# **Supplementary information**

## Strategy of regulating electrophilic/nucleophilic ability by ionic ratio

## in poly(ionic liquid)s to control the coupling reaction of epoxide

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#### FTIR spectra of PVIM and PIL-ACs

PVIM and PIL-ACs were measured by Thermo Fisher Nicolet FT-IR instrument at room temperature. In PVIM, the FTIR spectra showed the characteristic bands of imidazole ring at 3112 cm<sup>-1</sup> (C-H bond stretch), 1643 cm<sup>-1</sup> (C=C bond stretch) and 1500 cm<sup>-1</sup> (C=N bond stretch) which was consisted with the previous research. The characteristic bands of PIL-ACs were consisted with PIL-Brs which showed a new peak at 1705cm<sup>-1</sup> represent the C-O bond stretch from anion species.

### NMR of PVIM

PVIM could be dissolved in  $D_2O$ , thus, PVIM were measured in  $D_2O$  solution using a 600 MHz AVANCE III NMR spectrometer at room temperature. It showed the signals appeared between 1.8 and 3.6 was corresponding to the backbone, and those showed at around 6.4 and 7.0 ppm attributed to imidazole ring.

#### **TG of PIL-Brs**

Thermogravimetry analysis of PIL-Brs was recorded on a NETZSCH STA 449C instrument under nitrogen atmosphere at a heating rate of 10 °C/min.



Figure S1: FTIR spectra of PVIM



Figure S2: The full <sup>1</sup>H NMR spectra of PVIM in D<sub>2</sub>O



Figure S3: FTIR spectra of PIL-ACs from 4000 cm<sup>-1</sup> to 1000 cm<sup>-1</sup>



Figure S4: Thermogravimetry analysis of PIL-Brs ranging from 100 °C to 800 °C