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Electrical and Magnetic Properties of Liquid Crystalline Molecular Materials: Lithium and Lutetium Phthalocyanine Derivatives[⊥]

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The synthesis and characterization of bis(phthalocyaninato)lutetium (Pc_2Lu) and lithium phthalocyanine (PcLi) substituted with long alkyl chains are reported. They form columnar liquid crystals over an extended domain of temperature. Oxidation of the lutetium derivative to the corresponding ionic compound $(s\text{-}Pc_2Lu)^+,BF_4^-$ leads to a more stable mesophase. The magnetic properties of $(s\text{-}Pc)_2Lu$ are determined by electron paramagnetic resonance (EPR) spectra demonstrating the influence of the disorder on the EPR line width. Electrical properties of the solid and liquid crystalline phases have been measured in the frequency range 10^{-3}–10^5 Hz. The intracolumnar order is shown to determine the frequency dependence of the conductivity: $\omega^{0.8}$ for the disordered columnar liquid crystalline phase and $\omega^{0.5}$ for the corresponding ordered one.

I. Introduction

Bis(phthalocyaninato)lutetium (Pc_2Lu) and lithium phthalocyanine (PcLi) were the first known examples of intrinsic molecular semiconductors.[1-4] They show an exceptionally high intrinsic conductivity when compared to most other molecular compounds.[5,6] This peculiarity is associated with their radical nature; diphenylpicrylhydrazyl (DPPH), a well-known standard for electron paramagnetic resonance (EPR), demonstrates a similar behavior.[7] Since it was known that long alkyl chain substituted phthalocyanines form columnar liquid crystals,[8,9] synthesis of substituted Pc_2Lu and PcLi should yield mesomorphic one-dimensional semiconductors (Figure 1).

The conduction properties of liquid crystals of rod-shaped molecules are well established. Extensive studies have shown that these materials are insulators and that any conductivity present is ionic in nature.[10] Several recent attempts have been reported for making conducting liquid crystals.[8,11-14] The ac electrical properties of liquid crystalline charge transfer complexes were reported,[13] demonstrating a mesophase conductivity of the same order of magnitude as in the solid powder (10^{-3} Ω^{-1} cm^{-1}) but with noticeable degradation in the mesophase. A copper complex derived from bis(3,4-nonyloxybenzoyl)methane was shown to demonstrate conductivities, probably extrinsic, of the order of 10^{-8} Ω^{-1} cm^{-1} in a columnar mesophase.[15]

In this paper the synthesis and the characterization of the dodecyloxy derivatives of lithium and lutetium complexes are described. The domains of stability and the structure of the liquid crystalline phases are determined by X-ray diffraction at small angles, optical microscopy, and differential scanning calorimetry (DSC). The magnetic properties of the mesomorphic materials are characterized by electron paramagnetic resonance. Finally, the electrical properties are measured in the frequency range 10^{-3}–10^5 Hz in the solid, liquid crystalline, and isotropic phases. A model for the electrical conduction in one-dimensional columnar mesophases is proposed.

II. Synthesis and Characterization of the Discogens

The syntheses of the octakis(octadecyloxymethyl)lutetium derivatives (**3** in Figure 1) have been previously described.[16,17] Octakis(dodecyloxy)phthalocyanine was prepared either chemically[18,19] or electrochemically.[20] The electroreduction of 4,5-bis(dodecyloxy)phthalonitrile yields octakis(dodecyloxy)lithium phthalocyanine (**2**).[20] The bis[octakis(dodecyloxy)phthalocyaninato]lutetium (**1**) is obtained in 20% yield by heating under reflux a mixture of 4,5-bis(dodecyloxy)phthalonitrile, $^1/_8$ equiv of lutetium acetate, and $^1/_2$ equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene in 1-hexanol. A mono[octakis(dodecyloxy)phthalocyaninato]lutetium complex is produced in addition to the product; it is separated by chromatography. The neutral complex (**1**) is oxidized with nitrosyl tetrafluoroborate

$$[(C_{12}O)_8Pc]_2Lu + NO^+, BF_4^- \rightarrow [(C_{12}O)_8Pc]_2Lu^+, BF_4^- + NO$$

The radical nature of the $s\text{-}Pc_2Lu$ and s-PcLi derivatives has been established by EPR and optical spectroscopy. In dilute solution ($\simeq 10^{-6}$ M), $s\text{-}Pc_2Lu$ **1** and **3** show a single EPR line with an apparent peak-to-peak line width of 10.2 G, similar to that observed in the unsubstituted complex (11 G in chloroform).[21] This broad line arises from an unresolved hyperfine coupling with the lutetium atom ($I = ^7/_2$).[22] The line is considerably narrowed by an exchange mechanism when the concentration is increased (ΔH_{pp} = 8 G at 10^{-4} M). The oxidized complex 1^+, BF_4^- in the solid state shows a small residual concentration of neutral complex (0.3%). In heptane solution, part of the oxidized complex is

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TABLE I: Mesomorphic Properties of the Various Discogens Used in the Present Study[a]

