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Dimeric Substituted Copper Phthalocyanine Liquid Crystals. Synthesis, Characterization and Magnetic Properties[†]

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Abstract: The synthesis and the characterization (gel permeation chromatography, FAB mass spectrometry, NMR spectroscopy) of a bisphthalocyanine derivative substituted with twelve (2-ethylhexyl)oxy side chains are described. This compound and the corresponding copper complex are shown to form mesophases, probably related to a nematic order. Electron spin resonance (ESR) studies demonstrate a highly anisotropic rotation of the molecule in solution; in the mesophase, both intramolecular antiferromagnetic and intermolecular ferromagnetic couplings have been observed.

The engineering of molecular materials[1-4] is nowadays one of the most active field of research. The degree of sophistication of molecular organizations is such that analogies with some naturally occurring biological systems can now be found. At the same time, physicists explore and modelize multiprocesses interconnected by numerous parameters. While a precise and detailed knowledge of every process is important for designing molecular materials, an overview of the whole problem is also necessary even though it can be only qualitative and approximate (systemic approach).[5]

Among the various molecular units which can be chosen for fabricating molecular materials, it has been previously shown[6-11] that the phthalocyanine moiety is one of the most versatile, owing both to the physicochemical characteristics of the subunit (polarity, polarizability, redox behavior, etc.) and to the types of condensed phases it can lead to (single crystals, mesophases, thin films, etc.).

Phthalocyanines substituted with long alkyl chains have been shown to form columnar liquid crystals.[6,7] These mesophases provide quasi-one-dimensional materials in which electron transport[8,9] and singlet[10] or triplet energy[11] migrations have been shown to occur. These systems may be considered as submicronic[12] wires that can be used in electronic devices[13] at the nanometer scale.

In order to further increase the number of adjustable physicochemical parameters of the subunit, the synthesis of the dodecasubstituted planar dimer of phthalocyanine has been achieved (Figure 1).

This paper describes the synthesis and the characterization of the metal-free (**1**) and the corresponding copper complex (**2**) of new bisphthalocyanine derivatives. Their structure has been identified by gel permeation chromatography (GPC) and fast ion bombardment (FAB) mass spectrometry. The liquid crystalline properties of **1** and **2** have been determined by optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction at small angles. Electron spin resonance (ESR) studies have been carried out in solution on complex **2**, and it demonstrates an intramolecular antiferromagnetic coupling between the Cu(II) metallic ions. In the mesophase, an intermolecular ferromagnetic coupling between the metallic subunits has been observed.

Experimental Section

Synthesis. The 4,5-bis((2-ethylhexyl)oxy)-1,2-phthalonitrile (**3**) was synthesized as previously reported.[14,15] The bis(diiminoisoindole) (**4**) was prepared by reacting 1,2,4,5-tetracyanobenzene, dissolved in ethyl alcohol, with ammonia under slight pressure[16] (2 bars). The pressure was maintained constant during the reaction of NH_3 by a Logilap system (Roussel Uclaf).

Laterally bridged bisporphyrins[17] and bisphthalocyanines[18] were previously described. A closely related chemical pathway has been used for synthesizing the alkyl-substituted bisphthalocyanines.

3 (2.3 g, 6 mmol) and **4** (45 mg, 0.21 mmol) are mixed for reaction in 10 cm^3 of freshly distilled *N*,*N*-dimethylaminoethanol[19] under nitrogen at 150 °C for 20 h. The reaction mixture is poured into 20 cm^3 of EtOH and the residue is filtered off and dissolved in CH_2Cl_2. The organic layer is washed with a 0.1 M HCl aqueous solution and with distilled water. The organic layer is dried over $MgSO_4$. Purification of the crude product is carried out by column chromatography over alumina (eluent CH_2Cl_2). A final purification is achieved by preparative thin layer chromatography (TLC, SiO_2; eluent CH_2Cl_2/heptane 90:10 (v/v); $R_f = 0.5$) leading to 12.5 mg (0.005 mmol; yield 2.4%) of the substituted metal-free dimer **1**. Elemental analysis for $C_{154}H_{222}N_{16}O_{12}\cdot 4CH_2Cl_2$ (M_w 2829). Calcd: C, 67.02; H, 8.13; N, 7.92. Found: C, 66.07; H, 8.89; N, 6.11.

