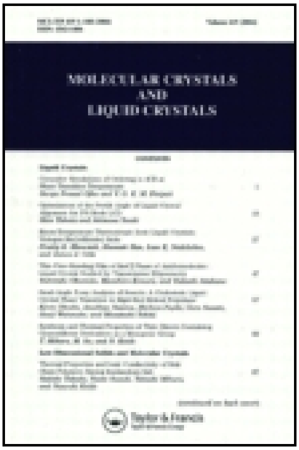


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Charge Migration in Supramolecular Stacks of Porphyrins and Phthalocyanines

Pieter G. Schouten [a], John M. Warman [a], Matthijs P. De Haas [a], Horn-Long Pan [b] & Marye Anne Fox [b]

[a] Radiation Chemistry Department, IRI, Delft University of Technology, Mekelweg 15, 2629, JB Delft, The Netherlands

[b] Department of Chemistry, University of Texas, Austin, Texas, 7812, USA

Version of record first published: 05 Dec 2006.

To cite this article: Pieter G. Schouten, John M. Warman, Matthijs P. De Haas, Horn-Long Pan & Marye Anne Fox (1993): Charge Migration in Supramolecular Stacks of Porphyrins and Phthalocyanines, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 235:1, 115-120

To link to this article: http://dx.doi.org/10.1080/10587259308055182

Mol. Cryst. Liq. Cryst. 1993, Vol. 235, pp. 115–120
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CHARGE MIGRATION IN SUPRAMOLECULAR STACKS OF PORPHYRINS AND PHTHALOCYANINES

PIETER G. SCHOUTEN*, JOHN M. WARMAN*, MATTHIJS P. DE HAAS*,
HORN-LONG PAN+ AND MARYE ANNE FOX+
* Radiation Chemistry Department, IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.
+ Department of Chemistry, University of Texas, Austin, Texas 7812, USA

Abstract Information on the factors controlling the mobility of charge carriers in columnar aggregates of aromatic macrocycles is obtained from studies of the radiation-induced and dark microwave conductivity.

INTRODUCTION

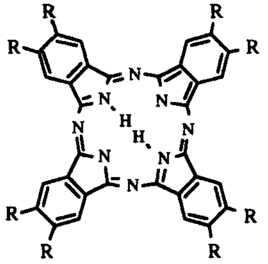
Porphyrin (P) and phthalocyanine (Pc) macrocyclic moieties tend to form columnar stacks in the solid phase. When long aliphatic chains are substituted at the periphery of the macrocycles the stacked molecules in many cases do not melt directly to an isotropic liquid, where all the structural order is lost, but first form a liquid crystalline phase over a rather large temperature range.[1,2] In this mesophase the columnar structure is preserved but there is more motional freedom since the hydrocarbon chains are completely molten.

As has been recognized the close packed aromatic macrocycles are capable of conducting charge along the columnar axis due to the π-π overlap. With the increased tractability of the liquid crystalline material, the fabrication of one dimensional organic conductors which could serve as molecular wires in future molecular electronic devices becomes possible.

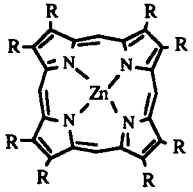
In our group we are attempting to obtain a fundamental understanding of charge carrier migration and recombination within these self-organizing aggregates in relation to microscopic details of their molecular structure. The introduction of charge carriers by chemical doping is often accompanied by structural changes making it difficult to obtain an insight into the conductive properties of the unperturbed material.[3] To circumvent this problem we make use of the ionizing power of high energy radiation to produce low concentrations, less than 10 μM, of charge carriers in the undoped materials. After a nanosecond pulse of the radiation, changes in the conductivity due to the presence of mobile charge carriers are monitored using the time resolved microwave conductivity (TRMC) technique.

EXPERIMENTAL

The compounds studied in the present paper are shown in figure 1. Small angle X-ray scattering, differential scanning calorimetry and polarization microscopy show that the molecules stack in columns both in the solid (K) and the mesophase (M).[2,4] On heating, the mesophase is entered at 91 °C for **1**, at 79 °C for **2** and at 102 °C for **3**. On further heating **2** and **3** reach an isotropic phase at 260 °C and 152 °C respectively while for **1** decomposition of the material occurs prior to melting at 290 °C.



R = $-O-C_{12}H_{25}$ **1**
R = $-CH_2-O-C_{12}H_{25}$ **2**



R = $-CH_2CH_2-O-C_9H_{19}$ **3**

FIGURE 1 The compounds studied in the present work

Indexation of the X-ray reflections for **1**[4] shows the columns to be packed in an orthorhombic lattice in the solid. In a column the molecules are tilted with a stacking period of 4.3 Å along the columnar axis. In the mesophase the orientation changes to horizontal stacking with a period of 3.4 Å. This detilting leads to a hexagonal packing of the columns with a center to center distance between the columns of 35 Å.

