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Microstructure of Monolayered Aggregate of 5-(4-Carboxyphenyl)-10,15,20-triphenylporphine Self-Assembled at the Toluene/Water Interface

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5-(4-Carboxyphenyl)-10,15,20-triphenylporphine (TPPCOOH) was acid-dissociated and its salt with alkali metal ions (TPPCOO⁻M⁺, M⁺ = Li⁺, Na⁺, and K⁺) formed ordered needle-like monolayered aggregates at the toluene/water interface under alkaline conditions. The light absorption of the aggregates at 451 nm depended on the polarization direction. The dependence revealed two types of TPPCOO⁻M⁺ aggregates with different growth direction, but their microstructure and interfacial concentration were almost the same. The height of the aggregates measured by atomic force microscopy was approximately equivalent to that of titled TPPCOO⁻.

Keywords: liquid/liquid interface, porphyrin aggregate, aggregate microstructure, polarized light, atomic force microscopy

The active center of heme proteins has a porphyrin backbone. Chlorophyll, the active center of photosynthesis, is also a porphyrin analog. Porphyrins are one of the most extensively studied groups of substances and typically have the following chemical, biochemical, and photochemical properties:¹ an extended and conjugated 18 π electron system, which produces the characteristic Soret band with a high molar absorption coefficient ($> 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$). These many π -electrons undergo a variety of redox reactions. Porphyrin complexes are formed with various metal ions, each of which exhibits different physicochemical properties.

The above properties have been studied for porphyrin monomers. Pasternack, et al. found in 1972 that the aggregate of tetraphenylporphine trisulfonate exhibited a specific light absorption.² Ohno, et al. characterized the aggregate of tetraphenylporphine tetrasulfonate formed in acidic solutions in 1993.³ These studies have led to active researches on porphyrin aggregates. At present, porphyrin aggregates are known to form by hydrogen bonding, electrostatic interaction, π - π stacking, van der Waals force, and metal-ligand bonding.⁴ Porphyrins are highly light-absorbing, and thus porphyrin monomers and aggregates are expected to be beneficial to light-involved science and technology, including photoconductivity,⁵ photocatalysis,¹ photovoltaic devices,^{6,7} highly sensitive analytical reagents,¹ and phototherapy.¹

Almost all the previous studies dealt with 3-dimensional porphyrin aggregates in solutions. If ordered 2-dimensional porphyrin aggregates are formed, different properties between in-plane and out-of-plane would appear and their new functionality is expected. Interface is considered to be an effective reaction field in the formation of 2-dimensional aggregates. In the present study, we pay attention to the oil/water interface where hydrophobic substances can react with hydrophilic substances.

Oil/water interfaces play an essential role in a variety of fields such as solvent extraction chemistry, colloidal chemistry, membrane chemistry, development of surfactants, paints, inks, cosmetics, and emulsifiers (food additives). A wide range of studies, from fundamental to applied, have been carried out in each field.

Thermodynamic interfacial tension has been the predominant method for measuring substances at oil/water interfaces from the past to the present. Recently, a variety of spectroscopy are developed for substances at oil/water interfaces.⁸ These measurements were mainly conducted from a macroscopic viewpoint, collecting averaged information about interfacial substances. However, to better evaluate the physical properties of interfacial substances, microscopic information of individual aggregates obtained by optical microscopy and/or probe microscopy is required.

The resolution of optical microscopy is about 100 nm at best, and that of probe microscopy is about 1 nm at best. Since substances at oil/water interfaces move by diffusion or convection, optical microscopy, not probe microscopy, is more suitable for in situ measurements of interfacial substances. If substances are transferred from oil/water interfaces to a solid substrate, probe microscopy becomes a powerful tool.

The authors were the first in the world to do in situ microscopic measurements of porphyrin aggregates formed at an oil/water interface by optical microscopy in 2001.⁹ Subsequently, they have continued to do in situ microscopic or microspectroscopic measurements of substances at oil/water interfaces by optical microscopy to the present.¹⁰⁻¹⁸

It was reported that hydrophobic 5,10,15,20-tetraphenylporphine (TPP) reacted with hydrophilic H⁺ to form TPP aggregates at oil/water interfaces.^{15,19-21} These aggregates are ordered 2-dimensional, but they are formed under highly acidic conditions ($\geq 4 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) and are therefore quite difficult to take out. In the present study, we investigated new porphyrin aggregates formed at the toluene/water interface by in situ microspectroscopy and measured them by atomic force microscopy (AFM), one of the probe microscopies, after taking them out.