	K_1		K_2		M		I
$(C_{18}OCH_2)_8PcH_2$				62 (50)	hexagonal D, 36; L, 4.7	193	
$[(C_{18}OCH_2)_8Pc]_2Lu$				51 (70)	hexagonal ? D, 37; h, 7.3 L, 4.3, 4.1	56 (26)	
$[(C_{18}OCH_2)_8Pc]_2Lu^+$, $SbCl_6^-$				56		132	
$[(C_{12}O)_8Pc]_2Lu$		41 (16)	orthorhombic a, 29; b, 24.6	85 (14)	hexagonal D, 34.6; h, 3.30 L, 4.6	189 (2)	
$[(C_{12}O)_8Pc]_2Lu^+$, BF_4^-				−3 (7)	hexagonal D, 34.6; h, 3.30 L, 4.5	253	
$(C_{12}O)_8PcLi$			tetragonal a, 25.5	92 (20)	hexagonal D, 34.9; h, 3.35 L, 4.6	269	

[a] The transition temperatures are in °C (enthalpy in kcal/mol), the distances are in Å. Key: K, crystal; M, mesophase; I, isotropic liquid; D, intercolumnar distance; L, correlation length of disordered side chains; h, stacking period along the columns.

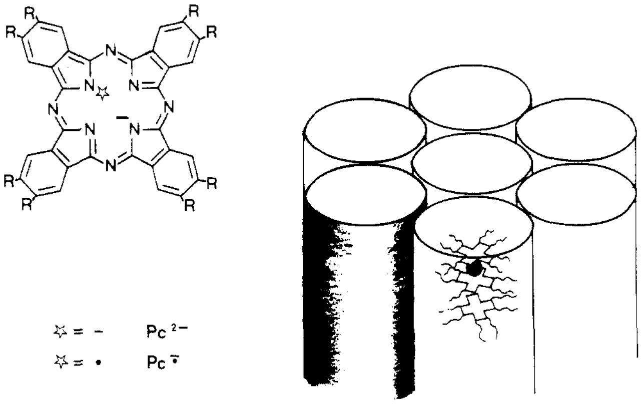

Figure 1. Discogens synthesized and schematic representation of the corresponding mesophases. For R = $C_{12}H_{25}O$–: $[(C_{12}O)_8Pc]_2Lu$ (**1**) and $(C_{12}O)_8PcLi$ (**2**). For R = $C_{18}H_{37}OCH_2$–: $[(C_{18}OCH_2)_8Pc]_2Lu$ (**3**).

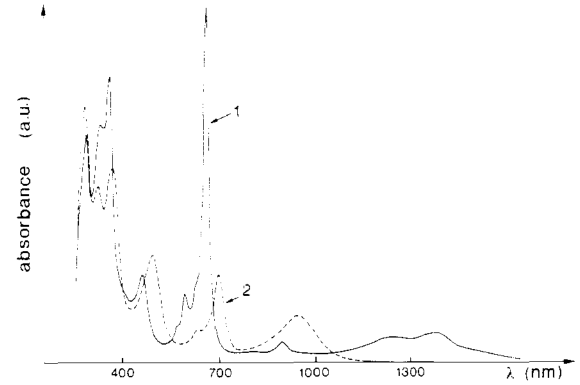

Figure 2. Absorption spectra in arbitrary units of $[(C_{12}O)_8Pc]_2Lu$ (**1**) and $[(C_{12}O)_8Pc]_2Lu^+,BF_4^-$ (**2**) in heptane. For neutral species λ_{max} (log ϵ) are 1370 (4.1), 1250 (4.0), 900 (3.8), 655 (5.2), 595 (4.4), and 460 (4.6) and for oxidized species λ_{max} (log ϵ) are 940 (4.3), 695 (4.6), 530 (4.2), and 495 (4.7) (wavelengths in nm).

degraded back to its neutral form (10%) whose apparent line width is unexpectedly narrow (5.9 G). The presence of traces of nitrogen monoxide is revealed by its characteristic triplet.

Diluted in dichloronaphthalene (10^{-6} M), $(C_{12}O)_8PcLi$ shows a single EPR line, with a peak-to-peak line width of 6.2 G, very similar to that observed for the unsubstituted compound (ΔH_{pp} = 6.3 G[23]). The Gaussian shape is characteristic of an unresolved hyperfine structure with both nitrogen and hydrogen atoms. The low solubility does not allow observation of concentration effects.

The near-IR and visible absorption spectra in heptane of $[(C_{12}O)_8Pc]_2Lu$ (Figure 2) present the same bands at 1370 nm (log ϵ = 4.1) and 1250 nm (4.0), reported for the parent complexes.[24,25] They correspond to an intramolecular charge transfer between the two macrocycles of the complex which disappears upon oxidation, indicating the probable symmetrical nature of the oxidized complex. The optical spectrum of substituted and unsubstituted PcLi demonstrated similar behavior.[23]

III. Mesomorphic Properties

Octaalkyloxymethyl-substituted free phthalocyanines have been shown to lead to hexagonal columnar liquid crystals that are stable in a large temperature range.[8,26] For the lutetium complexes, only a restricted domain of stability (51–56 °C) was obtained[16] for the octadecyloxymethyl neutral derivative (Table I). Oxidation led to far more stable mesophases, the liquid crystalline domain extending over 100 °C.[16] In all cases, the interplanar distance within the columns yielded halos by X-ray diffraction at small angle, indicating the lack of intracolumnar periodicity.

