluble tetrasubstituted metallophthalocyanines. For example, pure isomers may show interesting NLO properties, which can not be investigated in the mixture of all four isomers.[6]

Phthalocyanines are well known as disc-like molecules and form one dimensional columnar structures in the condensed phases. The first thermotropic discotic liquid crystalline phthalocyanine was reported in 1982[7] and since then numerous liquid crystalline phthalocyanine derivatives have been synthesized with the aim of producing more easily controllable macroscopic structures.[8] Although there are many studies on the liquid crystalline properties of octa- and tetrasubstituted phthalocyanines, this work is the first study of the mesogenic properties of the one pure (C_{4h}) isomer.

In the present work, we describe the separation and characterization of sterically hindered non-peripheral (1(4),8(11),15(18),22(25)-tetra(13,17-dioxanonacosan-15-yloxy)-substituted Ni(II) phthalocyanine (Fig. 1) using preparative thin layer chromatography and a chiral HPLC column. The liquid crystal properties of the pure (C_{4h}) isomer were determined by differential scanning calorimetry, optical polarizing microscopy and single angle X-ray diffractometry.

Experimental

Materials

3-Nitrophthalonitrile,[9] 15-hydroxy-13,17-dioxanonacosane,[10] 3-(13,17-dioxanonacosan-15-yloxy)phthalonitrile and 1(4), 8(11),15(18),22(25)-(13,17-dioxanonacosan-15-yloxy)phthalocyaninato nickel(II) was prepared according to literature

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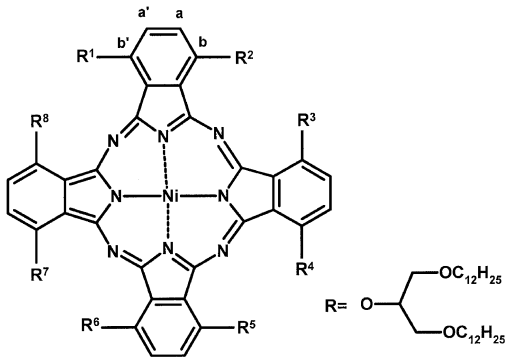

Isomer	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
C_{4h}	H	R	H	R	H	R	H	R
C_{2v}	H	R	R	H	R	H	H	R
C_s	H	R	H	R	H	R	R	H
D_{2h}	H	R	R	H	H	R	R	H

Fig. 1 The four structural isomers of 1(4),8(11),15(18),22(25)-(13,17-dioxanonacosan-15-yloxy) phthalocyaninato nickel(II) with point groups.

procedures.[11] All other reagents and solvents were reagent-grade and HPLC-grade quality, and were obtained from commercial suppliers.

Methods

Preparative thin layer chromatography was performed on Merck Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. HPLC was performed with a Agilent 1100 series HPLC system (ChemStation software) equipped with a G 1311A pump and G1315B diode array detector monitoring the range 254–900 nm. The HPLC column used was a reversible chiral column-(*R*,*R*)-whelk-01 (250 × 4.6 mm) from Regis Tech. Inc. The whelk-01 chiral stationary phase (CSP) is derived from 4-(3,5-dinitrobenzamido) tetrahydrophenanthrene covalently bound to silica. The mobile phase was a 98 : 2 (v/v) mixture of hexane–THF, respectively. The flow-rate was set at 1 ml min^{-1} and the sample was dissolved in hexane at a concentration 20 μg ml^{-1} for the chiral column. All separations were carried out at room temperature. UV–Visible spectra were provided by the ChemStation program. ^{1}H NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer. Transition temperatures were determined with scan rates of 10 °C min^{-1} using Mettler Toledo Star^e Thermal Analysis System/DSC 822^e System differential scanning calorimeter calibrated with indium from 1–2 mg samples under a nitrogen atmosphere. Optical textures were observed with the polarizing microscope Leitz Wetzler Orthoplan-pol equipped with a hot stage Linkam TMS 93 and temperature-controller Linkam LNP. X-Ray measurements were performed with Cu-Kα-radiation using a Rigaku Kristalloflex diffractometer (D_{max} 2200) at room temperature.

Results and discussion

Generally, the substituted phthalocyanines are prepared by cyclotetramerization of substituted 1,2-dicyanobenzene or 1,3-diimino-1*H*-isoindoles. Peripheral 2(3),9(10),16(17),23(24)-tetrasubstituted phthalocyanines can be synthesized from 4-substituted phthalonitriles while non-peripheral 1(4),8(11),15(18),22(25)-tetrasubstituted phthalocyanines are obtained from 3-substituted analogues.[1] In both cases a mixture of four possible structural isomers are obtained.[1] The four probable isomers can be designed by their molecular symmetry as C_{4h}, C_{2v}, C_s and D_{2h}. The 2(3)-substituted compounds always occur in the expected statistical mixture of 12.5% C_{4h}, 25% C_{2v}, 50% C_s and 12.5% D_{2h} isomers. But for the 1(4)-substituted ones the composition depends on the central metal ion and the structure of the peripheral substituent.

