ChemComm
FEATURE ARTICLE

Functional supramolecular materials: self-assembly of phthalocyanines and porphyrazines

Cornelius F. van Nostrum* and Roeland J. M. Nolte

N.S.R. Center, Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Phthalocyanines and related compounds can self-assemble into columnar structures in the solid and liquid crystalline state, in Langmuir–Blodgett films and in solution. This paper presents an overview of supramolecular architectures that have been constructed using several phthalocyanine and porphyrazine building blocks substituted with hydrocarbon chains and/or crown ether units. The most interesting applications of such highly organized columnar assemblies are in the field of one-dimensional transport of energy, charge and ions.

Introduction

The construction of functional materials from molecular building blocks as part of the field of supramolecular chemistry has gained increasing interest over the last decade.[1] Currently, many research groups world-wide are exploring the concepts of self-organization to assemble molecules into organized states,[2] *e.g.* wires and channels.[2c–f] The formation of supramolecules is based on molecular recognition phenomena, which make use of molecular information such as shape, flexibility, polarizability, polarity and the possibility of hydrogen bond formation and aromatic π-stacking. The strength of a non-covalent bond is 1–3 orders of magnitude weaker than a covalent bond and comparable with thermal energies. Supramolecules can only be stable, therefore, if many non-covalent interactions or large interacting areas are involved. Moreover, these interactions must be stronger than interactions with solvent molecules and energetically more favourable than the entropic advantages of dissociation.[2a]

Supramolecular chemistry can be divided into two main and partly overlapping areas. One is the area of host–guest chemistry, which involves the association of two or more complementary molecules. The discovery of cation-binding crown ethers in the mid 1960's had a great impact on organic chemistry,[3] since when hundreds of receptors which can bind substrate molecules selectively have been designed and synthesized. This binding, based on molecular recognition, can be followed by a chemical reaction, a transport process, or a detectable signal, *i.e.* a change in conformation or a change in electronic, ionic or optical properties. The second area in supramolecular chemistry concerns the formation of large molecular aggregates, in solution, or in the solid state, in thermotropic and lyotropic liquid crystals, and in monolayers and multilayers.[1b,c]

This paper presents a review of self-assembled structures that have been obtained from the phthalocyanine (Pc) and porphyrazine (Pz) building blocks (Fig. 1). These molecular units are highly versatile in having special catalytic, electronic and optical properties.[4] Pcs and Pzs owe their self-organizing abilities mainly to the strong attracting forces between their aromatic rings—also called π-π stacking interactions—and, in solution, to solvophobic effects. The overlap between the π-orbitals within a well organized stack of Pc molecules may result in interesting uni-dimensional materials with conducting properties.

Two separate or combined methods have been employed to organize the phthalocyanines and porphyrazines, *i.e.* with the help of the property of liquid crystallinity and by attaching crown ether rings to the above macrocycles. These methods will be described more fully in the following sections. The crowned Pcs can be used as materials for highly sensitive and fast gas sensors. How Pcs can be processed with the help of the Langmuir–Blodgett technique will be indicated briefly in the final section.

Liquid crystalline phthalocyanines

Structure and dynamics of the mesophase

In general, phthalocyanines and porphyrazines substituted with long flexible hydrocarbon side chains form so-called discotic mesophases at elevated temperatures. The first mesogenic Pc, *i.e.* a peripheral octa(alkoxymethyl) substituted Pc, was synthesized in 1982 by Piechocki *et al.*[5] Later, van der Pol *et al.*[6] synthesized Pcs substituted peripherally with eight alkoxy side chains [Fig. 2(*a*)], which can form a well-defined mesophase [Fig. 2(*b*)] according to X-ray powder diffraction measurements. The discotic molecules were stacked in columns, with the planes of the molecules perpendicular to the columnar axis. The intracolumnar separating distance amounted to 3.4 Å, which is close to the van der Waals distance of aromatic molecules. The columns had a hexagonal arrangement as shown in Fig. 2(*b*). This structure is classified as a D_h mesophase. The mesophase structure of the alkyl and alkoxymethyl analogues has been discussed.[7] The large-angle X-ray band found with these compounds, which corresponds to a spacing of 4.9 Å, has been attributed to the intracolumnar stacking period with the molecules tilted by an angle of 46° (D_t phase). Pcs substituted with alkyl or alkoxymethyl chains on the non-peripheral sites exhibit D_h mesophases.[8]

An alteration from a tilted to a non-tilted stacking of the molecules and melting of the hydrocarbon chains characterize the transition from the solid to mesophase in Pcs with peripheral alkoxy side chains. In the solid phase a number of sharp hydrocarbon reflections are visible in the X-ray diffractogram, whilst in the mesophase only a very broad and diffuse halo indicative of disordered aliphatic chains is present. The melting of the hydrocarbon chains can also be followed by temperature dependent solid state ^{13}C NMR spectroscopy.[9] These measurements also revealed another interesting feature, *viz.* that the

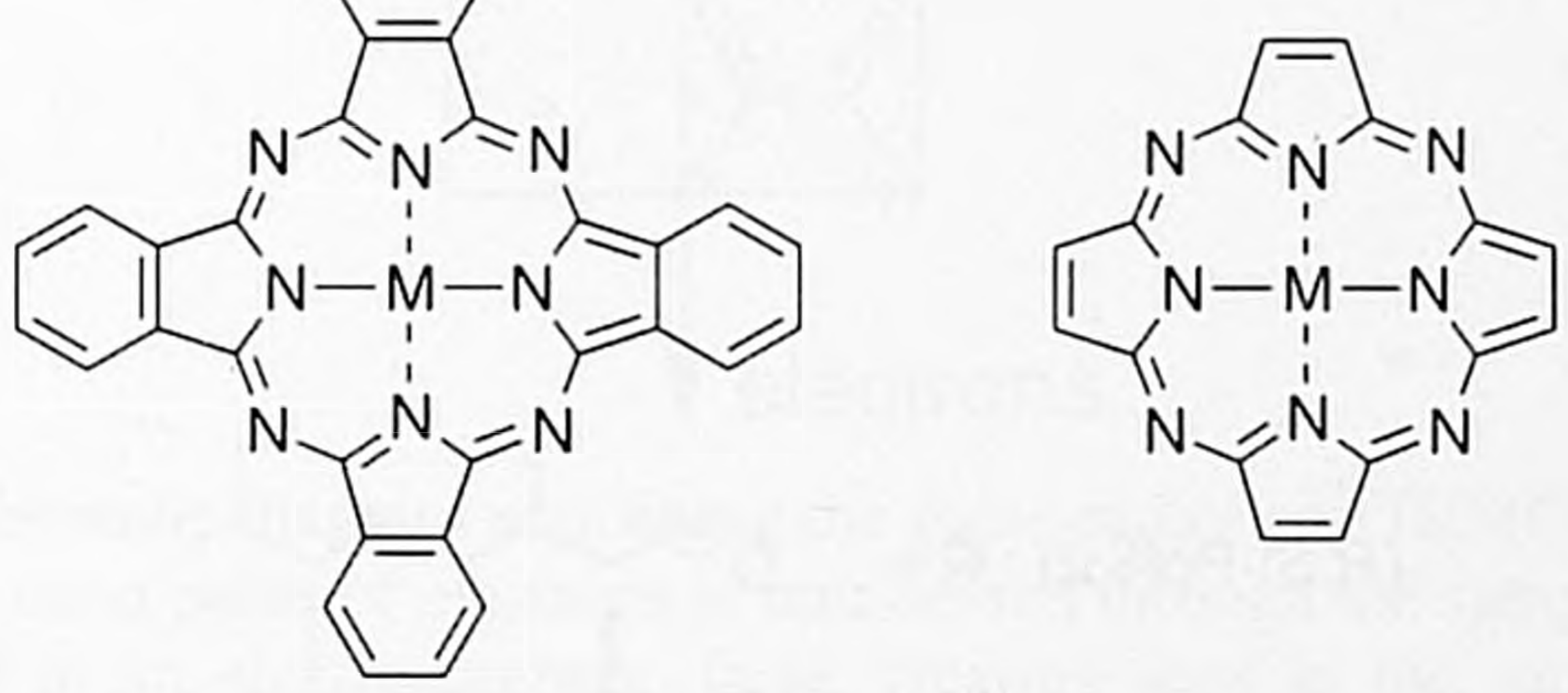

Fig. 1 Chemical structures of phthalocyanine (left) and porphyrazine (right)

molecules in the mesophase rotate around their columnar axes. The upper limit of 6.3 kHz for the frequency of rotation was derived from an analysis of the spectra.

Liquid crystalline porphyrazines containing alkylthio side chains have been synthesized recently by other groups.[10] These compounds also form hexagonal discotic mesophases.

Few phthalocyanines are known to be liquid crystalline at room temperature.[11] Several have branched hydrocarbon chains, which probably introduce disorder and hence a decrease in the transition temperature. The compound (*R*,*S*)-Pc(8,2) (Fig. 3), for example, forms a supercooled mesophase at room temperature, which then crystallizes after a few hours.[11c] The corresponding Pc with unbranched side chains, *i.e.* octa(octoxy)Pc, displays a reversible crystalline to mesophase transition at 94 °C with only slight hysteresis.[6b] The property of being liquid crystalline at ambient temperature may be important for some applications, *e.g.* in the construction of Langmuir–Blodgett films (see final section).