Copper complex **2** is obtained by mixing the phthalonitrile **3** (2.31 g; 6 mmol) with 1,2,4,5-tetracyanobenzene (0.178 g, 1 mmol) in the presence of an excess of copper metal in quinoline at 250 °C under nitrogen for 5 h. The reaction mixture is poured into 20 cm^3 EtOH, and the solution is filtered; the residue is dissolved in CH_2Cl_2. The organic phase is washed with a 0.1 M HCl aqueous solution and with distilled water. The organic layer is dried over $MgSO_4$. Purification is achieved by two repetitions of preparative TLC over alumina (eluent CH_2Cl_2, $R_f = 1$; eluent toluene, $R_f = 0$) leading to 18.5 mg (0.007 mmol; yield 0.7%) of dimeric complex **2**.

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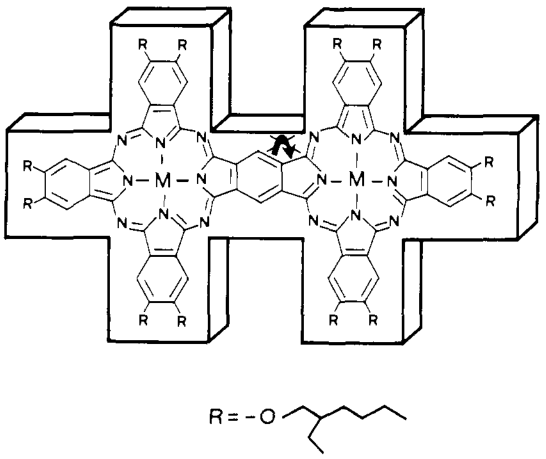


Figure 1. Chemical representation of the dodecasubstituted phthalocyanine derivatives synthesized (**1**, M = 2H; **2**, M = Cu).

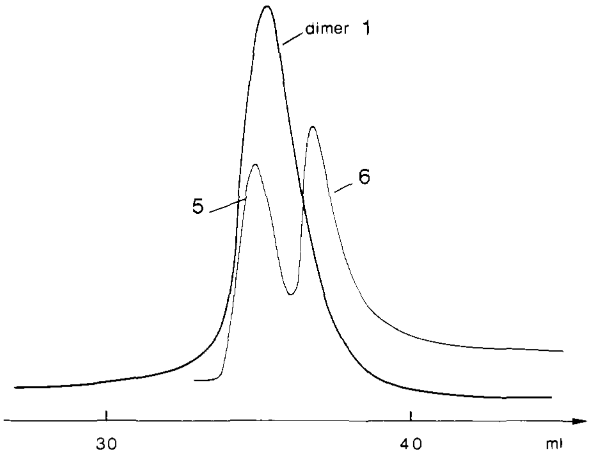


Figure 2. Gel permeation chromatograms obtained for the reference compounds $[(RO)_8Pc]_2Lu$ (**5**: R = 2-Et-C_6, M_w = 3251), $(RO)_8PcH_2$ (**6**: R = 2-Et-C_6, M_w = 1540) and for the metal-free dimer **1**.

Identification of 1 and 2. (a) Gel Permeation Chromatography. This method is reliable for determining the molecular weight of polymers or mesomolecules when reference compounds of very closely related structure may be found for calibration. In our case, the monophthalocyanines $(RO)_8PcH_2$ (R = 2-Et-C_6; M_w = 1540.27; R = C_6; M_w = 1315.83) and the bisphthalocyanine $[(RO)_8Pc]_2Lu$[20,21] (R = 2-Et-C_6; M_w = 3251.45) are used. Four columns (grain diameter 100, 50, 100, 500 Å) of microstyragel are employed as stationary phases with toluene as solvent (pressure 1.2 psi). The detection is achieved with a Waters R 401 differential refractometer.

The profile of the GPC peak obtained for **1** demonstrates that it is not composed of a mixture of products of various molecular weights (Figure 2). A linear extrapolation leads to a value of 2510 for the molecular weight of **1** (theoretical value 2489.55).