The separations of the C_{4h} and D_{2h} isomers of 1(4),8(11),15(18),22(25)-(13,17-dioxanonacosan-15-yloxy)phthalocyaninato nickel(II) were achieved by preparative thin layer chromatography with CH_2Cl_2–*n*-hexane (5 : 2) as eluent. On the other hand, the C_{2v} and C_s isomers were separated by HPLC with a chiral column. The isomer mixture was separated by HPLC with a chiral stationary phase (Fig. 2) according to the Experimental section. In order to separate the isomer mixture it was subjected to HPLC using a chiral analytical column because they could not be separated by using the normal analytical columns such as C_{18} or Lichrosorb-SI-60 columns. A semi-preparative separation was achieved by repeated injection and collection of the respective fractions from the analytical column to give a few milligrams of C_{2v} and C_s, allowing characterization by ^{1}H NMR spectroscopy. Fig. 2 shows that the HPLC chromatogram of the isomer mixture consists of 2.6% D_{2h}, 57.8% C_s, 19.7% C_{2v} and 19.9% of the C_{4h} isomer. The D_{2h} isomer has the lowest proportion (2.6%) in the isomer mixture. One reason for this is the steric hindrance of the respective neighboring alkoxy groups in the D_{2h} isomer (see Fig. 1). In order to prevent aggregation, the ^{1}H NMR spectra of the nickel(II) phthalocyanine were recorded as very dilute solutions. The individual isomers were assigned on the basis of the ^{1}H NMR signals of the aromatic protons H^a, $H^{a\prime}$ and H^b or $H^{b\prime}$ of the phthalocyanine ring system. The ^{1}H NMR parameters used to

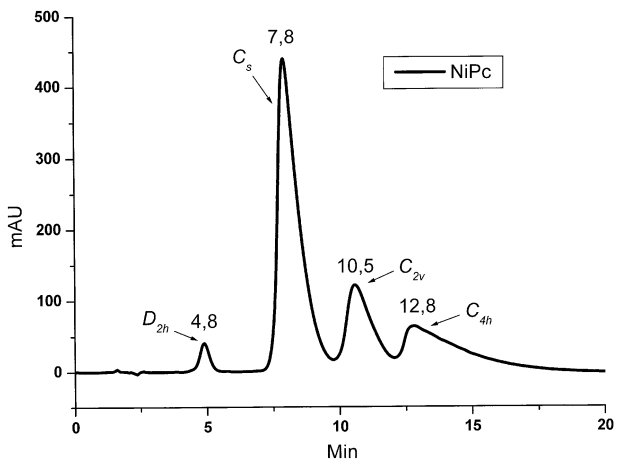

Fig. 2 HPLC chromatogram of the 1(4),8(11),15(18),22(25)-(13,17-dioxanonacosan-15-yloxy)phthalocyaninato nickel(II) using a chiral column (250 × 4.6 mm) and a solvent system of 98% *n*-hexane–2% tetrahydrofuran at a flow-rate of 1 ml min^{-1}.

Table 1 The ^{1}H NMR parameters of the aromatic regions of the four separate isomers (500 MHz, $CDCl_3$)

Isomer	D_{2h}	C_{2v}	C_s	C_{4h}
δ (H^b or $H^{b'}$)	8.95 (d, ^3J = 7.3 Hz, 4 H)	9.07 (d, ^3J = 7.4 Hz, 2 H) 9.03 (d, ^3J = 7.4 Hz, 2 H)	9.08 (d, ^3J = 7.3 Hz, 1 H) 9.06 (d, ^3J = 7.6 Hz, 1 H) 9.04 (d, ^3J = 7.6 Hz, 1 H) 9.00 (d, ^3J = 7.6 Hz, 1 H)	9.04 (d, ^3J = 7.4 Hz, 4 H)
δ ($H^{a'}$)	7.90 (dd, ^3J = 7.6 Hz, 4 H)	8.20 (overlap, 4 H)	7.97 (dd, ^3J = 7.6 Hz, 1 H) 7.96 (d or overlap, 2 H) 7.95 (dd, ^3J = 7.6 Hz, 1 H)	7.95 (dd, ^3J = 7.7 Hz, 4 H)
δ (H^a)	7.78 (d, ^3J = 8.4 Hz, 4 H)	7.76 (d, ^3J = 7.4 Hz, 2 H) 7.26 (d, ^3J = 7.4 Hz, 2 H)	7.79 (d, ^3J = 8.5 Hz, 1 H) 7.76 (d, ^3J = 4.4 Hz, 1 H) 7.73 (d, ^3J = 4.7 Hz, 1 H) 7.72 (d, ^3J = 5.4 Hz, 1 H)	7.71 (d, ^3J = 8.0 Hz, 4 H)

