

Electronic Supplementary Information

## **Complex Phase Behavior of Dihydroxyl-Functionalized Ionic Liquids at low temperature**

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## Supplementary Note 1

### Materials

4-Hydroxypyridine ( $C_5H_5NO$ , 97%), 4-(2-hydroxyethyl) pyridine ( $C_7H_9NO$ , 98%), Ethylacetate ( $C_4H_8O_2$ , 99.5%), Ethanol ( $C_2H_6O$ ,  $\geq 99.8\%$ ) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 2-Bromoethanol ( $C_2H_5BrO$ , 96%), Acetonitrile ( $C_2H_3N$ ,  $\geq 99.5\%$ ), Silver-bis(trifluoromethanesulfonyl)imide ( $AgNTf_2$ , 98%) were bought from Shanghai Macklin Biochemical Co., Ltd. Dimethyl Sulfoxide- $d_6$  ( $DMSO-d_6$ , D, 99.9%), Acetonitrile- $d_3$  ( $C_2D_3N-d_3$ , D, 99.5%) were purchased from Cambridge Isotope Laboratories, Inc. All reagents and solvents were used as received without further purification.

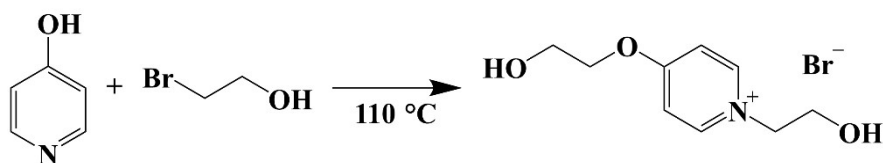
### Ionic Liquids Synthesis

Synthesis of ILs with bromine anion: Under  $N_2$  atmosphere, a certain molar ratio of pyridine derivatives and 2-bromoethanol were mixed and heated to  $110^\circ C$  for 2h. Upon cooling, the mixture began to crystallize. The crude product was washed, recrystallized or double-solvents recrystallized, dried and other operations to obtain pure crystalline products.

Synthesis of ILs with bis(trifluoromethanesulfonyl)imide anion: Equimolar amounts of the onium bromide and Silver-bis(trifluoromethanesulfonyl)imide were mixed as aqueous solutions for 1h. Silver bromide was removed by filtration and two phases were obtained, the lower one was washed several times with water until no residual bromine could be detected with silver nitrate solution. The obtained ILs were dried for several hours in vacuum at  $60^\circ C$ .

### Synthesis of the specific compounds

#### 1-(2-hydroxyethyl)-4-(2-hydroxyethoxy)pyridinium-bromide (IL-1)

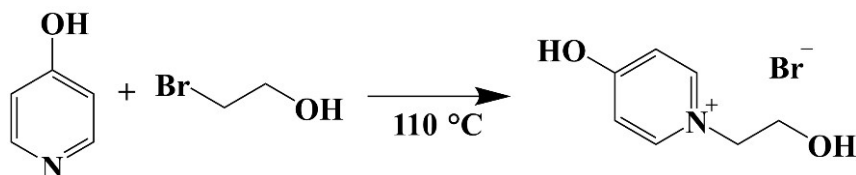


With continuous stirring at room temperature, 1.9608 g (20 mmol) of 4-hydroxypyridine and 2.9550 mL (40 mmol) of 2-bromoethanol were mixed in a 15 mL thick-wall pressure-resistant bottle. The resulted solution was stirred at  $110^\circ C$  for 2 hours. After natural cooling, the crude product was mixed with 50 ml of ethylacetate and stirred thoroughly to form a light yellowish precipitate. The precipitate was dissolved again in acetonitrile-ethylacetate binary mixed solvent, double-solvents recrystallized and dried under vacuum at  $60^\circ C$  overnight.

ESI-MS Calculated:  $m/z$ : 184.0969 ( $C_9H_{14}NO_3^+$ ); found:  $m/z$ : 184.0910. ESI-MS Calculated:

$m/z$ : 78.9188 ( $\text{Br}^-$ ); found:  $m/z$ : 78.9233.  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.77 (d,  $J = 7.4$  Hz, 2H), 7.64 (d,  $J = 7.4$  Hz, 2H), 4.48 (t,  $J = 5.1$  Hz, 2H), 4.39 (t,  $J = 4.6$  Hz, 2H), 3.79 (q,  $J = 5.2, 4.7$  Hz, 4H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{DMSO-}d_6$ )  $\delta$  170.16, 146.40, 113.30, 72.47, 61.06, 59.90, 58.93.