For **2**[4] the packing of the columns is also orthorhombic in the solid with a tilted 4.3 Å stacking period. In the mesophase Ohta et al.[4] report a hexagonal packing of the columns with an intercolumnar distance of 31 Å but without a 3.4 Å reflection. Weber et al.[5] have concluded that the molecules remain tilted in the mesophase with a (pseudohexagonal) orthorhombic lattice and a stacking period of 4.9 Å.

The absence of a 3.4 Å reflection for **3** was taken to indicate that the porphyrin moieties have a tilted conformation in both the solid and the mesophase similar to the alkoxymethyl Pc.[6] The shortest intercolumnar distance in the mesophase is 26.3 Å.[6]

To study the conductive properties the materials were irradiated with 3 MeV electrons from a Van de Graaff accelerator using pulses of 2-20 ns duration and beam currents up to 4 A. The energy deposited per unit volume within the sample, D, was 580 J/m^3 per nanocoulomb. Any change in the conductivity of the material was monitored using the time resolved microwave conductivity technique (TRMC) which has been fully described elsewhere.[7,8] Measurements were made in the 26.5 - 38 GHz region.

The background microwave conductivity without irradiation, σ_b, was measured by comparing the power reflected by the cell with and without the sample present. σ_b is related to the dielectric loss, ε'', by $\sigma_b = \omega\varepsilon_0\varepsilon''$ with ω the radian microwave frequency and ε_0 the permittivity of vacuum.

RESULTS

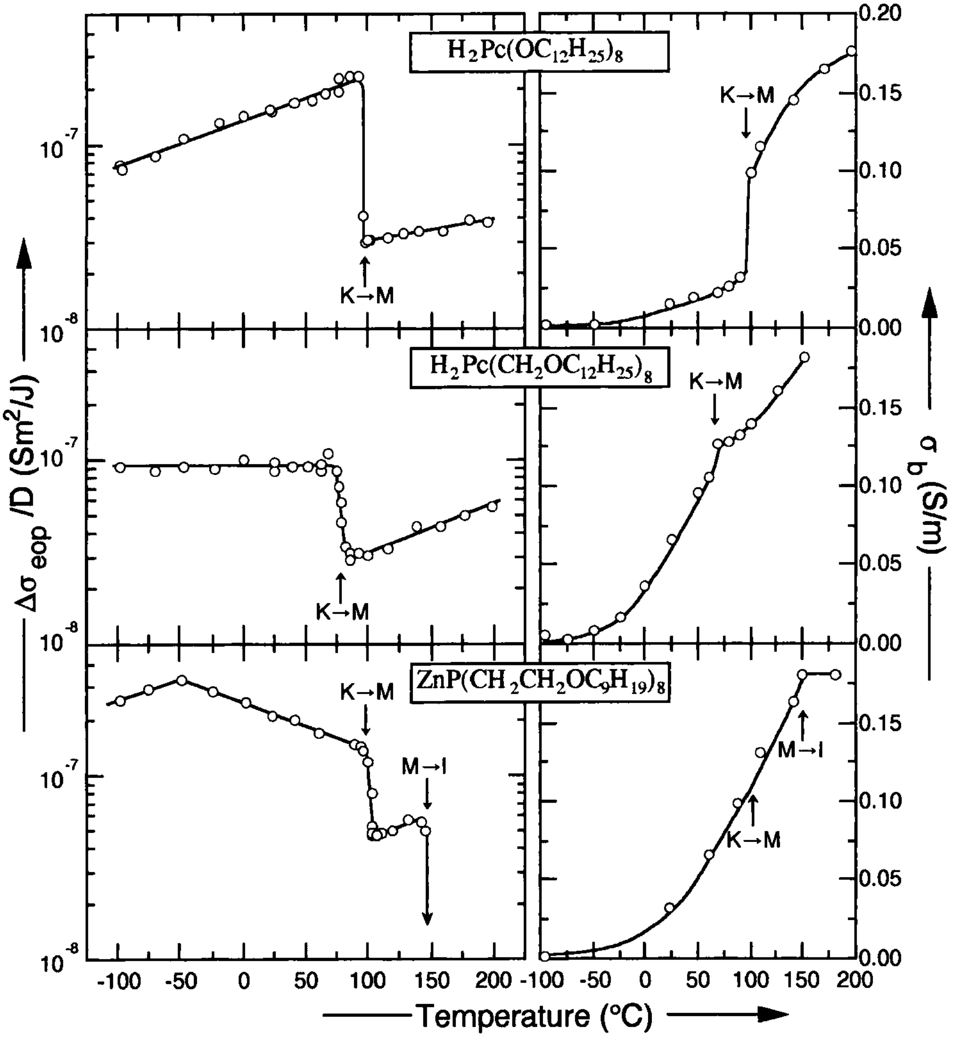


FIGURE 2 The temperature dependences (heating trajectory) of the radiation-induced conductivity per unit dose (left) and the dark, background microwave conductivity (right) of the compounds shown in figure 1

