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Supplementary Information for

Terahertz Dynamics Interfaces to Ion-lipid Interaction Confined in Phospholipid Reverse Micelles

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Experimental Procedures

Sample

1,2-dioleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) and 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPG and DOPC, respectively) used as surfactant for the preparation of reverse micelle purchased from Avanti Polar lipids, Inc., and anhydrous hexadecane used as nonpolar solvent from Sigma-Aldrich were used to prepare the reverse micelle emulsion. Millipore water was used to prepare all of the buffers, solutions, and suspensions. The samples investigated in reverse micelles were prepared in the same procedure to obtain dispersed phase before dispersed in oil phase. The phospholipids were dissolved in chloroform and evaporated with nitrogen gas to obtain the thin film of lipids, then which were dissolved in hexadecane to definite concentration. Millipore water, as dispersed phase in emulsion system, was injected in the phospholipid/hexadecane solution. The homogeneous emulsion would be obtained after a series of vortex and sonicate. Besides, Cu^{2+} and Mg^{2+} were prepared to investigate ions-phospholipids interactions.

Terahertz time-domain spectroscopy

The main experimental methods used in this study to investigate confined water are terahertz time-domain spectroscopy (THz-TDS). THz-TDS is a technique in which the time dependent electric field of a THz pulse is measured after it interacts with a sample. the samples are placed in a liquid cell (fused quartz cuvette) with a thickness of 0.5 mm. To avoid water vapor absorption, the THz setup is enclosed in a box which is purged with dry air-purged (RH=1.2%) and temperature-controlled conditions (21.5±0.2 °C). The detected THz pulse trace of the dry air-purged system versus time delay is shown in Fig. S1(a). The according Fourier transform spectrum is illustrated in Fig. S1(b). The noise floor allows high quality spectral measurements up to 3.5 THz

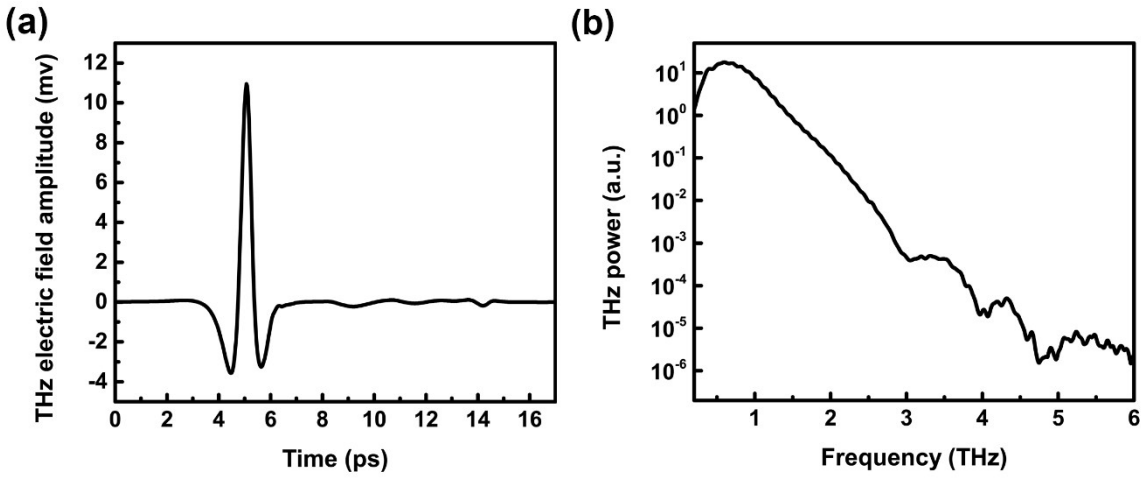

Figure S1. (a) Measured wave form of THz pulse under dry air. (b) Power spectrum of the Fourier transform of the pulse shown in (a).

From a measurement with THz-TDS, the electric field of the THz beam as a function of time $E_{THz}(t)$ is recorded. A fast Fourier transformation of $E_{THz}(t)$ yields the frequency dependent power and phase of the transmitted pulse. Subsequently, the frequency

dependent refraction index n, absorption coefficient α, real dielectric constant ε' and imaginary dielectric constant ε" can be deduced. [1, 2]

The absorption coefficient $\alpha(\nu)$ can be derived as follows:

$$\alpha(\nu) = d^{-1} \ln\left[I_r(\nu)/I_s(\nu)\right] \tag{1}$$

where d is the optical path length of the cell, $I_r(\nu)$ and $Is(\nu)$ are the intensity of reference and sample solutions, respectively.

The refractive index $n(\nu)$ can be derived as follows:

$$n(\nu) = n_r(\nu) + c(2\pi\nu d)^{-1}\left(\phi_s(\nu) - \phi_r(\nu)\right) \tag{2}$$

where $n_r(\nu)$ is the refractive index of the reference, $\Phi_r(\omega)$ and $\Phi_s(\omega)$ are the phase of reference and sample, respectively.

