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Orientational Order and Linear Dichroism of a Water Soluble Porphine in a Lyotropic Nematic Liquid Crystal

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Aqueous lyotropic nematic liquid crystals can be homogeneously oriented by magnetic fields and are therefore well suited to be used as anisotropic solvents for optical polarization studies of water soluble dye molecules. The potassium laurate (KL)/KCl/H_2O nematic phase, composed of rod-like or cylindrical micelles, was used as a matrix for the study of orientational order and linear dichroism of a substituted free-base porphine ($TPPS_4$). The results indicate that a significant portion of porphine molecules are incorporated into the micelles with their planes on the average perpendicular to the optic axis of the lyotropic rods. The order parameter of $TPPS_4$ is much higher in this system than in other nematic lyophases such as KL/decanol/H_2O in which preferential hydrogen bonding occurs between $TPPS_4$ molecules and the hydroxyl groups of decanol molecules which presumably occupy the surface of the cylindrical micelles. All observed electronic transitions in the 350–700 nm range are found to be polarized in the plane of the porphine ring.

INTRODUCTION

Lyotropic nematic mesophases have been extensively used for the determination of the structure of oriented molecular or ionic species by NMR spectroscopy.[1] Measurements have also been reported[2] on polarized absorption spectra of water soluble dyes in several magnetically oriented aqueous lyotropic nematic liquid crystals such as : (A) disodium cromoglycate[3] (DSCG)/water, with negative diamagnetic anisotropy ($\Delta\chi < 0$), or (B) potassium laurate[4,5] (KL)/1-decanol/water ($\Delta\chi > 0$). Both nematic phases are composed of rod-like or cylindrical micelles (N_c phases)[6] at room temperature and are readily oriented into homogeneous planar textures by magnetic field or surface interactions. Thus the polarized differential absorption spectra (the linear dichroism, $A_{\parallel} - A_{\perp}$, where $\parallel$ denotes light polarized parallel and $\perp$ perpendicular to the major optic axis) of water soluble guest molecules in oriented samples can easily be recorded.

In an earlier study,[2a] it was found that a water soluble free-base porphine (Figure 1), tetrasodium-meso-tetra(4-sulfonatophenyl)porphine ($TPPS_4$), orients with its plane (xy axes) in (A) and (B) systems approximately perpendicular to the optic axis of the lyotropic rods with a low order parameter ($S_{xy} = -0.006$). The low order parameter of $TPPS_4$ was attributed to the size and shape of porphine molecules and the presence of phenyl groups, which, because of steric hindrance, are rotated[7,8] about 61–63.1° with respect to the plane of the porphine nucleus.

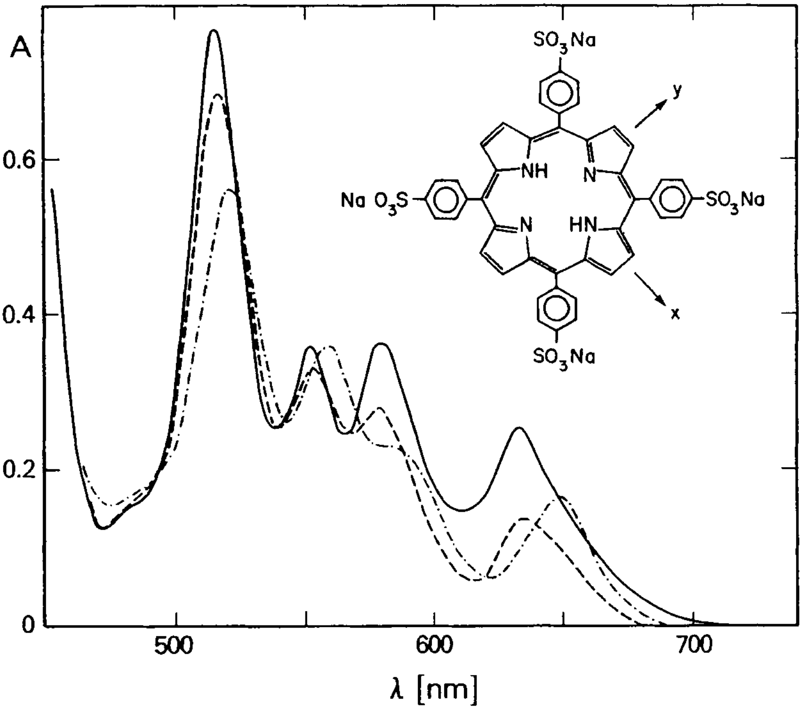

FIGURE 1 Superimposed absorption spectra of different concentrations of $TPPS_4$ in water (pH ~ 5.5): 5 × 10^{-5}M (1 cm cell, —), 5 × 10^{-4}M (0.1, - - -), 2.5 × 10^{-3}M (0.02, -·-·-).

