

Microcrystals engineering using assemblies of di-protonated *meso*-tetraphenylporphine dimers under Zundel cations operation



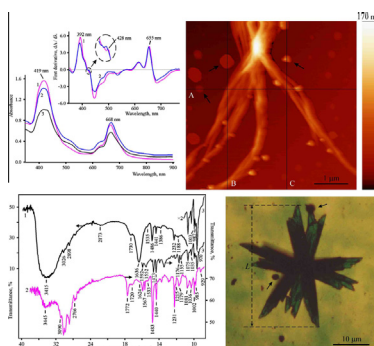
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HIGHLIGHTS

- A destroying of shell around protonated dimers is needed to complete di-protonation.
- Two H_3O_2^+ ions embedded between TPP units change the shape of their assemblies.
- Assemblies of di-protonated TPP dimers looked like rods crystallized in a thin layer.
- The size of these green crystals produced by the assemblies varies within 30–35 μm .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 September 2014
Received in revised form 13 December 2014
Accepted 15 December 2014
Available online 23 December 2014

Keywords:

Di-protonated TPP dimers
Ordered assemblies
Microcrystals
AFM

ABSTRACT

New approach based on the usage of self-organized assemblies of di-protonated *meso*-tetraphenylporphine (TPP) dimers under Zundel cations action is suggested for the microcrystals engineering. Properties of the assemblies consisting of water and the protonated dimers, as produced in aqueous HCl in the presence of a small concentration of water-soluble organic solvent were investigated by UV–Vis and infrared spectroscopy and atomic force microscopy (AFM) in thin films. The self-organized assemblies consisting of water and di-protonated TPP dimers looked like long rods produced green crystals. These crystals were found by light microscopy. The ordered assembled structures crystallized into thin layers at open air at relative humidity of least 60%. Three acts of the microcrystals engineering actions are needed to obtain the green crystals that are (i) self-assembling of protonated TPP dimers under Zundel cations operation; (ii) generation of pure rod precursor in the di-protonated state and (iii) application of gaseous water to initiate the crystallization in order to Zundel cations action in the surface layer could occur. The size of the green crystals produced by the self-organized assemblies varies within 30–35 μm .

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Introduction

Self-organization and self-assembly of different supramolecular structures are of major interest in different fields of research and scanning probe microscopy revealed new views [1–6]. Hydrogen

bonding, π – π interactions, and cooperative effects play an important role in the self-organizing and self-assembling processes. A wave-cluster model was suggested for successfully explaining how liquid water properties influence the molecular organization processes when for example minute clay particles are sticking together [7,8]. Thus, the investigation of unique features of the liquid water structure [9–11] may help to clarify self-organization processes that are not yet understood on the molecular level. In this connection the cooperative and vibrational characteristics of

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water clusters [12–14] and in particular of small-size protonated water clusters [15,16] represent the most promising perspective for the molecular understanding. The protonated water dimer (H_5O_2^+), the well-known “Zundel cation” exhibiting a characteristic doublet vibration near 1000 cm^{-1} in the infrared spectrum is generally accepted as evidence for the small-size protonated water cluster [15–17]. Such Zundel cations are involved in proton sharing when connecting the TPP units in their protonated clusters [18].

It has been proposed that water clusters with their tetrahedral network of hydrogen bonds influence upon the self-organization processes in aqueous solution via cooperative interactions, because the fine structure on the surface of ordered porphyrin aggregates has an intimate relation to the unique liquid water structure [18]. For example, the water–porphyrin matrix structure fixed cooperative molecular motions on the surface of protonated TPP aggregates after solvent evaporation. Furthermore, spherical nanoparticles of different size were found by contact AFM [19], this implies protonated TPP aggregates self-assembling from the dimers. The water–porphyrin matrix ordering by the structure self-organization with the tetrahedral network of water hydrogen bonds has mainly to proceed in solution. It is already known that di-protonated TPP dimer with parallel configuration of the transition dipole moments in the neighboring molecules exists [20]. However, those results with di-protonated TPP dimers were obtained with somewhat different rate of mixing of the aqueous HCl and tetrahydrofuran containing TPP. Herein we study the effect of double charge in TPP dimers on the self-organization processes into ordered structures and present an interpretation of IR data by a small-size water complex incorporated into di-protonated porphyrin dimer. Emphasis is on the analysis of structural organization of assemblies of protonated TPP dimers and nanoparticles when these are produced in water–organic solutions with hydrochloric acid at concentrations of 0.8 N or 2 N. The major techniques are UV–Vis spectroscopy of solutions and contact AFM of thin solid films. The crystals are characterized by light microscopy.

