Liquid-crystalline phthalocyanines revisited

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A Commentary on the paper "Homologous series of liquid-crystalline metal free and copper octa-*n*-alkoxyphthalocyanines", by J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser and S. J. Picken. First published in *Liquid Crystals*, **6**, 577-592 (1989).

Our work on liquid-crystalline compounds started some 25 years ago after a discussion with Professor Rijk Zijlstra and Dr. (now Professor) Daan Frenkel from the Physics Department of the University of Utrecht, The Netherlands. Our colleagues wanted to study the deformation modes in liquid-crystalline phases of disc-like mesogens and approached us for the compounds. We had never been involved with mesogenic compounds and decided, after a literature search, to focus on the synthesis of mesogenic triphenylenes and truxenes. We discovered, by chance, a new truxene derivative that displayed an interesting physical property, namely, a re-entrant isotropic phase [1]. Such behaviour had been observed before, but only in mixtures of liquid-crystalline compounds and not in a pure mesogen. Experimental studies revealed that for the nematic discotic (N_D) phases of our truxenes the bend mode was the easiest deformation mode as had been predicted theoretically. Our physicist colleagues were quite happy with the results obtained and for us these studies opened a completely new field. We decided to embark on some general studies of liquid-crystalline compounds, but also to focus specifically on electron transport in stacks of discotic mesogenic molecules, which had not been studied before. We carried out some initial experiments on the triphenylene derivatives [2] we had synthesized, and then looked for other disc-shaped compounds, in particular discs that could bind metal centres. We hoped that these would be better conductors than the triphenylenes, which turned out to be rather poor conducting materials. This is how we stumbled upon the liquid-crystalline phthalocyanines. As is described in our 1989 *Liquid Crystals* paper and in a paper by the group of Simon in Paris [3], these compounds form well-behaved liquid-crystalline phases,

which, according to our complex impedance spectroscopy measurements, were semi-conducting ($\sigma = 10^{-3}$– 10^{-8} S/m depending on whether or not they were doped) with a conductivity that was somewhat lower in the mesogenic phase than in the crystalline phase. In subsequent studies we also synthesized and investigated different types of polymerized liquid-crystalline phthalocyanines and studied their physical properties including electrical properties [4]. Having established that liquid-crystalline phthalocyanines and their polymerized counterparts were electron conducting we looked to set up a collaboration with experts on electrical measurements. This brought us in contact with Drs. John Warman and Mathijs de Haas of Delft University of Technology. John and Mathijs had developed a very useful Time Resolved Microwave Conductivity Technique, which was subsequently used to study, in great detail, the electrical properties of our liquid-crystalline phthalocyanines. The properties studied included the hopping time of charges in the stacks and the recombination of charges (free electrons and electrons residing on separate stacks) as a function of the distance between the stacks. The latter could be controlled by varying the length of the hydrocarbon chains attached to the phthalocyanine discs. A paper summarizing many of these studies was published in 1994 [5].

Another topic we had been working on was that of chiral polymeric materials. Our expertise in this area influenced us to synthesize chiral liquid-crystalline phthalocyanine stacks, the objective being to investigate whether such chiral stacks would conduct electrons differently when compared to normal achiral stacks. The compound which we prepared is shown in Figure 1. It was found to form a new columnar hexagonal phase (Col$_h$*), which under the polarizing microscope was visible as spiral patterns. For comparison we also synthesized the phthalocyanine compound with (*R*, *S*)
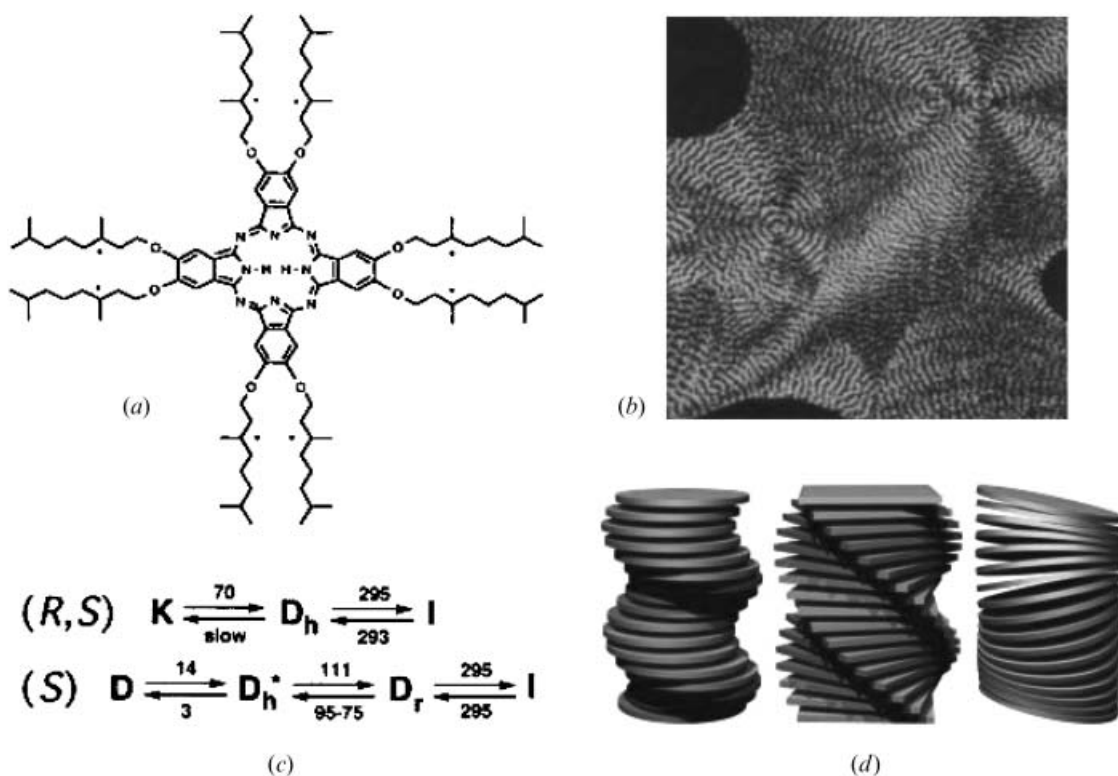
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Figure 1. Structure of the chiral phthalocyanine (a) and spiral pattern displayed by the Col_h^* phase under the polarizing microscope (b). Phase behaviour of the ''racemic'' and chiral liquid-crystalline phthalocyanines (c) and possible helical arrangements of the phthalocyanine discs in the Col_h^* phase (d). The helical structure with the tilted discs is the most likely arrangement.

tails. This mesogen, which is a mixture of 43 stereo-isomers (16 enantiomeric pairs and 11 meso compounds), surprisingly displayed a much simpler phase behaviour than the chiral one, which consists of only a single stereoisomer. The reason for this behaviour is still not understood. For the new chiral Col_h^* phase three possible structures were proposed (see figure 1). From circular dichroism studies and studies on model compounds in which the position of the discs was fixed by polymerization, we were able to conclude that the discs in the Col_h^* columns have a tilted orientation, where the tilt angle changes in a helical fashion when moving in the direction of the stacking axis (see figure 1d, right). Electron conductivity studies revealed that the helical columnar stacks were poorer transporters of charges (electrons and holes) than normal columnar stacks. On the other hand energy migration appeared not to be hampered by the helical structure of the stacks and was similar to that in the normal stacks [6].

