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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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1 5-(4-Carboxyphenyl)-10,15,20-triphenylporphine
2 (TPPCOOH) was acid-dissociated and its salt with alkali
3 metal ions (TPPCOO⁻M⁺, M⁺ = Li⁺, Na⁺, and K⁺) formed ordered
4 needle-like monolayered aggregates at the toluene/water
5 interface under alkaline conditions. The light absorption
6 of the aggregates at 451 nm depended on the polarization direction.
7 The dependence revealed two types of TPPCOO⁻M⁺
8 aggregates with different growth direction, but their micro-
9 structure and interfacial concentration were almost the same.
10 The height of the aggregates measured by atomic force micro-
11 scopy was approximately equivalent to that of titrated TPP-
12 COO⁻.

13 **Keywords:** liquid/liquid interface, porphyrin aggregate, ag-
14 gregate microstructure, polarized light, atomic force micro-
15 scopy

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

27 The above properties have been studied for porphyrin
28 monomers. Pasternack, et al. found in 1972 that the aggregate
29 of tetraphenylporphine trisulfonate exhibited a specific light
30 absorption.² Ohno, et al. characterized the aggregate of tetra-
31 phenylporphine tetrasulfonate formed in acidic solutions in
32 1993.³ These studies have led to active researches on porphy-
33 rin aggregates. At present, porphyrin aggregates are known
34 to form by hydrogen bonding, electrostatic interaction, π - π
35 stacking, van der Waals force, and metal-ligand bonding.⁴
36 Porphyrins are highly light-absorbing, and thus porphyrin
37 monomers and aggregates are expected to be beneficial to
38 light-involved science and technology, including photocon-
39 ductivity,⁵ photocatalysis,¹ photovoltaic devices,^{6,7} highly
40 sensitive analytical reagents,¹ and phototherapy.¹

41 Almost all the previous studies dealt with 3-dimensional
42 porphyrin aggregates in solutions. If ordered 2-dimensional
43 porphyrin aggregates are formed, different properties be-
44 tween in-plane and out-of-plane would appear and their new
45 functionality is expected. Interface is considered to be an ef-
46 fective reaction field in the formation of 2-dimensional ag-
47 ggregates. In the present study, we pay attention to the oil/wa-
48 ter interface where hydrophobic substances can react with hy-
49 drophilic substances.

50 Oil/water interfaces play an essential role in a variety of
51 fields such as solvent extraction chemistry, colloidal chemis-
52 try, membrane chemistry, development of surfactants, paints,
53 inks, cosmetics, and emulsifiers (food additives). A wide
54 range of studies, from fundamental to applied, have been car-
55 ried out in each field.

56 Thermodynamic interfacial tension has been the pre-
57 dominant method for measuring substances at oil/water inter-
58 faces from the past to the present. Recently, a variety of spec-
59 troscopy are developed for substances at oil/water interfaces.⁸
60 These measurements were mainly conducted from a macro-
61 scopic viewpoint, collecting averaged information about inter-
62 facial substances. However, to better evaluate the physical
63 properties of interfacial substances, microscopic information
64 of individual aggregates obtained by optical microscopy
65 and/or probe microscopy is required.

66 The resolution of optical microscopy is about 100 nm at
67 best, and that of probe microscopy is about 1 nm at best. Since
68 substances at oil/water interfaces move by diffusion or con-
69 vection, optical microscopy, not probe microscopy, is more
70 suitable for *in situ* measurements of interfacial substances. If
71 substances are transferred from oil/water interfaces to a solid
72 substrate, probe microscopy becomes a powerful tool.

