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UV–Vis and AFM Study of Tetrakis (4-sulfonatophenyl) Nano-Porphyrin Aggregation

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ABSTRACT

In this study, aggregation of - tetrakis(4-sulfonatophenyl)porphyrin ($TSPP_4$) in acidic solution were examined. The spatial structure of $TSPP_4$ put on the surface was imaged using scanning atomic force microscopy (AFM). The aggregation of $TSPP_4$ was studied using UV-Vis spectroscopy. The $TSPP_4$ nanotubes could be used in future as electronic devices.

Key words: UV-Vis, nanotube, tetrakis, AFM, $TSPP_4$, heme

INTRODUCTION

Porphyrins and porphyrin derivatives present in all living systems of biochemistry. They form the main structure of pigments like chlorophyll and heme, which involved in important processes of life. Self-assembled nanostructures are of great current interest (Whitesides *et al*., 1995). Porphyrins are attractive building blocks for these nanostructures because of their electronic, optical, catalytic properties and medical applications of porphyrins like photodynamic therapy.

Substantial amount of researches has been done on the medical applications of porphyrins (Okada and Segawa, 2003). In this present study, we worked 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 (Augulis *et al*., 2008; Rahimi and Hambright, 1998).

One type of molecular assemblies is called J-aggregates . The aggregates are characterized by one 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 (Okada and Segawa, 2003). The structure of-$TSPP_4$ porphyrin molecule in acid aqueous solution was illustrated in Fig. 1. In the presence of chiral groups, the

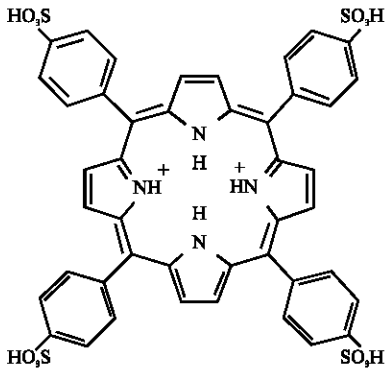

Fig. 1: The structure of the $TSPP_4$ porphyrin diacid ($H_6TSPP_4^{2+}$) in pH = 1 solution

structure has the optical activity of J-aggregates .The supramolecular J-aggregate structures are not completely understood yet and hence, the spectroscopic determination of aggregation numbers doesn't correspond to the geometrical size of - aggregates. This conclusion was supported by the results of picoseconds spectroscopy, suggesting large aggregates composed of thousands of dye monomers (Herzog *et al.*, 2003).

MATERIALS AND METHODS

Experiment was carried out during 2008-2009 at amir-kabir laboratory Tehran, Iran. The J-aggregate solutions were prepared by dissolving $TSPP_4$ in acidic aqueous medium (HCl was used to adjusting the pH value at 1) in the range of concentration between 1×10^{-4} to 2×10^{-6} M. To stabilization of the aggregates formation, the solution was kept at room temperature (25°C) for about 10 days. The nanotubes deposited on the glass surface using setting it in TSPP solution for 5 min. The glass dried in oven at 70°C for 30 min. Atomic Force Microscopy confirmed the results of J-aggregates of TSPP4. UV-Vis spectroscopy used for study of absorption changes at different acidic solutions and different time of aggregation.

RESULTS AND DISCUSSION

Acid aggregation in $TSPP_x$ derivatives: It was found that H_2TSPP_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. In this present study, $TSPP_x$ derivatives in 0.1 M HCl was studied and it founded that the aggregation is in the order of trans-$TSPP_2$ (fully aggregated)>>cis-$TSPP_2$>$TSPP_3$~$TSPP_4$ (Valanciunaite *et al.*, 2007). The order of porphyrin solubility was H_2TSPP_4 (very soluble)>H_2TSPP_3 (soluble)>cis-H_2TSPP_2 (slightly soluble)>trans-H_2TSPP_2 (very slightly soluble)>>H_2TSPP_1 (fairly insoluble). The comparison of these two series shows that the order of porphyrin solubility was in contrast to aggregation. By filtering the aggregated $TSPP_4$ through a 0.45 μm Millipore filter, the porphyrin di-acid passed through and the aggregation form was left in the filter as shown in Fig. 2. The H_4TSPP_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.

