Effect of Adding Lecithin and Nonionic Surfactant on α-Gels Based on a Cationic Surfactant-Fatty Alcohol Mixture

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Abstract: α-Gels are often used as base materials for cosmetics and hair conditioners. α-Gel–based commercial products typically contain many types of additives, such as polymers, electrolytes, oily components, and other surfactants, in addition to the three basic components. However, few systematic studies have been conducted on the effect of such additives on α-gels. In this study, we chose surfactant as an example to initiate the effect of such additives on the structure and rheological properties of α-gel samples formulated using cetyl alcohol (C₁₆OH) and cetyltrimethylammonium chloride (CTAC). Optical microscopy analysis demonstrated that the size of the vesicles in the α-gel samples in this study was decreased via the addition of hydrogenated soybean lecithin (HSL) and penta(oxyethylene) cetyl ether (C₁₆EO₅), a nonionic surfactant, to them. Rheological measurements revealed that at high C₁₆OH/CTAC ratios, the viscosity and yield stress of the α-gel samples decreased owing to the addition of surfactants to them. Conversely, at low C₁₆OH/CTAC ratios, the opposite tendency was observed. Small-angle X-ray scattering analysis indicated that for the α-gel samples with high C₁₆OH/CTAC ratios, the addition of HSL or C₁₆EO₅ to them decreased the interlayer spacing of their lamellar bilayer stack, which led to the changes in the rheological properties of the α-gel samples.

Key words: α-gel, bilayer structure, rheological property, surfactant self-assembly

1 Introduction

When higher alcohols, such as stearyl and cetyl alcohols, are hydrated, they form α-type hydrated crystals with hexagonal subcell structure and long-period lamellar bilayer structure.¹ When an ionic or a nonionic surfactant is mixed with a higher alcohol, the α-type hydrated crystal retains a large amount of water owing to the electrostatic repulsion between its lamellar bilayers.² When excess water is added to the α-type hydrated crystal, an "α-gel" that contains a large amount of water in the bilayer network is formed.³ α-Gels are self-standing at rest, but their fluidity increases under shear, which is a beneficial feature for cosmetic and pharmaceutical formulations. α-Gels formulated with alkyl quaternary ammonium salts and higher alcohols are commonly used for hair conditioners.⁴ The small-angle X-ray scattering (SAXS) profiles of α-gels are similar to those of lyotropic lamellar liquid crystals, and present a series of Bragg peaks, which are attributed to their lamellar structure.⁵ Conversely, the wide-angle X-ray scattering (WAXS) profiles of α-gels are different from those of lyotropic lamellar liquid crystals, for which the hydrophobic part is in liquid state, which present a sharp peak at q = 15 nm⁻¹ (q is the absolute value of the scattering vector). This is attributed to the hexagonal subcell structure of the α-type hydrated crystals, which is the same as that of the α-type crystals of fats and lipids.⁶ Furthermore, the structure and properties of α-gels have been investigated using methods, such as thermal analysis⁷, electron microscopy⁸, and rheological measurements.⁹ Watanabe et al. evaluated the state of the water molecules retained between the lamellar bilayers and in the bulk aqueous phase using a combination of self-diffusion nuclear magnetic resonance (NMR) and SAXS measurements.¹⁰ Sakai et al. analyzed the effects of tempera-
ture and shear on the structure of α-gels using SAXS, small-angle neutron scattering, and NMR spin–spin relaxation measurements\(^{19}\). In addition to surfactant-higher alcohol systems, α-gels were obtained using surfactants such as linear monoalkyl phosphoric acid and L-arginine\(^{19}\) or mono-(or poly-)-glyceryl alkyl ethers\(^{20}\).

Most studies on α-gels have focused on simple water-surfactant-higher alcohol ternary systems. However, the α-gels used in commercial products, such as hair conditioners, contain many types of additives, such as polymers, electrolytes, oily components, and other surfactants, in addition to the three basic components. The effects of additives on α-hydrated crystals and α-gels is not well understood. Therefore, we studied the effect of the addition of hydrogenated soybean lecithin (HSL) and penta(oxyethylene) cetyl ether (C\(_{16}\)EO\(_{5}\)), which can be used for cosmetic formulation, to α-gel samples formulated using a mixture of cetyltrimethylammonium chloride (CTAC), a cationic surfactant, and cetyl alcohol (C\(_{16}\)OH), a higher alcohol, to elucidate the effects of additives on the structure of the α-type hydrated crystals and viscoelastic properties of the α-gels.