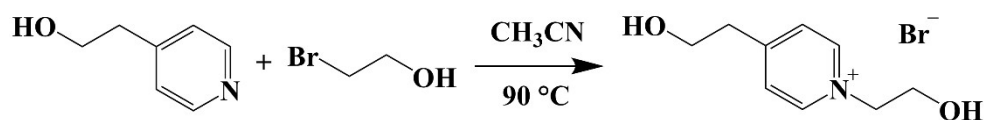
**1-(2-hydroxyethyl)-4-hydroxypyridinium-bromide (IL-2)**



0.08 mol of 4-hydroxypyridine and 0.1 mol of 2-bromoethanol were mixed at room temperature in nitrogen atmosphere. The obtained mixture was refluxed and condensed at 110°C for 72 hours. When the reaction began, the white suspension gradually changed into a light yellow homogeneous liquid and finally into a dark brown homogeneous liquid. After natural cooling to room temperature, the crude product was dissolved in 50 ml acetonitrile, and 300 ml ethylacetate was added to precipitate brown powder. The brown precipitate was washed several times with acetonitrile-ethylacetate binary mixed solvent and dried under vacuum at 60°C overnight.

**ESI-MS** Calculated:  $m/z$ : 140.0707 ( $\text{C}_7\text{H}_{10}\text{NO}_2^+$ ); found:  $m/z$ : 140.0685. **ESI-MS** Calculated:  $m/z$ : 78.9188 ( $\text{Br}^-$ ); found:  $m/z$ : 78.9193.  $^1\text{H NMR}$  (600 MHz, Acetonitrile- $d_3$ )  $\delta$  8.23 – 8.19 (m, 2H), 7.50 – 7.47 (m, 2H), 4.26 – 4.23 (m, 2H), 3.78 – 3.74 (m, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{DMSO-}d_6$ )  $\delta$  170.68, 146.09, 142.87, 114.22, 113.95, 60.67, 59.96.

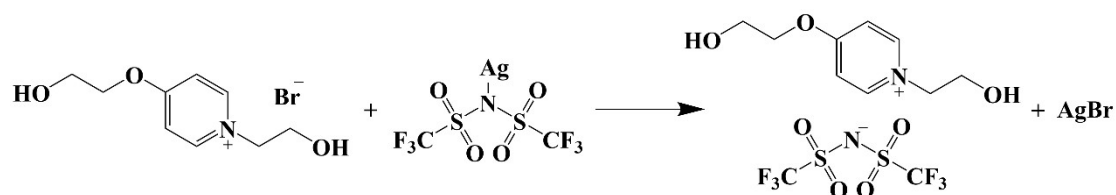
**1,4-bis(2-hydroxyethyl)pyridinium-bromide (IL-3)**



With continuous stirring at room temperature, 0.815 mL (0.011mol) of 2-bromoethanol was added to a solution of 1.155 mL (0.01mol) of 4-(2-hydroxyethyl) pyridine and 30 mL of acetonitrile through a constant pressure dropping funnel within 10 minutes. The obtained mixture was refluxed and condensed at 90°C for 12 hours in nitrogen atmosphere. The initial system was orange-yellow transparent homogeneous solution, and the color gradually deepened with the reaction. After natural cooling to room temperature, two phases were formed, the lower one was washed several times with ethylacetate and dried under vacuum at 60°C overnight.

**ESI-MS** Calculated:  $m/z$ : 168.1020 ( $\text{C}_9\text{H}_{14}\text{NO}_2^+$ ); found:  $m/z$ : 168.1065. **ESI-MS** Calculated:  $m/z$ : 78.9188 ( $\text{Br}^-$ ); found:  $m/z$ : 78.9129.  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.90 (d,  $J = 6.7$  Hz, 2H), 8.02 (d,  $J = 6.7$  Hz, 2H), 5.24 (s, 1H), 4.90 (s, 1H), 4.62 (t,  $J = 5.0$  Hz, 2H), 3.84 (t,  $J = 5.0$  Hz, 2H), 3.76 (t,  $J = 6.1$  Hz, 2H), 3.03 (t,  $J = 6.1$  Hz, 2H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{DMSO-}d_6$ )  $\delta$  160.61, 144.09, 127.88, 62.34, 59.96, 59.84, 38.15.

