strictions dictated by solubility, availability, or cost.

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Energy Transfer in Solid Phases of Octasubstituted Phthalocyanine Derivatives[†,1]

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Octasubstituted phthalocyanine derivatives are well known to form columnar mesophases by segregation of the rigid aromatic cores and the flexible paraffinic side chains[2,3] (Figure 1). In the case of the dodecyl derivatives, the copper complex demonstrates a mesophase from 53 to more than 300 °C and the metal free compound from 80 to 260 °C.[2] It is possible to incorporate the copper complex $(C_{12}OCH_2)_8PcCu$ into the dihydrogeno compound $(C_{12}OCH_2)_8PcH_2$ as to form either mixed liquid crystals or solid solutions.[4] X-ray determinations at small angles have shown that the mesophases consist of ^{2}D hexagonal arrays of columns separated by about 31 Å.[2] In the solid phases present at room temperature, the columnar structure is preserved while a tilting angle of about 24° between the macrocycles and the axis of the columns induces an orthorhombic structure (a = 24.5 Å; b = 30.4 Å).[5] ESR studies have shown that the copper complex is randomly distributed within the columns composed of the metal free derivative.[4] In this paper the luminescence properties of the corresponding solid solutions are studied (Figure 2). The fluorescence of the dihydrogeno derivative is quenched in the presence of the copper complex in the solid[6,7] or in the solution.[13] Concentrations of Cu^{II} not inferior to 0.05% (m/m) could be attained due to the fact that copper cyanide is used in the chemical pathway leading to the final macrocycles.[3] For 16% of copper complex, the luminescence of $(C_{12}OCH_2)_8PcH_2$ is almost entirely quenched showing that energy migration processes are involved. For comparison, in unsubstituted phthalocyanine thin films, singlet excitation migrates over a distance of 300–500 Å.[8]

The exciton diffusion length may be estimated knowing the probability $N(n)$ of having a sequence of n metal free molecules as a function of the copper concentration. It may be demonstrated that for a ^{1}D system if P_{ba} represents the probability of having the species A after the species B, then

$$N(n) = P_{ba} P_{aa}^{n-1} P_{ab} \qquad (1)$$

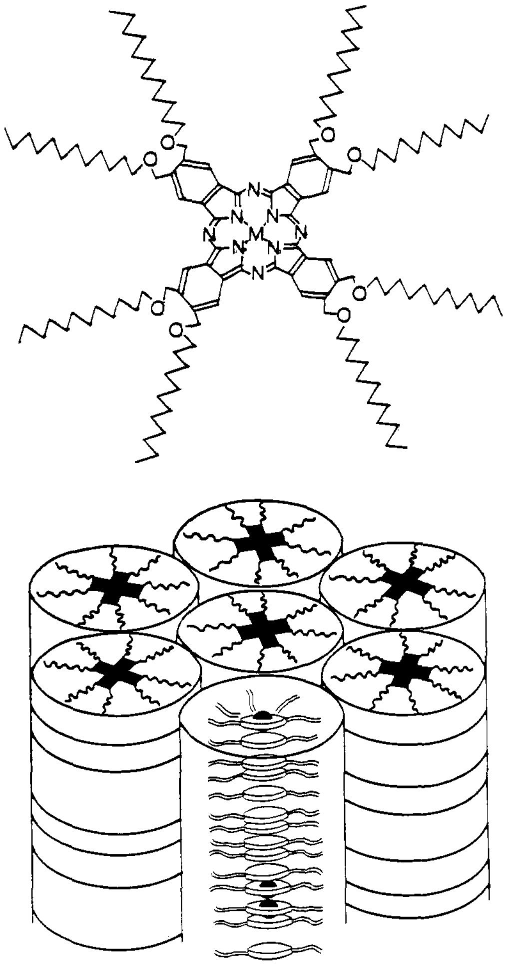

Figure 1. Schematic representation of the octadodecylphthalocyanine derivatives used: M = H_2, $(C_{12}OCH_2)_8PcH_2$; M = Cu^{II}, $(C_{12}OCH_2)_8PcCu$, and the structure of the corresponding columnar mesophases of mixed copper (solid circles) and metal free compounds.

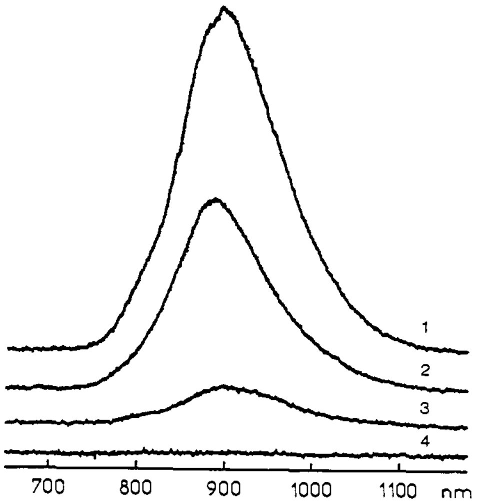

Figure 2. Fluorescence spectra of mixtures of $(C_{12}OCH_2)_8PcCu$ into $(C_{12}OCH_2)_8PcH_2$ at room temperature (excitation wavelength:514.5 nm): 1:0.05% (m/m); 2:0.45%; 3:4.5%; 4:16%.

