Supporting Information

Molecular Level Insights into the Microstructure of a Hydrated and Nano-confined Deep Eutectic Solvent

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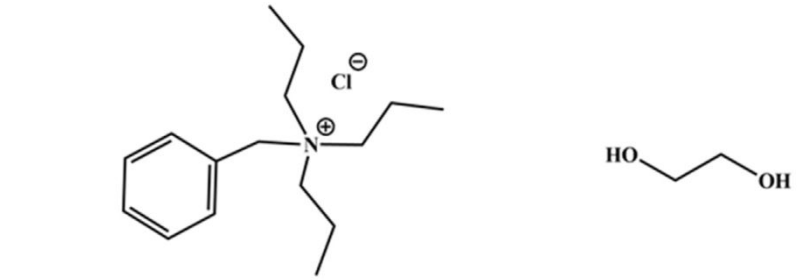

Benzyltripropylammonium chloride Ethylene glycol

Fig. S1. Structures of the ammonium salt and the hydrogen bond donor.

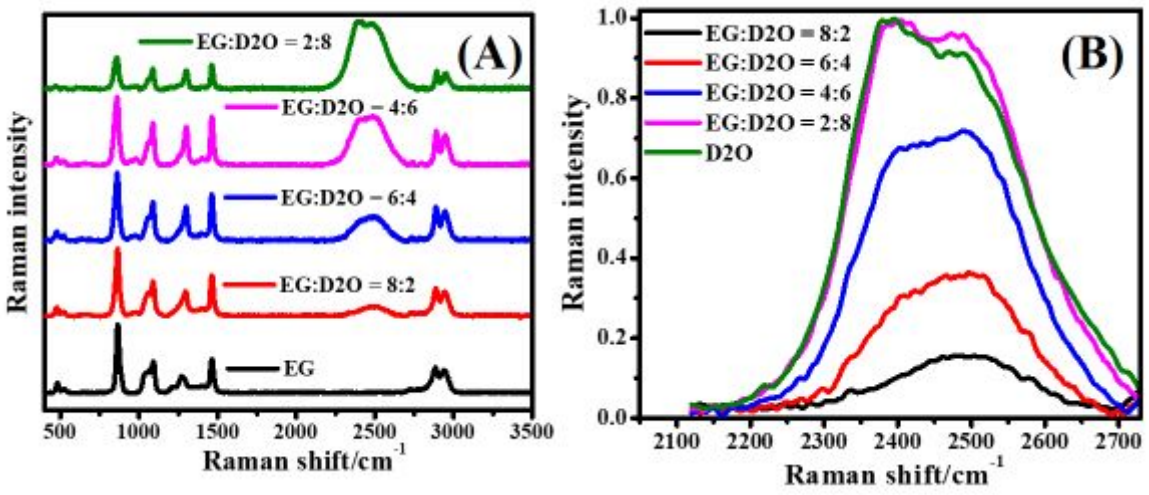

Fig. S2. Raman spectra of EG as a function of water volume fraction in the frequency window of **(A)** 500-3500 and **(B)** 2100-2700 cm^{-1} at 298 K.