When the paraffinic side chain is directly linked via an oxygen atom (alkoxy derivatives), ordered hexagonal columnar liquid crystals are obtained.[18,19] The ordered character is evidenced by the presence of a fairly narrow peak at large angles in the X-ray diffraction patterns. The mesormorphic properties of octakis(dodecyloxy)phthalocyanine of lithium (**2**), bis[octakis(dodecyloxy)phthalocyaninato]lutetium (**1**) and **1**$^+$, BF_4^- have been determined (Table I). For all the complexes, the range of stability of the mesophase is more extended than for the alkoxymethyl derivatives. The neutral lutetium complex, for instance, forms a mesophase from 85 to 189 °C, whereas $[(C_{18}OCH_2)_8Pc]_2Lu$ leads to liquid crystals between 51 and 56 °C. For s-PcLi and oxidized s-Pc_2Lu, the mesophase to liquid transition is irreversible and a decomposition reaction partly leads to s-PcH_2 and s-Pc_2Lu, respectively.

Crystalline $(C_{12}O)_8PcLi$, like the parent PcLi,[27] possesses a tetragonal lattice (a = 25.5 Å). The solid phase of $[(C_{12}O)_8Pc]_2Lu$ has an orthorhombic unit cell (a = 29 Å, b = 24.6 Å). In the mesophase, all the systems present the characteristics of an ordered

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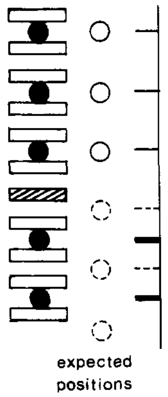

Figure 3. J. Prost's model for the periodic structure evidenced by X-ray diffraction on bis(phthalocyaninato)lutetium derivatives and illustration of the dephasing introduced by monocyclic impurities.

hexagonal columnar structure. The intercolumnar distance is in the range 34.6–34.9 Å. Since a value around 31 Å was found for $(C_{12}OCH_2)_8PcH_2$,[26] we conclude it is the oxygen linkage that leads to our significantly larger intercolumnar distance. The conjugation of the oxygen atom with the aromatic macrocycle seems to stiffen the anchoring point of the paraffinic chain. An intense and fairly narrow peak occurs at large angles, corresponding to a stacking periodicity within the columns for all the discogens. The van der Waals radius of the aromatic derivatives is approximately 3.4 Å, whereas single crystals of PcNiI show an interplanar spacing around 3.24 Å.[28] The intracolumnar periodicity occurs between these two limiting values (Table I). The periodicity of 3.30 Å observed for the lutetium complexes is perhaps surprising since the repeating unit is the bis macrocyclic complex whose size is of the order of 6.8 Å. For the corresponding alkyloxymethyl derivatives, a period of around twice the van der Waals distance was indeed observed (h = 7.3 Å and 6.75 Å for the neutral and oxidized complexes, respectively). The periodicity of 3.30 Å therefore seems to be related to a regular intermacrocyclic spacing uncorrelated to the position of the lutetium ion. If some monocyclic impurities such as $(C_{12}O)_8PcH_2$ are incorporated within the columns, a dephasing of the position of the lutetium ion is introduced. If the concentration of impurity leads to unperturbed column lengths smaller than the spatial coherent domain of the incident X-ray beam (200–300 Å),[29] X-ray diffraction will only detect the intermacrocyclic distance, which is not altered by the incorporation of the impurity[30] (Figure 3). In consequence, the concentration of monocyclic impurities must be in the percent range.

IV. Magnetic Properties

The EPR signal line width of π-radical systems depends on the strength of the spin exchange interaction (J_s) and on the degree of order. In the exchange narrowing limit, the line width varies as

$$\Delta\omega \propto (\Delta\omega_{dip}^2 + \Delta\omega_{hf}^2) J_s^{-n}$$

if, in the absence of exchange, the overall line width is an additive function of the dipolar ($\Delta\omega_{dip}$) and hyperfine ($\Delta\omega_{hf}$) contributions. The parameter n depends on the packing dimensionality: for a 3D spin system $n = 1$ and for 1D $n = 0.5$.[31,32] In all cases the line width decreases when the exchange integral increases.