(b) FAB Mass Spectrometry. The measurements have been carried out in the "Service de spectrométrie de masse de Strasbourg" (spectrometer Zab, V.G.). FAB measurements were previously known on unsubstituted phthalocyanines.[22]

The derivative $(RO)_8PcH_2$ (R = 2-Et-C_6, **6**) was first studied to determine the fragmentation pattern of substituted phthalocyanines. The molecular peak (M_w = 1540) was observed as well as the following fragmentations: 1510 (M − 28), 1428 (M − 110), 1410 (M − 128), 1397 (M − 110 − 30), 508 (unsubstituted Pc-6; very strong).

The same studies have been carried out on the metal-free derivative **1**, *M* = 2486. The peaks are the following: 2348 (M′ = M − 110 − 28), 1964 (M′ − 3 × 128), 1564 (M′ − [6 × 128 + 17]).

Due to its instability, the molecular peak of **1** is not observed; however, the reference compound **6** and the derivative **1** show exactly the same fragmentation pattern. The highest molecular weight observed for **1** is 2348, which corresponds to (M − 110 − 28), this fragmentation is observed for **6** and corresponds to the mechanism in Scheme I.

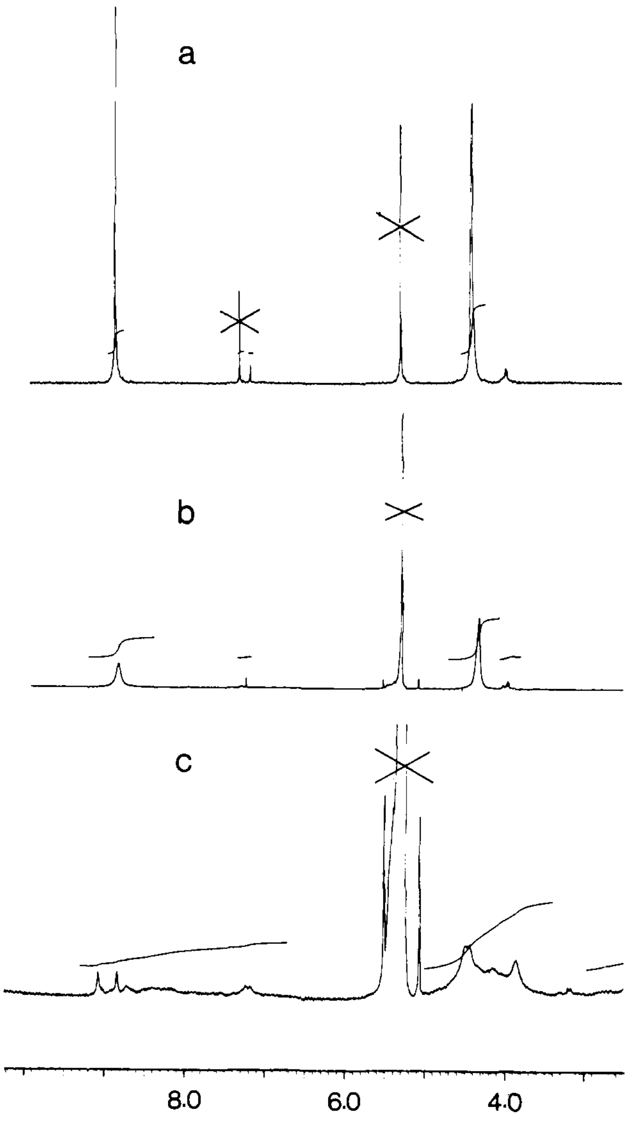
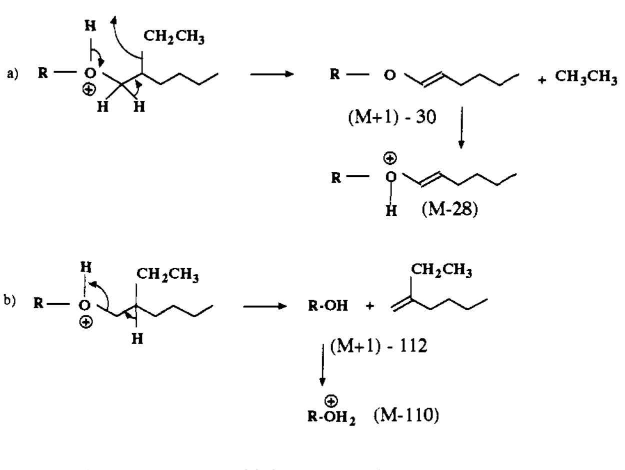


Figure 3. ^1H NMR spectra of $(2\text{-Et-}C_6O)_8PcH_2$ (**6**) in (a) CS_2 at 310 K, (b) CD_2Cl_2 at 300 K, and (c) CD_2Cl_2 at 183 K. Only the regions corresponding to the aromatic protons and to $-OCH_2CH-$ are shown. The solvent peaks are crossed.

