basic agreement with our findings. Currently, we are examining quantitatively the sequential kinetics[12] for the resolution of enantiomeric diols to enable us to define more precisely the stereospecificity of this unique biocatalytic lactonization process.

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Laser Induced Triplet Excitons in the Columnar Phases of an Octasubstituted Metal Free Phthalocyanine

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Columnar mesophases are interesting systems for the study of one-dimensional energy migration. In these phases, chromophores which constitute the central rigid part of the mesogenic molecules are stacked in columns surrounded with flexible hydrocarbon chains; the intercolumnar distance is much larger than the intermolecular distance within the columns.[1-3] Energy migration has been recently reported for the columnar phases of the 2,3,6,7,10,11-hexa-*n*-hexyloxytriphenylene; singlet excitons are generated by fusion of triplet excitons, and delayed fluorescence is observed.[4] Moreover the singlet exciton diffusion length has been determined in columnar phases formed with solid solutions of metal free and copper(II) octasubstituted phthalocyanines.[5]

The present communication describes the properties of laser induced triplet excitons observed in both the crystalline and the liquid crystalline phases of the octakis(octadecyloxymethyl)metal free phthalocyanine, **1** (Figure 1), determined by nanosecond absorption spectroscopy.[7]

Laser excitation of **1** (Q band) in homogeneous benzene solutions or in pure columnar mesophases gives transient differential absorption spectra typical of a phthalocyanine triplet–triplet absorption[8,9] (Figure 2). The triplet lifetime in benzene solutions (10^{-6} M) is 120 ± 10 μs. This value is in agreement with the ones previously reported for the nonsubstituted metal free phthalocyanine.[8,10] When the pure compound thin films are excited with low energy laser pulses a monoexponential decay of the transient absorption is observed, yielding a triplet lifetime of 7.5 ± 0.5 μs at 25 °C. This lifetime continuously decreases down to 4.2 ± 0.3 μs when the temperature increases up to 84 °C.

For high-energy pulses, the transient decay obeys second-order kinetics. The differential spectrum obtained under these conditions is the same as the one obtained with low-energy excitation. Triplet–triplet annihilation therefore occurs: $T + T \rightarrow 2S_o$. The

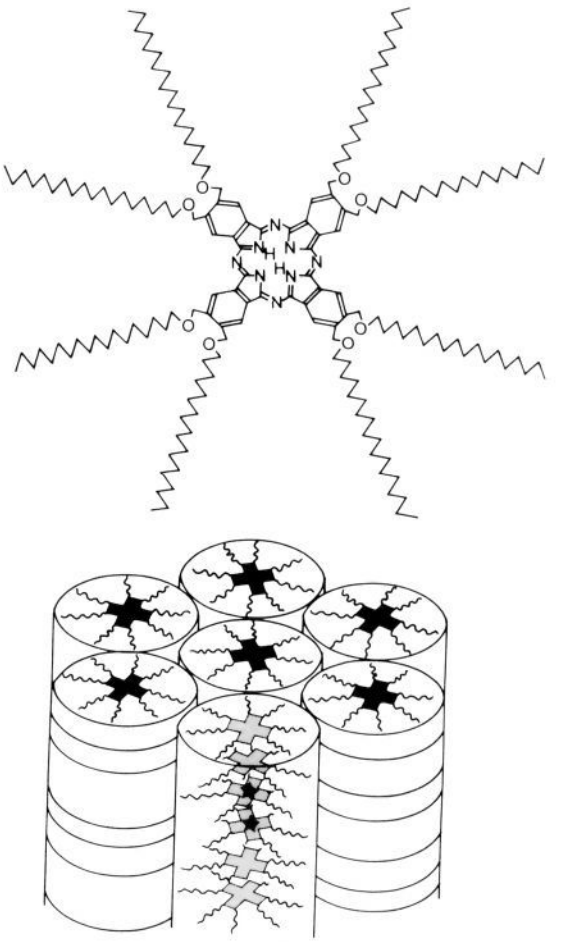

Figure 1. Schematic representation of the octakis(octadecyloxymethyl)metal free phthalocyanine used, $(C_{18}OCH_2)_8PcH_2$ (**1**).

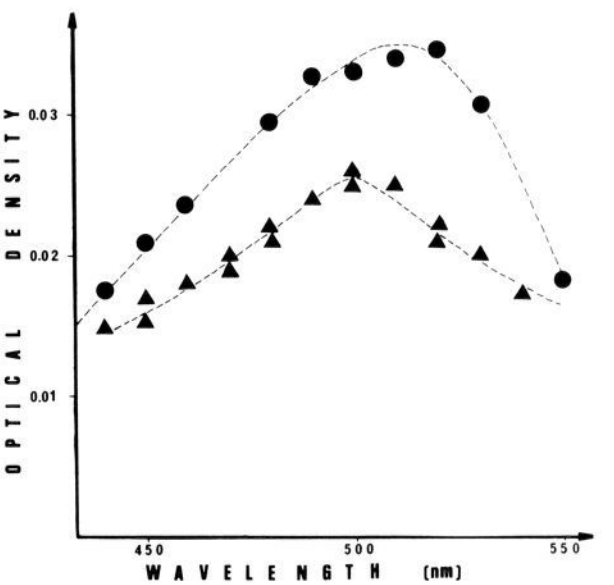

Figure 2. Transient differential absorption spectra at $t = 0.2$ μs of pure $(C_{18}OCH_2)_8PcH_2$ excited at 532 nm: (●) 25 °C, (△) 77 °C. Phase transitions: crystal $\xrightarrow{62\ °C}$ mesophase (D_{hd}) $\xrightarrow{193\ °C}$ isotropic liquid.

