

SUPRAMOLECULAR ARCHITECTURES FROM PHTHALOCYANINE BUILDING BLOCKS

C.F. van Nostrum and R.J.M. Nolte*

Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

Abstract: Different procedures for preparing columnar stacks and layered structures from phthalocyanine molecules are presented and discussed, including organization of the molecules by one of the following means: (i) with the help of liquid crystallinity, (ii) by using crown ether rings attached to the phthalocyanine core, (iii) by polymerization, and (iv) by Langmuir-Blodgett film formation.

INTRODUCTION

Phthalocyanines (Pc's) are interesting building blocks for the construction of molecular materials with special optical and electrical properties.¹ To prepare these molecular materials the Pc molecules must be organized to form well-defined (supra)molecular structures, *e.g.* one-dimensional stacks, which can conduct electrons in the stacking direction.² In this review we describe some examples of supramolecular phthalocyanine architectures which we have recently constructed, with the aim of developing low-dimensional conductors.

1. LIQUID CRYSTALLINE PHTHALOCYANINES

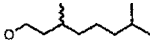
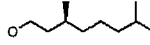
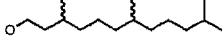
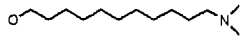
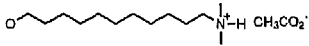
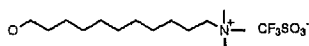
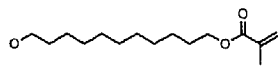
Mesogenic properties

Phthalocyanines peripherally substituted with long hydrocarbon chains form discotic mesophases. The transition temperature from the solid to the mesophase as well as the liquid-crystalline arrangement of the molecules depend on the nature of the substituents.

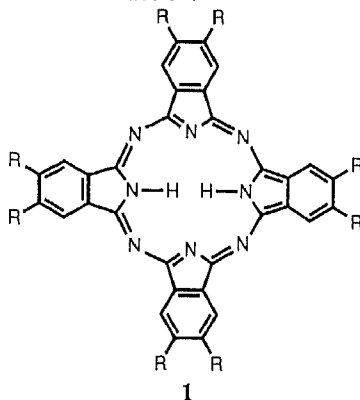
A selection of liquid-crystalline Pc's we have studied is presented in Table 1, together with the phase transitions that have been observed. The Pc's **1a(n)** which are substituted with linear chains (n=6-12) show phase transitions from the crystalline to the mesophase between 80 and 120 °C.³ The mesophase consists of hexagonally arranged, ordered (D_{h0}) columns. The Pc molecules are closely packed with their planes perpendicular to the column axis (Figure 1). The intracolumnar distance

between the molecules is 3.4 Å, close to the VanderWaals distance of aromatic molecules.

Table 1: Phase transitions of some alkoxy substituted Pc's

Compound	R	Phase transition ^a	Ref.
1 a(n)	OC _n H _{2n+1}	K.80-120.D _{ho}	3
1 b		K.70.D _{hd} .295.I	4
(S)-1 b		?16.D _{ho} *.111.D _γ .295.I	5
1 c		D _{ho} .34.D _{hd} .173.D _γ .185.I	4
1 d		K.79.D.265.I	-
1 d-acetate		K.71.D _{ho} .270.I	-
1 e		not determined	-
1 f		K.54.D _{ho}	6

^a The transition temperatures (°C) are determined by DSC and optical microscopy. The structures of the different phases are established by small angle X-ray powder diffraction.



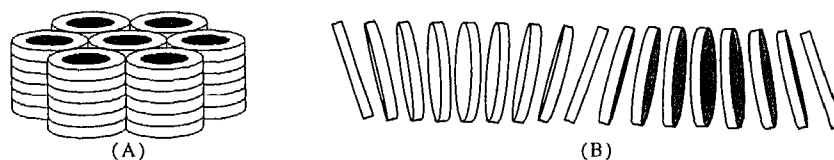


Fig. 1: Structure of the D_{h0} (A) and chiral D_{h0}^* (B) mesophase.

