

## Interfacial Molecular Structure of LB Films of Fatty Acids Studied by *in-situ* Sum Frequency Generation (SFG) Spectroscopy

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The *Langmuir-Blodgett* (LB) technique is an important fabrication methods for solid surfaces using ordered ultra thin organic film and has been widely applied in the studies of molecular electronics, nonlinear materials, and biosensors.<sup>1</sup> Although the bulk structures of LB films have been extensively investigated, a number of issues about their surface molecular structures are still not clear. Sum frequency generation (SFG) is an intrinsically interface sensitive vibrational spectroscopy technique<sup>2</sup> and has been applied to explore the interfacial structures of the LB films of fatty acids both in air and in solution.<sup>3-5</sup>

In the present study, the interfacial molecular structures of LB films of stearic acid on the hydrophilic solid substrates have been characterized by SFG measurements both in air and in buffer solution.<sup>3,4</sup> The *in situ* SFG measurements clearly demonstrate that  $\text{Cd}^{2+}$  cations can induce an interfacial structural change of the stearic acid LB films. On the basis of the SFG measurements using the combination of hydrogenated (H) and deuterated stearic acid (D) molecules, the reorganization mechanism by the  $\text{Cd}^{2+}$  cation is discussed in detail.<sup>4</sup>

Figure 1(Left panel) shows a series of *in situ* SFG spectra of the DH bilayer on a fused quartz surface for different immersion periods in a buffer solution (pH=6.6) containing  $\text{Cd}^{2+}$ . As shown in Fig. 1a, only two intense peaks were observed, which can be attributed to the C-H stretching modes of terminal  $\text{CH}_3$  group in the top layer H, indicating that a well-ordered H layer was formed as a second layer at the initial stage. However, intensities of these two peaks became weaker with increasing immersion time in the solution (Figs. 1a-e: left). After 5 hr. immersion, peak intensities decreased to ca. one third of its original values (Fig. 1e), suggesting that the structure of the top layer (H) of the stearic acid DH bilayer considerably changed during the immersion process in the subphase solution. On the other hand, intensities of the SFG peaks were almost the same with increasing immersion time in the same solution but without  $\text{Cd}^{2+}$  cation during 4.5 hr. (Figs. 1f-j: right).

A schematic model (Fig. 2) is proposed to explain the structural change at the outermost-layer of the LB films of stearic acid induced by the  $\text{Cd}^{2+}$  cation.<sup>4</sup> When the even-layered LB film was deposited on the hydrophilic substrate surface, an ideal bilayer structure is formed in the initial stage. This bilayer structure is stabilized both by the hydrophobic interaction between the long alkyl tails and by the hydrophilic interaction between the water molecules and carboxylate headgroup. However, the stabilization interaction will be even higher by the strong electrostatic interaction between the carboxylate headgroup via the divalent  $\text{Cd}^{2+}$  cation, which can form a stable chelating structure ( $\text{COO}^-:\text{Cd}^{2+}:\text{COO}^-$ ). To reach an energetically stable state, the topmost-layer of the LB film is flipped over to form a new bilayer structure. The present results strongly suggest the extremely important role of the  $\text{Cd}^{2+}$  ion in the reorganization process of the

LB films of stearic acid on the solid surface.<sup>4</sup>

A detailed recent results using different divalent metal cations will be also given in the presentation.

### References

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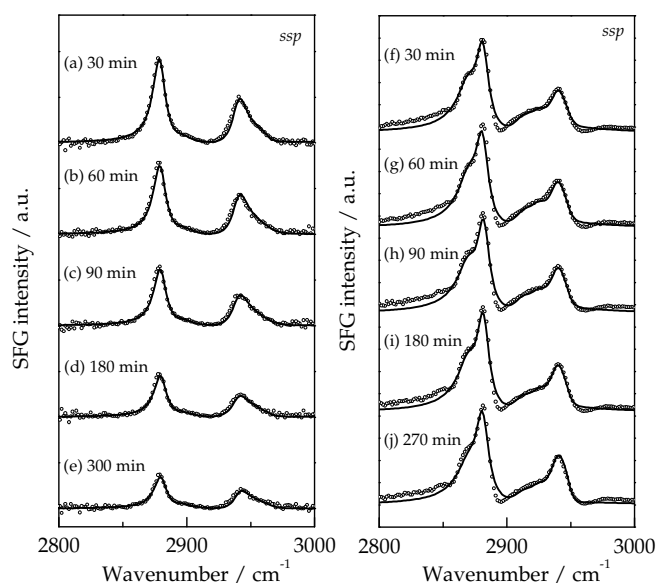


Fig 1. *In situ* SFG spectra of LB films on a fused quartz surface of DH bilayer in 0.3 mM  $\text{NaHCO}_3$  with 0.2 mM  $\text{Cd}^{2+}$  cation (Left panel) and in 0.3 mM  $\text{NaHCO}_3$  without 0.2 mM  $\text{Cd}^{2+}$  cation (Right panel) for different immersion periods. The polarization combination is s-SFG, s-visible, and p-infrared.

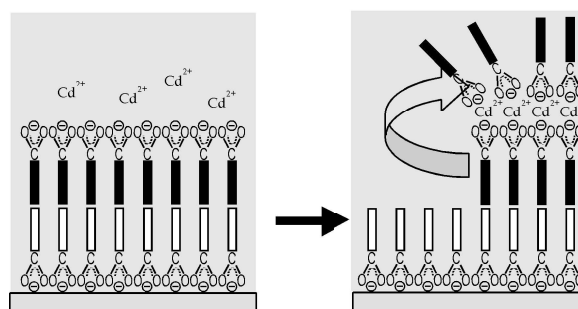


Fig 2. Proposed model for the interfacial structural change at the outermost-layer of even-numbered LB films of stearic acid in the subphase containing  $\text{Cd}^{2+}$ .