5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin (TPPCOOH) was purchased from Tokyo Chemical Industry (purity 98%) and used as received. TPPCOOH is an amphiphilic porphyrin with a large hydrophobic moiety and a small hydrophilic moiety. The large hydrophobic moiety is a porphyrin-ring known for its various optical, redox, and complexing functions, as mentioned above. Water was purified with a Milli-Q system (Milli-Q Sp. Toc., Millipore). All other reagents were of analytical reagent grade. TPPCOOH was dissolved in toluene at a concentration of $5 \times 10^{-7} - 5 \times 10^{-5}$

1 mol L⁻¹, and the solutions were used as the organic phase. Aqueous solutions of LiCl–LiOH (pH 10–11) were prepared by dropwise addition of 5×10^{-3} mol L⁻¹ LiOH to an aqueous LiCl solution until the desired pH was obtained. Aqueous solutions of pH 12–13 were prepared by dropwise addition of 1.0 mol L⁻¹ LiOH to an aqueous LiCl solution. Aqueous solutions of NaCl–NaOH or KCl–KOH were prepared by the same procedure. The concentrations of all salts were adjusted in the range of 0.25–2.0 mol L⁻¹, and these alkaline solutions were used as the aqueous phase. The pH values were measured with a pH meter (F-55, Horiba).

The TPPCOOH toluene solution (5.0×10^{-5} mol L⁻¹, 1.0 mL) and the aqueous solution (pH 10–13, 1.0 mL) were added to a glass vial (diameter 2 cm, height 5 cm) and allowed to settle for 1 h until equilibrium was reached. The color of the toluene phase changed from pink to light pink, and the fading became more pronounced with an increase in pH. The aqueous phases were colorless at all pH. Yellow substances were observed at the toluene/water interface at pH 11, 12, and 13, and yellow precipitates were observed at the bottom at pH 13 (Section S1 in SI). This pH dependence suggests that acid-dissociated TPPCOOH, TPPCOO⁻, was adsorbed at the toluene/water interface. The light absorption spectra of the toluene and aqueous phases suggested that most of the TPPCOOH was adsorbed at the toluene/water interface at pH 12 (Section S2 in SI).

Since the pK_a (K_a : acid-dissociation constant) of TPPCOOH is about 5,²² TPPCOOH is dissolved in alkaline solutions to become TPPCOO⁻. In the presence of alkali metal ions (M⁺), its salt (TPPCOO⁻M⁺) can be formed. Under appropriate conditions, TPPCOO⁻M⁺ will be adsorbed at the toluene/water interface as shown in Figure 1.

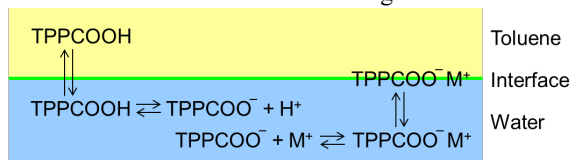


Figure 1. Schematic illustration of the distribution and adsorption equilibria of TPPCOOH in the toluene/water system. M⁺ = Li⁺, Na⁺, or K⁺.

Figure 2 shows the two-phase microcell used for microscope observation of the liquid/liquid interface (Section S3 in SI).²³ The lower hole was filled with the aqueous solution and then the upper larger hole was filled with the toluene solution. The microspectroscopy equipment consisted of an inverted microscope (IX-51, Olympus) with an objective lens (UPlanFL, 10×, NA 0.30, Olympus), a xenon lamp (UXL-75XB, power 75 W, Olympus), a linear polarizer, a monochromatic CCD camera (INFINITY3-1M, Lumenera), a monochromator (RA-401, Photal), and a spectrophotometer with an optical fiber (BRC1K, B&W Tek, Inc.). In the case of measurements with monochromatic polarized light, white light from the xenon lamp was introduced into the monochromator and the resulting monochromatic light was irradiated to the sample with an optical fiber. The polarizer was placed between the output face (bottom end) of the optical fiber and the sample. All microscopic measurements were carried out with the

microcell on a microscope thermostated plate (MAT-555MRO-KU, Tokai Hit) at 15.0 ± 0.5 °C.