Pc's with branched alkoxy chains (compounds **1b** and **1c**) were found to have liquid-crystalline properties different from those of **1a(n)** (see Table 1).⁴ However, Pc's **1b** and **1c** are mixtures of a large number of stereoisomers, due to the presence of chiral carbon atoms in the chains. For example, **1b** is a mixture of 16 enantiomers and 11 meso forms. In order to avoid this complication, we synthesized the optically pure compound (*S*)-**1b** and found that the phase transitions displayed by this compound are very different from those of the mixture of stereoisomers (Table 1).⁵ From X-ray diffraction measurements we were able to derive for (*S*)-**1b** a D_{h0}^* phase at 80 °C. Additional X-ray reflections were observed, which can be explained by assuming an extra periodicity of 55 Å (16 molecules) in the direction of the columnar axis. This extra periodicity is probably the result of a helical distortion of the columns (Figure 1b). The presence of a helix structure was confirmed by the fact that a thin solid film of (*S*)-**1b** showed a circular dichroism spectrum.

Phthalocyanines **1d** and **1e** contain dimethylamino and trimethylammonium functions at the end of their aliphatic side chains and were shown to form lyotropic liquid crystalline phases. The UV-vis spectrum of **1d** in 10% aqueous acetic acid solution displays a broad absorption maximum at ~600 nm which is absent in a chloroform

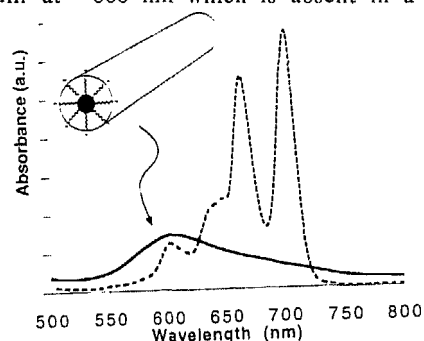


Fig. 2: Absorption spectra of **1d** in 10% aqueous acetic acid (—), and in chloroform (---). Inset: Structure of the rod-like micelle formed from **1d**-acetate and **1e** in water.

solution of this compound (Figure 2), indicating that the molecules of **1d** are strongly aggregated in dilute acetic acid. The critical aggregate concentration was determined to be 3.4×10^{-7} M, which is an extremely small value. Electron microscopy suggests that rod-like micelles are present in solution (Figure 2), which have further aggregated to supramolecular structures. Similar results were obtained for **1e**.

Intra-columnar charge transport

Charge migration in the above-mentioned stacks of Pc's was measured by pulse radiolysis time-resolved microwave conductivity (PR-TRMC) measurements.⁷ With this method low concentrations of free charge carriers are created by a short pulse of high energy electrons. The mobility of these charge carriers is monitored by the absorption of microwave power. For the alkoxy substituted Pc's a decrease in the microwave conductivity was found at the crystalline to mesophase transition,⁸ a result of an increase in molecular motion, which is unfavorable for charge carrier migration within the columns.

The optically pure (*S*)-**1b** displays a microwave conductivity that is lower than the conductivity of the mixture of stereoisomers **1b**,⁵ which suggests that the helical distortion of the columns lowers the one-dimensional charge migration.

Molecular dynamics

¹³C solid state NMR experiments have been performed on compounds **1a**(11), **1a**(12) and (*S*)-**1b** to investigate the molecular interactions and the molecular motions in the mesophases of these compounds. A reduction of the heteronuclear dipolar interaction of the aromatic core carbons with neighboring protons was observed indicating that in the mesophase the Pc molecules rotate around their columnar axes.⁹ The frequency of this molecular rotation was observed to be 5 kHz.¹⁰ The alkoxy chains were found to be very mobile in the mesophase, displaying a liquid-like order.

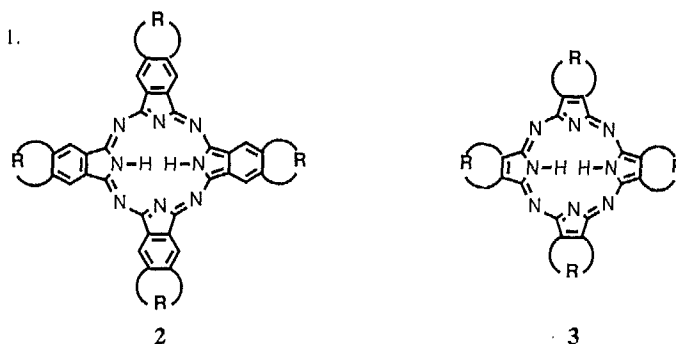
2. CROWN ETHER PHTHALOCYANINES AND PORPHYRAZINES

Structure of metal complexes

Crown ether rings attached to the Pc core can assist in the creation of supramolecular structures. We have shown that the crown ether substituted Pc's **2a**(n) (Chart 1) form aggregates in the presence of alkali metal salts.¹¹ The structure and conductivity of these complexes depend