Due to the low order parameter of $TPPS_4$, it was not possible to measure the linear dichroism spectra of this porphine in the visible region of the spectrum. However, large red shifts were noted in the low energy visible (Q_x) bands and also the near ultraviolet Soret (B) band in the absorption spectrum of $TPPS_4$ dissolved in either KL(B) or DSCG (A) system. Analogous red shifts of the same absorption bands are observed in alcoholic solutions of $TPPS_4$, which are known[10] to disperse porphine aggregates and are presumably due to strong specific interactions (hydrogen bonding) of a porphine nucleus with the hydroxyl groups of DSCG or the decanol of the KL (B) system. $\pi \rightarrow \pi^*$ bands of hydrogen donors are known[11] to undergo red shifts with hydrogen bond formation. Such "oriented" hydrogen bonding in nematic phases could have a significant effect on the order parameter of $TPPS_4$.

In this study we report on polarized absorption spectra and order parameter of $TPPS_4$ dissolved in another (OH group relatively free) lyotropic nematic N_c phase[12] (C): KL (35.31 wt %) – KCl (2.36) – H_2O (62.32); $\Delta\chi > 0$. The porphyrins and metalloporphyrins form the central structures of haemoproteins and chlorophylls and their visible absorption spectra have been studied for many years.[13]

The in-plane polarization of two visible Q bands and one near ultraviolet Soret (B) band in the absorption spectra of metalloporphyrins (D_{4h} symmetry) have generally been agreed on by various theoretical models of their electronic structure.[14] These $\pi \rightarrow \pi^*$ transitions are ascribed, in terms of simple MO theory, as being due to the excitation of an electron from the highest-filled a_{2u} and a_{1u}-type symmetry orbitals to the lowest-empty double degenerate e_g-type orbitals. Both Soret band ($a_{1u} \rightarrow e_g$) and lower energy Q band ($a_{2u} \rightarrow e_g$) are assumed to be electronic (0-0) transitions having a vibronic envelope (1-0) at higher energy. While Q bands are strongly split into their components Q_x and Q_y (Figure 2) in going from metalloporphyrins to free base porphyrin ($D_{4h} \rightarrow D_{2h}$), the Soret band is split to a much lesser extent and is not well resolved in the absorption spectrum.

Experimentally there has been a parallel effort to confirm the relative polarization and absolute assignment of electronic transitions in observed spectra. However negative linear dichroism components at 400, 551 and 641 nm, corresponding to out of plane ($z-$) polarized transitions have been observed by Norden and Davidsson,[15] in the case of tetraphenylporphine (TPP), in oriented polymer matrices. Anex and Uman,[16] using the technique of polarized reflection spectroscopy on a single TPP crystal, also detected z-polarized compo-