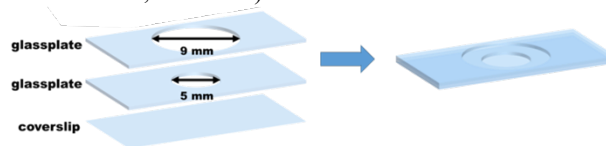


Figure 2. Schematic illustration of the thin-layer two-phase microcell.

Figures 3a-c show the microscope images of TPPCOO⁻M⁺ aggregates formed at the toluene/water interface with different alkali metal ions. The initial TPPCOOH concentration of 3.0×10^{-7} mol L⁻¹ and pH 12 were used for further investigations because these conditions provided aggregates of a size suitable for microspectroscopic measurements. The aggregate shape was needle-like with a length of 50–100 μm, and rarely branched aggregates were formed. The aggregate length increased with time. Below pH 12, the aggregates were not observed. At pH higher than 12, large amorphous precipitates (> 100 μm in size) were formed in the aqueous phase. Instead of toluene, dodecane, CH₂Cl₂, or 1-butanol was investigated, but no TPPCOO⁻M⁺ aggregates were observed at the interface (Section S4 in SI).

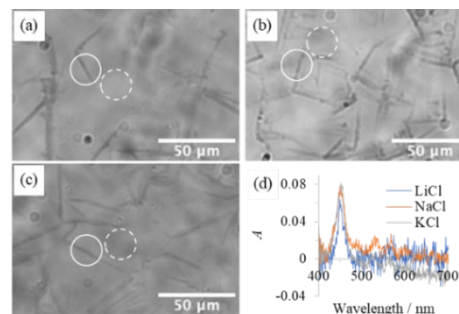


Figure 3. Microscope images of aggregates at the interface at 30 min after the preparation with the TPPCOOH toluene solution (3.0×10^{-7} mol L⁻¹) and 1.0 mol L⁻¹ (a) LiCl–LiOH, (b) NaCl–NaOH, or (c) KCl–KOH aqueous solution (pH 12). Unpolarized white light was used as a light source. (d) Absorption spectra of single aggregates in (a), (b), and (c).

We investigated the effects of alkali metal ion concentration at pH 12. The interfacial aggregates were not formed at 0.25, 0.30, 0.50, and 0.75 mol L⁻¹, but they were formed at 1.0 and 2.0 mol L⁻¹ for Li⁺, Na⁺, and K⁺. These facts support the equilibrium shown in Figure 1 and the formation of TPPCOO⁻M⁺ at the interface. Such high concentrations of alkali metal ions are essential to reduce the electrostatic repulsion between TPPCOO⁻ at the interface. Instead of alkali metal ions, Mg²⁺, Ca²⁺, or Ba²⁺ was used, but no aggregates were observed (Section S4 in SI).

In order to obtain the absorption spectra of the single interfacial aggregates, the intensities of the light passing through two areas indicated by the solid circle (I) and the dotted circle (I_0) in Figures 3a-c were measured by the spectrophotometer with unpolarized white light. The solid circles represent the area with one aggregate and the dotted circles represent the area without aggregates. Absorbance (A) values were calculated with Eq. (1) and the absorption spectra are

1 shown in Figure 3d. All interfacial aggregates showed ab-
 2 sorption maxima at the wavelengths (λ_{\max}) of 450 – 452 nm
 3 (the Soret band), regardless of the salt type.

$$A = -\log \frac{I}{I_0} \quad (1)$$

5 The λ_{\max} of the Soret band of TPPCOO^- in the aqueous
 6 phase is 447 – 448 nm at pH 12 (Section S5 in SI). Small
 7 absorbance (0.008 – 0.06) with a 1.0 cm path length indicated
 8 that the TPPCOO^- concentration in the aqueous phase was
 9 quite low. Porphyrins have two orthogonal and almost equiv-
 10 alent transition dipole moments for absorption in the porphy-
 11 rin-ring at the Soret band.^{24,25} Therefore, two new absorption
 12 bands, blue-shifted H-band and red-shifted J-band, appear
 13 simultaneously when porphyrins have a strong mutual inter-
 14 action.^{20,25,26} In the present case, the interfacial $\text{TPPCOO}^- \text{M}^+$
 15 shows only one absorption at the Soret band in Figure 3d,
 16 suggesting that the interfacial $\text{TPPCOO}^- \text{M}^+$ do not have a
 17 strong mutual interaction. This can also be understood from
 18 the fact that the λ_{\max} of the Soret band of the interfacial TPP-
 19 $\text{COO}^- \text{M}^+$ is close to that of TPPCOO^- in the aqueous phase.

