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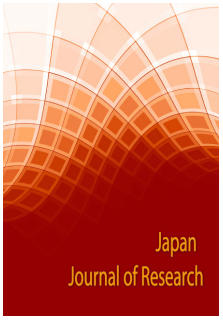

Quasi-Crystal Structure Formation is the Prerequisite for Organic Liquid Micro- and Nano-Crystal Engineering

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Abstract

Formation of liquid micro-crystals based on self-organized water-porphyrin assemblies found earlier is usually accompanied by generation of hole polaron. Hole polaron movement along the wires of hydrogen bonds through the liquid crystalline structure creates the water network squeezing around the porphyrin dimers. Possibility of the latter has been investigated by IR spectroscopy with two supports for the self-organized assemblies deposited on fluorite or germanium plates. The obtained IR spectra exhibit two different behaviors of the TPP self-organized assemblies. In the case of Ge plate, only protonated TPP dimers without aqueous cover are found in the corresponding IR spectrum that excludes the formation of liquid micro-crystals. The observed destruction of the self-organized assemblies was the reason to study a thin aqueous layer found by IR spectroscopy on Ge plate. The obtained experimental results and theoretical estimations based on polaronic exciton concept allowed to conclude that the thin aqueous layer on Ge plate has the quasi-crystal structure also. Bound state energy of polaronic exciton in this structure has the fewer barriers than the energy gap in germanium that is the cause of the electron leaving from the quasi-particle. However, liquid crystal engineering requires the quasi-particle preservation, i.e. the state of electron coupled with the hole for stabilization of hole polaron movement.

Introduction

Evolution of the matter properties from organic molecules to crystals can be described in terms of two steps, namely, from molecules to clusters and from clusters to crystals. Crystallization of molecules or compounds from their solutions is usually initiated from the formation of nucleation centers or germs and this process has been well studied [1]. Nucleation and growth of different crystals or micro- and nano-crystals and their properties and properties of liquid crystals have been investigated by many research groups [2–6]. This area of research attracts the attention of many investigators because of crystals and liquid crystals are widely used in many devices. In semiconductors, where broad bands of the allowed electron and hole states are separated by a forbidden gap, properties of the crystals and nano-crystals are mainly determined by the band gap energy [2, 4]. A self-organization process of the inner structure is often necessary for the production of liquid crystals or liquid micro-crystals [5, 7]. No doubt that important role in the processes of the substance self-assembling and structure self-organization belongs to ordinary water [7, 8].

Hydrated proton in liquid water is usually exists as Zundel cation $(H_5O_2)^+$ and the proton has unordinary high mobility. The presence of these ions is universally adopted to explain the high mobility and proton tunneling along wires of hydrogen bonds [9, 10]. It is found that in the presence of Zundel cations in supramolecular structures, which contain water and protonated porphyrin dimers, protons move along water hydrogen bonds of the tetrahedral network. This moving produces cooperative motions of the molecule and self-organization of the water-porphyrin matrix [11,12]. As a result, tracks of the cooperative motions or highly ordered unique structures of the water-porphyrin aggregates were observed by scanning electron microscopy. The structure of the aggregates was fixed after removing of water excess from the surface. And physical state of the aggregates are found depending on the support used for the deposited molecular assemblies [11]. In the case of solid support, their properties were found like the solid object with quasi-crystal structure, while their properties were revealed resemble to liquid water confined in the aggregates on the liquid support (Vaseline oil). These features and the doublets of the confined water were explained by the presence of proton-donating

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and proton-accepting water molecules in the water-porphyrin matrix because of the presence of large amounts of protons. In this work possibility of the squeezing of the hydrogen bonds producing quasi-crystal structure has been investigated by IR spectroscopy with two different supports for the self-organized water-porphyrin assemblies, which were deposited on fluorite or germanium plates. Structure of thin aqueous layer found on germanium surface was studied by IR spectroscopy too.

Experimental details

Synthesis of *meso*-tetraphenylporphine (TPP) was carried out according to the procedures described elsewhere [13]. Tetrahydrofuran (THF) and other chemicals, and organic solvents were of high-grade purity. The porphyrin was dissolved in THF and its solution was used for procedure of self-assembling and self-organization of water-porphyrin particles, where the porphyrin is remained with the protonated macrocycle. Distilled or double distilled water was used without additional purification. The procedure of self-organization of water-porphyrin assemblies was performed with the use of 0.4N HCl final concentration. The TPP solution was carefully poured on the wall of a vessel with the aqueous HCl to allow di-protonation of the porphyrin before the mixing. This procedure excludes TPP aggregation in the assemblies with the following precipitation because of the hydrogen bonding between the TPP units, which is provided by small-size water cluster embedded in the cage between the units [14]. In this case TPP forms protonated dimers under the self-assembling as displayed in Figure 1 (panel b), where only one singly protonated macrocycle of a porphyrin molecule is remained after the self-assembling of the water-porphyrin particles. Thus, the protonated state of TPP before the mixing provides at least one $(H_5O_2)^+$ ion embedded in the cage of the dimers during the fast self-assembly process [15]. So, mainly mono-protonated TPP dimers are usually observed on HCl concentrations between 0.4N and 0.8N [11, 12, 14]. The thin layer of protonated TPP dimers self-assembled into the particles with the confined water was not fully dried to preserve water in the aggregates, i.e. drying was interrupted as soon as water was disappeared from the surface.

Infrared spectra of samples were recorded with a Specord M-80 spectrophotometer with an accuracy of 2-3 cm^{-1} at room temperature that was ~295K. Estimation of a thickness of thin aqueous layer on germanium plate was performed with the extinction coefficient of 1668 cm^{-1} band averaged with two values. The upper threshold of 19.4±3.7 mol^{-1} l cm^{-1} was obtained for the H–O–H bending vibrations for water confined in the aggregates dispersed in Vaseline oil [11]. The below threshold of 2.2 mol^{-1} l cm^{-1} of the coefficient was calculated for H–O–H bending vibrations of water confined in the not fully dried aggregates producing quasi-crystal structure [11], where extinction coefficient for water stretching vibrations is 8.5±0.5 mol^{-1} l cm^{-1} [16]. Then the averaged value is (2.2+19.4)/2=10.8 mol^{-1} l cm^{-1}. The other estimation of the extinction coefficient was obtained for the same 1668 cm^{-1} band, observed in IR spectrum of Vaseline oil with minor amounts of water, which is 4.4 mol^{-1} l cm^{-1}. Thus, the thickness of the thin aqueous layer is found to be between 0.60 μm for each side of germanium plate obtained with the latter coefficient until to 0.25 μm with the former. Note that the extinction coefficient for the same vibrations but at 1645 cm^{-1} of liquid water is 20.8 mol^{-1} l cm^{-1} [17].

