Water Hydrogen-Bonding Dynamics at Different Phases of Lipid Multibilayer: Femtosecond Mid-IR Pump-Probe Spectroscopy

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The water hydrogen-bonding dynamics at different phases of lipid-multibilayer are studied by femtosecond Mid-IR pump-probe spectroscopy. We observe existence of two different vibrational lifetime components (phosphate-associated water and choline-associated water). Vibrational lifetime of phosphate-associated water remains constant, whereas other component slows down in a sigmoidal fashion upon lipid phase transition.

Membrane water is a potential reaction site for many biochemical reactions. A molecular level understanding of water structure and dynamics at different phases of lipid membrane is essential to understand the biological reactions. Up to now, all of the measurements at the membrane have mainly concentrated on measuring the effect of changing the hydration level with water concentration as control variable[1,2]. However, there is no ultrafast vibrational spectroscopic study on water dynamics with changing the structure of the membrane. Here, we prepare phospholipid multibilayer as a model system, and employing femtosecond mid-IR pump-probe spectroscopy with HDO infrared probe to study the water hydrogen-bond network and dynamics at different temperatures. By changing temperature, the phase transition from gel phase to liquid crystal phase can be realized.

Here we observe existence of two significantly different vibrational lifetime components. One is phosphate-associated (red color at Fig 1a) and other is choline-associated water (blue color at Fig 1b). Figure 1b represent the cartoon picture of these two kinds of water and chemical structure of lipid head part. With increasing temperature, the vibrational lifetime of phosphate-associated water remains constant, but other component slows down in a sigmoidal fashion, indicating a noticeable change of water environment around the lipid multibilayer upon phase transition (shown in Fig 1c).

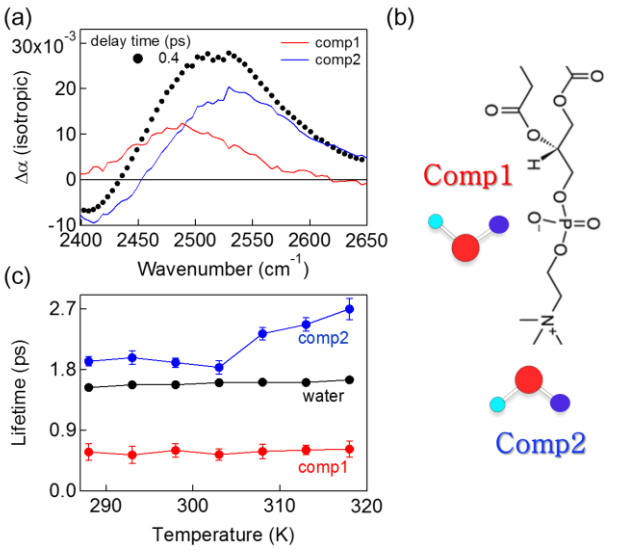

Fig.1 (a) Decomposed of IR PP spectrum (0.4 ps, black circles) at the zwitterionic lipid multibilayer into two decay components (comp1: red and comp2: blue) and at 288 K. (b) Chemical structure of the head part of zwitterionic lipid and cartoon representation of the phosphate-associated and choline-associated water. (c) The vibrational decay time constants for two decay components (comp1: red, comp2: blue) in zwitterionic lipid multibilayer and in isotopically diluted bulk water as a function of temperature.

[1] Z. Wei *et al*., J. Am. Chem. Soc. **130,** 13927 (2008).
[2] M. Bonn *et al*., J. Am. Chem. Soc. **132,** 14971 (2010).