Scheme I



(c) NMR Spectrometry. ^1H NMR of **6** is broadened due to the formation of aggregates[16] at low temperature in CD_2Cl_2 (Spectrometer AM 400, Bruker) (Figure 3).

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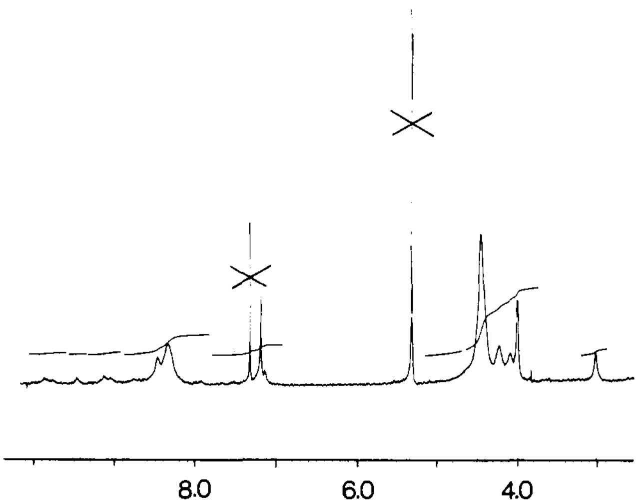

Figure 4. ^1H NMR spectrum of the metal-free derivative **1** in CS_2 at 310 K.

In the case of the dimeric metal-free derivative **1**, aggregation is always observed whatever the solvent or the temperature used (Figure 4) (concentration 5×10^{-3} M).

In all cases, the integration of the different protons corresponds to the expected values. The $-OCH_2CH-$ coupling constant is of the order of 4 Hz for both **1** and **6** derivatives.

^{13}C NMR of **6** strictly follows the expected spectrum. In particular one peak is observed at 106 ppm downfield from TMS for the aromatic CH. In the same region **1** shows one broad peak at 104 ppm and one narrow peak at 106 ppm.

Physicochemical Properties of 1 and 2. X-ray diffraction has been carried out with the Cu Kα radiation using Dutertre equipment. The mesogens were observed with a light polarized microscope equipped with a heating plate controlled by a thermoregulator (Mettler FP 80). The mesomorphic properties were studied with a Differential Scanning Calorimeter (Perking-Elmer DSC 7). The ESR spectra have been recorded using a Bruker ESP 200 band spectrometer. Spin susceptibility is obtained by double integration of the ESR signal and compared with a calibration sample.

Results and Discussion

Derivatives **1** and **2** may be obtained in one step from the corresponding substituted phthalonitrile and 1,2,4,5-tetracyanobenzene. The purification of the products necessitates several chromatographies to isolate only minute amounts (yields 0.7–2.5%) of the desired products. Several years ago,[16] the synthesis of these compounds was attempted. The isolation of the derivatives was unsuccessful due to the unexpected optical absorption characteristics of **1** and **2**: in the dimeric derivative, one could expect a strong coupling between the two phthalocyanine macrocycles which should lead to a red shift of the spectra since, in the simplest models,[23,24] the maximum absorption wavelength is proportional to the number of π-conjugated electrons.

In fact, the maximum wavelength of **1** and **2** (Figure 5) occurs around 670 nm as for the monomeric copper complex **7**.

As a matter of fact, while π-conjugation occurs in the whole molecule, delocalization of the double bonds cannot take place simultaneously between the two phthalocyanine subunits (Figure 1). (An alternative explanation to the absence of red shift could be the protonation after reduction of the benzene ring linking the Pc macrocycles.)