Background microwave conductivity

The temperature dependence of σ_b for the different compounds is shown in figure 2. For **1** a small σ_b is apparent which at the K→M transition increases abruptly by a factor of approximately 4.[9,10] For **2** σ_b is much larger than for the alkoxy derivative in the solid phase. At the K→M transition only a very small (ca 10%) sudden rise in σ_b is observed.

For **3** σ_b is similar in magnitude and temperature dependence to that for **2** compound. No discontinuity is however observed at the K→M phase transition. The background microwave conductivity of **3** is seen to remain at the same level in the isotropic phase after melting.

Radiation induced microwave conductivity

Upon pulsed irradiation the three compounds show large conductivity changes. The conductivity decays on a timescale much longer than the pulse width. In the present article we are concerned with the value of the change in conductivity at the end of the radiation pulse normalized to the dose, $\Delta\sigma_{eop}/D$.

In figure 2 the values of $\Delta\sigma_{eop}/D$ are plotted as a function of temperature. As can be seen a sudden drop in $\Delta\sigma_{eop}/D$ occurs for all three compounds at the K→M transition by approximately a factor of 8 for **1** and 3 for **2** and **3**. When the isotropic phase is entered for **3** at 150 °C the conductivity signal disappears completely.

While all the compounds show a gradual increase in $\Delta\sigma_{eop}/D$ with increasing temperature in the mesophase a marked difference in the temperature dependence is found in the solid state as can be seen in figure 2.

DISCUSSION

Background microwave conductivity

Even for large aromatic molecules such as phthalocyanines, the band-gap within the columnar cores of the stacked macrocycles is estimated to be as high as 2 eV.[11] As expected therefore these materials are insulators in their pure state with DC conductivities, even in the presence of oxygen, many orders of magnitude lower than the microwave conductivities found in the present work. It is unlikely therefore that the background conductivities observed are caused by the presence of thermally produced, highly mobile charge carriers. This conclusion is supported by results on materials for which the effect of complete melting can be studied, such as the present zinc-porphyrin.[6,10] The fact that σ_b remains unaffected by melting suggests that it is not related to charge carrier mobility since this would be expected to be greatly reduced on loss of long-range columnar order.

Because of the symmetry of the Pc and P moieties, any dipolar contribution to σ_b most probably arises from motional freedom of the ether coupling groups which have individual dipole moments of approximately 1.2 Debye.[12] The value of $\sigma_b \approx 0.1$ S/m found for all three compounds in their liquid crystalline phases corresponds to a dipole relaxation time of approximately 100 ps.[9]

The large values of σ_b for compounds **2** and **3** below T(K→M) indicate substantial freedom of movement of the ether groups even in the solid phase for which the motion of the alkyl tails is considered to be "frozen". The dipolar motion in compound **1** appears however to be substantially inhibited in the solid phase.

Radiation induced microwave conductivity

Evidence has been provided in previous publications[6,13,14] for a model which explains the long-lived radiation-induced conductivity transients found for the present type of materials. This involves ionization to form electron-hole pairs, e^--h^+, for some of which the electron and the hole become localized within the macrocyclic cores of separate columns. Charge recombination for these pairs is retarded by the intervening saturated hydrocarbon mantle resulting in the long (up to milliseconds) lifetimes observed. While localized within the core of a column the charge carriers can still display a high mobility by rapid one-dimensional motion along the core axis.

The absolute value of $\Delta\sigma_{eop}/D$ is related to the sum of the mobilities of the carriers, $\Sigma\mu$, and the average energy required to produce one charge carrier pair, E_p (in eV), by (1). For high energy radiation E_p is expected to be approximately 25 eV.[15] Since not all initial electron hole pairs will become separated on different columns[14], only a lower limit to $\Sigma\mu$, $\Sigma\mu_{min}$, is obtained

$$\Sigma\mu \geq E_p\, \Delta\sigma_{eop}/D = \Sigma\mu_{min} \qquad (1)$$

Values of $\Sigma\mu_{min}$ just below and above the K→M transition temperature are listed in table I

TABLE I Lower limits to the sum of the charge carrier mobilities ($10^{-6}m^2/Vs$) in the solid 10 °C below and in the mesophase 10 °C above the K→M transition for the different compounds using equation (1) with E_p =25 eV.