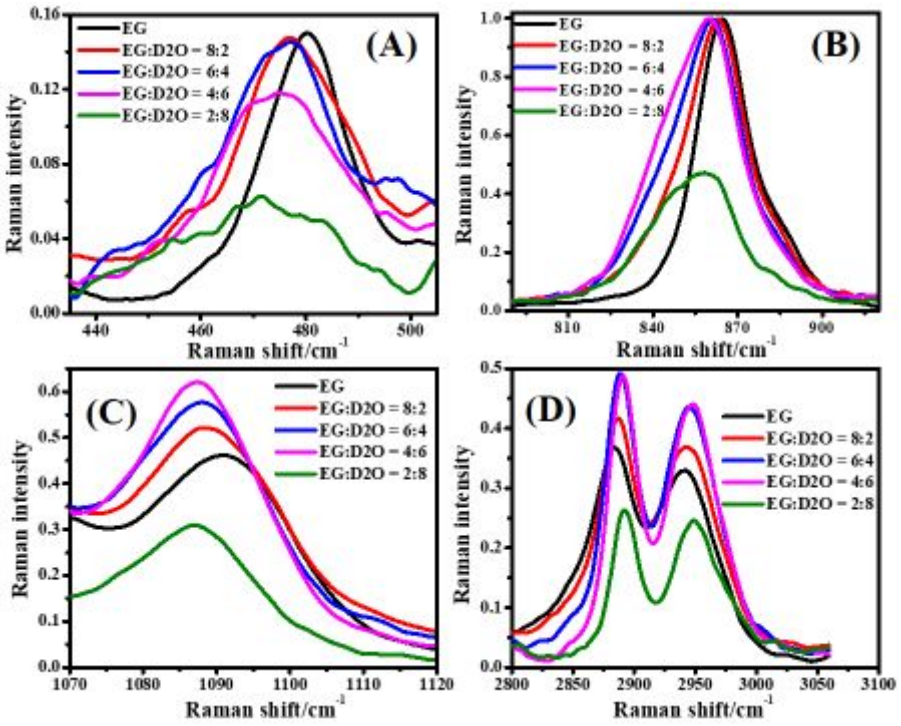

Fig. S3. Raman spectra of EG as a function of water volume fraction in the frequency window of **(A)** 420-520, **(B)** 800-910, **(C)** 1070-1120, and (D) 2800-3050 cm^{-1} at 298 K.

Raman spectra of EG in EG-water binary solutions with varying mixing volume ratios are shown in Figure S2. Figures S3A-C show the spectra of the binary solutions, which includes all the peaks related to the C-C-O bending, C-C stretching and CH_2CH_2-O stretching modes, respectively.[1] In general, the assigned peaks are shifted towards lower wavenumbers in the spectra of the mixtures with increasing water fraction. Presumably, the frequency changes are induced by the formation of hydrogen bonds between the EG oxygen atom and a water hydrogen atom rather than by self-association of the EG molecules. The hydrogen bonds formed result in a reduction of the electronegativity of the EG oxygen atom, which is accompanied by a bond elongation and a decrease of the force constant of the corresponding bonds.[2] Finally, this leads to a red shift of the assigned frequencies (Figures S3A-C).

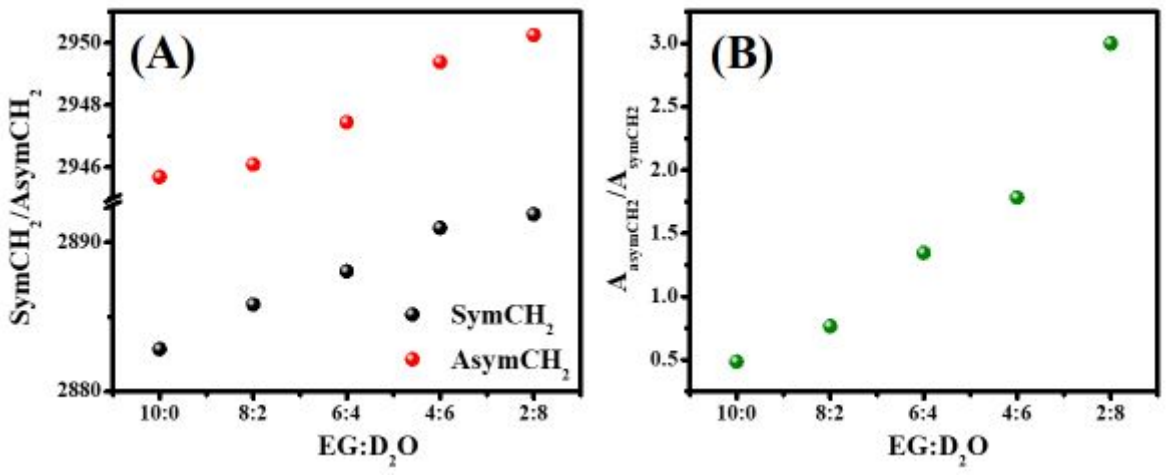

Fig. S4. (A) The changes of symmetric and asymmetric C-H stretching Raman bands of EG, and **(B)** their area ratio as a function of water.

The C-H stretching region of the Raman spectra of EG with different amounts of water are shown in Figure S4. The two peaks around 2882 and 2945 cm^{-1} refer to the symmetric and asymmetric CH_2 stretching vibrations in EG molecules, respectively.[3] The symmetric and asymmetric stretching of EG are sensitive to the molecular structure and ambient conditions. An interesting result that can be extracted from Figure S4A is the blue-shift of the symmetric and antisymmetric stretching modes with increasing water concentration. The observed blue-shifts of the $(CH_2)_{sym}$ and $(CH_2)_{asym}$ upon dilution indicate that water weakens the H-bonding associations between EG molecules.[4] Furthermore, the area ratio between the two Raman peaks, $A_{asymCH2}/A_{symCH2}$, reflects qualitatively the structural change of EG molecules induced by interaction with surroundings. An increase in the ratio with addition of water (Figure S4B) can be qualitatively related to the strengthening of interaction between EG and water in the solution.[5,6]