73 The authors were the first in the world to do *in situ* mi-
74 croscopic measurements of porphyrin aggregates formed at
75 an oil/water interface by optical microscopy in 2001.⁹ Subse-
76 quently, they have continued to do *in situ* microscopic or mi-
77 crospectroscopic measurements of substances at oil/water in-
78 terfaces by optical microscopy to the present.¹⁰⁻¹⁸

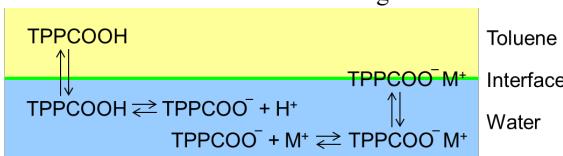
79 It was reported that hydrophobic 5,10,15,20-tetra-
80 phenylporphine (TPP) reacted with hydrophilic H⁺ to form
81 TPP aggregates at oil/water interfaces.^{15,19-21} These aggre-
82 gates are ordered 2-dimensional, but they are formed under
83 highly acidic conditions ($\geq 4 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) and are there-
84 fore quite difficult to take out. In the present study, we in-
85 vestigated new porphyrin aggregates formed at the toluene/water
86 interface by *in situ* microspectroscopy and measured them by
87 atomic force microscopy (AFM), one of the probe microscop-
88 ies, after taking them out.

89 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin
90 (TPPCOOH) was purchased from Tokyo Chemical Industry
91 (purity 98%) and used as received. TPPCOOH is an am-
92 phiphilic porphyrin with a large hydrophobic moiety and a
93 small hydrophilic moiety. The large hydrophobic moiety is a
94 porphyrin-ring known for its various optical, redox, and com-
95 plexing functions, as mentioned above. Water was purified
96 with a Milli-Q system (Milli-Q Sp. Toc., Millipore). All other
97 reagents were of analytical reagent grade. TPPCOOH was
98 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. 2 Aqueous solutions of LiCl–LiOH (pH 10–11) were prepared 3 by dropwise addition of 5 × 10⁻³ mol L⁻¹ LiOH to an aqueous 4 LiCl solution until the desired pH was obtained. Aqueous solutions of pH 12–13 were prepared by dropwise addition of 6 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 9 in the range of 0.25–2.0 mol L⁻¹, and these alkaline solutions 10 were used as the aqueous phase. The pH values were measured 11 with a pH meter (F-55, Horiba).

12 The TPPCOOH toluene solution (5.0 × 10⁻⁵ mol L⁻¹, 1.0 13 mL) and the aqueous solution (pH 10–13, 1.0 mL) were 14 added to a glass vial (diameter 2 cm, height 5 cm) and allowed 15 to settle for 1 h until equilibrium was reached. The 16 color of the toluene phase changed from pink to light pink, 17 and the fading became more pronounced with an increase in 18 pH. The aqueous phases were colorless at all pH. Yellow 19 substances were observed at the toluene/water interface at pH 11, 20 12, and 13, and yellow precipitates were observed at the bottom 21 at pH 13 (Section S1 in SI). This pH dependence suggests 22 that acid-dissociated TPPCOOH, TPPCOO⁻, was adsorbed at 23 the toluene/water interface. The light absorption spectra of 24 the toluene and aqueous phases suggested that most of the 25 TPPCOOH was adsorbed at the toluene/water interface at pH 26 12 (Section S2 in SI).

27 Since the pK_a (K_a : acid-dissociation constant) of TPP- 28 COOH is about 5,²² TPPCOOH is dissolved in alkaline solutions 29 to become TPPCOO⁻. In the presence of alkali metal ions (M⁺), its salt (TPPCOO⁻M⁺) can be formed. Under appropriate 30 conditions, TPPCOO⁻M⁺ will be adsorbed at the 31 toluene/water interface as shown in Figure 1.