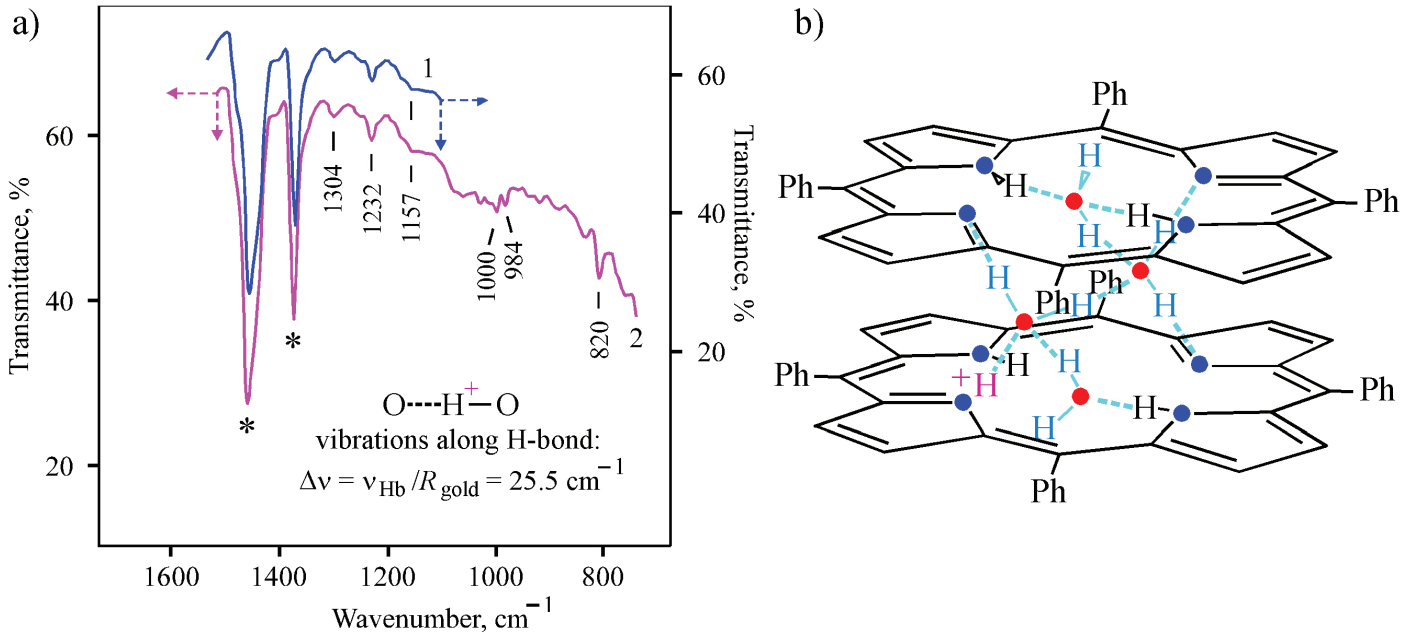

Figure 1. *Panel a): Infrared spectra of protonated TPP dimers self-assembled into water-porphyrin aggregates, which were obtained after evaporation of 0.86 mol l^{-1} aqueous THF containing 0.4N HCl, recorded in water-free Vaseline oil (right scale) (1); and the same sample recorded in the transmittance range of 0-50% with zero adjustment (left scale) (2); where vHb = 41.262389 cm^{-1} (see Appendix 1). The bands of oil are marked by asterisk. Panel b): Structure of mono-protonated TPP dimer with small-size water cluster embedded in the cage between TPP units with antiparallel orientation of the porphyrin units. A water coating around the TPP dimer is not depicted.*

Theory

Water has a high polarizability that is why many substances dissolved in water are hydrated. Hydrophilic substance containing a polar group in their chemical structure that is further polarized or ionized due to the interaction with water is a necessary prerequisite for the hydration. The polaron problem arises due to the motion of electrons in conduction band of a polar semiconductor or ionic crystals. Not a large band gap E_g = 0.66 eV in germanium at T = 300K [2], or E_g = 0.67 eV [18] favors overcome of electrons through the band gap to the conduction band. However, bound state energy of polaronic exciton in the self-organized assemblies is ca. –0.33 eV. This barrier for the electron leaving from the polaronic exciton state is considerably less than the band gap of 0.67 eV in germanium that is the barrier for electron injection to the conduction band. Therefore, electrons involved in the polaronic excitons in the self-organized assemblies will be preferably injected into the germanium conduction band as compared with the electrons in Ge valence band. Only this suggestion can explain the obtained below IR spectra, when the self-organized assemblies are deposited on Ge plate. Most probably similar effect takes place when water vapor from air is condensed on germanium surface, while strongly polarized water molecules on the surface under the interactions generate polarons. The bound state energy of polaronic exciton as estimated below is found to be $E_{b\text{-}ex}$ = –0.3282 eV (see Appendix 2). In this case electrons coupled with hole polarons can preferably be injected into germanium conduction band. Infrared spectra obtained in this work support the presence of the holes, i.e. protons in the aqueous layer on germanium surface. In fact, the electrons in the conduction band are actually moving. Therefore, the hydrated protons can move in the aqueous layer like polaron depending on polaron energy. If there is sufficient quantity of protons in the surface layer, then we can observe absorption of *LO* phonons in the case if protons move through the lattice of quasi-crystal structure. The latter can be formed in the presence of sufficient quantity of protons in the layer on germanium surface. The quasi-crystal structuring of the thin aqueous layer follows from the presence of two doublets of water vibrations in the observed IR spectrum, which is interpreted in terms of proton-donating and proton-accepting water molecules. If hole polaron in the quasi-crystal structure moves rather like proton sharing in liquid water with energy $E_{v,sh}$, then we can estimate the energy of the *LO* phonons as follows. Namely, this energy ($\hbar\omega'_{LO}$) should be approximately as the difference $E_{v,sh} - E_g$, where vibration energy ($E_{v,sh}$) of the proton sharing is 0.81422 eV [19]. The energy of the vibrational system ($E_{v,sh}$) has been earlier calculated in approximation of elastic interaction with proton according to the binding force $F = -k_e x^2$. Note that the proton sharing is accompanied by the nucleus spin turnover, energy of which along the direction of the hydrogen bonded water molecules is ν_{Hb} [20]. Hence, in the case of the hole polaron moving, the energy $\hbar\omega'_{LO}$ should be diminished by the value of ν_{Hb}. Then the exact energy should be written as $\hbar\omega'_{LO} = E_{v,sh} - E_g - \nu_{Hb}$ = 1121.95 cm^{-1}, where E_g = 0.67 eV and ν_{Hb} =41.262389 cm^{-1} (see Appendix 1). The obtained exact value of $\hbar\omega'_{LO}$ is less than the energy of the lowest Frank-Condon states (E_{FC}) [21], through which the coupled electron moves. Therefore, hole polaron most probably moves within a local structure like water tetrahedrons. In this case the same *LO* phonon energy ($\hbar\omega'_{LO}$) can be obtained using the energy of the lowest Frank-Condon states (E_{FC}) and electronic bonding energy ($E_{e\text{-}Hb}$) in the moiety O–H$^+$...O [21, 22]. Hence, we can write the following relation.

