# Electronic Supporting Information (ESI)

# for

# Two-Dimensional Measurements of the Solvent Structural Relaxation Dynamics in Dipolar Solvation

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**Figure S1**

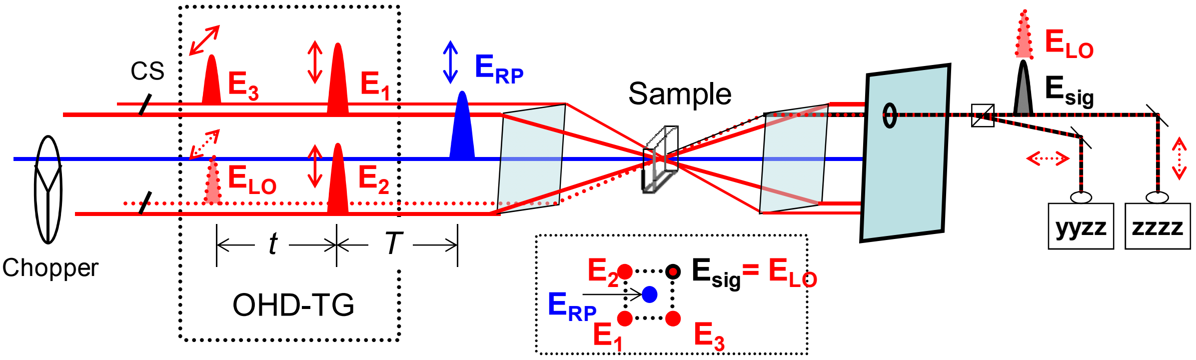

**Figure S1.** Schematic illustration of RP-PORS. RP-PORS is based on the optical heterodyne detected transient grating (OHD-TG) spectroscopy ($\mathbf{E}_1$, $\mathbf{E}_2$, $\mathbf{E}_3$, and $\mathbf{E}_{LO}$) with an additional resonant pump beam ($\mathbf{E}_{RP}$). The resonant pump beam ($\mathbf{E}_{RP}$), which is only resonant with the solute (C153), is used to excite the solute at $T$= 0ps. After a time delay of $T$, the OHD-TG spectroscopy is performed to measure the solvation response around the solute. In OHD-TG spectroscopy, two pump pulses ($\mathbf{E}_1$ and $\mathbf{E}_2$) are spatially and temporally overlapped at the sample generating transient grating along the sample. Time-delayed probe pulse ($\mathbf{E}_3$) is scattered off from the grating and is detected as a signal. $S_{zzzz}(T,t)$ and $S_{yyzz}(T,t)$ are measured at the same time with two almost identical detectors. CS is a 150 μm thick cover slip that is used to control the phase between the signal ($\mathbf{E}_{sig}$) and local oscillator ($\mathbf{E}_{LO}$). At a given $T$, $S(t,\phi=\pi/2)$ and $S(t,\phi=-\pi/2)$ are collected with two phases ($\phi=\pi/2$ and $\phi=-\pi/2$). The RP-PORS signal at a given $T$ is obtained by

$$S^{\text{RP-PORS}}(t) = S(t,\phi=\pi/2) - S(t,\phi=-\pi/2)$$

This is called “dual phase scan method”. See Figure S2 for the dual phase scan method.

**Figure S2**

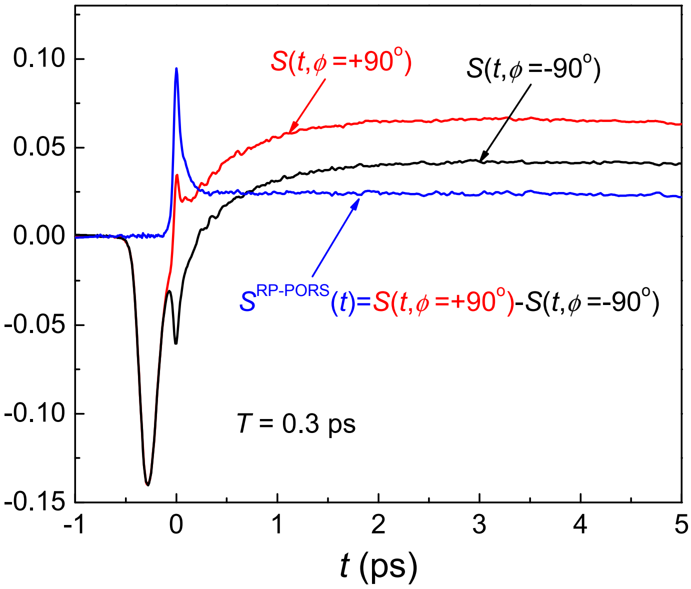

**Figure S2.** Illustration of dual phase scan method to measure the solvation response at $T$=0.3 ps. Two OHD-TG signals with $\phi$=±90 (red and black) are obtained at $T$=0.3 ps by chopping the resonant pump. The RP-PORS signals (solvation responses) are superimposed on top of the resonant signals of C153 with opposite phases. The resonant signal of C153 may result from the excited state absorption ($S_1 \rightarrow S_2$). Note that the resonant pump beam ($\mathbf{E}_{RP}$) and the LO ($\mathbf{E}_{LO}$) in our RP-PORS make a pump-probe geometry and thus the resonant signal of the solute is measured. The pure solvation response (blue) at $T$=0.3 ps is obtained by subtracting $S(t,\phi=-90)$ from $S(t,\phi=+90)$. The resonant signal of the solute is removed from the overall signal. Therefore, the solvation response induced by the resonant pump beam can be only obtained by the dual phase scan method.

