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Photophysical Properties of Amphiphilic Porphyrins in Different Media

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ABSTRACT

Photophysical properties (absorption spectra, fluorescence spectra, lifetimes and quantum yields) have been studied for several amphiphilic porphyrins bearing hydrophilic pyridinium and hydrophobic long-chain alkyl groups in different media. These amphiphilic porphyrins are characterized by reduced fluorescence quantum yields, aggregating appreciably in nonpolar solvents and biexponential fluorescence decay. The observed biexponential fluorescence decay of these porphyrin derivatives can be interpreted in terms of mixing of the S_1 *and a CT state in which an electron is transferred from the porphyrin core to the electron-deficient pyridinium group.*

Keywords: amphiphilic porphyrins, aggregating, biexponential fluorescence decay.

1 INTRODUCTION

Recently, considerable effort has been directed towards finding chemical process that are capable of conversion and storage of light energy. Porphyrins, the structural cogeners of cholophylls, have been extensively used in model studies [1]. One approach to this involves the photolysis of water by

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means of dye-sensitized electron-transfer reactions, as in photosynthesis. Amphiphilic porphyrins seem to be promising for such reactions. Development of photosensitizers requires knowledge of the photophysical properties. While extensive studies exist for several naturally occurring porphyrins in nonaqueous media or water-soluble porphyrins in aqueous solution [2], similar studies on amphiphilic porphyrins are sparse. Preparation of some surfactant porphyrins has been reported [3]. However, there remained some difficulties in purification. Toward development of amphiphilic porphyrins photosensitizers, in the present study we report the improved purification of amphiphilic porphyrins and studies on the photophysical properties of several amphiphilic porphyrins (Fig. 1) in $CHCl_3$, CH_3OH and Triton X-100 micellar solution.

2 EXPERIMENTAL SECTION

2.1 Materials

The precursor porphyrin TPyP was synthesized by condensing pyrrole with pyridine-4-carboxaldehyde in propionic acid [4]. The synthesis of the amphiphilic TC$_{16}$PyP was accomplished by the quaternization of appropriate TPyP with 1-bromohexadecane [5]. Okuno *et al.* [5] obtained the pure product by repeated gel chromotagraphy over Sephadex LH-20. In this study, the purifications were made via fractionated crystallizations in CH_3OH, and then chromatographed on a silica gel column using CH_2Cl_2/CH_3OH(9:1) as eluent. Using a similar procedure, the dodecyl (TC$_{12}$PyP) and hexanyl (TC$_6$PyP) derivatives were prepared by employing 1-bromododecane and 1-bromohexane, respectively. The methyl derivatives (TC$_1$PyP)

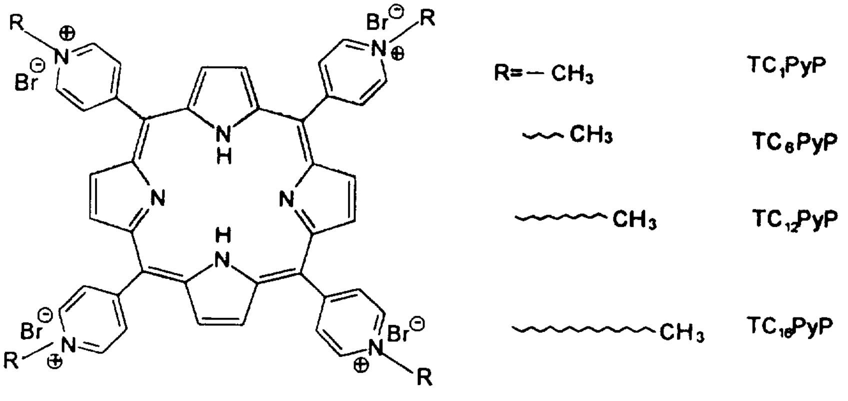

Fig. 1. Structure of porphyrin amphiphiles.

was prepared according to the described procedure [6] and recrystallized from methanol. All the samples were characterized by elemental analysis and the homogeniety of the samples confirmed by TLC.

2.2 Photophysical methods

UV-Vis absorption spectra were measured using a Shimadzu UV-160A spectrophotometer. Fluorescence spectra were recorded on a Hitatch MPF 4F Spectrofluorimeter. Fluorescence quantum yields were determined using T(4-OH)PP in ethanol ($\Phi_f = 0.126$) [7] as standard. Fluorescence lifetimes were determined on a HORIBA NA ES-1100 time-correlated single-photon counting unit. The lifetimes were calculated from the decay curves by using the least-squares method. For all the fluorescence measurements, the excitation wavelength was chosen at the maximum of the Soret band, and nitrogen gas was bubbled in for 30 min prior to measurements.

