Ordered Microdomain of Diprotonated Tetraphenylporphine Aggregate Formed at Dodecane/Aqueous H_2SO_4 Interface Measured by Microspectrophotometry

Yukio Kamiya, Satoshi Tsukahara,* and Terufumi Fujiwara
Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526

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In situ microscopic measurements showed that rhombic microdomains of diprotonated 5,10,15,20-tetraphenylporphine aggregates were formed at a dodecane/aqueous H_2SO_4 interface. The size and thickness of the microdomains were about 10–100 μm and a monolayer level, respectively. The microscopic absorption anisotropy of individual microdomains revealed that they had an ordered structure, like single crystals.

Liquid/liquid interfaces are extensively investigated in recent years, because they show specific functions in colloidal chemistry, biochemistry, and solvent extraction chemistry. Nowadays, direct measurements of species at liquid/liquid interfaces are done by many spectroscopic techniques; these methods usually assume homogeneous interfaces. However, we found some inhomogeneous phenomena at liquid/liquid interfaces by in situ microscopy, for example, the formation of assemblies of palladium(II)–tetrapyridylporphine complexes at the toluene/water interface.[1] It is expected that the inhomogeneous phenomena are the specificities that will appear under a concentrated condition at the interfaces; a higher interfacial concentration is easily attained, which is hard to be realized in solutions.

Porphyrins have been studied actively, because they take essential roles in physiological phenomena. In recent years, it is investigated that photovoltaic and photoconductive porphyrin aggregates can be applied to solar cells and photoelectronic nano-devices, respectively.[2] 5,10,15,20-Tetraphenylporphine (tpp) is also known to be adsorbed and aggregated at liquid/liquid interfaces when acidic aqueous solutions are used.[3,4] The present study will show ordered microdomains of diprotonated tpp aggregates formed at the dodecane/aqueous H_2SO_4 interface measured by microspectrophotometry.

Tpp was purchased from Aldrich Chem. Water was purified with a Milli-Q system (Milli-Q Sp. Toc., Millipore). Other reagents were of analytical reagent grade. The present study employed a dodecane solution of tpp and an aqueous H_2SO_4 solution (6.0 mol dm^{-3}) as the organic and aqueous phases, respectively. The tpp concentration was 5.0×10^{-7}–5.0×10^{-5} mol dm^{-3}. Figure 1 shows the equilibria of the H_2tpp^{2+} aggregation in the dodecane/aqueous H_2SO_4 system.[3,4]

An inverted microscope (IX-51, Olympus) with an objective (UPlanFl, 10×, NA 0.30), a linear polarizer, a CCD camera (WAT-100, Watec) and a fiber spectrophotometer (SM-240, CVI Laser; resolution 1 nm) was mainly used for in situ observations and measurements for the liquid/liquid interface. A mercury lamp (100 W), a tungsten halogen lamp (100 W) or a light emitting diode (LED; wavelength 390–430 nm, 45 mW) was employed as a light source. A monochromator (H-10VIS, Horiba) was used for the selection of wavelength. The polarizer was placed between the light source and sample.

Figure 2 shows a used thin-layer two-phase microcell, which was fabricated in a similar way to the previous study.[5] It allows one to locate the position of the dodecane/aqueous H_2SO_4 interface within the working distance of the objective; consequently, we can do in situ microscopic measurements for the interface under high magnification. In addition, sealing the microcell with a coverslip has an advantage that the interface is stable and nonfluctuated. In the present microscopic apparatus, the acceptance face of the CCD camera and that of the fiber spectrophotometer are placed on the conjugated position of the specimen this allows one to measure the spectral intensity of light transmitted through a microregion of the specimen, whose size depends on the magnification (10×) and diameter (400 μm) of the optical fiber. The size at the specimen is about 40 μm in diameter. The position of the measured region is changeable with the microscopic stage.

