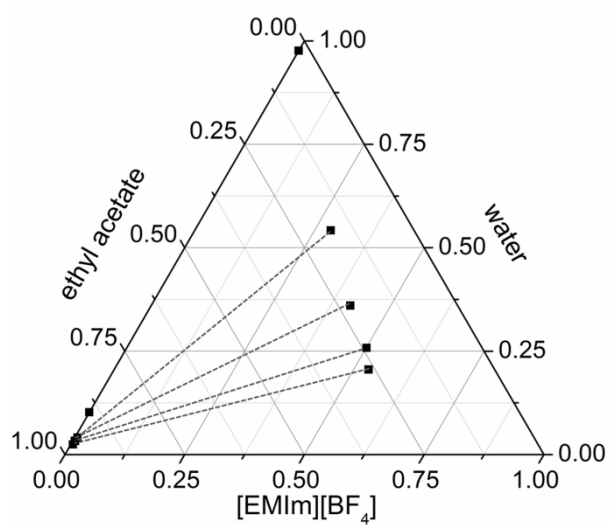


## Supplementary Information

### Phase equilibrium procedure

Phase equilibriums of [EMIm]BF<sub>4</sub> + water + ethyl acetate ternary mixture were carried out in a jacketed glass vessel connecting to a temperature controlled circulating bath ( $\pm 0.1$  K). The temperature in the cell was measured with a mercury thermometer ( $\pm 0.1$  K). After the temperature was adjusted, equal volumes of ethyl acetate and IL–water solution of known composition were added to the vessel. The mixture was stirred magnetically for 1 h and left to settle for at least 3 h. Then samples were taken from the upper and lower phases with a syringe.

The water content in both phases was determined by Karl-Fisher titrator. Phase compositions of IL and ethyl acetate were determined by HPLC. The Waters HPLC system included a 1525 binary HPLC pump, a thermostat, a 717 plus autosampler, a 2487 dual absorbance UV detector, and a 2414 refractive index detector. Analysis of IL and ethyl acetate was performed on a Sunfire C18 column (Waters, 4.6×250 mm i.d., 5  $\mu$ m). The mobile phase was methanol and the flow rate was 0.5 ml·min<sup>-1</sup>. The oven temperature was 308.2 K. The concentration of ethyl acetate in the ethyl-acetate-rich phase and IL in the IL-rich phase was detected by RI detector. Ethyl acetate in the IL-rich phase was detected by UV detector at 207 nm.



**Fig.S1** Experimental tie-lines of the ternary systems [EMIm]BF<sub>4</sub> + water + ethyl acetate at 303.2 K.