20 Figures 4 and 5 show microscope images of the interfa-
 21 cial aggregates with monochromatic polarized light as a func-
 22 tion of polarization direction. The brightness of the needle-
 23 like aggregates changes uniformly depending on the polariza-
 24 tion direction in all cases, indicating that all the TPPCOO^-
 25 M^+ constituting one interfacial aggregate are oriented in one
 26 direction, like a two-dimensional crystal. Since the light ab-
 27 sorption is expressed with the transition dipole moments for
 28 absorption (vector μ), we can discuss the orientation of TPP-
 29 $\text{COO}^- \text{M}^+$ of the interfacial aggregates. The transition possi-
 30 bility (p) for absorption is expressed as:¹⁵

$$p \propto |\mu \cdot \mathbf{E}|^2 = |\mu|^2 |\mathbf{E}|^2 \cos^2 \theta \quad (2)$$

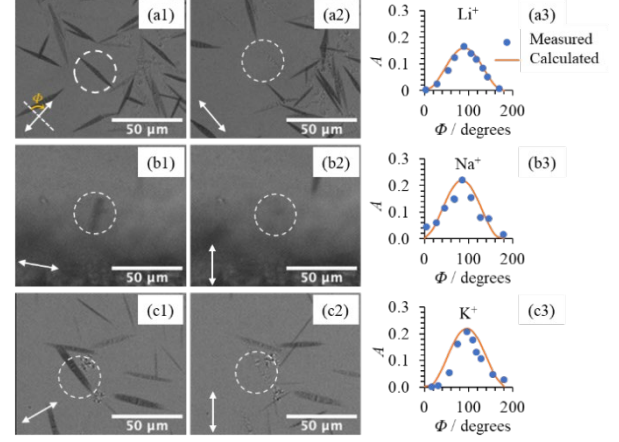
32 where \mathbf{E} is the electric field vector of the incident light and θ
 33 is the angle between μ and \mathbf{E} .

34 The brightness (I) of one aggregate indicated by circles
 35 and the brightness (I_0) without aggregates in Figures 4 and 5
 36 were obtained from the digital images, and the absorbance
 37 values (A) of the aggregate were calculated with Eq. (1). Fig-
 38 ures 4(a3,b3,c3) show that A of one aggregate depends on the
 39 angle (Φ) from the major axis of the aggregate to the polar-
 40 ization direction. Positive Φ indicates clockwise direction.
 41 The dependences are well fit with Eq. (2), meaning that one
 42 μ of $\text{TPPCOO}^- \text{M}^+$ of the aggregate was observed. The max-
 43 ima at $\Phi \approx 90^\circ$ ($92^\circ \pm 5^\circ$, $83^\circ \pm 10^\circ$, and $97^\circ \pm 10^\circ$ for Li^+ , Na^+ ,
 44 and K^+ , respectively, mean \pm confidence interval with 95%
 45 confidence level) indicate that the μ direction is almost per-
 46 pendicular to the major axis of the aggregate. We call these
 47 aggregates type S.

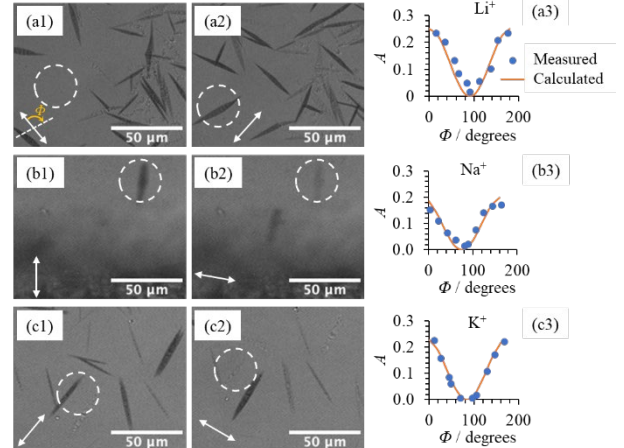
48 Figures 5(a3,b3,c3) also show the absorbance depend-
 49 ence of one aggregate on Φ . In these cases, the maxima exist
 50 at $\Phi \approx 0^\circ$ ($9^\circ \pm 7^\circ$, $-17^\circ \pm 6^\circ$, and $-5^\circ \pm 3^\circ$ for Li^+ , Na^+ , and
 51 K^+ , respectively), indicating that the μ direction is almost par-
 52 allel to the major axis. We call these aggregates type P.