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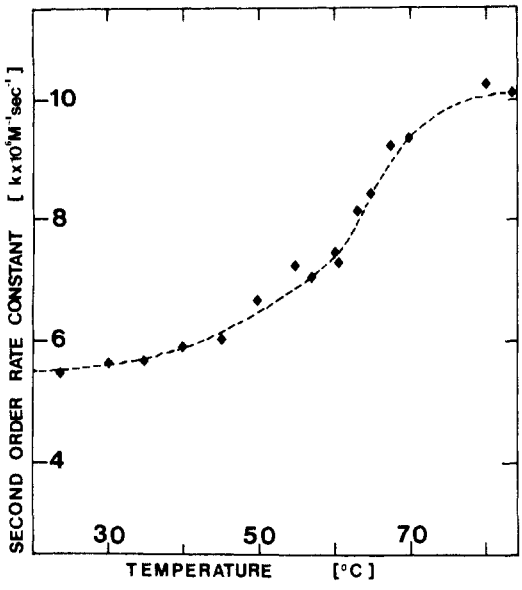

Figure 3. Temperature variation of the second-order rate constant obtained with pure $(C_{18}OCH_2)_8PcH_2$: λ_{ex} = 532 nm.

plot of the second-order rate constant k versus temperature (Figure 3) shows that k increases with increasing temperature: it is (5.5 ± 1.0) × 10^6 M^{-1} s^{-1} at 25 °C and (10.0 ± 1.0) × 10^6 M^{-1} s^{-1} at 84 °C. The inflection point at 62 °C corresponds to the crystal → liquid crystal transition. Thus triplet–triplet annihilation is twice as efficient in the liquid crystal than in the crystal.

The minimum number of absorbed mole-photons necessary to obtain second-order decay kinetics has been determined from laser energy variation experiments. Assuming a triplet yield of 0.14,[8,11] the minimum triplet molar fraction needed is 0.0070 at 25 °C and 0.0067 at 77 °C. As triplet exciton migration occurs only via a short range (<15 Å) interaction[12a] and because in the examined phases the intercolumnar distance is 36 Å,[13] such an interaction is possible only for the molecules belonging to the same column. The average distance between the macrocyles inside the column being 4.5 Å,[14] the exciton path length can be calculated: 640 Å at 25 °C, 670 Å at 77 °C. The exciton diffusion coefficient for one-dimensional energy migration[12b] is found to be respectively 16 × 10^{-6} cm^2 s^{-1} and 10 × 10^{-6} cm^2 s^{-1} at 25 °C and 77 °C. Like the second-order decay rate constant, the diffusion coefficient is higher in the liquid crystalline phase than in the crystalline one by a factor 1.6, consistent with a more efficient exciton migration in the liquid crystal than in the crystal.

The exciton path length, as expected, is higher than the one determined for singlet excitons (100–200 Å) in similar systems,[5] but it remains low compared to the triplet exciton path lengths determined for organic single crystals in which typical values are of the order of a few microns.[12a] It is tempting to assign the shortening of the triplet exciton path length to an exciton trapping when the one-dimensional way is interrupted, i.e., when the continuity of the column breaks down. Therefore the path length determined in the columnar phases should be correlated with the column length: the columns would be made of 140–150 phthalocyanine molecules. The column length determined by this method is expected to be higher than the coherence length given by X-ray diffraction,[15] because distortions of the column axis are allowed as far as the one-dimensional migration is preserved.

These experimental results have been treated on the basis of mean values. A statistical treatment taking into account the distribution of the various parameters is in progress.

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Supplementary Material Available: Sample and laser pulse characteristics, boundary conditions for a second-order decay kinetics, and determination of the exciton diffusion coefficient (A) (1 page). Ordering information is given on any current masthead page.

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Carboxylic Acid Complexation by a Synthetic Analogue of the "Carboxylate-Binding Pocket" of Vancomycin

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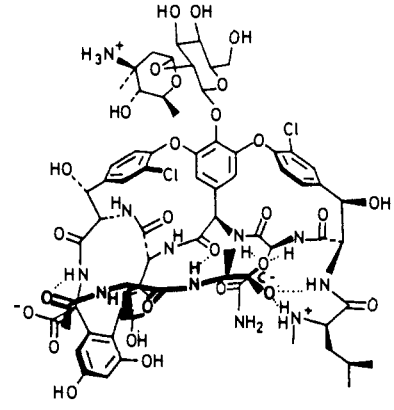
Vancomycin[1] is a clinically important antibiotic that disrupts bacterial cell wall biosynthesis by binding to the terminal D-Ala-D-Ala sequence of one of the peptidoglycan precursors.[2] The active complex **1** involves six hydrogen bonds between vancomycin



1

and the dipeptide substrate[3] (bold lines in **1**). In addition nonbonded interactions between the alanine methyl groups and hydrophobic regions of the antibiotic may account for its strong substrate- and stereospecificity.[1b,3,4] Five of the six hydrogen bonds in **1** are found near the right-hand ring of the antibiotic, and they form a binding pocket for the carboxylate region of the terminal D-alanine.[3]

In an effort[5] to determine the minimal functional unit of vancomycin we have synthesized an analogue **2** of the right hand ring and shown that it binds to carboxylic acids by a similar mechanism to the antibiotic. Two key structural features of this model[5] are an N-terminal amino group[3] and a bulky substituent on the central amino acid,[6] both of which are thought to play important roles in binding.[3]

Receptor **2** was prepared in six steps from amino acid starting materials.[7] Protection of 3,5-dinitro-L-tyrosine as its *tert*-but-

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