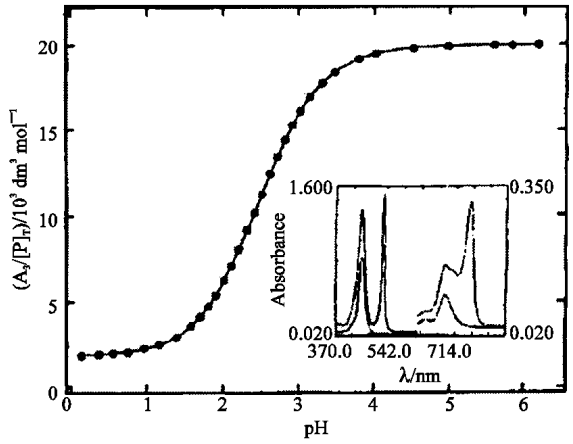

Fig. 2: pH profile of the protonation reactions of $H_2T(2,6\text{-F})PPS$ (0.1 M $NaNO_3$). Insert: the four-band spectrum of aggregated $TSPP_4$ after passage through a 0.45 μm millipore filter

H_2P porphyrin molecules protonate at the central nitrogen atoms to formation of 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:

$$H_4P^{2+} \rightleftharpoons H_3P^+ + H^+, \qquad K_4 \tag{1}$$

$$H_3P^+ \rightleftharpoons H_2P + H^+, \qquad K_3 \tag{2}$$

To decrease the presence of dimmers, the total porphyry's 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:

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

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

UV-Vis and AFM studies of $TSPP_4$ aqueous acid 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).

AFM image of $TSPP_4$ samples deposited on silica, prepared from $TSPP_4$ aqueous acid solutions at pH = 1. The dispersion of nanotubes on glass substrate is given in Fig. 4 and AFM image (from above) of $TSPP_4$ sample on silica. Is shown in Fig. 5. The size of nanotubes from section analysis calculated by section analysis (Fig. 6), was about (20×100×200 nm).

Comparison between spectroscopic data and AFM images implies that the absorption band at 423 nm and the J-band at 490 nm both together reflect the formation of the ordered structure of TSPP tube - like aggregates (Valanciunaite *et al.*, 2007). UV-Vis absorption spectra of $TSPP_4$ 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. 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

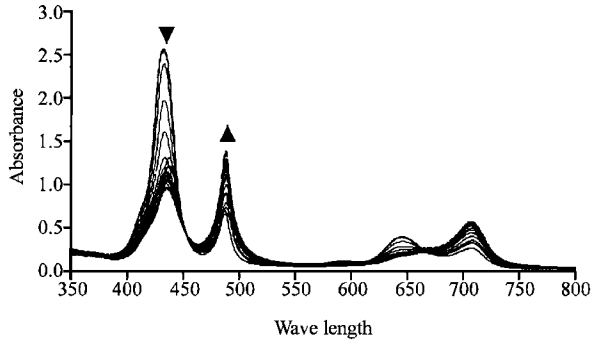

Fig. 3: UV-Vis absorption spectra of TSPP4 solution by changing the pH from 4 to 1

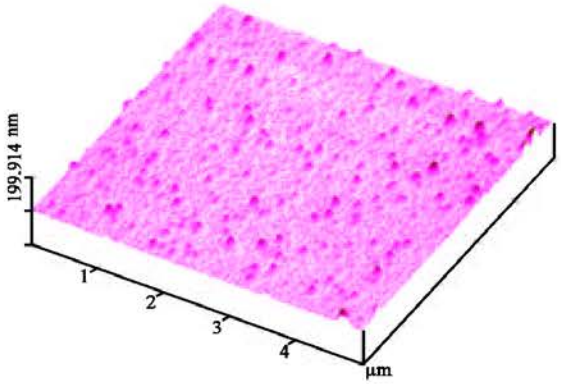

Fig. 4: AFM image of $TSPP_4$ sample on silica prepared from $TSPP_4$ aqueous acid solutions (pH = 1)