on the type of metal ion (Figure 3). Rb^+ ions give rise to extended stacks with relatively high a.c. conductivities. The divalent Ba^{2+} ion causes the formation of networks, which have a low conductivity.

Chart 1.



Compound	R	Ref.
2a(n)	$n=3-5$	11
2b		-
3a(n)	$n=3,4$	12
3b(n)	$n=0,2$	-

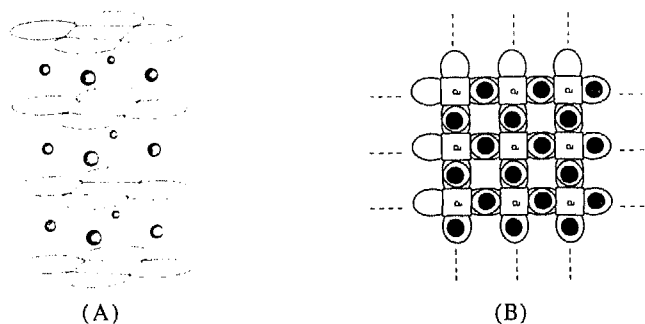
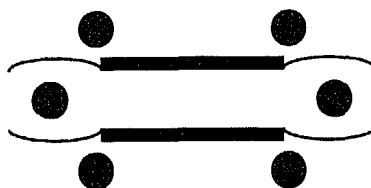


Fig. 3. Schematic structures of complexes of Pc 2a(4): (A) with Rb^+ picrate, (B) with Ba^{2+} picrate.

The porphyrazines (Pp's) **3a(n)** and **3b(n)** with sulfur containing crown ether rings attached to the aromatic cores are able to complexate silver and mercury ions.¹² The structure proposed for a dimer formed from **3a(4)** and silver perchlorate in a 5% methanol/chloroform solution is shown in Figure 4.

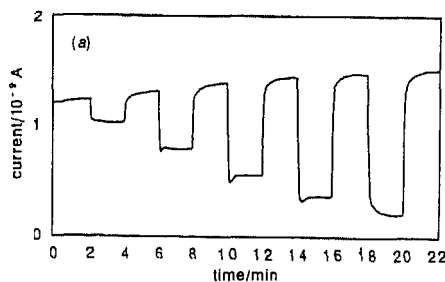
Fig. 4. Schematic cross-section of the proposed structure of the dimeric complex of **3a(4)** with silver perchlorate.



Crown ether phthalocyanines as a gas sensor

It is well known that semiconductors, including Pc's can be used as gas sensor materials.¹ This property results from the change in conductivity that occurs when electron donating or electron accepting gasses are absorbed on these materials. Casted films of the crown ether Pc's **2a(n)** treated with potassium chloride showed remarkably good gas sensing properties.¹³ A very fast response and a good reversibility was observed on exposure of the sensor to 1-5 ppm NO₂ in air, and subsequent exposure to clean air (Figure 5). The signal has an almost linear dependence on the gas concentration. These unprecedented gas sensing characteristics are probably the result of the high degree of order present in the crown ether Pc complexes.

Fig. 5. Conductivity changes of KCl treated Pc **2a(5)** exposed to five NO₂ concentration cycles of 1-5 ppm in clean air.