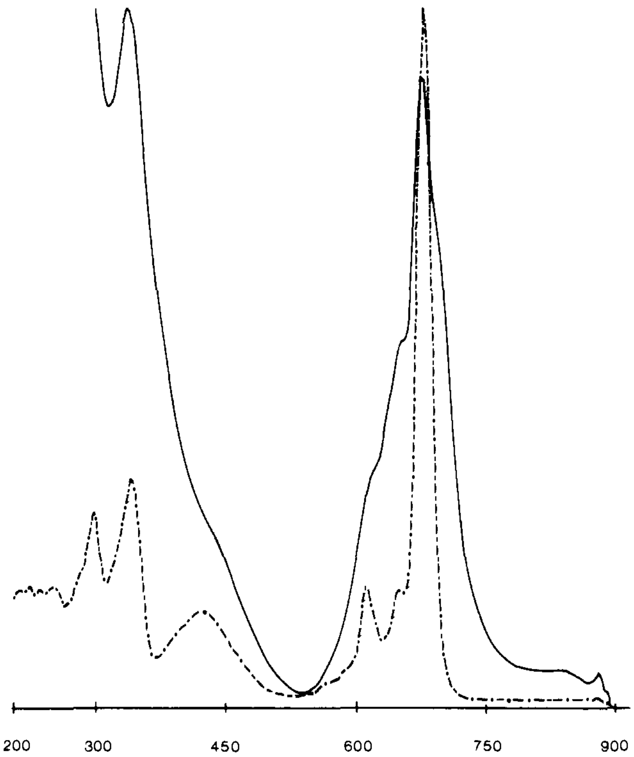

Figure 5. Optical absorption spectra of monomeric $(2\text{-Et-}C_6O)_8PcCu$ (**7**) (dotted line) and of dimeric copper complex **2** (solvent CH_2Cl_2). (No dilution effect has been noticed; $c \sim 10^{-5}$–10^{-6} M.)

The mesomorphic properties of **1** and **2** have been determined by optical microscopy and differential scanning calorimetry. **1** shows a birefringent fluid mesophase from room temperature to 240 °C where an isotropic phase forms. With cooling, the anisotropic phase reappears (Figure 6). The texture is closely related to those found for substituted monophthalocyanines[15] and for uroporphyrin derivatives.[29]

No transitions have been detected by DSC. **2** shows a birefringent fluid mesophase from room temperature to 300 °C. In both cases, solid phases must occur below room temperature and are hardly detected due to the viscosity of these high molecular weight compounds at such temperatures. X-ray diffraction has been carried out on **1** at room temperature and at 40 °C. In both cases, a fairly narrow line at 21.6 Å and broader peaks at 7.7 and 4.1 Å are observed (Figure 7).

The X-ray pattern is very closely related to the one observed for the nematic phase of $(2\text{-Et-}C_6O)_8PcH_2$.[15] However, the peak at 21.6 Å is slightly narrower. This can be due to a higher organization state in a direction perpendicular to the long axis of the molecular unit, as shown in Figure 8. Such a structure is probably related to a smectic type phase with a nematic order within the lamellar plane (Figure 8).

In this case, rotation around the C_2 axes of the molecule would be prevented. This hypothesis is substantiated by the ESR studies on **2** described in the next section. An analogy with a previously reported mesomorphic structure can be noticed.[25]

The ESR characteristics of monomeric substituted copper phthalocyanines have been previously described.[26] $(2\text{-Et-}C_6O)_8PcCu$ (**7**) presents the same ESR pattern. At room temperature, the condensed phase of **7** presents a single line ($\Delta H_{pp} = 54$ G; $g = 2.054$), corresponding to approximately one spin $^1/_2$ per molecule. The intensity of the signal varies as $\chi = C/(T - \theta)$ with no significant magnetic coupling ($\theta = 0$). When the sample is diluted in a diamagnetic matrix, the ESR pattern characteristic of a square-planar copper complex ($I_N = 1$; $I_{Cu} = {}^3/_2$) is observed.[26] In a solution of chloronaphthalene, at room temperature, only the