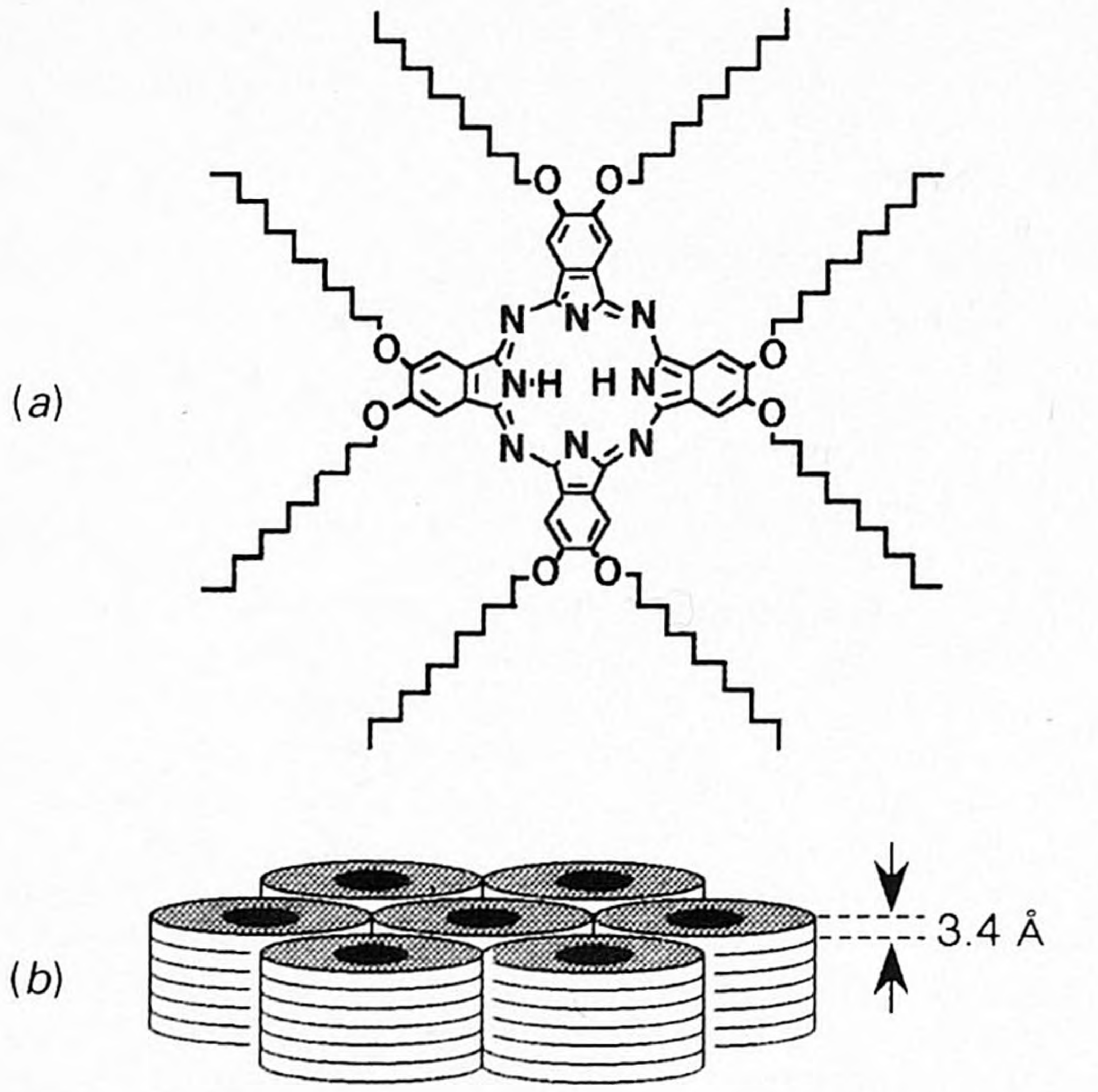

Fig. 2 (*a*) Example of an octaalkoxy Pc forming a D_h mesophase and (*b*) schematic representation of the one-dimensional stacks of Pc units formed in the D_h mesophase

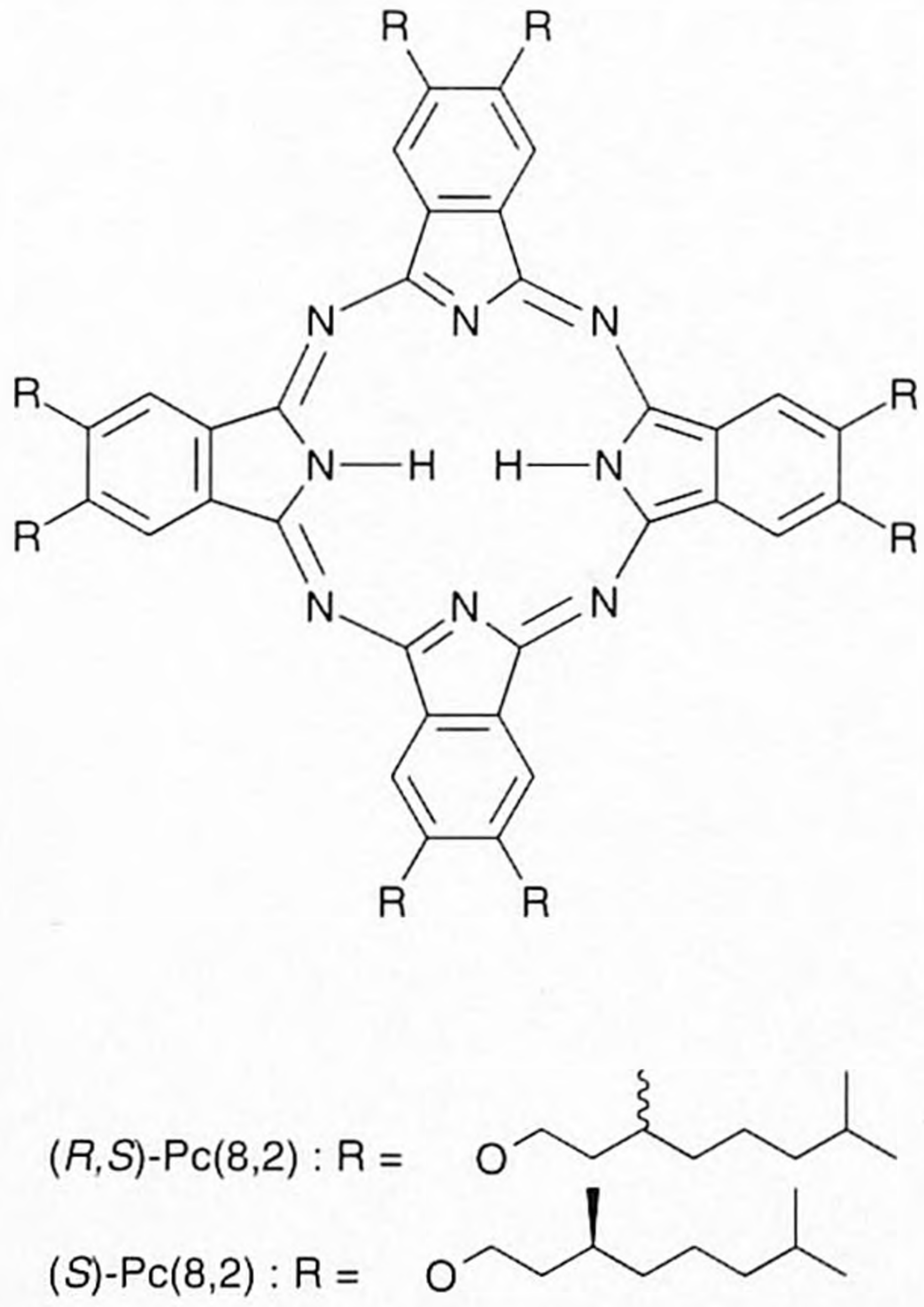

Fig. 3 Chemical structures of (*R*,*S*)-Pc(8,2) and (*S*)-Pc(8,2)

Molecular and mesophase chirality

The above mentioned compound (*R*,*S*)-Pc(8,2) is actually a mixture of 43 stereoisomers (16 pairs of enantiomers and 11 *meso* compounds), due to the presence of the eight chiral centres (one in each side chain). It was decided, therefore, to prepare one of these individual stereoisomers, *viz.* (*S*)-Pc(8,2) (Fig. 3), which would enable investigation of the influence of optical purity on the mesophase properties.[12]

The differences between the chiral compound (*S*)-Pc(8,2) and the mixture of stereoisomers are remarkable. The optically active material, unlike (*R*,*S*)-Pc(8,2), showed no crystalline phase to mesophase transition, but appeared to be liquid crystalline from the isotropic transition temperature at 295 °C down to 3 °C. The structure of the mesophase is probably retained below this temperature, but the molecular mobility characteristic for the mesophase is much reduced.[12b]

The first indication that the chiral Pc forms a chiral (D_h*) mesophase resulted from viewing the textures visible under a polarizing microscope. These showed spiral structures (Fig. 4). Additional information was obtained from X-ray powder diffraction data, which revealed the presence of a helical superstructure along the columnar axis with a pitch of 57 Å (including *ca.* 16 molecules). Other observations that indicated such a helical mesophase came from solid state ^{13}C NMR experiments, conductivity measurements, and circular dichroism (CD) studies. The conformation of the molecules in the D_h* phase was derived from the NMR data. The methyl groups at the chiral centres of the side chains are positioned alternately above and below the molecular plane, thus resulting in a propeller-like structure [see Fig. 5(a)]. The CD spectra showed that the Pc molecules are stacked in a left-handed helix. The most probable structure of the mesophase is shown schematically in Fig. 5(*b*): the normal to the Pc plane makes an angle with the columnar axis and, moving along the columnar axis, the normal rotates around this axis.[12b]

Energy transport

One-dimensional energy (exciton) migration in mesogenic metal-free phthalocyanines has been studied by Simon and coworkers and by Blasse.[13] Excitons are created by absorption of light. They can travel through the stacks of the Pc molecules

