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Aggregation of two carboxylic derivatives of porphyrin and their affinity to bovine serum albumin

Yao-Bing Yin, Yi-Nong Wang, Jian-Biao Ma *

Key Laboratory of Functional Polymer Materials (Ministry of Education), Nankai University, Tianjin 300071, PR China

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Abstract

Aggregation of two porphyrin derivatives with carboxylic groups, 4-oxo-4-((4-(10,15,20-triphenyl-21*H*,23*H*-porphin-5-yl)phenyl)amino)-butanoic acid (MAC) and 4,4′,4″,4‴-[21*H*,23*H*-porphine-5,10,15,20-tetrayltetrakis(4,1-phenyleneimino)]tetrakis(4-oxo-butanoic acid) (TA4C), and their affinity to bovine serum albumin were investigated via absorption spectrometry, ^{1}H NMR and fluorescence spectrometry. MAC and its complexes with β-cyclodextrin could form aggregates in an aqueous solution while TA4C was self-associated loosely. From the absorbance profiles of MAC in the titration of bovine serum albumin, hypochromicity was observed without any shift of the maximum absorbance wavelength. In both absorption spectra of TA4C in aqueous solutions and in solid state, three Q bands appeared in the visible region. In the measurements of absorption and fluorescence spectra upon titration of BSA, some spectral changes of TA4C were observed. The whole procedure of titration could be divided into three successive stages. The three-banded profiles of TA4C might be explained according to a loose dimer model.

Keywords: Aggregation; Binding modes; Three-banded Q bands; Fluorescence; Absorption spectrum

1. Introduction

Aggregation of porphyrin derivatives is known to play an important role in biological events, such as photosynthetic light energy conversion, oxygen transport, and biological catalysis. Their affinity to biological molecules is often involved in the transportation and metabolism of porphyrins in human bodies. It is found that the formation of porphyrin aggregates in aqueous solutions is often affected by the chemical structure of porphyrins, ionic strength, temperature, pH and surfactants [1]. The affinity of some porphyrins to bovine serum albumin or human serum albumin was studied [2–6]. Especially, much attention was paid on protoporphyrin IX [7], deuteroporphyrin [8] and other carboxylic porphyrins [9,10] in the past decades. Moreover, some cyclodextrin derivatives could bind water-soluble porphyrins [11,12] so as to preclude the porphyrin–porphyrin aggregation [13].

On the other hand, three Q bands as an interesting spectral characteristic of tetracarboxyphenylporphine (TCPP) in an aqueous solution occurred in the visible region [14]. The influence of substituents, monoprotonation and steric hindrance on the three-banded phenomena was observed. The three-banded Q bands existed in the UV–vis spectra of some monoprotonated porphyrins [15], 5,15-di(4-hydrocyphenyl)-10,20-di(4-hexadecyloxyphenyl)porphyrin [16], five tri-(*N*-methyl-4-pyirdiniumyl) porphyrins with an amino acid or peptide side-chain on the fourth meso aromatic substituent [17] and four protoporphyrin IX derivatives with 2-aminoglycosamide group [18] in aqueous media. In the absorption spectrum of tetra-(*p*-*N*,*N*-diphenylamino)phenylporphine ($TDPAPPH_2$) in chloroform solution, three Q bands also occurred due to non-planar distortion of the porphine ring originated from big steric hindrance [19]. Unfortunately, the nature and the significance of three-banded profile of different porphyrins are not clear up to date.

In the present study, an attempt is to gain more insight into the aggregation behavior of some porphyrins and their interaction with biological molecules. Two porphyrin derivatives with butanoic acid groups, 4-oxo-4-((4-(10,15,20-triphenyl-21*H*,23*H*-porphin-5-yl)phenyl)amino)butanoic acid (MAC) and 4,4′,4″,4‴-[21*H*,23*H*-porphine-5,10,15,20-tetrayltetrakis(4,1-phenyleneimino)]tetrakis(4-oxo-butanoic acid) (TA4C), as illustrated in Chart 1, were studied via absorption spectrometry, ^{1}H NMR and fluorescence spectrometry. The effect of

* Corresponding author. Tel.: +86 22 23507746; fax: +86 22 23502749.
E-mail address: jbma@nankai.edu.cn (J.-B. Ma).

