

Dimerization of Metal-free Sulfonated Phthalocyanines in Aqueous Methanol Solution

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Phthalocyanines can be used as dyes, optical and electrical materials, catalysts and models for naturally existing macrocycles^[1], especially it can be one of the possible candidates for photodynamic therapy^[2] (PDT). Particular attention has focused on its sulfonated derivatives because they are highly water-soluble and show great promise in PDT since they can be retained by tumor tissues. However, as with other water-soluble dyestuffs^[3], the sulfonated phthalocyanines tend to dimerize in aqueous solutions. These aggregates will depress the photoactivity of these dyes and phototoxicity towards biological tissues since their major pathway of deactivation is through internal conversion process to the ground state^[4]. Thus, it is important to evaluate quantitatively the influence of sulfonation on aggregation^[5] and other photophysical properties of phthalocyanine dyes.

In the present work, we try to illustrate the effect of sulfonation degree on dimerization for metal-free sulfonated phthalocyanines (HSPCs). The dimerization equilibrium constant (K) and the percentage of monomer in the solution (α) were obtained spectrophotometrically. The quantum yield of fluorescence (Φ_f) and the lifetime of the singlet excited state (τ_f) of these sulfonated phthalocyanines have also been measured. These confirm an inverse order between the extent of dimerization and the sulfonation degree for these sulfonated phthalocyanines.

1 Experimental

1.1 Instruments and methods

Ultraviolet-Visible (UV-Vis) absorption spectra were recorded by a HP8452A diode-array spectrophotometer. X-ray photoelectron spectra (XPS) were obtained on a PHI-5300 X-ray photoelectron spectrometer. Elemental analysis for S and N were performed at Beijing Institute of Chemistry, Academia Sinica.

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Fluorescence measurements were carried out with a PE LS50 B luminescence spectrometer. Fluorescence quantum yields (Φ_f) were determined by a comparative calibration method using unsubstituted ZnPC as standard ($\Phi_f=0.3$) with an excitation wavelength at 610 nm and excitation and emission slit widths of 7.5 nm. Singlet excited state lifetimes (τ_f) were measured on SLM 48000_{TM}S multiple frequency lifetime spectrometer. All the measurements were carried out in methanol containing 30% phosphate buffer (PBS, pH=7.4) at 20 °C.

1.2 Synthesis

(a) 29H, 31H-Phthalocyanine H₂PC. It was prepared by the method of Brach^[6]. Anal. Calcd. for C₃₂H₁₈N₈: C, 74.70; H, 3.53; N, 21.77. Found. C, 74.55; H, 3.33; N, 22.11.

(b) Sulfonated 29H, 31H-Phthalocyanines HSPCs. HSPCs were prepared by sulfonation with fuming (20–25% SO₃) sulfuric acid^[7]. A series of HSPCs with different sulfonation degree can be obtained by varying the temperature and time of reaction.

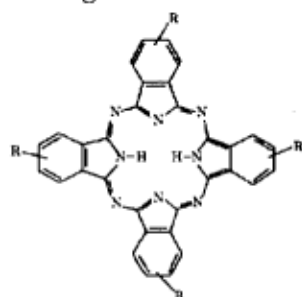


Fig.1 Chemical structure of HSPC, R=H or SO₃H dependent upon sulfonation degree

2 Results and Discussion

2.1 Absorption spectra and aggregation behaviour of HSPCs

The sulfonation degree of HSPCs was determined according to the ratio of S atom to N atom in the molecules by means of XPS and elemental analysis, the results are listed in Table 1.

Table 1 Degree of sulfonation and UV-Vis absorption of HSPCs

HSPC	Reaction condition ^a	S/PC ^b	S/PC ^c	λ_{ab}/nm^d
A	40 °C × 1	1.1	1.0	682 650 628* 332
B	60 °C × 1	1.6	1.3	684 652 628* 334
C	80 °C × 1	2.0	1.8	686 656 630* 338
D	80 °C × 2	2.8	2.6	686 656 630* 340
E	80 °C × 3	3.7	3.4	688 656 630* 342

Note a: Reaction condition is expressed as temperature × reaction time (hour);

b, c: Number of sulfonate per molecule determined by XPS and elemental analysis, respectively;

d: The absorption of HSPCs in methanol containing 30 % PBS, the values marked with star referred to the absorption of dimers.

