Electronic Supplementary Information

Reversible tuning of the hydrophobic-hydrophilic transition of hydrophobic ionic liquids by means of an electric field

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1. Table for the Force Field Parameters

Table S1. Detailed force field parameters used for the Lennard-Jones interactions, including the atoms in both the cation and anion

Atom type	σ (Å)	ε (kJ/mol)	charge(e)
NA	3.250	0.7113	0.1350
CT1(bonded to nitrogen)	3.550	0.2929	-0.1530
CT2	3.550	0.2929	0.0090
CT3(terminal alkyl carbon)	3.550	0.2929	-0.1620
HC1 (bonded to CT1)	2.500	0.1255	0.1170
CT(other alkyl carbon)	3.550	0.2929	-0.1080
HC(other alkyl hydrogen)	2.500	0.1255	0.0540
CR	3.550	0.2929	-0.0990
HA (hydrogen in ring)	2.420	0.1255	0.1890
NB	3.250	0.7113	0.1350
CV	3.550	0.2929	-0.1170
P (anion)	3.540	0.8368	1.2060
F (anion)	2.918	0.2552	-0.3510

2. The Ion Mobility

We also have noticed that the ion mobility of the cation and the anion are swiftly promoted by the electric field, especially in the z-axis. This can be evaluated by contrasting the diffusion coefficients at the z-axis D_z (parallel to the electric field direction) and the lateral diffusion coefficients D_{xy} (normal to the electric field direction). In Figure S1, we plotted the ratio D_z/D_{xy} for the ions and water as a function of electric field. It can be observed from Figure S1 that, whether the cation or the anion, the diffusion along the z-axis is much faster than that of the xy plane direction over the critical electric field 0.2V/nm, and the motion of the water remains almost unchanged in different directions over the critical electric field. However, these results are dependent on the periodic boundary condition (pbc) of z-direction. Due to the pbc of z-direction, the ions can move freely in or out the z-direction cell by the electric field. This ion motion tuned by the electric field direction was also reported in the previous papers.[1, 2] It will induce the ions spreading into the water phase fast, i.e. forming a mixing phase. However, these results do not result in the hydrophobic-to-hydrophilic transition but only accelerate the mixing process.

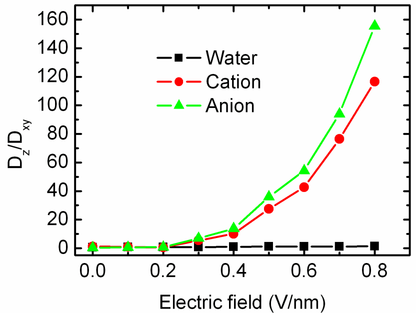

Fig. S1. The ratio D_z/D_{xy} of the diffusion coefficients along different directions as a function of electric field.

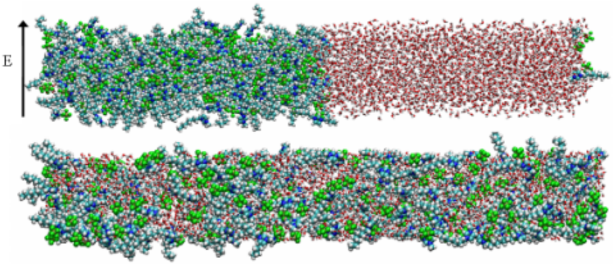

Fig. S2. The snapshots of the system applied in x-directional electric field. The upper one is the initial topology. The lower one is the final snapshot of system run by 15 ns.

To validate this conclusion, the new simulation with an x-directional electric field of 0.8 V/nm was applied to the two-phase system (parallel to the water/IL layers). Other parameters were the same as in our previous simulation. The system was run by 15ns. Figure S2 shows the initial topology and the final snapshot box of the system. The snapshot of the final production presents the well-mixed phase. Although, the mixing equilibrium process is much slower than the system with electric field applied in z direction. This is due to the fact that the diffusion of the ions along z direction (normal to the electric field x direction) is much lower comparing to those in x direction. The diffusion coefficients of cation and anion along the z-axis are $4.07\times10^{-5}cm^2.s^{-1}$ and $2.47\times10^{-5}cm^2.s^{-1}$ respectively. In contrast, the diffusion coefficients of cation and anion along the x-axis, i.e. electric field direction are $309.3\times10^{-5}cm^2.s^{-1}$ and $163.4\times10^{-5}cm^2.s^{-1}$, about 2 orders of the magnitude larger than those along the z-axis. These results are similar to the simulation results with electric field applied in z-axis (normal to the IL/water layer). Both the ion diffusions of the electric field direction are much larger than those in lateral directions. Moreover, the simulation results of well-mixed system are the same as previous results of z-direction electric field expected from the mixing time.