33 **Figure 1.** Schematic illustration of the distribution and adsorption equi- 34
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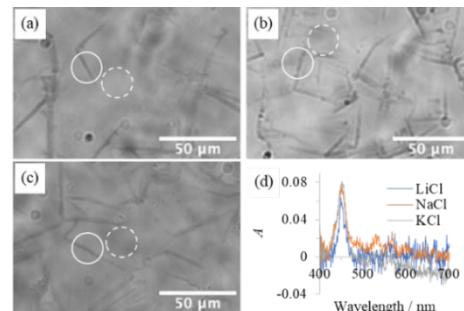
Figure 2 shows the two-phase microcell used for microscope observation of the liquid/liquid interface (Section S3 in SI).²³ The lower hole was filled with the aqueous solution and then the upper larger hole was filled with the toluene solution. The microscope equipment consisted of an inverted microscope (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, Photol), 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

52 microcell on a microscope thermostated plate (MAT- 53 555MRO-KU, Tokai Hit) at 15.0 ± 0.5 °C.



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

55 Figures 3a-c show the microscope images of TPPCOO⁻ 56 M⁺ aggregates formed at the toluene/water interface with dif- 57 ferent alkali metal ions. The initial TPPCOOH concentration 58 of 3.0 × 10⁻⁷ mol L⁻¹ and pH 12 were used for further inves- 59 tigations because these conditions provided aggregates of a 60 size suitable for microspectroscopic measurements. The ag- 61 ggregate shape was needle-like with a length of 50–100 μm, 62 and rarely branched aggregates were formed. The aggregate 63 length increased with time. Below pH 12, the aggregates were 64 not observed. At pH higher than 12, large amorphous precip- 65 itates (> 100 μm in size) were formed in the aqueous phase. 66 Instead of toluene, dodecane, CH₂Cl₂, or 1-butanol was in- 67 vestigated, but no TPPCOO⁻M⁺ aggregates were observed at 68 the interface (Section S4 in SI).



69 **Figure 3.** Microscope images of aggregates at the interface at 30 min 70 after the preparation with the TPPCOOH toluene solution (3.0 × 10⁻⁷ mol 71 L⁻¹) and 1.0 mol L⁻¹ (a) LiCl–LiOH, (b) NaCl–NaOH, or (c) KCl–KOH 72 aqueous solution (pH 12). Unpolarized white light was used as a light 73 source. (d) Absorption spectra of single aggregates in (a), (b), and (c).

74 We investigated the effects of alkali metal ion concen- 75 tration at pH 12. The interfacial aggregates were not formed 76 at 0.25, 0.30, 0.50, and 0.75 mol L⁻¹, but they were formed at 77 1.0 and 2.0 mol L⁻¹ for Li⁺, Na⁺, and K⁺. These facts support 78 the equilibrium shown in Figure 1 and the formation of TPP- 79 COO⁻M⁺ at the interface. Such high concentrations of alkali 80 metal ions are essential to reduce the electrostatic repulsion 81 between TPPCOO⁻ at the interface. Instead of alkali metal 82 ions, Mg²⁺, Ca²⁺, or Ba²⁺ was used, but no aggregates were 83 observed (Section S4 in SI).

84 In order to obtain the absorption spectra of the single 85 interfacial aggregates, the intensities of the light passing 86 through two areas indicated by the solid circle (I) and the dotted 87 circle (I_0) in Figures 3a-c were measured by the spectro- 88 photometer with unpolarized white light. The solid circles 89 represent the area with one aggregate and the dotted circles 90 represent the area without aggregates. Absorbance (A) values 91 were calculated with Eq. (1) and the absorption spectra are

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

$$4 A = -\log \frac{I}{I_0} \quad (1)$$

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 equivalent
10 transition dipole moments for absorption in the porphyrin-ring at the Soret band.^{24,25} Therefore, two new absorption
11 bands, blue-shifted H-band and red-shifted J-band, appear
12 simultaneously when porphyrins have a strong mutual interaction.^{20,25,26} In the present case, the interfacial TPPCOO^-M^+
13 shows only one absorption at the Soret band in Figure 3d,
14 suggesting that the interfacial TPPCOO^-M^+ do not have a
15 strong mutual interaction. This can also be understood from
16 the fact that the λ_{\max} of the Soret band of the interfacial TPPCOO^-M^+
17 is close to that of TPPCOO^- in the aqueous phase.
18