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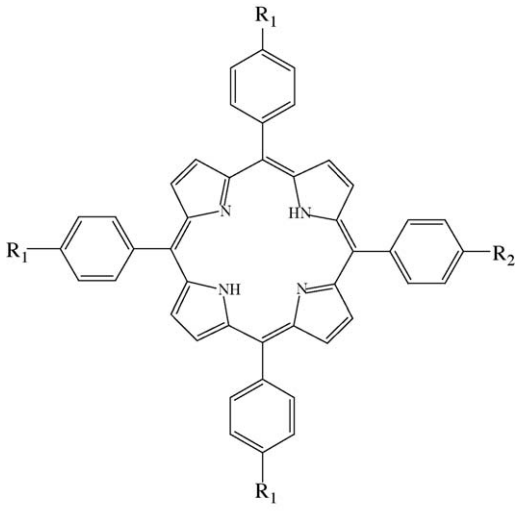

MAC R_1=H, R_2=- $NHCOCH_2CH_2COOH$

TA4C R_1=R_2=-$NHCOCH_2CH_2COOH$

Chart 1. Structures of two porphyrin derivatives with carboxylic groups.

β-cyclodextrin on aggregation of MAC in an aqueous medium was investigated. The spectral characteristic of the three Q bands was observed and discussed to elucidate the aggregation of TA4C in an aqueous solution and the binding of TA4C to BSA.

2. Experimental

2.1. Materials

Monomethoxy poly(ethylene glycol) was supplied by Sigma Chemical Company. Bovine serum albumin (BSA) was purchased from Institute of Hematology, Chinese Academy of Medical Sciences. All chemicals were of analytic grade and purified prior to use. 5,10,15,20-tetrakisphenylporphyrin (TPP) was prepared according to the previous literature. 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin (*p*-TAPP) [20] and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (*p*-MAPP) [21,22] were prepared from the corresponding nitro-substituted benzaldehyde and pyrrole [23] via the condensation and successive reduction with $SnCl_2$ in 12 mol dm^{-3} HCl–acetic acid (1:1, v/v) at 65 °C. TA4C and MAC were synthesized via esterification of *p*-TAPP and *p*-MAPP with succinic anhydride.

2.2. Instruments

Proton NMR spectra were measured on a Varian UNITY Plus-400 spectrometer. Reflective solid UV–vis spectra were recorded with a JASCO U-570 spectrophotometer. Ultraviolet–visible (UV–vis) spectra were obtained on a SHIMADZU UV-2101PC spectrophotometer where the temperature of the solutions was maintained by the use of a constant-temperature circulation pump (Tulabo F12) and a variable-temperature cell holder (Hitachi). Steady-state fluorescence spectra were measured using JY FluoroMax-P spectrofluorometer after the samples were equilibrated for 1 h.

2.3. Spectra titration

A stock solution was prepared by dissolving TA4C in phosphate buffer at pH 7.4. A stock solution of MAC was prepared by successive dissolution of MAC into THF, addition of distilled water, and removement of THF via evaporation in vacuo. The quartz cuvettes were cleaned in 3 mol dm^{-3} nitric acid overnight and washed with distilled water, ethanol, distilled water, and the sample solution before any measurement. Both the porphyrins fluorescence and absorbance were titrated with protein solutions. All experiments were carried out at pH 7.4 in phosphate buffer containing 0.01 mol dm^{-3} NaCl at 25 °C. The concentration of porphyrin derivatives maintains 1×10^{-6} mol dm^{-3}.

3. Results and discussion

3.1. Beer's law

The Beer's law titrations of the TA4C at pH 7.4 (Fig. 1) and MAC at pH 7.4 in the presence and the absence of β-CD were performed respectively at a suitable wavelength. As seen in Fig. 1, the photophysical properties of TA4C poorly adhere to the Beer's law in the present case, indicating that molecules of TA4C form aggregates even in a dilute aqueous solution. Remarkable deviation from the Beer's law is observed for MAC both in the presence and the absence of β-CD (plots not shown). In fact, it is difficult to measure the spectral absorption of MAC because it is per se insoluble in distilled water. Although β-cyclodextrin as protective molecules can preclude the porphyrin–porphyrin interaction [13], deviation from the Beer's law is significant for MAC in the presence of β-CD. The result implies that the tetraphenylporphyrin with only one butanoic acid group predominantly trends to aggregate in aqueous media owing to its poor hydrophilicity. It is in line with the previous results that the increased lipophilicity of porphyrins with long nonpolar alkyl