3. POLYMERIC PHTHALOCYANINES

We have synthesized polysiloxanes from the dihydroxysilicon derivatives of **1a(n)** and **2a(n)**.^{14,15} These polymers contain a linear chain of stacked Pc molecules (Figure 6A). Polysiloxane-**1a(n)** is soluble

in organic solvents and conducts electrons. The polymer derived from **2a**(5) was shown to be an electron conductor as well as an ion conductor.¹⁵

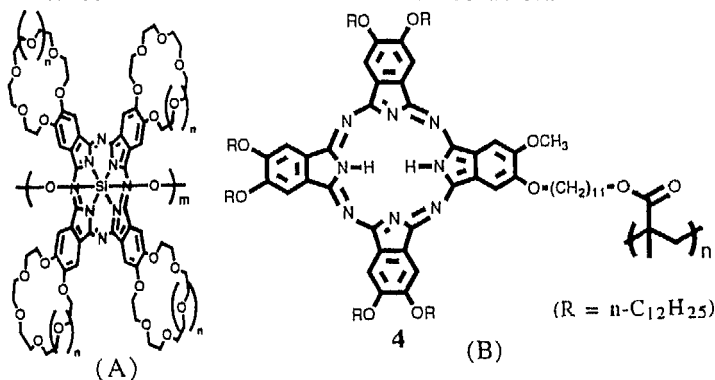


Fig. 6. Molecular structure of a phthalocyanine polysiloxane (A) and a polymethacrylate containing phthalocyanine side chains (B).

Other types of polymers have been obtained from Pc's with alkoxy chains terminating in acrylate or methacrylate functions. For instance, radical polymerization of compound **1f** in the mesophase resulted in a highly cross-linked network polymer.⁶ The value of the electrical conductivity of this network was 2 orders of magnitude higher than that of **1a**(12). Polymerization of a Pc with one methacrylate function gave a linear side chain polymer (**4**, Figure 6B).¹⁶ Both poly-**1f** and **4** retain their liquid crystalline (D_{h0}) structures upon cooling to room temperature, as was shown by X-ray diffraction measurements.

4. LANGMUIR-BLODGETT FILMS

Certain substituted monomeric and polymeric Pc's are known to form stable monolayers at the air-water interface.¹ These can be transferred layer by layer onto solid substrates to give Langmuir-Blodgett (LB) films, in which the Pc molecules are uniformly oriented. The monolayer properties and preparation of LB films of some of the previously mentioned Pc's have been investigated in detail.

Compound (*S*)-**1b** forms a monolayer at the air-water interface that can be transferred onto hydrophobic glass slides.⁵ The Pc molecules are oriented edge-on with respect to the water surface. Spectroscopic studies indicate that in the multilayer sample of (*S*)-**1b** the director on the Pc rings is aligned parallel to the transfer direction.

Phthalocyanine **1d** also forms stable monolayers. In this case the molecules have a side-on orientation with respect to the water surface (see pressure-area isotherm, Figure 7). Transfer onto hydrophobic glass is also possible for **1d**.

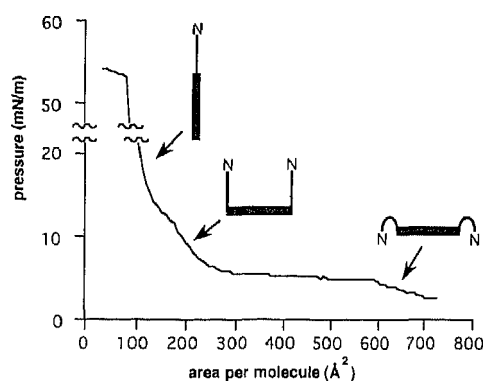


Fig. 7. Pressure-area isotherm of **1d** and proposed molecular conformations in the different phases.

The crown ether Pc **2a(4)** is too soluble in water to form monolayers. However, compound **2b** (Chart 1), which contains additional decoxy chains attached to the crown ether moieties, gives a stable monolayer that can be transferred. Both pressure-area isotherms (area per molecule = 230 \AA^2) and infrared spectroscopy studies reveal that the molecules of **2b** adopt a side-on orientation on the water surface. The monolayers of **2b** are able to bind alkali metal ions.

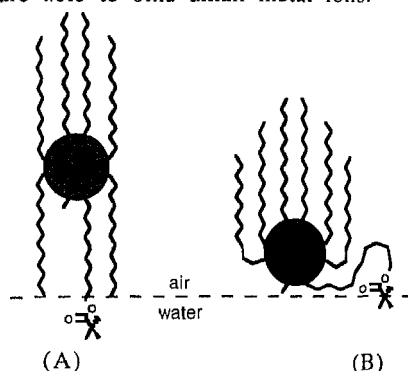


Fig. 8. Schematic representation of the conformation of a polymer repeating unit of poly-4 at the air-water interface: (A) in a non-expanded monolayer; (B) in an expanded monolayer.

