

Mesomorphic molecular materials for electronics, opto-electronics, iono-electronics: Octaalkyl-phthalocyanine derivatives

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Abstract : Molecular materials are made from molecular units, separately synthesized and subsequently organized into some condensed phases. Because of their very nature, the electrical properties (ferro- and antiferroelectricity, semiconductivity) and the optical properties (polarizability and hyperpolarizability) of the molecular materials may be deduced from the physicochemical characteristics of the isolated molecular units (symmetry, polarity, redox potentials, absorption spectrum). Octaalkyl-phthalocyanine derivatives lead to columnar and nematic lenticular mesophases. These liquid crystalline phases are shown to be usable in the domains of electronics, opto-electronics and iono-electronics.

Molecular materials (ref. 1-3) are made from molecular units, which can be separately synthesized and which are in a subsequent step organized into some condensed phases : single crystals, thin films, liquid crystals...

The notion of material is unavoidably correlated with some finalities or applications. In this paper, liquid crystalline phases of *octaalkyl-phthalocyanine derivatives* (ref. 4, 5) will be shown to be usable in the three domains of *electronics, opto-electronics and iono-electronics*.

Phthalocyanine is a particularly versatile subunit since more than 70 different complexes are known. The ground state *dipole moment* of the subunit may be either absent, within the molecular plane or perpendicular to the macrocycle depending upon the type of complexes formed and/or the nature of the substituents (Fig. 1).

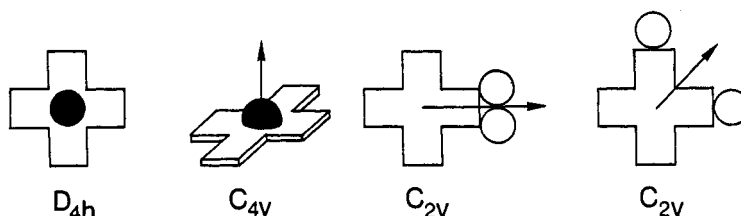


Fig. 1. Representation of various polar phthalocyanine subunits. For D_{4h} symmetry, $M = Zn^{II}, Ni^{II}, Cu^{II}...$; for C_{4v} symmetry, $M = Pb^{II}, Sn^{II}$; for C_{2v} symmetry, $O = CN$ for example.

The polar character may be employed in several types of mesophases. *Nematic lenticular mesophases* (ref. 8, 9) based on the phthalocyanine subunits were observed (ref. 10); the use of in-plane or out-of-plane dipolar molecules should allow the obtainment of new types of liquid crystalline phases (Fig. 2).

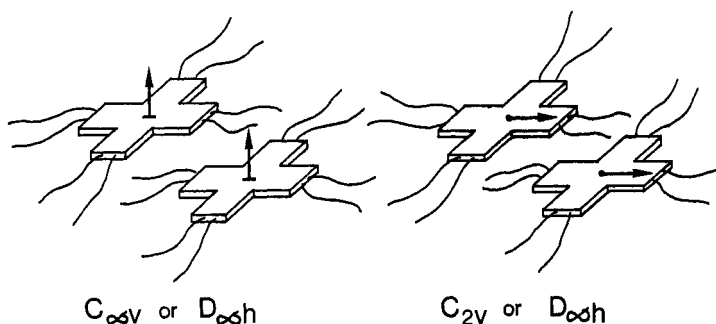


Fig. 2. Nematic mesophases which can be obtained from polar phthalocyanine macrocycles whose syntheses are described in ref. 6 and 7. The symmetry of the mesophase depends on the relative orientations of the dipole moments.

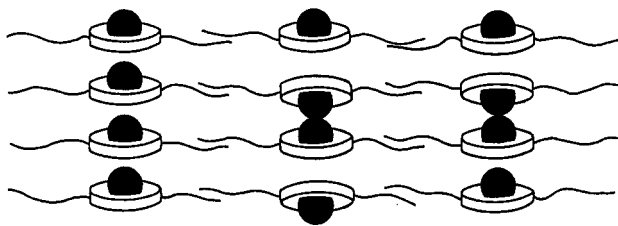


Fig. 3. The various ways of organizing out-of-plane dipolar phthalocyanine derivatives in columnar liquid crystals.