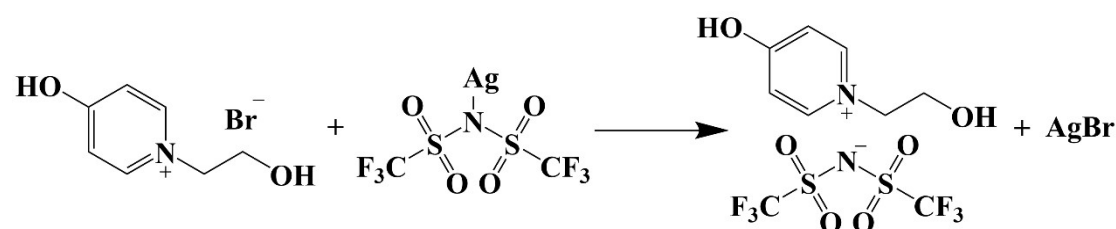
**1-(2-hydroxyethyl)-4-(2-hydroxyethoxy)pyridinium-bis(trifluoromethanesulfonyl)imide (IL-4)**



At room temperature, 2.0010 g (0.0076 mol) of **IL-1** was dissolved in 5 ml of H<sub>2</sub>O, and 2.9996 g (0.0076 mol) AgNTf<sub>2</sub> was added. The mixture was stirred for 12 hours. Two phases were obtained after filtration by a needle filter, and the lower one was washed several times with water until no residual bromine was detected with silver nitrate solution. The obtained liquid was dried under vacuum at 60°C overnight.

**ESI-MS** Calculated: *m/z*: 279.9178 (NTf<sub>2</sub><sup>-</sup>); found: *m/z*: 279.9322. **<sup>13</sup>C NMR** (151 MHz, DMSO-*d*<sub>6</sub>) δ 170.17, 146.39, 142.79, 120.54, 118.40, 114.01, 113.30, 72.47, 61.08, 59.91, 58.93.

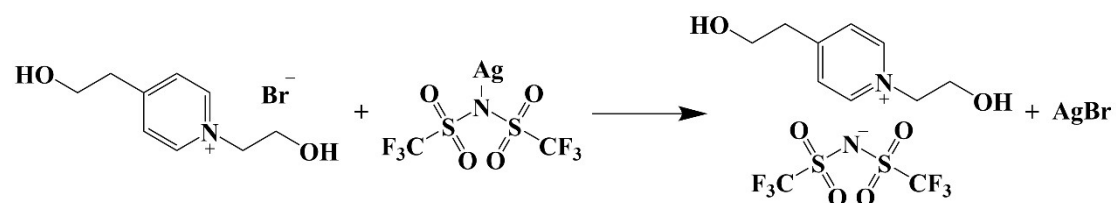
**1-(2-hydroxyethyl)-4-hydroxypyridinium-bis(trifluoromethanesulfonyl)imide (IL-5)**



At room temperature, 1.1395 g (0.0052 mol) of **IL-2** was dissolved in 5 ml of H<sub>2</sub>O, and 2.0294 g (0.0052 mol) of AgNTf<sub>2</sub> was added. The mixture was stirred for 12 hours. Two phases were obtained after filtration by a needle filter, and the lower one was washed several times with water until no residual bromine was detected with silver nitrate solution. The obtained liquid was dried under vacuum at 60°C overnight.

**ESI-MS** Calculated: *m/z*: 279.9178 (NTf<sub>2</sub><sup>-</sup>); found: *m/z*: 279.9141. **<sup>13</sup>C NMR** (151 MHz, DMSO-*d*<sub>6</sub>) δ 170.86, 145.97, 142.81, 120.54, 118.41, 114.29, 114.00, 60.62, 59.97.

**1,4-bis(2-hydroxyethyl)pyridinium-bis(trifluoromethanesulfonyl)imide (IL-6)**



At room temperature, 1.8411 g (0.0074 mol) of **IL-3** was dissolved in 5 ml of H<sub>2</sub>O, and 2.9082 g (0.0074 mol) of AgNTf<sub>2</sub> was added. The mixture was stirred for 12 hours. Two phases were obtained after filtration by a needle filter, and the lower one was washed several times with water until no

residual bromine was detected with silver nitrate solution. The obtained liquid was dried under vacuum at 60°C overnight.

