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Investigation on disassociation of porphyrin J-aggregates induced by β-cyclodextrins using absorption and fluorescence spectroscopy

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Abstract

In this paper, interaction of meso-tetra-(4-sulfonatophenyl) porphyrin ($H_4TPPS_4^{2-}$) with three kinds of cyclodextrins, including β-cyclodextrin (β-CD), hydroxypropyl-β-cyclodextrin (HP-β-CD) and methyl-β-cyclodextrin (Me-β-CD) is investigated by absorption and fluorescence spectra. J-aggregates of $H_4TPPS_4^{4-}$ show a sharp peak at 490 nm in UV–vis spectra, while they have no fluorescence emission. The experimental results demonstrate that β-CDs efficiently break aggregates and lead to decrease at 490 nm and increase at 436 nm in absorption spectra, with gradually increasing fluorescence emission. Both inclusion ratios and inclusion constants are correspondingly calculated based on the "double reciprocal method".

Keywords: Meso-tetra-(4-sulfonatophenyl) porphyrin; J-aggregates; Cyclodextrins; Absorption spectra; Fluorescence

1. Introduction

Molecular aggregation behaviors are very interesting and important in understanding the fundamental process of living organisms and exploring better ways to photodynamic therapy of cancer. Under appropriate ionic strength or acidity, porphyrins, cyanine dyes and their analogues can form highly ordered aggregates, such as H-, J-type and so on [1–5]. In H-aggregates, molecule components are stacked one dimensionally in a "plane-to-plane" way, and there appears a hypsochromic band in absorption spectra. In the case of J-aggregation, strongly coupled monomers are self-assembled in an "end-to-end" manner to show a sharp peak at a red-shifted wavelength compared with that of monomers. Generally speaking, there often exist several mixed aggregates forms containing J-, H- or cyclic arrangement of three dimers in porphyrins, and it is hydrophobic effects and electrostatic attracting force that contribute to the aggregation process of water-soluble porphyrins [6,7]. Excitonic coupling theory and schematic representative presentation have been proposed to elucidate the structures of these aggregates and their spectral properties [8–10]. More experimental results are needed to gain further insight into such interaction between porphyrin monomers. Herein the breaking behaviors of porphyrin aggregates induced by β-CDs are reported in detail to explore more information.

Cyclodextrins (CDs) are of great importance as useful host molecules due to their characteristic structure, namely interior hydrophobic cavity and exterior hydrophilic groups, and thus find wide applications in photophysics, photochemistry as well as photobiology field. The structural features of CDs can be used to control monomer/dimer equilibrium and aggregation behaviors of dyes, and thus affect absorption, luminescence and electrochemical properties of dyes. The cavity of CDs shows different inclusion behaviors dependent on the size matching degree between host and guest, so binding models vary from partial to total penetration of guest molecules [11–13].

Herein we carefully study the interaction between porphyrin J-aggregates and three kinds of cyclodextrins, including β-cyclodextrin (β-CD), hydroxypropyl-β-cyclodextrin (HP-β-CD) and methyl-β-cyclodextrin (Me-β-CD) using electronic spectra and stead-state fluorescence spectra. The

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ability of CDs is studied to disassociate porphyrin J-aggregates, and correspondingly some inclusion parameters are also calculated to give a clearer comparison on their complex ability.

2. Experimental details

2.1. Reagents

The free-base species known as $H_2TPPS_4^{4-}$, shown as Fig. 1 and purchased from Alfa Aesar Reagent Company, is prepared into 1×10^{-4} M aqueous solution and then diluted to a certain concentration when used. β-CD (95%, Yunan Gourmet Factory) is recrystallized before use. Both HP-β-CD and Me-β-CD are kindly presented by Mr. I.P. Peter of Wacker Co. and used without further purification. Hydrogen chloride, nitric acid and sulfuric acid are bought from Tianjin Chemicals Factory, and the stock solution is 3 M. All the other reagents are of analytical-reagent grade made in China, and the experimental water is doubly distilled.

2.2. Apparatus

The absorption spectra are measured on TU-1901 spectrophotometer (PGeneral, Beijing), and all the auto-corrected fluorescence spectra are conducted on LS-55 luminescence spectrometer (Perkin-Elmer Co.) equipped with a pulse xenon lamp. To get satisfactory signals, auto-corrected fluorescence measurement is carried out under the condition of 1% attenuator, and the excitation and emission slits are typically set at 10 and 15 nm, respectively. The experimental results are got at $22 \pm 1\,^{\circ}C$.