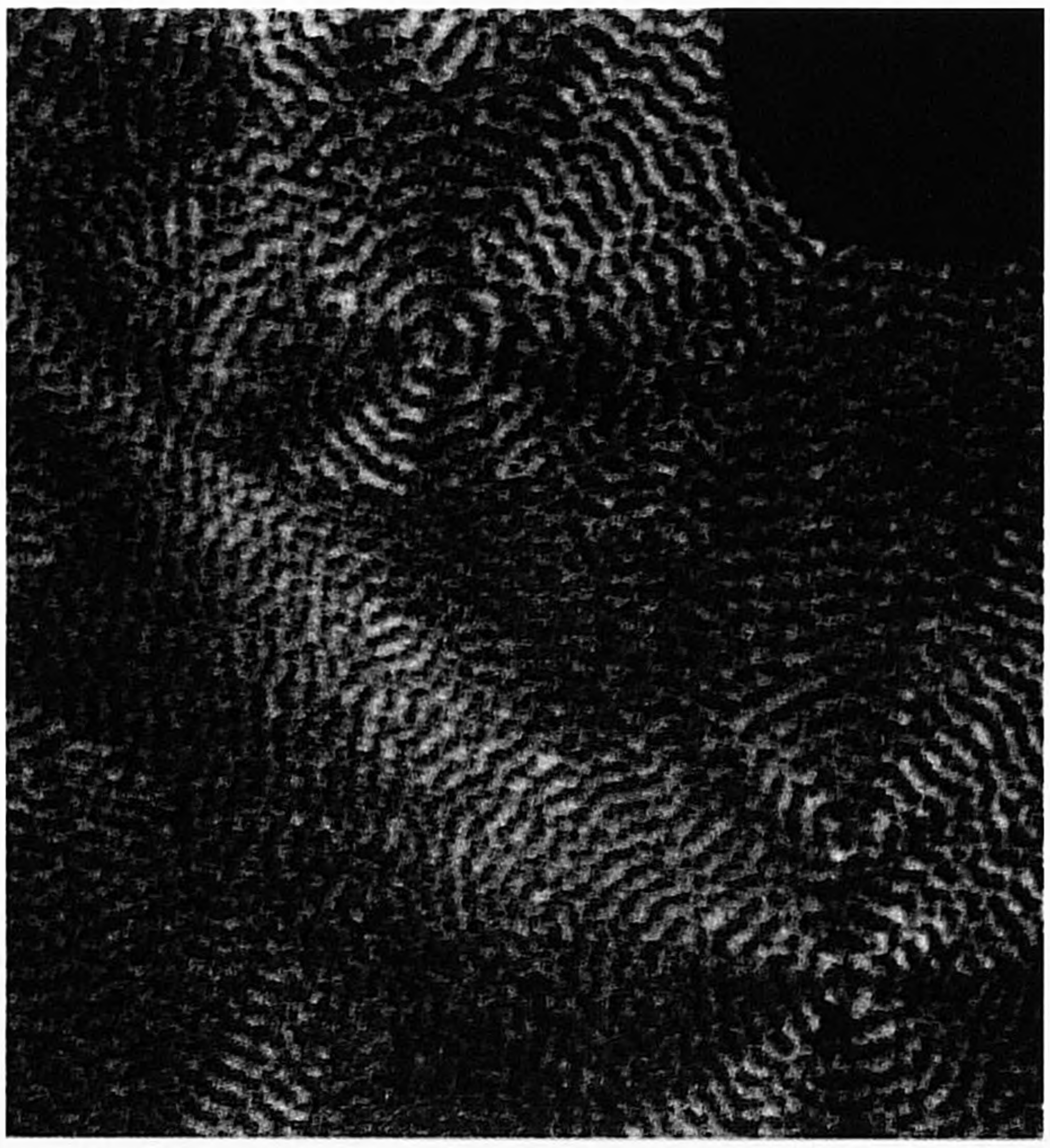

Fig. 4 Texture of (*S*)-Pc(8,2) observed between crossed polarizers at room temperature

until they reach a so-called intrinsic or extrinsic site where they decay to the ground state with emission of light (luminescence), or reach quenching sites which leads to non-radiative decay. It has been calculated from luminescence studies that at room temperature the exciton migration length is in the order of a micrometer, which means that the stacks must also have similar lengths.[13b,c] A sudden decrease in luminescence intensity was found to take place at the crystalline to mesophase transition for alkoxymethyl Pc,[13a,c] alkoxy Pc[13b] and the above mentioned branched alkoxy Pc (*R*,*S*)-Pc(8,2).[12b] The decrease can be explained by the fact that in the mesophase, unlike the crystalline phase, the Pc molecules are oriented perpendicularly to the columnar axes, which leads to a faster migration of the excitons and, consequently, to more rapid trapping at the quenching sites. A gradual disappearance of the luminescence was observed between 65 and 90 °C for a sample of the optically active (*S*)-Pc(8,2) that had been freshly precipitated from solution.[12b] This result is probably due to the introduction of disorder in the mesophase during the precipitation process, followed by an improvement of the stacking and energy migration when the compound is heated. The helical structure does not apparently cause a measurable reduction of the energy migration rate.

When phthalocyanines are cooled from the mesophase, exciton mobility normally decreases when re-entering the crystalline phase. It is noteworthy that crystallization could be prevented in several ways, *i.e.* by polymerization of liquid crystalline Pcs in the mesophase,[14a,b] by using bulky terminal groups on a flexible side chain[14c] and by using the optically active (*S*)-Pc(8,2).[12b] It was shown that the polymers and (*S*)-Pc(8,2) display fast energy migration down to cryogenic temperatures due to the preservation of the mesophase structure upon cooling, which makes these compounds interesting for future applications as energy guides.

Charge transport

Charge carriers, *i.e.* free electrons and holes, in phthalocyanines and porphyrins can be generated in various ways: thermally (intrinsic), chemically by doping (extrinsic), photochemically, or by high energy electron irradiation. We and others have studied charge carrier transport by dc, ac and the time-resolved microwave conductivity (TRMC) techniques.[6b,15,16] The TRMC technique makes use of the absorption of electromagnetic waves of high frequencies (microwave region, *ca.* 30 MHz) to monitor the conductivity in a material, and is useful to obtain information about both intra- and inter-columnar charge transport.[16] To overcome the problem of inducing structural changes in a material on chemical doping, charge carriers were created by ionization with short (nanosecond) pulses of high energy electrons (see Fig. 6). In the case of octaalkoxy Pc the so-called end-of-pulse conductivity decreases sharply at the crystalline phase to mesophase transition.[16a] This effect was explained by an increase of the molecular motion in the mesophase, which more than counteracted the expected increase in charge migration due to improved π–π overlap between the Pc rings. The conduction process can best be described in terms of a hopping model. An average jump time of 0.28 ps has been calculated from the charge mobility values.[16c] At the mesophase to isotropic phase transition the conductivity dropped to zero, supporting the idea that a columnar structure is necessary for charge transport.[16b] In the pulse-radiolysis TRMC experiments the conductivity decays after the pulse with high energy electrons [Fig. 7(*a*)].[16d] From the observation that the lifetime of the conductivity transients is exponentially dependent on the length of the alkoxy side chains it was concluded that intercolumnar charge transport probably occurs *via* a tunneling mechanism through the hydrocarbon mantles [Fig. 7(*b*)].

When the end-of-pulse conductivities in the mesophases of compounds (*R*,*S*)-Pc(8,2) and (*S*)-Pc(8,2) (Fig. 3) are compared, the most obvious difference is that the conductivity values of (*S*)-Pc(8,2) are lower than those of (*R*,*S*)-Pc(8,2).[12b,16c] It seems that the helically distorted columns in the D_h* phase of optically active (*S*)-Pc(8,2) are less favourable for intracolumnar charge migration than are the linear columns in the D_h phase of the mixture of stereoisomers.

In general, the TRMC technique proved to be a valuable tool for studying the relationships between structure, dynamics and charge transport in columnar stacks of liquid crystalline phthalocyanines and porphyrins. The results may be important for future design and development of devices based on discotic liquid crystals.

Crown ether substituted phthalocyanines and porphyrazines

Cation induced aggregation

Porphyrins containing pendant crown ether macrocycles were first described by Thanabal[17] and by Kobayashi.[18] Phthalocyanines β-substituted with four oxacrown ether rings [Fig. 8(*a*)] were reported later by the groups of Nolte,[19] Bekâroglu[20] and Kobayashi.[21] Other crown ether substituted Pcs have been described in recent years, among them several thiacrown ether[22] and azacrown ether Pcs.[23] The synthesis and properties of thiacrown ether substituted porphyrazines [Fig. 8(*b*)] were reported recently by us[24] and by Hoffman *et al.*[25] Single-crystal structures of the free 18-membered ring compound[24b] and of the $(AgBF_4)_8$ complex of the 15-membered ring compound[25] were determined.

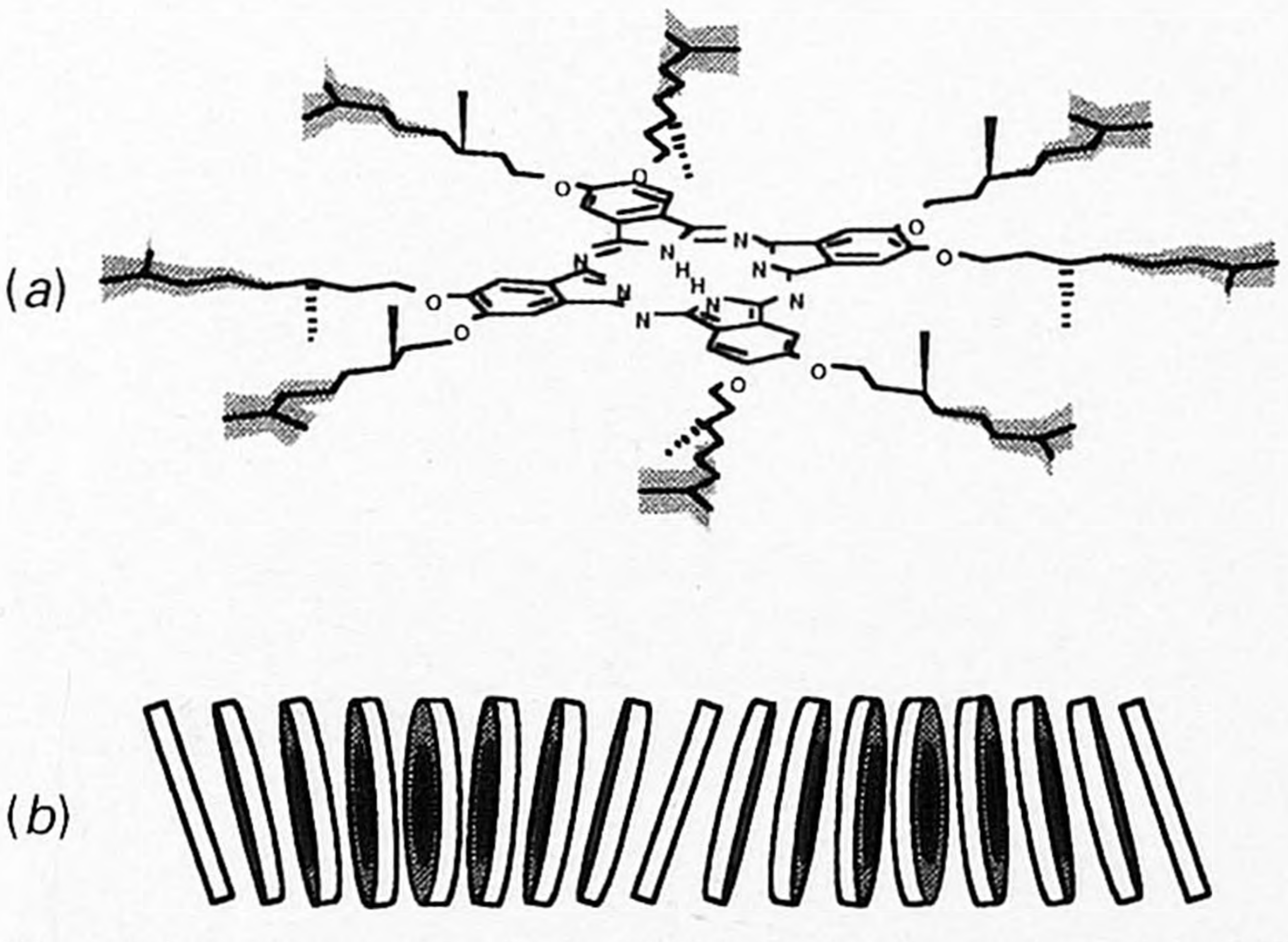

Fig. 5 Schematic representations of (*a*) the molecular conformation of (*S*)-Pc(8,2) and (*b*) the proposed columnar structure, in its D_h* mesophase, showing the unique helical arrangement of the molecules in one column