**Figure S3**

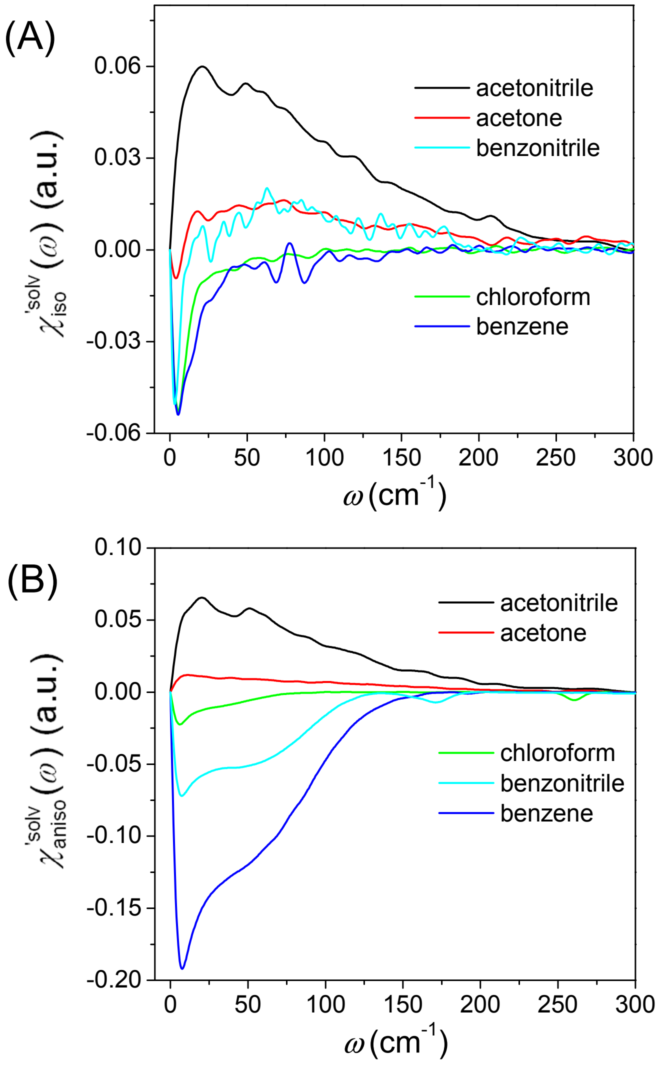

**Figure S3.** Solvation polarizability spectra obtained with C153 in different solvents by RP-PORS. (A) Isotropic solvation polarizability spectra. (B) Anisotropic solvation polarizability spectra. Solvation responses at different solvents can be directly compared. Solvation polarizability spectra are solvent-dependent. This indicates that the RP-PORS signal results not from the solute but from the solvation process.

**Figure S4**

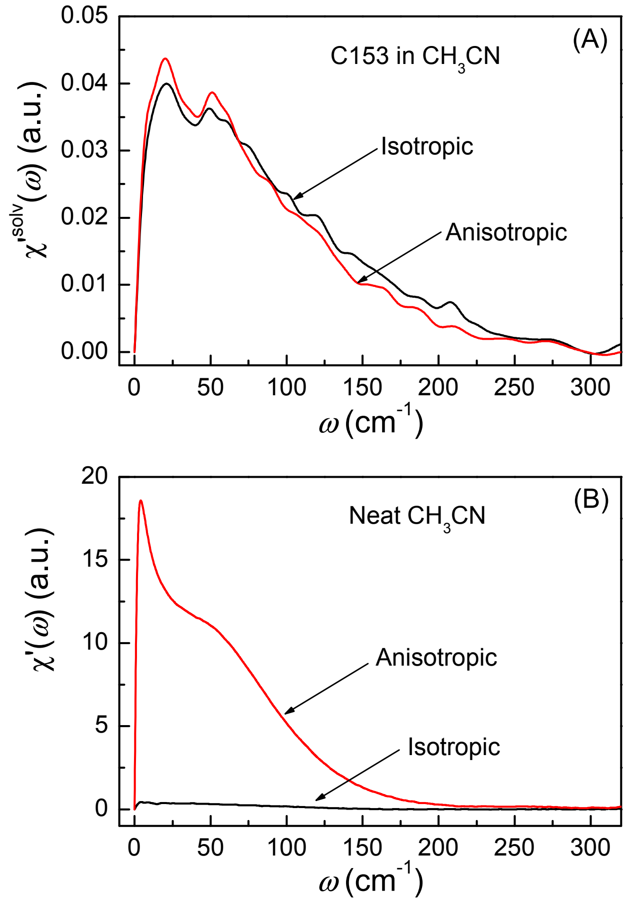

**Figure S4.** Polarizability spectra obtained with (A) C153 in acetonitrile and (B) neat acetonitrile. The amplitudes of polarizability spectra can be directly compared. In (A), the overall isotropic and anisotropic solvation polarizability spectra measured with C153 in acetonitrile were shown. During the solvation of C153, the isotropic and anisotropic responses were almost equally driven. In (B), polarizability responses were measured with neat acetonitrile. The anisotropic response is observed to be predominant in neat acetonitrile. See the main text in Ref.[4] for more detail. The relative magnitude of the solvation and bulk solvent polarizability response can be directly determined by calculating the areas of the polarizability spectra. We found that the relative amplitude of the solvation polarizability responses with respect to the solvent polarizability response is 0.72%.