510   *Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 5

Communications to the Editor

References

1. Hirota, E. *High Resolution Spectroscopy of Transient Molecules*; Springer-Verlag: Berlin, Germany, 1985.
2. Droege, A. T.; Engelking, P. C. *Chem. Phys. Lett.* **1983**, *96*, 316.
3. Engelking, P. C. *Rev. Sci. Instrum.* **1986**, *57*, 2274.
4. Lee, S. K. *Bull. Korean Chem. Soc.* **1993**, *14*, 340.
5. Lee, S. K. *Bull. Korean Chem. Soc.* **1994**, *15*, 349.
6. Blazier, C. R. *J. Mol. Spectrosc.* **1996**, *177*, 90.
7. Suh, M. H.; Lee, S. K.; Rehfuss, B. D.; Miller, T. A.; Bondybey, V. E. *J. Phys. Chem.* **1991**, *95*, 2727.
8. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 262.
9. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 277.
10. Lee, S. K.; Miller, T. A. *The 52nd International Symposium on Molecular Spectroscopy*; Columbus, Ohio, RI09, June 16-20, 1997.
11. Cossart, D.; Cossart-Magos, C. *J. Mol. Spectrosc.* **1990**, *141*, 59.
12. Cossart, D. *J. Mol. Spectrosc.* **1994**, *167*, 11.
13. Xu, D.; Li, X.; Shen, G.; Wang, L.; Chen, H.; Lou, N. *Chem. Phys. Lett.* **1993**, *210*, 315.
14. Yu, H.; Gu, Y.; Yin, Y.; Li, X.; Shen, G.; Wang, L. *Chem. Phys. Lett.* **1994**, *230*, 243.
15. Tokeshi, M.; Nakashima, K.; Ogawa, T. *Chem. Phys.* **1996**, *206*, 237.
16. Ha, Y. M.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1997**, *18*, 692.
17. Choi, I. S.; Ha, Y. M.; Lee, S. K. *Bull. Korean Chem. Soc.* **1997**, *18*, 1285.
18. Okamura, T.; Charlton, T. R.; Thrush, B. A. *Chem. Phys. Lett.* **1982**, *88*, 369.
19. Heaven, M.; DiMauro, L.; Miller, T. A. *Chem. Phys. Lett.* **1983**, *95*, 347.
20. Fukushima, M.; Obi, K. *J. Chem. Phys.* **1990**, *93*, 8488.
21. Lin, T.-Y. D.; Tan, X.-Q.; Cerny, T. M.; Williamson, J. M.; Cullin, D. W.; Miller, T. A. *Chem. Phys. Lett.* **1992**, *167*, 203.
22. Carrick, P. G.; Selco, J. I. *J. Mol. Spectrosc.* **1990**, *139*, 449.
23. Han, M. S.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 991.
24. Wiese, M. L.; Smith, M. W.; Glennon, B. M. *Atomic Transition Probabilities*; NSRD-NBS4, 1966.
25. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1990**, *137*, 13.
26. Cossart-Magos, C.; Leach, S. *J. Chem. Phys.* **1976**, *64*, 4006.
27. Cossart-Magos, C.; Leach, S. *J. Chem. Phys.* **1972**, *56*, 1534.
28. Zachwieja, M. *J. Mol. Spectrosc.* **1995**, *170*, 285.
29. Cossart-Magos, C.; Goetz, W. *J. Mol. Spectrosc.* **1986**, *115*, 366.

Unique Feature on the New J-Aggregate Formation of Tetrakis(2,6-difluorophenyl)porphyrin

Jongwan Yu, Eunyoung Nam, Byoung Soo Yu*, Kapsang Cheong[†], Hosoeb Choi[†], Dong Hee Kim[†], Soo-Chang Yu[†], and Ai-Ran Hahn[‡]

Department of Chemistry, Medical Resources Research Center, Wonkwang University, Iksan, Chonbuk 570-749, Korea
[†]*Department of Chemistry, Kunsan National University, Kunsan, Chonbuk 573-701, Korea*
[‡]*Division of Material Analysis, National Institute of Technology and Quality, Kwacheon, Kyunggi-Do 427-010, Korea*
Received February 3, 1997