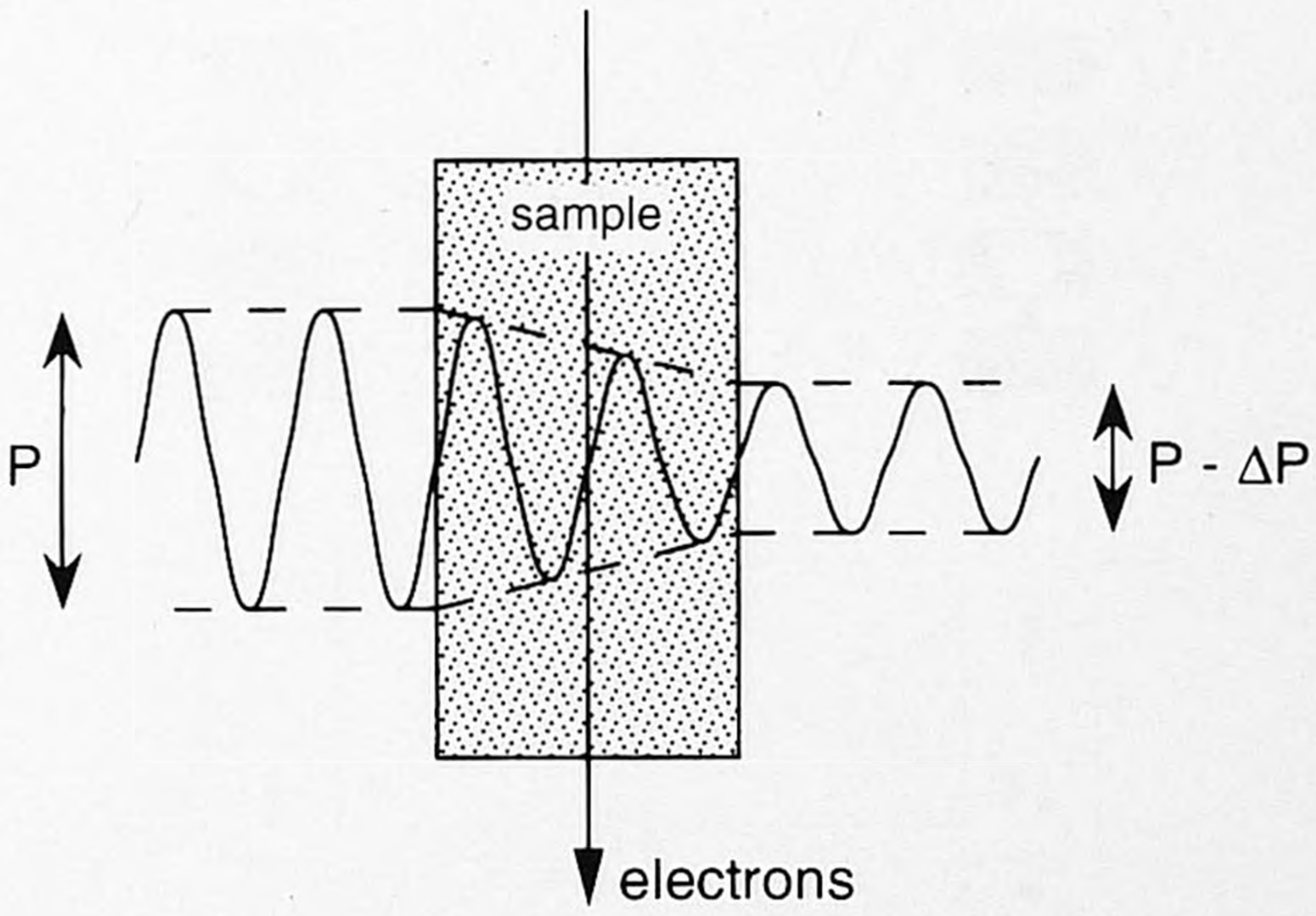

Fig. 6 Schematic diagram explaining the pulse-radiolysis TRMC measurements. A short pulse of electrons is transmitted through the sample, which is placed in an electromagnetic field, creating ions in the sample. The concentration and motion of these ions is detected by a decrease in the field power (P).

The aggregation behaviour of crowned phthalocyanines has been studied extensively. The molecules form aggregates in polar solvents, which can be seen from the blue shifts of the absorption bands in the UV–VIS spectra.[26] The addition of metal salts to solutions of these phthalocyanines also causes aggregation, due to complexation of the cations by the crown ether rings.[26,27] We have isolated and investigated complexes of crown ether Pcs with several alkali metal picrates.[28] These solid materials consist of untilted stacks of eclipsed Pc molecules [Fig. 9(*a*,*b*)]. Non-cofacial aggregates are formed with barium picrate [Fig. 9(*c*)].[29] The conductivities of these complexes were measured by ac impedance spectroscopy.[28–30] The electrical conductivities of the K^+, Rb^+ and Cs^+ complexes of 18-crown-6 Pc were two to three orders of magnitude higher than that of the free host, with the Rb^+ complex displaying the highest conductivity. The latter result is in agreement with the fact that the smallest distance between the Pc macrocycles, 3.3 Å, was found for the Rb^+ complex by X-ray diffraction. A further increase in conductivity was observed upon doping with iodine. The conductivity of the Ba^{2+} complex was found to be much lower than those of the other complexes, which is in agreement with the non-cofacial structure of the former compound. A positive co- operative binding effect was observed when Rb^+ was complexed with $(18\text{-crown-6 Pc})_2Lu$,[31] and it has been suggested that this could be an important step in the realization of neural networks and molecular switches.

Transition metal ions can be complexed by phthalocyanine derivatives containing nitrogen or sulfur atoms in their crown ether rings.[22,32] The thiacrown ether porphyrazines shown in Fig. 8(*b*) appeared to display especially interesting binding behaviour, as indicated from UV–VIS and EPR spectroscopic data.[24*b*] Non-linear complexation of silver(I) and mercury(II) perchlorates with porphyrazines having varying crown ether sizes and metal centres was observed. Dimers are formed, in which the porphyrazine molecules are held together by the ions that are sandwiched between neighbouring crown ether rings. The dimers initially formed from the compounds with the 18-membered crown ether rings dissociate upon further addition of the metal salts to form 6 : 1 guest–host complexes eventually. Hoffman isolated single crystals of a 8 : 1 complex of $AgBF_4$ with a nickel porphyrazine containing 15-membered crown ether rings.[25] Four silver ions were bound in the crown ether rings and four ions were situated in the *meso*-pockets of the compound.

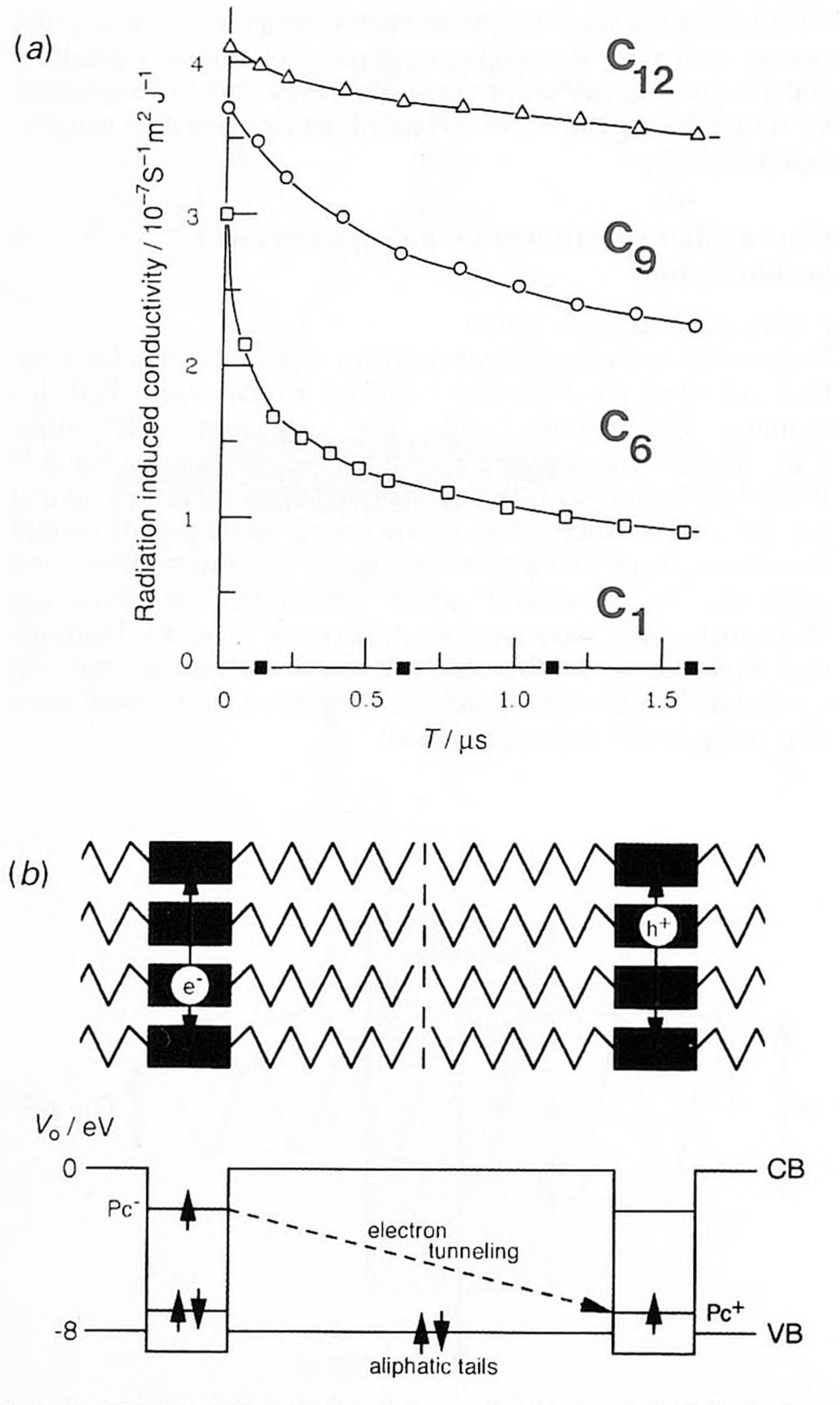

Fig. 7 (*a*) Decay of the radiation induced microwave conductivity in time for octaalkoxy Pcs with various side chain lengths (number of carbon atoms in the side chains). (*b*) Schematic diagram showing the charge recombination in Pcs *via* electron tunneling through the peripheral hydrocarbon mantle.