As we have shown liquid-crystallinity can be used as a tool to arrange molecules in a stack structure. In a parallel project we applied the host-guest binding properties of crown ether rings attached to the periphery of phthalocyanine molecules for this purpose [7]. Crown ethers are known to bind alkali metal ions, such as potassium ions, and addition of these ions to the crown ether phthalocyanines resulted in extended stacks with the sandwiched alkali metal ions acting as glue and holding the structure together. Impedance spectroscopy on these stacks showed that they were electron conducting with a conductivity that depended on the size of the alkali metal ion. The highest conductivity was displayed when rubidium ions were used as guest ions. X-ray studies revealed that in the rubidium case the distance between the phthalocyanine rings in the stacks was the smallest of all the alkali metal ions tested. This smaller distance leads to a better overlap of the π-electrons of the phthalocyanine rings and hence to a higher conductivity [8].

Studies on the aggregation behaviour of the liquid-crystalline phthalocyanines reported in our 1989 *Liquid Crystals* paper indicated that these compounds only formed stacks in their mesophases and not in solution. We were intrigued by this and reasoned that in solution the π-π stacking interactions between the discs were probably too weak to compete with the interactions of solvent molecules with the discs. We therefore decided
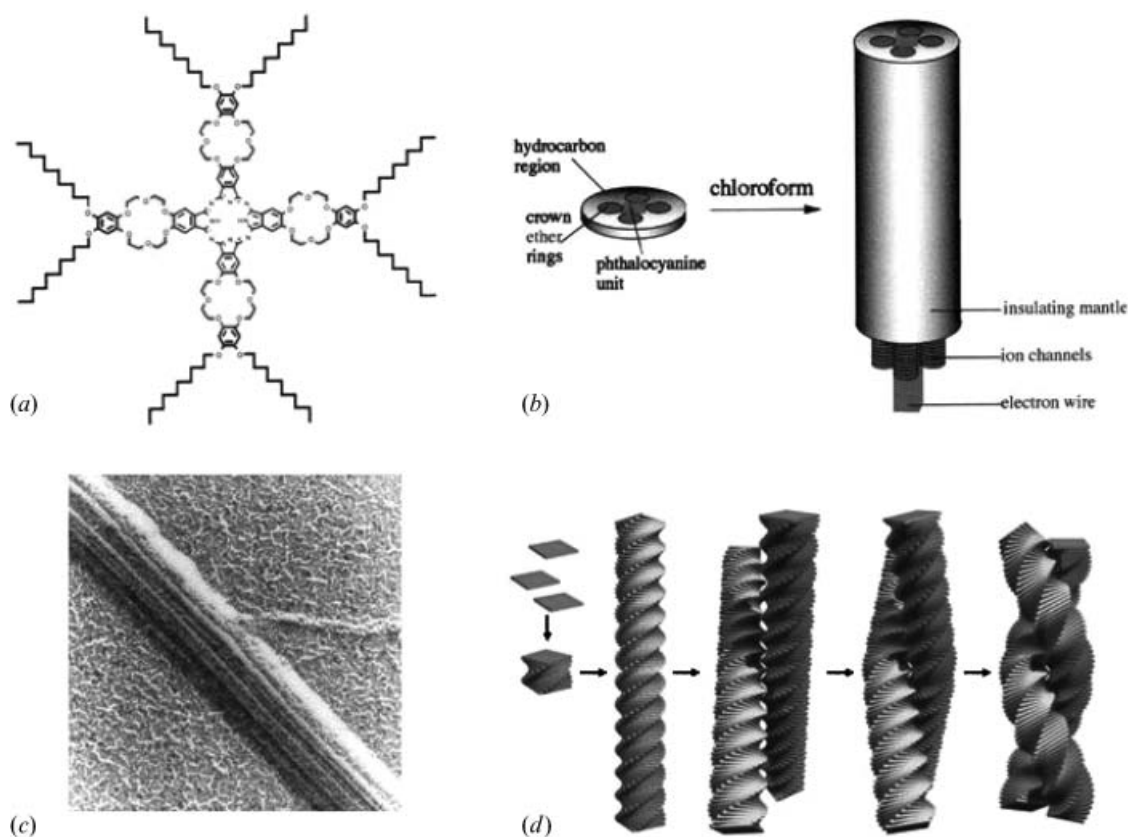
Figure 2. Liquid-crystalline crown ether phthalocyanine (a) and a molecular cable formed from molecules of this compound by self-assembly in organic solvents (b). Electron micrograph showing a bundle of single fibres, each of which is 6 nm in diameter (c). Schematic representation of the hierarchical stepwise assembly of the chiral crown ether phthalocyanine molecules (d).

to extend the size of the phthalocyanine core with benzocrown ether rings to construct a larger disc which, including the tails, measured 6 nm in diameter (see figure 2). This new compound was found to form a liquid-crystalline phase over a large temperature range and to our delight it also self-assembled in organic solution to yield a gel, which contained very long fibres composed of thousands of stacked molecules [9]. Electron microscopy revealed that the fibres had a diameter corresponding to the diameter of the single disc, i.e. 6 nm, suggesting that by self-assembly a molecular cable with a central conducting core and an isolating mantle of paraffinic chains had been formed (see figure 2). The entholpy of association, ΔH, of the molecules was measured and amounted to 125 kJ/mola, which is relatively large but in line with the idea that the large crown ether phthalocyanine discs interact more strongly by π-π stacking interactions than their smaller counterparts without crown ether rings. In a subsequent study we made a crown ether phthalocyanine containing chiral tails and this compound turned out to display very interesting aggregation behaviour [10]. In organic solvents it was also found to self-assemble, but now in

the form of right-handed single fibres that further assemble to generate left-handed super helices. Apparently, the chiral (S) centres in the floppy tails were able to transfer chiral information stepwise; first to the discs, then to the single fibre and finally to the super structure. It was found that the alkali metal ions can block this chirality transfer process. These ions bind in between two crown ether rings forcing the discs, which have a staggered orientation, to become eclipsed leading to a loss of helicity. This process could be followed by electron microscopy [10].