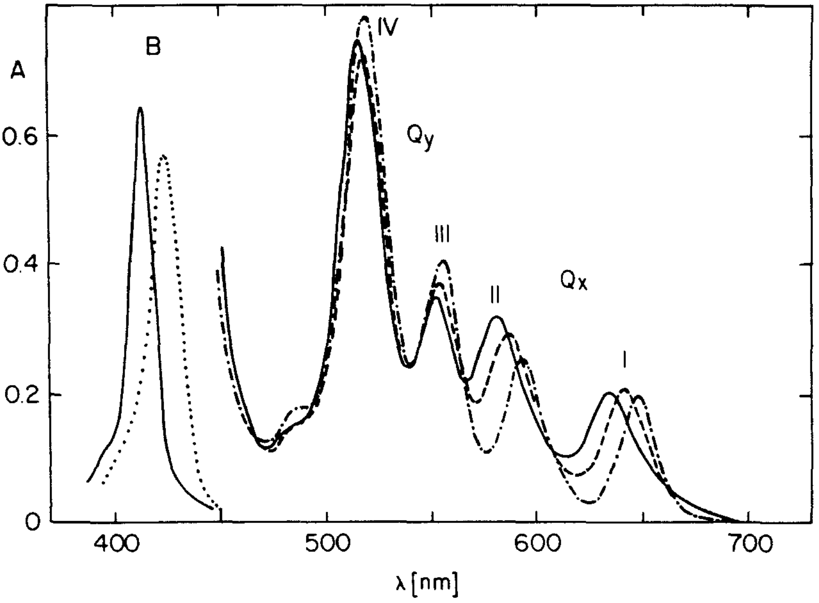

FIGURE 2 The effect of different concentrations of DSCG on absorption spectra of TPPS$_4$ (pH ~ 5.5): (—) 0.001 M DSCG: 5 × 10^{-5}M TPPS$_4$ (1 cm cell), Soret (B) band, 1.4 × 10^{-5}M TPPS$_4$ (0.1); (1 cm, - - -) 0.01 M DSCG, 5 × 10^{-5}M TPPS$_4$; 0.24 M DSCG: 2.5 × 10^{-3}M TPPS$_4$ (0.02, —·—·—), 6 × 10^{-5}M TPPS$_4$ (0.02, ·····).

nents at about 552 and 650 nm. Contrary to these observations Gale et al[17] found, using polyethylene and thermotropic liquid crystals as the orienting solvents, that all observed electronic transitions are polarized in the plane of the porphine ring.

From the studies of polynuclear porphyrins[18] and chlorophyll a aggregates[19] it has now been generally agreed that the observed out of plane polarized transitions should be interpreted with caution as they are probably due to strong electronic interaction between the rings in free-base porphyrin crystals or aggregates present in polymer films.[20] These optical effects may arise from exciton, exchange and or charge transfer interaction between the rings. It has also been shown[20] that elongation of the polymeric film may cause the increase in the amount of aggregates. It should therefore be of prime importance to establish that the studied molecules are monomeric.

EXPERIMENTAL

The preparation of KL[5] and nematic mixtures is described elsewhere.[2] Stock solutions of TPPS$_4$ in water, 1.5 × 10^{-4} and 1 × 10^{-3}M respectively, were used for preparation of the KL/KCl/H_2O system. The samples were placed in either 0.2 mm glass capillaries and sealed with a torch or into 1 mm spectroscopic cells and aligned in a magnetic field of up to 20 kG. Uniform alignment was obtained within hours. A Nikon polarizing microscope was used to examine the samples for homogeneity and alignment before measurement of the polarized absorption spectra. The transition temperatures of the KL/KCl/H_2O system were only slightly lowered by the presence of low concentrations of $TPPS_4$ and were in both cases well above 30°C for $N_c \leftrightarrow N_c$ + M transition, where M denotes middle soap.

The polarized absorption spectra were recorded on a Cary 14 spectrophotometer. Glan-Foucault polarizing prisms in the reference and cell compartments were placed in front of and behind the sample to correct for instrumental polarization and sample depolarization effects. The absorbancy (A) was recorded with light polarized either parallel ($A_{\|}$) or perpendicular ($A_{\perp}$) to the liquid crystal optic axis (director).

RESULTS AND DISCUSSION

The large red shifts of low energy I (0-0) and II (1-0) Q_x bands and B (Soret) band are demonstrated in Figure 2 for increasing concentrations of DSCG. The frequency shifts to the longer wavelength are analogous to those observed in alcoholic solutions of $TPPS_4$ or KL/decanol/H_2O system.[21] These red shifts for $\pi \rightarrow \pi^*$ transitions correspond to the energy difference between the hydrogen bond energies in the ground and the Frank-Condon excited states. Significantly lower frequency shifts Q_x bands in the spectrum of $TPPS_4$ are observed in KL/KCl/H_2O nematic phase (Figure 3) indicating much lower concentration of hydroxyl (OH) groups, which in this system are present presumably due to the hydrolysis of KL, as indicated by the value of pH ~ 9 of the nematic phase.