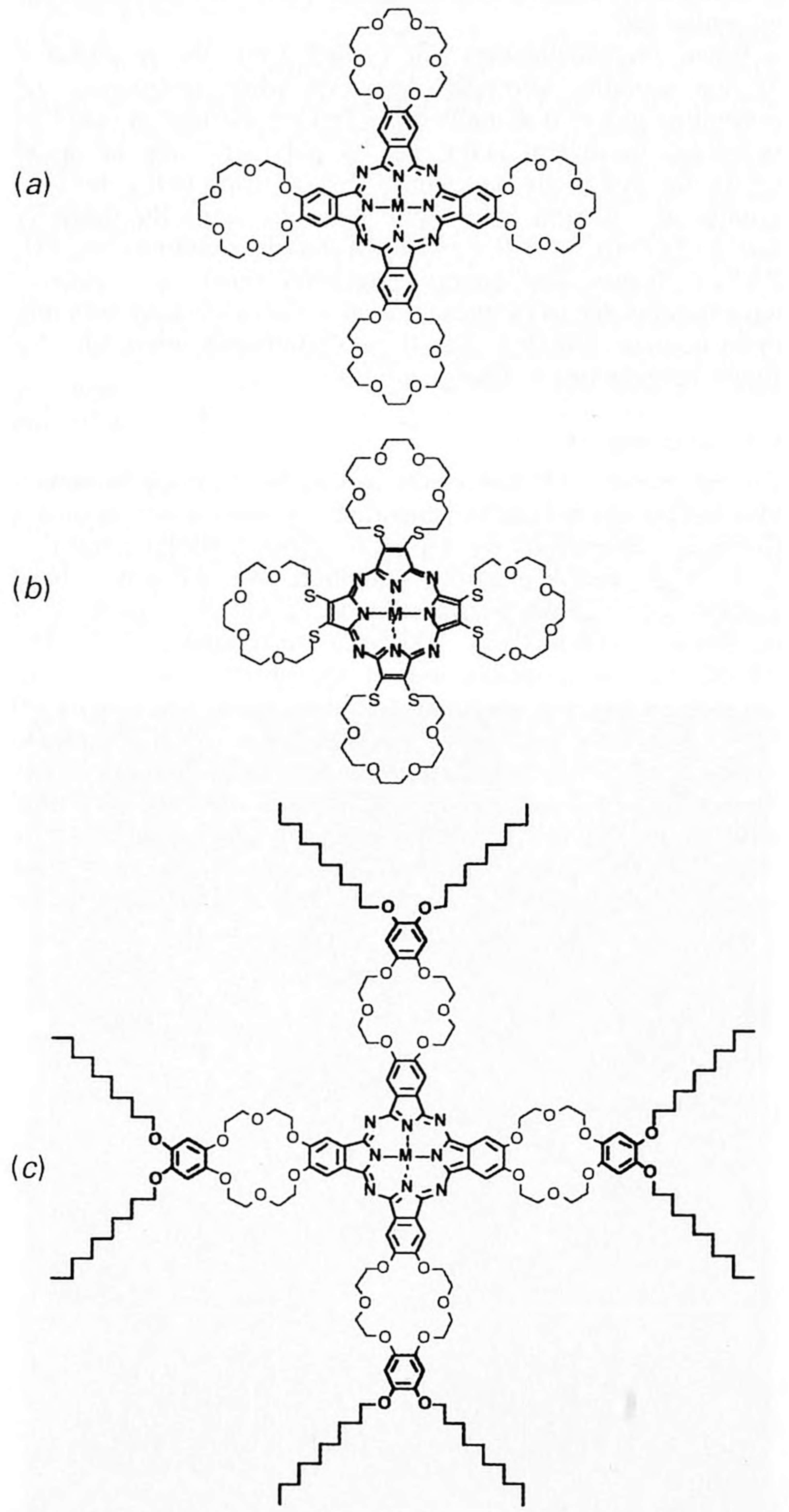

Fig. 8 Chemical structures of several crowned phthalocyanines and porphyrazines

The great variety of complexation behaviour observed for the crowned phthalocyanines and porphyrazines may be interesting for future applications of these compounds in molecular ionics.[1a] This is especially so in the case of nonlinear complexation of ions, *e.g.* when (de)aggregation takes place above a critical concentration of ions. It may be possible to obtain molecular switching devices in this manner.[31,33,34]

Supramolecular wires and channels

Crown ether phthalocyanines can be easily converted into dihydroxy silicon derivatives, which on heating in the presence of a catalyst undergo a polycondensation reaction to give polysiloxanes with crown ether substituents.[35] The crown ether rings are stacked to form four channels which have been shown to transport small alkali metal ions (Fig. 10).[35]

The aforesaid liquid crystalline and crown ether Pcs display their conduction and transport properties in bulk. As part of our efforts to obtain real nanostructured functional materials, it was of interest that we were able to isolate and visualize *single* supramolecular stacks from a crowned phthalocyanine building block having liquid crystalline properties [Fig. 8(*c*)].[34] This compound was prepared by connecting long hydrocarbon chains to the crown ether rings. In the solid phase the crown ether units are stacked one on top of another, thereby forming channels. The compound displays a transition to the D_h mesophase at a temperature of 148 °C. The large disk-like molecule (molecular weight 2890 Da) self-assembled in chloroform to form an organogel in which a network of extremely long stacks of molecules was present. The heat of association was determined by UV–VIS spectroscopy to be -125 kJ mol^{-1}. This high value indicates that very strong intermolecular attracting forces are responsible for this peculiar behaviour. The individual stacks of molecules have a length of more than one micrometer and a molecular thickness of *ca.* 6 nm. They contain more than ten thousand molecules and can be visualized by electron microscopy[34] and atomic force microscopy (Fig. 11). These stacks may be considered as being supramolecular cables containing a central wire of Pc molecules and four ion channels of stacked crown ether units in view of their structural resemblance with the afore mentioned crowned phthalocyaninato-polysiloxanes. The peripheral hydrocarbon chains can act as an insulating mantle [see Fig. 11(*c*)].

Applications and outlook

Phthalocyanines have received much attention as gas sensing materials because they are reactive towards reducing and oxidizing gases. Their electrical conductivity depends on the gas concentration, but sufficiently high gas adsorption and desorption rates were not achieved.[36] The use of linear stacks of KCl–crown ether phthalocyanine complexes, however, gave highly organized materials with excellent gas sensing characteristics at room temperature (see Fig. 12).[37] A hand-held gas sensing device based on the surface plasmon resonance technique using crown ether Pcs has been recently developed.[38]

The previous example shows that it is important to use well organized materials for practical applications. An attractive method to prepare ultra-thin organized films of phthalocyanines is the Langmuir–Blodgett (LB) technique. There are many reports on the preparation of LB films from monomeric and polymeric phthalocyanines displaying several degrees of organization and orientation of the molecules within the films.

Discotic liquid crystals have been suggested to be very suitable for the construction of such films.[39] The orientation and conformation of phthalocyanine molecules in a monolayer on a water surface depends on whether the molecules have predominantly LC or amphiphilic character (Fig. 13). Mesogenic α-octaalkyl Pcs form rigid films which cannot be deposited onto substrates,[40] but when two chains at one side of the phthalocyanine are modified with hydroxy or carboxylic acid functions the molecule becomes amphiphilic and forms stable and transferable monolayers.[40,41] The optically active (*S*)-Pc(8,2) is liquid crystalline at ambient temperature. This feature appeared to be favourable for the formation of stable bilayers on a water surface, wherein the planes of the molecules are arranged perpendicularly to the water surface.[12b] These bilayers can be readily transferred onto solid substrates to form oriented multilayers with LC structure. An amphotropic phthalocyanine, *i.e.* a liquid crystalline derivative containing amphiphilic side chains (see Fig. 14), was shown to adopt both perpendicular as

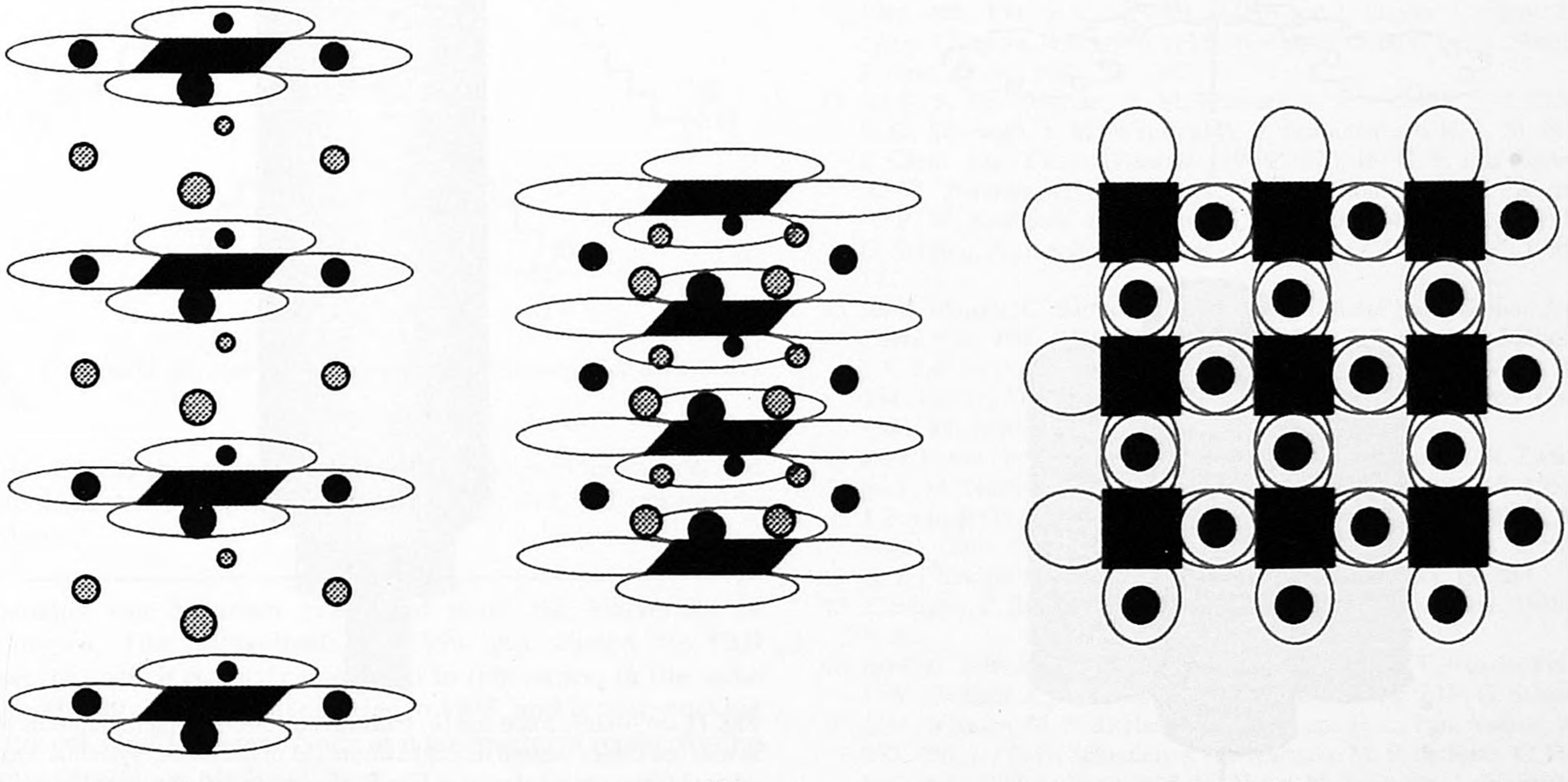

Fig. 9 Schematic representations of (*a*) the stacked complexes of 18-crown-6 Pc with K^+ picrate, (*b*) 18-crown-6 Pc with Rb^+ and Cs^+ picrate, and (*c*) network complex formed with Ba^{2+} picrate. The filled circles are the cations and the dotted circles the picrate anions.