Compound	1		2		3	
	T	$\Sigma\mu_{min}$	T	$\Sigma\mu_{min}$	T	$\Sigma\mu_{min}$
Solid	85	5.4	70	2.3	92	3.6
Mesophase	105	0.75	90	0.75	112	1.20

The order of magnitude of the mobilities indicates a high degree of localisation at individual macrocyclic sites, with the hopping of charge carriers between adjacent Pc or P macrocycles in a column occurring on a timescale of a few picoseconds or less.[6,14]

At the transition to the isotropic phase all of the long range order is lost. The disappearance of $\Delta\sigma_{eop}/D$ at the M→I transition, as measured for **3** therefore provides definite evidence that molecular ordering is a necessity for the mobility of charge carriers in both the solid and the mesophase. The fact that even during the nanosecond pulse almost no microwave conductivity could be measured indicates that in the isotropic phase any ordering which exists can only be short range and of a very transitory nature.

The lower values of $\Delta\sigma_{eop}/D$ in the mesophase compared to the solid indicate that the enhanced freedom of movement of the molecules has a negative influence on the charge carrier mobilities. This observation agrees with theoretical predictions that perturbations in ideal columnar stacking such as tilting, rotation, and longitudinal and lateral displacement should increase the "resistivity" towards charge migration.[16]

Rather surprisingly $\Sigma\mu_{min}$ for **1** and **2** are similar in the mesophase despite horizontal stacking for the former and tilted for the latter.

We think that the much larger sudden decrease in $\Delta\sigma_{eop}/D$ on entering the mesophase for **1** compared with either **2** or **3** may be related to the large stepwise increase in freedom of movement of the ether groups of the alkyl chains for **1** as indicated by the sharp increase in σ_b. Since little change occurs in σ_b and the macrocycles remain tilted at T(K→M) for **2** and **3**, we conclude that the factor of approximately 3 decrease in $\Delta\sigma_{eop}/D$ for these compounds is due to an increase in the freedom of motion of the macrocycles which resulting from the melting of the outer hydrocarbon regions of the side chains.

The differences in the temperature dependence of $\Delta\sigma_{eop}/D$ in the solid phase of **1**, **2** and **3** may also reflect differences in the freedom of motion of the ether coupling units as evidenced by the σ_b values. The slight positive temperature activation of $\Delta\sigma_{eop}/D$ for **1** may be associated with close to complete rigidity of the peripheral alkoxy groups while the lack of activation for **2** and the eventual negative activation for **3** may reflect a reduction in charge carrier mobility related to increasing perturbation in the columnar stacking due to freedom of movement of the ether units, as evidenced by the large, thermally activated σ_b values.

REFERENCES

1 C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, J. Am. Chem. Soc., 104, 5245 (1982)
2 B.A. Gregg, M.A. Fox and A.J. Bard, J. Am. Chem. Soc, 111, 3024 (1989)
3 T.J. Marks, Angew. Chem. Int. Ed. Engl., 29, 857 (1990)
4 K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio and J. Simon, New J. Chem., 12, 751 (1988)
5 P. Weber, D. Guillon and A. Skoulios, Liq. Crystals, 9, 369 (1991)
6 P.G. Schouten, J.M. Warman, M.P. de Haas, M.A. Fox and H.L. Pan, Nature, 353, 736 (1991)
7 J.M. Warman and M.P. de Haas, in Pulse Radiolysis, (CRC press, 1991), p.101.
8 J.M. Warman, M.P. de Haas and H.M. Wentinck, Radiat. Phys. Chem., 34, 581 (1989).
9 J.F. van der Pol, M.P. de Haas, J.M. Warman and W. Drenth, Mol. Cryst. Liq. Cryst., 183, 411 (1990); 195, 307 (1991)
10 P.G. Schouten, C. Wenming, J.M. Warman, M.P. de Haas, J.F. van der Pol and J.W. Zwikker, Synt. Metals, 2665 (1991)
11 N.N. Usov and V.A. Benderskii, Phys. Status Solidi., 20, 481 (1967)
12 A.L. McClellan, Tables of Experimental Dipole Moments, Volume 2, (Rahara Enterprises, 1974).
13 J.M. Warman, M.P. de Haas, J.F. van der Pol and W. Drenth, Chem. Phys. Lett., 164, 581 (1989).
14 P.G. Schouten, J.M. Warman, M.P. de Haas, J.F. van der Pol and J.W. Zwikker, J. Am. Chem. Soc., accepted for publication
15 W.F. Schmidt and A.O. Allen, J. Phys. Chem., 72, 3730 (1968)
16 W.J. Pietro, T.J. Marks and M.A. Ratner, J. Am. Chem. Soc., 107, 5387 (1985)