19 Figures 4 and 5 show microscope images of the interfacial
20 aggregates with monochromatic polarized light as a function
21 of polarization direction. The brightness of the needle-like
22 aggregates changes uniformly depending on the polarization
23 direction in all cases, indicating that all the TPPCOO^-M^+
24 constituting one interfacial aggregate are oriented in one
25 direction, like a two-dimensional crystal. Since the light absorption
26 is expressed with the transition dipole moments for
27 absorption (vector μ), we can discuss the orientation of TPPCOO^-M^+
28 of the interfacial aggregates. The transition possibility (p) for absorption is expressed as:¹⁵

$$31 p \propto |\mu \cdot E|^2 = |\mu|^2 |E|^2 \cos^2 \theta \quad (2)$$

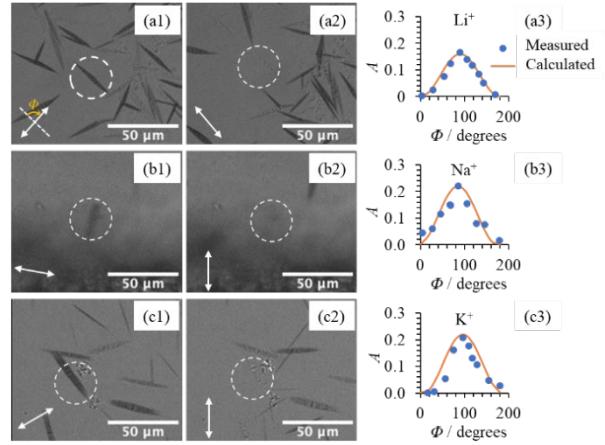
32 where E is the electric field vector of the incident light and θ
33 is the angle between μ and E .

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). Figures
38 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 polarization
40 direction. Positive Φ indicates clockwise direction. The dependences
41 are well fit with Eq. (2), meaning that one μ of TPPCOO^-M^+ of the aggregate was observed. The maxima at $\Phi \approx 90^\circ$ ($92^\circ \pm 5^\circ$, $83^\circ \pm 10^\circ$, and $97^\circ \pm 10^\circ$ for Li^+ , Na^+ ,
42 and K^+ , respectively, mean \pm confidence interval with 95%
43 confidence level) indicate that the μ direction is almost per-
44 pendicular to the major axis of the aggregate. We call these
45 aggregates type S.

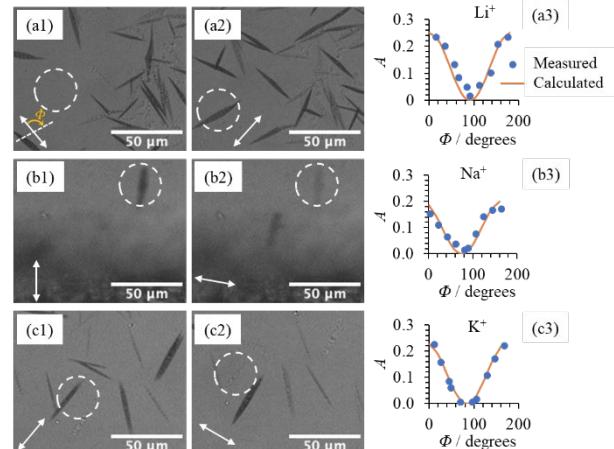
46 Figures 5(a3,b3,c3) also show the absorbance dependence
47 of one aggregate on Φ . In these cases, the maxima exist
48 at $\Phi \approx 0^\circ$ ($9^\circ \pm 7^\circ$, $-17^\circ \pm 6^\circ$, and $-5^\circ \pm 3^\circ$ for Li^+ , Na^+ , and
49 K^+ , respectively), indicating that the μ direction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