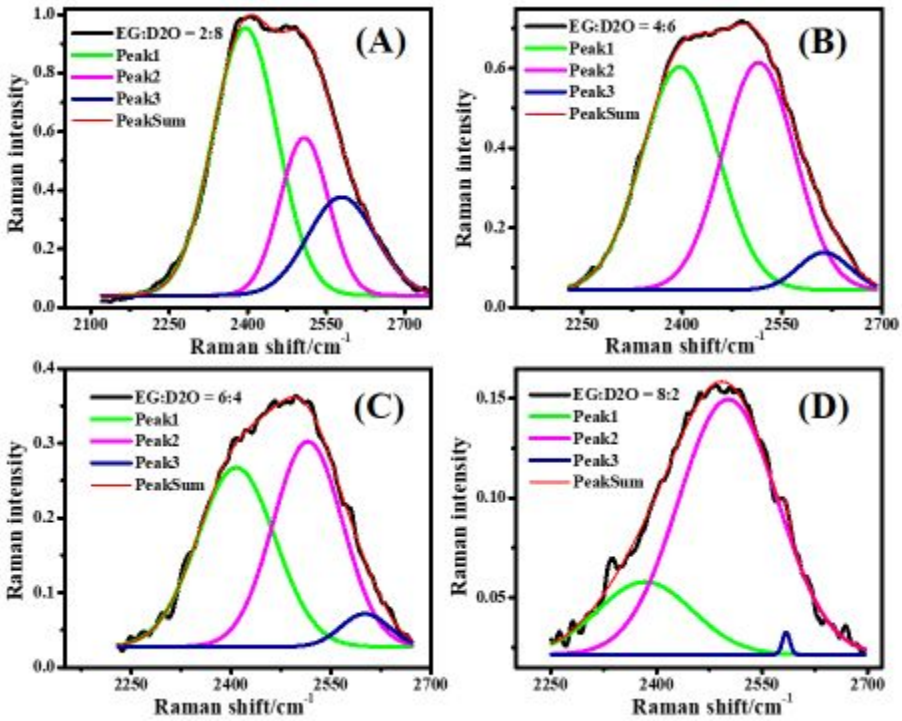

Fig. S5. Gaussian deconvoluted Raman bands of EG as a function of water volume fraction in the O-D frequency region showing various states of water (green, magenta and blue lines indicate network, intermediate and multimer water, respectively) at a particular ratio of EG and water, such as **(A)** 2:8, **(B)** 4:6, **(C)** 6:4, and **(D)** 8:2.

