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

Mohammad Gilaki
Department of Chemistry, University of Mazanderan, Babolsar, Iran

ABSTRACT
In this study, aggregation of tetrakis(4-sulfonatophenyl)porphyrin (TSPP₄) in acidic solution were examined. The spatial structure of TSPP₄ put on the surface was imaged using scanning atomic force microscopy (AFM). The aggregation of TSPP₄ was studied using UV-Vis spectroscopy. The TSPP₄ nanotubes could be used in future as electronic devices.

Key words: UV-Vis, nanotube, tetrakis, AFM, TSPP₄, heme

INTRODUCTION
Porphyrls 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 TSPP₄ porphyrin molecule in acid aqueous solution was illustrated in Fig. 1. In the presence of chiral groups, the

Fig. 1: The structure of the TSPP₄ porphyrin diacid (H₅TSPP₄²⁺) 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 picosecond 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 TSPP₄ 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 TSPPₓ derivatives: It was found that H₂TSPP₄ 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, TSPPₓ derivatives in 0.1 M HCl was studied and it founded that the aggregation is in the order of trans-TSPP₂ (fully aggregated)>>cis-TSPP₂>TSPP₁~TSPP₄ (Valanciunaite et al., 2007). The order of porphyrin solubility was H₂TSPP₄ (very soluble)>H₂TSPP₂ (soluble)>cis-H₂TSPP₂ (slightly soluble)>trans-H₂TSPP₂ (very slightly soluble)>>H₂TSPP₁ (fairly insoluble). The comparison of these two series shows that the order of porphyrin solubility was in contrast to aggregation. By filtering the aggregated TSPP₁ 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 H₂TSPPₓ 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 H₂T(2,6-F)PPS (0.1 M NaNO₃). Insert: the four-band spectrum of aggregated TSPP₁ after passage through a 0.45 µm millipore filter](image-url)
$\text{H}_2\text{P}$ porphyrin molecules protonate at the central nitrogen atoms to formation of $\text{H}_3\text{P}^+$ or $\text{H}_4\text{P}^{2+}$ in the acidic medium with pH values range of 0 to 3. The equilibrium constants for protonation reactions are:

$$\text{H}_4\text{P}^{2+} \rightarrow \text{H}_3\text{P}^+ + \text{H}^+, \quad K_1$$

$$\text{H}_3\text{P}^+ \rightarrow \text{H}_2\text{P} + \text{H}^+, \quad K_3$$

To decrease the presence of dimmers, the total porphyrin's concentrations were near $10^{-2}$ 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 $[\text{H}^+]$ is:

$$\frac{A_x}{[P]_t} = \frac{c_s K_s + c_1 K_1 [\text{H}^+] + c_2 [\text{H}^+]^2}{(K_1 K_s + K_2 [\text{H}^+] + [\text{H}^+]^2)}$$

where, $c_s$, $c_1$, and $c_2$ are the molar absorbivities of the free base, mono- and di-cations, respectively. Figure 2 shows a plot of $A_x/[P]_t$ versus pH for $\text{H}_2\text{T}(2,6\text{-F})\text{PPS}$.

**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 (200×100×200 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](image-url)
Fig. 4: AFM image of TSPP₄ sample on silica prepared from TSPP₄ aqueous acid solutions (pH = 1)

Fig. 5: AFM image (from above) of TSPP₄ sample on silica

Fig. 6: AFM section analysis of TSPP₄ samples on silica

Fig. 7: UV-Vis absorption spectra of TSPP₄ 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