The aggregation of porphyrin compounds has been extensively studied because of its importance in the application to the biological and medicinal researches as well as the photoelectric applications.[1-5] Porphyrins with hydrophilic side chains are well known to form the aggregate in aqueous solution; porphyrins having anionic,[6-8] cationic,[9,10] or non-ionic[11-13] side chains form dimer or higher molecular aggregates, depending on the chemical structure of side chains upon the increase in solute concentration or the addition of acid, salt or surfactant. The aggregation is usually spectroscopically characterized by the appearance of the

blue shifted (H-aggregate) or the red shifted (J-aggregate) Soret band. According to the molecular exciton theory, the frequency shift in the absorption spectrum is interpreted in terms of the angle between the aggregation axis and the transition dipole moment of each chromophore.[14] For porphyrin compounds, the H- and J-aggregates are formed when the aggregation occurs with face-to-face and edge-to-edge interactions between the neighboring units, respectively. Especially for the dicationic porphyrins with anionic side chains, the aggregation is closely related to the intermolecular ionic interaction as well as the π-π interaction, which strongly favors the J-aggregate formation.[8]

In this work, we report for the first time the aggregation

---

*Author to whom correspondence should be addressed.

of free base tetrakis(2,6-difluorophenyl)porphyrin (F_8-TPP) in acetone/water mixture. Contrary to the previously reported aggregations of organic compounds which occur so rapidly on the time scale of microseconds,[15,16] the aggregation of F_8-TPP occurs so slowly that we can monitor the aggregation process on a real-time scale by steady state spectroscopies. Moreover, the aggregate is stable enough in aqueous solution such that it is not destroyed at elevated temperatures or upon dilution with excess amount of water.

F_8-TPP was prepared by the standard pyrrole-arylaldehyde condensation in propionic acid.[17] The compound was identified by UV/Vis and NMR spectroscopies. At low concentration, F_8-TPP exists as a monomeric form in both acetone and water solutions; it is water-insoluble, but is easily solvated by water molecules with small amount of acetone as a cosolvent. As the acetone/water volume % fraction in the solution was adjusted to between 50:50 to 20:80, a unique spectral profile resulted, in which the Q and Soret bands are significantly red shifted relative to both its acetone-only and almost-water solutions.

A 200 μL of the 2×10^{-4} M F_8-TPP/acetone solution was mixed with 3.0 mL acetone, and then 7.0 mL HPLC grade pure water was added and mixed immediately. A portion of the solution was transferred to an absorption cell, and then its absorbance change was measured by a HP-8453 photodiode array type spectrophotometer. As the time advanced, the 417 nm Soret band decreased while the newly generated 441 nm band increased with an isosbestic point at 434 nm (Figure 1). The absorbance change was completed in 15 min, and it is considered to result from the formation of molecular J-aggregate because the newly generated Soret band is significantly shifted to red.

The formation of molecular aggregates was also confirmed by the resonance light scattering (RLS) experiment, which has been widely employed to probe chromophore aggregation.[18] A PTI fluorophotometer was used to measure the RLS by collecting the excitation fluorescence spectrum with the emission slit positioned to collect the zeroth order of the light beam diffracted from the grating. In order to

minimize self-absorption effect, the unaggregated and, aggregated solutions were diluted by distilled water to the concentration of 1×10^{-7} M. The spectral profile of the instrumental response was checked by observing the excitation spectrum for an aqueous colloidal silica solution, which showed some spectral peaks characteristic to the lamp with generally higher intensity over the blue wavelength region than over the red wavelength region. However, the corrected RLS spectra obtained by dividing the raw data with the reference were found to be inclined over the red wavelength region due to the colloidal silica-related artifact, so we adopted the uncorrected RLS data. The RLS spectral profiles of both the unaggregated and aggregated solutions are very similar to their respective absorption profiles, however, the peak RLS intensity of the aggregated solution is more than 5 times stronger than the unaggregated solution even though the latter has the bigger peak absorbance than the former, demonstrating the enhancement of resonance light scattering due to aggregation (Figure 2).