2 Experimental

2.1 Materials

CTAC (>99.0% purity) was purchased from Kanto Chemical Co., Inc. (Japan), C\(_{16}\)OH (98.0% purity) was acquired from Tokyo Chemical Industry Co., Ltd. (Japan), C\(_{16}\)EO\(_{5}\) was supplied by Nihon Emulsion Co., Ltd. (Japan), C\(_{16}\)SarNa was procured from YMC Ingrid Co., (Japan). No specific information of chemical contents and compositions are provided. Sodium palmitoylsarcosinate (C\(_{16}\)SarNa) was obtained from Nippon Surfactant Co., Ltd. (Japan), and sodium palmitate (C\(_{16}\)COONa, >97.0% purity) was attained from Tokyo Kasei Kogyo Co., Ltd. (Japan). All chemicals were used as received, without further purification. Deionized water was prepared using an Elix3 (Nihon Millipore, Japan) water purification system and was used for all experiments.

2.2 Sample preparation

Predetermined amounts of reagents were added to a screw cap test tube, which was subsequently heated at 95°C. Afterward, the content of the test tube was stirred and mixed using a vortex mixer to prepare the samples. All the samples were kept in an incubator at 25°C for a week. Table 1 lists all samples analyzed in this study.

2.3 Optical microscopy

Polarized light optical microscopy observations were performed using a CX31-P (Olympus, Japan) differential interference microscope in the temperature range 15–30°C.

2.4 Cryogenic scanning electron microscopy (cryo-SEM)

A JSM-7800(JEOL, Japan) Schottky field emission scanning electron microscope with an Alto 2500 (Gatan, UK) cryo transfer system was used for cryo-SEM analysis. The samples were snap frozen and were analyzed after etching their fractured surface.

2.5 SAXS and WAXS measurements

A SAXSess (Anton Paar, Austria) SAXS and WAXS camera was used to analyze the prepared samples. The X-rays (Cu Kα, λ = 0.1542 nm) employed to irradiate the samples were generated utilizing a sealed glass X-ray tube and were collimated using a block optical system. A glass capillary sample cell (sample thickness of 1 mm) was used as sample cell, and the scattered X-rays were detected using an image plate. The image plate was analyzed using a Cyclone (Perkin Elmer, USA) imager, and the one-dimensional spectra of the samples were obtained using the SAXSQuatt (Anton Paar, Austria) software. The measurements were performed at the X-ray generator voltage and current of 40 kV and 50 mA, respectively, and at the X-ray irradiation time of 10 min.

2.6 Differential scanning calorimetry (DSC)

A DSC6200 (SII Nano Technology, Japan) heat flux-type DSC instrument was used for the DSC experiments. We weighed 8–12 mg of samples and sealed them in alodined alumina sample pans. Air (empty sample pan) was used as reference. DSC thermograms were recorded from −50°C to 100°C with 5°C min\(^{-1}\) of the temperature ramp.

2.7 Rheological measurements

Dynamic viscoelasticity measurements were performed utilizing the strain control method using a combination of cone (diameter of 40 mm) and plate geometries. To measure the yield stress, the angular velocity (ω) was set at 10 rad s\(^{-1}\) and the storage modulus (G') was measured at an oscillating stress in the range 0.1–1000 Pa. The strain at the elastic-to-viscous transition point was determined and was used to measure G' and the loss modulus (G'\(^{\prime}\)) at ω in the range 0.01–1000 rad s\(^{-1}\).

