Soft X-ray Polarization Measurements of Phospholipid Multilayers Supported on Hydrophilic Si Surfaces

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Lipid membranes supported on substrates are promising systems for use in biological sensing, biocompatibility, bioelectronics [1]. The idea that ordered lipid molecules can be prepared by several convenient methods, like freeze-thaw and spin-coating methods [2]. We also confirmed that the phospholipid multilayers made by simple dropping of acetone solution onto hydrophilic Si substrates under atmospheric pressure and moisture and room temperature conditions forms well-ordered multilamellar structures. But the quality of ordering as well as formation process of ordered lamellar structure during such a short period is not well understood.

X-ray absorption spectroscopy (XAS) is one of powerful tools to investigate local structural and dynamical information because of its element selectivity. Especially, one can easily get orientation structure around X-ray absorption center by using linearly polarized X-ray beam. In this study, polarization dependence of XAS measured for phospholipid multilayers supported on hydrophilic Si surfaces was investigated in order to quantify the orientation quality.

Measurements of near edge X-ray absorption fine structure (NEXAFS) have been performed at BL-13 of HiSOR, where is a soft X-ray beamline with a Dragon-type spherical grating monochromator developed to investigate soft X-ray spectroscopy for surface organic materials. During measurements, the experimental chamber had a base pressure less than 1×10^{-9} Torr. NEXAFS spectra around the C K-edge were recorded in total electron yield (TEY) mode by measuring a sample drain current by changing incident angle of synchrotron radiation. Polarization at BL-13 is horizontal due to bremsstrahlung from a bending magnet and the polarization factor P was determined to be 0.95 [3] by measuring azimuthal angle-dependent NEXAFS spectra of a highly oriented pyrolytic graphite (HOPG) [4].

DPPC and DOPC phospholipid molecules were used to form supported lipid membranes from 10 to 1000 multilayer by changing the dropping volume of lipid solution onto hydrophilic Si substrates, and moreover for getting the bilayer membranes, multilayers on substrates were considerably washed by immersing Milli-Q water. DPPC and DOPC molecules are shown in Fig. 1, consisting of a polar zwitterionic hydrophilic group and two non-polar carbon chains. So, molecules in aqueous solution form bilayers with the carbon chains facing each other due to hydrophobic interaction. It is understood that bilayers of DPPC with saturated carbon chains form crystalline-like gel phase at room temperature, while DOPC with unsaturated chains composes liquid crystalline phase. Fig. 2 shows typical polarization dependent NEXAFS spectra measured for (a) DPPC and (b) DOPC on Si surfaces at C K-edge. Although DPPC shows clear polarization dependence, the dependence of DOPC in not so dominant. Tendency of such polarization dependence does not depend on the layer number of lipids. So, the different degree of

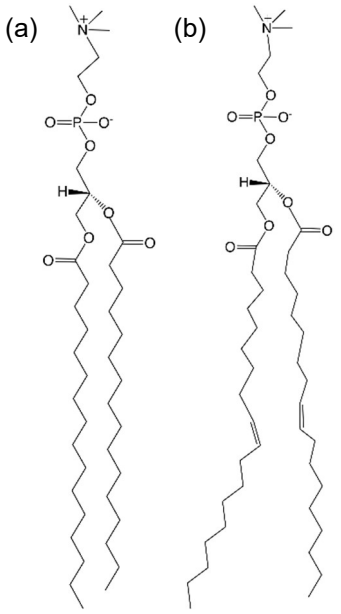

FIGURE 1. Molecular structures of phospholipids (a) DPPC and (b) DOPC.

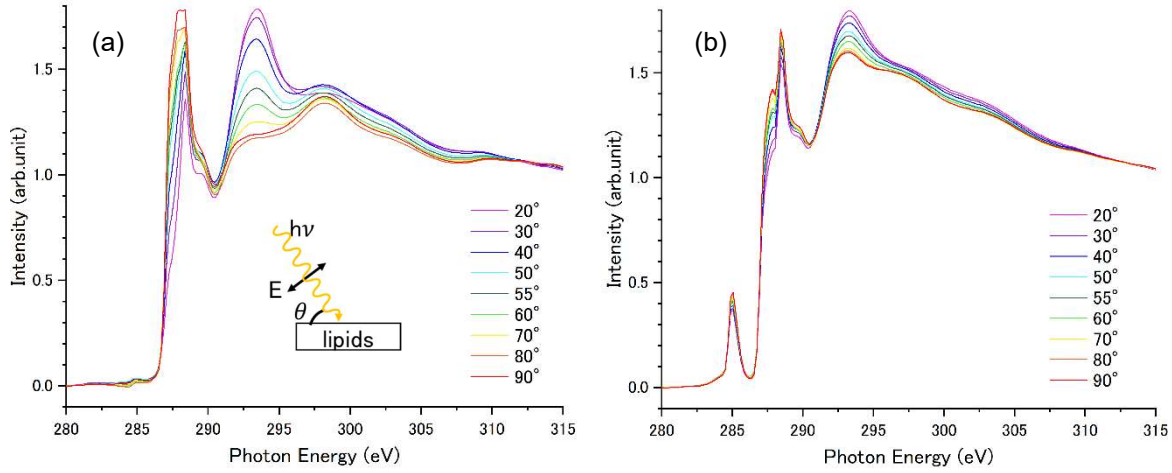

FIGURE 2. Polarization dependent NEXAFS spectra of (a) DPPC and (b) DOPC phospholipids multilamellar membranes measured at C K-edge. These membranes consist of about 100 bilayers, which are confirmed by simple molar consideration and interference of reflected visible light. Incident angle θ from the surface, and therefore the angle of electric vector from the surface normal, is defined like inset.

polarization dependence reflects not only the orientation angles themselves but also the different phase (ordering quality) of lipid membranes. On the basis of above consideration and the careful analysis of polarization dependence of each resonant peaks, DPPC bilayers (that is gel phase) consist of 60% ordered component and 40% non-ordered one, while DOPC bilayers (liquid phase) contain 80% non-ordered carbon chains. This is the first quantitative analysis of phospholipid bilayers of DPPC and DOPC by means of strong advantage of polarization quality and element selectivity of soft-X ray synchrotron radiation.

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