



# Polaronic exciton in self-organized assemblies of protonated *meso*-tetraphenylporphine dimers and water at room temperature

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## ARTICLE INFO

### Article history:

Received 15 May 2016

Received in revised form

5 July 2016

Accepted 8 July 2016

Available online 11 July 2016

### Keywords:

Protonated TPP dimers

Self-assembly

Confined water

Polaron

Polaronic exciton

## ABSTRACT

Assemblies consisting of protonated *meso*-tetraphenylporphine (TPP) dimers and water have been investigated by UV–vis and infrared (IR) spectroscopy and by atomic force microscopy (AFM) in thin layers. Features of electronic absorption spectra of the assemblies are interpreted in terms of hole polaron combined with exciton theory using quantum well with parameters obtained from the dimer structure. It appears to be hole polaron moving defines kinetic energy of polaronic exciton confined in a quantum well when the electron absorbs photon. Hole polaron characteristics such as polaron self-energy, energy of Frank–Condon transitions, and radius of hole polaron moving through water are found to be 1.38 eV, 0.2445 eV, and 0.246 Å, respectively. A doublet at 1944, 1960  $\text{cm}^{-1}$  (0.2412, 0.2432 eV) observed in IR spectra matches the energy of Frank–Condon transitions. Excitation energies estimated using molecular parameters for polaronic excitons in pure water and in the TPP dimers are found in a good agreement with the experimental data.

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## 1. Introduction

Polaron concept has been developed to describe physical behavior of electron and hole and the charges transport in polar crystals and ionic semiconductors [1–4]. Conventional polaron is a quasiparticle consisting of electron or hole and the self-induced polarization that is able to move together with the charge carrier generating longitudinal optical (LO) phonons. A bound pair of electronic and hole polarons can form new quasiparticle called polaronic exciton [5]. Behavior of polaron is characterized by the interaction with the self-induced polarization, so polaron movement through a lattice occurs via localized states. Free-base porphyrins have hydrogen atoms that can move within the macrocycle under NH-tautomeric transitions and the rate of the transitions is strongly dependent on temperature [6]. Although in this case the movement takes place via localized states but no LO phonons are found, since there is no polarization moving together with hydrogen atom under the transitions. Porphyrin protonation makes the difference, but the electronic structure of singly protonated macrocycle of a monomer is unstable, while the electronic

structure stabilization can be provided by the dimer formation with hydrogen bonding of the porphyrin units.

In liquid water proton has unordinary high mobility that is due to the presence of so-called Zundel cation,  $(\text{H}_5\text{O}_2)^+$  [7]. The high proton mobility is universally adopted to explain by the formation of wires of hydrogen bonds and proton tunneling along the wires [7,8]. Proton behavior changes the electronic spectra of the protonated porphyrin, when one or two  $(\text{H}_5\text{O}_2)^+$  ions are embedded in the cage between two porphyrin units under the dimers formation [9–11]. In aqueous solutions protonated *meso*-tetraphenylporphine (TPP) dimers are quickly self-assembled with further self-organization of the assemblies' structure and microcrystals formation [10–12]. Note that the inner structure ordering of water-porphyrin matrix must be fully completed for crystallization, otherwise crystallization would be impossible. Zundel cation and water play important role in these processes, so proton moving through water confined in the assemblies and their aggregates plays a key role in the structure self-organization [11]. Characteristic features found in electronic absorption spectra of the assemblies at 77 K, which suggested proton moving via localized states in mono-protonated TPP dimers together with the self-induced polarization, have been interpreted in terms of polaron theory [13]. Further results of the investigation of self-assembled protonated TPP dimers in solution at room temperature by UV–vis

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spectroscopy and the assemblies by IR spectroscopy and atomic force microscopy in thin layers are reported in the present paper.

## 2. Materials and methods

Synthesis of *meso*-tetraphenylporphine (TPP) was carried out according to the procedure described elsewhere [14]. Tetrahydrofuran (THF) and other chemicals or organic solvents were of high-grade purity. Assemblies of protonated TPP dimers were produced under the mixing of aqueous HCl and a THF solution of TPP taking into account the aliquot of the TPP solution that did not exceed 7% (v/v) [12]. The TPP solution was carefully poured on the wall of a vessel with aqueous HCl to allow the porphyrin diprotonation that manifested by appearance of Soret band at 445 nm. The following mixing of the solutions results in quick formation of protonated TPP dimers and their self-assembling. So this procedure excludes the presence of aggregated TPP in the assemblies since all the molecules are bound in the dimers via hydrogen bonds. For IR spectroscopy a thin layer of the assemblies was prepared by evaporation of the solvent with a warm stream of air, further details can be found elsewhere [11,15]. For atomic force microscopy (AFM) thin layers of the assemblies were prepared on mica by evaporation of the solvent at open air.

A Perkin–Elmer Lambda 15 or a Specord M-40 spectrophotometer were used for registration of electronic absorption spectra. Porphyrin solutions containing the assemblies of protonated TPP dimers were mixed just before measurements of the spectra. An extinction coefficient of  $\epsilon^{360} = 3.86 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$  obtained for the broad band at 360 nm, when mainly mono-protonated and only an admixture of di-protonated TPP dimers compose the assemblies, was used for estimation of exact final TPP concentration. Infrared spectra of dried samples were recorded with a Specord M-80 spectrophotometer. Contact AFM images were recorded with a Nanoscope II (Digital Instruments Inc.) at ambient conditions. A V-shaped cantilever of 200  $\mu\text{m}$  in the length with a  $\text{Si}_3\text{N}_4$  tip (spring constant 0.12 N/m) was used to probe the surface. Images of the assemblies in thin layer 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 (z-direction). All measurements were carried out at room temperature that was between 20 and 25 °C.