The presence of water may induce aggregation by exerting the hydrophobic interaction[19] to form the π-π interaction between porphyrin molecules. Also the presence of an enough amount of acetone is crucial for the aggregation to occur. The role of acetone in the aggregation may be explained in terms of a couple of solvation effects; firstly, it acts as a good solvent to make the molecular structure of porphyrin more flexible, and secondly it weakens the hydrogen bonding between F_8-TPP and water molecules to enable the formation of hydrogen bonds between the neighboring porphyrin molecules. Once aggregated, the aggregate had existed as a very stable form at room temperature for more than one month. Also it remained intact at lower temperatures down to 5 °C and at elevated temperatures above 60 °C. Addition of an enough amount of acetone into the aggregated solution destroyed the aggregate to restore its monomeric absorption profile. However, the aggregate was not destroyed by the addition of acetone/water (30:70 vol%) mixture solvent or neat water at any amount. This implies that the aggregate is formed by tightly holding its monomeric units together, and the intermolecular locking can only be released by the addition of an enough amount of acetone,
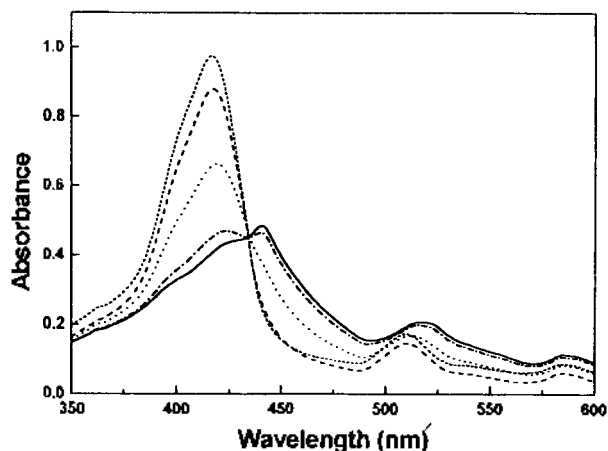

Figure 1. Time-dependent absorption measurement of the aggregation of 4×10^{-6} M F_8-TPP in 30:70 vol% acetone/water solution at 25 °C. Data were collected after addition of water; 90 s (short dashed), 240 s (long dashed), 480 s (dotted), 720 s (dot-and-dashed), and 960 s (solid), respectively.
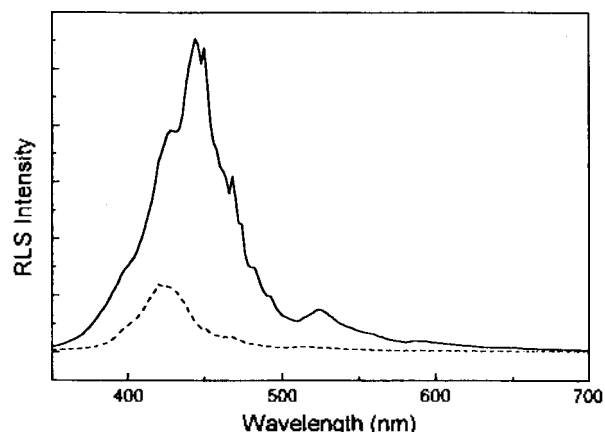

Figure 2. Uncorrected RLS spectra of the aggregated (solid) and unaggregated (dashed) solutions of 1×10^{-7} M F_8-TPP in water.
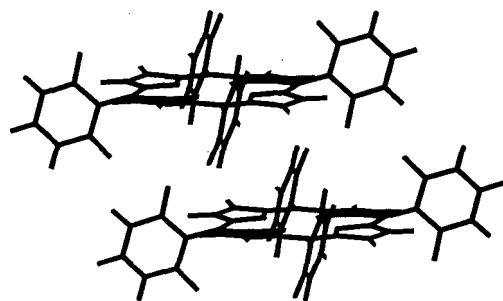
Figure 3. Diagram for molecular aggregation of F_8-TPP.

which can assist in the unlocking by enhancing the solvation of each monomeric unit.