characterize the point groups of the four separated isomers are summarized in Table 1. Three signals (two doublets, one doublet of doublets) are observed for the D_{2h} (reference isomer) and C_{4h} isomers for the three aromatic protons H^a, $H^{a'}$ and H^b or $H^{b'}$ as expected. This confirms that the first elution at 4.8 min (2.6%) is the isomer with D_{2h} symmetry. Although six signals (four doublets, two doublets of doublets) are expected for the C_{2v} isomer, the ^{1}H NMR spectrum exhibits two doublets for H^b or $H^{b'}$, a broad signal for $H^{a'}$, and two doublets for H^a. The broad signal at 8.2 ppm whose integration corresponds to four protons could be proven by changing the concentration of the solution, thus it could be observed as two doublets of doublets. Similar behavior was observed for the $H^{a'}$ protons of the C_s isomer; the ^{1}H NMR spectrum of the C_s isomer demonstrates four doublets between 9.08–9.00 ppm for H^b or $H^{b'}$, an overlap signal between 7.97–7.92 (two doublets of doublets and/or a doublet) for $H^{a'}$ which corresponds to four protons and four doublets between 7.79–7.72 ppm for H^a (Fig. 3). The UV–Visible spectra of the four structural isomers of the nickel(II) phthalocyanine show that they do not differ significantly as expected.[3] Their UV–Vis spectra have similar maxima at 694, 692 and 690 for D_{2h}, C_s/C_{2v} and C_{4h} isomers, respectively.

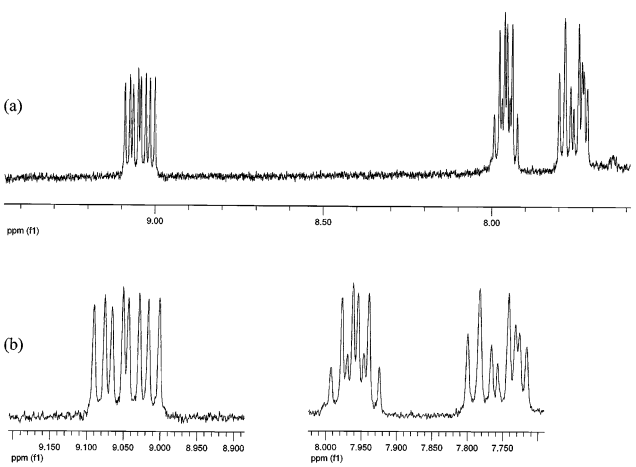

Fig. 3 (a) The ^{1}H NMR spectrum of the C_s isomer (resonance range of the aromatic protons) (b) Expanded ^{1}H NMR spectrum of the C_s isomer.

The pure (C_{4h}) isomer exhibited liquid crystalline properties at room temperature while the other isomers are liquid at the same conditions. One reason for the difference in physical properties of C_{4h} might be the spatial arrangement of the neighboring isoindoline units. The phase transition behavior of the C_{4h} isomer was determined by differential scanning calorimetry (DSC) and polarizing microscopy observations. Phase transition temperature and enthalpy change (in parentheses) of this product are 69 °C (152.23 kJ mol^{-1}) for the first heating. The thermogram of this isomer recorded with increasing temperature showed clearly one endothermic peak. We assume that this peak is related to the transition from the discotic mesophase to the isotropic liquid phase. When cooling the sample only one peak was observed at 26 °C for the first cooling. The second and third heating/cooling cycles gave similar results (Fig. S1–S3 and Table S1, ESI†).These investigations indicate that the C_{4h} isomer exhibits thermotropic liquid crystalline behavior at room temperature.

When observed using the polarizing optical microscope, the C_{4h} isomer was seen to become a highly viscous, birefringent fluid above 50 °C. The exact temperature of the transition from the solid to the mesophase was not optically observable due to the high viscosity. On further heating, the birefringent texture was maintained and the sample became less viscous until the transition into the isotropic phase at about 70 °C. The transition was reversible and on slow cooling (5 °C min^{-1}) from the isotropic phase, the birefringent texture emerged in the form of petals which coalesced to produce a flower-like texture at about 51 °C. This texture remained on cooling to room temperature observed by polarizing optical microscopy for the C_{4h} isomer and is very similar to those described in the literature.[12] The textures of the C_{4h} isomer under polarizing optical microscopy at room temperature are presented in Fig. 4.