Absorption spectra for these HSPCs in methanol containing 30% PBS are shown in Fig.2. The absorption maximum wavelength is red-shift and the band at 630 nm drops as the increasing of sulfonation degree. Slight deviations from Beer's law were observed for all these HSPCs with increasing concentration since the formation of dimer in the concentration range selected (1×10^{-6} – 1×10^{-5} mol⁻¹·L), HSPC-C is served as a typical example (Fig.3). It also indicates that the tendency towards aggregation is in the order: A>B>C>D>E.

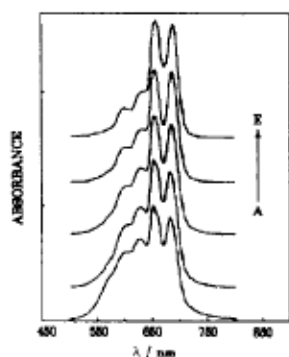


Fig.2 Absorption spectra of HSPCs in methanol containing 30 % PBS

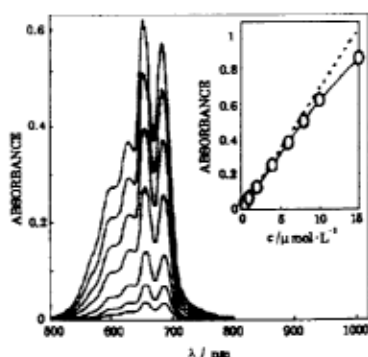


Fig.3 Negative deviation from Beer's law for absorption maximum of HSPC-C with increasing concentration

2.2 Determination of dimerization equilibrium constant K of HSPCs in methanol-water solution

Supposing that the dimer is the main aggregate under the conditions given, the equilibrium between monomer (M) and dimer (D) and the dimerization equilibrium constant K are described by



$$K = \frac{[D]}{[M]^2} = \frac{([M]_0 - [M])}{2[M]^2} \quad (2)$$

where $[M]_0$, $[M]$ denote the initial and equilibrium concentration of monomer, respectively, and $[D]$ is the equilibrium concentration of dimer in solution. The percentage of monomer in the solution under equilibrium α and the molar absorptivity of monomer ϵ_M are

$$\alpha = \frac{[M]}{[M]_0} \quad (3)$$

$$\epsilon_M = \frac{A}{[M] \cdot l} \quad (4)$$

where A is the absorbance of the solution at the maximum absorption wavelength of monomer (λ_{max}), l is the length of the optical path. Eq(4) is on the assumption that the absorption at λ_{max} is mainly attributed to the monomer, which can be satisfied in the case of HSPC-B, C, D, E (*vide infra*). However, it is impossible to calculate ϵ_M by eq. (4) since $[M]$ is unknown. It is convenient to introduce the "effective" absorption coefficient $\epsilon_{eff}^{[8,9]}$, which neglects partial association of the monomer and can be expressed as

$$\epsilon_{eff} = \frac{A}{[M]_0 \cdot l} \quad (5)$$

Eq. (2)–(5) can be combined to give

$$\epsilon_{eff} = \epsilon_M - \frac{2K}{\epsilon_M} \cdot \epsilon_{eff}^2 \cdot [M]_0 \quad (6)$$

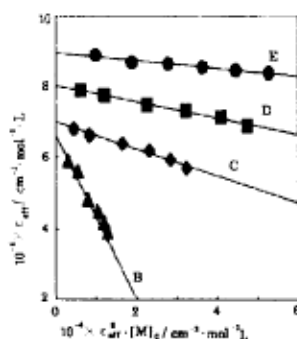


Fig.4 Plots of ϵ_{eff} versus $\epsilon_{\text{eff}}^2 \cdot [M]_0$ for HSPC (B-E) in methanol-water solution

Plots of ϵ_{eff} versus $\epsilon_{\text{eff}}^2 \cdot [M]_0$ are shown in Fig.4. In all the cases except A, a straight line is obtained with statistical R coefficient >0.99 . This confirms that the contributions of dimer to the absorbance at the λ_{max} of monomer are practically negligible for HSPC-B, C, D, E in the concentration range studied. However, for HSPC-A, the existence of higher percentage of dimer results a contribution in absorbance at the λ_{max} of monomer and hence a manifest deviation to eq. (6).