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

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



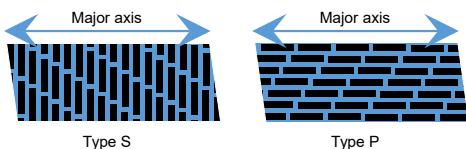
61 **Figure 4.** Microscope images of needle-like aggregates at the interface
62 at 30 min after preparation. (a1,a2) 1.0 mol L⁻¹ LiCl–LiOH; (b1,b2) 1.0
63 mol L⁻¹ NaCl–NaOH; (c1,c2) 1.0 mol L⁻¹ KCl–KOH. TPPCOOH, 3.0×10^{-7} mol L⁻¹. Polarized light at 451 nm was used as the light source. Double
64 arrows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

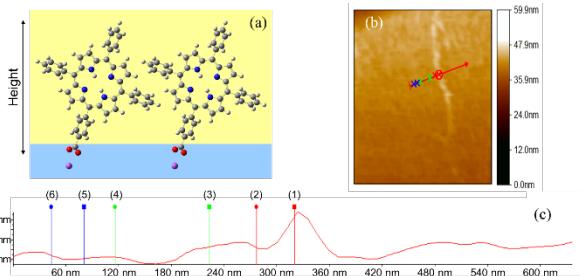
74 As mentioned above, porphyrins have two orthogonal
75 and almost equivalent μ at the Soret band. If the porphyrin-
76 ring lies parallel to the interface, the two μ should be ob-
77 served under the present experimental conditions. In fact,
78 only one μ was observed, which means that the porphyrin-
79 ring stands perpendicular to the interface, as shown in Figure
80 6. The porphyrin-ring of TPPCOO^-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

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



12 **Figure 6.** Partial microstructures of the interfacial type S and P aggre-
 13 gatest of TPPCOO-M⁺ (top view). The black rectangles represent the por-
 14 phyrin-ring of TPPCOO-M⁺ standing at the interface.

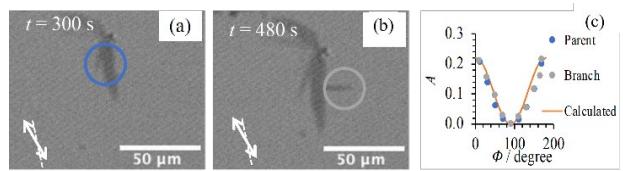
15 Using the A_{\max} values in Figures 4 and 5, the interfacial
 16 concentration (Γ) of TPPCOO-M⁺ was calculated with the
 17 modified Lambert-Beer's law, $A_{\max} = \varepsilon_1 \Gamma$ ^{15,27} where ε_1 is the
 18 molar absorption coefficient for light polarized parallel to one
 19 μ . The ε_1 value of TPPCOO-M⁺ was estimated to be $6.62 \times$
 20 $10^4 \text{ mol}^{-1} \text{ m}^2$ (Section S7 in SI), and the Γ values were calcu-
 21 lated to be 3.5, 3.3, and $3.5 \times 10^{-6} \text{ mol m}^{-2}$ for Li⁺, Na⁺, and
 22 K⁺, respectively. To compare the Γ values, the chemical
 23 structures of two TPPCOO-Na⁺ in vacuo and water were opti-
 24 mized with B97D/6-31G by Gaussian 09W²⁸ (Section S8 in
 25 SI). When the interfacial TPPCOO⁻ is tilted at about 20° from
 26 90°, as shown in Figure 7a, the neighboring phenyl-groups do
 27 not overlap, and the height, width, and thickness of TPPCOO⁻
 28 were estimated to be 2.0₃, 1.4₇, and 0.36 nm, respectively.
 29 The cross-section is 0.529 nm² (= 1.4₇ nm × 0.36 nm). When
 30 a close-packed TPPCOO⁻ monolayer is formed, the Γ
 31 value is calculated to be $3.19 \times 10^{-6} \text{ mol m}^{-2}$, which is approx-
 32 imately in agreement with the experimental values.



33 **Figure 7.** (a) Interfacial TPPCOO-M⁺ estimated based on the
 34 experimental results and DFT calculation with Gaussian 09W. (b) An AFM
 35 image of one TPPCOO-K⁺ aggregate transferred to a silicon substrate (1
 36 × 1 μm). The experimental conditions were the same as in Figure 4c. (c)
 37 The height profile along the red line in (b).

