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# SUPRAMOLECULAR ASSEMBLIES FROM LIQUID-CRYSTALLINE PHTHALOCYANINES

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Abstract Some novel liquid crystalline phthalocyanines form extraordinary supramolecular structures. These include an amphiphilic phthalocyanine displaying lyotropic as well as thermotropic behavior, a chiral phthalocyanine forming a helical mesophase at room temperature, and a liquid crystalline phthalocyanine containing crown ether rings which forms large columnar aggregates in solution. All these compounds can be used to prepare Langmuir-Blodgett films with varying arrangements of the molecules.

## 1. INTRODUCTION

Liquid crystalline phthalocyanines (LC Pcs) were prepared for the first time about fifteen years ago.[1] Since then they have been widely investigated, most of the studies being related to the one-dimensional semiconducting properties of these molecules. The discotic phthalocyanines in the mesophase are stacked to form columns, which can be considered as being supramolecular wires[2] because charge can travel through the stacks by a hopping process.[3] In general, the molecules, *e.g.* **1** (Figure 1), are provided with alkyl chains at their peripheral positions, which not only serves to induce LC behavior, but also creates a conduction barrier around the phthalocyanine cores. The effects of structural modifications in these side chains on the phase behavior and conducting properties have been investigated by Schouten *et al.*[3]

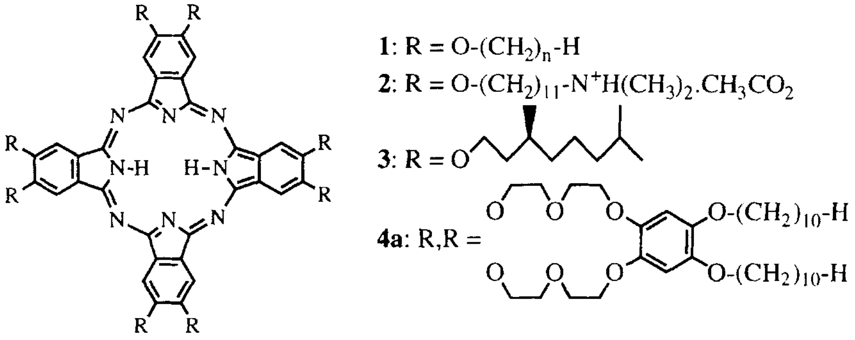


FIGURE 1 Liquid crystalline phthalocyanines discussed in this paper.

Recent work in our laboratory[4] aims at the preparation of novel LC Pcs in which special functionalities are introduced. This paper describes how these functionalities are responsible for the formation of interesting supramolecular architectures such as columnar aggregates in solution, monolayers at the air-water interface, ion channels, and a chiral mesophase.

## 2. AMPHOTROPIC PHTHALOCYANINE [5]

### 2.1. Phase behavior

Phthalocyanine **2** (Figure 1) contains amphiphilic side chains, *i.e.* lypophilic alkyl chains terminating in a polar head group. The thermotropic LC behavior of this compound (Table I) does not appreciably deviate from that of unfunctionalized alkoxy substituted Pcs, apart from a minor phase transition from an as yet unknown mesophase (M) to the common hexagonal columnar mesophase ($D_h$).

TABLE I Transition temperatures ($T_{tr}$/°C) of the Pcs discussed in this paper.[a]

| Comp. | phase | $T_{tr}$ | phase | $T_{tr}$ | phase | $T_{tr}$ | phase |
|---|---|---|---|---|---|---|---|
| **1**(n=12) | K | 83 | $D_h$ | | | 309 | I |
| **2** | K | 73 | M | 89 | $D_h$ | 270 | I |
| **3** | G | 14 | $D_h^*$ | 111 | $D_r$ | 295 | I |
| **4a** | K | 148 | $D_h$ | | | | |

[a] $T_{tr}$ observed on heating; K=crystalline, M=mesophase, $D_h$=hexagonal columnar, $D_h^*$=chiral hexagonal columnar, $D_r$=rectangular columnar, I=isotropic, G=glass.