Actually, $n(\nu)$ is the real part of the complex refractive index, moreover, the imaginary part of the complex refractive index can be calculated from the following equation:

$$\kappa(\nu) = \alpha(\nu)/2\pi\nu \tag{3}$$

Using these estimated complex refractive indices, the real ε'(ν) and imaginary ε"(ν) dielectric constants of the samples can be obtained, as follows:

$$\varepsilon'(\nu) = n^2(\nu) - \kappa^2(\nu) \tag{4}$$

$$\varepsilon''(\nu) = 2n(\nu)\cdot\kappa(\nu) \tag{5}$$

Results

Millipore water and hexadecane

THz technology is finding use in an increasingly wide variety of applications in biology science. However, one of the major hurdles for biomedical applications lies in the poor THz transmittance of polar liquids, such as water, which makes it difficult to extract information about solute molecules.[3] Water as a very strong absorber in the terahertz region has been reported in previous work.[1] Fortunately, the solvent for reverse micelles is oil (nonpolar liquid), and absorption of which in THz range is much weaker than that of water.[4]

In our work, Millipore water and anhydrous hexadecane were used as dispersed phase and nonpolar solvent in emulsion system. Figure S2 demonstrates the THz pulses through Millipore water and hexadecane, which were studied with liquid cells of different thickness ((a) 0.1 mm, (b) 0.2 mm, (c) 0.5 mm, (d) 1.0 mm). With thickness increasing from 0.1 mm to 1.0 mm, the electric field amplitude of hexadecane can be considered to maintain invariable, but that of Millipore water would be greatly affected. The electric field amplitude of Millipore water is about 0.4 in 0.1mm cell, 0.1 in 0.2 mm cell, 0.01 in 0.5 mm cell,

and almost zero in 1.0 mm cell. The corresponding transmission spectra for the temporal profiles of Fig. S2(a) and S2(d) are shown in Fig. S3. The range of quality spectral measurements is about 2 THz for reverse micelles. We have measured refraction index $n(v)$ and power absorption coefficient $\alpha(v)$ of Millipore water and hexadecane in the range covering 0.2-2 THz. Figure S4 presents $n(v)$ and $\alpha(v)$ for these two liquids. The difference between two kinds of absorption spectrum in Fig. S4 is significant. Therefore, the absorption of THz electric waves by hexadecane is much weaker than that by water.