Octasubstituted lead phthalocyanine derivatives (ref. 6, 11) form *columnar liquid crystals* in which the out-of-plane dipole moments may be arranged into a *ferroelectric* or *antiferroelectric* order (Fig. 3).

The ferroelectric arrangement within the columns has been shown on the monoclinic form of unsubstituted Pc's (ref. 12) to yield *switching devices* under the influence of an electric field. The low conducting "off-state" is due to the thermal creation of head-to-head dimers within the columns, these defects being cured in the presence of an electric field.

Lutetium bisphthalocyanine and lithium phthalocyanine have been shown to be the first examples of *intrinsic molecular semiconductors* (ref. 13, 14) in which the generation of charge carriers occurs through a *disproportionation* reaction :



The concentration of ions pairs A^+ , A^- is high enough to lead to intrinsic semiconductors, whenever the molecular unit is both easily oxidized and easily reduced (ref. 14). The corresponding alkyl-derivatives have been prepared and shown to form columnar liquid crystals (ref. 15, 16) (Fig. 4).

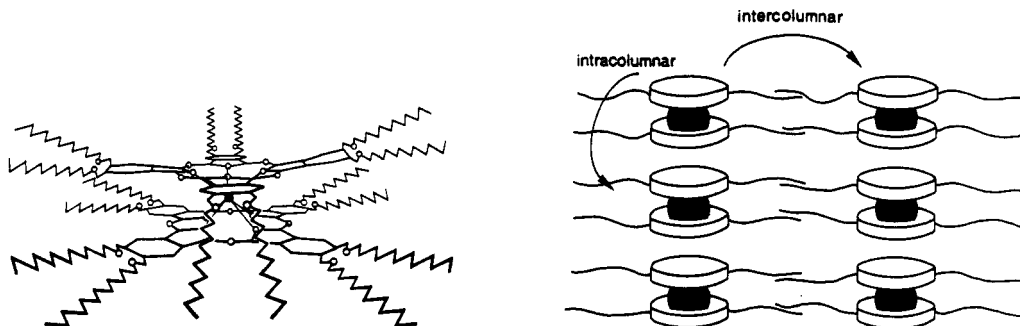
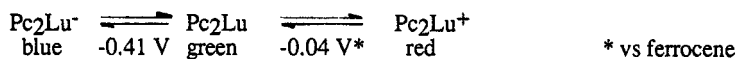


Fig. 4. Molecular structure of the alkyl-substituted complex of lutetium and schematic representation of the intracolumnar and intercolumnar conduction processes in the liquid crystalline phase (after ref. 16).

Semiconductors are mainly used in *electronics* for making devices such as : Schottky contacts, p-n junctions or transistors. A thin film *field effect transistor* based on lutetium phthalocyanine (Pc_2Lu) has been shown to demonstrate performances comparable to those of amorphous silicon (ref. 17). It is well established on the other hand that Pc_2Lu (ref. 18) and its substituted counterpart (ref. 19) show exceptional electrochromic properties :



Substituted Pc_2Lu therefore permits to combine transistor effect, electric field orientation of liquid crystals and *electrochromism*; many new electronic devices, while still hypothetical, may be elaborated from appropriately substituted lithium or lutetium phthalocyanine complexes.

The *polarizability* and the *optical absorption* characteristics of molecular units are closely related (ref. 3, 20). Two of the main optical transitions involving the π -orbitals and d-orbitals of PcM 's in a D_{4h} symmetry are : $a_{1u}(\pi) \rightarrow e_g(\pi)$ (660 nm) and $b_{2g}(d_{xy}) \rightarrow b_{1u}(\pi)$ (280 nm) (ref. 20) (Fig. 5).