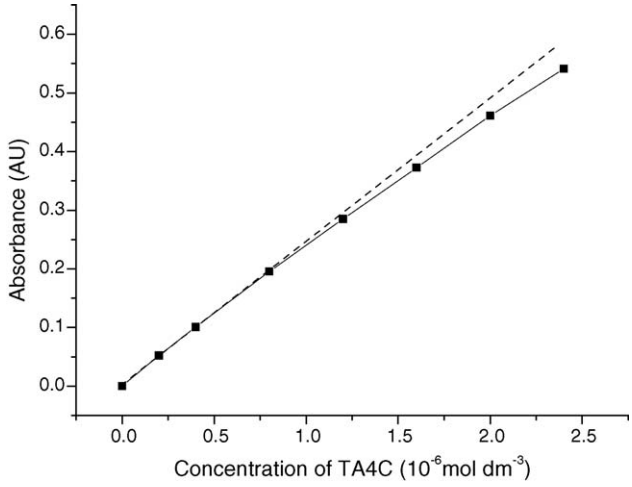

Fig. 1. Beer's law titration of TA4C.

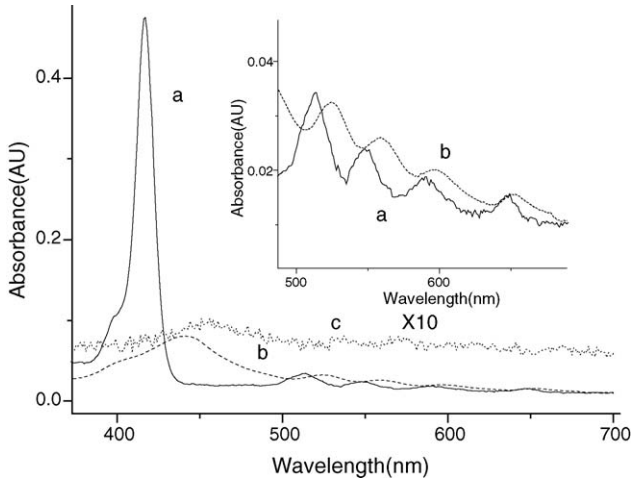

Fig. 2. Absorption spectra of MAC. (a) MAC in THF (solid line); (b) MAC-β-CD in water (dash line); (c) MAC in water (dot line); The inset is the magnified Q bands of MAC.

chain would result in a pronounced tendency toward the aggregation [24].

3.2. Aggregates

The UV–vis absorption spectra of MAC in tetrahydrofuran solution and in an aqueous solution in the presence and the absence of β-cyclodextrin are displayed in Fig. 2. It can be clearly seen that the absorbance intensities of MAC in the aqueous solution are lower for the Soret band and higher or equal for Q bands than those in the organic solution, respectively. The result suggests that intensity transfer from the B- to the Q-band region occurs owing to an excitonic coupling between B and Q transition [25]. Moreover, a blue-shifted shoulder appears at 403 nm for MAC both in the organic solution and in the aqueous solution in the presence of β-cyclodextrin, while the absorption of Q-bands in the visible region exhibits a slight red shift. These spectral profiles indicate the formation of porphyrin aggregates. In comparison with the data in the absence of β-cyclodextrin, the corresponding bands exhibit red shift and slightly higher intensities after MAC interacts with β-cyclodextrin. This result is attributed to the inclusion complexes of the porphyrin with β-cyclodextrin, which is consistent with the previous studies [11,12]. In addition, the absorption spectrum of this inclusion complex is not changed after addition of equimolar BSA solution (absorption spectra not shown), suggesting that the complex of MAC with β-cyclodextrin can not bind to BSA.

At a higher concentration of TA4C than 1×10^{-4} mol dm^{-3} in an aqueous solution, a remarkable deviation from the Beer's law was observed owing to the formation of TA4C aggregates. Further evidence for the aggregates was observed in the ^{1}H NMR measurement of TA4C. ^{1}H NMR spectra of TA4C in DMSO-d_6 and in phosphate buffer (pH 7.4) at a concentration of 1×10^{-5} mol dm^{-3} are shown in Fig. 3. In the molecular solution of TA4C in DMSO-d_6, the molar ratio of porphine/ethylene, calculated from integration values, is 0.25 (Fig. 3a). At a lower concentration in the buffer, however, the