For a random distribution , the following is obtained[9] with y being the molar concentration of the species A in B.

$$N(n) = y^n(1 - y) \qquad (2)$$

The luminescence will be considered as quenched when the photon is absorbed in a region extending over $n_c/2$ A molecules

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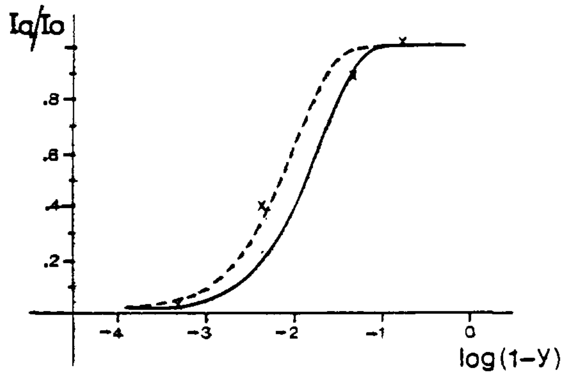

Figure 3. Proportion of fluorescence quenching (I_q/I_0) as a function of the logarithm of the concentration of quencher B, ($1 - y$), into A (m/m) for a ^{1}D randomly distributed system. Solid line: $n_c/2 = 25$; dashed line: $n_c/2 = 50$ (see eq 3).

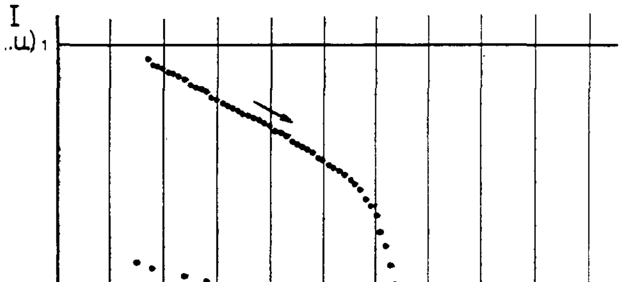

Figure 4. Fluorescence intensity (in arbitrary units) of condensed phases of $(C_{12}OCH_2)_8PcH_2$ as a function of temperature.

from the quencher B. The quenching efficiency I_q/I_0 is then given by

$$I_q/I_0 = \left(\sum_{n=1}^{n_c} ny^n + n_c \sum_{n=n_c+1}^{\infty} y^n\right) \Big/ \left(\sum_{n=1}^{\infty} ny^n\right) \qquad (3)$$

Experimental points have been fitted to eq 3 leading to $n_c/2$ of the order of 25–50 and, correspondingly, to an exciton diffusion length in the range 100–200 Å (Figure 3).

The luminescence of $(C_{12}OCH_2)_8PcH_2$ has been studied as a function of temperature (Figure 4) indicating a strong fluorescence decrease when going from the solid to the mesophase. A hysteresis effect is observed by cooling down from the mesomorphic state and the characteristics of the solid are restored only after a few weeks. The effect of the incorporation of copper complex in the liquid crystal domain could not be accurately studied because of the low intensity of fluorescence. Luminescence properties of $(C_{12}OCH_2)_8PcH_2$ and the corresponding unsubstituted derivatives were studied in different phases: monomer or aggregates in solution, thin films, single crystals; these studies demonstrate that the least-ordered states yield to the lowest luminescence quantum yields. The low intensity of fluorescence in the mesophase is therefore probably related to a more disorganized state.[10]

In the present publication, the energy migration processes involved in ^{1}D molecular materials have been studied. This is a first step toward molecular superlattices in which two different molecular materials would be periodically alternated. Since the mean free path of charge carriers is of the order of 10 Å at room temperature in the case of molecular materials,[11] the superlattice period must be of the same order of magnitude.[14] Polymeric phthalocyanine derivatives have been synthetized for this purpose.[12]

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Dioxygen–Copper Reactivity: Hydroxylation-Induced Methyl Migration in a Copper Monooxygenase Model System

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In this report, we describe a system in which a copper-ion mediated hydroxylation of an arene exhibits a mechanistic similarity to that known for the iron-dependent monooxygenases such as phenylalanine hydroxylase and cytochrome P-450. The overall process of hydroxylation-induced migration is reminiscent of the "N.I.H. shift"[1-3] and suggests that the reaction proceeds by the electrophilic attack of a $Cu(I)_n/O_2$ derived species upon the aromatic substrate.

We have previously described a chemical system in which an aromatic ring, which is part of a dinucleating ligand, is hydroxylated.[4,5] Here, the dinucleating ligand, *m*-XYL (**1**), in which two tridentate PY2 units (PY2 = bis[2-(2-pyridyl)ethyl]amine, **9**) are connected by a *m*-xylyl group, is employed. The three-coordinate dinuclear copper(I) complex **2** reacts with dioxygen, resulting in the oxygenation of the ligand and concomitant formation of the phenoxo- and hydroxo-bridged dinuclear Cu(II) complex **3**. The free phenol **4** can be isolated by leaching out the copper ions using a base extraction procedure.[4] The hydroxylation reaction, **2** + $O_2 \rightarrow$ **3**, is analogous to the reactions mediated by the copper monooxygenases such as tyrosinase[6,7] and dopamine β-hydroxylase[6b-8] since labeling studies on the enzymes and this

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