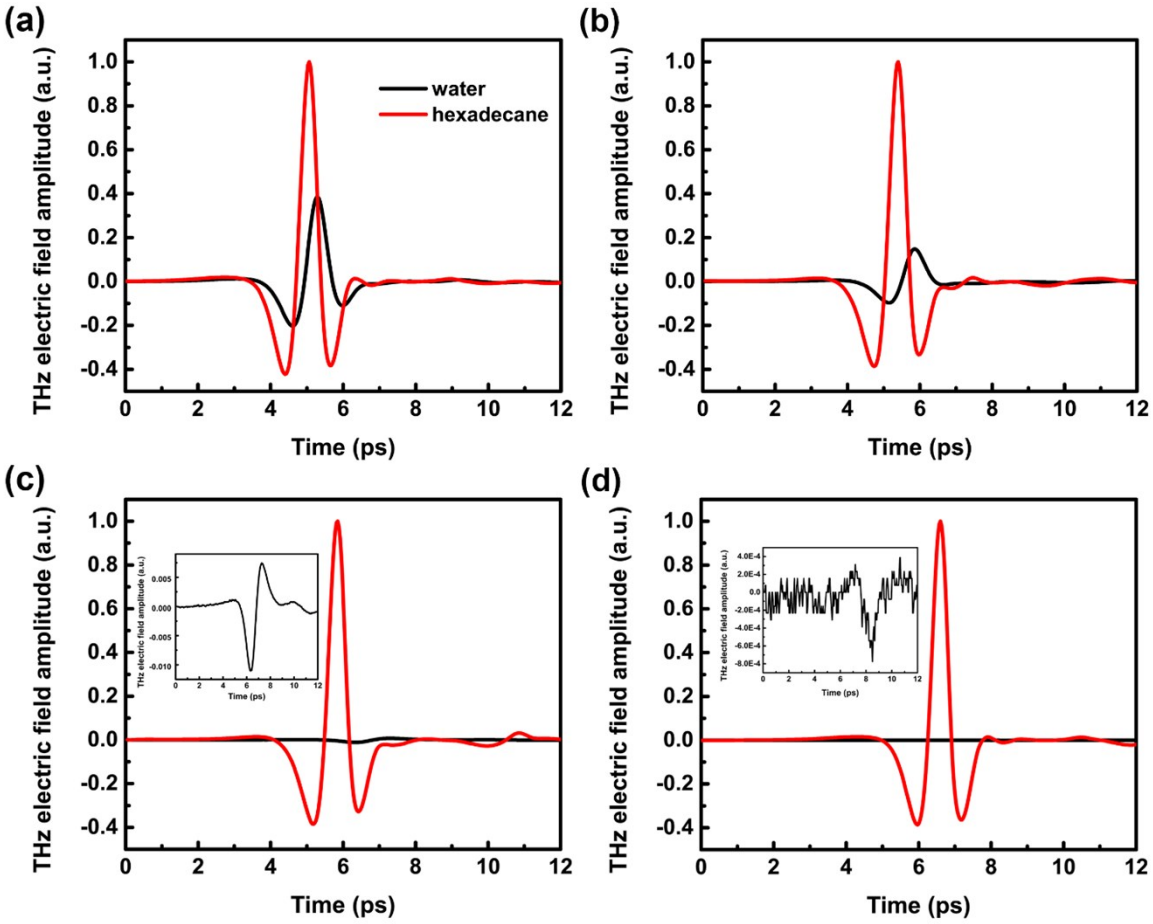

Figure S2. The temporal profiles of electric field with Millipore water (black line) and hexadecane (red line) (a) in 0.1 mm cell, (b) in 0.2 mm cell, (c) in 0.5 mm cell, and (d) in 1 mm cell.

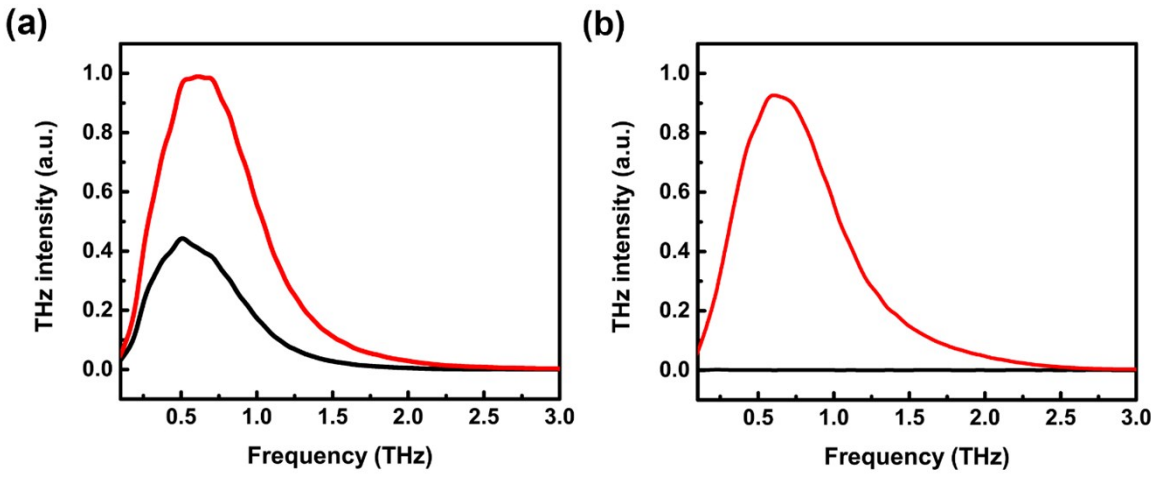

Figure S3. Corresponding transmission spectra for the temporal profiles of electric field of Fig. S1(a) and S1(d) with Millipore water (black line) and hexadecane (red line). (a) 0.1 mm cell and (b) 1 mm cell.

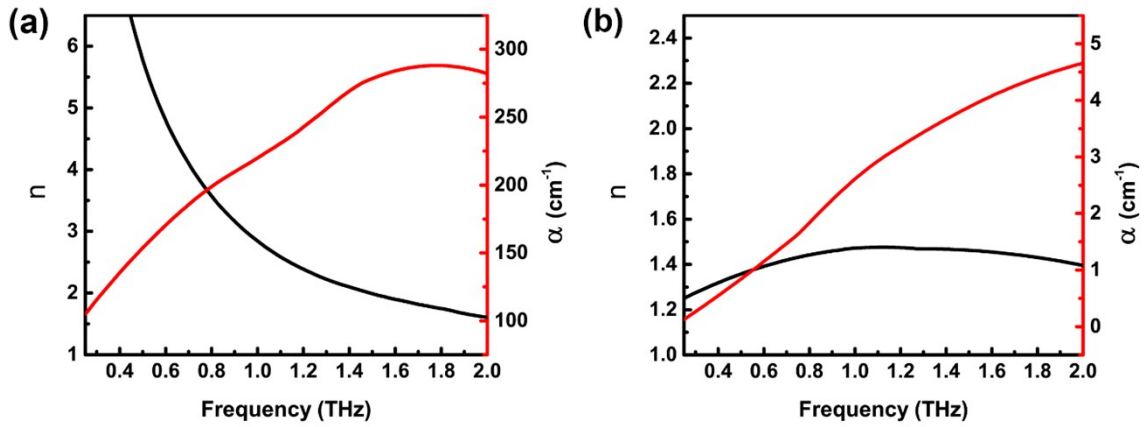

Figure S4. Frequency-dependent refraction index (black line) and power absorption coefficient (red line). (a) Millipore water and (b) hexadecane.

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