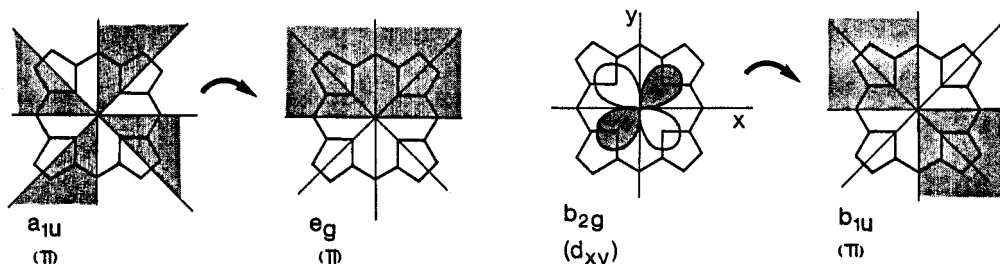


Fig. 5. Schematic representation of the symmetry of the orbitals involved in the absorption spectra of metallophthalocyanines.

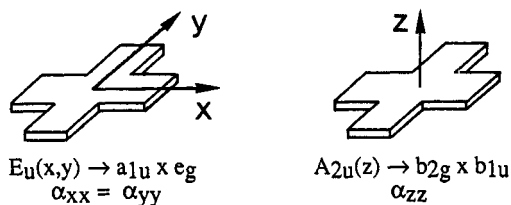


Fig. 6. Symmetry of the transition moments involved in the optical absorption spectra of metallophthalocyanines and the corresponding polarizability coefficients.

The corresponding transition moments will be of $E_u(x,y)$ and $A_{2u}(z)$ symmetries leading to polarizability coefficients (ref. 20) $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$, respectively.

In the same way, the *hyperpolarizability* coefficients β_{ijk} may be determined from the ground and excited states orbital symmetries of a given molecular unit (ref. 20). Non-centrosymmetric units are required for obtaining second order polarizability coefficients different from zero (Fig. 6).

The synthesis of C_{4v} (ref. 6, 21) and C_{2v} (ref. 7) phthalocyanine based molecular units has been described. The calculation of the β -value (β_{zzz}) was performed in the case of an amino-nitro-substituted planar C_{2v} Pc (ref. 22). However, *opto-electronic* properties arise from materials and the macroscopic properties must be derived from those of the molecular unit.

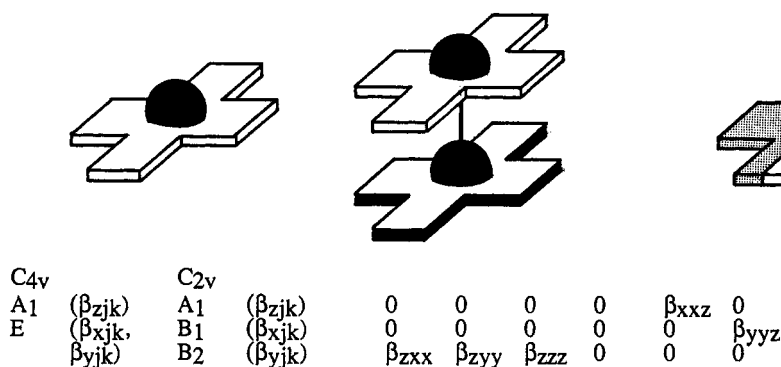


Fig. 7. Determination of the symmetry-allowed hyperpolarizability tensor coefficients β_{ijk} as a function of the molecular unit symmetry and the corresponding transition moment symmetries associated with the optical absorption spectra.

When the molecular material is less symmetrical than the molecular unit, the number of symmetry elements which are in common is given by the ratio of the order of the material symmetry class upon the number of molecular units in the primitive cell. In the case of mesophases however, the condensed phases are only partially organized and the statistical distribution of molecules along certain directions yield highly symmetrical materials (Fig. 8). Fully oriented nematic phases have the same symmetry than C_{2v} molecular unit; the macroscopic properties of polarizabilities and hyperpolarizabilities may therefore be straightforwardly deduced from the molecular unit symmetry. Unoriented nematic and isotropic phases possess higher symmetries and the macroscopic characteristics are obtained by averaging in some or all directions the molecular unit characteristics.