2.3. Procedures

Typically, porphyrin solution of 100 μL and appropriate amount of different acids are transferred into a comparison tube. And throughout the experiment, porphyrin concentration is 2 μM. Appropriate volume of CDs is subsequently added and thoroughly shaken, following enough equilibrium time for 30 min, and the solution is diluted to the final volume of 5 mL with doubly distilled water. Then the working solution is transferred into a 1 cm × 1 cm quartz cell with a cover to record absorption and fluorescence spectra.

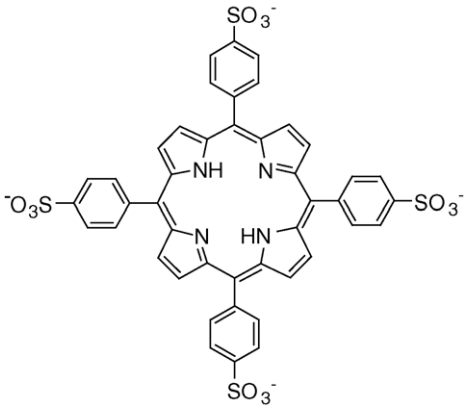

Fig. 1. Structure of meso-tetra-(4-sulfonatophenyl) porphyrin ($H_2TPPS_4^{4-}$).

3. Results and discussion

3.1. Influence of acids on aggregation of $H_4TPPS_4^{2-}$

The planar and large surfaces of porphine in porphyrin molecules belong to hydrophobic chromophores, and they are easily stacked to form large aggregates [14]. In the peripheral parts of $H_2TPPS_4^{4-}$, the phenylsulfonic groups are of high enough polarity to convert the whole macro-circular molecule into water-soluble species. For the protonated diacid, namely $H_4TPPS_4^{2-}$, the pK_a is ca. 5 [15], and under our experimental conditions, the minimal concentration of acids is 0.06 M, which makes pH value below 5. Obviously, nitrogens in porphine cycle can be protonated upon the addition of acids, and the whole porphyrin is both positive at the center of porphyrin ring and negative charges at the peripheral sulphonic groups. So electrostatic attracting force will be an aid to form much highly ordered aggregates, namely the porphyrin J-aggregates, which has the characteristic absorption peak at 490 nm.

Fig. 2 clearly shows the absorption bands of $H_4TPPS_4^{2-}$ upon the varying concentrations of HCl. Within a certain concentration range, the more hydrogen ions are added in the measurement system, and the stronger intensity of J-aggregates at 490 nm is. Because there exists the equilibrium between $H_4TPPS_4^{2-}$ monomers and J-aggregates, five isobestic points appear in the absorption spectra, inclusive of an obvious point at 450 nm and another at 660 nm. Interestingly, after about one-day incubation time, green precipitates appear at the bottom of comparison tube due to the poor water solubility of J-aggregates. The upper solution does not absorb lights at 490 nm but regains light absorbing ability after slight shaking and mixing procedures, which further proves

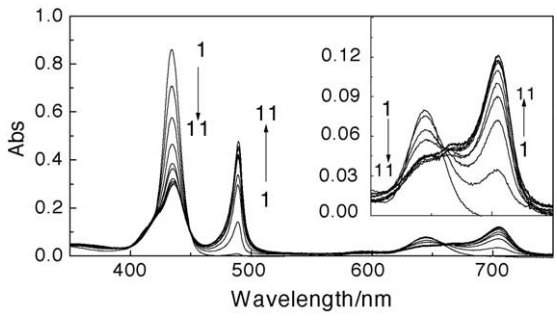

Fig. 2. Absorption bands equilibrium of changing HCl (the variation of $[H^+]$ is from 0.12 to 1.2 M, and the arrows indicate the varying peaks at 436, 490, 644 and 704 nm).

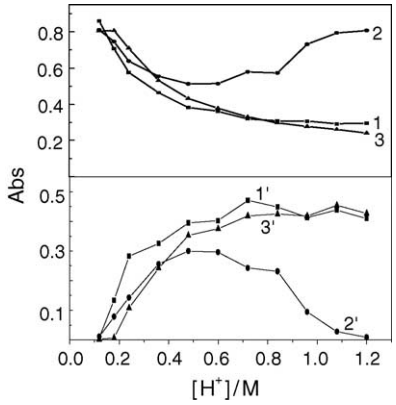

Fig. 3. Varying absorbance at 436 nm (above) and 490 nm (below) upon the addition of different acids (from 1 to 3, the curves stand for HCl, HNO_3, and H_2SO_4, respectively, with the $[H^+]$ of from 0.12 to 1.2 M).

that aggregated forms cause the sharp absorption increase at a red-shifted wavelength.