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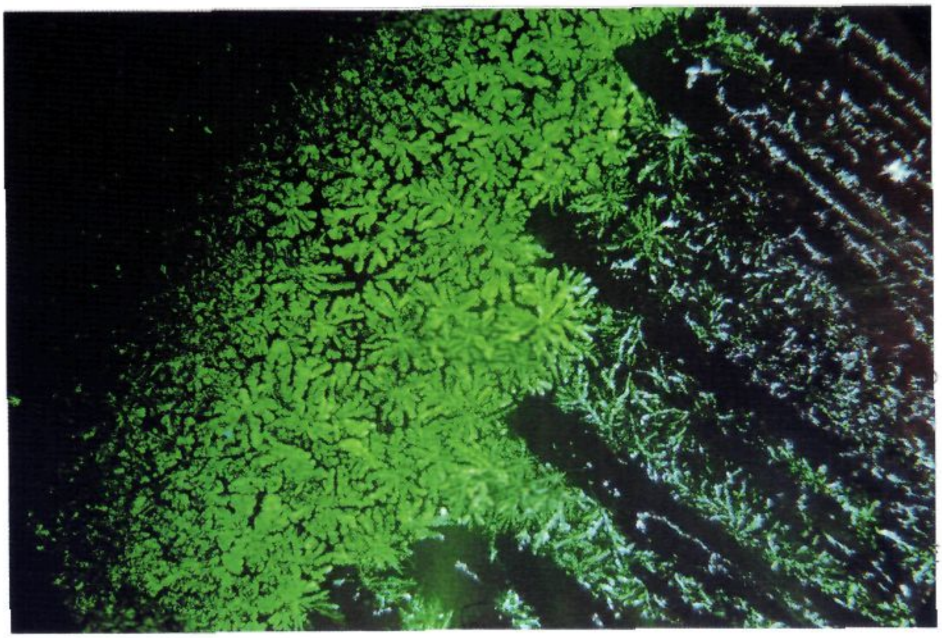

Figure 6. Texture observed for the dimeric metal-free derivative **1** in polarized light microscopy.

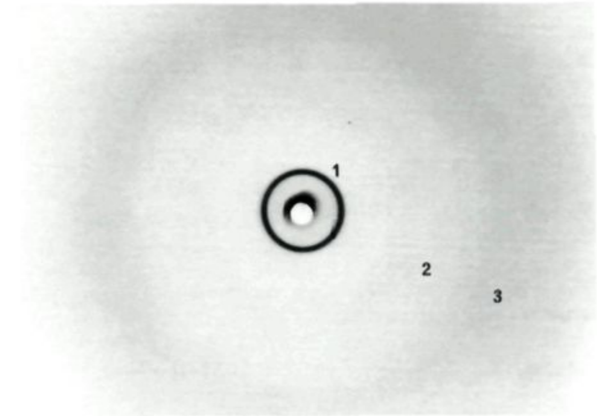

Figure 7. X-ray diffraction pattern of **1** at room temperature: (1) 21.6 Å; (2) 7.7 Å; (3) halo at 4.1 Å.

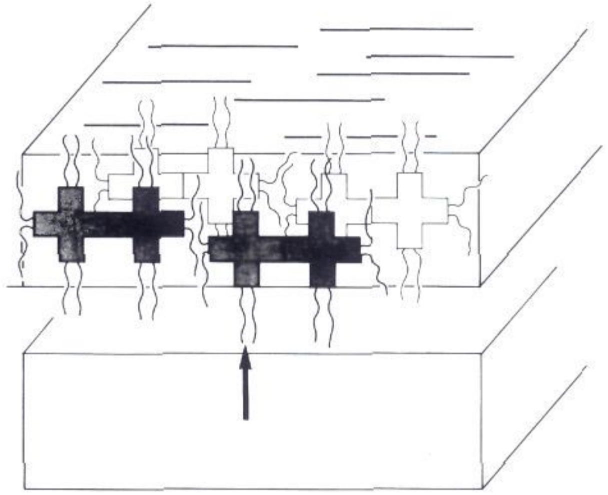

Figure 8. Schematic representation of the structure of the mesophase exhibited by **1**.

coupling with the copper nucleus can be observed (Figure 9).

The ESR spectrum of the copper complex of *N,N'*-bis(2-aminoethyl)-1,3-propanediamine[27] is nearly identical. In both cases, free isotropic rotation occurs with a longer correlation time for **7**.