### 2.2. Properties

The presence of polar ammonium acetate groups in **2** makes the compound soluble in water. The UV/Vis spectrum of an aqueous solution of **2** showed that the molecules are highly aggregated. From the blue shift of the absorption maximum an aggregation number of 24 was calculated. It is believed that the hydrophobic cores of the molecules self-assemble in water to form columnar stacks, while the ammonium groups constitute a hydrophilic shell.

Another interesting property of **2** is the fact that it forms a lyotropic mesophase at high concentrations in water at room temperature. Probably the columnar aggregates are elongated at high concentration, the surrounding water molecules providing these assemblies with enough flexibility to form a mesophase.

### 2.3. Monolayer behavior

The free base derivative of **2** forms a monolayer at the air-water interface. According to the surface pressure - surface area isotherm three different conformations are possible, depending on the applied surface pressure. The conformation at low surface pressure, with the molecules entirely parallel to the water surface, is not stable. The monolayer with the side chains oriented perpendicularly to the water surface could be transferred onto hydrophobized glass by a Z-type deposition (only transfer at vertical upstroke movement of the substrate).

## 3. OPTICALLY ACTIVE PHTHALOCYANINE [6]

### 3.1. Phase behavior and mesophase structure

Phthalocyanine **3** (Figure 1) is a compound with eight chiral centers each of them having the (*S*)-configuration. This optically active compound displays a phase behavior that is entirely different from that of Pcs with unbranched side chains (Table I). First of all, **3** shows no crystalline phase. A mesophase is present at room temperature whose structure freezes into a glass when cooled down. On heating, a phase transition to a second mesophase is observed before the compound becomes isotropic. The room temperature mesophase has an unprecedented structure. According to polarizing microscopy, X-ray diffraction, and circular dichroism studies, the molecules are stacked in a left-handed helix with a pitch of ca. 57 Å. The most probable structure of this helix is shown in Figure 2.

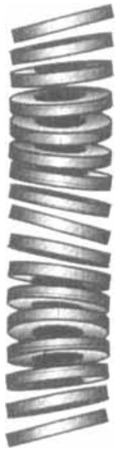


FIGURE 2 Structure of the helical mesophase formed by **3**.

### 3.2. Properties

Two properties of compound **3** have been studied in detail, *viz.* the one-dimensional transport of energy and the transport of charge. The results can be summarized as follows. Due to the fact that the molecules are cofacially stacked in the mesophase at ambient and lower temperatures, fast energy migration is possible over a wide temperature range, as judged from luminescence spectroscopy studies. Energy migration is known to be delayed in the crystalline phase of other mesogenic Pcs. On the contrary, the intracolumnar hopping of charges in Pcs is more favorable in the more rigid crystalline phase than in the mesophase.[3] As a consequence, similar high conduction levels as reported for crystalline Pcs can not be reached with compound **3**. Moreover, it was found that the conductivity of **3** is even further decreased due to the helical distortion of the columnar stacking.

### 3.3. Monolayer behavior

The surface pressure - surface area isotherm of **3** on a water subphase is shown in Figure 3. Two phase transitions can be seen in this figure. A monolayer is present at a low surface pressure, in which the molecules are oriented perpendicularly to the water surface. On decreasing the surface area, a transformation to a bilayer was observed. This bilayer was sufficiently stable to be uniformly transferred onto various substrates, via Y-type deposition. The columns in each layer of the resulting Langmuir-Blodgett film were preferentially oriented in the transfer direction.

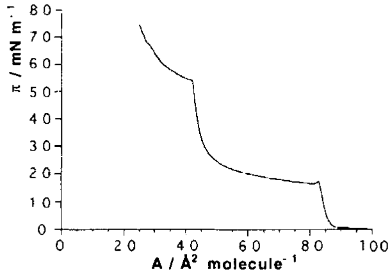
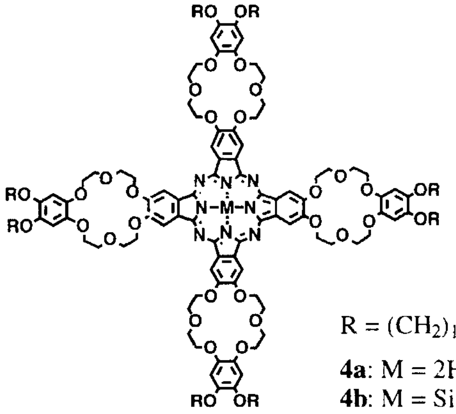


FIGURE 3 Surface pressure - surface area isotherm of phthalocyanine **3** on water.