well as parallel orientations on the water surface, depending on the applied surface pressure.[42]

The use of oligomers and polymers for LB films has the advantage that the Pc units are pre-organized.[41a,43] Wegner *et al.* used tetra(methoxy)tetra(octoxy)Pc–polysiloxane as building blocks to prepare highly organized LB films.[43a] The axes of the rod-like polymer molecules are positioned parallel to the water surface in a monolayer. The polymers arrange themselves parallel to the transfer direction upon deposition of these monolayers on to solid substrates. This lateral orientation is due to monolayer flow during the dipping process.[44]

Only two crown ether phthalocyanine derivatives have been applied so far in LB films, *i.e.* an octa(15-crown-5)-lutetium bisphthalocyanine[45] and the dihydroxysilicon derivative of the previously mentioned liquid crystalline Pc shown in Fig. 8(*c*).[34] An interesting feature of the latter compound is the non-linear complexation of cations that has been observed in Langmuir monolayers.

In summary, it can be concluded that liquid crystalline phthalocyanines and crown ether phthalocyanines are very attractive compounds for applications in functional materials

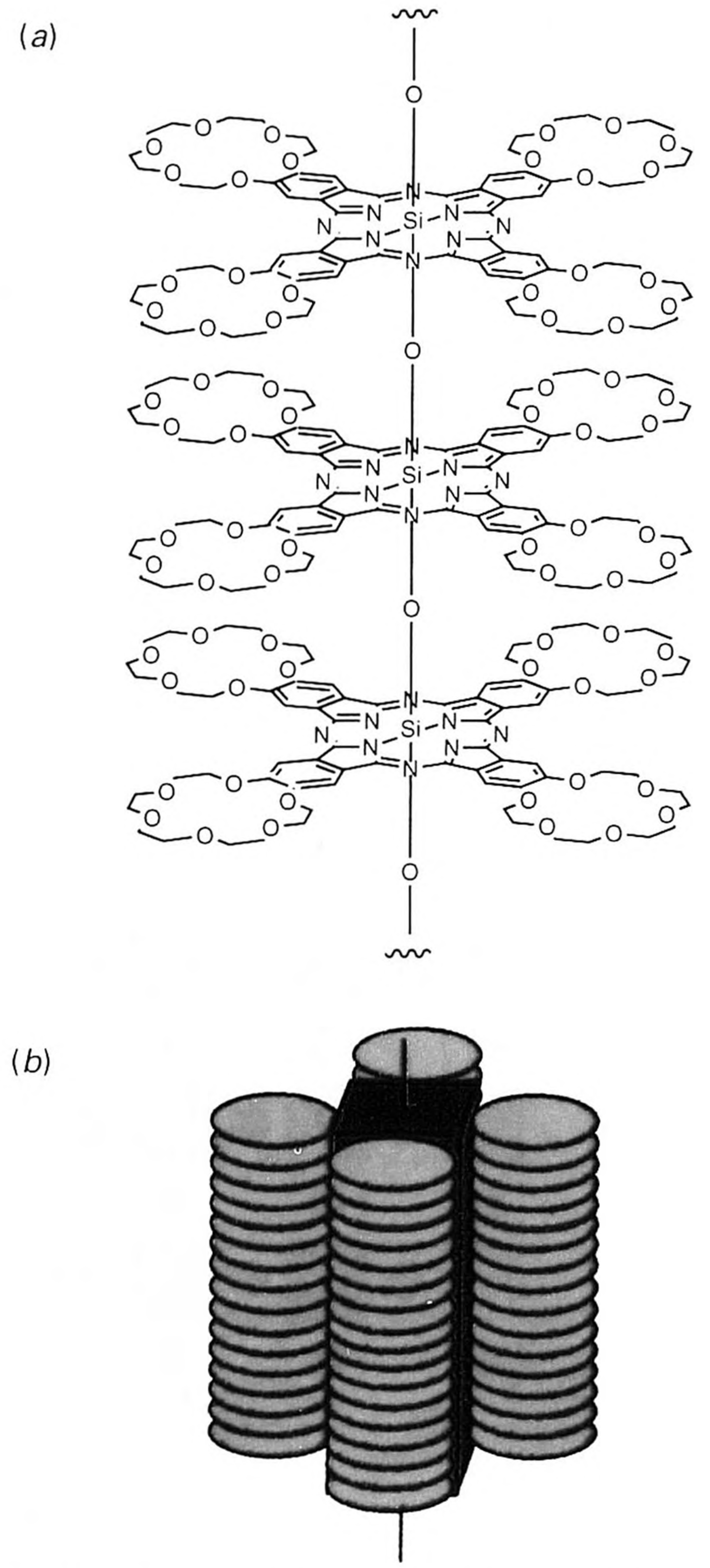

Fig. 10 (*a*) Chemical structure and (*b*) schematic representation of the ion channels of a (crown ether phthalocyaninato)polysiloxane

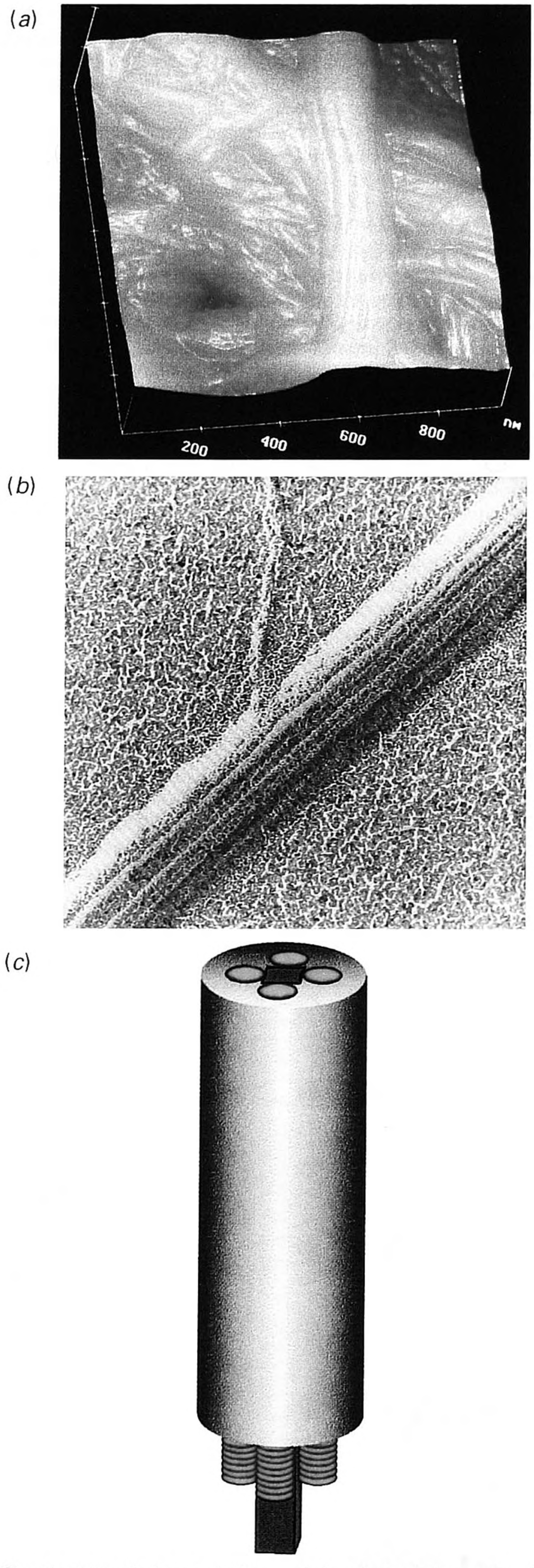

Fig. 11 (*a*) Atomic force and (*b*) transmission electron micrographs of self-assembled cables present in a chloroform gel of the liquid crystalline crown ether phthalocyanine shown in Fig. 8(*c*) (reproduced with permission from ref. 34). The pictures display bundles of fibers. The smallest fibers have diameters close to the molecular diameter. (*c*) Schematic structure of the self-assembled cables.