For the sake of comparison, normal tetraphenylporphyrin (TPP) and tetrakis(2-fluorophenyl)porphyrin (F_4-TPP) were tried to get the aggregate by employing the same aggregation scheme used for F_8-TPP, but it turned out to yield the aggregates which showed only the increase of broad baseline absorption accompanied by the loss of original absorption bands of the porphyrins. Moreover, the aggregates of TPP and F_4-TPP were easily destroyed by the addition of either water or acetone, implying that the aggregates are colloidal particles formed by loose interaction. So it is reasonable to say that the unique feature in the aggregation of F_8-TPP is closely related to the presence of fluorine atoms on the ortho positions of its phenyl rings. To rationalize the experimental results, we performed a simple molecular modeling study,[20] which shows that F_8-TPP has the highest possibility to form the aggregate among these three porphyrin compounds since it can provide the closest contact between the monomeric units as well as the strongest intermolecular hydrogen bonding between fluorine and hydrogen atoms as shown in Figure 3. Compared with the J-aggregate of dicationic tetrakis(4-sulfonatophenyl)porphyrin (H_4^{2+}TPPS) which is formed majorly by ionic interaction between the dicationic internal ring and the anionic side group,[8] the aggregation of F_8-TPP is considered to be dominated by the π-π interaction with the assistance of the hydrogen bonding, which would result in the aggregation geometry much less skewed than H_4^{2+}TPPS as exemplified by the difference in the degree of red shift between the two aggregates (1305 cm^{-1} of F_8-TPP compared with 2645 cm^{-1} of H_4^{2+}TPPS).

In conclusion, this report presents the formation of a new aggregate from F_8-TPP, which occurs on the time scale of minutes. Contrary to the previously reported ionic porphyrin aggregates, this aggregate is found to be very stable against heating or dilution, implying that the aggregation is an irreversible process. Among the free base TPP derivatives, the irreversible aggregate formation occurs uniquely for F_8-

TPP, which is supported by a simple molecular modeling study.

References

1. Pasternack, R. F.; Bustamante, C.; Collings, P. J.; Giannetto, A.; Gibbs, E. J. *J. Am. Chem. Soc.* **1993**, *115*, 5393.

2. Hildebrandt, P.; Tamiaki, H.; Holzwarth, A. R.; Schaffner, K. *J. Phys. Chem.* **1994**, *98*, 2192.

3. Scherz, A.; Parson, W. W. *Biochim. Biophys. Acta*, **1984**, *766*, 666.

4. Shelnutt, J. A.; Bobry, M. M. *J. Phys. Chem.* **1983**, *87*, 3012.

5. Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Fox, M. A.; Pan, H.-L. *Nature* **1991**, *353*, 736.

6. Pasternack, R. F.; Huber, P. R.; Boyd, P.; Engasser, G.; Francesconi, L.; Gibbs, E.; Fasella, P.; Venturo, G. C.; Hinds, L. de C. *J. Am. Chem. Soc.* **1971**, *94*, 4511.

7. Akins, D. L.; Zhu, H.-R.; Cao, C. *J. Phys. Chem.* **1994**, *98*, 3612.

8. Ribo, J. M.; Crusats, J.; Ferrera, J.-A.; Valero, M. L. *J. Chem. Soc., Chem. Commun.* **1994**, 681.

9. Gibbs, E. J.; Tioco, Jr., L; Maestre, M. F.; Elliana, P. A.; Pasternack, R. F. *Biochem. Biophys. Res. Commun.* **1988**, *157*, 350.

10. Kano, K.; Takei, M.; Hashimoto, S. *J. Phys. Chem.* **1990**, *94*, 2181.

11. Barber, D. C.; Freitag-Beeston, R. A.; Whitten, D. G. *J. Phys. Chem.* **1991**, *95*, 4074.

12. Barber, D. C.; Woodhouse, T. E.; Whitten, D. G. *J. Phys. Chem.* **1992**, *96*, 5106.

13. Fuhrhop, J.-H.; Demoulin, C.; Boettcher, C.; Koning, J.; Siggel, U. *J. Am. Chem. Soc.* **1992**, *114*, 4159.

14. Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. *Pure Appl. Chem.* **1965**, *11*, 371.

15. Dewey, T. G.; Raymond, D. A.; Turner, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 5822.

16. Das, R. R.; Pasternack, R. F.; Plane, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 3312.

17. Nanthakumar, A.; Goff, H. M. *Inorg. Chem.* **1991**, *30*, 4460.

18. Pasternack, R. F.; Collings, P. J. *Science* **1995**, *269*, 935.

19. Rick, S. R.; Berne, B. J. *J. Phys. Chem. B* **1997**, *101*, 10488.

20. Molecular modeling of F_8-TPP were performed on a Silicon Graphics Indigo^2 workstation using Cerius^2. Solvent effects were not considered in this work.