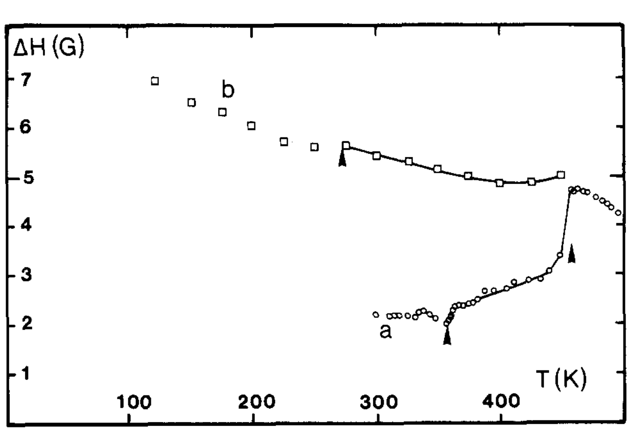

Figure 4. Temperature dependence of the apparent peak-to-peak EPR line width of (a) $[(C_{12}O)_8Pc]_2Lu$ (○) and (b) $[(C_{12}O)_8Pc]_2Lu^+,BF_4^-$ (□). This product contains approximately 0.3% of the neutral radical derivative. The EPR signal is due to this latter. The solid lines visualize the mesophase domain for each system and the arrows the transition temperatures.

The spin exchange integral between electrons delocalized on two molecules A and B is mainly determined by the orbital overlap of these atoms of A and B which are in close contact.[33] For parallel molecules in which p_z orbitals are concerned, the spin exchange integral may related to the overlap integral S_{AB} by

$$J_s = J_{s0} S_{AB}^2 \propto e^{-2\alpha r}$$

J_{s0} is characteristic of the couple AB of interacting sites, α is a parameter, and r is the distance between the two sites. J_s strongly depends on the spin densities, on the distance, and on the reciprocal orientation of the successive sites.

Thus, the J_s term is an averaged site to site exchange integral for the overall interacting spin system. Any reduction of the orbital overlap in this system decreases the local exchange integral, which affects the line width. Such a broadening has been reported for conducting polymers and radical ion salts.[34,35] The apparent peak-to-peak line width is therefore very sensitive to disorder, particularly in 1D systems.

The columnar mesophases are highly anisotropic systems with intracolumnar distances approximately 10 times smaller than intercolumnar values. These materials may therefore be considered as quasi 1D spin systems. The magnitude of J_s is expected to be large since the interplanar distance is smaller than the van der Waals value. In the solid state, the columnar nature is probably preserved.[19] On the contrary in the isotropic phase, small 3D interactions must take place, each radical being separated from the neighboring by the paraffinic molten chains.[36]

The variation of the line width of the EPR signal of $[(C_{12}O)_8Pc]_2Lu$, and its oxidized product, as a function of temperature is shown in Figure 4. The transition crystal–mesophase has no effect on the line width, whereas the transition between the mesophase and the liquid is revealed by an important broadening from 3.2 to 4.7 G at 450 K. It can be concluded that the mesophase and solid structures are closely related. A hysteresis effect is observed when the sample is first heated at 500 K in the isotropic liquid phase and then cooled down to room temperature (ΔH_{pp} = 2.2 G before heating, ΔH_{pp} = 3.2 G after heat treatment). On the contrary in alkyloxymethyl derivatives $[(C_{18}OCH_2)_8Pc]_2Lu$ the line width is very similar in the liquid crystal and in the isotropic phase[16] (5 G). This observation corroborates the X-ray determination studies, which indicated a strong difference in the ordering within the columns for alkoxy or alkyloxymethyl derivatives. The EPR line width of the radical isolated within a column has been obtained by diluting the mixture $[(C_{12}O)_8Pc]_2Lu/[(C_{12}O)_8Pc]_2Lu^+,BF_4^-$ into $(C_{12}O)_8PcH_2$; a value

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of 3.3 G was found. Since in this last case no exchange interaction can occur, the EPR line widths are mainly governed by dipolar interactions. In particular, the difference in line width between liquid crystals and isotropic liquids is due to the difference in dipolar interaction associated with the structural change. The undiluted mixture of neutral and oxidized complexes shows a different comportment: the EPR line width is larger in the mesophase ($\simeq 5$ G) and increases up to 7 G in the crystalline phase. These two facts seem to indicate an exchange contribution to the line width. This consequently implies the presence of a biradical on the oxidized lutetium complex. The magnetic state of s-Pc_2Lu^+ is not thoroughly elucidated by the previous results. The disappearance of the intermacrocyclic charge transfer band in the optical absorption spectrum of the oxidized species also favors the formation of a symmetrical biradical, whose ground state can be singlet ($S = 0$, EPR silent) or triplet ($S = 1$). All attempts to observe directly a triplet state were, however, unsuccessful: neither dipolar splitting nor $\Delta M = \pm 2$ transition could be observed in the temperature range 100–500 K. However, as such spectra are usually very broad, triplet species may be undetected.

The integrated intensity of the signal follows a Curie law up to 400 K (i.e. showing a constant spin concentration). At this temperature, an irreversible increase of the concentration of radicals is observed demonstrating the reduction of the oxidized species back to the neutral form.

V. Electrical Properties

The intrinsic generation of charge carriers in a molecular material may be represented by the reaction[6]

$$AAA \rightleftarrows A^+A^-A \rightleftarrows \text{free carriers}$$

where A is the molecular unit.