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

43 parent major axis. The length of the parent and the branch
 44 increased with time and Figure 8b was obtained. From Figure
 45 8b, the absorbance dependences of the parent and the branch
 46 on Φ were obtained in a similar way (Figure 8c), where Φ
 47 was the angle between the polarization direction and the parent
 48 major axis. The parent and branch major axes are almost
 49 perpendicular, but the absorbance dependences are almost
 50 identical. This fact means that the orientation directions of
 51 TPPCOO-M⁺ are the same and only the direction of growth
 52 is different. This relationship is the same as that between the
 53 types S and P. In other words, the parent and the branch parts
 54 correspond to the types P and S, respectively. If there is a
 55 trigger, only the direction of growth changes, without change
 56 in the orientation direction of TPPCOO-M⁺. As for the trigger,
 57 some consideration is given in Section S6 in SI.



58 **Figure 8.** Microscope images of a branched aggregate at the interface at
 59 (a) 300 s and (b) 480 s after preparation with polarized light at 451 nm.
 60 (c) Absorbances of the parent and the branch parts as a function of Φ ,
 61 which is the angle between the polarization direction and the parent ma-
 62 jor axis. The line corresponds to the fitting curve of Eq. (2). The experi-
 63 mental conditions were the same as in Figure 4c.

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

76 In conclusion, we confirmed that TPPCOO-M⁺ formed
 77 ordered needle-like monolayered aggregates at the tolu-
 78 ene/water interface by two independent analytical methods,
 79 in situ microspectroscopy and AFM. Furthermore, the chem-
 80 ical structure of the interfacial TPPCOO-M⁺ was estimated
 81 based on the experimental results and DFT calculation
 82 (B97D/6-31G) with Gaussian. Most studies of liquid/liquid
 83 interfaces have been based on the interfacial tension (or
 84 the interfacial pressure). However, when the heterogeneous
 85 adsorption of substances occurs, as in the present study, it is
 86 difficult to know the nature of the interfacial substances only
 87 by the interfacial tension. In the future, it is expected that the
 88 microstructure of more interfacial substances will be eluci-
 89 dated by combining various analytical methods.

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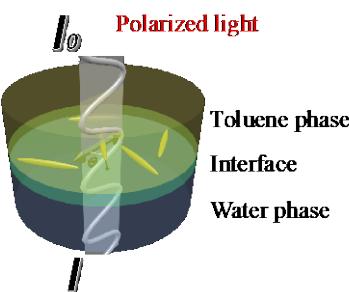
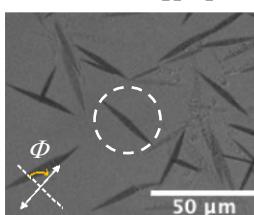
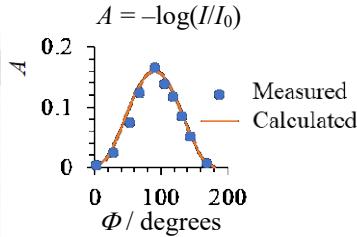
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You are requested to put a brief abstract (50-60words, one paragraph style) with the graphical abstract you provided, so that readers can easily understand what the graphic shows.

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 ($\text{TPPCOO}^-\text{M}^+$, $\text{M}^+ = \text{Li}^+$, 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 $\text{TPPCOO}^-\text{M}^+$ 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 Avienda Gusman and Satoshi Tsukahara	
Graphical Information		
 <p>Polarized light Toluene phase Interface Water phase</p>	 <p>TPPCOO-M⁺ Aggregates</p>	 <p>$A = -\log(I/I_0)$</p> <p>Measured Calculated</p> <p>$\Phi / \text{degrees}$</p>
<p>Polarized light absorption dependence of interfacial TPPCOO-M⁺ aggregates</p>		

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