The water-soluble porphyrins are known[10] to aggregate at either higher concentration or ionic strength. The changes in the absorption spectra with increased concentration of $TPPS_4$ in water, as demonstrated in Figure 1, are ascribed to aggregation (ring stacking), and exciton theory has been used to calculate the electronic spectral properties of, for example, chlorophyll a aggregates.[19] Contrary to this, the spectrum of monomeric $TPPS_4$ was observed in all lyotropic mesophases, as is apparent from Figures 2 and 3.

However, as is seen in Figure 3, much higher values of the linear dichroism for $TPPS_4$ were obtained in KL/KCl/H_2O lyotropic nematic

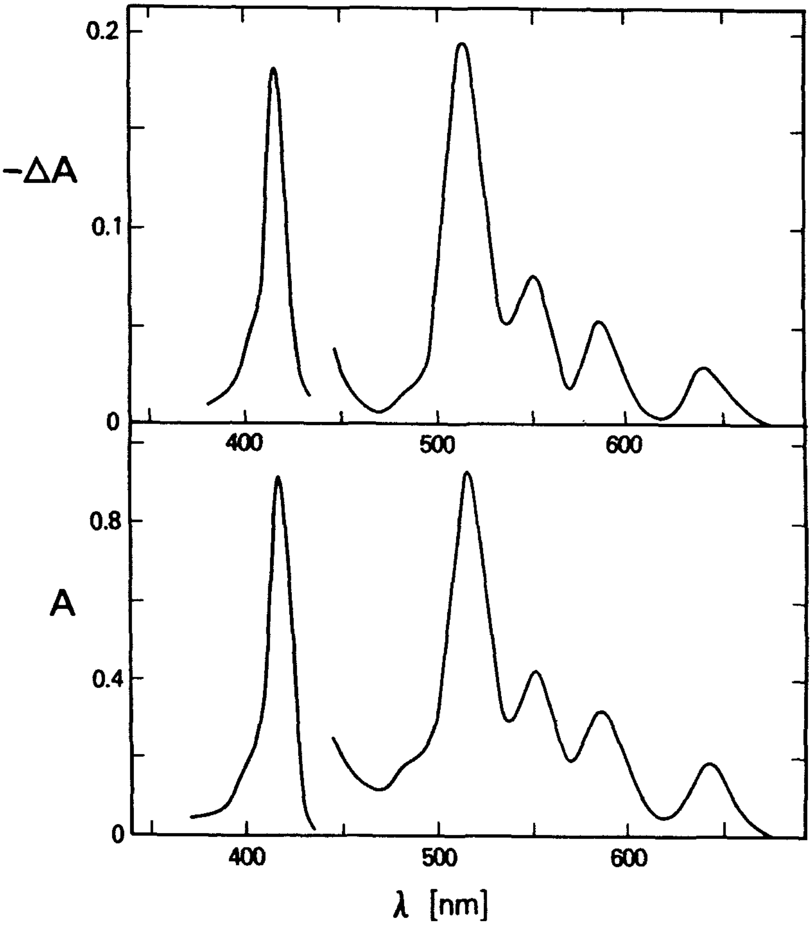

FIGURE 3 The linear dichroism (upper curves) and absorption spectra (lower curves) of $TPPS_4$ in $KL/KCl/H_2O$ lyotropic nematic phase.

phases as compared to DSCG (A) or $KL/decanol/H_2O$ (B) systems. The average orientation (degree of orientation, S) of the corresponding transition axis (i,j) with respect to the liquid crystal optic axis $(\hat{n})$ may be expressed in terms of the Saupe order matrix[22-24]

$$S_{ij} = \frac{1}{2} \langle 3 \cos \theta_i \cos \theta_j - \delta_{ij} \rangle \qquad (1)$$

where $i,j = x,y,z$ and $\delta_{i,j} = 1$ or 0 for $i = j$ or $i \neq j$, respectively.