More recently we have used stacks of liquid-crystalline phthalocyanines as components in a new type of sensor material that allows the naked eye detection of small amounts (down to the nanomolar level) of compounds. This material was discovered by chance as part of a project aimed at the development of new procedures for making alignment layers for liquid-crystalline displays. Alignment layers traditionally are prepared by a rubbing process which has been used since the 1920's. This rubbing process is simple but requires clean room facilities which is a drawback. We found that alignment layers can easily be made under
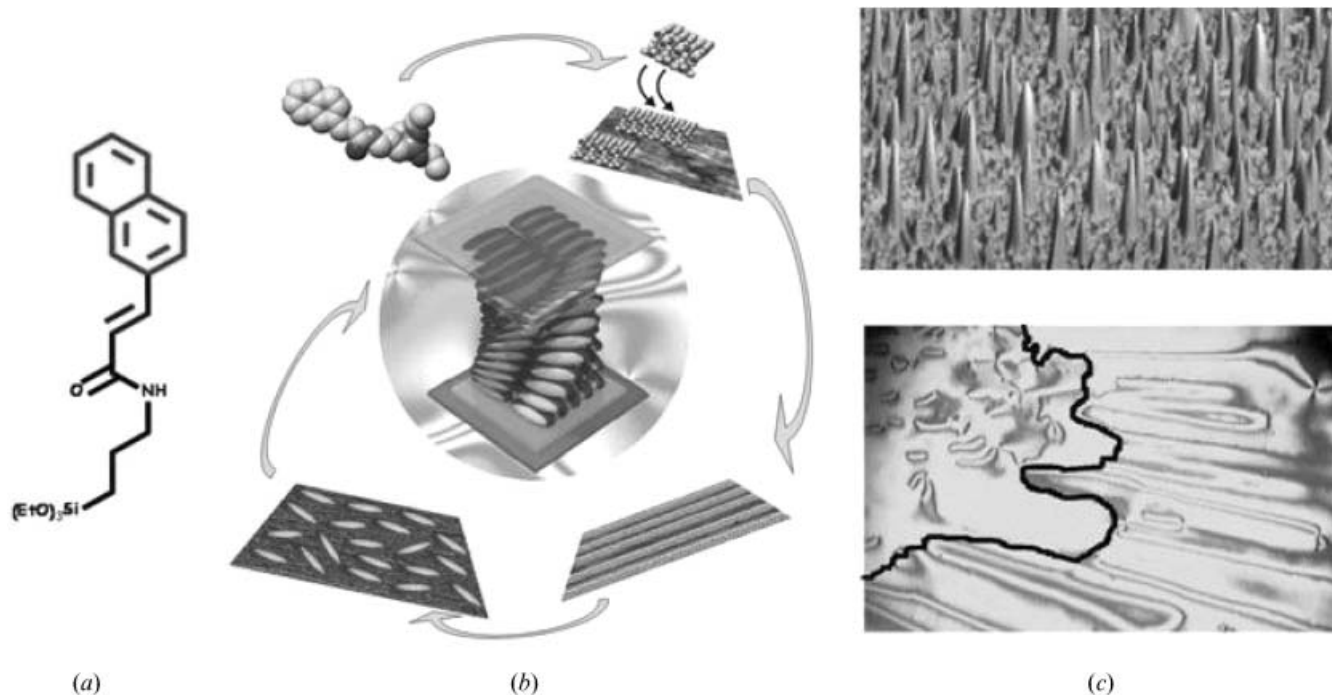
Figure 3.   Siloxane derivative (a), which forms self-assembled alignment layers on an ITO surface. These layers can be used to construct a twisted-nematic liquid-crystal display (b). Alignment layers prepared form a pyridine containing siloxane are capable of templating the epitaxial growth of highly ordered columnar stacks of mesogenic zinc phthalocyanine molecules as shown by AFM (c, top). Addition of compounds that coordinate to the zinc centres in the phthalocyanine molecules destroys the stacks, which can be detected by the naked eye (c, bottom); the solid line separates areas where the stacks are intact (right) and destroyed (left).

laboratory conditions without the need of clean room facilities by a hierarchical self-assembly process from solution. When an indium tin oxide (ITO) plate is immersed in a solution of a siloxane functionalized with aromatic rings (benzene, naphthalene or pyridine) an alignment surface is generated without external stimuli (i.e. rubbing or photoalignment). This surprising result turned out to involve a self-assembly process in which siloxane oligomers formed in solution and precipitated on to the ITO surface and then grown further by self-assembly to yield micrometer-sized grooves. In this process parallel nanometer-sized grooves, already present on the ITO surface as a result of the manufacturing process, act as templates. During the self-assembly process the size and ordering of these nanogrooves are amplified over several orders of magnitude. These self-assembled alignment surfaces were shown to align uniformly mesogenic molecules and could be used in the construction of standard twisted-nematic liquid-crystal displays rivaling industrially manufactured displays in terms of interaction energy between the alignment layer and the liquid-crystalline matrix [11].

When the self-assembled layers are prepared from pyridine containing siloxanes an alignment surface is obtained that contains metal binding sites. We used this surface to template the epitaxial growth of highly ordered columnar aggregates of mesogenic zinc phthalocyanine molecules from solution (see figure 3). The height of the aggregates could be controlled by varying the time of immersion of the grooved ITO surface in the phthalocyanine solution. The anchoring energy, which is a measure of the interaction strength between the alignment layer and the mesogen, was found to increase substantially in the presence of the stacks and was dependent on the stack height. The alignment properties of the zinc phthalocyanine layers could be changed by association with molecules that are capable of coordinating to the zinc centres. Addition of such molecules (amines and amino acids) caused the stacks to disassemble and to dissolve in the liquid-crystalline matrix. This process could be seen by the naked eye (see figure 3) [12] and, therefore, opens the possibility to construct versatile sensor systems for naked eye detection of a variety of analytes including biomolecules like toxins and proteins.

Conclusion

Looking back we realize that our article on liquid-crystalline phthalocyanines published in *Liquid Crystals* in 1989 has been one of our most innovative papers. From the humble beginning of studying a series of

simple discotic mesogens, a myriad of research topics has evolved, ranging from conducting molecular wires and functional command layers to new concepts of helical communication. In hindsight this paper opened a new world for us and inspired us to set out new lines of research, which gave us great pleasure and, as shown above, interesting results.

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Homologous series of liquid-crystalline metal free and copper octa-*n*-alkoxyphthalocyanines

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Two series of discotic liquid crystals, one based on metal-free and the other on copper containing phthalocyanine (Pc) as the central core and eight peripherally *n*-alkoxy groups (C_6–C_{12}) as substituents have been synthesized and their mesomorphic properties and structural parameters have been determined. These compounds represent a series totally devoid of polymorphism, the mesophase in all cases being D_{ho}. In the solid state an orthorhombic two dimensional lattice with four molecules per unit cell and a presumably tilted stacking is present, while in the mesophase the planes of the molecules are on average perpendicular to the direction of the stacks. The aggregation behaviour of the C_8, C_{10} and C_{12} homologues was studied as a function of solvent polarity and of concentration. The electrical properties of the copper complexes of the *n*-dodecoxy and *n*-octoxy derivatives have been determined by means of complex impedance spectroscopy and compared with those of the non-mesogenic CuPc.

1. Introduction

The discovery of thermotropic liquid crystals in 1888 by Reinitzer [1] led to considerable interest in these materials [2, 3]. Much is known about the influence of chain length in the case of rod-like liquid crystals [4]. Generally, at a certain temperature, increase in the chain length leads to more organized mesophase structures [4, 5]. Thus, nematic phases are more stable with short chains, while smectic phases are thermodynamically favoured when longer chains are present. Compounds with intermediate chain length sometimes show polymorphism. In addition the influence of chain length on the structure and physical properties of some disc-like mesogens has been investigated. Examples include derivatives of benzene [6], truxene [7], triphenylene [8], penta-O-*n*-alkanoylglucopyranose [9] and metal complexes such as bis(3,4-*n*-alkoxybenzoyl)methanatocopper(II) [10], porphyrins [11], and phthalocyanines (Pc's) [12–17]. In all cases the length of the alkyl chain has a remarkable influence on the structure of the mesophase. Mesomorphic structures which have been

identified are nematic [18] (N_D), lamellar (D_L) [19, 20] and columnar (ordered or disordered hexagonal, rectangular, oblique and cholesteric) [21–23]. Here we report the effect of alkyl chain length of two series of discotic liquid-crystalline octa-*n*-alkoxy-Pc's, **1** and **2**. The octoxy and dodecoxy derivatives have already been independently reported [12, 14–16].

Mesogenic phthalocyanines are of interest as potential one dimensional conductors [24]. However, thus far conductive properties have only been reported in the literature for bis(octa-*n*-octadodecoxymethylphthalocyaninato)lutetium [17]. Within the present series electrical conductivity measurements have been performed on the C_8 and C_{12} homologues in their respective mesophases.

|	M
1	2H
2	Cu

R = -OC$_n$H$_{2n+1}$

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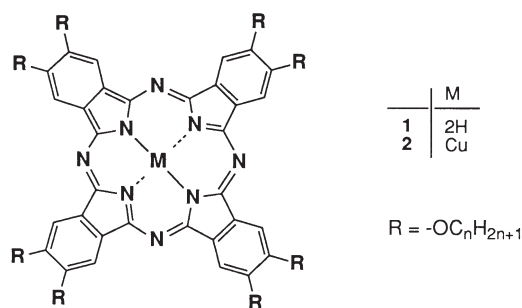
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2. Synthesis

The metal-free phthalocyanines studied were synthesized and characterized as before [12]. Copper-Pcs were prepared from the free ligands by deprotonation with sodium pentanolate in pentanol and subsequent reaction with anhydrous copper(II) chloride.

$$1 \xrightarrow[\text{CuCl}_2]{\text{NaOC}_5\text{H}_{11}/\text{C}_5\text{H}_{11}\text{OH}} 2$$
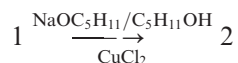
After Soxhlet extraction with acetone pure **2** was isolated. Copper complexes **2** are less soluble in organic solvents than the free ligands **1**.