Additionally, we investigate different influence aroused by three kinds of acids. As shown in Fig. 3, HCl, HNO_3, and H_2SO_4 at lower concentrations demonstrate similar variation in absorbance, but those anions might partially function as regulating factors. In the case of HNO_3, decreasing tendency at 490 nm might be attributed to the fact that hydrophilic sulfuric groups also can be protonated under extremely high acidity, and then the absorbent species become totally positive to show disaggregation signals as indicated as curve 2 in Fig. 3.

J-aggregates of $H_4TPPS_4^{2-}$ have a sharp and intense absorption band at 490 nm, while they do not emit fluorescence. And it is probable that in the aggregates, absorbed energy might experience intrinsic transfer among those monomer units in a non-luminous way. However, experimental evidence is needed to elucidate this matter. Fig. 4 shows the decreasing fluorescence emission in the same measurement system. With the addition of HCl, it is obvious that J-aggregates will reach its maximal value, and the monomers will not disappear completely owing to the presence of the aforementioned equilibrium but be at their lowest level. So it is easy to understand the decreasing emission intensities as shown

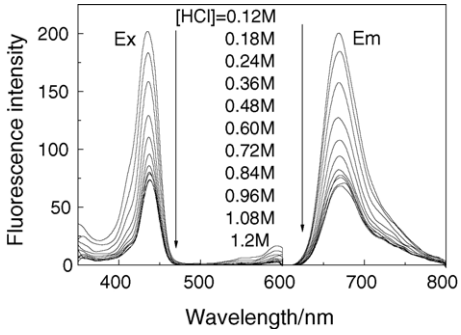

Fig. 4. Fluorescence variation during changing HCl (under the same condition stated as Fig. 2.).

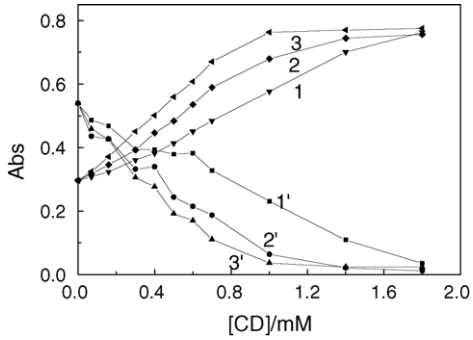

Fig. 5. Absorbance variation at 436 nm (above) and 490 nm (below) with the addition of different CDs (from 1 to 3, the curves stand for β-CD, HP-β-CD and Me-β-CD of the concentration from 0 to 1.8 mM).

in Fig. 4, which is consistent with the same tendency as observed in absorption spectra.

3.2. Influence of CDs on $H_4TPPS_4^{2-}$ J-aggregates

When CDs are added into the working solution, absorption spectra show reverse changes as the influence of different acids, namely there appears increasing absorbance at 436 nm and decreasing one at 490 nm, as shown in Fig. 5. The characteristic structure of β-CDs is both hydrophobic in their cavities and hydrophilic in those outside hydroxyl groups, which has appropriate ability to break the J-aggregates that appear a most distinct and sharp peak at 490 nm in absorption spectra. The addition of β-CDs witnesses the diminishing peaks at 490 nm, accompanied with increasing absorbance at 436 nm corresponding to monomeric molecules. The stability of CD complexes is believed to depend on many cooperative forces, mainly including electrostatic, van der Waals forces, hydrogen bonding, hydrophobic interaction, and the release of distortion energy of CD ring upon guest binding [16]. As far as HP-β-CD and Me-β-CD are concerned, those substituents increase accommodation ability of CD for the peripheral phenylsulfonic groups, and Fig. 5 shows that the two chemically modified cyclodextins witness greater changes than β-CD. J-aggregates are easily broken in organic solvents, and we think that CDs' breaking aggregation in that they provide such similar microenvironment to hinder porphyrin monomer assembling to aggregates, and some detailed discussion is expressed in the following section.