$$\hbar\omega'_{LO} = E_{v,sh} - (E_{e\text{-}Hb} + E_{FC} + \nu_{Hb}) \quad (1)$$

Eq. (1) means that the electron has been coupled with the hole polaron within water tetrahedron because of the lack of E_{FC} energy. The latter indicates the electron cannot move via the lowest Frank-Condon excited states along hydrogen bonds through water structure. With $E_{e\text{-}Hb}$ = 0.425566 eV [22] and E_{FC} = 0.244358 eV [21] Eq. (1) gives $\hbar\omega'_{LO}$ = 0.139180 eV (1122.56 cm^{-1}). Deviation of this estimate from the experimental value of 1157 cm^{-1} is 3% in the self-assembled aggregates or 0.1% from experimental 1124 cm^{-1} observed in thin aqueous layer on Ge plate. While the experimental shoulder at 1157 cm^{-1} displayed in Figure 1 (panel a) rather is the vibrations of four-chain protonated water cluster in the cage between TPP units, but not *LO* phonon energy.

Polaronic exciton generation occurs under photon interaction with water when an electron absorbing a photon perceives its momentum that becomes angular momentum of the electron (see Appendix 3). Consideration of photon interaction with water molecule allows to derive a coefficient (β), which characterizes the interactions in polaronic exciton depending on angular momentum quantum number [21, 23]. In this case the interaction of photon with the particle becomes quasi-elastic, therefore the interactions can be described in terms of Compton effect that involves Compton wavelength, $\lambda_C = h/(m_e c)$ = 2.426310215×10^{-12} m. This coefficient assumes the meaning of spin-orbit coupling because of it is estimated using proportionality of the Compton wavelength depending on the angular momentum quantum number. The Compton coefficient can be also introduced because the hydrogen bonding is a prerequisite for spin-orbit coupling between the electron and hole, which form a quasi-particle called polaronic exciton. In the case if angular momentum quantum number equals 7 the calculated coefficient is β = 1.19100654 [21, 23]. The spin-orbit coupling for electron or proton separately can be expressed via the coefficient $\beta^{1/2}$ that gives β for the spin-orbit coupling in the polaronic exciton.

The charge separation between the states of electron and hole in the solid germanium can be described at the first approximation alike the formation of electron and hole in the surface aqueous layer that can occur via the first excited state of the hydrogen (E_1^*). An energy of the first excited state of hydrogen atom is 3/4Ryd, i.e. 3/4(13.60569172 eV), namely E_1^* = 10.204269 eV. On the other hand, the charge separation in the aqueous environment can also be described with extreme splitting of the electric charges (ΔE_{spl}) [22] and the constant (β_q) of spin-orbit coupling depending on quaternary molecule coordination, where β_q = 3.741657387 [20, 23, 24]. Hole polaron moving within water tetrahedron of the quasi-crystal structure on germanium surface can generate *LO* phonons with the energy $\hbar\omega'_{LO}$ as mentioned above. In this case the energy required for the charge separation in the surface layer should be written as $\beta_q \Delta E_{spl} - \hbar\omega'_{LO}$. At the first approximation both energies, namely $\beta_q \Delta E_{spl}$ and $E_1^* + \hbar\omega'_{LO}$ should be equal, where ΔE_{spl} = 2.764566 eV [22].

$$E_1^* + \hbar\omega'_{LO} = \beta_q \Delta E_{spl} \quad (2')$$

Thus, we can find the energy $\hbar\omega'_{LO}$ also by the other way for the case of hole polaron moving within water tetrahedron.

$$\hbar\omega'_{LO} = \beta_q \Delta E_{spl} - E_1^* \quad (2)$$

In the case if hole polaron moves through the lattice with the generation of *LO* phonons with the energy $\hbar\omega_{LO}$ = 0.368491 eV,

the hole polaron movement provides the electron moving via the lowest Frank-Condon excited states (E_{FC}) because of the strong coupling between the charges [21]. Then we can use the energy E_{FC} to connect the energies of different *LO* phonons generated by different modes of hole polaron moving, namely $\hbar\omega_{LO}$ and $\hbar\omega'_{LO}$ (see calculation of the E_{FC} energy in Appendix 4). In this case the following relation is expected, where the coefficient $\beta^{1/2}$ means one-dimension walk of the proton in the moiety O–H^+...O that generates *LO* phonons and β means the spin-orbit coupling between the opposite charges in the polaronic exciton.

$$\beta^{1/2}\hbar\omega'_{LO} = \beta(\hbar\omega_{LO} - E_{FC}) \quad (3'),$$

or

$$\hbar\omega'_{LO} = \beta^{1/2}(\hbar\omega_{LO} - E_{FC}) \quad (3)$$

With the energy $\hbar\omega_{LO}$ = 0.37658 eV of *LO* phonons, shoulder of which is observed in the absorption spectrum at 524 nm at room temperature [7] and E_{FC} = 0.244358 eV Eq. (3) gives $\hbar\omega'_{LO}$ = 0.144296 eV (1163.8 cm^{-1}). In the case of the energy $\hbar\omega_{LO}$ = 0.368491 eV, Eq. (3) yields somewhat close value, $\hbar\omega'_{LO}$ = 1092.6 cm^{-1}. The similarity of these values and estimated above implies similar structure of aqueous layers on germanium plate and in water-porphyrin aggregates, in which molecular ratio of water/porphyrin is 630/1 [16].

