Asian Journal of Chemistry Vol. 21, No. 5 (2009), 3988-3994

Characterization of Nano Tetrakis(4-sulfonatophenyl)porphyrin Aggregation Through Atomic Force Microscopy and UV-Vis Spectroscopy Methods

RAHMATOLLAH RAHIMI*, MARYAM JEDDI and SAYYED MOHAMMAD REZA RAVANFAR
College of Chemistry, Iran University of Science and Technology, Tehran, Iran
E-mail: rahimi.rah2008@gmail.com

The biological roles of porphyrins and metalloporphyrins as biological model compounds are known since the significant biological macromolecules like hemoglobin and chlorophyll were discovered. The known biological roles for these compounds are in photosynthesis and respiration processes. In addition, the porphyrins have been applied at different fields such as photoconverter, photocatalysts, photosensitizes in diagnosis and photodynamic therapy and also, as an anti Aids (HIV) drugs. In this work the tetrakis(4-sulfonatophenyl)-porphyrin ($TPPS_4$) was synthesized and metallated according to the reference method, for this compound is very active model of biological porphyrins. The aggregations of $TPPS_4$ in acidic solution were investigated by two methods, atomic force microscopy (AFM) and ultra violet -visible spectroscopy (UV-Vis). The synthesized compound of $TPPS_4$ was deposited on the surface of glass and the spatial structure was imaged by scanning on atomic force microscopy. The size of nanotubes calculated by section analysis was about (20 nm × 100 nm × 200 nm). Atomic force microscopy confirmed the *J*-aggregations of $TPPS_4$. The UV-Vis spectroscopy method was also used for investigation of $TPPS_4$ aggregation. The measured UV-Vis spectrum of the aggregated form of the compound in acidic solutions has shown maximum absorption at 433, 490 and 705 nm, which has to be attributed to the formation of *J*-aggregates (490 nm). The synthesized $TPPS_4$ nanotubes can be used in future as electronic devices.

Key Words: Tetrakis(4-sulfonatophenyl)porphyrin, Aggregation, Nanotube, Porphyrin, Atomic force microscopy.

INTRODUCTION

Porphyrins and porphyrin derivatives present in biochemistry of all living systems. They form the main structure of pigments like chlorophyll and heme, which involved in important processes of life[1]. Self-assembled nanostructures are of great current interest[2-4]. Porphyrins are attractive building blocks for these nanostructures because of their electronic, optical, catalytic properties and medical applications like photodynamic therapy.

Substantial amount of researches has been done on the medical applications of porphyrins[5-7]. In our previous work, we have discussed on metalloporphyrins as anti-cyanide agents. It was founded that nickel(II) and copper(II) can be removed from their N-methyl-tetra(4-sulfonato)porphyrins using cyanide and hydrogen cyanide[8]. Enthalpically interaction between the π-systems of porphyrins caused to self-association and formation of molecular's stacks in aqueous solutions[9].

One type of molecular assemblies is called *J*-aggregates[10], the aggregates which are characterized by an optical absorption band (*J*-band), which has a red shift with respect to the absorption band of the monomers at about 400 nm (known as the Soret band) and several weaker absorptions (Q-bands) at higher wavelengths[11-17]. The structure of $TPPS_4$ porphyrin molecule in acidic aqueous solution is illustrated in Fig. 1. In the presence of chiral groups, the structure has the optical activity of *J*-aggregates[14,18]. The supramolecular *J*-aggregate structures are not completely understood yet and hence, the spectroscopic determination of aggregation numbers does not correspond to the geometrical size of aggregates[19,20]. This conclusion was supported by the results of Yao and coworkers[21], suggesting that large aggregates are composed of thousands of dye monomers.