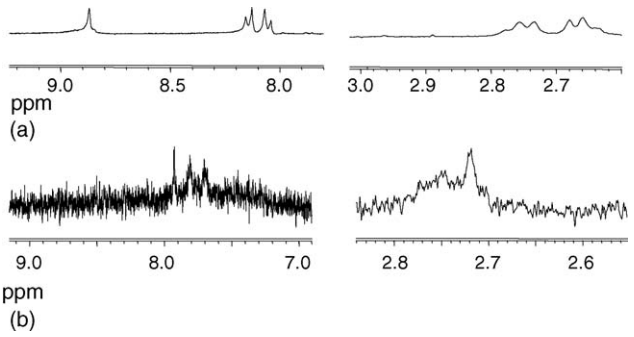

Fig. 3. Representative profile of ^{1}H NMR of TA4C: (a) in DMSO-d_6; (b) 1×10^{-5} mol dm^{-3} in D_2O.

ratio of porphine/ethylene decreases dramatically to 0.05 at room temperature (Fig. 3b). ^{1}H NMR spectrum of TA4C at a higher concentration give only the ethylene peak at 2.70–2.80 ppm and the proton peaks of the porphyrin residues can not be observed even though the solution of TA4C is green and exhibits the characteristic porphyrin bands in its electronic spectrum (^{1}H NMR spectrum not shown). This phenomenon suggests that TA4C do not present as free molecules in an aqueous solution at a higher concentration, which is in good agreement with the recent study on porphyrinic polymer in another group [26].

The number of butanoic acid groups influences aggregation of MAC and TA4C in solid state. Their reflective UV–vis spectra are displayed in Fig. 4. It can be seen that the spectral profile of MAC is similar to that of TPP, but the spectral profile of TA4C is distinctly different from that of MAC. The absorption band of MAC and TPP are 374, 523, 560, 600, 657 nm and 353, 509, 552, 592, 650 nm, respectively. A butanoic acid group renders the reflective peaks of MAC red shift. Soret bands of MAC and TPP occur at shorter wavelengths (374 and 353 nm, respectively). This indicates that molecules of MAC and TPP exist in aggregates in solid state. In contrast with this result, the Soret band of TA4C splits into two peaks at 431 and 467 nm because TA4C exist in the monomolecular state and aggregates. The Q bands of TA4C precipitated from an aqueous solution surpris-

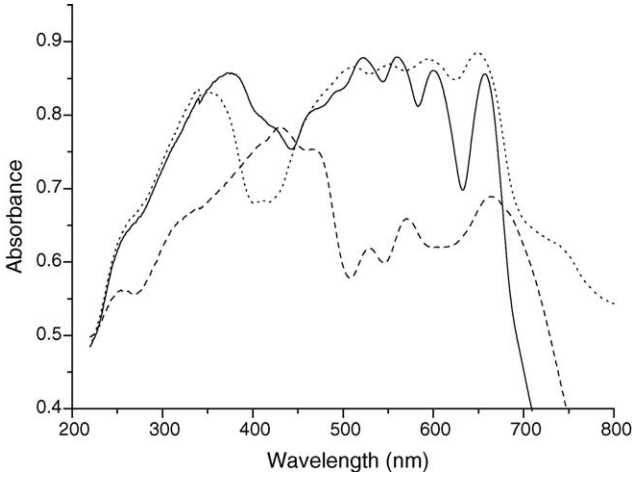

Fig. 4. Reflective UV–vis spectra of TPP (dot line), MAC (solid line) and TA4C (dash line).

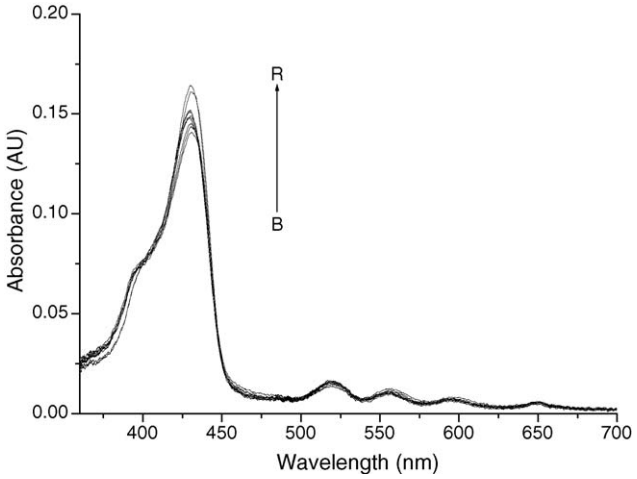

Fig. 5. Absorption spectra of MAC upon titration with BSA in phosphate buffer (pH 7.4). BSA concentration (in mol dm^{-3}) increases in the order 0.0 (B), 0.02×10^{-6} (D), 0.05×10^{-6} (F), 0.1×10^{-6} (H), 0.15×10^{-6} (J), 0.2×10^{-6} (L), 0.3×10^{-6} (N), 0.5×10^{-6} (P), 1.0×10^{-6} (R) for curves B–R.

ingly show three peaks at 529, 571, and 665 nm, respectively. A similar spectral profile in visible region also occurs for the TA4C aqueous solution.