3 RESULTS AND DISCUSSION

3.1 Absorption spectra

For a comprehensive understanding of the photophysical properties, it is essential to have information on the ground-state absorption and aggregation properties. In this study we summarize absorption spectra data of the amphiphilic porphyrins in $CHCl_3$, CH_3OH and Triton X-100 micellar solution in Table 1. Absorption intensities are correlated in terms of the relative peak ratios normalized with respect to the Qy (1,0) band, for it is known [8, 9] that this Qy (1,0) band is rather insensitive to the nature of the substituents. Following Spelane *et al.* [9], we give the absorbance ratio Q(0,0)/Q(1,0) [eqn (1)] in the last column of Table 1 as a measure

$$Q(0,0)/Q(1,0) = [Qx(0,0) + Qy(0,0)]/[Qx(1,0) + Qy(1,0)] \qquad (1)$$

of the substituent effect on the absorption properties. For comparison, we include similar data on the TPyP and water-soluble TC_1PyP in Table 1.

Examination of the absorption data shows several features:

1. the absorption spectra of all the porphyrin amphiphiles are strikingly similar under the same conditions, indicating that the differences in the length of long-chain alkyl do not affect greatly the ground-state absorption properties;

TABLE 1

Absorption Spectral Features of the Porphyrin Amphiphiles in Different Media[a]

Porphyrin	*Medium*	*B (0,0)*	*Qy (1,0)*	*Qy (0,0)*	*Qx (1,0)*	*Qx (0,0)*	*A [Q(0,0)]/ [Q(1,0]*
TPyP	$CHCl_3$	418 (5.60) [25.2]	514 (4.29) [1.0]	547 (3.71) [0.29]	588 (3.70) [0.28]	644 (3.56) [0.21]	0.39
TC1PyP	CH_3OH	418 (5.44) [14.8]	516 (4.28) [1.0]	552 (3.84) [0.36]	592 (3.83) [0.35]	645 (3.27) [0.10]	0.34
	Triton X-100	420 (5.24) [13.2]	516 (4.12) [1.0]	549 (3.72) [0.40]	590 (3.71) [0.39]	643 (3.29) [0.15]	0.40
TC6PyP	$CHCl_3$	434 (5.02) [13.7]	522 (3.91) [1.0]	560 (3.37) [0.29]	594 (3.49) [0.38]	653 (3.07) [0.14]	0.31
	CH_3OH	425 (5.44) [16.6]	516 (4.22) [1.0]	556 (3.56) [0.22]	590 (3.63) [0.26]	646 (3.29) [0.12]	0.27
	Triton X-100	428 (5.19) [12.8]	519 (4.08) [1.0]	557 (3.60) [0.33]	593 (3.62) [0.35]	647 (3.16) [0.12]	0.33
$TC_{12}PyP$	$CHCl_3$	434 (4.99) [12.6]	524 (3.89) [1.0]	556 (3.25) [0.23]	594 (3.35) [0.29]	652 (3.06) [0.15]	0.29
	H_3OH	427 (5.42) [15.5]	517 (4.23) [1.0]	553 (3.65) [0.26]	590 (3.62) [0.25]	645 (3.27) [0.11]	0.30
	Triton X-100	429 (5.11) [12.2]	522 (4.02) [1.0]	555 (3.61) [0.39]	593 (3.60) [0.38]	650 (3.20) [0.15]	0.39
$TC_{16}PyP$	$CHCl_3$	435 (5.09) [13.8]	523 (3.96) [1.0]	556 (3.28) [0.21]	593 (3.39) [0.27]	652 (3.06) [0.13]	0.26
	CH_3OH	426 (5.39) [16.0]	517 (4.29) [1.0]	554 (3.58) [0.24]	592 (3.60) [0.31]	646 (3.43) [0.14]	0.29
	Triton X-100	430 (5.16) [14.8]	520 (3.99) [1.0]	552 (3.55) [0.36]	592 (3.53) [0.35]	645 (3.00) [0.10]	0.34

[a] λ in nm; value in parentheses refers to log ε and in square brackets to relative intensity ratio.