$^{13}\text{C}$  NMR (151 MHz, DMSO- $d_6$ )  $\delta$  160.63, 144.09, 127.89, 120.54, 118.41, 62.37, 59.97, 59.85, 38.16.

### Thermal Analyses

Simultaneous Thermal Analyzer (STA, NETZSCH STA 449 F3) was used to detect the thermal properties of as-prepared ILs sample, which can provide simultaneous signals from TG and DSC. Measurements were carried out with approximately 6 mg of sample at a heating rate of 10°C min<sup>-1</sup> over a temperature range from room temperature to 800°C. In order to accurately describe the thermochemical properties of ILs, the onset decomposition temperature ( $T_{\text{onset}}$ ) is defined at which a 5% mass loss has occurred. Melting temperature ( $T_{\text{m}}$ ) is determined from the peak temperature of the corresponding DSC curve.

Differential scanning calorimetry (DSC, NETZSCH DSC 214) was used to investigate the phase transition behavior of the ILs between -170 and 150°C. The measurements were conducted under a N<sub>2</sub> atmosphere (40 mL min<sup>-1</sup>) using a concave aluminum closed crucible with a scanning rate of  $\pm 5^\circ\text{C min}^{-1}$ . Liquid nitrogen was used as the coolant fluid. Each sample (~ 6 mg) was subjected to three thermal cycles, including three heating programs and three cooling programs, with a 2-min isothermal step between them:

- (a) heating from 25°C to 150°C at 5°C min<sup>-1</sup>,
- (b) isothermal step at 150°C during 2 minutes,
- (c) cooling from 150°C to -170°C at 5°C min<sup>-1</sup>,
- (d) isothermal step at -170°C during 2 minutes,
- (e) heating from -170°C to 150°C at 5°C min<sup>-1</sup>,
- (f) isothermal step at 150°C during 2 minutes,
- (g) cooling from 150°C to -170°C at 5°C min<sup>-1</sup>,
- (h) isothermal step at -170°C during 2 minutes,
- (i) heating from -170°C to 150°C at 5°C min<sup>-1</sup>,
- (j) isothermal step at 150 °C during 2 minutes and
- (k) cooling from 150°C to -170°C at 5°C min<sup>-1</sup>.

Throughout this work, the onset temperature of thermal anomaly is defined as the transition temperature.

## Structural Analyses

Temperature-dependent powder X-ray diffraction was conducted for the as-prepared sample using X-ray diffractometer (XRD, Rigaku SmartLab 9 kW, Tokyo, Japan) equipped with a medium and low temperature in-situ diffraction analysis accessory. The  $2\theta$  range for the XRD measurements was set from 5 to 60°, and measurements were taken at 5° min<sup>-1</sup>. A monochromatic Cu K $\alpha$  ( $\lambda = 1.540593 \text{ \AA}$ ) radiation was used as the X-ray source. The temperature range measured was between -180 and 140 °C at a temperature change rate of  $\pm 5.0^\circ\text{C min}^{-1}$  under vacuum, and measurements were performed after 10 minutes of stabilization at every 20 °C. Liquid nitrogen was used as the coolant fluid. Each sample was subjected to six ramps, three in cooling and three in heating mode.

## Temperature-dependent Raman

Raman measurements were carried out using a confocal Raman microscopy (LabRAM HR Evolution, HORIBA Scientific, France) equipped with its high throughput 800 mm single stage spectrometer. Temperature and environmental control are achieved through a Linkam microscope stages (CAP500, Linkam scientific instruments, United Kingdom). Measurements were carried out in the temperature range between -180 and 150 °C at a scanning rate of  $\pm 5.0^\circ\text{C min}^{-1}$  under a N<sub>2</sub> gas flow. The excitation was triggered by a green laser with excitation power of 20 mW (wavelength of 532 nm). The spectral resolution was 1 cm<sup>-1</sup>. Routine calibration of the monochromator was performed by using single crystal silicon. HORIBA Scientific's LabSpec 6 software delivers a unique environment for complete instrument control and data processing.