Side-chain polymer poly-4 displays interesting properties at the air-water interface.¹⁷ A monolayer of this polymer is not stable, but expands slowly with time. The Pc molecules in the monolayer have an edge-on orientation, which remains the same after expansion. Spectroscopic data indicate that the expansion is the result of a change in conformation of the alkoxy chains on the Pc rings (Figure 8). The poly-4 monolayer can be deposited on various substrates if it is mixed with arachidic acid.

CONCLUSIONS

Various methods are now available to construct supramolecular structures from phthalocyanine molecular units. The next step will be complete control over the organization of the systems and fine-tuning of the properties of the materials, allowing for the development of novel molecular devices. Work along these lines is in progress in our laboratory.

ACKNOWLEDGMENT

We acknowledge important contributions from Drs. A.P.M. Kentgens, A.J. Schouten, P.G. Schouten, J.M. Warman, J.F. van der Pol, O.E. Sielcken, J.D. Wright and Professor W. Drenth.

REFERENCES

- (1) C.C. Leznoff, A.B.P. Lever (eds.), Phthalocyanine. Properties and Applications, VCH Publishers; New York (1989)
- (2) R.J.M. Nolte, W. Drenth, in Inorganic and Organometallic Polymers with Special Properties, R.M. Laine (ed.), Kluwer Academic Publishers, pp. 223-239 (1992)
- (3) J.F. van der Pol, E. Neeleman, J.W. Zwikker, R.J.M. Nolte, W. Drenth, J. Aerts, R. Visser, S.J. Picken, Liq. Cryst. **6**, 577 (1989)
- (4) P.G. Schouten, J.F. van der Pol, J.W. Zwikker, W. Drenth, S.J. Picken, Mol. Cryst. Liq. Cryst. **195**, 291 (1991)
- (5) C.F. van Nostrum, A.W. Bosman, G.H. Gelinck, S.J. Picken, P.G. Schouten, J.M. Warman, A.J. Schouten, R.J.M. Nolte, J. Chem. Soc. Chem. Commun., submitted for publication
- (6) J.F. van der Pol, E. Neeleman, J.C. Miltenburg, J.W. Zwikker, R.J.M. Nolte, W. Drenth, Macromolecules **23**, 155 (1990)

- (7) J.M. Warman, de Haas, Pulse Radiolysis of Irradiated Systems, Reidel; Dordrecht, The Netherlands, pp. 129-161 (1982)
- (8) P.G. Schouten, J.M. Warman, M.P. de Haas, J.F. van der Pol, J.W. Zwikker, J. Am. Chem. Soc. **114**, 9028 (1992)
- (9) A.P.M. Kentgens, B.A. Markies, J.F. van der Pol, R.J.M. Nolte, J. Am. Chem. Soc. **112**, 8800, (1990)
- (10) A.W. Bosman, A.P.M. Kentgens, R.J.M. Nolte, to be published
- (11) O.E. Sielcken, W. Drenth, R.J.M. Nolte, Recl. Trav. Chim. Pays-Bas **109**, 425 (1990)
- (12) C.F. van Nostrum, F.B.G. Benneker, R.J.M. Nolte, J. Chem. Soc. Chem. Commun., submitted for publication
- (13) P. Roisin, J.D. Wright, R.J.M. Nolte, O.E. Sielcken, S.C. Thorpe, J. Mater. Chem. **2**, 131 (1992)
- (14) J.F. van der Pol, J.W. Zwikker, J.M. Warman, M.P. de Haas, Recl. Trav. Chim. Pays-Bas **109**, 208 (1990)
- (15) O.E. Sielcken, L.A. van de Kuil, W. Drenth, J. Schoonman, R.J.M. Nolte, J. Am. Chem. Soc. **112**, 3086 (1990)
- (16) J.F. van der Pol, E. Neeleman, R.J.M. Nolte, J.W. Zwikker, W. Drenth, Makromol. Chem. **190**, 2727 (1989)
- (17) C.F. van Nostrum, R.J.M. Nolte, M.A.C. Devillers, G.T. Oostergetel, M.N. Teerenstra, A.J. Schouten, Macromolecules, in press