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Construction of J- and H- Aggregates of *meso*-Tetrakis (4-hydroxyphenyl) porphyrin Diacid (H_4THPP^{2+})

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Abstract: UV-Vis spectrum was utilized to study the aggregation behaviors of H_4THPP^{2+} in DMF-chloroform mixture and water. It was found that J-aggregation of H_4THPP^{2+} was formed in DMF-chloroform mixture and H-aggregate was formed in aqueous solution with high ionic-strength, as indicated by different spectral characteristics of different H_4THPP^{2+} aggregates.

Keywords: H_4THPP^{2+}, aggregation, UV-Vis spectrum.

Solvent, salt and pH have essential but different effects on the aggregation of porphyrin, which can be utilized to control the aggregation behaviors of porphyrin, such as aggregate size[1], and furthermore, the geometric arrangement of porphyrin monomer in aggregate[2].

Result and Discussion

The absorption spectrum of H_4THPP^{2+} monomer in DMF-chloroform mixture (1:1, v/v) has a strong Soret band at 455 nm and a weak Q band at 698 nm (see **Figure 1**a). Further increasing of chloroform volume percentage yields distinct changes in the absorption spectrum of H_4THPP^{2+} solution. Upon increasing chloroform percentage, two new peaks at 492 and 765 nm appear and become more intensive at the expense of 455 nm and 698 nm, respectively (see **Figure 1**). In the Soret band, the red shift is a sign of J-aggregation formation whereas the blue shift is a sign of H-aggregation formation[3]. The evolution of the absorption spectrum of H_4THPP^{2+} with chloroform percentage indicates the formation of J-aggregation, in which the angle between the molecule transition dipole moment and the line joining the molecular centers is less than 53.7° [4]. Two isosbestic points at about 471 and 720 nm are the characteristic of the quantitative transformation of H_4THPP^{2+} monomer to J-aggregation. The hydrogen bond formed between hydroxyl and the protons in the porphyrin diacid center is considered as the main cause of the formation of J-aggregation.

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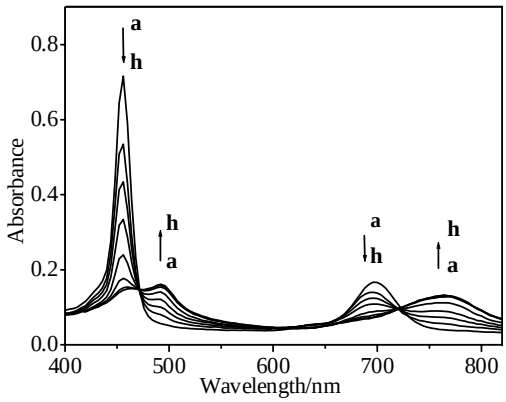
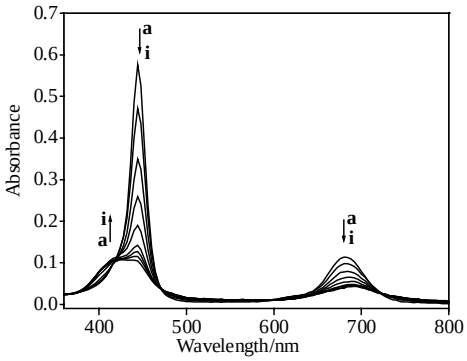
Figure 1 UV-Vis absorption spectra of H_4THPP^{2+} in DMF-chloroform mixture



$[H_4THPP^{2+}]=1.8\times10^{-6}$mol/L, [HCl]=0.005mol/L, the volume percentage of chloroform: a. 50%; b. 70%; c. 78%; d. 82%; e. 86%; f. 90%; g. 92%; h. 95%.

Figure 2 UV-Vis absorption spectra of H_4THPP^{2+} aqueous solution.



$[H_4THPP^{2+}]=1.5\times10^{-6}$mol/L, pH=2, [KCl]: a. 0.00 mol/L; b. 0.03 mol/L; c. 0.05 mol/L; d. 0.08 mol/L; e. 0.11 mol/L; f. 0.14 mol/L; g. 0.17 mol/L; h. 0.20 mol/L; i. 0.24 mol/L.

The Soret band and Q band of H_4THPP^{2+} monomer in aqueous solution is at 445 and 682 nm, respectively (see **Figure 2**a). The slight shift from the corresponding bands in DMF-chloroform solution is due to the different solvation effect. The addition of KCl to H_4THPP^{2+} aqueous solution induces the changes of absorption spectrum as showed in **Figure 2**. As the concentration of salt increased, the absorption band at 455 nm decreases and a shoulder grows in blue wavelength at 425 nm, meanwhile Q band shifts upward from 682 nm to 690 nm with concomitant decrease of intensity. The evolution of the absorption spectrum of H_4THPP^{2+} with increase of addition of KCl is similar to that of the dimeriazation of tetracationic porphyrins[5], and the blue shift of Soret band indicates the formation of H-aggregation, in which the angle between the molecule transition dipole moment and the line joining the molecular centers is larger than 53.7° [4]. The π-σ interaction between two porphyrin rings is generally thought as the main driving force to the formation of H-aggregation.

Acknowledgments

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