Results and Discussion

Spectroscopy of the self-assembled protonated TPP dimers

Proton sharing in the O–H^+...O moiety is a prerequisite for proton (or hole) moving through the confined water in the water-porphyrin assemblies [12]. This moving is a reason for self-organization and the inner structure ordering. A molecular mechanism is previously suggested for the proton moving to explain highly ordered structures of the water-porphyrin aggregates [11, 12]. This molecular mechanism manifests that protons move through the confined water forming domain of submicroscopic or microscopic proportions and protons can avoid encounters to each other due to the moving as a wave along hydrogen bonded water molecules with tetrahedral coordination [12]. Water molecules with different vibration characteristics of their doublets are assigned to proton-accepting and proton-donating species that implies the quasi-crystal structure formation [11]. In contrast, in the aggregates dispersed in Vaseline oil, i.e. on the liquid support, similar doublets are not observed and therefore such separation of the water molecules is not possible [11, 25]. At the same time the bands of C–H vibrations of TPP units in the dimer are observed in both cases. A doublet associated with proton sharing is observed at 984, 1000 cm^{-1} in the spectra in Figure 1 (panel a), where the energy gap between the components is 16 cm^{-1}. Proton moving initiated in the moiety O–H^+...O results in polaronic exciton generation and theoretical energy gap between two vibrational states is ν_{Hb} =41.262389 cm^{-1} for liquid water. The energy gap of 25.5 cm^{-1} as displayed in Figure 1 (panel a) is observed due to strong coupling between the opposite charges [11, 24]. Hence, the further enhancement accompanied by a decrease of the energy gap under the interactions (i.e. 16 cm^{-1} = 25.5 cm^{-1}/R_{gold}) is associated with quasi-crystal structure formation. And actually this enhancement of the interactions is independent on which support is used. The peak produced by the secondary nitrogen atom (N_s) interacting with water in the moiety N_s–H...OH_2 is located at 1232 cm^{-1} [12] as displayed in Figure 1 (panel a, curve 2). The latter position but not at ca. 1260 cm^{-1} indicates its electron in the bound-state with hydrogen bonding in the cage between TPP units. Then a shoulder at 1157 cm^{-1} can be assigned to the energy of longitudinal optical (*LO*) phonons (i.e. vibrations extending in the direction of the propagation) that takes place in the cage. Alternatively, the shoulder at 1157 cm^{-1} can be vibrations of O–H group associated with the confined water.

A shoulder at 535.5 nm as displayed in Figure 2 or the same broadened 533 nm shoulder in Figure 2 (curve 1) is originated from the hole polaron movement and is observed at 77K [15]. The latter or proton moving with the self-induced polarization through the lattice of frozen aqueous solution containing glycerol and assemblies of protonated TPP dimers generates *LO* phonons. As known the *LO* phonons are usually generated when a charge moves in solid substance under the interaction with the polarization of the lattice that is moving together with the charge. Thus, the *LO* phonons with the energy $\hbar\omega_{LO}$ = 0.3704 eV has been assigned to hole polaron moving within the conjugated π-system of the TPP macrocycle [15]. At the same time, energy of *LO* phonons under hole polaron moving through the lattice of the aqueous solution at 77K is found to be 0.3564 eV. In contrast, the other *LO* phonons with lower energy $\hbar\omega'_{LO}$ = 1157 cm^{-1} as displayed in Figure 1 (panel a) are originated rather under hole polaron moving within water tetrahedron intercalated with the proton. In this case the moiety O---H^+N_t, where N_t is tertiary nitrogen atom, which is hydrogen-bonded with small-size water cluster, connects two TPP molecules in the dimer [12].

In the case of hole polaron moving through water confined in water-porphyrin particles or aggregates, proton or hole moves along hydrogen bonds via the localized states. The direction of its movement coincides with that of proton sharing between two water molecules. However, proton bypasses the neighboring water molecule in the course of the movement, which results in

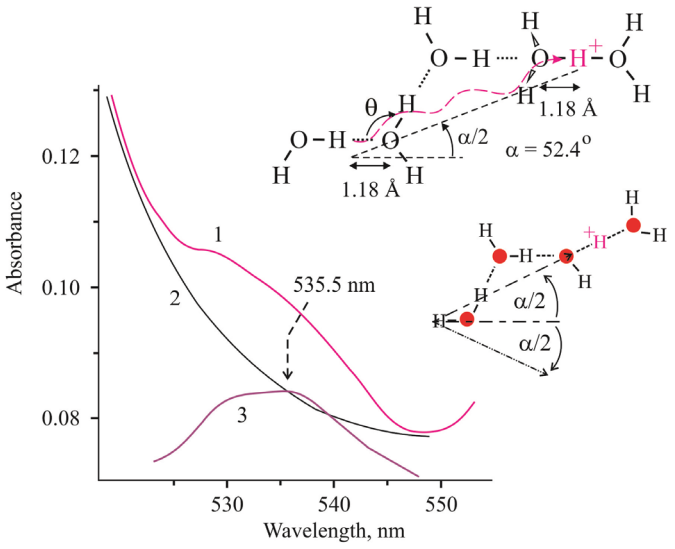

Figure 2. *Electronic (1) and difference (3) absorption spectra of protonated TPP dimers in aqueous glycerol with 24 mol L^{-1} water and 0.74 mol L^{-1} THF in the presence of 0.4 N HCl at 77K: curve (3) is curve (1) minus the base line, curve (2), which is the wing of the band around 467 nm at 293K. Energy of the generated LO phonons is E = ħ(c/λ) that yields 0.368491 eV. Inset shows a way of hole moving through water that explains slanting cross of a half of the tetrahedral angle, where 2.98Å is oxygen-oxygen distance in liquid water structure (see details in the text).*