3. Mesomorphic properties

In order to establish the phase behaviour the compounds synthesized were investigated by polarizing microscopy and differential scanning calorimetry (D.S.C.). Upon heating above a certain temperature, the solid material melts into a highly viscous mass. In all cases polarization microscopy reveals the presence of a mosaïc texture. The metal-free derivatives show a transition to the isotropic liquid for $n=10$, 11 and 12. Upon fast cooling ($20°$C/min) the isotropic melt of these derivatives, linear birefringent defects appear, which are characteristic of (uniaxial) D_{ho}-phases [25]. Upon slow cooling ($2°$C/min) digitate stars, as reported before for hexa-n-alkoxytriphenylenes [26] are observed when the analyser and the polarizer are parallel (see figure 1 (a)). These stars grow faster at the points where the positive curvature is large, which causes their particular shape. Eventually, the stars coalesce to a homeotropic aligned sample, in which linear defects are sometimes present (see figure 1 (b)). In figure 2 we propose a structure for these linear defects; in this the main deformation is a bend mode. We expect bend (elastic constant K_3) to be the easiest mode in analogy with rod-like molecules where splay (elastic constant K_1) is usually the easiest mode [26, 27]. This has in fact been observed in the N_D phase of discotic materials based on truxene derivatives by Warmerdam *et al.* [28, 29], and was predicted theoretically by Sokalski and Ruijgrok [30] in 1982. Moreover, Warmerdam *et al.* [28, 29] observed that at the $N_D \rightarrow D_{rd}$, transition the ratio K_1/K_3 approaches unity. Apparently, in our case of columnar D_{ho} mesophases the ratio K_1/K_3 does not approach unity, but K_1 is still larger than K_3. In addition, no twist deformations are observed in the textures indicating that in our case the elastic constant for twist (K_2) is larger than K_3.

The transition temperatures and enthalpies were measured by D.S.C. Only one transition was detected for all compounds. The observed transition
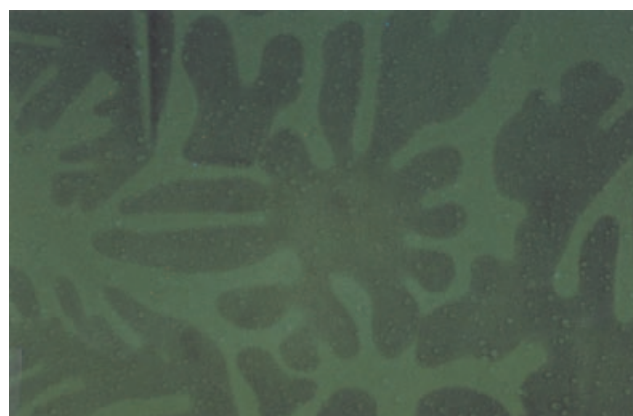
(*a*)
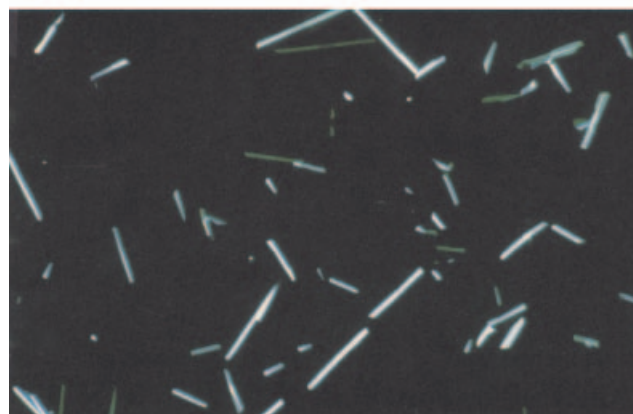
(*b*)

Figure 1. Micrographs of (*a*) digitate stars observed under a polarizing microscope upon slow cooling ($2°$C/min) of compound **1** ($n=11$) from the isotropic phase. Polarizer and analyser are parallel. (*b*) Linear birefringent defects; crossed polarizers.
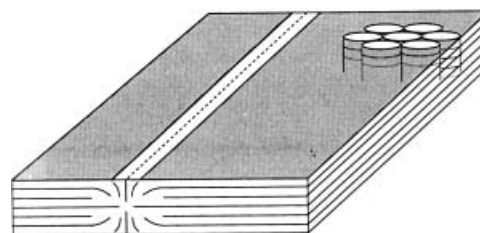

Figure 2. Schematic representation of the proposed molecular arrangement around a birefringent defect, the planes indicate the alignment of the Pc molecules and the stacks are perpendicular to these planes.

temperatures, enthalpies and calculated entropies for the solid→mesophase transition are given in table 1. This table also gives the temperatures at which the mesophase→isotropic liquid transition takes place for three of the free ligands. The latter temperatures were

Table 1. Mesomorphic properties of peripherally octa-*n*-alkoxy substituted phthalocyanines $MPc(OC_nH_{2n+1})_8$: transition temperatures and thermodynamic parameters†.

			Transition temperature °C					
M	n	C	D_{ho}		I	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}	$\Delta S/R$
2H	6	●	119[86] ●	‡	–	72	182	21.9
Cu	6	●	120[101] ●	‡	–	70	177	21.3
2H	7	●	104[75] ●	‡	–	86	228	27.4
Cu	7	●	110[78] ●	‡	–	73	190	22.9
2H	8	●	94[77] ●	‡	–	98	239	28.8
Cu	8	●	112[85] ●	‡	–	83	216	26.0
2H	9	●	101[71] ●	‡	–	94	251	30.2
Cu	9	●	106[71] ●	‡	–	93	245	29.5
2H	10	●	94[78] ●	345§	●	102	278	33.6
Cu	10	●	104[75] ●	‡	●	108	286	34.4
2H	11	●	83[66] ●	334§	●	108	303	36.5
Cu	11	●	92[70] ●	‡	–	101	277	33.3
2H	12	●	83[65] ●	309§	–	109	307	36.9
Cu	12	●	95[76] ●	‡	–	108	295	35.5

†Transition temperatures and enthalpies are observed during second and subsequent heating runs. Transition temperatures measured during a cooling run are given between square brackets. C is the crystalline phase, D_{ho} is the hexagonal ordered phase and **I** is the isotropic phase. Heating and cooling rate 10 K/min. ‡No transition to the isotropic phase was visible under a polarizing microscope at temperatures below 345°C. §Only observed under the polarizing microscope with accompanying decomposition.

determined by hot stage (Mettler F52) polarization microscopy. These transitions could be detected by inserting a sample between two glass slides into the hot stage at 300°C and subsequently increasing the temperature at a rate of 10°C/min. Simultaneously, severe decomposition was observed at the edges of the sample. For all other compounds no transition to the isotropic liquid was detected. In figure 3 the measured crystalline to mesophase transition temperatures of **1** and **2** are plotted as a function of the number of carbon atoms *n* in the side chain. The transition temperature decreases with increasing *n*, except for some odd-even alterations. Qualitatively similar behaviour was observed for non-peripherally *n*-alkyl substituted Pc's [18]. In figure 4 the
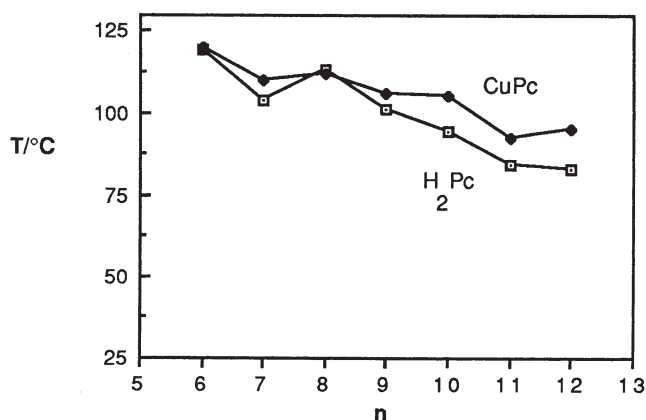
transition enthalpy and entropy are plotted as a function of *n*.