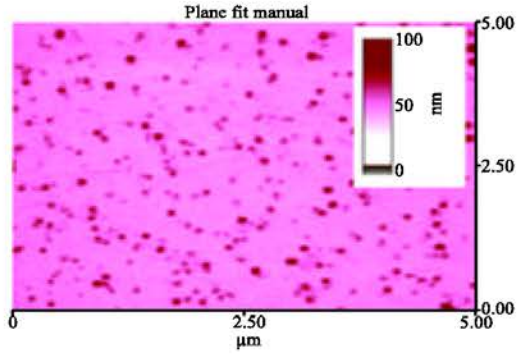

Fig. 5: AFM image (from above) of $TSPP_4$ sample on silica

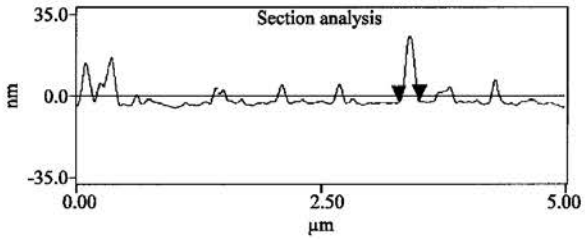

Fig. 6: AFM section analysis of $TSPP_4$ samples on silica

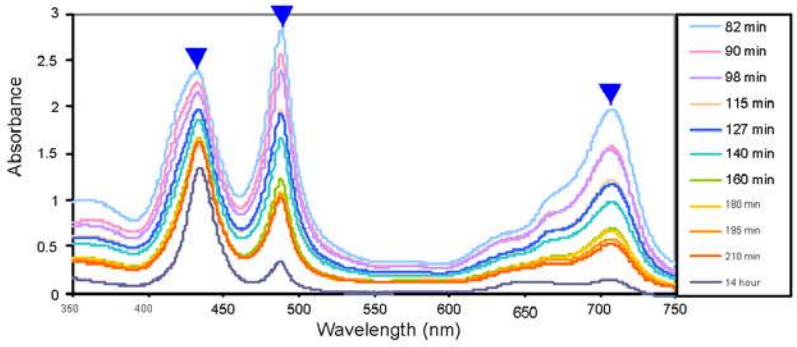

Fig. 7: UV-Vis absorption spectra of $TSPP_4$ solution by the different time of aggregation

of size-limited aggregated structures. The necessary conditions for the co-precipitation seem to require the presence of $TSPP_4$ monomers as well as highly aggregated species serving as a substrate finalizing the cohesion.

CONCLUSIONS

Aggregated porphyrin materials studied showed nanoporous surfaces and their applications are promising. Due to the high surface area, nanoporphyrins usually act high efficiency for sensing devices and using 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 growing the nanowire. Wide ranges of such properties have been explored, including various non-linear optical behavior and low-dimensional electric conduction.

REFERENCES

Augulis, R., S. Valentinas and R. Rotomskis, 2008. Self-assembled (TPPS) 4 nanostructures revealed by atomic force microscopy. Solid State Phenomena, 97-98: 191-194.

Herzog, B., K. Huber and H. Stegemeyer, 2003. Aggregation of a pseudoisocyanine chloride in aqueous NaCl solution. Langmuir, 19: 5223-5232.

Okada, S. and H. Segawa, 2003. Substituent-control exciton in j-aggregates of protonated water-insoluble porphyrins. J. Am. Chem. Soc., 125: 2792-2796.

Rahimi, R. and P. Hambright, 1998. Anti-cyanide drugs: kinetics of the removal of copper(II) and nickel(II) from N-methyl-tetra(4-sulfonatophenyl)porphyrins by cyanide. LD50s of common metalloporphyrins and metallophthalocyanines. J. Porphyrins Phthalocyanines, 2: 493-499.

Valanciunaite, J., V. Poderys, S. Bagdonas, R. Rotomskis and A. Selskis, 2007. Protein induced formation of porphyrin (TPPS4) nanostructures. J. Physics: Conf. Ser., 61: 1207-1211.

Whitesides, G.M., E.E. Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen and D.M. Gordon, 1995. Noncovalent synthesis: Using physical organic chemistry to make aggregates. Acc. Chem. Res., 28: 37-44.