the proton is captured by water molecule with a deviation [12]. This peculiar is most probably associated with that the proton is shared as a particle, while the proton moving happens as a wave as suggested earlier. In Figure 2 (inset) upper scheme is used to estimate a deviation of proton propagation angle relative to the proton sharing direction that is found to be 26.2° [12]. The other scheme in Figure 2, inset (below) shows the direction of proton propagation after single proton-hopping step between the localized states. The same deviation of proton propagation to the right relatively the direction of the initial proton sharing, which yields α=52.4° in the sum with that to the left, implies that the deviation and therefore the self-induced polarization are dependent on the proton spin direction. It follows from that proton spins and the self-induced polarization both are preserved in the course of hundreds jumping steps during the movement producing the ordered structure. The sharp angle of the slanting cross observed in the self-organized structures is 55°±3° [11]. Hence, the estimated value of the angle is found in a good agreement with the experiment.

Thus, two modes of hole polaron moving, namely far-distance and the moving within water tetrahedron, are possible in the water-porphyrin assemblies possessing quasi-crystal structure. The latter structure is remained only on the solid support.

IR spectroscopy of thin water layer on germanium plates

Water interaction with germanium surface discussed above is accompanied by carbon dioxide binding with water because of specificity of the semiconductor possessing the energy band gap of 0.67 eV. Infrared spectra of single and two Ge plates with both components (water and CO_2) adsorbed on the plates are displayed in Figure 3. The picture of the spectrum in Figure 3 (curve 2) resembles Fraunhofer diffraction when two Ge plates with a slit between the plates have perpendicular orientation relative to the wave propagation. Carbon dioxide adsorption between two germanium plates and the splitting of water bands make the spectra complicated. The content of CO_2 is quite large according to the intense band at 2365 cm^{-1} in the spectrum (curve 2), but the slit between the plates is not fully completed that makes effect alike Fraunhofer diffraction because CO_2 and

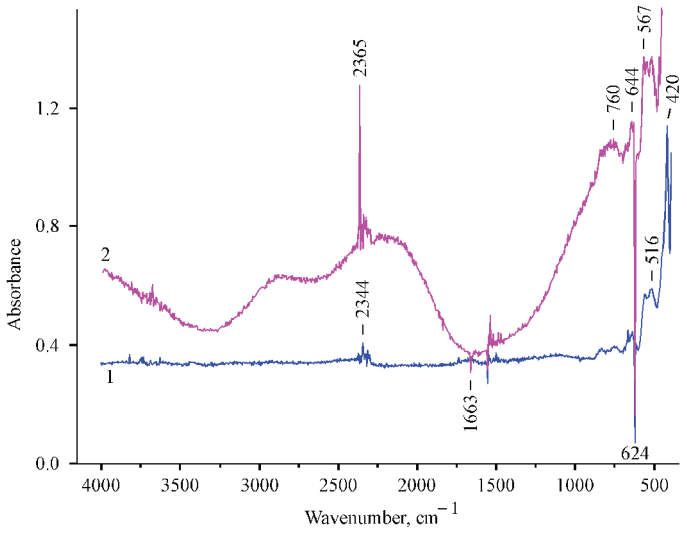

Figure 3. Infrared spectra of germanium at room temperature: one plate (1); and two plates together (2).

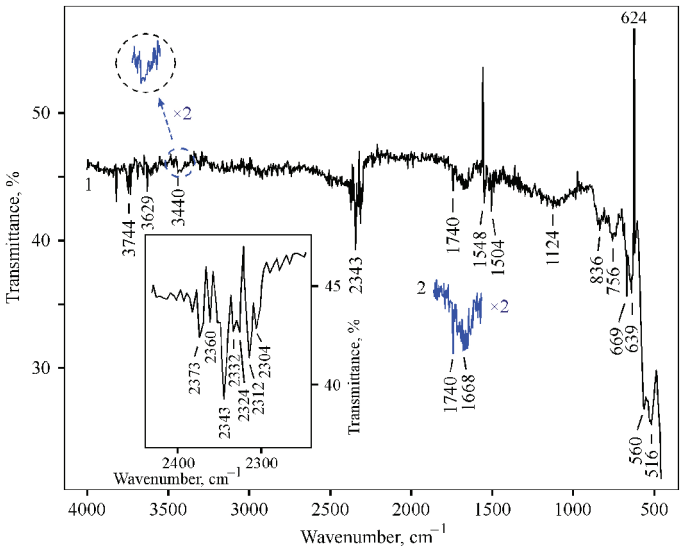

Figure 4. *Infrared spectrum of germanium recorded in transmittance mode (1); and area of H–O–H bending vibrations shown at the other scale (2). Inset shows the area of carbon dioxide vibrations.*

water creates a fluid mixture. The thin aqueous layer as displayed in Figure 3 (curve 1) and in Figure 4 mainly contains proton-donating water molecules producing vibration band at 1668 cm^{-1}. In this case the band of the O–H stretching vibrations at 3440 cm^{-1} is enough small in the magnitude. The latter indicates small extinction coefficient because of tight water like on the surface of water-porphyrin assemblies, where a layer of tight water did not allow observing submicroscopic grains with non-contact atomic force microscopy [26]. The tight water in the thin layer on germanium surface is apparently the reason of that the band at 1740 cm^{-1} displayed in Figure 4 is proved appreciably narrowed, like in gas-phase [27] but which here is most probably produced by vibrations of protonated water clusters bound with carbon dioxide. A large amount of carbon dioxide according to the magnitude of the stretch vibrations at 2365 cm^{-1} in Figure 3 (curve 2) is rather localized in the slit between Ge plates. As known the peak of carbon dioxide stretching vibrations shifts from 2350 cm^{-1} in gas phase to 2342 cm^{-1} when it is dissolved in ionic liquid, while the bending mode of CO_2 in air is observed at 667 cm^{-1} [28].