4. Structure

In the solid state, the synthesized compounds have a microcrystalline morphology, as was shown by electron microscopy (see figure 5) and electron diffraction. From the electron diffraction pattern it was deduced that the molecules stack in a direction parallel to the needle axis.

We have performed X-ray diffraction experiments on samples cooled from the mesophase to room temperature. An indexing scheme had to satisfy the following criteria: (i) Compounds **1** and **2** with equal side chains fitting the same scheme; (ii) all observed lines indexed; (iii) a reasonable number of molecules per unit cell; (iv) reasonable cell parameters; (v) reasonable calculated densities. In most cases approximately 20 lines varying in intensity from medium to weak were present, which could be indexed by an orthorhombic lattice with $Z=2$. In addition approximately five very weak rings were present which could only be indexed by assuming an orthorhombic unit cell with $Z=4$. The calculated densities vary between 1.1 for $n=12$ and 1.4 for $n=6$ for compounds **2**, which is in line with observed values of 1.6 for CuPc [32] and 1.1 for octa(dodecoxymethyl)phthalocyanine [33]. In all cases the 001 reflection corresponds to approximately 4.3 Å, which is the distance between two neighbouring Pc molecules within one stack. In figure 6 the calculated cell parameters a and b have been plotted against *n*. On average, both *a*
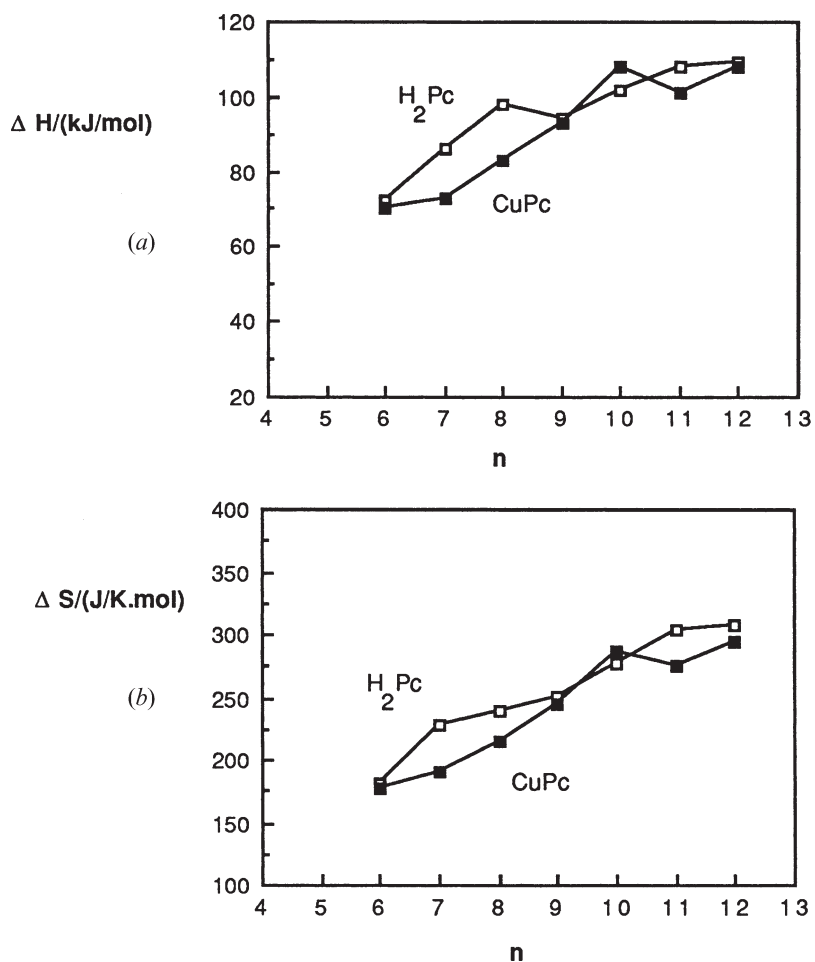
Figure 3. Transition temperature as a function of *n* for compounds **1** and **2**.

Figure 4. Enthalpy of transition ΔH (*a*) and entropy of transition ΔS (*b*) plotted as a function of *n*.
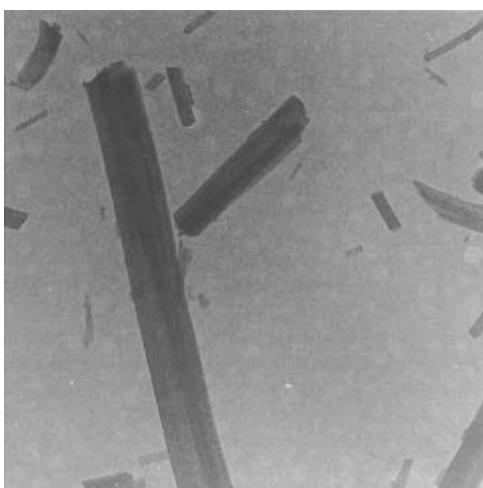

Figure 5. Electron microscopy micrograph of the morphology of monocrystals of compound **2** (*n*=12) at room temperature.
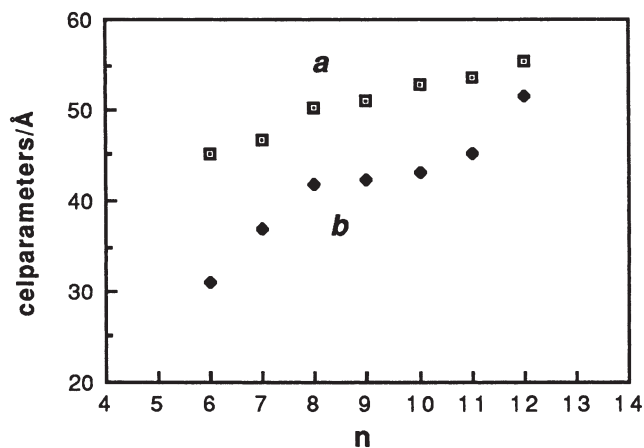

Figure 6. Cell parameters *a* and *b* of the orthorhombic lattice as a function of *n*.

and *b* increase with increasing *n*, although the variation in *b* is somewhat more pronounced than that in *a*. This might be explained by assuming that the molecules in the solid phase have a preferred tilt around the *b* axis, we will come back to this later. The difference between *a* and *b* becomes less with increasing *n*.