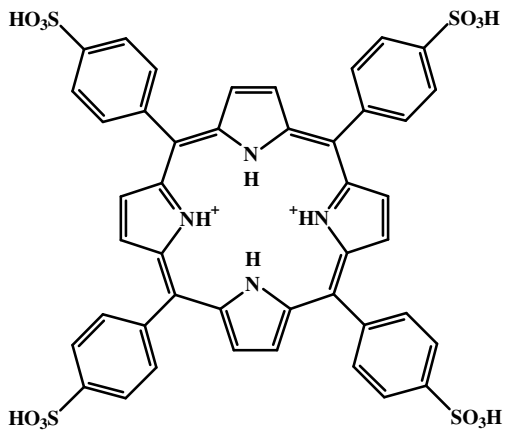

Fig. 1. Structure of the $TPPS_4$ porphyrin diacid ($H_6TPPS_4^{2+}$) in pH = 1

EXPERIMENTAL

Tetraphenylporphine was synthesized by the method of Adler[22], then sulfonated[23] and metalated[24]. The *J*-aggregate solutions were prepared by dissolving $TPPS_4$ in acidic aqueous medium. HCl was used to adjust the pH value at 1, the concentration range of $TPPS_4$ was varied between 1×10^{-4} to 2×10^{-6} M. To stabilize the aggregate formation the solution was kept at room temperature (25 ºC) for *ca.* 10 d. The nanotubes deposited on the glass surface by setting it in $TPPS_4$ solution for 5 min. The glass dried in oven at 70 ºC for 0.5 h. Atomic force microscopy confirmed the *J*-aggregations of $TPPS_4$ and UV-Vis spectroscopy was also used for studying the absorption changes at different acidic solutions and different time of aggregation.

RESULTS AND DISCUSSION

Aggregation of $TPPS_x$ derivatives in acidic solution: Fleischer[25] found that H_2TPPS_4 in acidic media at pH = 4, forms a di-acid porphyrin. The related bands were observed at 435, 593 and 645 nm and at pH values less than 2, the bands appeared at 435, 491, 645 and 707 nm as shown in Fig. 2. Pasternack[26] reported about aggregation of H_2TPPS_3 in different ionic strength solutions and reported the extent depending on the identification of the cation used to produce the ionic media. In our previous work[27], other $TPPS_x$ derivatives in 0.1 M HCl was studied and was found that the aggregation is in the order of *trans*-$TPPS_2$ (fully aggregated) >> *cis*-$TPPS_2$ > $TPPS_3$ ~ $TPPS_4$. The order of porphyrin solubility was H_2TPPS_4 (very soluble) > H_2TPPS_3 (soluble) > *cis*-H_2TPPS_2 (slightly soluble) > *trans*-H_2TPPS_2 (very slightly soluble) >> H_2TPPS_1 (fairly insoluble[27]). The comparison of these two series shows that the order of porphyrin solubility was in contrast to aggregation. By filtering the aggregated $TPPS_4$ through a 0.45 μm Millipore filter, the porphyrin di-acid passed through and the aggregation form was left on the filter as shown in Fig. 2. The H_4TPPS_x compounds could overlap in an edge-to-edge aggregation larger than 0.45 μm and cause a red shift in the Soret band of absorption spectra.

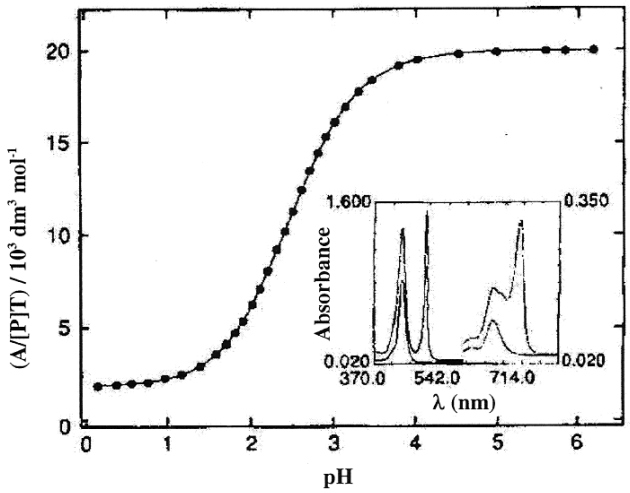

Fig. 2. pH profile of the protonation reactions of $H_2T(2,6\text{-F})PPS$ (0.1 M $NaNO_3$). Insert is the 4-band spectrum of aggregated $TPPS_4$ after passage through a 0.45 μm millipore filter

H_2P porphyrin molecules protonate at the central nitrogen atoms to form H_3P^+ or H_4P^{2+} in the acidic medium with pH values range of 0 to 3. The equilibrium constants for protonation reactions are:

$$H_4P^{2+} \rightleftharpoons H_3P^+ + H^+; \qquad K_4 \qquad (1)$$

$$H_3P^+ \rightleftharpoons H_2P + H^+; \ K_3 \quad (2)$$

To decrease the presence of dimers, the total porphyin concentrations were near 10^{-7} M. The absorption spectra were plotted as a function of pH. The relationship between the observed absorbance A_x, the total porphyrin concentration, $[P]_T$ and $[H^+]$ is:

$$\frac{A_x}{[P]_T} = \frac{\left(\varepsilon_2 K_3 K_4 + \varepsilon_3 K_4 [H^+] + \varepsilon_4 [H^+]^2\right)}{\left(K_3 K_4 + K_4 [H^+] + [H^+]^2\right)} \quad (3)$$

where ε_2, ε_3 and ε_4 are the molar absorptivities of the free base, mono- and di-cations, respectively. Fig. 2 shows a plot of $A_x/[P]_T$ *versus* pH for $H_2T(2,6\text{-F})PPS$.