3.3. Interaction with BSA

It is difficult to carry out the titration of MAC with an aqueous BSA solution since MAC is insoluble. A simple experiment on the interaction of the water-insoluble porphyirn with BSA was performed adopting an organic solvent evaporation method as applied for preparing polymeric nanoparticles [27]. In order to investigate interaction of MAC with BSA, a series of MAC solutions were prepared through dissolving tetrahydrofuran solutions of MAC in distilled water and then removing almost all of organic solvent by evaporation. The yellow transparent suspensions were obtained finally and the absorption spectra revealed the formation of aggregates of MAC (absorption spectrum not shown). These suspensions of MAC were employed to perform the titration with BSA solution and the spectral changes of MAC are showed in Fig. 5. It is seen that the Soret band exhibits slight hyperchromicity without any obvious shift of the maximum absorbance wavelength. The shoulder peak at 394 nm as the spectral adsorption of MAC aggregates becomes weaker accompanied with hyperchromicity of the Soret band, suggesting that the aggregates are broken partially after interaction with protein.

In Fig. 6, it is observed that the Soret band and four Q bands of TA4C change upon titration with gradually increasing concentrations of BSA. The most obvious change occurs in the Soret region of the absorption spectrum, where the intense band at 417 nm undergoes a red shift of 8 nm upon addition of BSA. No isosbestic point is observed, which indicates the presence of more than one type of porphyrin–BSA complexes in equilibrium with free porphyrins. As also illustrated in Fig. 6, there are three successive stages of the spectral change during the titration, and one near isosbestic point exists during the second stage of the titration as follows. At the first stage, the initial porphyrin

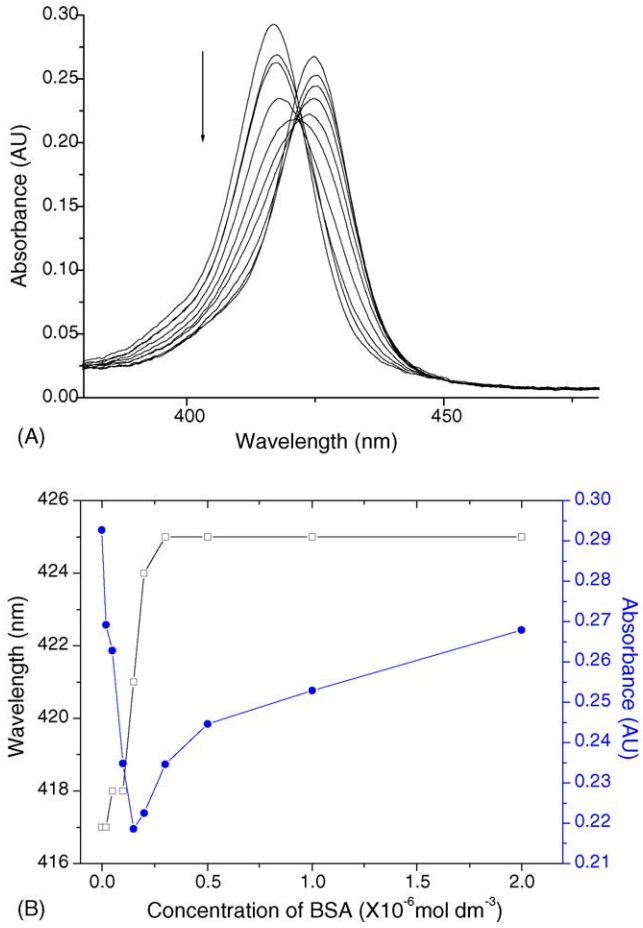

Fig. 6. Absorption spectra of TA4C upon the titration of BSA. (A) Concentration of TA4C is 1×10^{-6} mol dm^{-3} and the concentrations of BSA as arrowhead are 0, 0.02×10^{-6}, 0.05×10^{-6}, 0.1×10^{-6}, 0.15×10^{-6}, 0.2×10^{-6}, 0.3×10^{-6}, 0.5×10^{-6}, 1.0×10^{-6}, 2.0×10^{-6} mol dm^{-3}, respectively; (B) the same titration expressed in the forms of a plot of the absorbance (●) and a plot of wavelength (□) of the Soret band vs. concentration of BSA, respectively. Equalized for 60 min.

