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The role of Zundel-like ions in the supramolecular self-organization of porphyrin assemblies

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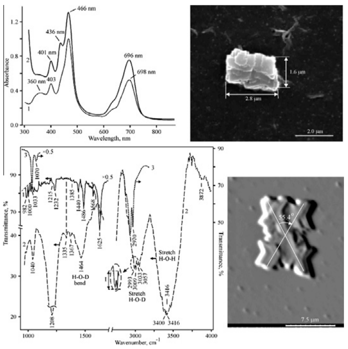
HIGHLIGHTS

- IR spectra indicate that $H_5O_2^+$ ions embedded in the cage between TPP units form stable clusters.
- A doublet at 2993, 3009 cm^{-1} confirms deuterium labeling of water clusters in the cage.
- IR studies of aggregates identify a doublet at 982, 1000 cm^{-1} with proton sharing in $H_5O_2^+$ ions.
- A mechanism for proton moving in water is suggested to explain a slanting cross with 55°.
- An estimate of proton hopping time of 6.4-7.9 ps supports this mechanism in the aggregates.

GRAPHICAL ABSTRACT



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ABSTRACT

Aggregates mainly consisting of mono-protonated *meso*-tetraphenylporphine (TPP) dimers and water self-assembled from the dimers in 0.4 N aqueous HCl with 0.86 mol L^{-1} tetrahydrofuran have been investigated by means of infrared spectroscopy (IR), electronic absorption spectroscopy, and scanning electron microscopy (SEM). IR studies using deuterium labeling of small-size protonated water clusters located in the cage between TPP in the dimers allow for the assignment of a doublet at 2993, 3009 cm^{-1} to stretching vibrations of $H\cdots O{-}DH$ and $H\cdots O^{+}{-}DH$, respectively. In the absence of heavy water in the thin film a doublet at 982, 1000 cm^{-1} with the same energy gap of 16–18 cm^{-1} is identified with proton sharing in the $O{-}H^{+}\cdots O$ moiety of the cluster. The main features of the dimers, which provide their hydration, are the protonated $-N=$ groups of pyrrole rings observed in the IR near 1486 cm^{-1} that are involved in the conjugated π-system of the porphyrin macrocycle. Stabilization of the electronic structure in the mono-protonated dimers occurs by $H_5O_2^+$ ions present in the cage between TPP units and charge delocalization through hydrogen bonding. It is proposed that together with the cooperative structure of the cluster the $H_5O_2^+$ ions are responsible for efficient self-assembling and self-organization of the highly ordered aggregates obtained. Based on surface studies a molecular mechanism for proton mobility is suggested to explain the origin of a slanting cross with the angle of 55° ± 3°, half the tetrahedral angle, on the surface of the aggregates in the solid state. Estimated proton hopping times of within 6.4–7.9 ps supports this molecular mechanism.

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Introduction

Water is a prerequisite for life and plays a central role in the determination of the structure and properties of living cells. As a result the vibrational characteristics of protonated water clusters have been investigated by many researchers to understand water's unique properties [1–5]. Small-size water clusters usually interact with a hydrogen ion to form species such as $H_5O_2^+$ or $H_9O_4^+$, the so-called Zundel and Eigen cations, respectively. The importance of these ions is their ability of proton sharing between water molecules in these small-size clusters [1–3]. In vibrational spectra of Zundel-like ions proton sharing is identified by a specific doublet near 1000 cm^{-1} that is connected with the proton-transfer mode [3–4]. Such a doublet was observed in resonance Raman and IR spectra of protonated TPP aggregates assembled from water–porphyrin dimeric complexes in solution and thin films [5]. These aggregates show an ordered surface structure including a slanting cross on the surface of the aggregates with an angle of 55° ± 3°, half the tetrahedral angle, but the origin of this structure was not well understood because of the absence of a molecular mechanism capable of explaining the angle of the slanting cross. In this paper we present further results revealing new features, which indicate that self-organization of water–porphyrin dimeric complexes into supramolecular structures can be explained by the specific properties of Zundel cations.