Figure 3a shows a microscopic picture of the interface with a transmitted light. Many rhombic microdomains were formed at the interface, whose size was 10–100 μm, and they grew up gradually within 60 min at this concentration. When toluene was used instead of dodecane, the formation of microdomains was also observed. When the tpp dodecane solutions at the higher concentrations were employed, many smaller rhombic microdomains were formed at a shorter time. Consequently, a tpp dodecane solution at 5.0×10^{-7} mol dm^{-3} was mainly used, because the microdomain size was suitable for the microscopic measurements. Figure 3b shows the in situ absorption spectrum of a single microdomain. The spectral light intensities passing through the solid and dotted circle regions (I and I_0) in Figure 3a were measured and the absorbance (A) of the single microdomain was obtained with

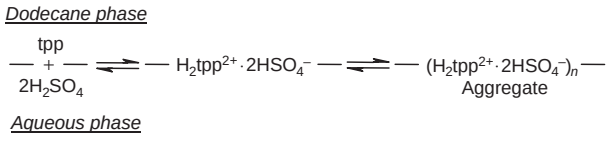

Figure 1. Adsorption and formation equilibria of diprotonated tpp and its aggregate at the dodecane/aqueous H_2SO_4 interface.

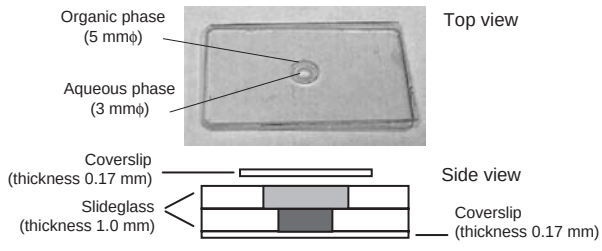

Figure 2. Photograph and schematic illustration of the thin-layer two-phase microcell. The lower three glass plates were stuck with adhesive.

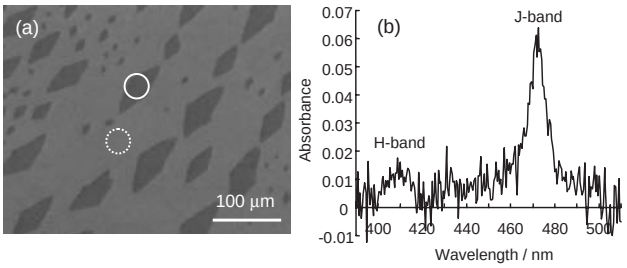

Figure 3. (a) Microscopic picture of one section of the dodecane/aqueous H_2SO_4 interface after 60 min with an unpolarized transmitted light at 470–475 nm, which was supplied with the mercury lamp and the monochromator. The initial tpp concentration in dodecane was 5.0×10^{-7} mol dm^{-3}. (b) In situ absorption spectrum of a single microdomain with unpolarized light. The light source was the LED (390–430 nm) and the tungsten halogen lamp (430–510 nm). The spectral light intensities in the solid and dotted circle regions in Figure 3a were measured.

$$A = -\log(I/I_0) \quad (1)$$

Microscopic light absorption measurements confirmed that tpp and H_2tpp^{2+} monomers did not exist both in the dodecane phase and at the interface where the microdomains were absent. The absorption maxima at about 410 and 473 nm in Figure 3b are caused by one kind of H_2tpp^{2+} aggregate; these absorption bands are called H-band and J-band, respectively.[6] There are no absorptions of tpp and H_2tpp^{2+} monomers in Figure 3b, revealing that the microdomains consist of only H_2tpp^{2+} aggregates.[3]

Figure 4a shows microscopic pictures of the interface with a polarized incident light as a function of its polarization direction. The absorption of each microdomain changes homogeneously. The transition possibility (P) for an absorption transition dipole moment ($\boldsymbol{\mu}$) is expressed as:

$$P \propto |\boldsymbol{\mu} \cdot \boldsymbol{E}|^2 = |\boldsymbol{\mu}|^2 |\boldsymbol{E}|^2 \cos^2\theta, \quad (2)$$