Previous results

The structure of protonated TPP assemblies is defined in solution by irreversible self-assembling from different ionized TPP dimers [21], configuration of which and number of protons bound in the dimers are occurred under an organic TPP and aqueous HCl solutions mixing. The procedure of the solutions mixing has been earlier modified [22] relative to the previous in [21] so that to exclude the presence of neutral TPP molecules in the assemblies, since otherwise an irreversible aggregation took place. The electronic absorption spectra reported in [22] evidently indicate repulsion of excess ions from the porphyrin macrocycle upon the mono-protonated TPP dimers formation since di-protonated TPP was used in the modified procedure. Some questions of the dimers solvation and interactions with counterions can be somewhat clarified from the following comparison of the absorption and fluorescence properties of different metal free porphyrins presented in Table 1. In this connection dimerization of metal free TPP in aqueous–organic solutions in the presence of HCl represents a special interest because it involves Zundel ions in the cage between TPP in a dimer, while alternatively not ionized TPP species were aggregated and precipitated from a solution [21]. Earlier it has been established that H_5O_2^+ and H_3O_2^+ are the simplest ions in aqueous solutions of acids and bases [23] while in fact H_3O^+ and OH^- are absent. Therefore, two H_5O_2^+ ions have to be located in the cage of di-protonated TPP dimer with $\lambda_{\text{max}} = 437\text{ nm}$ of Soret band.

The maximum of the band of the lowest electron transition, $Q_x(0,0)$, in the $\text{TPP}_2\text{H}_2^{2+}\uparrow\downarrow$ dimer is blue-shifted by 11 nm relative to that of the monomeric TPPH_2^+ with the same charged state (see Table 1). In contrast, the interaction with different counterions

in mono-protonated TPP dimers causes a bathochromic shift. An excitation energy of 1.92 eV observed for $\text{TPP}_2\text{H}_2^{2+}\uparrow\downarrow$, which is the same as that for TPP in dioxane without a counterion, indicates not only a large hydration of the dimer but also perhaps an expulsion of the chloride anion from the cage of the dimer. In contrast, the excitation energy for the aminoporphyrin dimers that is within 1.72–1.60 eV, i.e. lower by 0.2–0.32 eV, is an evidence of a large solvation of the porphyrin macrocycles under interaction with the counterions as displayed in Table 1. The latter feature is supported by 2–3-fold larger Stokes shift observed for the fluorescence of TAPP species relative to that of $\text{TPP}_2\text{H}^+\uparrow\downarrow$.

Materials and methods

Synthesis of *meso*-tetraphenylporphyrin was carried out according to the procedures described in [27]. Tetrahydrofuran (THF) and other chemicals or organic solvents were of high-grade purity. The porphyrin was dissolved in THF. Distilled water was used without additional purification. Assemblies of protonated TPP dimers were produced in solution by addition of the TPP solution to the aqueous HCl with somewhat higher concentration than 0.8 N or 2 N to make the exact those concentrations taking into account the aliquot of the TPP solution added. The aliquot of TPP solution added to the HCl one did not exceed 7% (v/v) from the final volume, so the properties of associated water clusters were kept. The modified procedure of the TPP solution and aqueous HCl mixing was used in this work, when di-protonated TPP is involved in the dimers formation and their self-assembling that excludes the presence of neutral TPP in assemblies. Pure assemblies of di-protonated TPP dimers were produced by a strong shaking of the solution with the initially formed assemblies to destroy them and induce an additional protonation of the mono-protonated TPP dimers. After that the solution was kept for 24 h at room temperature. Details of thin films preparation can be found in [20,22]. The crystals in this work were prepared at relative humidity of 60%, or thin layers of the assemblies on mica were placed in a box with saturated humidity for 2–3 h and then let at open air for 24 h. The high humidity induced crystallization of the assemblies giving crossed swallow-tailed green crystals (Figs. 13 and 14).

A Perkin–Elmer Lambda 15 or a Specord M-40 (Carl Zeiss Jena, Germany) spectrophotometer was used for the registration of electronic absorption spectra in 2-mm cuvettes without reference cuvette in the comparison channel. Infrared spectra of dried films on CaF_2 or CsI were recorded with a Perkin–Elmer FT-IR 1720 instrument. Porphyrin solutions containing the green assemblies were mixed just before the measurements of the spectra. Thin films of the porphyrin assemblies for IR spectroscopy were prepared by evaporation of the solvent with a warm (30–40 °C) stream of air both on CaF_2 and CsI. After measurement of the electronic spectra, the mixture of porphyrin assemblies was then poured on mica and thin layers formed by evaporation at open air without the warm stream for AFM investigation. Contact AFM images were recorded with a Nanoscope II (Digital Instruments Inc.) at ambient conditions. A V-shaped cantilever of 200 μm length with a Si_3N_4 tip (spring constant 0.12 N m^{-1}) was used to probe the surface. Images of porphyrin assemblies were recorded in the height mode (constant force) and the voltage was applied to the piezo elements, in order to keep the probing force constant for the topographic surface images.

Results

UV–Vis absorption spectroscopy of assemblies of protonated TPP dimers in solutions

Absorption spectra of assemblies of protonated TPP dimers in aqueous organic solution are strongly changed at considerably dif-

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