Previous results

In the dimeric complex [5] there are four —N= groups of pyrrole rings that can be protonated upon full protonation. However, in fact the full protonation does not take place because a squeeze of the network of the hydrogen bonds around TPP dimers and the hydrogen bonds connecting two TPP units restrict the full protonation. This hydrogen bonding defines only two configurations of the TPP dimers, with parallel and anti-parallel orientation of the dipole moments. So that the existence of two pairs of the positive charges in the cage between two hydrophobic TPP units upon full protonation is impossible simultaneously with the hydrogen bonding due to that the complex exists. Thus, in fact the features of the complexes formation restrict the full protonation of the dimers. That is why the dimers of this type were called as restrictively protonated species [6]. So-called restrictively protonated porphyrin dimers were initially found in solutions of *meso*-tetra(*p*-aminophenyl)porphine (TAPP) and TAPP covalently bound with a copolymer [7–8]. TAPP molecules in organic solvents usually form associated species because they contain amino-groups in *para*-position so that TAPP units are connected by hydrogen bonds via water molecules. For example, a monocation of the amino-porphyrin, which exists mainly in the dimeric state (λ_{max} = 430 nm for Soret band), has been found in aqueous dimethylformamide–ethanol solution by titration of a TAPP bound with a copolymer [7]. In this case two main absorption bands with λ_{max} = 462 and 757 nm were observed in the electronic spectra. The mono-cation radical of the TAPP dimer with λ_{max} = 463 and 735 nm was found when the porphyrin was oxidized with molecular bromine [8]. A di-protonated TPP dimer with λ_{max} = 437 nm for Soret band was observed in 50% (v/v) aqueous dioxane in a study of the dimerization of TPP resulting in the formation of $TPP_2H_2^{2+}$ [6], with a high dimerization constant of 1.9 × 10^9 mol^{-1} L. Mono-protonated TPP dimers with Soret bands at 403 and 465 nm related to parallel and anti-parallel configurations of their dipole moments, respectively, have been found at a higher water concentrations [6,9], when hydrophobic interaction between TPP molecules is considerably stronger. The pK_a for the protonation of —N= groups of pyrrole rings in a hydrophobic environment is considerable diminished, and a pK_a = 0.8 was found upon titration of TAPP bound to a hydrophobic/hydrophilic copolymer [10]. A doublet at 1000, 1025 cm^{-1} with the narrowed 1000 cm^{-1} component and a slightly higher intensity relative to the neighboring one was revealed in resonance Raman spectra of protonated TPP aggregates [11]. IR spectra of the aggregates in thin films usually demonstrate a doublet at 984, 1000 cm^{-1} [5]. The aggregates obtained were characterized using infrared and electronic spectroscopy and by scanning electron microscopy.

Materials and methods

All chemicals and organic solvents were of high-grade purity. Highly purified de-ionized water with a resistance of more than 18 MΩ was used for the producing of protonated TPP aggregates in aqueous 0.4 N HCl with a small concentration of tetrahydrofuran (THF). Thin films were obtained under evaporation of a solvent from the solution containing the aggregates with a warm stream of air to fix tracks of molecular motions on the surface. In this study our aim was to obtain aggregates with tracks on their surface that suggests a water–porphyrin matrix ordering. In these studies drying was needed to remove weakly bound water from the largely hydrated aggregates. However, complete drying of the layers creates aggregates that cannot be used for X-ray diffraction because they are possibly amorphous. A criterion of complete drying is a splitting of the bands of stretching and H—O—H bending vibrations of ordinary water as observed in IR spectra [9]. This requires an additional 2–3 min drying after water has disappeared from the surface. The splitting indicates that only water firmly bound in the aggregates is present. Typical approximately 1200 water molecules are found in the aqueous shell around each protonated TPP dimer in a completely dried thin film [9]. Weakly bound water in the films remains when the drying was stopped as soon as water has been disappeared from the surface of a film. Therefore, the water content in such not completely dried films is usually larger by 20% relative to that in a film obtained after complete drying of the sample [9]. IR spectra were recorded with a Specord M-80 spectrophotometer with an accuracy of 2–3 cm^{-1}. The complete drying method was also applied for thin films intended for SEM. Images of porphyrin aggregates were obtained with a Hitachi S-520 scanning electron microscope. The microphotographs were obtained with a side illumination for the images contrasting. All other experimental details have been reported before [5,9,12].

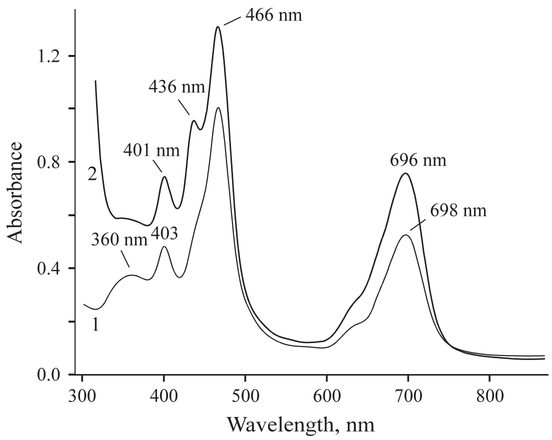

Fig. 1. Electronic absorption spectra of protonated TPP aggregates in (1) 0.4 N aqueous HCl with 0.86 mol L^{-1} THF; and in (2) D_2O containing 0.4 N HCl with 1.9 mol L^{-1} H_2O and 0.80 mol L^{-1} THF.