Supporting information

## An ionic liquid-based synergistic extraction strategy for rare earths

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extractant	density (g/cm <sup>3</sup> )	viscosity (mPa·s)	average molecular weight			
[A336][NO <sub>3</sub> ]	0.9126	199.9	432			
DEHEHP	0.9022	10.52	418			

Table S1 Some physical properties of [A336][NO<sub>3</sub>] and DEHEHP (298 K)

Table S2 Viscosity of IL phase under the different Pr-loaded concentrations at the different temperatures

II phase	$[\Pr]_{IL}(M)$	Viscosity (mPa·s)			
IL pliase		298 K	303 K	308 K	318K
[A336][NO <sub>3</sub> ]	0		105.6394		
	0.30		gel (> 2000)		
[A336][NO <sub>3</sub> ]-DEHEHP ( $V_A:V_D = 2:3$ )	0	48.9121	38.9032	31.3979	21.3152
	0.33		150.7841		
	0.57		565.4734		



Fig. S1. The fitting plots of  $C_e/q_e$  vs  $C_e$  at different temperature for the extraction of Pr(III) according to Langmuir model.



**Fig. S2.** Effect of temperature on the adsorption equilibrium constants for Pr(III) by ionic liquid phase 0.2ml [A336][NO<sub>3</sub>] and 0.3ml DEHEHP.  $C_{LiNO3} = 3 \text{ M}$ ,  $pH_e = \sim 3.5$ ,  $C_{Pr} = 0.48 - 48 \text{ mmol/l}$ ,  $V_{aq} = 10\text{ml}$ .



Fig. S3. The fitting plots of  $t/q_t$  vs t for the extraction of Pr(III) according to pseudo-

second-order rate equation.



**Fig. S4.** Digit-photos for (AD) Pr-loaded [A336][NO<sub>3</sub>]-DEHEHP (0.33 M [Pr]<sub>IL</sub>) and (A) Pr-loaded [A336][NO<sub>3</sub>] (0.30 M [Pr]<sub>IL</sub>).



Fig. S5. The relationship between pseudo-second-order rate constant  $k_2$  and 1/T.



**Fig. S6.** IR spectra. (A) DEHEHP and Pr(III)-loaded DEHEHP. (B) [A336][NO<sub>3</sub>] and Pr(III)-loaded [A336][NO<sub>3</sub>].

As seen in Fig. S6A, the characteristic band at 1249 cm<sup>-1</sup> ( $v_{P=O}$ ) in DEHEHP has shifted to 1180 cm<sup>-1</sup> in the Pr(III)-loaded DEHEHP. Thus, the strong interaction between the P=O group and Pr(III) shifts the stretching vibration peak of the P=O group to a lower wavenumber. While as both the characteristic bands at ~1000 cm<sup>-1</sup> ( $v_{P-O-C}$ ) and ~870 cm<sup>-1</sup> ( $v_{P-C}$ ) for DEHEHP underwent no obvious change, this indicates that the P-O-C and P-C groups are not involved in the coordination reaction. In addition, new peaks at 1490cm<sup>-1</sup> and 1288cm<sup>-1</sup> in the spectra of Pr-loaded DEHEHP can be attributed to  $v_{as,O-NO2}$  and  $v_{s,O-NO2}$ , respectively. This suggests that the nitrate groups are involved into the neutral extracted species. Moreover, in the spectra of Pr-loaded DEHEHP, a minimal H<sub>2</sub>O peak is observed, thus, indicating that pure DEHEHP does not extract H<sub>2</sub>O. Therefore, contrary to traditional molecular solvent extraction, pure DEHEHP extracts Pr(III) without following a microemulsion extraction mechanism due to the absence of H<sub>2</sub>O molecules. While as in the IR spectra of [A336][NO<sub>3</sub>] and Pr-loaded [A336][NO<sub>3</sub>] (Fig. S6B), 1640 cm<sup>-1</sup> is attributed to  $\delta_{H2O}$ . 1464 cm<sup>-1</sup> is from  $\delta_{as,CH3}$  and  $\delta_{as,CH2}$ . ~ 1380 cm<sup>-1</sup> probably comes from  $v_{as,NO3}$  and  $v_{s,CH3}$ . 1332 and 1040 cm<sup>-1</sup> belong to  $v_{C-N}$ . 830 cm<sup>-1</sup> is from  $\delta_{NO3}$ . Finally, 722 cm<sup>-1</sup> can be attributed to  $\delta_{(CH2)n}$  (n>4). The two new peaks identified at 818 and 734 cm<sup>-1</sup> were probably produced by bending and deformations of Pr-NO<sub>3</sub> bonds.