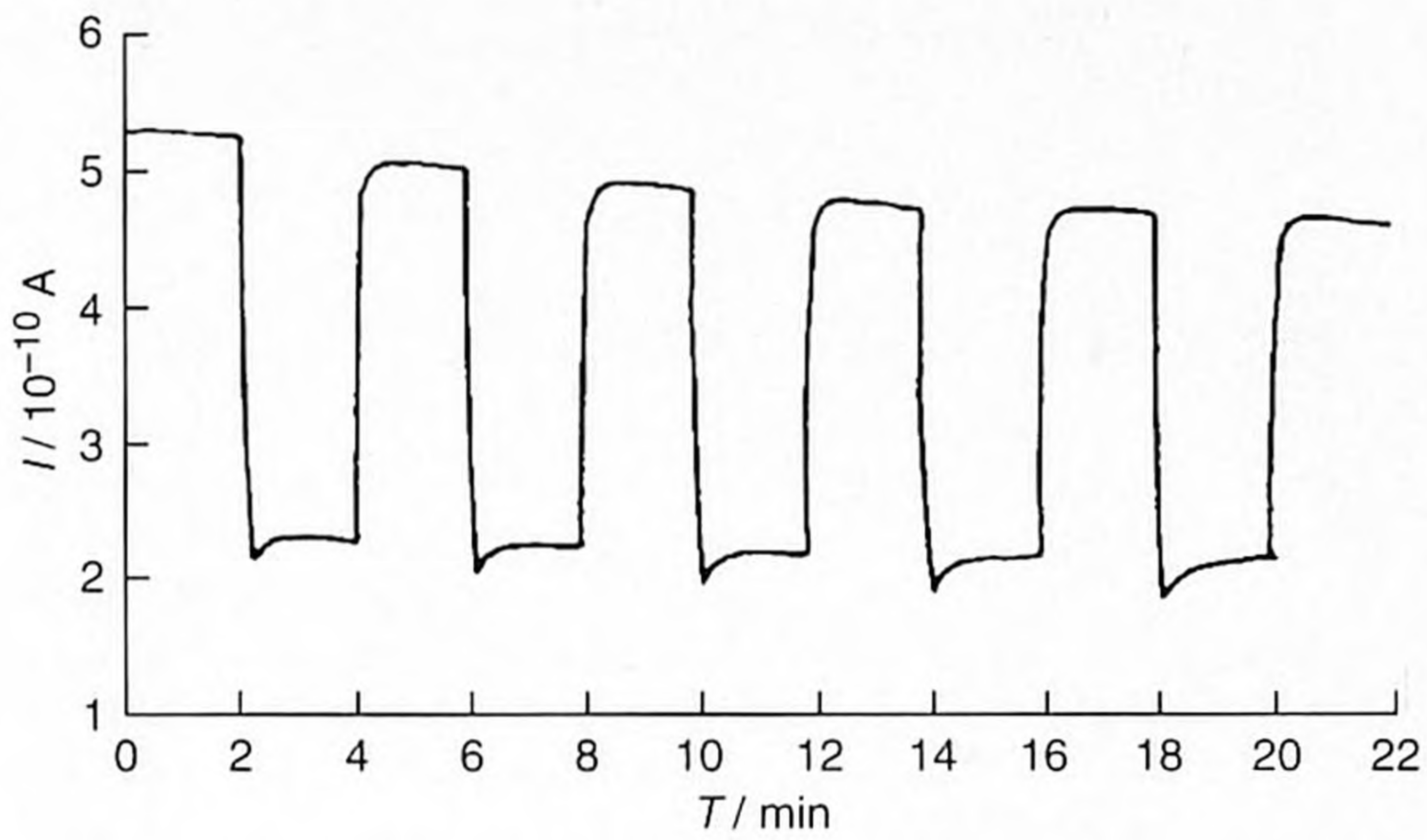

Fig. 12 Conductivity changes of a film of 15-crown-5 Pc mixed with KCl upon 2 min exposure cycles to 5 ppm of NO_2

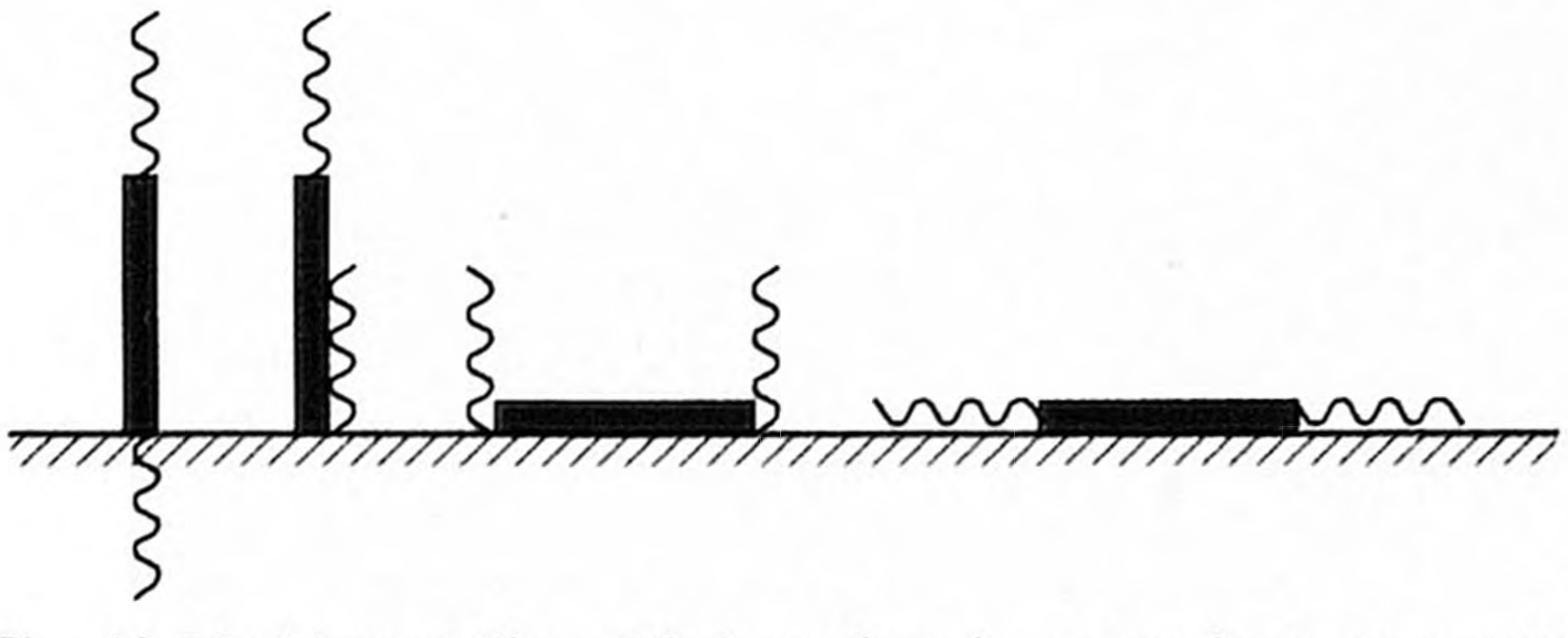

Fig. 13 Liquid crystalline phthalocyanines in a monolayer on a water surface. The drawing shows the possible orientations of the macrocyclic core and the hydrocarbon chains.

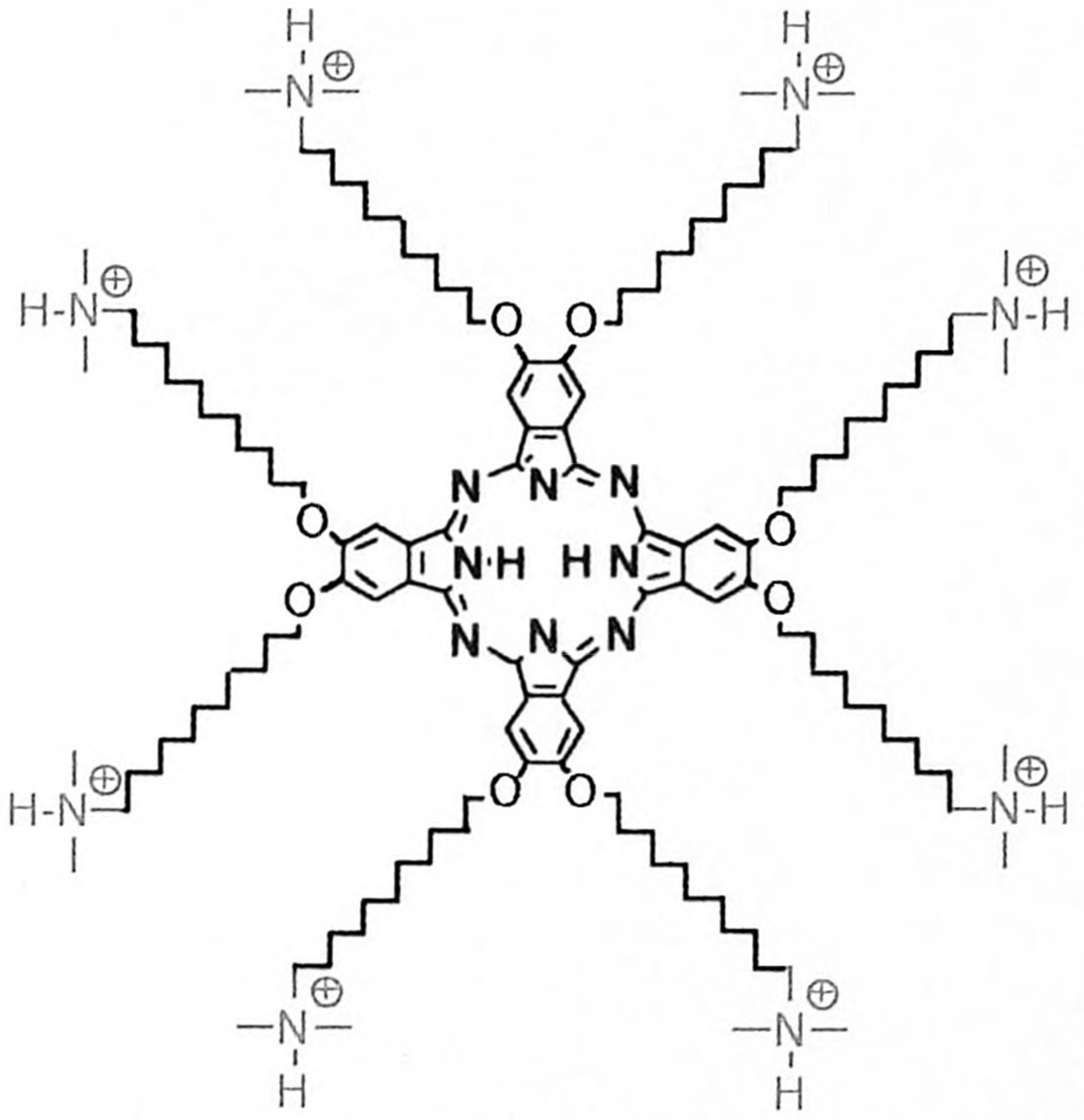

Fig. 14 Chemical structure of the amphotropic phthalocyanine used in this work

which are capable of transporting charge, ions, or electrons, due to their intrinsic properties as well as their rich self-organizing abilities.

Cornelus van Nostrum graduated from the University of Nijmegen, The Netherlands, in 1990 and started his PhD research, which is partly described in this paper, in the same year. He obtained his PhD degree in 1995, and is now working in the group of Professor Nolte as a postdoctoral researcher on liquid-crystalline photopolymers.

Roeland Nolte is Professor of Organic Chemistry at the University of Nijmegen. He was educated at the University of Utrecht (PhD in 1973) and did postdoctoral work with D. J. Cram at U.C.L.A. His research interests include molecular recognition phenomena, electron conducting molecular materials, chiral polymers and metal-catalysed epoxidation reactions.

References

1 (*a*) J.-M. Lehn, *Angew. Chem.*, 1988, **100**, 91; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; (*b*) H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem.*, 1988, **100**, 117; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 113; (*c*) J. Simon, J.-J. André and A. Skoulios, *New J. Chem.*, 1986, **10**, 295.