The ionized pair A^+A^- is thermally or photochemically generated and the thermal activation energy of conduction, E_{act}, may be estimated from the redox potentials of isolated molecules in solution[37]

$$A \rightleftarrows A^+ + e^- \qquad E_{1/2}{}^{ox}$$

$$A + e^- \rightleftarrows A^- \qquad E_{1/2}{}^{red}$$

$$E_{act} = e\left(E_{1/2}{}^{red} - E_{1/2}{}^{ox}\right) + E_p$$

where e is the electron charge. E_p corresponds to the difference in solvation energy between the solution and the solid or liquid crystalline phases. The equation is valid for weak interaction energy between molecular units, which justify the neglect of collective electronic states. The difference in oxidation and reduction potentials is about 2 V in divalent complexes of phthalocyanines PcM (M = Cu, Ni, Zn, ...)[6] but much less in Pc_2Lu and PcLi: 0.48 and 0.83 V, respectively. The concentration of charge carriers can be estimated from[38]

$$n = n_0 \exp\left[-\frac{\Delta E_{1/2}}{2kT}\right]$$

where $n_0 \simeq 10^{21}$ per cm^3 for molecular materials. For divalent complexes with $\Delta E_{1/2} = 2$ eV, $n = 1.5 \times 10^4$ carriers/cm^3, for Pc_2Lu, $n = 9 \times 10^{16}$ carriers/cm^3, and for PcLi, $n = 10^{14}$ carriers/cm^3.

The ac electrical properties of the condensed phases of s-Pc_2Lu and s-PcLi were determined between two planar electrodes separated by 20 µm (Figure 5). The average size of the single domains in liquid crystals is of the order of 1 µm, while the interrupted column length is approximately 500 Å.[39] Depending on the frequency range considered, the conductivity of the various local structures can be determined. The conductivity (σ) and capacitance (Cp) as function of the frequency for the various mesogens are displayed in Figures 6 and 7.

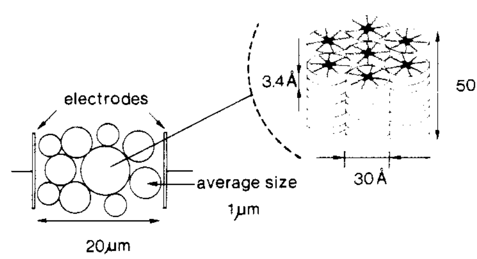

Figure 5. Measurement of the ac electrical properties of columnar liquid crystals: the main characteristic distances important for determining the electrical behavior are figured.

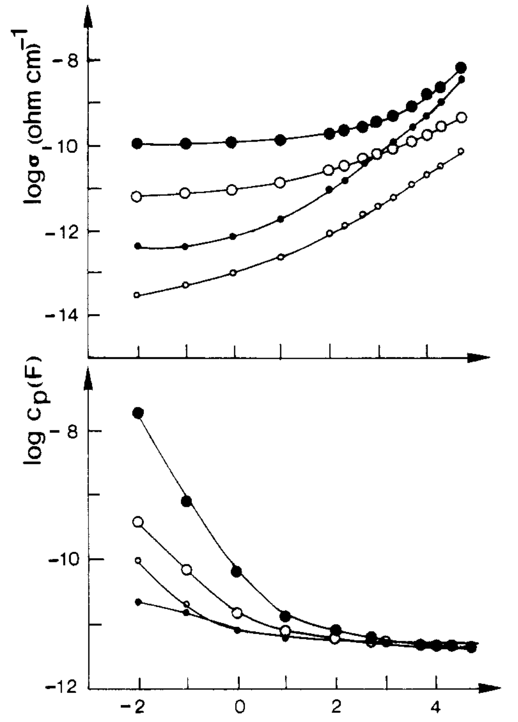

Figure 6. Dielectric spectra of the solid (K) and liquid crystalline (M) phases of the lutetium and lithium alkyloxyphthalocyanine complexes at 300 and 373 K, respectively: ●, $[(C_{12}O)_8Pc]_2Lu$ (M); ○, $(C_{12}O)_8PcLi$ (M); •, $[(C_{12}O)_8Pc]_2Lu$ (K); ∘, $(C_{12}O)_8PcLi$ (K).

Many mechanisms can be operative for charge carrier transports in molecular compounds. However, in molecular materials with interunit distances of the order of the van der Waals value, the individual units constitute spatially localized states for charge carriers. The following discussion will therefore focus on hopping processes. The hopping conduction mechanism was first postulated by Pollack and Geballe in 1961 to explain the ac conductivity of doped silicon.[40] Since then, a considerable number of experimental data concerning the frequency-dependent conductivity of a large variety of materials—covalently or ionically bonded amorphous solids, moleculaf materials—have been accumulated which verify the empirical relation[41-43]

$$\sigma(\omega) = A(T)\omega^{n(T)}$$

where $0.5 < n(T) < 1$.