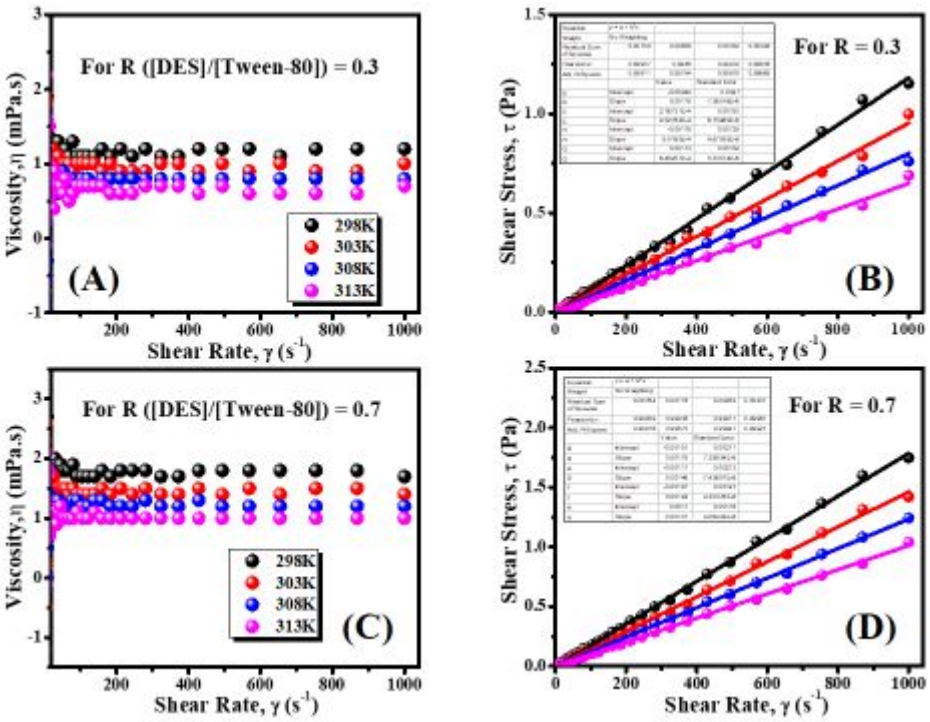

Fig. S6. Variation of viscosity (η) [**(A)** and **(C)**] and shear stress (τ) versus steady shear rate (γ) [**(B)** and **(D)]** plots for BTEG/Tween-80/Cy RMs at different molar ratios of BTEG to surfactant (R = 0.3 and 0.7) as a function of temperature.

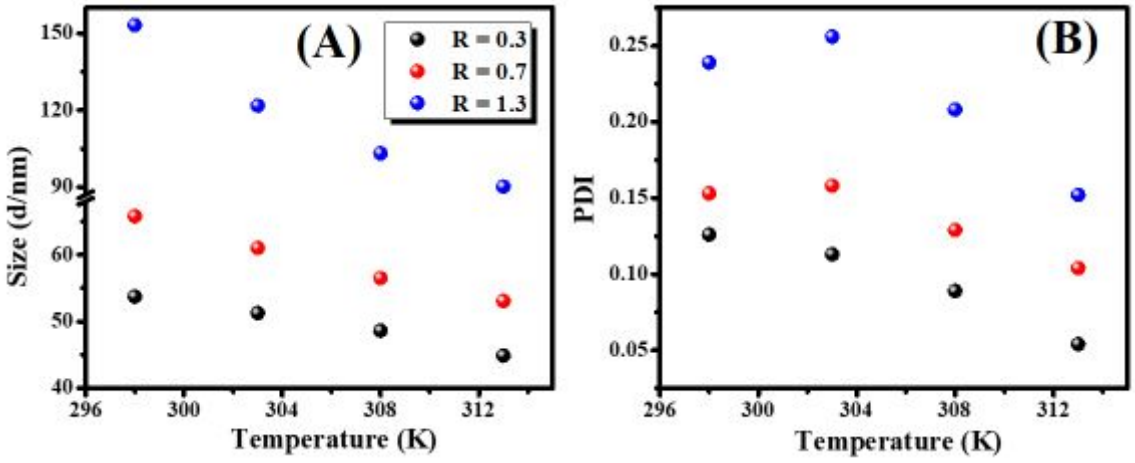

Fig. S7. (A) Droplet size and **(B)** polydispersity index (PDI) of BTEG/Tween-80/Cy RMs as a function of the molar ratio of IL to surfactant (R) at different temperatures.

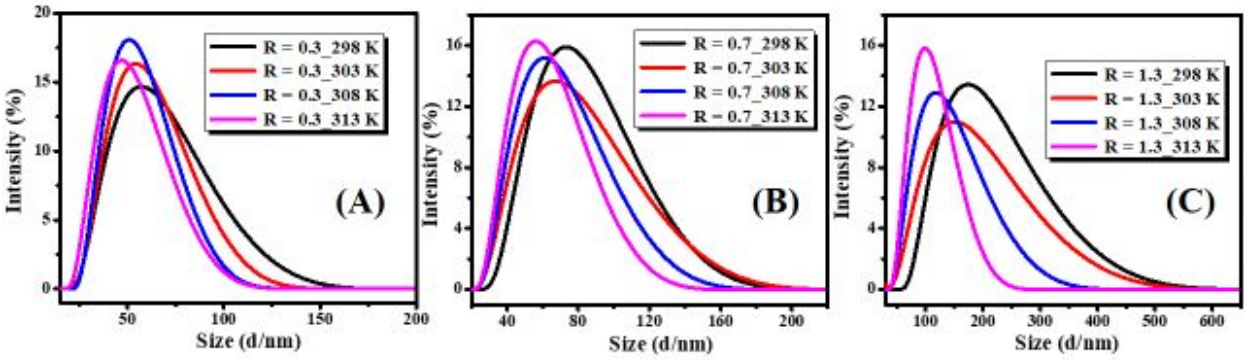

Fig. S8. Size distribution plots of Tween-80/Cy reverse micellar systems as a function of temperature at fixed of molar ratios of BTEG to surfactant (R), such as **(A)** 0.3, **(B)** 0.7, and **(C)** 1.3.

References

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