In the case of single plate, the carbon dioxide is dissolved in the thin aqueous layer on the Ge surface because the stretch vibrations are observed at 2343 cm^{-1} in Figure 4, while the band of CO_2 bending vibrations at 669 cm^{-1} is shifted to 639 cm^{-1}. Carbon dioxide exhibiting a peak of bending vibrations at 669 cm^{-1} is rather located on the surface of the aqueous layer covered Ge plate. While CO_2 dissolved in the aqueous layer exhibits the second component at 639 cm^{-1}, which is most probably appeared because of the hydrogen bond formation. These hydrogen bonds are apparently weak since the hydrogen bond is broken producing the negative peak at 624 cm^{-1} position in the wing of the component as displayed in Figure 4. The breaking means that the carbon dioxide is not involved in the intermolecular interactions with polarons that enhances the hydrogen bonds in the aqueous layer.

As mentioned above, enhancement of proton-donating and proton-accepting affinity of water molecules produces a higher

ordering of the structure, which can be observed by scanning electron microscopy [11, 12]. Similar separation of water molecules into proton-donating and proton-accepting species takes place in the aqueous layer on germanium surface because the doublets of librations at 836, 756 cm^{-1}, and 560, 516 cm^{-1} are present in the IR spectrum in Figure 4. The librations of water molecules are not restricted in the same extent as the stretching and bending vibrations in the tight water. The H–O–H bending vibrations at 1668 cm^{-1} rather with proton-donating affinity provide proton moving in the thin layer on germanium. The proton motion within water tetrahedrons of the quasi-crystal structure generates *LO* phonons with the energy $\hbar\omega'_{LO}$ = 1124 cm^{-1}, a broad band of which is shown in the spectrum in Figure 4. Theoretical estimation with Eq. (2), where ΔE_{spl} = 2.764566 eV, β_q =3.741657387, and E_1^* =10.204269 eV gives $\hbar\omega'_{LO}$ = 0.1397898 eV (1127.48 cm^{-1}) that is in the good agreement with the experimental value, a deviation is 0.3%. Thus, the quasi-crystal structuring occurs in the thin aqueous layer covered germanium because electrons from the surface are injected into the conduction band that produces hole polaron accumulation in the layer. In this case the broad band at 1124 cm^{-1} in the IR spectrum is the consequence of proton moving within the water tetrahedrons.

Influence of the thin water layer covered germanium on the behavior of the self-assembled protonated TPP dimers

The doublets of water stretching and H–O–H bending vibrations observed in Figure 5 (curve 1) are characteristic evidence for quasi-crystal structure of water-porphyrin aggregates on the solid support [11, 12]. The splitting of these bands means pronounced separation of water molecules into proton-accepting and proton-donating species due to hydrogen ions involving in the network of hydrogen bonds of water confined in the particles.

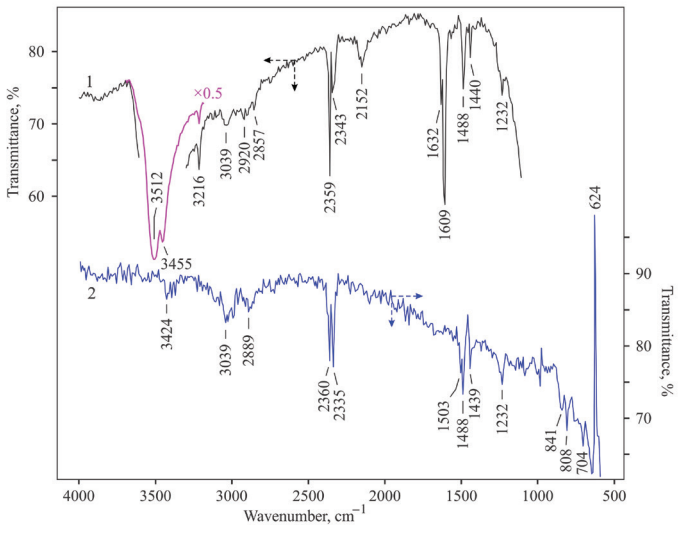

Figure 5*. Infrared spectra of TPP self-assembled into water-porphyrin submicroscopic particles obtained after evaporation of 0.86 mol l^{-1} aqueous THF containing the self-assembled protonated TPP dimers, which were prepared in the presence of 0.4N HCl and deposited on: CaF_2 plate (1); and Ge plate (2).*

The doublet observed at 1440, 1488 cm^{-1} in Figure 5 (curve 1) is the characteristic evidence for the presence of porphyrin macrocycle [11, 29]. The latter component is shifted from 1473 cm^{-1} of neutral TPP to 1488 cm^{-1} position of the mono-protonated TPP dimers while the former component is practically remained not shifted. The IR spectrum undergoes crucial change if the water-porphyrin aggregates were deposited on germanium plate as displayed in Figure 5 (curve 2). The change is seen even by eye because there are no the aggregates on the germanium plate but only minute blue-violet crystals like those of neutral TPP. Besides, the spectrum (curve 2) does not exhibit the doublets of the stretching and bending vibrations of water, but only small 3424 cm^{-1} band that indicates main water content has been disappeared. At the same time the doublet at 1439 (or 1440), 1488 cm^{-1}, which is characteristic for the presence of protonated TPP dimers, is remained in the spectrum in Figure 5 (curve 2). Therefore, the protonated TPP dimers do not destroy, because the small-size protonated water clusters are retained in the cages between the TPP molecules. This fact means that the hydrogen bonding in the cluster embedded between hydrophobic TPP units is stronger under connection of the TPP units via hydrogen bonds. The presence of the 1232 cm^{-1} band in this spectrum indicates the preservation of the electrons in the moiety N_s–H... OH_2, which are remained in the coupled state with the hole polarons. Note that the aqueous thin layer is most probably preserved only on the opposite side of the Ge plate because the doublet at 841, 808 cm^{-1} of water librations is present in the spectrum in Figure 5 (curve 2). The doublet at 704, 648 cm^{-1} of CO_2 interacting with water and another doublet of water librations at 560, 520 cm^{-1} (results are not shown) are also observed. Thus, it seems that the decay of polaronic exciton takes place only in the water confined in water-porphyrin aggregates, when they are deposited on germanium plate. It means that the electrons involved in the polaronic exciton as the quasi-particles go out from the water-porphyrin aggregates into conduction band of germanium as suggested above. Thus, as soon as the spin-orbit coupling of electrons with the holes vanishes, immediately the electrons involved in the polaronic exciton can be injected into germanium conduction band. The bound state energy ($E_{b\text{-}ex}$ = –0.3282 eV) of polaronic exciton as calculated below, see Eq. (5), cannot be a barrier for the electrons as compared with germanium band gap of 0.67 eV.