3 Results and Discussion

3.1 Gelation testing

The appearances of the samples are illustrated in Table 2 and Fig. S1. Samples that did not flow when the test tubes containing them were tilted were considered gelled samples (α-gel samples). Samples A-1–A-4, which presented different CTAC and C\(_{16}\)OH contents were all gelled. Surfactants were added to the basic CTAC-C\(_{16}\)OH samples to examine the effect of a second surfactant on the formation of α-gels, and the obtained samples were classified as
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Table 1  Composition of samples (by weight); here C₁₆OH, CTAC, HSL, C₁₆EO₅, C₁₆COONa, and C₁₆SarNa denote cetyl alcohol, cetyltrimethylammonium chloride, hydrogenated soybean lecithin, penta(oxyethylene)cetyl ether, sodium palmitate, and sodium palmitoylsarcosinate, respectively.

| Sample | A-1  | A-2  | A-3  | A-4  |
|--------|------|------|------|------|
| Water (wt.%) | 90   | 90   | 90   | 90   |
| C₁₆OH | 5    | 6    | 7    | 8    |
| CTAC  | 5    | 4    | 3    | 2    |
| C₁₆OH/CTAC (mol/mol) | 1.32 | 1.98 | 3.09 | 5.28 |

Table 2  Appearance of the prepared samples.

| Sample | A-1  | A-2  | A-3  | A-4  |
|--------|------|------|------|------|
| State  | Gel  | Gel  | Gel  | Gel  |
| Sample | B-1  | B-2  | B-3  | B-4  |
| State  | Sol  | Gel  | Gel  | Gel  |
| Sample | C-1  | C-2  | C-3  | C-4  |
| State  | Sol  | Gel  | Gel  | Gel  |
| Sample | D-1  | D-2  | D-3  | D-4  |
| State  | PS   | PS   | PS   | PS   |
| Sample | E-1  | E-2  | E-3  | E-4  |
| State  | PS   | PS   | PS   | PS   |

follows: samples B-1 and C-1 were fluid and could not be gelled, samples B-2–B-4 and C-2–C-4 were gelled, and the phases of samples D-1–D-4 and E-1–E-4 (which were anionic surfactant-added systems) separated. The anionic surfactants added to the basic CTAC-C₁₆OH samples formed complexes with CTAC, which is a cationic surfactant, and the complexes precipitated as solids. Moreover, as the C₁₆OH fraction increased, the amount of precipitated solid increased, which suggested that C₁₆OH crystals could have also formed.

3.2 Polarized light optical microscopy and cryo-SEM
Optical microscopy observations were conducted for all systems except for the anionic surfactant-added ones, and the results are depicted in Fig. 1. Maltese crosses were observed for all samples, and they indicated the formation of
multilayer vesicles in the size range of several micrometers to several tens of micrometers. When the samples with the same C16OH/CTAC ratios were compared, the vesicle size of the HSL- or C16EO5-added samples were smaller than those of the basic CTAC-C16OH samples. The reason for the size differences is unknown because vesicular aggregates should be formed by shear during agitating samples at a high temperature. The aggregate size could mainly be dependent on viscosity at the agitation temperature, which we do not have experimental data in this study.

**Figure 2** illustrates the cryo-SEM images of samples A-1, A-4, B-1, and B-4. For samples A-1 and B-1, the sheet-like structure formed complex networks and held a large amount of bulk water (the black gaps in Fig. 2). The cryo-SEM images in this study were similar to those reported for other α-gel systems, and we concluded that the sheet-like network consisted of a stack of bilayers. Furthermore, the samples presented partial vesicle-like structure, which was in agreement with the conclusions drawn from analyzing the optical micrographs of the samples. The network structures of samples A-4 and B-4 were more elaborate than those of the other samples and the vesicle-like structures of these samples were smaller than those of the other samples.

### 3.3 SAXS and WAXS

The structure of the α-gel samples was analyzed at 25°C using SAXS and WAXS measurements. **Figure 3** presents the plot of $q$ in the small-angle region with respect to the scattering intensity. **Table 3** lists the peak positions ($q_n$, where $n$ is the diffraction order) and interlayer spacings ($d_1$) calculated using $q_n$. The ratios of the peak positions of all samples were integral multiples, which confirmed that the samples presented lamellar structure.

The SAXS profiles of samples A-1, B-1, and C-1 contained higher-order peaks than the other samples; moreover, the peaks became sharper. These findings indicated that the higher the fraction of cationic surfactant in the samples, the higher the correlation between their $d_1$ values. In addition, the $d_1$ values of samples A-1, B-1, and C-1 were smaller than those of the other samples, which indicated that the amount of water retained between the bilayers of these samples was small due to small electrostatic repulsion. When the distance between the bilayers was small, the fluctuations of the bilayers were suppressed, and consequently, the bilayer stacks were highly regular.