2. the molar extinction coefficients of the Soret and Q bands are significantly lower than that of their parent TPyP. This may be the result of the quaternization of the pyridyl nitrogen atoms. Earlier studies [12] with isomeric substituted TPPs showed that the electron-withdrawing character of substituents in the meso-TPPs reduced the absorption intensities, whereas electron-donating character increased them;
3. it is noted that the absorption position are similar in CH_3OH and Triton X-100 micellar solution, while the ε value in Triton X-100 micellar solution is lower than that in CH_3OH;
4. both the B and Q bands are red-shifted in $CHCl_3$ relative to in CH_3OH and Triton X-100 micellar solution (Fig. 2). The red-shifted of the bands,with concomitant decreases in the ε values and broadening of the bands in $CHCl_3$ solutions, suggest the presence of porphyrin-porphyrin interchromophore interactions, characteristic of aggregate formation. [10–12].

3.2 Fluorescence spectra and quantum yields

Fluorescence spectra of the porphyrin amphiphiles were also examined in $CHCl_3$, CH_3OH and Triton X-100 micellar solution at room temperature. Quantitative data on the emission maxima, relative intensities and quantum yields are given in Table 2; for comparison, emission data on the TPyP and water-soluble TC1PyP are also shown.

In analogy with the absorption spectra, the values of the emission maxima and quantum yields for all the porphyrin amphiphiles are rather similar under the same conditions. In $CHCl_3$, all the amphiphilic porphyrins exhibit two fluorescence bands around 665 and 721 nm, corresponding to the Q (0, 0) and Q (1, 0) transitions, respectively; in CH_3OH, the Q (0, 0) and Q (1, 0) fluorescence bands appeared around 656 and 717 nm, respectively; in Triton X-100 micellar solution, the Q (0, 0) and Q (1, 0) around 660 and 718 nm, respectively (Fig. 3). Addition of methanol to the chloroform solution shifted the bands to the blue region, with an increase in intensity. Thus, with increase in solvent polarity, both Q (0, 0) and Q (1, 0) bands shifted to shorter wavelengths. The blue-shifted emission bands signify partly disaggregation as a consequence of increase in the polarity of the solvent. Moreover, the Φ_f value in $CHCl_3$ was found to be lower than that observed in CH_3OH. These observations lead to the suggestion of self-aggregation of porphyrin amphiphiles in $CHCl_3$.

Moreover, all the amphiphilic porphyrins studied exhibited weak fluorescence, with a quantum yield in the range of 0.01–0.04. These Φ_f values are distinctly lower as compared to those found for TPyP and TPP (Table 2); the decrease in the Φ_f value may be the result of quaternization of the pyridyl nitrogen atoms.

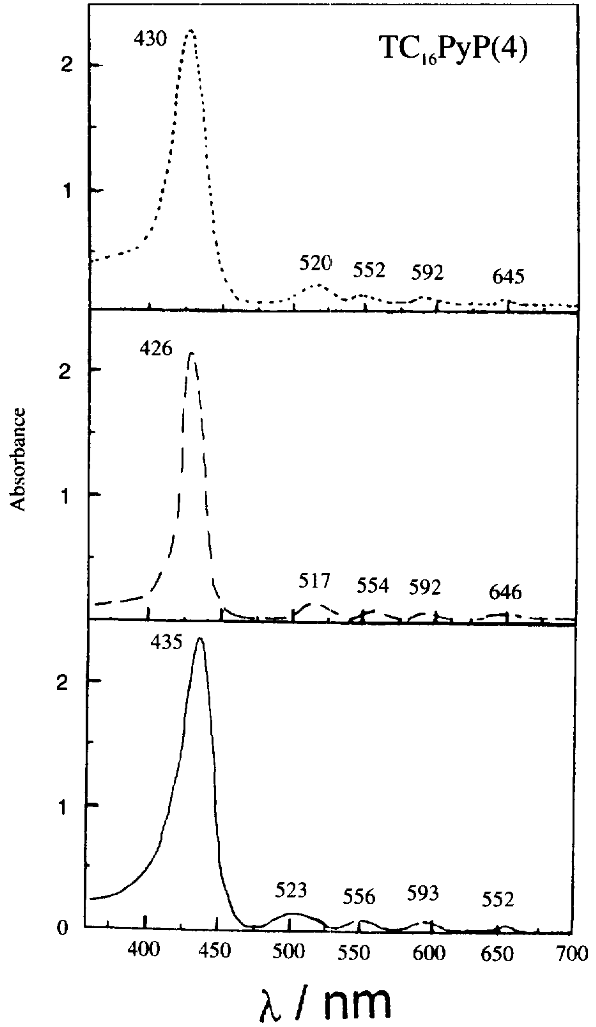

Fig. 2. Absorption spectra of TC$_{16}$PyP in (a) $CHCl_3$ (—), (b) CH_3OH (- - -), (c) Triton X-100 micellar solution (····).