## 4. CROWNED PHTHALOCYANINE [7]

### 4.1. Phase behavior

Crown ether substituted phthalocyanines are known for about ten years,[8] but apart from one claim of a metastable monotropic mesophase[9] they are in general not liquid crystalline. Therefore, compound **4a** was synthesized, which displayed a hexagonal columnar mesophase from 148 °C upto its decomposition temperature at 320 °C (the crystallization temperature was found to be at 105 °C).



$R = (CH_2)_{10}H$

**4a**: M = 2H

**4b**: M = $Si(OH)_2$

### 4.2. Properties

Compound **4a** is barely soluble in organic solvents, which was quite surprising since crown ether and alkoxy substituted Pcs are highly soluble compounds. When a boiling solution of **4a** in chloroform was cooled down to room temperature a gel was formed. The UV/Vis spectrum (Figure 4a) showed that the molecules are aggregated in the gel. From the concentration and temperature dependence of the absorption maximum it was calculated that the heat of association amounted to -125 kJ mol$^{-1}$, which is a rather high value. The structure of the gel in chloroform was investigated by atomic force and electron microscopy. A network of fibers was observed, in which micrometer long stacks of single molecular diameter were visible. Given the molecular structure of **4a**, each columnar stack can be considered as being a molecular cable (Figure 4b). The crown ether rings in this cable form channels through which small cations may migrate. Similar ion conducting channels were shown to be present in a polymeric crown ether substituted phthalocyanine.[10]

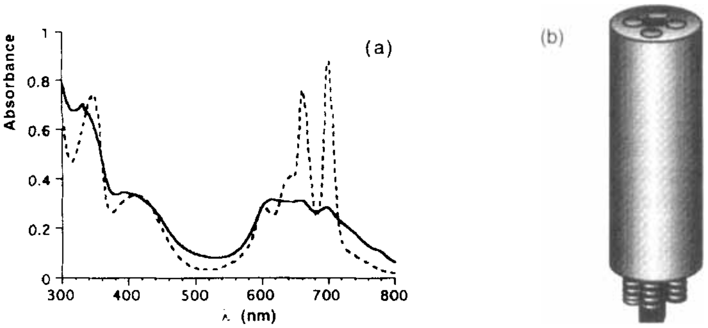


FIGURE 4 (a) Absorption spectra of **4a** in chloroform at 20 °C (gel, solid line) and 50°C (solution, broken line). (b) Structure of the columnar aggregates of **4a** in chloroform.

### 4.3. Monolayer behavior

Since **4a** easily forms aggregates in solution it cannot form a monolayer on a water surface. However, aggregation can be prevented by introducing a dihydroxysilicon group in the center of the phthalocyanine unit as in compound **4b**. The latter compound forms a stable monolayer at the air-water interface, in which the phthalocyanine and crown ether units are in contact with the subphase, while the alkoxy side chains are oriented perpendicularly to the water surface. This monolayer could be transferred onto a hydrophobic glass substrate via Y-type deposition. A special property of the monolayer is its capability to bind potassium ions that are present in the subphase, which could be detected by an increase in the area per molecule. From the cation concentration dependence of the area per molecule, a binding constant of 48 M$^{-1}$ was calculated. This value is close to the binding constant of the complex between potassium and dibenzo-18-crown-6 in water.

## 5. CONCLUDING REMARKS

This paper shows that various supramolecular structures can be constructed by modification of liquid crystalline phthalocyanines. One completely novel mesophase structure was obtained from a chiral phthalocyanine. Well-defined columnar aggregates are formed in solutions of an amphiphilic and a crown-ether substituted phthalocyanine. Such supramolecular aggregates are of interest for future applications as energy guides or as conducting supramolecular wires if they can be alligned or spatially situated.

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