The $d_1$ values of the samples with the same C16OH/CTAC ratio were compared, and it was concluded that the $d_1$ values of the HSL-added systems were smaller than those of the basic CTAC-C16OH systems. HSL is a mixture of anionic, cationic, and amphoteric phospholipids; however, the zeta potential of the liposomes formed by HSL in water was reported to be negative, and therefore, the average HSL charge is negative in water because of the contribution of an acidic phospholipid, phosphatidylinositol which is one of the main ingredients in a general soybean lecithin. In the present samples, pH of present α-gel samples is 4, indicating protonation of phospholipids. Hence, when HSL was incorporated into the C16OH-CTAC–based α-type crystal bilayers, the electrostatic repulsions between the bilayers was suppressed. Consequently, the $d_1$ values of the HSL-added systems were smaller than those of the basic CTAC-C16OH systems. The $d_1$ values of all C16EO5-added...
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Fig. 2  Cryo-SEM images of samples A-1, A-4, B-1, and B-4.

Fig. 3  SAXS profiles of samples A-1–A-4, B-1–B-4, and C-1–C-4 at 25°C.

Table 3  Interlayer spacings ($d_i$) and peak positions ($q_1$–$q_6$) of samples A-1–A-4, B-1–B-4, and C-1–C-4.

|     | $d_i$/nm | $q_1$/nm$^{-1}$ | $q_2$/nm$^{-1}$ | $q_3$/nm$^{-1}$ | $q_4$/nm$^{-1}$ | $q_5$/nm$^{-1}$ | $q_6$/nm$^{-1}$ |
|-----|----------|----------------|----------------|----------------|----------------|----------------|----------------|
| A-1 | 24.1     | 0.261          | 0.528          | 0.789          | 1.06           | 1.32           | 1.60           |
| B-1 | 22.9     | 0.274          | 0.554          | 0.841          | 1.12           | 1.40           | 1.68           |
| C-1 | 19.3     | 0.326          | 0.646          | 0.978          | 1.30           | 1.62           | 1.95           |
| A-2 | 40.0     | 0.157          | 0.313          | 0.463          |               |               |               |
| B-2 | 35.7     | 0.176          | 0.346          | 0.535          |               |               |               |
| C-2 | 35.7     | 0.176          | 0.352          | 0.528          | 0.887          | 1.06           | 1.21           |
| A-3 | 38.5     | 0.163          | 0.339          |               |               |               |               |
| B-3 | 34.3     | 0.183          | 0.378          |               |               |               |               |
| C-3 | 38.5     | 0.163          | 0.339          | 0.509          | 0.678          |               |               |
| A-4 | 43.9     | 0.143          | 0.287          |               |               |               |               |
| B-4 | 34.3     | 0.183          | 0.352          | 0.541          |               |               |               |
| C-4 | 40.0     | 0.157          | 0.313          | 0.470          | 0.626          | 0.783          |               |
systems, except for sample C-3 were smaller than those of the basic CTAC-C_{16}OH samples. The oligo-oxyethylene groups of C_{16}EO_5 neighboring CTAC reduce hydration of CTA^+ anion, which prevented the dissociation of the cat-
ionic groups and reduced the electrostatic repulsions.

Figure 4 presents the WAXS profiles of samples A-1–A-4, B-1–B-4, and C-1–C-4. A sharp peak at q = 15 nm^{-1} was ob-
served in the profiles of all the analyzed samples. The lattice constant of the subcell(2D-hexagonal) in the α-type
hydrated crystal in surfactants, lipids and alcohol-surfact-
tant mixtures are usually around 0.41-0.42 nm. Therefore,
the present WAXS results indicate the existence of α-type
hydrated crystal, which support the gel samples are α-gels.

3.4 DSC measurements

Figure 5 presents the results of the DSC measurements
of samples A-1–A-4, B-1–B-4, and C-1–C-4, and Table 4
summarizes the endothermic peak temperatures of the
samples. The endothermic peak temperature in the range
55–65°C should indicate the melting of the α-type crystals
because the melting temperatures of the CTAC and C_{16}OH
hydrated crystals are 1122 and 47°C11, respectively. For all
the analyzed systems, the endothermic peak temperature
increased as the C_{16}OH/CTAC ratio increased, and became
to a sharper peak. The endothermic peak temperature increased with the addition of HSL and decreased with the
addition of C_{16}EO_5 to the basic CTAC-C_{16}OH samples.