3.3 Fluorescence lifetimes

It is very important to probe the excited-state lifetimes of such species, since their magnitude plays a decisive role in the efficiency of photosensitization reactions. Table 3 summarizes the fluorescence lifetime data of the amphiphilic porphyrins in $CHCl_3$, CH_3OH and Triton X-100 micellar solution. Interestingly, while the unquaternized TPyP exhibits a single-exponential fluorescence decay, all the porphyrin amphiphiles were found to be exhibit biexponential decay, irrespective of the solvent media, viz, methanol, chloroform and Triton X-100 micellar solution (Fig. 4). The two lifetimes are

TABLE 2
Emission Spectral Features of the Porphyrin Amphiphiles in Different Media[a]

Porphyrin	*Medium*	*Q (0, 0)*	*Q (1, 0)*	ϕ_{fl}
TPyP	$CHCl_3$	653 (1.78)	712 (1.0)	0.069
TC1PyP	CH_3OH	655 (2.62)	715 (1.0)	0.059
	Triton X-100	657 (2.42)	716 (1.0)	
TC6PyP	$CHCl_3$	664 (2.52)	720 (1.0)	0.014
	CH_3OH	657 (2.34)	714 (1.0)	0.038
	Triton X-100	659 (2.32)	717 (1.0)	
$TC_{12}PyP$	$CHCl_3$	666 (1.90)	722 (1.0)	0.010
	CH_3OH	656 (2.05)	717 (1.0)	0.027
	Triton X-100	660 (1.97)	719 (1.0)	
TC16PyP	$CHCl_3$	665 (2.32)	721 (1.0)	0.013
	CH_3OH	656 (1.93)	717 (1.0)	0.034
	Triton X-100	660 (2.20)	719 (1.0)	

[a] λ in nm; excition at Soret maximum; value in parentheses refers to Q (0.0)/Q (1.0) ratio.

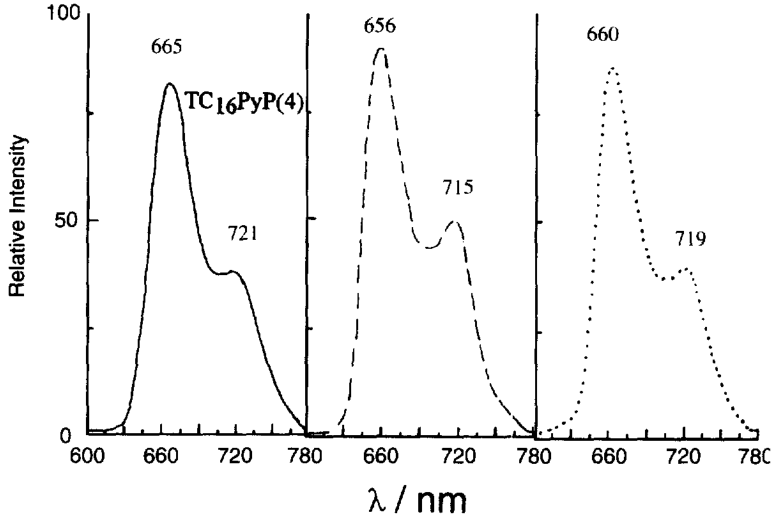

Fig. 3. Fluorescence spectra of $TC_{16}PyP$ in (a) $CHCl_3$ (—), (b) CH_3OH (- - -), (c) Triton X-100 micellat solution (····).

designated as τ_l (long) and τ_s (short), and the amplitudes of the two components as A_l and A_s, respectively. The magnitude and amplitudes of the two lifetimes of all the porphyrin amphiphiles did not vary significantly with changes of the alkyl chain (C_6–C_{16}) under the same conditions. Similar biexponential decay were observed for water-soluble TMPyPs; Kemnitz [13] studied the fluorescence decay was from a monomer–dimer equilibrium. The

TABLE 3
Single Excited-state Decay Data of the Amphiphilic Porphyrins in Different Media[a]