spectrum and spectra at very low BSA concentrations obviously do not exhibit an isosbestic point. Remarkable hypochromicity accompanied by a slight red shift at the Soret band is observed. At this stage, the behavior of BSA is similar to that of water-soluble macromolecules such as polyethylene glycol (PEG). Absorption spectra of TA4C upon addition of PEG ($M_n = 5000$) aqueous solution show hypochromicity only under the same experimental condition (absorption spectra not shown). The second stage shows a near isosbestic point at 421.8 nm in the spectra profile. It can be clearly observed that addition of BSA solution induces a significant red shift of the Soret band, and that the Soret maxima displays slight hypochromicity then followed by hyperchromic shift. At even higher BSA concentrations, a gradual hyperchromicity of the Soret band can be observed during the third stage. Even though a large excess of BSA is introduced into the TA4C solution, the absorption spectral profile of the porphyrin exhibits slight hyperchromicity instead of a red shift of the Soret band.

Moreover, usual curve fitting analysis for the observed absorbance changes during the second stage gives the asso-

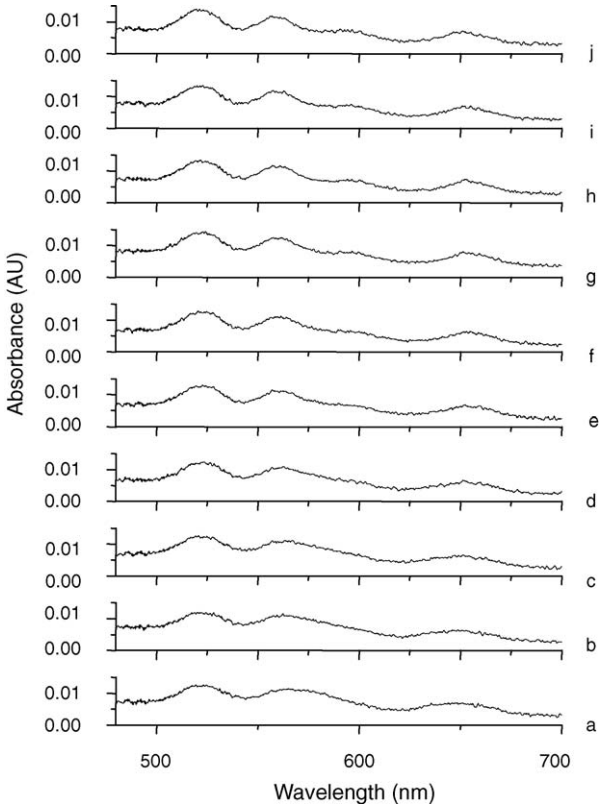

Fig. 7. Q bands of TA4C upon the titration of BSA. For curves a–j, BSA concentration (in mol dm^{-3}) was 0.0, 0.02×10^{-6}, 0.05×10^{-6}, 0.1×10^{-6}, 0.15×10^{-6}, 0.2×10^{-6}, 0.3×10^{-6}, 0.5×10^{-6}, 1.0×10^{-6}, 2.0×10^{-6}, respectively. Equalized for 60 min.

ciation constant to be 4.3×10^7 dm^3 mol^{-1} at 298 K. The affinity of TA4C to BSA is stronger than that of other carboxylic porphyrins and common tetraphenylporphyrin derivatives ($K = 10^4$–10^6 dm^3 mol^{-1}). The reason may be that besides π–π stacking interaction, hydrophobicity, hydrogen bonds generating from carboxyl groups and low aggregation, the additional hydrogen bonds generating from four amide bonds enhance the ability of TA4C binding to BSA.