However, the transition enthalpy increased with the addition
of either surfactant to the basic CTAC-C_{16}OH samples. Note
that the peak sharpness increased as the C_{16}OH
content increases, suggesting the increase in crystallinity
in the α-type crystal.

|       | T / °C | ΔH / J · g^{-1} |
|-------|-------|----------------|
| A-1   | 54.5  | 18.0           |
| B-1   | 55.5  | 19.8           |
| C-1   | 54.7  | 28.9           |
| A-2   | 59.4  | 48.1           |
| B-2   | 60.3  | 89.9           |
| C-2   | 58.9  | 76.1           |
| A-3   | 62.7  | 68.5           |
| B-3   | 63.4  | 58.1           |
| C-3   | 59.7  | 44.6           |
| A-4   | 62.9  | 24.7           |
| B-4   | 64.0  | 40.9           |
| C-4   | 60.5  | 54.9           |

Fig. 4 Wide-angle X-ray scattering profiles of samples A-1–A-4, B-1–B-4, and C-1–C-4 at 25°C.

Fig. 5 Differential scanning calorimetry thermograms of samples A-1–A-4, B-1–B-4, and C-1–C-4.
3.5 Rheological measurements

Samples A-1–A-4, B-1–B-4, and C-2–C-4 were subjected to dynamic viscoelasticity measurements, and the results are presented in Fig. 6. The rheological properties indicated that all samples presented elastic properties because \( G' > G'' \) for all samples regardless of \( \omega \). However, \( G' \) and \( G'' \) gradually increased with increasing \( \omega \); furthermore, \( G' \) and \( G'' \) came closer in the low frequency region for some samples. Therefore, the \( \alpha \)-gel samples presented gel characteristics, but were relatively weak gels. For samples A-1–A-4, the overall \( G' \) and \( G'' \) values increased as the C16OH/CTAC ratio increased. The same tendency was observed for the HSL- and C16EO5-added systems. Focusing on the effect of the addition of a surfactant, for example, in comparison of A-2, B-2, and C-2, addition of HSL increased \( G' \) and \( G'' \), but the addition of C16EO5, a nonionic surfactant, had the opposite effect. However, at higher C16OH/CTAC ratios, \( G' \) and \( G'' \) did not decrease when C16EO5 was added to the basic CTAC-C16OH samples.

The absolute values of the complex viscosity \( |\eta^*| \), which were calculated using Equation (1), were plotted against \( \omega \) (Fig. 7).

\[
|\eta^*| = \frac{G'^2 + G''^2}{\omega} 
\]

The results indicated that shear thinning decreased according to the power law with the increase in \( \omega \). Although sample A-1 was designated to be an \( \alpha \)-gel (Table 2), its viscosity was approximatively one order of magnitude lower than those of samples A-2–A-4. Similar, for the HSL- and C16EO5-added systems, the viscosities of the samples with small C16OH/CTAC ratios were lower than those of the other samples. The most optimal higher alcohol/surfactant molar ratio for industrial \( \alpha \)-gel formulations is 3:1. As presented in Table 1, the C16OH/CTAC ratios of samples A-3, B-3, and C-3 were close to 3:1. Therefore, the viscosity of the \( \alpha \)-gel decreased as the C16OH/CTAC ratio decreased because the stability of the crystal structure decreased. Furthermore, the viscosity of sample B-2, which contained HSL, was higher than that of sample A-2, and that of sample C-2, which contained C16EO5, was lower than that of sample A-2. However, at high C16OH/CTAC ratios, the effect of the addition of C16EO5, a nonionic surfactant, to the basic CTAC-C16OH samples on viscosity was weakened.