53 Furthermore, we investigated the absorbance depend-
 54 ence on Φ for 96 aggregates with 1.0 mol L⁻¹ NaCl–NaOH
 55 (pH 12). As the result, we found only two types, S or P, and
 56 we did not find any halfway types, such as 45° or 60° . The

57 numerical ratio of type S : P was 46 : 50, almost the same
 58 probability. Similar results were obtained for Li^+ and K^+ . Fur-
 59 thermore, the statistical distributions of the length of the ag-
 60 gregate major axis (l_{ma}) and the ratio ($R = l_{\text{mi}}/l_{\text{ma}}$, l_{mi} is
 61 the length of the minor axis) shown in Section S6 in SI mean that
 62 there is little difference in l_{ma} and R between types S and P.



63 **Figure 4.** Microscope images of needle-like aggregates at the interface
 64 at 30 min after preparation. (a1,a2) 1.0 mol L⁻¹ LiCl–LiOH; (b1,b2) 1.0
 65 mol L⁻¹ NaCl–NaOH; (c1,c2) 1.0 mol L⁻¹ KCl–KOH. TPPCOOH, $3.0 \times$
 66 10^{-7} mol L⁻¹. Polarized light at 451 nm was used as the light source. Double
 67 arrows indicate the polarization direction. (a3,b3,c3) A of single ag-
 68 gregates as a function of the angle Φ . The lines correspond to the fitting
 69 curves of Eq. (2). The aggregates moved randomly at the interface.



70 **Figure 5.** Microscope images of needle-like aggregates at the interface
 71 at 30 min after preparation. (a1,a2) LiCl–LiOH; (b1,b2) NaCl–NaOH;
 72 (c1,c2) KCl–KOH. The experimental conditions were the same as those
 73 in Figure 4.

74 As mentioned above, porphyrins have two orthogonal
 75 and almost equivalent μ at the Soret band. If the porphyrin-
 76 ring lies parallel to the interface, the two μ should be ob-
 77 served under the present experimental conditions. In fact,
 78 only one μ was observed, which means that the porphyrin-
 79 ring stands perpendicular to the interface, as shown in Figure
 80 6. The porphyrin-ring of $\text{TPPCOO}^- \text{M}^+$ is oriented perpendic-
 81 ular to the major axis of the type S, and it is oriented parallel
 82 to the major axis of the type P. The maximum absorbance
 83 (A_{\max}) and the λ_{\max} values in Figures 4 and 5 are almost the

same for the types S and P, and therefore the microstructures are almost identical. Only the direction of growth is different; with face-to-face and side-by-side growth for the types S and P, respectively. The driving forces for the formation of the types S and P are almost the same. The reason for the formation of the needle-like aggregates could be caused by an initial flow that is generated at the interface when the organic phase is manually added on the aqueous phase. Since TPPCOOH is supplied along the flow, small needle-like aggregates (cores) are initially formed in this direction, and they grow under the influence of their initial shape.

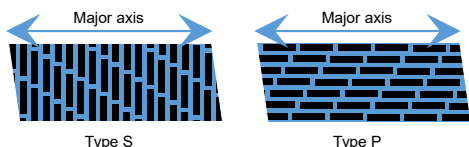


Figure 6. Partial microstructures of the interfacial type S and P aggregates of TPPCOO-M⁺ (top view). The black rectangles represent the porphyrin-ring of TPPCOO-M⁺ standing at the interface.