3.3. Formation constants of $H_4TPPS_4^{2-}$/CD complexes

The porphyrin system experiences the following equilibria with proton and CD to reach aggregation or disaggregation states.

$$H_2TPPS_4^{4-} + 2H^+ \rightleftharpoons H_4TPPS_4^{2-} \quad (1)$$

$$2H_4TPPS_4^{2-} \rightleftharpoons H_4TPPS_4^{2-}/H_4TPPS_4^{2-} \text{ (J-dimer)} \quad (2)$$

$$H_4TPPS_4^{2-}/H_4TPPS_4^{2-} + 2CD \overset{K}{\rightleftharpoons} 2H_4TPPS_4^{2-}/CD \quad (3)$$

Table 1
Formation constants of $H_4TPPS_4^{2-}$/CD in different CDs ([HCl] = 0.84 M)

	CDs		
	β-CD	HP-β-CD	Me-β-CD
K	286	754	894
R	0.998	0.992	0.996
The linear regression equations	$y = 0.00428 + 0.0150x$	$y = 0.00604 + 0.00801x$	$y = 0.00566 + 0.00633x$

Protonation occurs under a proper acidity, and the optimal concentration of HCl is to guarantee enough $H_4TPPS_4^{2-}$ to form J-aggregates as many as possible (Fig. 2). β-cyclodextrins are added to function as disaggregation reagents. So it is necessary to quantitatively investigate the competition between self-assembling and disaggregating processes.

Because CDs have no apparent influence on both absorption and fluorescence features of $H_4TPPS_4^{2-}$, it is feasible to calculate the inclusion parameters between CDs and J-aggregates. With regard to the sizes of those host and guest molecules, it is speculated that the inclusion interaction of those peripheral phenylsulphonic groups with β-CD might explain the breakage of J-aggregates, resulting in the equilibrium between monomers and aggregates of $H_4TPPS_4^{2-}$. However, it is noteworthy that such inclusion will not be a decisive aid to cause apparent changes of the monomer porphyrin's fluorescence emission, because our focused fluorescence peaks are not the results of the peripheral groups easily affected by CDs, but of the π–π* transitions of the porphine macrocycle with 18 well-conjugated electrons. Inclusion formation constant is a very important parameter to characterize the complex ability of CDs, which is closely connected with inclusion equilibrium constant. The constants of $H_4TPPS_4^{2-}$ with CDs, including β-CD, HP-β-CD and Me-β-CD are calculated based on the "double reciprocal method" proposed by Bright et al. [17,18]. The equation is listed as follows:

$$1/(F - F_0) = 1/\{KkQ[P]_0[\mathrm{CD}]_0\} + 1/(kQ[P]_0) \quad (4)$$

where F and F_0 stand for the fluorescence signals of $H_4TPPS_4^{2-}$ in the presence and absence of CD, respectively; $[P]_0$ is the initial concentration of $H_4TPPS_4^{2-}$ and $[\mathrm{CD}]_0$ is the analytical concentration of CDs; k is cited here as an instrumental constant; Q is the quantum yield for the inclusion complex. K is the formation constant of the complex. So from the slope and intercept, it is easily to calculate K value. The linear regression equations and inclusion formation constants are listed in Table 1. It shows that the stoichiometric ratio between $H_4TPPS_4^{2-}$ and CDs is 1:1, which has been indicated from Fig. 6. The formation constants for different CDs obey the following order: Me-β-CD > HP-β-CD > β-CD. The experimental results suggest that different chemical modification have changed CD's complex capacity, owing to larger and flexible cavities compared with parent CD.

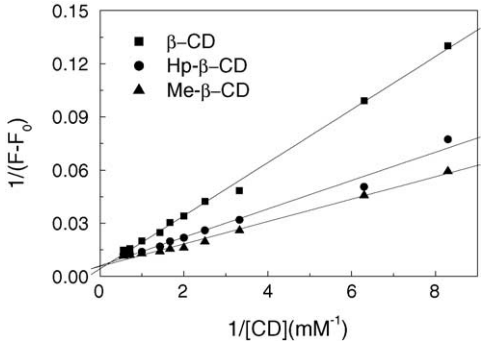

Fig. 6. Double reciprocal plots for $H_4TPPS_4^{2-}$/CD inclusion complexes in the case of different CDs.

4. Conclusions

Cyclodextrins inclusive of β-CD, HP-β-CD, and Me-β-CD can effectively break the porphyrin J-aggregates formed under appropriate acidity, showing relatively exquisite balance between 490 and 436 nm in absorption spectra. The gradually increasing fluorescence emission with the excitation wavelength at 436 nm can be used to roughly calculate the corresponding inclusion parameters. The experimental results might be of importance to understand the ubiquitous aggregation phenomenon in nature, and some relevant studies are still exploring in our laboratory.

Acknowledgments

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