In the mesophase X-ray diffraction gives 4 to 5 reflections at small angles ($l/d = 1$: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$: $\sqrt{9}$) corresponding to a hexagonal lattice, a broad and diffuse reflection around 4.6 Å as a consequence of the liquid-like order of the aliphatic chains and a strong and much sharper reflection at 3.4 Å which is ascribed, as before [13, 14, 15], to the ordering of discs within one column. In addition a broad and weak reflection with a spacing of 7.0 Å is present in all cases. With reference to work performed by De Jeu *et al.* [31] on monocrystals of hexa-*n*-hexylthiotriphenylene this reflection is ascribed to the presence of some kind of intracolumnar order. According to the nomenclature introduced by Destrade *et al.* [34] this structure is assigned the symbol D_{ho}, a picture of such a D_{ho} phase is presented in figure 7. Ordered columns are preferred for 2,3,9,10,16,17,23,24-octa-*n*-alkoxy-Pc-derivatives because of the low steric hindrance of the side chains, which allows a strong cohesion between the discs. Disordered columns are preferred for the corresponding *n*-alkoxymethyl substituted compounds, since their side chains point out of the plane of the aromatic Pc-nucleus [12, 15]. From the occurrence of only *hk*0 and 00*l* reflections it can be concluded that no correlations between molecules in different columns exist in contrast to what was observed for hexa-*n*-hexylthiotriphenylene, but here the driving mechanism for the existence of the correlations is probably the $D_{hd} \rightarrow D_{ho}$ transition, since general considerations predict that phase transitions are impossible in strictly one dimensional systems [35].

The dependence of the intercolumnar distance on alkyl chain length was studied at 200°C (see figure 8). As expected this distance increases with chain length. An apparently linear relationship, similar to that reported before for other homologous series of columnar mesophases, is found [7, 35]. Such an empirical correlation has no physical basis, however [35] instead,
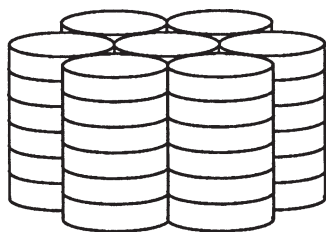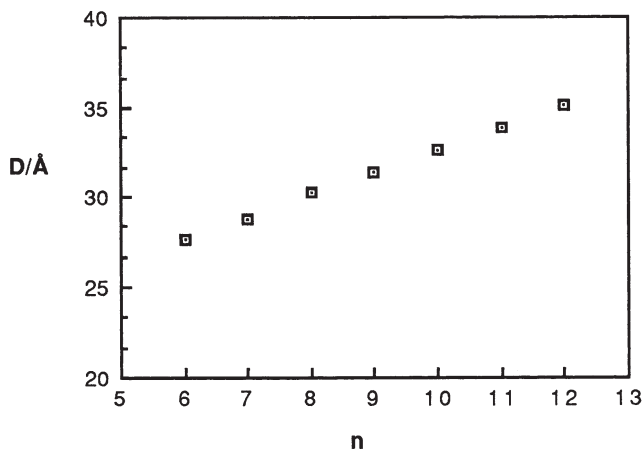

Figure 8. Intercolumnar distance as a function of *n* for compounds **1** and **2**.

D^2 should be studied as a function of *n*, as will be done from now on. For every additional methylene unit an average increase of 1.26 Å was found for both series **1** and **2**.

When the intercolumnar distance *D* and intercore distance *c* are known, the molecular volume, *V*, and density, ϱ of the lattice can be calculated according to

$$V = \frac{\sqrt{3}}{2} D^2 c$$

and

$$\varrho = M/(N_A V),$$

where *M* is the molecular weight. The dependence of these parameters on *n* is shown in figures 9 and 10. The lattice volume increases linearly with *n*, implying a constant increment per added methylene group. The lattice density decreases as a consequence of the fact
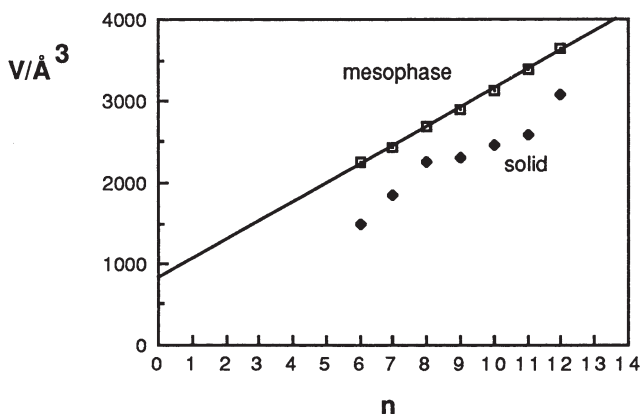

Figure 7. Schematic drawing of a D_{ho} phase.

Figure 9. Molecular volume *V* in the solid and liquid-crystalline state as a function of *n* for compounds **2**.

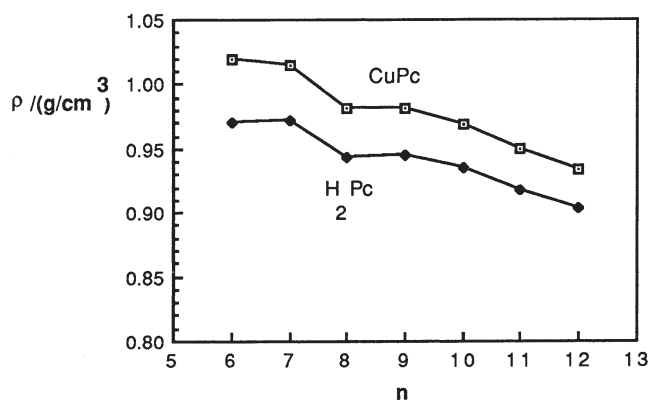Figure 10. Lattice density (ϱ) as a function of n for compounds **1** and **2**.

$$\pi cR^2_n = \pi cR^2_o + 8n\, V_{CH_2} \qquad R^2_n = R^2_o + \frac{8n\, V_{CH_2}}{\pi c}$$

Figure 11. Model corresponding to equation (1).

that the alkyl chains have a lower density than the Pc core. The volume of a molecule in the solid phase was calculated according to

$$V = abc/Z,$$

where Z is the number of molecules per unit cell, and this volume is also plotted in figure 9. The transition from solid to mesophase is thus accompanied by an increase in molecular volume.

The apparent Pc core size can be estimated from

$$D_n^2 = D_0^2 + 32nV_m/\pi c, \tag{1}$$

where D_n is the diameter of a column for the nth homologue, D_0 is the core diameter, including the ether oxygen and the excess volume of the terminal methyl group, and V_m is the mean volume of a methylene group (see figure 11). A plot of D_n^2 as a function of n (see figure 12) gives a straight line from which values of 16.8 Å for D_0 and 26.4 Å^3 for V_m can be calculated. The value of D_0 found in this study is consistent with the diameter of 13.9 Å calculated for unsubstituted Pc from X-ray studies [37] and the value of 17 Å estimated for D_0 from CPK models. Although rotation of the whole molecule around the normal to the molecular plane and fluctuations of this axis around the core direction might be possible in the mesophase, this agreement implies that in the mesophase the plane of the Pc nucleus is on average perpendicular to the column axis. This untilted stacking gives rise to interesting physical phenomena, such as efficient exciton and electron migration through the columns [38–40]. The observed diffuse diffraction feature, shows that in the mesophase the aliphatic side chains are in a molten state. For disordered side chains in hexa-n-alkoxytruxenes a value of 27.4 Å^3 is found for V_m at 80°C, suggesting that in our case the side chains are somewhat less disordered than for truxenes [41].
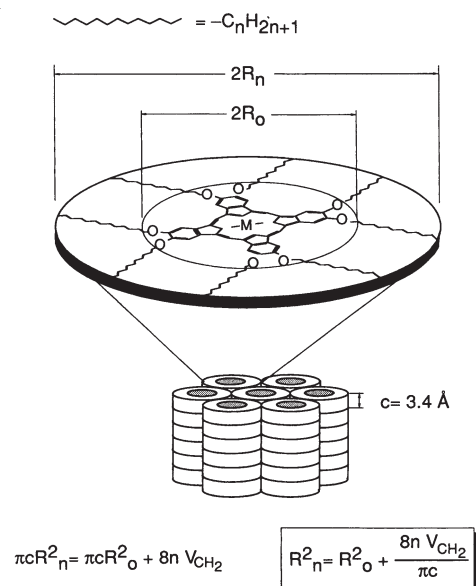
Temperature dependent FTIR and CPMAS NMR studies will further clarify this point [42].

