

Different J-Type Aggregates of *meso*-Tetrakis (4-hydroxyphenyl) porphyrin (H₂THPP) Formed in Different Solvents

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Abstract: The aggregation of *meso*-tetrakis(4-hydroxyphenyl)porphyrin (H₂THPP) in dimethylformamide (DMF)-water solution and in DMF-chloroform solution was studied by UV-vis absorption spectroscopy. The red shift of Soret band indicates the formation of J-type aggregates of H₂THPP in these two solutions. However, different shift extent of Soret band, 12 nm in DMF-water solution and 32 nm in DMF-chloroform solution, implies structural difference between these two J-type aggregates. The hydrogen bond between hydroxyl group and N-H bonds in porphyrin ring is thought as the main cause to the formation of J-type aggregate in DMF-chloroform solution, whereas the π - σ interaction between two adjacent porphyrin cores is thought as the main cause of the formation of J-type aggregate in DMF-water solution

Keywords: H₂THPP, aggregation, UV-Vis absorption spectrum.

The structure and spectroscopy of porphyrin aggregates are of much interest because of the possible technological application. A challenging aspect in this area is the possibility of controlling the arrangement and orientation of porphyrin monomer in the aggregates. The structure of porphyrin aggregate depends on peripheral substituent group of porphyrin ring^{1,2}, as well as on the experimental conditions (*i.e.*, solvent, ionic strength, pH and surfactant)³. Further study on the aggregation behaviors of porphyrin in different experimental conditions is necessary to perfect the techniques of controlling the aggregation of porphyrin. In this letter, different aggregations of H₂THPP in different solutions were studied.

Result and Discussion

The absorption spectrum of H₂THPP monomer in DMF solution has a strong Soret band at 420 nm and four weak Q bands at 518, 553, 594, and 650 nm (see **Figure 1a**). The addition of water to H₂THPP solution brings about distinct changes of the absorption spectrum of H₂THPP. Upon increase of water addition, both B band and Q bands shifted to longer wavelength accompanying with decrease of intensity. When the volume percentage of water increased to 85%, B band shifted to 432 nm and four Q bands shifted to 524, 565, 597, and 658 nm, respectively (see **Figure 1h**). In the Soret band region,

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the red shift is a sign of J-type aggregate formation whereas the blue shift is a sign of H-aggregate formation^{1,2}. The evolution of the absorption spectrum of H₂THPP with water percentage indicated that the formation of J-type aggregate, in which the angle between the molecule transition dipole moment and the line joining the molecular centers, is less than 53.7 degree⁴. The turbidity of solution after the addition of water also indicated the formation of aggregate.

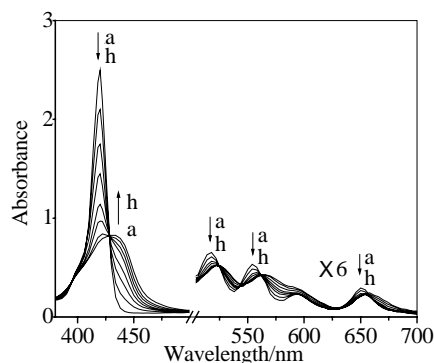
The absorption spectrum of H₂THPP in DMF solution was also observed upon addition of chloroform (see **Figure 2**), and the evolution of the absorption spectrum is similar to that with the addition of water. When the volume percentage of chloroform increased to 85%, B band shifts to 452 nm and four Q bands shift to 528, 566, 594, and 656 nm respectively, which confirming the formation of J-type aggregate of H₂THPP. The turbidity of solution with the addition of chloroform was also observed.

It should be noted that the red shift of Soret band of the J-type aggregates formed in DMF-chloroform solution is much larger than that in DMF-water solution. Theory predicts that the absorption frequency of the aggregate shifts according to equation (1)⁵.

$$\Delta\nu = \nu_M - \nu_A = \frac{1}{2\pi h \epsilon_0} \frac{(N-1)}{N} \frac{\langle M^2 \rangle}{r^3} (3 \cos^2 \theta - 1) \quad (1)$$

where ν_M and ν_A are the absorption frequencies of the monomer and aggregate, respectively, θ is the angle between the molecule transition dipole moment and the line joining the molecular centers, M is transition dipole moment, N is the spectroscopic aggregation number, and r is the center-to-center distance between adjacent transition dipole. In our experiment, the $\Delta\nu$ of J-type aggregate formed in DMF-water solution and in DMF-chloroform solution is 661 cm^{-1} and 1686 cm^{-1} , respectively. The latter is about 2.5 times larger than the former, which cannot be accounted solely by the difference of spectroscopic aggregation number. Therefore, different structural parameter (*i.e.*, r and θ) was thought to be responsible for the difference of $\Delta\nu$ between these two J-type aggregates, though the contribution of solvent effects could not be excluded. Furthermore, the molecular interactions driving the formation of these two

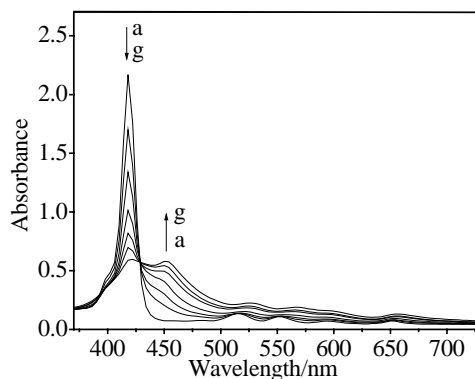
Figure 1 UV-Vis absorption spectra of H₂THPP in DMF-water solution



the volume percentage of water is: a. 0%; b. 50%; c. 69%; d. 76%; e. 80%; f. 82%; g. 84%; h. 85% ($[\text{H}_2\text{THPP}] = 1.8 \times 10^{-5} \text{ mol/L}$). The spectra larger than 500 nm are amplified by six times.

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Figure 2 UV-Vis absorption spectra of H₂THPP in DMF-chloroform solution



the volume percentage of chloroform is: a. 0%; b. 50%; c. 70%; d. 76%; e. 80%; f. 83%; g. 85% ($[H_2THPP]=1.8\times 10^{-6}$ mol/L).

J-type aggregates should be different. The hydrogen bond between hydroxyl group and N-H bonds in porphyrin core is thought as the main cause of the formation of J-type aggregate in DMF-chloroform solution, while the π - σ interaction between two adjacent porphyrin cores is thought as the main cause of the formation of J-type aggregate in DMF-water solution.

Acknowledgments

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References

1. K. Kano, K. Fukada, H. Wakami, *J. Am. Chem. Soc.*, **2000**, *122*, 7494.
2. D. M. Chen, T. He, D. F. Cong, *et al.*, *J. Phys. Chem. A*, **2001**, *105*(16), 3981.
3. M. Y. Choi, J. A. Pollard, M. A. Webb, J. L. Mchale, *J. Am. Chem. Soc.*, **2003**, *125* (3), 810.
4. D. C. Barber, T. A. Freitag-Beeston, D. G. Whitten, *J. Phys. Chem.*, **1991**, *95*, 4074.
5. N. C. Maiti, S. Mazumdar, N. Periasamy, *J. Phys. Chem. B*, **1998**, *102* (9), 1528.

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