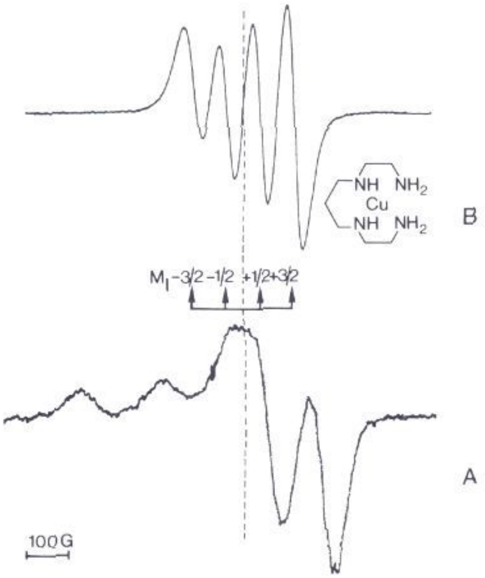

Figure 9. ESR spectra of copper complexes in solution: (A) monomeric complex $(2\text{-Et-}C_6O)_8PcCu$ (**7** in chloronaphthalene); (B) copper complex of *N,N'*-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) in water (from ref 26).

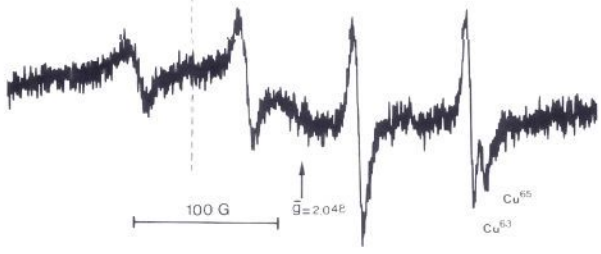

Figure 10. ESR spectrum of **2** in a chloronaphthalene solution (room temperature).

In chloronaphthalene solutions (room temperature), the ESR spectrum of **2** is significantly different (Figure 10).

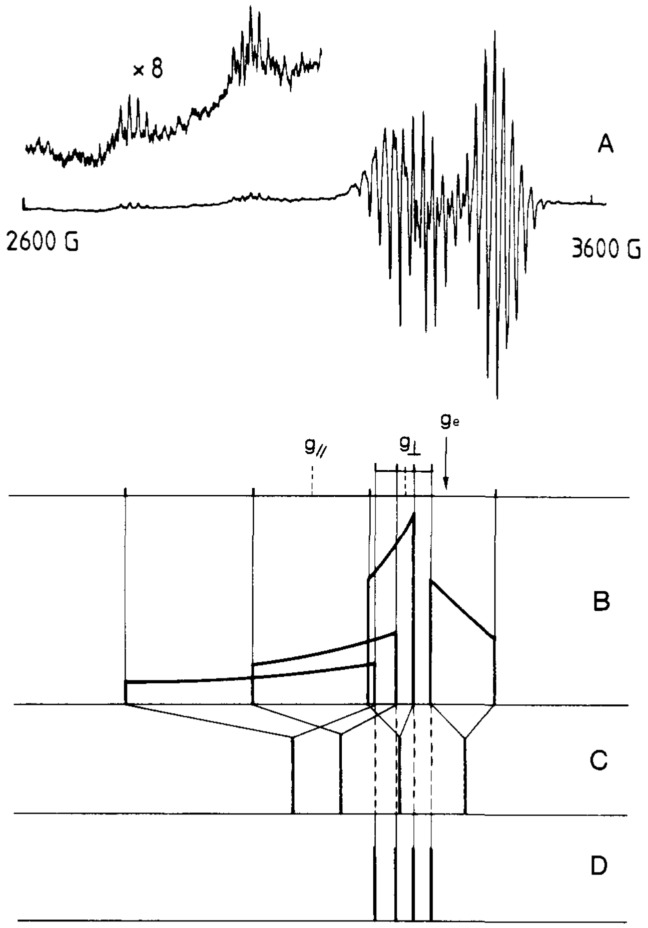

Figure 11. Illustration of the effect of rotation on the ESR spectra of copper phthalocyanine complexes: (A) $(C_{12}OCH_2)_8PcCu$ diluted into the corresponding metal-free derivative in the solid state (no rotation)—the assignment of $g_\parallel$ and $g_\perp$ is given (see ref 25 for further details); (B) representation of the absorption spectrum corresponding to part A; (C) absorption spectrum in the case of isotropic rotation; and (D) the same as part C, but rotation only occurs in the (x,y) macroscopic plane.