## Computational Details

Molclus<sup>1</sup> program was used to search the configuration. Density functional theory (DFT) was used to optimize the structure and calculate the energy of the searched configuration by MOPAC<sup>2</sup> and Gaussian16<sup>3</sup> program packages. B3LYP hybrid functional/6-311G (d,p) basis set was used to optimize the structure with dispersion correction. The energy of each structure was obtained by B2PLYP hybrid functional/def2-TVZP basis set, and then the proportions of different molecular conformations were calculated according to Boltzmann distribution. Vibrational analysis of the searched configuration was performed by Gaussian16, and Raman spectra were assigned by the Multiwfn<sup>4</sup> program. Further structural optimization was performed by Gaussian16 using the B3LYP hybrid functional/TZVP basis set with dispersion correction. Energy calculations were performed on the optimized structures by the M062X hybrid functional /ma-TZVPP<sup>5</sup> basis set. Interaction energies were calculated by Multiwfn program.

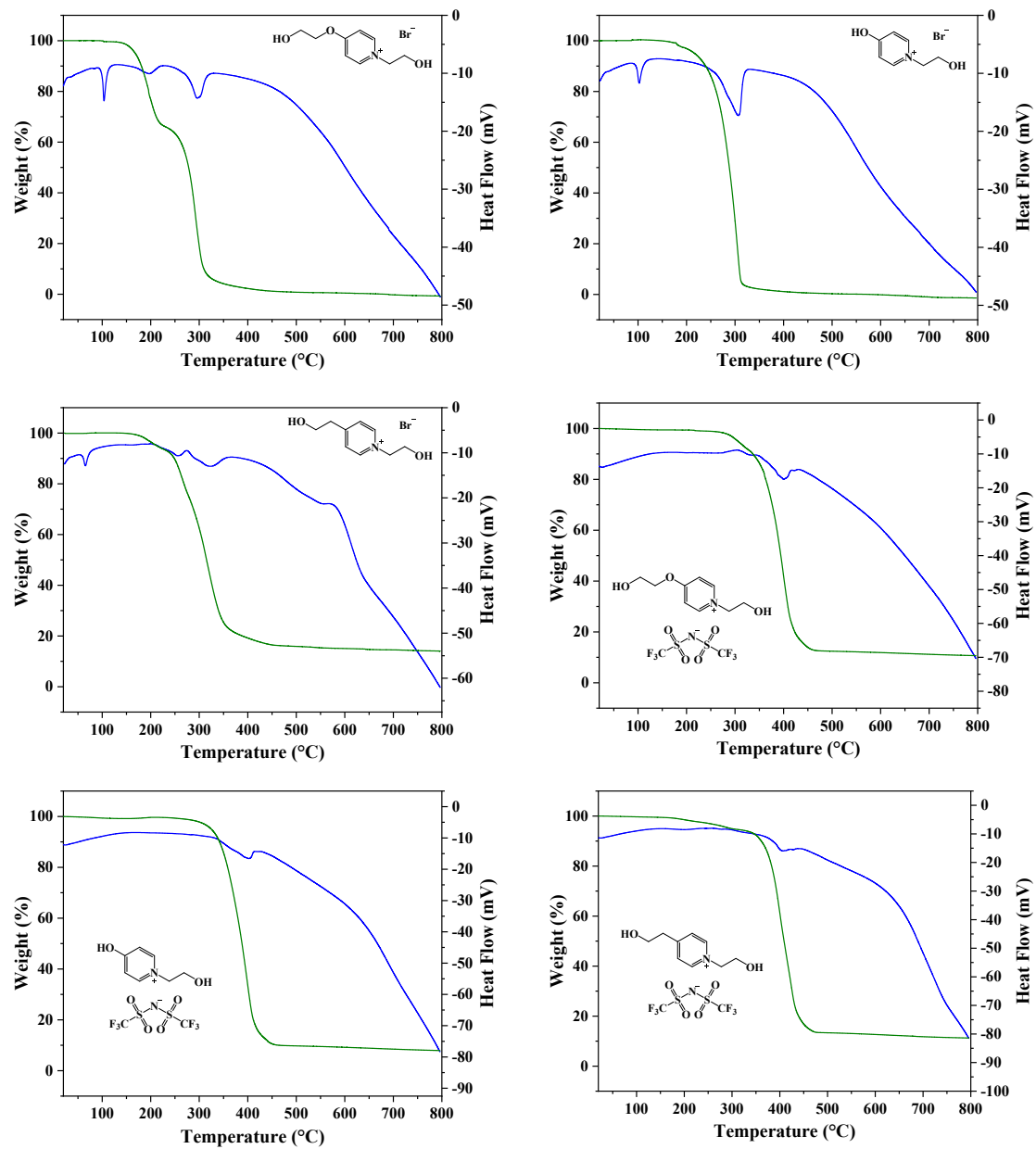