Using the A_{\max} values in Figures 4 and 5, the interfacial concentration (Γ) of TPPCOO-M⁺ was calculated with the modified Lambert–Beer’s law, $A_{\max} = \varepsilon_1 \Gamma l^{15,27}$ where ε_1 is the molar absorption coefficient for light polarized parallel to one μ . The ε_1 value of TPPCOO-M⁺ was estimated to be $6.62 \times 10^4 \text{ mol}^{-1} \text{ m}^2$ (Section S7 in SI), and the Γ values were calculated to be 3.5, 3.3, and $3.5 \times 10^{-6} \text{ mol m}^{-2}$ for Li⁺, Na⁺, and K⁺, respectively. To compare the Γ values, the chemical structures of two TPPCOO-Na⁺ in vacuo and water were optimized with B97D/6-31G by Gaussian 09W²⁸ (Section S8 in SI). When the interfacial TPPCOO⁻ is tilted at about 20° from 90°, as shown in Figure 7a, the neighboring phenyl-groups do not overlap, and the height, width, and thickness of TPPCOO⁻ were estimated to be 2.0₃, 1.4₇, and 0.36 nm, respectively. The cross-section is 0.52₉ nm² (= 1.4₇ nm × 0.36 nm). When a close-packed TPPCOO⁻ monolayer is formed, the Γ value is calculated to be $3.1_9 \times 10^{-6} \text{ mol m}^{-2}$, which is approximately in agreement with the experimental values.

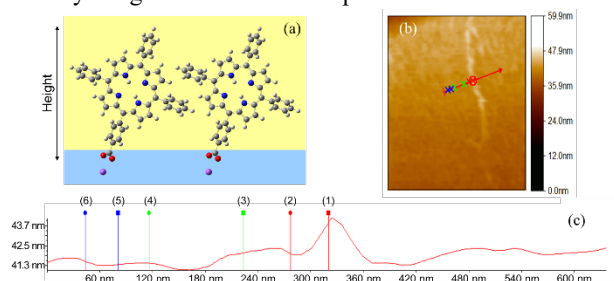


Figure 7. (a) Interfacial TPPCOO-M⁺ estimated based on the experimental results and DFT calculation with Gaussian 09W. (b) An AFM image of one TPPCOO-K⁺ aggregate transferred to a silicon substrate (1 × 1 μm). The experimental conditions were the same as in Figure 4c. (c) The height profile along the red line in (b).

As mentioned above, branched aggregates were rarely found. Figure 8 shows the formation and growth process of one branch. The aggregate had one major axis (parent, blue circle) at 300 s (a), and a branch (gray circle) was formed during 300 – 480 s with its major axis perpendicular to the

parent major axis. The length of the parent and the branch increased with time and Figure 8b was obtained. From Figure 8b, the absorbance dependences of the parent and the branch on Φ were obtained in a similar way (Figure 8c), where Φ was the angle between the polarization direction and the parent major axis. The parent and branch major axes are almost perpendicular, but the absorbance dependences are almost identical. This fact means that the orientation directions of TPPCOO-M⁺ are the same and only the direction of growth is different. This relationship is the same as that between the types S and P. In other words, the parent and the branch parts correspond to the types P and S, respectively. If there is a trigger, only the direction of growth changes, without change in the orientation direction of TPPCOO-M⁺. As for the trigger, some consideration is given in Section S6 in SI.

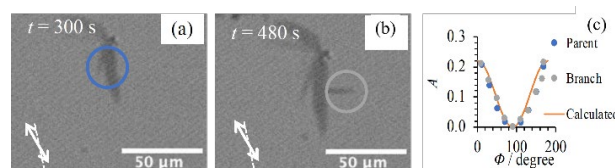


Figure 8. Microscope images of a branched aggregate at the interface at (a) 300 s and (b) 480 s after preparation with polarized light at 451 nm. (c) Absorbances of the parent and the branch parts as a function of Φ , which is the angle between the polarization direction and the parent major axis. The line corresponds to the fitting curve of Eq. (2). The experimental conditions were the same as in Figure 4c.

Interfacial TPPCOO-M⁺ aggregates were carefully transferred to a silicon substrate (coated with SiO₂ of 500 nm thickness) with a micropipette. After drying, atomic force microscope (AFM; JSPM-4200, JEOL) images were recorded using the soft-tapping mode. Figure 7b shows an example of the AFM image obtained. The TPPCOO-K⁺ aggregate seems to be a thread, and its width is about 60 nm. Figure 7c shows the height profile along the red line in Figure 7b. The aggregate height was determined to be 2.4 ± 0.4 nm by subtracting the mean height of points 2 – 6 from the height of point 1 in Figure 7c. This value is well in agreement with the above value obtained by Gaussian (2.0₃ nm).