Here $\theta_{i(j)}$ are the angles between the solute molecular axis (i,j) and

TABLE I

Absorbancies (A) and order parameters (S_{ij} ± 0.002) for selected bands of $TPPS_4$ in KL/KCl/H_2O nematic lyophase (t = 20 ± 2°C)

$TPPS_4$ concentration [mole l^{-1}]	Sample thickness [mm]	λ_{max} [nm]	$A_{\parallel}$	$A_{\perp}$	S_{xy}	S_{xx}	S_{yy}
~1.10^{-4}	0.2	416	0.890	1.072	−0.060	—	—
~6.10^{-4}	1.0	641	0.170	0.200	—	−0.053	—
		552	0.365	0.442	—	—	(−0.062)

the director $\hat{n}$ and the bracket denotes the ensemble average over all solute molecules. For solute molecules with C_{2v} or D_{2h} symmetry, the number of unknown parameters reduces to three and the order parameter can be determined from the equation

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{2}$$

We set x and y axes of the molecular coordinate system in the $TPPS_4$ plane (Figure 1) and z perpendicular to it.

The S-values, obtained by substituting for $A_{\parallel}$ and $A_{\perp}$ into (2) for the well-separated xy-polarized 416 nm Soret band and the (0-0) 641 nm Q_x (I) band, are summarized in Table I. It is seen indeed, that $TPPS_4$ orients with its plane (xy axis) on the average perpendicular to the director $\hat{n}$ (hence the negative value of S), but with a much higher order parameter (~ 10x) than in DSCG (A) or KL/decanol/water (B) nematic lyophases.

The low linear dichroism and order parameter of $TPPS_4$ in (A) and (B) systems may therefore be explained by preferential hydrogen bonding of the porphyrin molecules with the hydroxyl groups of the decanol or DSCG, which presumably occupy the surface of the cylindrical (in the case of DSCG, hollow[25]) micelles. This effect may be compared to the behavior of symmetrical molecules, such as dimedone, which is anisotropically oriented by hydrogen bonding with stretched polyvinyl alcohol.[26] Alternatively the formation of higher symmetry $TPPS_4$-DSCG (or decanol) solvates may be the reason for the low order parameter of $TPPS_4$ in these systems.

The increase in concentration of $TPPS_4$ (Table I) lowers the order parameter slightly as the relation $S_{xy} = S_{xx} = S_{yy}$ should hold. The value for the order parameter S_{yy} for 552 nm (0-0) Q_y (III) band is also included in Table I, although since there is an appreciable overlap of this band with other (1-0) vibrational bands, we consider this value of *S* to be less significant. The fairly high value of the order parameter of $TPPS_4$ in this system is rather surprising, considering the size (~ 20 *A*° in diameter)[27] and shape of this molecule.

It is plausible to assume that a significant portion of the porphyrin molecules are incorporated into the micelles, with their planes on the average perpendicular to the director and SO_3^- groups interacting with the interface region. It is well known[1] that the S-values for more water soluble aromatic compounds are considerably smaller than for molecules highly soluble in hydrocarbon solvents. Hence, for example, $TPPS_3$[28] with only three ionizing -SO_3Na groups should show an even higher order parameter than $TPPS_4$.

Contrary to the reported solubilization of hemin[29] by either cationic or anionic surfactants, we found[21] that the solubility of porphyrin with no ionizing groups such as tetraphenyl porphine (TPP) or meso-tetrapyridyl porphine in (A) or (B) lyotropic mesophase is very low ($\sim 2.5 \times 10^{-6}$M). The polarized absorption spectra of these molecules incorporated as guests in bilayer systems may provide more information about the bilayer thickness of certain lyotropic mesophases. Similar studies have been performed by ^{2}H NMR on α,ω-dicarboxylates[30] of varying chain length and provide unusual order-parameter profiles.

It may be possible to vary the diameter of porphyrin molecules by attaching hydrophobic groups of various length with ionizing groups on the periphery and/or to employ long chain azo-dyes of varying length, such as Congo Red, investigated in our previous work.[2a] Interestingly, recent low angle x-ray and neutron scattering studies[31] seem to indicate that the anisotropic micellar aggregates are of rather constant shape (oblate or prolate spheroids) of low dimensional anisotropy (e.g. length to width [~ 36 *A*°] ratio for KL/decanol/water system was estimated to be ~ 1.75).

Finally, as is seen from Figure 3, the linear dichroism spectrum of free-base water soluble porphine ($TPPS_4$) indicates that all observed transitions are found to be polarized in the plane of the porphyrin ring, supporting the observation of Gale et al.[17] The dichroic ratio ($A_{\parallel}/A_{\perp}$) was also constant within experimental error (6.5% at most) throughout the entire spectral range covered.

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