## **Electronic Supplementary Information (ESI)**

## Surfactant-free microemulsions of 1-butyl-3-methylimidazolium hexafluorophosphate, propylamine nitrate, and water

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## S1. Synthesis of Propylamine Nitrate (PAN)

*n*-Propylamine (AR, purity  $\geq$  99.0%) and nitric acid (AR, 65–63% in water) used were purchased from Tianjin Chemical Reagents Co., China. PAN was prepared in our laboratory through base-acid reaction between *n*-propylamine and nitric acid, as shown in Scheme S1. Nitric acid that was prediluted to 20–25% in water was dropwise added to the equimolar quantity of *n*-propylamine at ~4 °C under magnetic stirring. The mixture was kept magnetic stirring at ~4 °C for 1 h to achieve complete reaction. Water in the crude product was removed using a rotary evaporator, and the resultant product was then dried under vacuum at 65 °C until constant weight.



Scheme S1 Synthesis of propylamine nitrate (PAN).



Fig. S1 Molecular structures of (a) bmimPF<sub>6</sub> and (b) PAN.



**Fig. S2** <sup>1</sup>H NMR spectrum of PAN sample in  $D_2O$ .

 $\delta$  0.884 (3H, *t*, -C<u>H</u><sub>3</sub>), 1.588 (2H, *m*, -C<u>H</u><sub>2</sub>CH<sub>3</sub>), and 2.882 (2H, *t*, -C<u>H</u><sub>2</sub>NH<sup>3+</sup>). The H in -NH<sup>3+</sup> can exchange with D in D<sub>2</sub>O, so the peak of -N<u>H</u><sup>3+</sup> is covered up by the characteristic peak of the solvent at 4.7 ppm. No miscellaneous peaks are observed, indicating the so-obtained PAN sample has a high purity.



Fig. S3 (A) Diffusion coefficient  $(D_p)$  of K<sub>3</sub>Fe(CN)<sub>6</sub>, (B) intensity ratio  $(I_{393}/I_{373})$  of pyrene, and (C)  $\lambda_{max}$  of MO in microemulsions at  $R_{B/P} = 1/9$  as a function of  $f_w$ . Concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub>, pyrene, and MO were 0.65 g·L<sup>-1</sup>, 4.95×10<sup>-5</sup> mol·L<sup>-1</sup>, and 0.005 g·L<sup>-1</sup>, respectively.



Fig. S4 (A) Diffusion coefficient  $(D_p)$  of K<sub>3</sub>Fe(CN)<sub>6</sub>, (B) intensity ratio  $(I_{393}/I_{373})$  of pyrene, and (C)  $\lambda_{max}$  of MO in microemulsions at  $R_{B/P} = 2/8$  as a function of  $f_w$ . Concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub>, pyrene, and MO were 0.65 g·L<sup>-1</sup>, 4.95×10<sup>-5</sup> mol·L<sup>-1</sup>, and 0.005 g·L<sup>-1</sup>, respectively.



Fig. S5 (A) Diffusion coefficient  $(D_p)$  of K<sub>3</sub>Fe(CN)<sub>6</sub>, (B) intensity ratio  $(I_{393}/I_{373})$  of pyrene, and (C)  $\lambda_{max}$  of MO in microemulsions at  $R_{B/P} = 3/7$  as a function of  $f_w$ . Concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub>, pyrene, and MO were 0.65 g·L<sup>-1</sup>, 4.95×10<sup>-5</sup> mol·L<sup>-1</sup>, and 0.005 g·L<sup>-1</sup>, respectively.



Fig. S6 (A) Diffusion coefficient  $(D_p)$  of K<sub>3</sub>Fe(CN)<sub>6</sub>, (B) intensity ratio  $(I_{393}/I_{373})$  of pyrene, and (C)  $\lambda_{max}$  of MO in microemulsions at  $R_{B/P} = 4/6$  as a function of  $f_w$ . Concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub>, pyrene, and MO were 0.65 g·L<sup>-1</sup>, 4.95×10<sup>-5</sup> mol·L<sup>-1</sup>, and 0.005 g·L<sup>-1</sup>, respectively.



Fig. S7 (A) Diffusion coefficient  $(D_p)$  of K<sub>3</sub>Fe(CN)<sub>6</sub>, (B) intensity ratio  $(I_{393}/I_{373})$  of pyrene, and (C)  $\lambda_{max}$  of MO in microemulsions at  $R_{B/P} = 5/5$  as a function of  $f_w$ . Concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub>, pyrene, and MO were 0.65 g·L<sup>-1</sup>, 4.95×10<sup>-5</sup> mol·L<sup>-1</sup>, and 0.005 g·L<sup>-1</sup>, respectively.



Fig. S8 Viscosity of bmimPF<sub>6</sub>/PAN/water ternary system with  $R_{\rm B/P} = 2/8$  as a function of  $f_{\rm w}$ .



Fig. S9 Intensity ratio  $I_{393}/I_{373}$  of pyrene as a function of PAN volume fraction  $(f_{PAN})$  in bmimPF<sub>6</sub>/PAN binary solution. The pyrene concentration is  $4.95 \times 10^{-5}$  mol·L<sup>-1</sup>.



Fig. S10 MO  $\lambda_{max}$  as a function of  $f_{PAN}$  in bmimPF<sub>6</sub>/PAN and water/PAN mixture solutions. The MO concentration is 0.005 g·L<sup>-1</sup>.



Fig. S11 Photograph of  $\text{bmim}PF_6$ -water two-phase system containing MO. Bright orange of  $\text{bmim}PF_6$  phase (low phase) indicates that MO preferentially dissolves in  $\text{bmim}PF_6$  phase.



Fig. S12 Cryo-TEM images of samples with  $R_{B/P/W}$  of (a) 0.286/0.667/0.047 in W/IL subregion, (b) 0.164/0.656/0.180 in BC subregion, and (c) 0.056/0.500/0.444 in IL/W subregion.



Fig. S13 Size distributions of dispersed droplets for the samples  $a_2$ ,  $a_3$ ,  $c_2$ ,  $c_3$ , and  $c_4$  as marked in Fig. 1.