UV-Vis and atomic force microscopy studies of $TPPS_4$ in aqueous acidic solutions: The measured UV-Vis spectrum of the acid solutions (Fig. 3) has maximum absorption at 433, 490 and 705 nm, which has to be attributed to the formation of *J*-aggregates (490 nm).

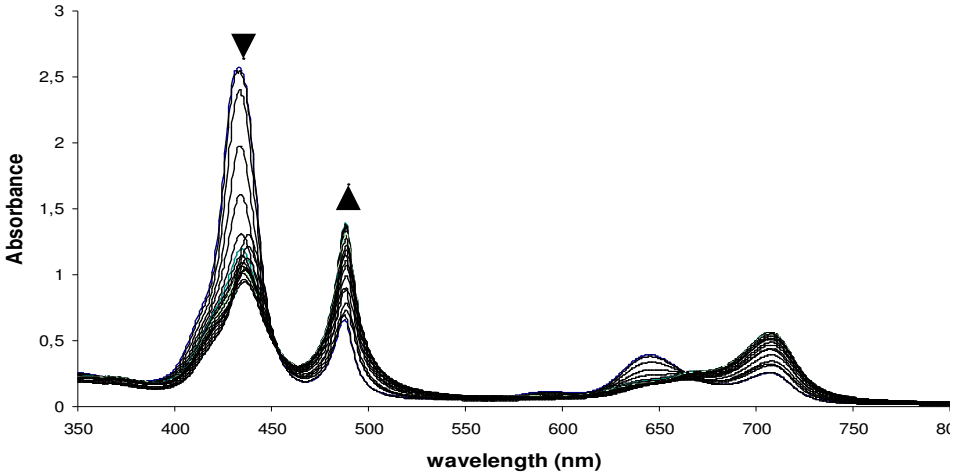

Fig. 3. UV-Vis absorption spectra of $TPPS_4$ solution by changing the pH from 4 to 1

Atomic force microscopy image of $TPPS_4$ samples deposited on silica, prepared from $TPPS_4$ aqueous acid solutions at pH = 1. The dispersion of nanotubes on glass substrate is given in Figs. 4 and 5. The size of nanotubes calculated by section analysis (Fig. 6) was about (20 nm × 100 nm × 200 nm).

Comparison between spectroscopic data and atomic force microscopy images implies that the absor-ption band at 423 nm and the *J*-band at 490 nm, both together reflect the formation of the ordered structure of TPPS tube-like aggregations[28]. UV-Vis absorption spectra of $TPPS_4$ solution recorded in the middle of aggregation as shown in Fig. 7. The absorption decreased by the time ahead and the final spectrum was the nanotube absorption bands.

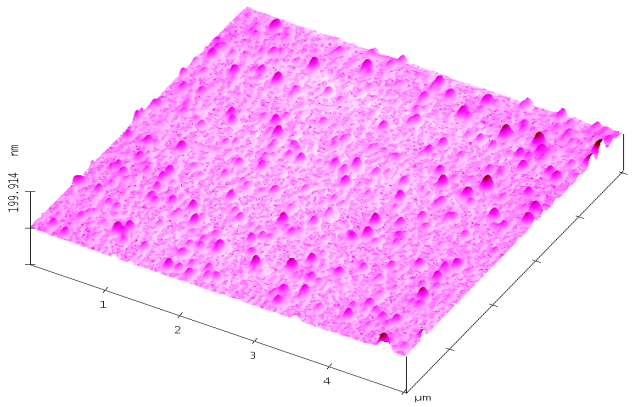

Fig. 4. Atomic force microscopy image of $TPPS_4$ sample on silica prepared from $TPPS_4$ aqueous acid solutions (pH = 1)