5. Aggregation behaviour in solution

In order to examine their aggregation behaviour in solution compounds **1** (n=8, 10, 12) have been studied by absorption and fluorescence spectroscopy as a function of solvent polarity in mixtures of chloroform and methanol and as a function of concentration in chloroform solution.

5.1. Solvent polarity

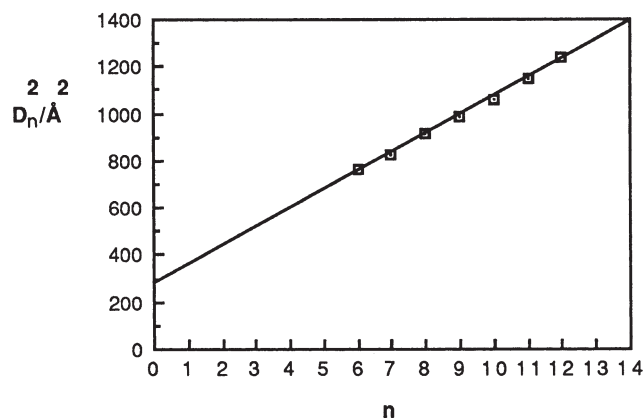Absorption spectra of metal-free mononuclear Pc in chloroform solution consist of two intense π–π^*

Figure 12. D_n^2 as a function of n for compounds **2**.

transitions at 664 and 700 nm (*Q* bands) with associated higher energy vibrational components, and a second intense and broader π–π^* transition at 300–360 nm called the Soret band [43]. The intensity of the *Q* bands decreases if the solvent is changed from chloroform to more polar solvents such as methylene chloride, DMF, acetone and methanol. Similar spectroscopic changes are also observed in mixed solvents, e.g. by mixing methanol with chloroform. This effect is illustrated for compound **1** (*n*=10) in figure 13; with increasing ratio of methanol to chloroform, the peak heights at 664 nm and 700 nm (mainly mononuclear species) decrease, but that at 625 nm (mainly aggregated species) [44, 45] increases. From the changes in absorption characteristics it can thus be concluded that aggregation becomes more important with increasing solvent polarity.

Mononuclear metal free Pc exhibits a fluorescent emission from the lowest π–π^* state (*Q*-band) near 707 nm (λ_1) [46]; this main band is accompanied by three other bands (λ_2=666, λ_3=742 and λ_4=786 nm). When these solutions are studied by fluorescence spectroscopy the main effect observed is a marked decrease in emission emission intensity, when methanol concentrations exceed 20 per cent v/v. This is illustrated in figure 14, where the intensity of the emission peak at 707 nm is plotted against the methanol content. The other characteristics of the emission spectra remain unchanged, i.e. the shape of the fluorescence spectra is
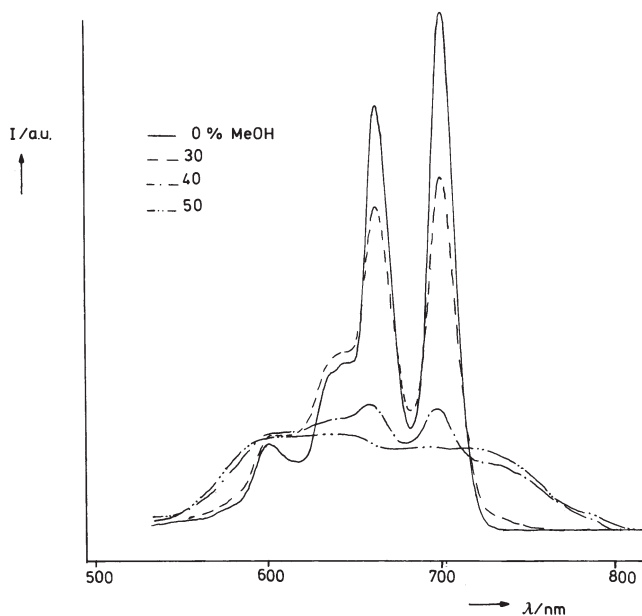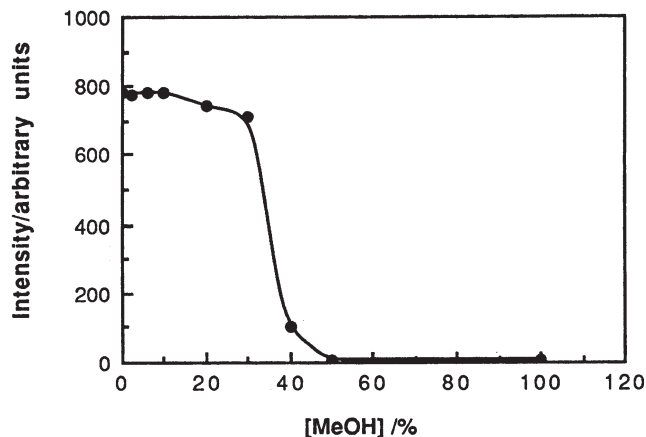

Figure 14. Decrease in emission intensity as a function of methanol content for compound **1** (*n*=10).

independent of methanol content. The residual emission intensity present when the methanol concentration exceeds 30 per cent v/v, has an excitation spectrum identical to that of the monomer species, indicating that the aggregated species does not emit. This conclusion is in line with aggregation studies of dinuclear, tetranuclear, and polynuclear Pc's [47, 48], and studies of cation-induced dimerization [49]. The near absence of emission intensity of the aggregates might be caused by more efficient self-quenching through several possible mechanisms including relaxation to triplet states [49] and nonradiative vibrational relaxation.

5.2. *Concentration study*

The absorption properties of the metal free derivatives **1** (*n*=8, 10, 12) have been studied in chloroform over the concentration range 6×10^{-4} to 10^{-6} mol/dm³. Within the concentration range studied, no significant changes in the absorption spectra occur and the species exhibit spectral typical of mononuclear Pc's. In contrast to this the luminescence spectra undergo a dramatic change upon increasing concentration. The emission maximum at λ_1 undergoes a red shift and the intensity of the emission spectra increases over the concentration range 10^{-6} and 10^{-5} mol/dm³. When the concentration is raised further the emission intensity decreases drastically, indicating that absorption processes become dominant. Simultaneously, the higher wavelength band becomes more dominant, the same behaviour is observed for the other homologues studied here. Similar effects have been observed by Knoesel *et al.* for $H_2Pc(CH_2OC_{12}H_{25})_8$ in benzene and 1-chloronaphthalene solution [51]. These authors interpret their observations in terms of aggregation of Pc-species. Aggregation is, however, not indicated by the absorption spectra. In line with the change in fluorescence

Figure 13. UV/Vis absorption spectra of **1** (*n*=10) in chloroform and in mixtures with increasing amounts of methanol: 0 per cent, 30 per cent, 40 per cent and 50 per cent, concentration of **1** is 1×10^{-6} mol/dm³.

characteristics upon aggregate formation when the solvent polarity is increased, a more feasible explanation might be based on reabsorption of emitted fluorescence intensity. Figure 15 shows that the absorption spectrum overlaps those luminescence bands which decrease in intensity upon increasing concentration.