The mesophases were identified by microscopic observation and X-ray diffraction measurements at 30 °C. The X-ray data are summarized in Table 2. Powder diffraction patterns of the C_{4h} isomer contain the typical reflections of a columnar mesophase of substituted phthalocyanines.[1] The low angle of the X-ray diffraction diagrams of the C_{4h} isomer show up to seven sharp Bragg reflections with d-spacing ratio 1 : $1/\sqrt{3}$: $1/\sqrt{4}$: $1/\sqrt{7}$: $1/\sqrt{9}$: $1/\sqrt{12}$: $1/\sqrt{13}$ (Table 2).[7,12] The lattice constant is 34.54 Å for the C_{4h} isomer. This result suggests a two-dimensional hexagonal lattice with disk-like molecules stacked in columns in the hexagonal arrangement. In the wide

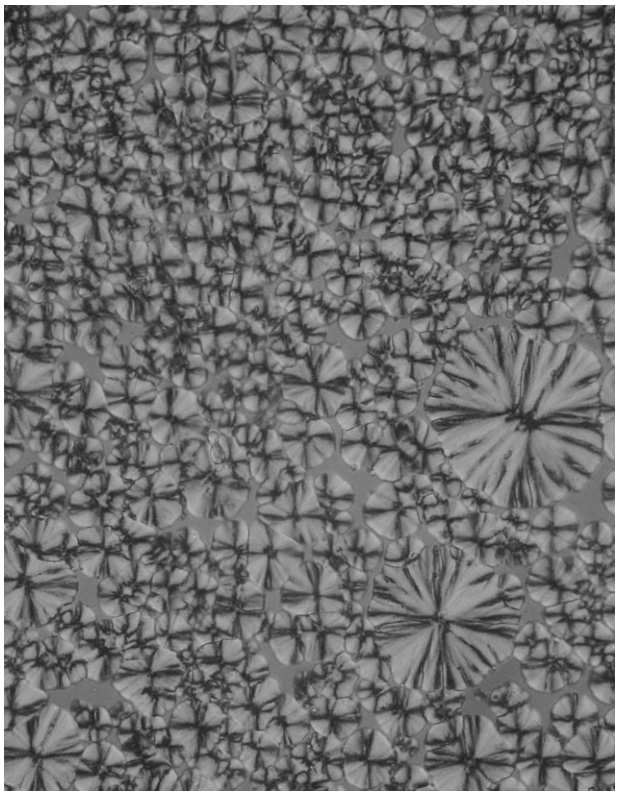

Fig. 4 Optical texture of the C_{4h} isomer of the non-peripheral substituted Ni(II) phthalocyanine observed at 25 °C (magnification ×25).

Table 2 X-Ray diffraction data of the C_{4h} isomer of the non-peripheral Ni(II) phthalocyanine

Spacing/Å				
$d_{observed}$	$d_{calculated}$	Ratio	Miller indices	Lattice constant
29.88	29.88	1 : 1	100	$a = 34.54$ Å
17.94	17.25	$\sqrt{3}$: 1	110	
14.49	14.94	$\sqrt{4}$: 1	200	
11.96	11.29	$\sqrt{7}$: 1	210	
9.59	9.96	$\sqrt{9}$: 1	300	
8.51	8.62	$\sqrt{12}$: 1	220	
8.39	8.28	$\sqrt{13}$: 1	310	
4.13				
3.91				

angle regions the compounds show a diffuse halo at 4.13 Å which is compatible with the disorder of the paraffinic tails in the side chain. An additional reflection at about 3.9 Å is observed which may be assigned to the packing of the macrocyclic subunits in the columns. The sharpness of this reflection for the C_{4h} isomer suggests good order within the columns and is consistent with the strong intramolecular periodicity associated with the discotic hexagonal ordered Col_{ho} mesophase.

Conclusions

In this work, we showed the separation of four possible structural isomers of non-peripheral substituted nickel phthalocyanine and their characterization. Non-peripheral substituted phthalocyanine isomers D_{2h}, C_{2v} and C_s are liquid at room temperature, whereas the C_{4h} isomer exhibits liquid-crystalline properties at the same temperature. The mesogenic properties of pure isomer C_{4h} were described. The pure C_{4h} isomer displays a discotic hexagonal ordered Col_{ho} mesophase at room temperature. Many other factors could be related to the observed effect, but our results indicated that isolated pure structural isomers may show different and better properties (spectroscopic and mesogenic) than isomer mixtures.

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