The above suggestion about proton spin requires more detail discussion. Hole polaron moving along hydrogen bonds in the quasi-crystal structure of water-porphyrin aggregates that is described with a good accuracy according to the scheme in Figure 2 (insets) implies one more peculiar. The matter is that the slanting cross as mentioned above is produced in the result of proton hopping steps, which are as many as hundreds of the steps with the same deviation to the left or only to the right because of microscopic proportions of the slanting cross [11, 12]. No doubt this effect can be connected with the proton spin direction taking into consideration features of the proton propagation along hydrogen bonds. Namely, if a proton has left spin then its propagation occurs only with the left deviation. And the self-induced polarization generated by hole polaron moving should have the spin also. Then, the polarization should have the opposite spin, since the self-induced polarization moves together with the hole [30]. It follows from that the hole polaron drags the lattice distortion with it as it moves through the quasi-crystal structure, so the spin of the self-induced polarization has the opposite direction relatively to that of the hole's spin. Alternatively, if the deviation angle of the hole propagation

would be independent from the hole spin direction, we could not observe the slanting cross of 55°±3° in the structure of water-porphyrin aggregates. But the fact is that the slanting cross is clearly observed in the experiments [11, 12].

Thus, the quasi-crystal structure of the thin aqueous layer on germanium plate is established due to far ordering of water molecules because of tetrahedral network of hydrogen bonds. In particular, the far ordering occurs because of a large amount of protons that induces the enhancement of proton-donating affinity of water molecules and produces the splitting of water bands into doublets.

Conclusions

The results presented above indicate a key role of polaronic exciton in the structuring of water-porphyrin matrix since a break of spin-orbit coupling between the opposite charges leads to the destruction of the aggregates. The obtained IR spectra exhibit two different behaviors of the TPP self-organized assemblies. In the case of Ge plate, only protonated TPP dimers without the aqueous coating are found in the corresponding IR spectrum. The latter means destruction of the self-organized assemblies because polaronic exciton on Ge plate loses electron coupled with the hole. Hence, hole polaron movement is only stabilized under the interaction with the electron in the quasiparticle. In this case the hole polaron movement along the wires of hydrogen bonds through water structure creates the network squeezing around the porphyrin dimers that therefore produces quasi-crystal structure or liquid microcrystals [7]. The presence of protons in thin aqueous layer on Ge enhances the interactions in the tetrahedral network of hydrogen bonds as well as it occurs in the water-porphyrin aggregates. The hole polaron moving via the localized states within water tetrahedrons generates *LO* phonons with the energy $\hbar\omega'_{LO}$ = 1127.48 cm^{-1} estimated theoretically or 1122.56 cm^{-1}. These estimations are found in a good agreement with experimental band observed at 1124 cm^{-1}. Besides, the self-induced polarization generated under the hole polaron moving implies that the polarization should have the opposite spin depending on that of hole polaron as suggested above.

Conflict of Interest

The authors declare no conflict of interest.

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Appendix

Appendix 1

The following Eq. (4) describes behavior of proton moving derived for the explanation of boson peak frequency observed in Raman and inelastic neutron scattering spectra, description in details can be found elsewhere [23]. The frequency of proton motion ($f_{Hb} = c/\nu_{Hb}^{-1}$) along the direction between the hydrogen-bonded water molecules in the dimer depends on polaronic exciton radius (r_{ex}), which is the average distance between the opposite charges.

$$f_{Hb} = [\hbar/(2\pi r_{ex}^2 m_r^*)]\beta(g_e/g_p)(m^h_{ef}/m_p)m \quad (4)$$

where $\hbar$ is the reduced Planck constant, m_r^* is the reduced effective mass of polaronic exciton, $m_r^* = m^h_{ef} m^e_{ef}/(m^h_{ef} + m^e_{ef})$, m^h_{ef} and m^e_{ef} are respectively the effective masses of hole and electronic polarons, g_e and g_p are electron and proton g-factors, respectively, and m is quantum number. In condensed matter the effective masses are $m^h_{ef} = 9.51 m_e$ for underlying hole polaron as the H_3O^+ particle and $m^e_{ef} = 0.5 m_e$, $m_e = 9.10938188 \times 10^{-31}$ kg [23]. The self-induced polarization for electronic polaron is defined by van der Waals radius of H_2O, the value of which (1.6×10^{-8} cm) is obtained exactly using $m^e_{ef} = 0.5 m_e$ [15]. The discussion of effective masses can be found elsewhere [15, 29]. With $\beta = 1.19100654$, $g_e = 2.002319304$, $g_p = 5.5856947$, $m_p = 1836.152667 m_e$, $r_{ex} = 2.63317$ Å for liquid water (see Appendix in Ref. [24]), and $m=1$ for proton with boson behavior, the calculated $f_{Hb} = 1.2370153$ THz or wavenumber $\nu_{Hb} = 41.262389$ cm^{-1}.

Appendix 2

Polaronic exciton moving over the conjugated π–system of TPP or within water cluster in the cage between TPP units and moving also through quasi-crystal structure, which generates *LO* phonons, occurs via the localized states. In this case consideration is alike the task about hydrogen atom with effective mass m_r^* and effective charge $e^* = e/(\varepsilon_{ef})^{1/2}$ [31]. Then the bound state energy ($E_{b\text{-}ex}$) of the polaronic exciton is defined by Eq. (5), where m_r^* is the reduced effective mass (see Appendix 1).

$$E_{b\text{-}ex} = -m_e e^4/(2\hbar^2)\,(m_r^*/m_e)\,(1/\varepsilon_{ef}^2) \quad (5)$$

In Eq. (5) $m^e_{ef} e^4/(2\hbar^2)$ is Rydberg constant (R_∞), $R_\infty = 13.605692$ eV and ε_{ef} is the effective dielectric constant, $\varepsilon_{ef}^{-1} = 1/\varepsilon_\infty - 1/\varepsilon_o$, ε_o ($\varepsilon_o = 78.4$) and ε_∞ ($\varepsilon_\infty = 4.2$) are respectively the static and the high-frequency dielectric constants. This ε_o value of water is quite acceptable because the aqueous layer covers germanium plate surface. The calculation according to Eq. (5) gives $E_{b\text{-}ex} = -0.3282$ eV.