3.4. Changes of the Q bands during absorption and fluorescence titration

In order to further probe characteristics of the three-banded spectra of TA4C, we analyzed the absorption spectra in visible region of TA4C upon the titration of BSA. The visible spectral changes of the Q bands upon the titration of BSA are shown in Fig. 7. It can be seen clearly that the number of Q bands changes from 3 to 4. Moreover, the species transformation occurs at the second stage of the absorption spectral change during the titration. These results evidence that the porphine ring is involved in the interaction of porphyrin with protein. It also can be seen that the blue shift of $Q_x(1,0)$ band, which is the major change, leads to formation of three-banded spectrum while the position of $Q_y(1,0)$ and $Q_y(0,0)$ bands remains almost unaltered. Meanwhile, companying with the changes of $Q_x(1,0)$ band, the $Q_x(0,0)$ band also undergoes a slight red shift followed by a

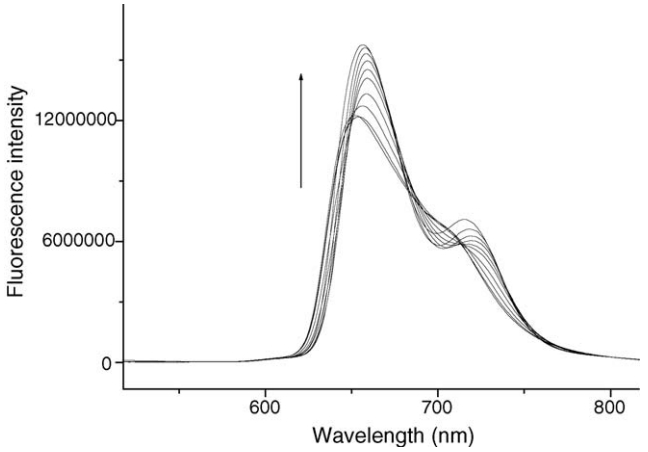

Fig. 8. Fluorescence emission spectra of TA4C upon the titration of BSA, measured at excitation wavelength $\lambda_{em} = 422$ nm. Concentration of BSA increases along with the direction of the arrowhead (in mol dm^{-3}): 0.0, 0.02×10^{-6}, 0.05×10^{-6}, 0.1×10^{-6}, 0.15×10^{-6}, 0.2×10^{-6}, 0.3×10^{-6}, 0.5×10^{-6}, 1.0×10^{-6}, and 2.0×10^{-6}. Equalized for 60 min.

more slight blue shift, and the half-peak width becomes narrow. This spectral change and changes occured in the mirror images in fluorescence emission spectra, as mentioned in the following section, exhibits that $Q_x(0,0)$ is also involved in the formation of the three-banded profile. Significantly, this phenomenon is not in line with the absorption spectral change of porphyrin-containing poly(*N*-isopropylacrylamide) in an aqueous solution, which displays bathochromic $Q_y(0,0)$ and $Q_y(1,0)$ bands so that the $Q_y(0,0)$ band partially overlaps with $Q_x(1,0)$ band [28].

Fig. 8. exhibits the fluorescence emission spectra of TA4C binding to BSA at different amount ratios measured at excitation wavelength $\lambda_{em} = 422$ nm. As inferred from Fig. 8, the fluorescence emission peaks of Q(0,1) significantly display three profiles, one profile is that the fluorescence emission intensity increases gradually, the other is that the half-peak width becomes narrow, the third is that the Q(0,1) peak appears red shift at the beginning and then blue shift. It can be also seen that the fluorescence emission peaks of Q(0,0) exhibit similar characteristics. These results imply that Q(0,1) and Q(0,0) peaks both are involved in the interaction procedure between porphyrin and BSA. It is known that the fluorescence emission spectrum sometimes appears the mirror image of the absorption spectrum. Taking together with the changes of the absorption spectra in the titration procedure, it can be concluded that the Q(0,0) involved in formation of the three-banded absorption spectra of TA4C in an aqueous solution.

3.5. Aggregation mode of TA4C

As induced from Figs. 7 and 8, the blue shift of $Q_x(1,0)$ and broadening of the half-peak width of $Q_x(0,0)$ are major changes during the formation of three-banded spectrum of TA4C. In other words, the formation of three-peaked Q bands results from that the blue-shifted $Q_x(1,0)$ merges with $Q_y(0,0)$, accompanying with that the blue-shifted $Q_x(0,0)$ becomes broad, which is in line with the case of TCPP [14]. The "face to face" model has been supported by a fluent of researches [29–32]. Based on our exper-

