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低濃度オゾン中における脂質単分子膜の構造と安定性

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Structure and Stability Studies of Mixed Monolayers of Saturated and Unsaturated Phospholipids under Low-level Ozone

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1. Introduction

Cell membranes play crucial roles in the functionality of cells such as mass transport, metabolism, information exchange, and energy conversion. The phospholipid bilayer, containing both saturated and unsaturated phospholipids, constructs the main frame structure for the cell membrane. The functionality of the membranes could be significantly affected by the stability of lipids, especially in an environment contaminated by oxidants such as ozone.[1,2] The concentration of ozone at the earth surface of troposphere are usually few tens of *ppb*, mainly formed upon photochemical reaction of nitrogen oxide (NO_x) and violated organic compounds (VOC) with UV light.[3] However, the influence of ozone on the lipid molecules have been mainly investigated in high concentration range (0.3 ~ 10 *ppm*) in the previous experiments.[1,2] In the present study, the structure and stability of lipid monolayer with both saturated and unsaturated lipids in *low concentration* of ozone (~20 ppb) have been explored by π-A isotherm, atomic force microscopy (AFM) and sum frequency generation (SFG) vibrational spectrscopy.[4]

2. Results and Discussions

The single or binary mixed monolayers of an unsaturated lipid (DOPC) and a saturated lipid (DPPC-d_{75}) were made by LB method on the water surface (22℃) in a chamber under environment control. Figure 1 shows the changes in the surface area as a function of exposure time to N_2 (0 ~ 60 min) and low-level O_3 (60 ~200 min) at a surface pressure of 30 mN/m. All the monolayers are stable in the nitrogen environment and show only very small decreases in the initial

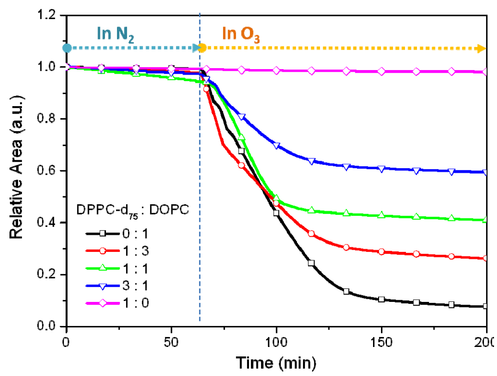

Figure 1. Stability of surface area for the DPPC-d_{75}/DOPC mixed monolayers at 30 mN/m exposed to N_2 (0~60 min) and O_3 (60~200 min).

60 min. However, when a small amount of ozone (~20 ppb) is introduced into the chamber, all the monolayers, except for the pure DPPC-d_{75}, show fast decays in the surface area, and become almost constant after a certain period (ca. 1 hr). The decrease in the surface area indicates the loss of molecules from the water surface and implies that DOPC or DOPC-contained monolayers are partially decomposed by the ozone exposure. Only a small surface area is remained for the pure DOPC monolayer. More surface area is remained with increase of DPPC-d_{75} in the mixed monolayer after exposure to O_3. The instability of the mixed monolayer seems to be related with the amount of the unsaturated DOPC in the monolayer. The origin for this is further investigated based on AFM and SFG observations.

SFG observations demonstrated that the DPPC-d_{75} monolayer construct a well-ordered structure and are stable in ozone. The pure DOPC monolayer showed a large amount of *gauche* defects in the monolayer and is unstable in ozone and most of the reaction products are dissolved in water to form micelle structure or evaporated into air, and only trace amount of oxidized phospholipid (oxPL) stay on the water surface (Fig. 2, upper). When the mixed monolayers were exposed to low-level ozone, DOPC molecules are also selectively oxidized but a small amount of DOPC is remained in the mixed monolayer (Fig. 2, lower), very different from the pure DOPC monolayer.[4] It is expected that the saturated DPPC components in the mixed monolayer can partially inhibit the ozone oxidation of unsaturated DOPC molecules. The *all-trans* hydrocarbon chains of DPPC can form a well-packed monolayer and are stable to ozone oxidation. On the other hand, by mixing with DPPC molecules, the packing density and orientation ordering of DOPC are largely improved and this can partially inhibit the ozone attack on the defect sites.

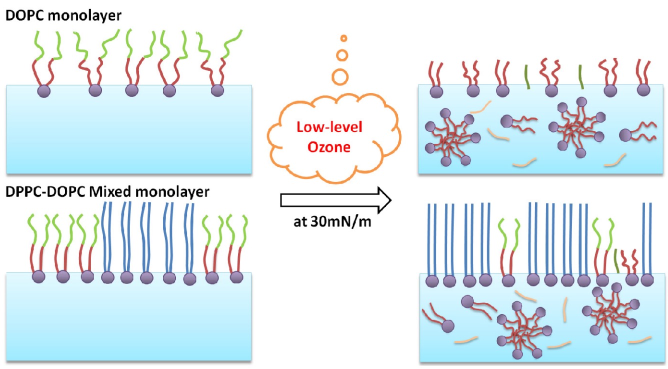

Figure 2. The schematic models for DOPC monolayer (upper) and DPPC-DOPC mixed monolayer (lower) on a water surface before (left) and after (right) exposure to a low-level ozone.

Detailed results and discussion will be given in the presentation.

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