Figure S1. STA profile of each ILs sample

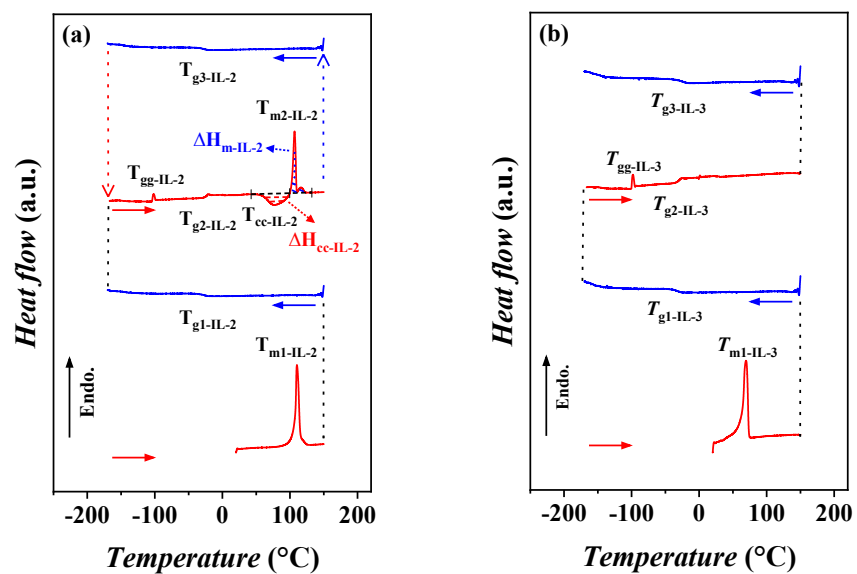


Figure S2. DSC traces for thermochemical behavior of IL-2 and IL-3

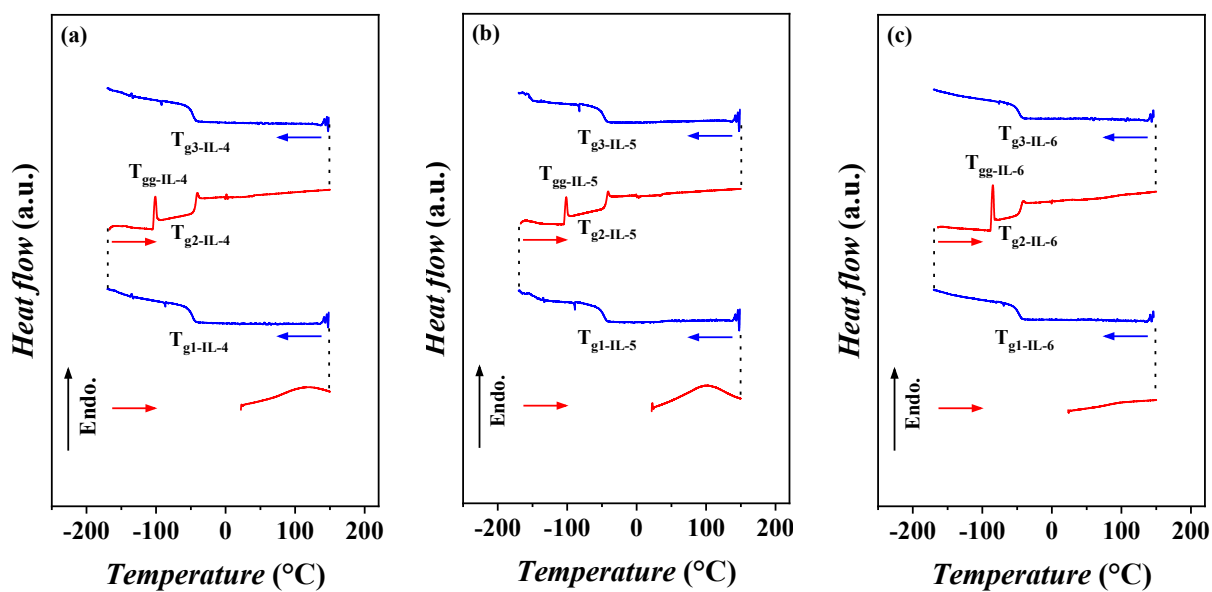


Figure S3. DSC traces for thermochemical behavior of IL-4, IL-5 and IL-6



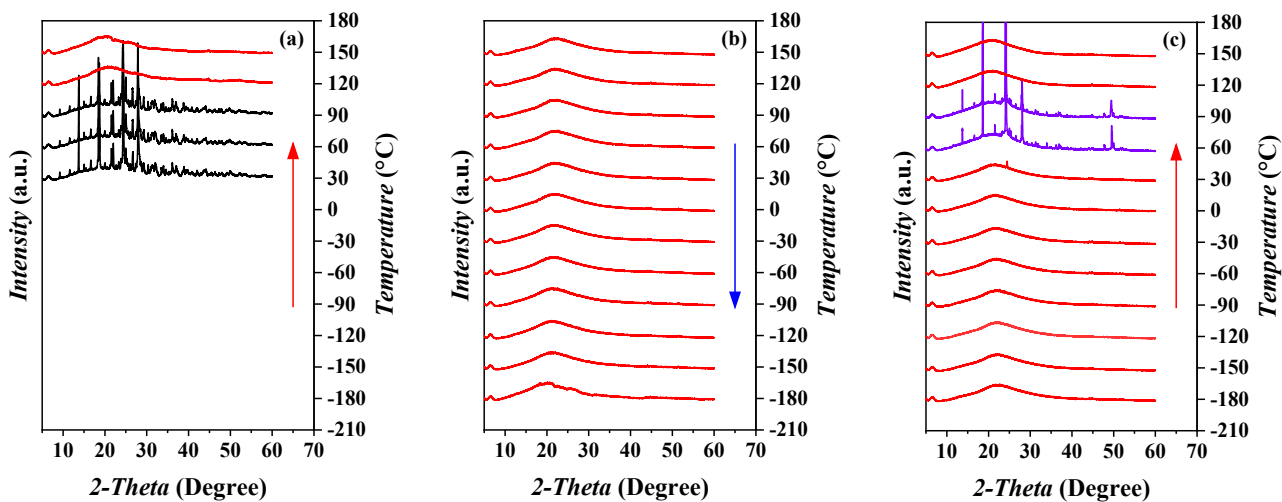


Figure S4. Thermal cycle XRD pattern and corresponding DSC curve of IL-2

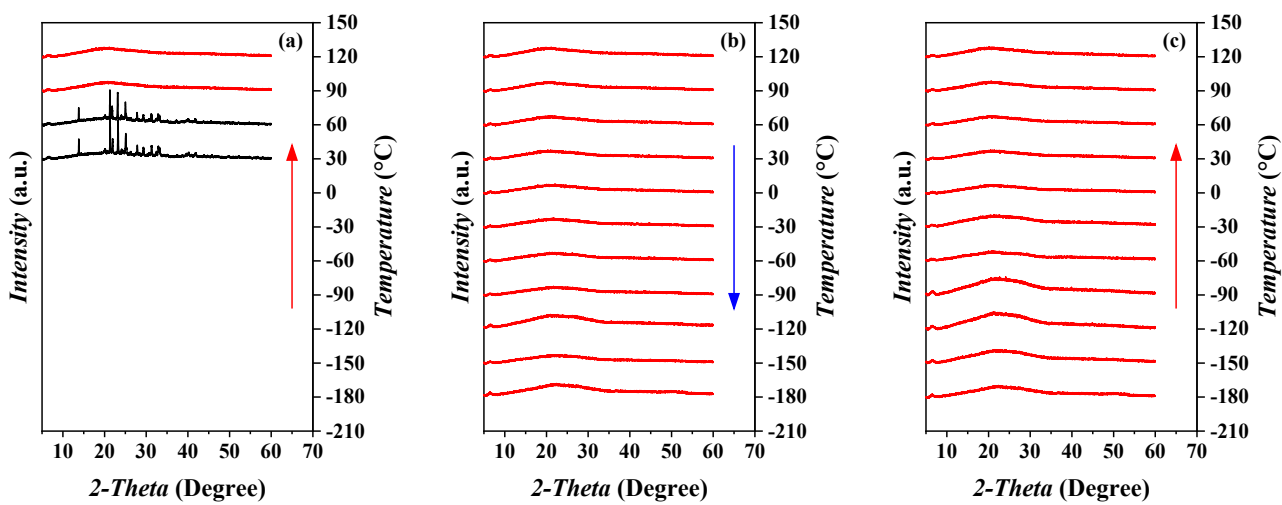


Figure S5. Thermal cycle XRD pattern and corresponding DSC curve of IL-3

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