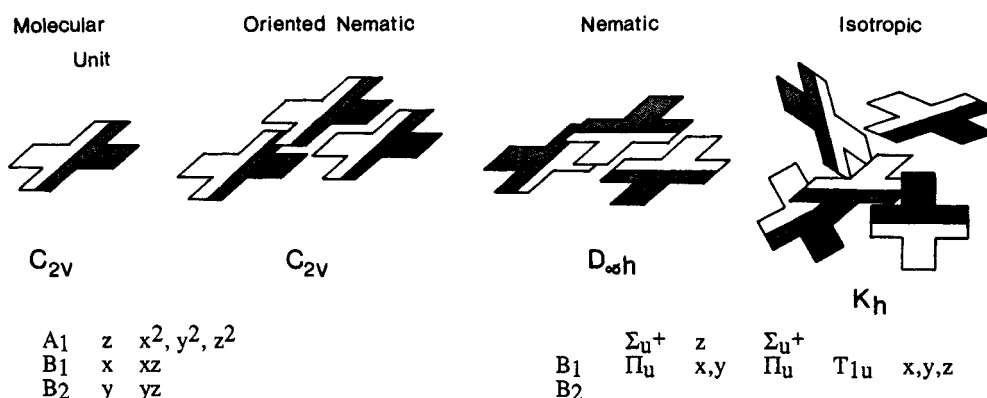


Fig. 8. Relationship between the transition moment symmetry of a molecular unit (C_{2v}) and the macroscopic characteristics of oriented nematic (C_{2v}), nematic ($D_{\infty h}$) and isotropic (K_h) phases.

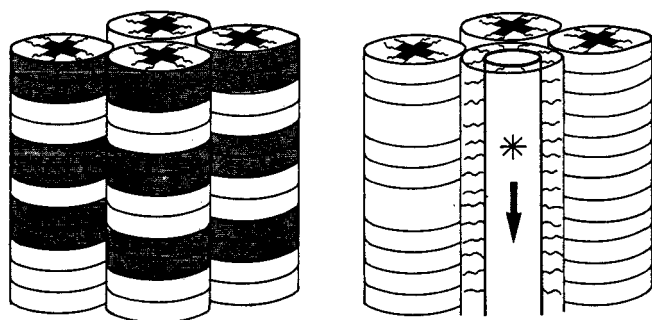


Fig. 9. Representation of the use of columnar liquid crystals for making molecular superlattices or waveguides.

Photons may also be used in devices such as quantum wells (ref. 23) or waveguides (ref. 24).

Superlattices (or quantum wells) consist of one-dimensional periodic structures in which charge carriers and/or photons may migrate. The periodicity of the superlattice intervenes on the transport whenever it is comparable or smaller than the mean free path of the carrier i.e. approximately 10 Å for electrons at room temperature (ref. 25). Such a small value imposes the use of "molecular periodicity" of the order of 3 Å. Polysiloxane derivatives of phthalocyanines were prepared for this purpose (ref. 26); the molecular period is the thickness of the phthalocyanine macrocycle (3.4 Å). The periodicity is ensured by selective dimerization of differently substituted compounds (ref. 21).

Molecular waveguides cannot be realized since visible photon wavelength is comprised between 300 nm and 1 μm. However, a photon may be absorbed and localized on a given molecular unit and subsequently transferred from macrocycle to macrocycle. In this way, photon energy may be transported over a few hundreds angstrom within the aromatic core of phthalocyanine-based columnar liquid crystals (ref. 27, 28).

Finally, all the pieces of the puzzle could be gathered to obtain a *molecular material based device* which would take advantage of the peculiarities of molecular compounds as compared to inorganic ones : high versatility of the types of organization, vast choice of molecular units, small mean free path of charge carriers, possibility of energy transfer ...