Three different frequency dependences, ω^0, $\omega^{0.5}$, $\omega^{0.8}$, were observed. The $\sigma \simeq \omega^0$ dependence seen at low frequency (<100 Hz) is associated with a macroscopic phenomenon, where carriers hop between crystallites of different sizes. In this case, the

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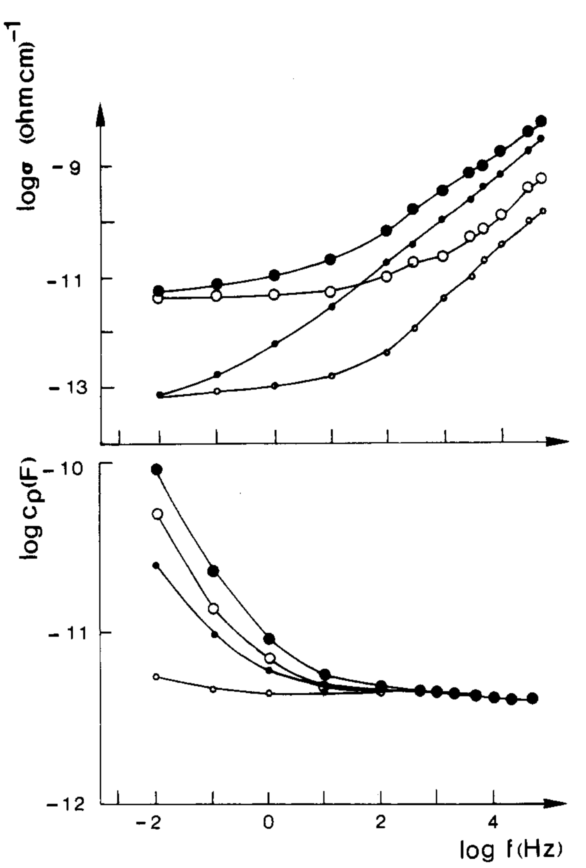

Figure 7. Dielectric spectra of the alkyloxymethyl complexes: ●, $[(C_{18}OCH_2)_8Pc]_2Lu$ (M); ○, $[(C_{18}OCH_2)_8]PcH_2$ (M); •, $[(C_{18}OCH_2)_8Pc]_2Lu$ (K); ∘, $[(C_{18}OCH_2)_8]PcH_2$ (K).

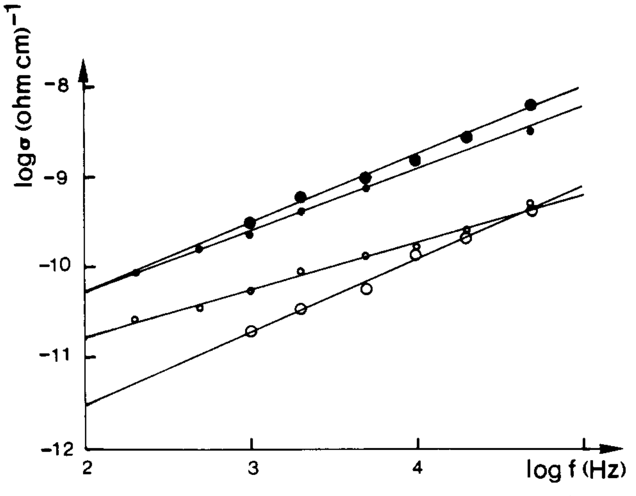

Figure 8. ac conductivity of $[(C_{18}OCH_2)_8Pc]_2Lu$ (●), $(C_{18}OCH_2)_8PcH_2$ (○), $[(C_{12}O)_8Pc]_2Lu$ (•), and $(C_{12}O)_8PcLi$ (∘) in the liquid crystalline domain in the frequency range 10^2–10^5 Hz; the slope is the value of n in $\sigma \simeq \omega^n$.

rate-limiting step for charge carrier migration is probably related to intercolumnar or intercrystallite transport properties. The importance of ionic contributions has been questioned. Translational diffusion in discotic mesophases of triphenylene derivatives has been studied by NMR.[44] The transport seen in our work is probably electronic in nature since (i) the corresponding thermal activation energy is fairly low ($\simeq$1 eV) (Table II), (ii) the capacitance is constant in the frequency range considered (10^{-3}–10^2 Hz), and (iii) translational diffusion of mesogens in discotic mesophases occurs below 5×10^{-2} Hz.[44]

TABLE II: Electrical Properties of the Various Discongens in Solid (K), Liquid Crystalline (M) or Isotropic (I) Phases[a]