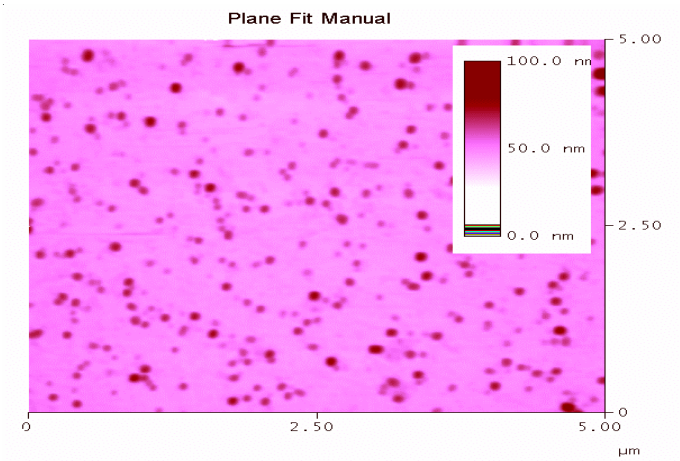

Fig. 5. Atomic force microscopy image from top of $TPPS_4$ sample on silica

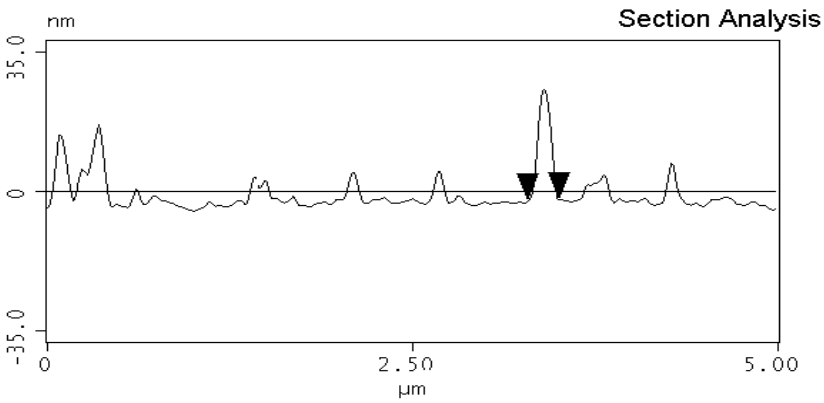

Fig. 6. Atomic force microscopy section analysis of $TPPS_4$ samples on silica

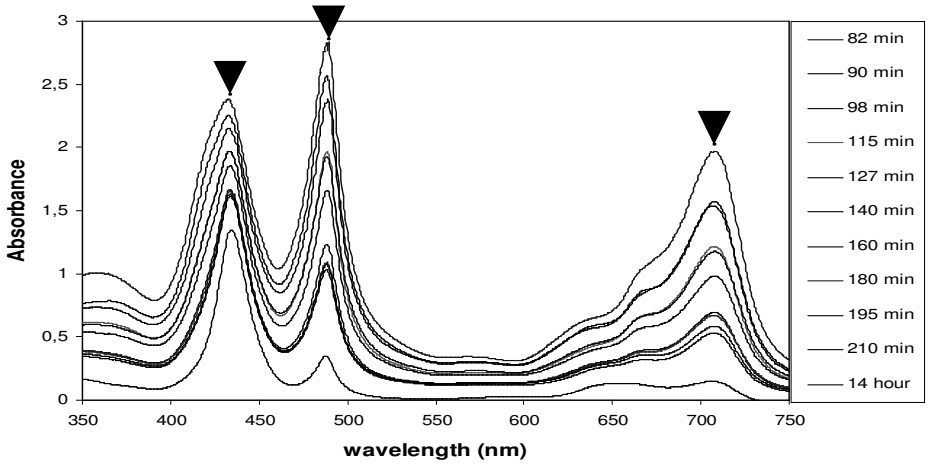

Fig. 7. UV-Vis absorption spectra of $TPPS_4$ solution by the different time of aggregation

The possible reasons for differences in spectral observed between *J*-aggregates present in aqueous solution and those formed in the presence of acid, could be related to the assembling and subsequent superficial localization of size-limited aggregated structures. The necessary conditions for the co-precipitation seem to require the presence of $TPPS_4$ monomers as well as highly aggregated species serving as a substrate finalizing the cohesion.

Conclusion

The studied aggregated porphyrin materials showed nanoporous surfaces and their applications are promising. Due to the high surface area, nanoporphyrins usually act high efficiency for sensing devices and with different metals makes them suitable for sensors. The *J*-aggregate composition of tube walls indicates strong electronic coupling of multiple porphyrin subunits, which might be expected to facilitate the electron transport that is necessary to grow the nanowire. The electronic reduction of porphyrin compounds were also studied by our group[29] which indicates that these bioinorganic compounds have electronic conductivity properties. Wide ranges of such properties have been explored, including various non-linear optical behaviour and low-dimensional electric conduction.