where $\boldsymbol{E}$ is a unit vector of the electric field of the incident light, and θ is the angle between $\boldsymbol{\mu}$ and $\boldsymbol{E}$. Figure 4b shows that the absorbance of the J-band depends on the angle Φ, which is the angle between the horizontal axis of the microscopic pictures and the polarization direction. These absorbances were calculated by eq 1 with the brightnesses of the microdomain and microdomain-free regions (I and I_0) in Figure 4a. The points in Figure 4b agree well with eq 2, meaning that the microdomain has one $\boldsymbol{\mu}$ for the J-band ($\boldsymbol{\mu}_J$). The angle of the absorption maximum (50°) agrees with the angle between the major axis of the rhombic microdomain and the horizontal axis of the pictures, meaning that the $\boldsymbol{\mu}_J$ is parallel to the major axis. Similar results were obtained for many other microdomains. One $\boldsymbol{\mu}_J$ of one direction in each microdomain means that it has a homogeneous structure, where H_2tpp^{2+} aggregates associate orderly and they have no freedom of rotation. Similar measurements for the H-band could not be accomplished because of the insufficient sensitivity and the weak light absorption.

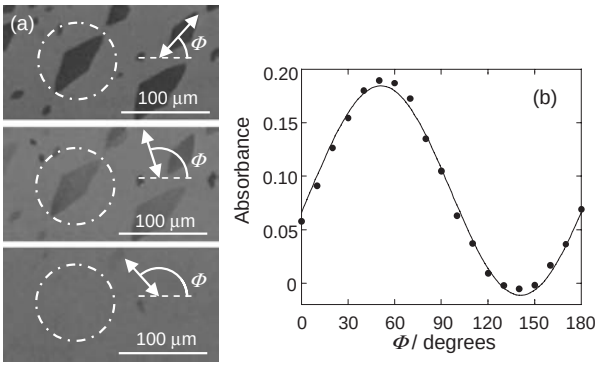

Figure 4. (a) Microscopic pictures of the interface as a function of the polarization direction of incidence light (white arrows) at 470–475 nm. (b) Dependence of absorbance of a single microdomain on the angle Φ. The encircled microdomain in Figure 4a was analyzed. The line expresses the fitting curve obtained by the least-squares method.

The thickness of the microdomains is determined on the basis of [1] light absorption, [2] mass balance, and [3] molecular size of tpp. [1] The Lambert–Beer's law is converted to $A = \varepsilon\Gamma$ for two-dimensional interfaces, where ε and Γ are molar absorptivity and interfacial concentration, respectively.[7] Since it was previously confirmed that $\boldsymbol{\mu}_J$ almost lay at the interface,[3] the maximum absorbance in Figure 4b was obtained with the polarized light whose polarization direction was parallel to $\boldsymbol{\mu}_J$. When this polarized light was used, ε of the J-band was 7.2×10^4 m^2 mol^{-1}.[3] From these values, Γ was determined to be 2.6×10^{-6} mol m^{-2} (Γ_1). [2] Almost all of tpp initially dissolved in the dodecane phase were adsorbed at the interface. The area occupied by the microdomains was one third area of the interface in Figure 3a, but it was about one half area of the whole interface. In this situation, Γ was estimated to be 2.8×10^{-6} mol m^{-2} (Γ_2). [3] The area and thickness of a tpp molecule were at 1.58 nm^2 and 0.4 nm, respectively, which were calculated by a molecular mechanics (MM2). If the porphyrin plane was parallel to the liquid/liquid interface and H_2tpp^{2+} molecules were contacted but not overlapped, Γ was 1.05×10^{-6} mol m^{-2} (Γ_3). The molecular thickness of the microdomains was expressed as Γ_1/Γ_3 and Γ_2/Γ_3, which were determined to be 2.5 and 2.6, respectively. The previous study showed that H_2tpp^{2+} molecules in the microdomains were overlapped and tilted,[3] and thus these values suggested that the thickness of the microdomain was a monolayer level, that is, about 1 nm. The structural analysis of such thin microdomains formed at liquid/liquid interfaces can not be done by other methods.

In conclusion, a unique liquid/liquid interfacial phenomenon was found out; the formation of the rhombic microdomains of H_2tpp^{2+} aggregates of a homogeneous structure, like single crystals. At liquid/liquid interfaces, randomly distributed precipitates or solids of μm-thickness have been formed so far. The present study, however, showed that the liquid/liquid interface was a reaction field of ordered microdomains of a monolayer level thickness by microspectroscopy for the first time. The microscopic quantitative analysis is highly required for future interfacial investigation.

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