compound	phase	n	σ_{RT}, $(\Omega\cdot cm)^{-1}$	E_{act}, eV
$(C_{12}O)_8PcH_2$	M	0.5	4.0×10^{-11}	1.2
		0	1.0×10^{-12}	1.4
	K	0.8	1.5×10^{-10}	0.42
		0	1.0×10^{-12}	0.8
$(C_{12}O)_8PcLi$	M	0.52	2.0×10^{-12}	0.8
		0	1.3×10^{-12}	1.4
	K	0.75	2.5×10^{-10}	0.46
		0	2.5×10^{-13}	1.2
$[(C_{12}O)_8Pc]_2Lu$	M	0.68	3.0×10^{-10}	0.56
		0	2.3×10^{-12}	1.6
	K	0.8	5.5×10^{-10}	0.32
		0	5.0×10^{-12}	1.6
$[(C_{12}O)_8Pc]_2Lu^+$, BF_4^-	M	0.56	7.0×10^{-10}	0.7
		0	2.0×10^{-10}	1.6
$(C_{18}OCH_2)_8PcH_2$	M	0.8	3.4×10^{-11}	0.63
		0	3.0×10^{-14}	1.6
	K	0.8	6.0×10^{-11}	0.4
		0	1.0×10^{-13}	1.12
$[(C_{18}OCH_2)_8Pc]_2Lu$	I	0	4.0×10^{-11}	0.8
	M	0.8	2.0×10^{-10}	0.1
		0	2.0×10^{-14}	
	K	0.8	6.0×10^{-10}	0.1
		0	1.0×10^{-13}	2.4

[a] n, frequency dependence parameter $\sigma \propto \omega^n$. σ_{RT}, conductivity at 10 kHz extrapolated to room temperature. E_{act}, thermal activation energy of conduction.

The number of charge carriers per unit volume can be estimated from $\sigma = ne\mu$ assuming that the mobility of carriers is between 10^{-6} and 10^{-2} cm^2/V·s.[6] By use of the highest value, the concentration of charge carriers is 10^{11} for $[(C_{12}O)_8Pc]_2Lu$ and $(C_{12}O)_8PcH_2$ and 10^{10} carriers/cm^3 for $(C_{12}O)_8PcLi$. On comparison of these numbers to the expected concentration of intrinsic charge carriers previously calculated, it may be concluded the intrinsic contribution is significant in the cases of s-Pc_2Lu and s-PcLi.

At higher frequencies (>10^2–10^5 Hz) the $\omega^{0.5}$ and $\omega^{0.8}$ dependencies are observed (Table II). The corresponding mechanisms can be associated with intracolumnar or intercolumnar processes. The ionization potentials and electron affinities of paraffinic and aromatic moieties are drastically different.[45–47] Charge carriers are therefore localized entirely on the aromatic subunits since the stabilization energy is higher than 2–3 eV for holes as well as for electrons. All electronic transport processes therefore involve the aromatic cores of the columns. It is necessary to determine the intracolumnar versus intercolumnar contributions. The hopping probability is related to the electronic exchange energy J through the equation[48]

$$W_H = \nu_j \exp(-E/kT)$$

where $\nu_j = J/2h$ and $J = J_0 \exp(-\alpha/r_0)$, with α the intermolecular potential barrier, r_0 the effective electron radius (estimated at 2 Å),[49] J the electronic exchange energy, J_0 the effective exchange interaction, and E the hopping activation energy.

By use of the distances determined by X-ray diffraction, it can be estimated that intracolumnar hopping probability is 10^7 times greater than the intercolumnar one for the same activation energy. The difference in frequency dependence ($\omega^{0.8}$ vs $\omega^{0.5}$) is moreover clearly related to the degree of order within the columns: the lower index corresponds in all cases to ordered columnar mesophases as determined by X-ray diffraction. This corroborates the fact that intracolumnar processes are observed at high frequencies. The conductivity at 10 GHz independently determined by a microwave technique[50] for $[(C_{18}OCH_2)_8Pc]_2Lu$ in the mesophase

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(T = 54 °C), was found to be equal to $3.9 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$. This value is equal to the conductivity found by extrapolation in the present study ($3.6 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$) assuming a $\omega^{0.8}$ dependency from 10^2 Hz to 10 GHz. This demonstrates that the same transport mechanism is effective over this frequency range. At 10 GHz, charge migration occurs over less than 1 Å and involves hops between only two localized sites, whereas multiple sites must be postulated in the low-frequency range.[43]

EPR studies have demonstrated that the incorporation in columnar liquid crystals of host molecules is statistical.[51] By assuming an intracolumnar mobility of charge carriers in the range 10^{-4}–10^{-2} cm^2/V·s, with the magnitude of the applied field (macroscopic electric field, 20 V/cm) and the estimated column length (500 Å), it can be calculated that the intracolumnar conduction process should be detected for frequencies higher than 10^2–10^4 Hz. This value is in good agreement with the experimental observations. In the mesophases, the thermal activation energies of conduction in the frequency range where intracolumnar processes are effective vary from 0.1 to 1 eV—with no apparent correlation with the difference in redox potential of the corresponding subunit s-PcH_2, s-Pc_2Lu, or s-PcLi. The thermal variation therefore reflects a detrapping of charge carriers.