In the high-field region, the coupling with the two copper ion isotopes can be detected: $a(^{63}Cu) = 78$ G (69%), $a(^{65}Cu) = 84$ G (31%). The coupling constants differ from the ones expected from measurements on related derivatives[26] ($a_\parallel = 213$ G, $a_\perp = 35$ G, $\bar{a} = 94$ G). The same discrepancy is observed for the g-factor: $g = 2.048$ for **2** instead of $\bar{g} = 2.090$.[26]

The anomalous coupling constants with the copper nucleus and the unusual g-factor found for dimer **2** are both in favor of a highly anisotropic rotation of the molecule in solution. In the case where rotation can only occur in the (x,y) plane of the molecule, the derivative signals observed by ESR mainly arise from the molecules oriented perpendicularly to the magnetic field, i.e. those for which the line is the narrowest (Figure 11). Consequently, the observed g-value (2.048) should be very close to $g_\perp$. This is indeed the case ($g_\perp = 2.052$).

ESR measurements have also been carried out on the condensed phases of $(2\text{-Et-}C_6O)_8PcCu$ (**7**) and dimeric copper complex **2**.

At room temperature, **7** is organized into an orthorhombic lattice[28] ($a = 23.4$ Å, $b = 16.3$ Å). The molecular planes are tilted relative to the column axis. The peak-to-peak line width is of the order of 54 G and the g-factor is 2.054. Such values are in agreement with those previously found for the condensed phase of $(C_{12}OCH_2)_8PcCu$: $g = 2.051$, $\Delta H = 50$ G.[26] The line width varies with temperature ($\Delta H_{pp} = 50$ G at 390 K and 70 G at 115 K) due to an intermolecular copper-to-copper interaction the magnitude of which depends on the mean distance between the metallic ions. The intensity of the signal follows a Curie law ($\theta \sim 0$), indicating a negligible antiferromagnetic or ferromagnetic coupling.

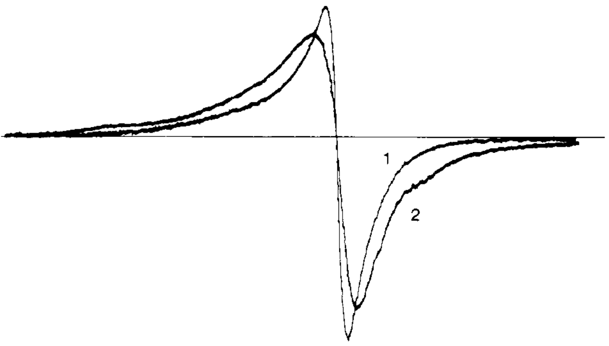

Figure 12. ESR spectra of the solid orthorhombic phase of $(2\text{-Et-}C_6O)_8PcCu$ (**7**) (curve 1) and the mesophase of dimeric copper complex **2** (curve 2).

The mesophase of dimer **2** leads to a surprisingly broad single ESR peak at room temperature ($\Delta H_{pp} = 96$ G) (Figure 12). In the temperature range 120–350 K, a Curie–Weiss law is observed with an antiferromagnetic coupling $\theta \sim -20$ K. At the same time, the line width remains constant contrary to the signal obtained for the monomeric complex. The weak coupling (1.72 meV) between the copper ions is therefore intramolecular since it is not affected by the expected variation of the lattice parameters with temperature.

In the temperature range 8–100 K, a $\Delta M = 2$ transition appears, which must correspond to an intermolecular ferromagnetic coupling.

Conclusion

The synthesis and the physicochemical properties of two new mesogens are described. They are based on a dimeric phthalocyanine molecular subunit. The corresponding mesophases have been characterized by conventional methods (DSC, optical microscopy) and X-ray diffraction at small angles.

The magnetic properties of the planar dimeric copper complex indicate that no rotation occurs around the C_2 axis in the molecular plane, both in solution and in the mesophase. In this case, a structurally related nematic liquid crystal is very probably obtained. Experiments are in progress in orientate the mesophase under the influence of electric or magnetic fields and by surface treatments. These studies should allow us to gain a deeper insight into the structure of the mesophase.

The formation of heterobinuclear complexes of the dimeric ligand should allow us to obtain two covalently linked conjugated macrocycles differing by their redox potentials. The use of such complexes for the dissociation of a photochemically excited state into an electron-hole pair is currently under study.

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