Appendix 3

When water molecule has seven electrons in the external electronic shell under the incident photon absorption, the angular momentum quantum number is $l_C = 7$ [23]. An electron absorbing a photon perceives its momentum, which becomes angular momentum of the electron moving about in its orbit. The orbit rotation occurs together with the self-induced polarization around Y-axis in the plane of the interaction θ angle related to the incident photon direction (see Scheme 1). The θ angle between the incident photon direction and the electron momentum directed in the plane of the rotation can therefore assume only the values.

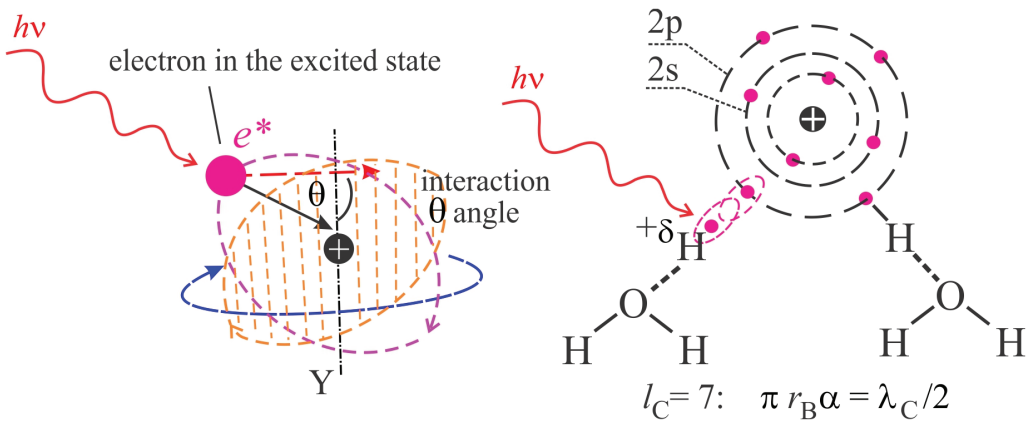
$$\theta = \cos^{-1}\{m/[l_C(l_C+1)]^{1/2}\} \quad (6),$$

where m is an integer in the range $7 \geq m \geq -7$ for $l_C = 7$. Then, the difference between the neighboring directions of the incident photon and electron momentum expressed as the difference between cos (θ_m) and cos (θ_{m-1}) is proportional to Compton wavelength and therefore is related to the Compton interaction parameter (r_C) by the equation.

$$r_C = \lambda_C/[2\pi(\cos\theta_m - \cos\theta_{m-1})] = \beta\, h/(m_e c) = \beta\,\lambda_C \quad (7),$$

$$\text{where } \beta = 1/[2\pi(\cos\theta_m - \cos\theta_{m-1})] \quad (7a)$$

And λ_C is Compton wavelength, $\Delta\cos\theta_m$ is invariable within $7 \geq m > -7$ ($\Delta\cos\theta_m = 0.13363062096$). The coefficient of proportionality β in Eq. (7) in fact assumes the meaning of the spin-orbit coupling, $\beta = 1.19100654$ for $l_C = 7$. It should be stressed that this parameter takes into account the spin-orbit coupling $\sqrt{\beta}$ for each particle possessing the spin, i.e. for the electron and the hole both that gives β for the coupled state in polaronic exciton.



Scheme 1. *Illustration of the incident photon interaction with water molecule that results in polaronic exciton generation, when proton of the same H_2O is borrowed for proton sharing (on the right) and the polaronic exciton rotation under the interaction with the incident photon (on the left).*

It should be noted that proton sharing in the moiety O–H$^+$...O is also prerequisite for polaronic exciton generation while theoretical energy gap between two vibrational states is ν_{Hb} =41.262389 cm^{-1} for liquid water as mentioned above.

Appendix 4

The properties of a polaron are defined by the following Eq. (8) describing the interaction between electrons (or holes) and phonons [30].

$$\alpha_F = (e^2/\hbar c)(m_{ef}c^2/2\hbar\omega'_{LO})^{1/2}(1/\varepsilon_\infty - 1/\varepsilon_o) \quad (8),$$

where α_F is the unitless Fröhlich coupling constant, ω'_{LO} is the *LO*-phonon angular frequency, m_{ef} is the effective mass of a charge carrier (electron or hole), ε_o and ε_∞ are respectively the static and the high-frequency dielectric constants, c and $\hbar$ are the speed of light and the reduced Planck constant, respectively. At a strong coupling, when α is much larger than 1, polaron is characterized by the self-energy (the energy of a polaron, E_p) and the energy of lowest Franck-Condon excited states (E_{FC}), which are given by Eqs. (9) [32] and (10), respectively [30].

$$E_p = 0.2\alpha_F^2\hbar\omega'_{LO} \quad (9)$$

$$E_{FC}=(\alpha_F^2/9\pi)\hbar\omega'_{LO} = 0.0354\alpha_F^2\hbar\omega'_{LO} \quad (10)$$

It should be noted that Fröhlich coupling constant as found earlier is 4.6 in the case of hole polaron [15], the effective mass for which was taken 10m_e. The latter obeys the strong-coupling mass (m^*) that is increased due to electron or hole polaron moving together with the lattice distortion and approximation of m^* is given as follows[30].

$$m^*/m_{ef} = 1 + 0.0227019\alpha_F^4 \quad (11)$$

With α_F =4.6 Eq. (11) gives 10.16m_{ef}. Hence, with $\hbar\omega'_{LO}$ = 0.1393583 eV (1124 cm^{-1}), m_{ef}=10m_e (m_e=9.10938188×10^{-31} kg) and the same ε_o and ε_∞ as in Appendix 2 we obtain α_F =7.0409677. Then with α_F =7.0409677 Eqs. (9) and (10) yield the self-energy E_p =1.381744 eV and the energy of lowest Franck-Condon excited states E_{FC}=0.244569 eV, a deviation is 0.09% from 0.244358 eV [21].