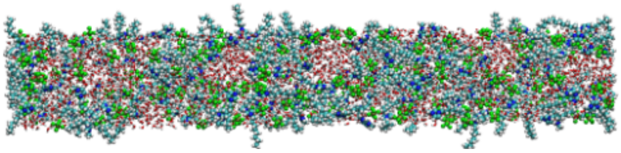

Fig. S3. The snapshot of the final simulation box of the 16 ns run.

3. The Periodic Boundary Conditions (PBC)

One may consider that the hydrophobic-to-hydrophilic transition will be affected by the pbc. Actually, if we turn off the pbc of z-direction, i.e. only pbc presented in xy directions, the two-phase system will present the mixed phase rather than the two separated phase. For further confirmation, we turned off the pbc of z-direction, and simulated in the same process like previous work at 0.6V/nm. Figure S3 shows the snapshot of the final simulation box of the 16 ns run. It can be seen that the system still present a mixed phase. We further calculated the diffusion coefficients of the ions. The diffusion coefficients of the cation and the anion along the z-axis are $0.3065\times10^{-5}cm^2.s^{-1}$and $0.3861\times10^{-5}cm^2.s^{-1}$, respectively. These values are adjacent to the value of the lateral diffusion coefficients obtained in xy direction, and much lower than of those in the z-direction of the pbc system. It means that the ions in this mixed system (no pbc in z-direction) diffuse homogeneously in different directions.

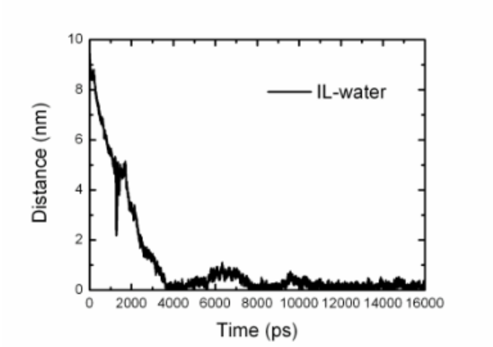

Fig. S4. The distance between the centers of mass of IL and the centers of mass of water as a function of time.

We also calculated the distance between the centers of mass of IL and the centers of mass of water as a function of time. If the phase separation occurs in the simulation, the distance between the IL and water will change. It's shown in Figure S4. We can find that the distance drops at a low value within the 4ns run. This time corresponds to such a mixing process between the IL and water. Above the 4ns, the distance is almost unaltered, showing no phase separation. This result may origin from a truth that interactions between ions in mixed phase are still strong enough to hold the mixed conditions. For electric field, the induced diffusion directions of cation and anion are opposite. If we want to obtain the directional ion motion, we must completely destroy the interaction between the cation and the anion in such no pbc system. But we know that the cation-anion correlations for IL electrolyte are very intense.[2-4] Furthermore, the ion motion will inevitably induce the chemical potential difference in this no pbc system. Due to the no pbc in z-axis, the ions can not move in or out the cell along the z-axis. This will limit the directional motion of the ions along the z-axis. Hence, the ions directional motion will not present in the well-mixed system (no pbc) and not induce the phase separation.

4. The Density Profiles in Phase Separation Simulation

Due to the very viscous ionic liquid without the electric field, the dynamics is slow to make a clear phase separation. In this study, the 50ns simulation presents a visible phase interface between water and IL in figure 8 of the text. This phase separation process can also be shown in density distribution of IL and water at different simulation time without the electric field. These results are shown in figure S5. It can be seen that the water-IL are well-mixed at the start of the simulation, shown in figure S5a. The mixed IL and water gradually separates each other along with the time without the electric field. The density distribution changes to undulance and heterogeneity, shown in figure S5b and S5c. Figure S5d shows a final visible phase interface between water and IL after 50 ns simulation. These density distributions can further validate the reversible hydrophobic-hydrophilic transition.