In conclusion, we confirmed that TPPCOO-M⁺ formed ordered needle-like monolayered aggregates at the toluene/water interface by two independent analytical methods, in situ microspectroscopy and AFM. Furthermore, the chemical structure of the interfacial TPPCOO-M⁺ was estimated based on the experimental results and DFT calculation (B97D/6-31G) with Gaussian. Most studies of liquid/liquid interfaces have been based on the interfacial tension (or the interfacial pressure). However, when the heterogeneous adsorption of substances occurs, as in the present study, it is difficult to know the nature of the interfacial substances only by the interfacial tension. In the future, it is expected that the microstructure of more interfacial substances will be elucidated by combining various analytical methods.

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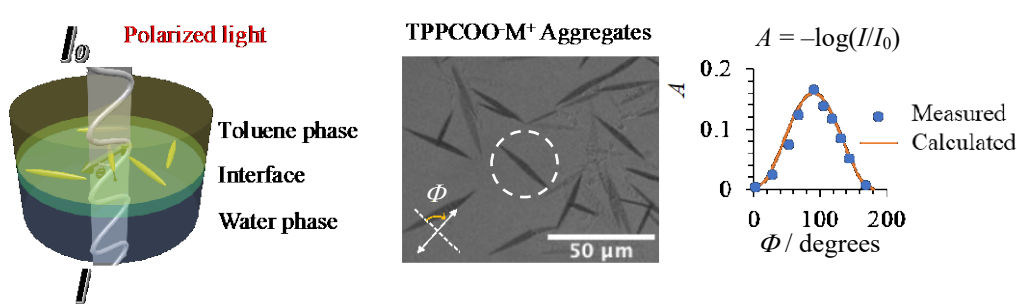
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NOTE The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge.

For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF.

If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.

You are requested to put a brief abstract (50-60 words, one paragraph style) with the graphical abstract you provided, so that readers can easily understand what the graphic shows.

Graphical Abstract	
Textual Information	
A brief abstract (required)	5-(4-Carboxyphenyl)-10,15,20-triphenylporphine (TPPCOOH) was acid-dissociated and its salt with alkali metal ions (TPPCOO ⁻ M ⁺ , M ⁺ = Li ⁺ , Na ⁺ , and K ⁺) formed ordered needle-like monolayered aggregates at the toluene/water interface under alkaline conditions. The light absorption of the aggregates at 451 nm depended on the polarization direction. The dependence revealed two types of TPPCOO ⁻ M ⁺ aggregates with different growth direction, but their microstructure and interfacial concentration were almost the same. The height of the aggregates measured by atomic force microscopy was approximately equivalent to that of titled TPPCOO ⁻ .
Title(required)	Microstructure of Monolayered Aggregate of 5-(4-Carboxyphenyl)-10,15,20-triphenylporphine Self-Assembled at the Toluene/Water Interface
Authors' Names(required)	Tania Avianda Gusman and Satoshi Tsukahara
Graphical Information	
 <p>The graphical abstract consists of three parts. On the left, a 3D schematic shows a cylindrical container with a green 'Toluene phase' on top and a blue 'Water phase' on bottom, separated by a horizontal 'Interface'. A vertical beam of 'Polarized light' (indicated by a double-headed arrow) passes through the interface. In the center, an AFM image shows 'TPPCOO-M⁺ Aggregates' as needle-like structures. A dashed circle highlights a region, and a scale bar indicates '50 μm'. An angle Φ is shown between two intersecting lines. On the right, a plot of absorbance A versus polarization angle Φ / degrees. The y-axis ranges from 0 to 0.2, and the x-axis ranges from 0 to 200. Blue dots represent 'Measured' data, and an orange line represents the 'Calculated' fit. The equation A = -log(I/I₀) is shown above the plot.</p> <p style="text-align: center;">Polarized light absorption dependence of interfacial TPPCOO-M⁺ aggregates</p>	
<p><Please insert your Graphical Abstract: The size is limited within 100 mm width and 30 mm height, or 48 mm square>(required)</p>	