The value of K and ϵ_M can be deduced from the plot's slope and intercept. In order to study the correlation between the extent of dimerization and sulfonation degree quantitatively, we should reform eq. (2) as:

$$K = \frac{1 - \alpha}{2\alpha^2[M]_0} \quad (7)$$

From eq. (7), we can get the value of α at given concentration, which provides a clear correlation between the sulfonation degree and the aggregation behaviour of these HSPCs.

Table 2 Photophysical parameters for HSPCs

HSPC	$10^{-4}K/\text{mol}^{-1} \cdot \text{L}$	$\lg \epsilon(\lambda_{\text{max}}/\text{nm})$	α^g	α^f	$\lambda_{\text{em}}/\text{nm}$	Φ_f	τ_f^g/ns
A	—	—	—	—	685	0.12	2.6
B	6.5166	4.83(684)	0.895	0.573	685	0.16	2.8
C	1.3423	4.85(686)	0.975	0.820	689	0.18	2.9
D	0.9183	4.90(686)	0.983	0.863	691	0.21	3.0
E	0.5494	4.94(688)	0.99	0.909	692	0.21	3.1

Note e, f: The values of α at $[M]_0=1 \times 10^{-6}$, $1 \times 10^{-5} \text{ mol}^{-1} \text{L}$, respectively;

g: These life times are fit by convoluting a double exponential decay

$A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$. However, τ_2 may be artificial, so τ_f referred to τ_1 .

2.3 Dependence of apparent Φ_f on aggregation

For an aggregated system, the measured apparent fluorescence quantum yield may show contributions from monomer and dimer, the correlation between Φ_f (apparent), Φ_M (monomer's) and Φ_D (dimer's) can be formulated as eq. (8):

$$I \Phi_f = I_M \Phi_M + I_D \Phi_D \quad (8)$$

As the total absorbed excitation light intensity I is the sum of I_M (absorbed by monomer) and I_D (absorbed by dimer), then

$$\begin{aligned} \Phi_f &= \left(1 - \frac{I_D}{I}\right) \Phi_M + \frac{I_D}{I} \Phi_D \\ &= \Phi_M + (\Phi_D - \Phi_M) \frac{I_D}{I} \end{aligned} \quad (9)$$

Since the major pathway of deactivation for dimer is radiationless decay, Φ_D will be much smaller than Φ_M . Therefore, when the extent of dimerization being higher, the I_D is more intense in the meanwhile the Φ_f becomes lower.

The maximum emission wavelength λ_{em} tends to red-shift more as increasing the sulfonation degree, which may be due to the higher percentage of monomer in solutions. However, the sulfonates have less effect on τ_f , this can be interpreted as the lower intensity of fluorescence from dimer with shorter lifetime, so the effect induced by dimer on τ_f can be negligible.

3 Conclusions

A number of factors can be proposed to account for the forces contributing to dimerization of dye molecules such as van der Waals forces, charge-charge interaction, hydrophobic interaction and the role of water. However, the correlation between sulfonation degree and dimerization rules out charge-charge interaction as a major contributor. Since the HSPC exists as $H_2PC(SO_3)_n^-$ in the methanol-water solution, the electrostatic interaction will lead to the repellency between the dye molecules. Accordingly, when the sulfonation degree of the molecule becomes higher, the larger interaction but the less dimerization will be resulted. A sizable contribution to the dimerization may come from the hydrophobic interaction of the backbone of the phthalocyanine molecules.

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磺化酞菁在甲醇 - 水溶液中的二聚作用研究

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摘要 研究了不同磺化度的酞菁在甲醇 - 水混合溶剂中的聚集行为. 通过紫外 - 可见光谱测定, 发现磺化度在 1.0 以上时染料在稀溶液中主要以单体和二聚体的形式存在, 并可用简便的方法计算出聚集平衡常数和平衡时单体所占的百分比, 得到磺化度越低越易聚集的结论. 有关激发态的实验表明, 增加酞菁磺化度有助于提高表观荧光量子产率, 但对荧光寿命影响较小.

关键词: 酞菁, 磺化, 二聚