\( G' \) was measured as a function of the stress at a constant \( \omega \) of 10 rad \( \cdot \) s\(^{-1} \), and the results are presented in Fig. 8. \( G' \) was constant in the low stress region and decreased sharply above a certain stress value. Comparing the yield stresses indicated by the arrows in Fig. 8, the yield stress of sample A-1 was smaller than those of the other basic CTAC-C16OH samples; however, the differences in the yield

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**Fig. 6**  Storage moduli \( G' \) (solid circles) and loss moduli \( G'' \) (open circles) of samples A-1–A-4, B-1–B-4, and C-2–C-4 at 25°C.
stresses of samples A-2, A-3, and A-4 were negligible. The same tendency was observed for the HSL- and C\textsubscript{16}EO\textsubscript{5}-added systems. As observed for the complex viscosity, the effect of the addition of a surfactant on the yield stress of the \(\alpha\)-gel samples was also dependent on the C\textsubscript{16}OH/CTAC ratio of the \(\alpha\)-gel samples.

As illustrated in Table 3, \(d_1\) of the \(\alpha\)-type crystals decreased when either surfactant was added to the basic CTAC-C\textsubscript{16}OH samples. This indicated that the water retained between the bilayer membranes was drained owing to the addition of the surfactant, and the amount of bulk water in the \(\alpha\)-type crystalline networks increased; viz., the gel network density of the \(\alpha\)-gel decreased. In addition, the surfactant (HSL or C\textsubscript{16}EO\textsubscript{5}) addition in the CTAC-C\textsubscript{16}OH \(\alpha\)-gel should lead the decrease in the Debye length around the bilayers since the mixing of HSL with a net negative charge (mentioned in Section 3.3) and non-charged C\textsubscript{16}EO\textsubscript{5} compensates or dilutes the positive charges of CTAC in bilayer. Therefore, the decrease in gel network density and Debye length could cause the decrease in viscosity and could explain the differences in viscosity between samples A-1 and B-1 or A-2 and C-2, but could not account for the increase in viscosity. To explain the increase in viscosity at higher C\textsubscript{16}OH/CTAC ratios, it was assumed that the rigidity of the bilayer membrane increased owing to the addition of surfactants, which caused the mechanical strength of the network to increase. However, the confirmation of such mechanisms using the experimental results of this study was not possible, and further studies would be necessary.

![Figure 7](image-url) Complex viscosity \(|\eta^*|\) dependence of angular velocity \(\omega\) of samples A-1–A-4, B-1–B-4, and C-2–C-4 at 25°C.

![Figure 8](image-url) Dependence of the storage moduli \(G'\) of samples A-1–A-4, B-1–B-4, and C-2–C-4 on the oscillating stress at an angular velocity of 10 rad·s\(^{-1}\) at 25°C.
4 Conclusion

We studied the effect of the addition of surfactants on the formulation, structure, and rheological properties of α-gel samples formulated using C16OH and CTAC. We added four surfactants to the basic CTAC-C16OH samples: HSL, C16EO5, which is a nonionic surfactant, and C16COONa and C8SarNa, which are anionic surfactants. The anionic surfactants destroyed the α-gel. The effect of the addition of surfactants on the size of vesicles of the basic CTAC-C16OH samples was confirmed. The effect of the addition of HSL and C16SarNa to the basic CTAC-C16OH samples on their rheological properties was not straightforward but depended on the C16OH/CTAC mass ratio. When the C16OH/CTAC mass ratio was small, the viscosity and yield stress decreased with the addition of HSL and C16SarNa, and the opposite tendency was observed when the C16OH/CTAC mass ratio was large. The reason for the dependence of the viscosity and yield stress on the C16OH/CTAC ratio could be ascribed to the simultaneous effect of two or more factors, and the contribution of each factor depended on the C16OH/CTAC ratio. One reason for the decrease in viscosity or yield stress was elucidated using our experimental results. The SAXS profiles of the samples revealed that the addition of HSL or C16SarNa to the α-gel samples reduced the interlayer spacing of the α-crystalline structure. Consequently, the water between the bilayers was squeezed out and the amount of bulk water in the gel network increased, which led to the viscosity and yield stress of the HSL- and C16SarNa-added samples being lower than those of the basic CTAC-C16OH samples. Another factor to be considered would be the increase in the mechanical strength of the gel network caused by the addition of surfactant, which could shift the mechanical properties of the α-gel samples in the opposite direction. However, we were unable to draw any conclusions to confirm the effect of this factor, and further studies should be conducted.

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Supporting Information

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