In the isotropic phase of $[(C_{18}OCH_2)_8Pc]_2Lu$, a ω^0 dependency is observed with an activation energy of 0.8 eV. Capacitance measurements indicate that ionic conduction takes place below 10 Hz for all mesophases and for isotropic phases. By assuming that the ion migrates over the interelectrode distance (20 μm), a mobility of 4×10^{-4} cm^2/V·s (for a field of 50 V/cm) may be calculated, corresponding to a diffusion coefficient D of 10^{-5} cm^2/s from $\mu = eD/kT$. This value is in agreement with conventional ionic mobilities in solution or in liquid crystals.[52]

VI. Conclusion

The synthesis and the characterization of new discogens $(C_{12}O)_8PcLi$, $[(C_{12}O)_8Pc]_2Lu$, and $[(C_{12}O)_8Pc]_2Lu^+,BF_4^-$ are reported. They form ordered columnar liquid crystals over extended ranges of temperature. The ionic derivative forms more stable mesophases than the neutral homologue; the stabilization of the columnar arrangement could arise from electrostatic contributions or partial orbital overlap within the columns. Since the anions are presumably located in the intercolumnar region, the electrostatic contribution should destabilize the columnar arrangement. The type of organization found, therefore, probably arises from the resonance type interactions between the macrocycles—as is the case for segregated charge transfer complexes.

The magnetic properties of the lutetium derivative has been investigated showing the influence of the disorder on the EPR line width. No conclusive evidence of the spin state of $[(C_{12}O)_8Pc]_2Lu^+,BF_4^-$ could be found; the derivative can be described either as a strongly coupled biradical or as a diamagnetic system. Static magnetic studies are in progress to elucidate this point.

The electrical properties of the three discogens have been determined in the frequency range 10^{-3}–10^5 Hz. In all cases, the macroscopic conductivities are extremely low (< 10^{-10}–$10^{-12}\ \Omega^{-1}\ \text{cm}^{-1}$). The transport properties are very probably governed by the presence of trapped charge carriers. However, it has been shown that, in the mesophase, electron transfer occurs within the columns and that the frequency dependence of this process is influenced by the degree of organization between the phthalocyanine macrocycles. Studies at 10 GHz and in the optical domains are in progress to determine the local electrical properties of these compounds.

VII. Experimental Section

Synthesis. $[(C_{12}H_{25}O)_8Pc]_2Lu$. A mixture of 4,5-bis(dodecyloxy)phthalonitrile (5 g, 10 mmol), lutetium acetate (0.45 g, 1.25 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.75 mL, 5 mmol) is stirred in 30 mL of 1-hexanol under reflux during 20 h. After evaporation to dryness, the green residue is dissolved in a few milliliters of chloroform and reprecipitated by addition of methanol. The solid is purified by chromatography over silica (eluent CH_2Cl_2), yield 20%, recrystallized from ethyl acetate. Anal. Calcd for $C_{256}H_{416}N_{16}O_{16}Lu$: C, 74.11; H, 10.11; N, 5.40; Lu, 4.22. Found: C, 73.71; H, 10.12; N, 5.29; Lu, 3.99.

$[(C_{12}H_{25}O)_8Pc]_2Lu^+,BF_4^-$. The neutral bis(phthalocyaninato)lutetium (97 mg, 23 μmol) is reacted in 5 mL of CH_2Cl_2 with nitroxyl tetrafluoroborate (5.7 mg, 46 μmol) to yield a red-brown solution of the oxidized complex. After evaporation, the remaining solid is dissolved in heptane and filtered: recrystallization, ethyl acetate; yield, 90%. Anal. Calcd for $C_{256}H_{416}N_{16}O_{16}LuBF_4$: C, 72.59; H, 9.90; N, 5.29; Lu, 4.13. Found: C, 71.41; H, 9.84; N, 5.12; Lu, 4.07.

Electrical Characterizations. Measurements were performed by using the cell described in ref 53, in the sandwich configuration. Electrodes consist of 150 nm thick vacuum-deposited gold films, spaced 15–50 μm apart (capacitor area of $S \simeq 7$ mm^2).

Sample conductance and capacitance were determined at different temperatures, using a 1621 General Radio capacitance–conductance bridge between 10 and 10^5 Hz and a semiautomatic apparatus between 10 and 10^{-3} Hz.[54]

The value of the temperature was taken in the vicinity of the sample by a Pt 100-Ω resistance temperature sensor and regulated with an analogic control system with a ±0.1 °C precision.

Electron Paramagnetic Resonance. The EPR experiments were performed on a Brüker ESP 300 X-band spectrometer provided with a NMR gaussmeter, a frequency meter, and a computer ESP-360 for data-handling facilities. The magnetic species concentration was determined by numerical double integrations of the EPR spectra. Sources of errors (saturation, modulation distortion, truncation by too narrow sweep field range) were taken into account and eliminated.

Registry No. $[(C_{12}O)_8Pc]_2Lu$, 122744-29-0; $[(C_{12}O)_8Pc]_2Lu^+,BF_4^-$, 122873-81-8; $(C_{12}O)_8PcLi$, 121477-35-8; 4,5-bis(dodecyloxy)phthalonitrile, 114364-56-6; lutetium acetate, 18779-08-3; 1,8-diazabicyclo[5.4.0]undec-7-ene, 6674-22-2; nitroxyl tetrafluoroborate, 14635-75-7.

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