6. Electrical conductivity

The electrical properties of phthalocyanine **2** were studied for $n=8$ and $n=12$ on pressed pellets by complex impedance measurements as described previously [52]. Measurements on pressed pellets were possible because of the very high viscosity of the mesophase, although some difficulties were encountered in maintaining good contacts. Electronically conducting CuPc was used as a reference compound. Figure 16 shows some typical impedance spectra taken at various temperatures for the derivative with $n=12$, similar spectra were obtained for the derivative with $n=8$.

The equivalent circuit to which the spectra could be fitted appear to be a *RCQ*-parallel. Here *R* is the resistance of the bulk material, *C* is the geometric capacitance and *Q* is a constant phase element $Q=Q_0 (i\omega)^\alpha$ where ω stands for frequency. The capacitance was almost constant for these experiments. From the formula for a plane plate capacitor $C=\varepsilon_0\varepsilon_r A/d$ the relative dielectric constant ε_r was calculated. In the columnar mesophase, the conductivity increases with increasing temperature, this behaviour is characteristic for semiconductive materials. The corresponding
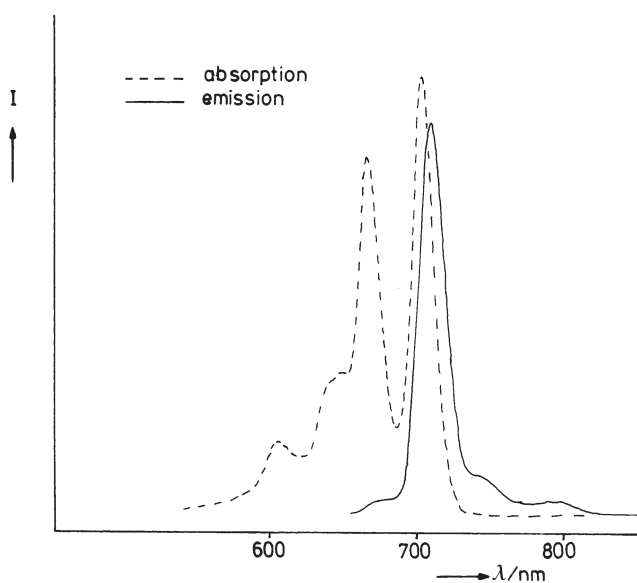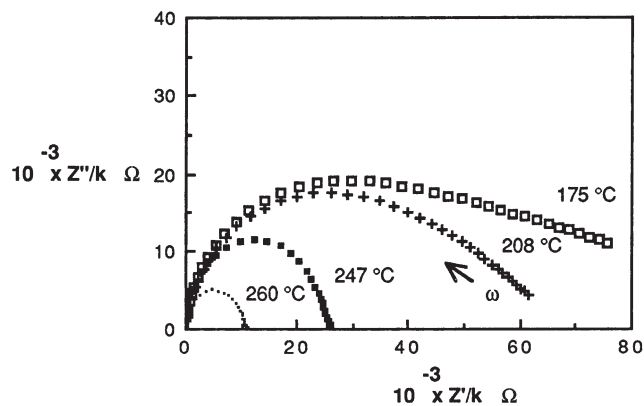

Figure 16. Impedance spectra as observed for compound **2** ($n=12$) at 175, 208, 247 and 260°C.

Arrhenius plots were constructed according to $\sigma=\sigma_0 \exp(-E_a/kT)$ and straight lines were obtained between 150 and 265°C for $n=8$. For $n=12$ a discontinuity in the Arrhenius plot (see figure 17) appears at approximately 250°C indicating a transition between an intrinsic transport regime at high temperatures (with a high activation energy) and an extrinsic one (with a lower activation energy) at low temperatures [53]. Extrinsic charge transport is found in most Pc's and is caused by the presence of trace impurities [53]. Upon going from the solid to the mesophase a slight decrease in conductivity was observed. The electrical conductivities at 175°C, activation energies for conduction and the preexponential factors σ_0 are presented in table 2. Conductivities found at 175°C are in the same range as for CuPc [54]. The activation energies are of the same order of magnitude as those found in columnar phases of hexa-*n*-alkoxytriphenylenes [55]. The activation energies given in table 2 are lower than those of the unsubstituted crystalline compounds. This difference

Figure 15. Fluorescence ($\lambda_{exc}=300$ nm) and absorption spectra of compound **1** ($n=10$) in chloroform solution, showing their overlap.
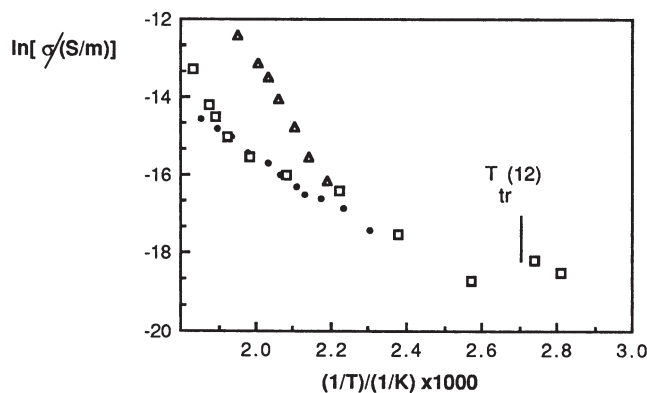

Figure 17. Arrhenius plots of the conductivity for CuPc, $\triangle$, and compounds **2** for $n=8$ denoted by ● and 12 represented by □.

Table 2. Electrical conductivity σ and relative dielectric constants at 175°C, activation energy of conduction and preexponential factors for $CuPcR_8$.

R	$\sigma_{175}/S\,m^{-1}$	$\varepsilon_r(175°C)$	E_a/eV	$\ln[\sigma_0/S\,m^{-1}]$
H	6×10^{-8}	6.8‡	1.4	20.0
$-OC_8H_{17}$	5×10^{-8}	8.2	0.6	2.6
$-OC_8H_{17}+I_2$†	3×10^{-3}	–	–	–
$-OC_{12}H_{25}$	7×10^{-8}	8.8	$T<250°C$: 0.5	4.7
			$T>250°C$: 1.7	21.6

†Measured at 40°C. ‡See [57].

might also be the result of a better orbital overlap between the Pc units in a stack, resulting in a substantial lowering of the gap between the valence and conduction bands of the material. This conclusion is in line with time resolved microwave conductivity measurements which have been performed on these compounds [56]. According to the work of Belarbi *et al.* [17] an activation energy of approximately 0.5 eV corresponds to intercolumnar electron hopping. Conductivities of both compounds studied are of the same order of magnitude within experimental error, indicating that bulk conductivity is not much dependent of side chain length.

Doping of molecular materials by strong electron donors or acceptors is expected to increase the conductivity, since free electrons or holes, respectively, are created in the conduction and valence bands. Doped samples were prepared by placing powdered **2** ($n=8$) in an iodine atmosphere for two to three days. The molar ratio of **2** ($n=8$) to I_2 was determined to be 1 to 1 by weight and by TGA. After this treatment the conductivity increases by at least four orders of magnitude (see table 2).

7. Conclusion

Two series of octa-*n*-alkoxyphthalocyanines have been synthesized. In the solid state these compounds are arranged in an orthorhombic lattice with four molecules per unit cell. At higher temperatures this lattice is converted to a hexagonal ordered columnar D_{ho} mesophase for all the compounds studied. Comparison of absorption and fluorescence measurements in solution have shown that in the concentration range 6×10^{-4} to 10^{-6} mol/dm^3, aggregation is not important. Conductivities of the derivatives with $n=8$ and $n=12$ have been determined and are of the order of 5×10^{-8} S/m. A slight decrease in conductivity is observed when going from crystal to mesophase. The activation energies for conduction are approximately 0.5 eV between 100 and 250°C. These low values might be related to an increased π–π overlap with respect to unsubstituted CuPc within a columnar stack.

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