## 3. Theory

Results obtained in this work are considered in terms of polaron theory [2,3,16] applied earlier for similar self-organized assemblies with details reported in Ref. [13]. Main positions of the polaron theory are reproduced here with further details in relation to aqueous solutions. When conventional polaron consisting of the electron or hole and the polarization of its surrounding moves, it generates longitudinal optical (LO) phonons extending in the direction of the carrier moving. So, electron or hole can interact with LO phonons creating a composite particle. The properties of a polaron are defined by the following eq. (1) describing the interaction between electrons or holes and the phonons [16].

$$\alpha = \epsilon_{ef}^{-1} \left( \frac{e^2}{\hbar c} \right) \left( \frac{m_{ef} c^2}{2\hbar\omega_{LO}} \right)^{1/2}, \quad (1)$$

where  $\alpha$  is the unitless Fröhlich coupling constant,  $\omega_{LO}$  is LO phonon angular frequency,  $\epsilon_{ef}$  is the effective dielectric constant,  $\epsilon_{ef}^{-1} = 1/\epsilon_\infty - 1/\epsilon_0$ ,  $\epsilon_0$  and  $\epsilon_\infty$  are respectively the static and the high-frequency dielectric constants,  $m_{ef}$  is the effective mass of a charge carrier (electron or hole),  $e$  is the elementary charge,  $c$  and  $\hbar$  are the speed of light and the reduced Planck constant. Relationship between the

effective mass of polaron in the ground state and the radius ( $r_p$ ) of the autolocalized polaron is defined by relation (2) [2].

$$1/r_p = 0.66 m_{ef} e^2 / (\hbar^2 \epsilon_{ef}) \quad (2)$$

For electronic polaron in vacuum (where  $\epsilon = 1$ ) the  $r_p$  value with the self-induced polarization is defined by van der Waals radius of  $\text{H}_2\text{O}$  that is  $1.6 \times 10^{-8} \text{ cm}$  [17]. This value ( $r_p = 1.6 \times 10^{-8} \text{ cm}$ ) is obtained exactly with eq. (2) for electronic polaron in vacuum using the effective mass  $m_{ef} = 0.5m_e$ , where  $m_e = 9.10,938 \times 10^{-28} \text{ g}$ . In contrast, the interaction of proton with  $\text{H}_2\text{O}$  is much more stronger, so its behavior in water clusters is often considered and described as a single particle [18]. The effective mass ( $m_{ef}$ ) of the hydrated proton as the  $\text{H}_3\text{O}^+$  particle is  $(1 + 18.015)/1$  relative to proton mass. Thus, the effective mass of the hydrated positive elementary charge with the self-induced polarization as underlying hole polaron is  $9.51m_e$  in comparison to that of electronic polaron possessing the same elementary but negative charge ( $m_{ef} = 19.015 \times 0.5m_e = 9.51m_e$ ). The obtained value is ca.  $10m_e$ , so the effective masses  $m_{ef}^h = 10m_e$  and  $m_{ef}^e = 0.5m_e$  were assumed for hole and electronic polarons, respectively [13]. Calculation with eq. (2) for underlying hole polaron with the effective mass of  $10m_e$ ,  $\epsilon_\infty = 4.2$ , and  $\epsilon_0 = 78.4$  yields  $r_p = 0.38 \times 10^{-8} \text{ cm}$  that is generally in agreement with proton radius of  $0.265 \times 10^{-8} \text{ cm}$  obtained under consideration of its moving through water [11].

At a strong coupling, when  $\alpha$  is much larger than 1, polaron is characterized by the self-energy ( $E_p$ ), i.e. the energy of a polaron, and the energy of lowest Franck–Condon (FC) excited states ( $E_{FC}$ ) of the LO phonons that are given by eqs. (3) and (4), respectively [16].

$$E_p = 0.2\alpha^2 \hbar\omega_{LO} \quad (3)$$

$$E_{FC} = \left( \alpha^2 / 9\pi \right) \hbar\omega_{LO} = 0.0354\alpha^2 \hbar\omega_{LO} \quad (4)$$

The electron (or hole) drags the lattice distortion with it as it moves creating a larger inertia. So, when the quasiparticle called a polaron is moving, the effective mass of such of a polaron becomes larger than the mass of the underlying electron (or hole). The strong-coupling mass ( $m^*$ ) that is increased due to the polaron moving together with the lattice distortion is given from an approximation as follows, eq. (5) [16].

$$m^* / m_{ef} = 1 + 0.0227019\alpha^4 \quad (5)$$

Inertia creating by hole polaron movement within the conjugated  $\pi$ -system has been found somewhat smaller ( $m^*/m_{ef} = 10.3$ ) than that ( $m^*/m_{ef} = 11.0$ ) calculated with eq. (5) for hole polaron moving through water [13]. An estimate of the polaron radius ( $r_{sph}$ ) as a spherical particle autolocalized in aqueous environment with minimal full energy (potential and kinetic) consisting of proton and the self-induced polarization, which moves together with the proton, can be obtained with formula (6) [2].

$$r_{sph} = \pi^2 \epsilon_{ef} \hbar^2 / (m^* e^2) \quad (6)$$

Application of polaron theory allows to calculate the charge mobility and conductivity assuming the effective mass not adjusted for polaronic effects [3,16]. Hole polaron of small radius plays important role in structure self-organization under diffusion in thin layers taking into account hopping mode of the charge migration [11]. So the theory development will be useful in many aspects concerning physical and biophysical implications.

The potential barrier under proton transitions between NH-tautomers has been evaluated within 0.35–0.4 eV [19] that

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