Porphyrin	*CH_3OH*			*$CHCl_3$*			*Triton X-100*		
TPyP					8.5 (1.00) [1.14]				
TC_1PyP	3.24 (0.36)	9.77 (0.64)	[1.13]				4.17 (0.43)	10.05 (0.57)	[1.32]
TC_6PyP	1.69 (0.22)	9.17 (0.78)	[0.96]	0.78 (0.31)	4.85 (0.69)	[1.22]	1.51 (0.38)	9.26 (0.62)	[0.96]
$TC_{12}PyP$	1.74 (0.18)	8.70 (0.82)	[1.05]	0.74 (0.35)	4.93 (0.65)	[0.97]	1.63 (0.27)	8.89 (0.73)	[1.19]
$TC_{16}PyP$	1.26 (0.11)	10.50 (0.89)	[1.31]	0.96 (0.28)	5.86 (0.72)	[1.11]	1.34 (0.40)	9.83 (0.60)	[1.26]

[a]Lifetime in ns and the amplitude is given in parentheses; χ^2 value are given in square brackets.

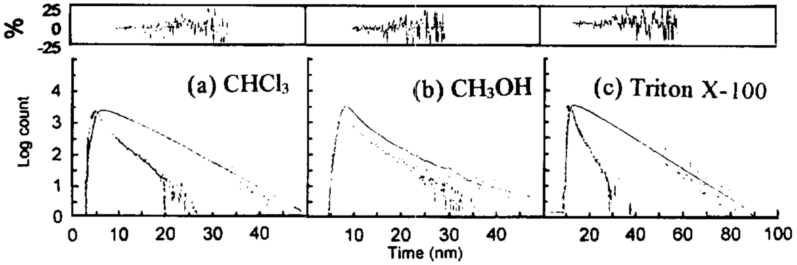

Fig. 4. Fluorescence decay profile of $TC_{16}PyP$ in (a) $CHCl_3$, (b) CH_3OH, (c) Triton X-100 micellar solution at room temperature.

same interpretation was made by Brookfield *et al.* [14], but, Vergeldt *et al.* [15] suggested that the biexponential fluorescence decay of TMPyP(2), TMPyP(3), TMPyP(4) could be accounted for by the presence of two types of porphyrins: (i) in solution, and (ii) absorbed at the surface of the quartz cuvette.

The latter could not explain the biexponential fluorescence decay of amphiphilic porphyrins in our experiments because of their good solubility in the solvents used. Moreover, the biexponential fluorescence decay could not also be explained in terms of the existence of different aggregate forms. If so, one would anticipate a single-exponential decay in Triton X-100 micellar solution, in which no any aggregate can form. So we can conclude that the observed biexponential decay is inherent in these amphiphilic porphyrins, and not dependent on other species existing in solution.

The biexponential decay observed for the amphiphilic porphyrins denotes the existence of the two components, quenched and unquenched, in solution. Then, where is the quenched component from? First, we note that the quaternary ammonium group, which is electrophilic in nature, can in principle abstract electrons from the porphyrin core, like the tertiary functional group [16] and the energy of the intramolecular CT state, (for which an electron is fully transferred, following optical excitation, from the porphyrin macrocycle to the pyridinium group) is close to the locally excited singlet state S_1. From the oxidation potential the free base porphine (≈1.0 eV vs NHE) and the reduction potential of *N*-alkylpyridinium, the energy of this CT state can be estimated. For *N*-alkylpyridinium we used the reduction potential of 3,3′- bis-(*N*-methylpyridinium) (−1.0 eV vs NHE) [17], which can be considered as a molecule with two weakly interacting *N*-methylpyridinium units. Using this assumption, the energy of the CT state is calculated as ≈2.0 eV, almost equal to the S_1 energy (1.9 eV). Because of the near-degeneracy of the S_1 and CT state, when sterically possible, rotation of pyridinium groups increases electronic mixing may between the S_1 and the energetically nearby CT state by a conformational change. Mixing of the S_1 and a CT state with higher energy, causing increased radiationless decay of the excited porphyrin, may result in a quenched component (τ_s) in the singlet emission decay measurements. Thus, the biexponential fluorescence decay in the present study could be explained in terms of the mixing of the S_1 and a CT state in which an electron is transferred from the porphyrin core to the electron-deficient pyridinium group.

4 CONCLUSIONS

Pronounced differences are observed in the photophysical properties (absorption, fluorescence, quantum yields and lifetimes) between amphiphilic porphyrins and their parent TPyP. Amphiphilic porphyrins are characterized by reduced fluorescence quantum yields, biexponential fluorescence decay and aggregating appreciably in nonpolar solvents. The biexponential fluorescence decay of these porphyrins can be interpreted in terms of mixing of the S_1 and a CT state, in which an electron is transferred from the porphyrin core to the electron-deficient pyridinium group.

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