A field effect transistor (ref. 17) is composed of a conductor (the grid) whose potential is varied as a function of an electrical signal to be amplified. It is isolated from two conducting electrodes (the source and the drain) by a thin insulating layer. The electrical connection between the two electrodes is ensured by a semiconductor. The signal applied to the grid will be recovered amplified in the source-to-drain current. This device may be designed by using only columnar phases of alkyl-substituted phthalocyanine derivatives (Fig. 10). While this device is yet to be realized, it is worth pointing out that (i) all the individual pieces of the puzzle have already been synthesized, (ii) all pieces possess the electrical properties required, (iii) the molecular material organization - through the use of columnar liquid crystals - is at least partly mastered. One thing is however missing, the possibility to store, over sufficiently long periods of time, the information which is treated. To this purpose, ions should be used since they can be readily moved over small distances with electrical fields. The time constant associated with their displacement is long enough to ensure a safe storage of the information. The synthesis of crown-ether substituted phthalocyanines (ref. 29, 30) has been described and their liquid crystalline properties studied (ref. 31).

In the case of benzo-15-crown-5 substituted phthalocyanine, a mesophase is formed in which the crown-ether macrocycles pile up to form channels in which ion transport can occur (ref. 31, 32). *Information storage and transmission* could be achieved by taking advantage of this one-dimensional ion migration. The field of *ionoelectronics* (ref. 33) would then be opened.

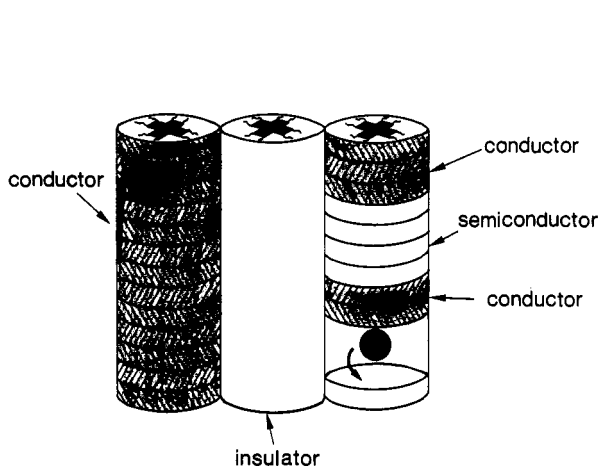


Fig. 10. Schematic representation of a molecular material based transistor (see text).

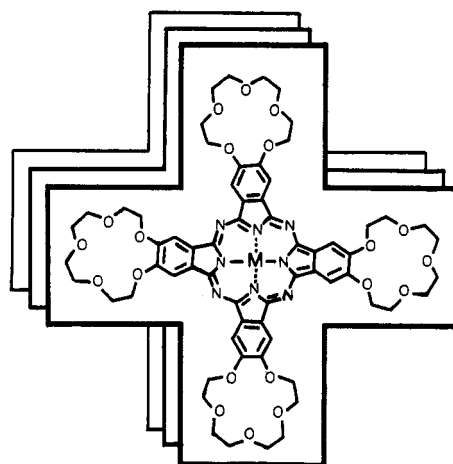


Fig. 11. Molecular structure of benzo-15-crown-5 substituted phthalocyanine and representation of the ion channel organization within the mesophase.

Acknowledgement

Many people contributed by their work to this paper, they are however too numerous to be cited here. Their name can be found in the reference list. I would like to express my extreme gratitude for their collaboration. This paper is an abstract of a conference presented at the University of Hamburg (Sept. 4-8, 1988); as a consequence, mainly the work arising from authors' laboratory has been cited in reference.

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33. In the same way opto-electronics concerns the use of photons for fabricating electronic devices, iono-electronics is concerned with ions. Mr. Greuze is acknowledged for helpful while sometimes misleading advices.