REFERENCES

1. F.E. Bulak, *Turk. J. Chem.*, **23**, 407 (1999).
2. G.M. Whitesides, J.P. Mathias and C.T. Seto, *Science*, **254**, 1312 (1991).
3. G.M. Whitesides, E.E.Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen and D.M. Gordon, *Acc. Chem. Res.*, **28**, 37 (1995).
4. J.M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990).
5. R.C. Lyons, P.J. Faustino, J.S. Cohen, A. Katz, F. Mornex, D. Colcher, S. Baglin, S. Koenig and P. Hambright, *Magn. Res. Med.*, **4**, 24 (1987).
6. N. J. Patronas, J.S. Cohen, R.H. Knop, A.J. Dwyer, D. Colcher, J. Lundy, F. Mornex, P. Hambright, M. Sohn and C.E. Meyers, *Cancer Treat. Rap.*, **70**, 391 (1986).

7. P.J. Bohdiewicz, D.K. Lavallee, R.A. Fawwaz, J.H. Newhouse, S.F. Oluwole and P.O. Anderson, *Invest. Radiol.*, **25**, 765 (1990).
8. R. Rahimi and P. Hambright, *J. Porphyrins Phthalocyanines*, **2**, 493 (1998).
9. J. Hofkens, L. Latterini, P. Vanoppen, H. Faes, K. Jeuris, S. DeFeyter, J. Kerimo, P.F. Barbara, F.C. DeSchryver, A.E. Rowan and R.J.M. Nolte, *J. Phys. Chem. B*, **101**, 10588 (1997).
10. T. Kobayashi, J-Aggregates, World Scientific Publishing, Singapore (1996).
11. O. Ohno, Y. Kaizu and H. Kobayashi, *J. Chem. Phys.*, **99**, 4128 (1993).
12. A. Pawlik, S. Kirstein, U. De Rossi and S. Dahne, *J. Phys. Chem. B*, **101**, 5646 (1997).
13. S. Okada and H. Segawa, *J. Am. Chem. Soc.*, **125**, 2792 (2003).
14. H. Kano, T. Saito and T. Kobayasashi, *J. Phys. Chem B*, **105**, 413 (2001).
15. K. Kano, K. Fukuda, H. Wakami, R. Nishiyabu and R.F. Pasternack, *J. Am. Chem. Soc.*, **122**, 7494 (2000).
16. R.F. Pasternack, C. Fleming, S. Herring, P.J. Collings, J. dePaula, G. DeCastro and E.J. Gibbs, *Biophys. J.*, **79**, 550 (2000).
17. R. Rubires, J. Crusats, Z. El-Hahemi, T. Jaramillo, M. Lopez, E.Valls, J.A. Farrera and J.M. Ribo, *New J. Chem*., **23**, 189 (1999).
18. X. Huang, K. Nakanishi and N. Berova, *Porphyrins Metalloporphyrins*, **2**, 237 (2000).
19. W.J. Harrison, D.L. Mateer and G.T. Tiddy, *J. Phys. Chem.*, **100**, 2310 (1996).
20. H. Yao, H. Ikeda and N. Kitamura, *J. Phys. Chem. B*, **102**, 7691 (1998).
21. B. Herzog, K. Huber and H. Stegemeyer, *Langmuir*, **19**, 5223 (2003).
22. A. Longo, F.R. Adler, J.D. Finarelli and J. Goldenmacber, *J. Assour, J. Org. Chem.*, **32**, 476 (1967).
23. M. Krishnamurthy, *Inorg. Chim. Acta*, **25**, 215 (1977).
24. M. Krishnamurthy, *Inorg. Chem.*, **17**, 2242 (1978).
25. E.B. Fleischer, J.M. Palmer, T.S. Srivastava and A. Chatterjee, *J. Am. Chem. Soc.*, **93**, 3162 (1971).
26. R.F. Pasternack, P.R. Huber, P. Boyd, G. Engasser, L. France-sconi, E. Gibbs, P. Fasella, G.C. Venturo and L.D. Hinds, *J. Am. Chem. Soc.*, **94**, 4511 (1972).
27. T.P. Sutter, R. Rahimi and P. Hambright, *J. Chem. Soc. Faraday Trans*, **89**, 495 (1993).
28. J. Valanciunaite, V. Poderys, S. Bagdonas, R. Rotomskis and A. Selskis, *J. Physics: Conference Series*, **61**, 1207 (2007).
29. G.P. Nets, P. Hambright and R. Rahimi, *Inorg. Chem.*, **31**, 4849 (1992).

(*Received*: 22 September 2008; *Accepted*: 23 February 2009) AJC-7276