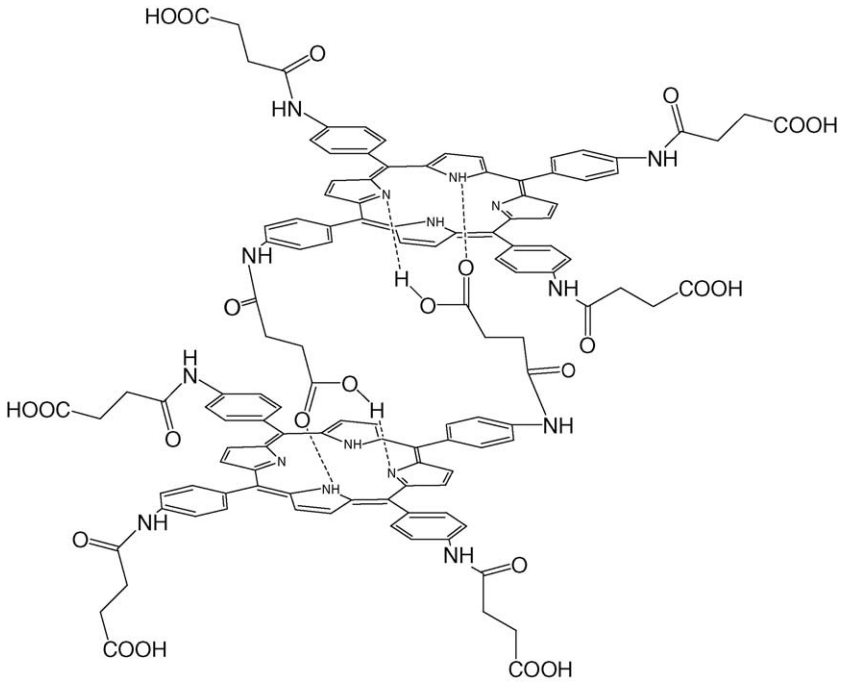

Fig. 9. Loose dimer of TA4C in an aqueous solution.

iments and the abovementioned understanding of three-peaks Q bands, we here propose a loose dimer model for association behavior of TA4C in an aqueous solution (Fig. 9). According to this loose dimer model, a face-to-face dimer of porphyrin is formed. Two carboxylic groups are hydrogen-bonded to the inner NH. Other six butanoic acid groups extend well-distributed towards the environmental space. Scolaro et al. proposed a similar hydrogen-bonding network but they were inclined to think that it was not a better model [7]. On considering the similar spectral profiles of TA4C in solid state, the slight deviation from the Beer's law and the hydrophobic–hydrophilic interaction, we think that the modified model could be more plausible for the case of TA4C. In this case, the added salt could enhance the hydrophobic–hydrophilic interaction and stabilize the aggregated species [1]. The blue-shift of $Q_x(0,1)$ can be interpreted as effects of hydrogen bonds on the conjugated system [33] of porphine ring, and a twisted conformation for porphine ring due to four carboxylic groups extending towards differently orientational space. Moreover, the loose dimer model can be utilized to explain the three-banded spectrum of TA4C in solid state. After precipitated from the aqueous solution, a loose dimer is stacked with another similar unit via hydrogen bonds among butanoic acid groups, leading to three-banded spectra (Fig. 4).

The loose dimer model would promote understanding the nature of the conjugated system of porphyrin. A series of strong well-defined Q bands in visible region were assigned to the $0 \rightarrow 0$ and $0 \rightarrow 1$ vibronic transitions of the distinct x and y components of the lowest $\pi \rightarrow \pi^*$ transition [34]. According to the previous literature, $Q_x(1,0)$ and $Q_x(0,0)$ both are involved in protonation of porphyrin [15]. Q(0,1) and Q(0,0) of metalloporphyrins have been measured and reached reasonable interpretation [35]. Up to date, the nature of $Q_x(1,0)$ remains unclear. In order to reach definitive conclusions concerning the nature of the changes observed, a more detailed experimental examination of these component transitions would be required.

4. Conclusions

In conclusion, the tight aggregates of MAC in an aqueous solution lead to slight hypochromicity and the absence of obvious red shift for MAC upon the spectral titration of BSA solution. The complexes of MAC aggregates with β-cyclodextrin cannot interact with BSA. The changes in the three-banded spectrum of TA4C in visible region during the spectral titration with BSA show that the titration of TA4C with BSA could be divided into three stages. The three-banded profile of TA4C both in an aqueous solution and in solid state may be explained on the basis of a loose dimer model.

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