2 (*a*) G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; (*b*) J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153; (*c*) J.-M. Lehn, *Angew. Chem.*, 1990, **102**, 1347; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; (*d*) M. R. Ghadiri, J. R. Granja and L. K. Buehler, *Nature*, 1994, **369**, 301; (*e*) M. Jørgensen, K. Bechgaard, T. Bjørnholm, P. Sommer-Larsen, L. G. Hansen and K. Schaumburg, *J. Org. Chem.*, 1994, **59**, 5877; (*f*) C. F. van Nostrum, S. J. Picken and R. J. M. Nolte, *Angew. Chem.*, 1994, **106**, 2298; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2173.

3 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.

4 *Phthalocyanines, Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989–1993, vol. 1–3.

5 C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245.

6 (*a*) J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 615; (*b*) J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser and S. J. Picken, *Liq. Cryst.*, 1989, **6**, 577.

7 (*a*) M. K. Engel, P. Bassoul, L. Bosio, H. Lehmann, M. Hanack and J. Simon, *Liq. Cryst.*, 1993, **15**, 709; (*b*) P. Weber, D. Guillon and A. Skoulios, *Liq. Cryst.*, 1991, **9**, 3.

8 M. J. Cook, *J. Mater. Sci., Mater. Electron.*, 1994, **5**, 117.

9 A. P. M. Kentgens, B. A. Markies, J. F. van der Pol and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1990, **112**, 8800.

10 (*a*) P. Doppelt and S. Huille, *New J. Chem.*, 1990, **14**, 607; (*b*) F. Lelj, G. Morelli, G. Ricciardi, A. Roviello and A. Sirigu, *Liq. Cryst.*, 1992, **12**, 941.

11 (*a*) A. N. Cammidge, M. J. Cook, K. J. Harrison and N. B. McKeown, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3053; (*b*) I. Cho and Y. Lim, *Mol. Cryst. Liq. Cryst.*, 1988, **154**, 9; (*c*) W. T. Ford, L. Sumner, W. Zhu, Y. H. Chang, P.-J. Um, K. H. Choi, P. A. Heiney and N. C. Maliszewskyj, *New J. Chem.*, 1994, **18**, 495; (*d*) D. Lelièvre, L. Bosio, J. Simon, J.-J. André and F. Bensebaa, *J. Am. Chem. Soc.*, 1992, **114**, 4475; (*e*) P. G. Schouten, J. F. van der Pol, J. W. Zwikker, W. Drenth and S. J. Picken, *Mol. Cryst. Liq. Cryst.*, 1991, **195**, 291; 1991, **208**, 109; (*f*) C. Sirlin, L. Bosio and J. Simon, *J. Chem. Soc., Chem. Commun.*, 1988, 236; (*g*) P. Weber, D. Guillon and A. Skoulios, *J. Phys. Chem.*, 1987, **91**, 2242.

12 (*a*) C. F. van Nostrum, A. W. Bosman, G. H. Gelinck, S. J. Picken, P. G. Schouten, J. M. Warman, A. J. Schouten and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1993, 1120; (*b*) C. F. van Nostrum, A. W. Bosman, G. H. Gelinck, P. G. Schouten, J. M. Warman, A. P. M. Kentgens, A. Meijerink, S. J. Picken, M. A. C. Devillers, U. Sohling, A.-J. Schouten and R. J. M. Nolte, *Chem. Eur. J.*, 1995, **1**, 171.

13 (*a*) B. Blanzat, C. Barthou, N. Tercier, J.-J. André and J. Simon, *J. Am. Chem. Soc.*, 1987, **109**, 135; (*b*) G. Blasse, G. J. Dirksen, A. Meijerink, J. F. van der Pol, E. Neeleman and W. Drenth, *Chem. Phys. Lett.*, 1989, **154**, 420; (*c*) D. Markovitsi, I. Lécuyer and J. Simon, *J. Phys. Chem.*, 1991, **95**, 3620.

14 (*a*) J. F. van der Pol, E. Neeleman, J. C. van Miltenburg, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Macromolecules*, 1990, **23**, 155; (*b*) J. F. van der Pol, J. W. Zwikker, J. M. Warman and M. P. de Haas, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 208; (*c*) K. E. Treacher, G. J. Clarkson and N. B. McKeown, *Liq. Cryst.*, 1995, **19**, 887.

15 Z. Belarbi, C. Sirlin, J. Simon and J.-J. André, *J. Phys. Chem.*, 1989, **93**, 8105.

16 (*a*) P. G. Schouten, J. M. Warman, M. P. de Haas, J. F. van der Pol and J. W. Zwikker, *J. Am. Chem. Soc.*, 1992, **114**, 9028; (*b*) P. G. Schouten, J. M. Warman, M. P. de Haas, M. A. Fox and H.-L. Pan, *Nature*, 1991, **353**, 736; (*c*) P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelinck, R. J. M. Nolte, M. J. Copyn, J. W. Zwikker, M. K. Engel, M. Hanack and W. T. Ford, *J. Am. Chem. Soc.*, 1994, **116**, 6880; (*d*) P. G. Schouten, J. M. Warman, G. H. Gelinck and M. J. Copyn, *J. Phys. Chem.*, 1995, **99**, 11 780.

17 V. Thanabal and V. Krishnan, *J. Am. Chem. Soc.*, 1982, **104**, 3643.

18 N. Kobayashi and T. Osa, *Heterocycles*, 1981, **15**, 675.

19 R. Hendriks, O. E. Sielcken, W. Drenth and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1986, 1464.

20 A. R. Koray, V. Ahsen and Ö. Bekâroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932.

21 N. Kobayashi and Y. Nishiyama, *J. Chem. Soc., Chem. Commun.*, 1986, 1462.

22 A. G. Gürek and Ö. Bekâroglu, *Helv. Chim. Acta*, 1994, **77**, 1616.

23 (*a*) E. Musluoglu, V. Ahsen, A. Gül and Ö. Bekâroglu, *Chem. Ber.*, 1991, **124**, 2531; (*b*) G. Gümüs, Z. Z. Öztürk, V. Ahsen, A. Gül and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1992, 2485; (*c*) A. G. Gürek, V. Ahsen, A. Gül and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1991, 3367; (*d*) M. Koçak, A. I. Okur and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1994, 323; (*e*) E. Hamuryudan and Ö. Bekâroglu, *J. Chem. Res. (S)*, 1993, 460.

24 (*a*) C. F. van Nostrum, F. B. G. Benneker, N. Veldman, A. L. Spek, A.-J. Schouten and R. J. M. Nolte, *Recl. Trav. Chim. Pays-Bas*, 1994, **113**, 109; (*b*) C. F. van Nostrum, F. B. G. Benneker, H. Brussaard, H. Kooijman, N. Veldman, A. L. Spek, J. Schoonman, M. C. Feiters and R. J. M. Nolte, *Inorg. Chem.*, 1996, **35**, 959.

25 J. W. Sibert, S. J. Lange, C. L. Stern, A. G. M. Barrett and B. M. Hoffman, *Angew. Chem.*, 1995, **107**, 2173; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2020.

26 O. E. Sielcken, M. M. van Tilborg, M. F. M. Roks, R. Hendriks, W. Drenth and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1987, **109**, 4261.

27 (*a*) N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, 1987, **109**, 7433; (*b*) V. Ahsen, E. Yilmazer, M. Ertas and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1988, 401.

28 O. E. Sielcken, H. C. A. van Lindert, W. Drenth, J. Schoonman, J. Schram and R. J. M. Nolte, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 702.

29 O. E. Sielcken, W. Drenth and R. J. M. Nolte, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 425.

30 O. E. Sielcken, R. J. M. Nolte and J. Schoonman, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 230.

31 T. Toupance, V. Ahsen and J. Simon, *J. Am. Chem. Soc.*, 1994, **116**, 5352.

32 A. Gürek, V. Ahsen, A. Gül and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1991, 3367.

33 J. Simon, M. K. Engel and C. Soulié, *New J. Chem.*, 1992, **16**, 287.

34 C. F. van Nostrum, S. J. Picken, A.-J. Schouten and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1995, **117**, 9957.

35 O. E. Sielcken, L. A. van de Kuil, W. Drenth, J. Schoonman and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1990, **112**, 3086.

36 High sensitivities have been reported, *e.g.* for unsubstituted lead phthalocyanines, but high operating temperatures (typically 150–200 °C) are required and even then the response is usually very slow. It can take several hours to reach saturation level. See, for example, T. A. Jones and B. Bott, *Sensors Actuators*, 1984, **5**, 43; A. Wilson and J. D. Wright, *Mol. Cryst. Liq. Cryst.*, 1992, **211**, 321.

37 P. Roisin, J. D. Wright, R. J. M. Nolte, O. E. Sielcken and S. C. Thorpe, *J. Mater. Chem.*, 1992, **2**, 131.

38 S. J. Peacock, V. Rivalle, J. D. Wright and H. C. Jaggers, in *Sensors VI: Technology, Systems and Applications*, ed. K. T. V. Grattan, Hilger, Bristol, 1993, p. 15.

39 A. Laschewsky, *Adv. Mater.*, 1989, **1**, 392.

40 N. B. McKeown, M. J. Cook, A. J. Thomson, K. J. Harrison, M. F. Daniel, R. M. Richardson and S. J. Roser, *Thin Solid Films*, 1988, **159**, 469.

41 (*a*) G. C. Bryant, M. J. Cook, C. Ruggiero, T. G. Ryan, A. J. Thorne, S. D. Haslam and R. M. Richardson, *Thin Solid Films*, 1994, **243**, 316; (*b*) R. H. Poynter, M. J. Cook, M. A. Chesters, D. A. Slater, J. McMurdo and K. Welford, *Thin Solid Films*, 1994, **243**, 346.

42 C. F. van Nostrum, P. T. J. H. ten Have, S. J. Picken, A. J. Schouten and R. J. M. Nolte, submitted for publication.

43 (*a*) T. Sauer, T. Arndt, D. N. Batchelder, A. A. Kalachev and G. Wegner, *Thin Solid Films*, 1990, **187**, 357; (*b*) C. F. van Nostrum, R. J. M. Nolte, M. A. C. Devillers, G. T. Oostergetel, M. N. Teerenstra and A. J. Schouten, *Macromolecules*, 1993, **26**, 3306.

44 S. Schwiegk, T. Vahlenkamp, Y. Xu and G. Wegner, *Macromolecules*, 1992, **25**, 2513.

45 M. L. Rodríguez-Méndez, J. Souto and J. A. de Saja, *J. Raman Spectrosc.*, 1995, **26**, 693.

Received, 22nd April 1996; 6/02753I