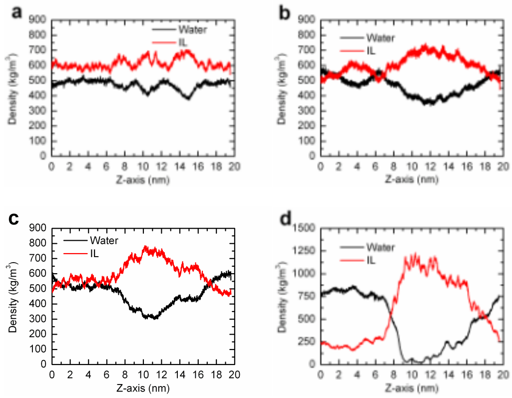

Fig. S5. Average density profile for OmimPF$_6$ and water along the z direction in phase separation simulation (without the electric field). (a) At 0 ps. (b) At 2 ns. (c) At 5 ns. (d) At 50 ns.

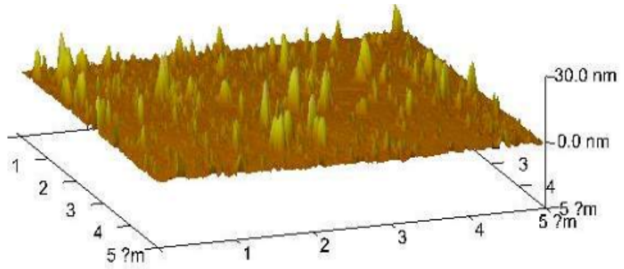

Fig. S6. Morphology of the IL nano-droplets on HOPG substrate after the methanol vaporized (5μm×5μm).

5. The Atomic Force Microscopy (AFM) images

AFM measurements were made to affirm the simulation results of the hydrophobic-to-hydrophilic transition. We first droped an IL solution onto the the HOPG substrate. After 10 min evaporation of the methanol, we found that many nano-droplets of IL were deposited on the substrate. It was shown in figure S6. In order to introduce the water phase, we injected the water to submerg the substrate in a closed cell. Hence, all the AFM images were obtained in liquid phase scanning. We also observed these nano-droplets under different electrical voltages in atmosphere condition (no water phase). These results were shown in figure S7. In the absence of the water phase, the nano-droplets were stable under the intensive electric field.

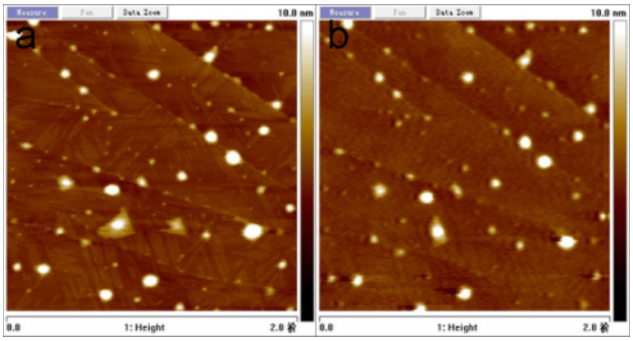

Fig. S7. A 2µm×2µm topographic image of IL nano-droplets remains in atmosphere condition. (a) Under 3 V. (b) Under 5 V.

6. The Effect of the Electrolytic Water

In AFM experiments, the water will be electrolyzed by the big bias (exceeding 1.23V). The electrolytic ions (H$^+$ and OH$^-$ ions) will inevitably present in this two-phase system. However, the ions effect especially the H$^+$ and OH$^-$ ions for water/ IL miscibility behaviours has been already studied by other papers. [5-7] It was suggested that the major effect on the IL-water system is salting-out and not salting-in. Therefore, it will not enhance the mixing ability of the hydrophobic IL and the water.

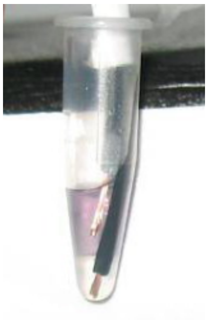

Fig. S8. A two-phase system consisted of hydrophobic OmimPF$_6$ (bottom phase) and the pink-dyed water after 1 hour electrolysis. The cathode and anode (both sheet copper) were submerged in IL and pink-dyed water, respectively. The DC voltage used here was 40V.

To further affirm the ion effect, we implemented a simple experiment by electrolyzing the water in an IL/water two-phase system. Firstly, a two-phase system in a centrifugal tube was constituted of hydrophobic IL OmimPF$_6$ (bottom phase) and the pink-dyed water. The cathode and anode (both sheet copper) were submerged in IL and pink-dyed water, respectively. Then different DC voltages of 5V, 10V, 25V and 40V were added in the system, respectively. Figure S8 shows a final result of the 40V voltages added in the system. Under such a strong voltage, many ions should be produced by the electrolysis. However, we found that the clear phase interface between the water and the hydrophobic IL was almost unchanged. Hence, the ions hardly affect the miscibility of the hydrophobic IL and the water.

References

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