

## **pH-regulated Reversible Phase inversion of Poly(ionic liquid) Aqueous Two-Phase Systems**

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## Materials and methods

Azobisisobutyronitrile (AIBN, 99%) was recrystallized from methanol twice before use. 1-Vinylimidazole (VIm, 98%) was purified by distilling under vacuum and stored in the fridge. Bromoethane, benzyl bromide (BnBr), ferrocenemethanol (FcCH<sub>2</sub>OH), 1-bromo-6-hexanol (BrC<sub>6</sub>H<sub>12</sub>OH), 2,6-di-tert-butyl-4-methylphenol (BHT), sodium hydroxide (NaOH), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), glacial acetic acid (CH<sub>3</sub>COOH), methanol, dichloromethane (DCM), petroleum ether, ether, acetone, hydrochloric acid (HCl, 36.5 wt%) were A.R. grade and used as received without further treatment. Deionized water was used to prepare the aqueous solutions.

### *Nuclear Magnetic Resonance (NMR) spectroscopy*

Proton and carbon nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) spectra were recorded on Bruker Advance AV 400 MHz spectrometer with chloroform-*d*, D<sub>2</sub>O and DMSO-*d*<sub>6</sub> as the solvents.

### *Fourier Transform Infrared (FT-IR) spectroscopy*

Fourier transform infrared (FT-IR) spectra were conducted on a Thermo Nicolet Nexus-470 spectrophotometer using KBr tables by signal-averaging 32 scans with a 4 cm<sup>-1</sup> spectral resolution. The data processing was performed by the software of OMNIC 8.0.

### *Ultraviolet-visible (UV-vis) spectroscopy*

UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer using a 1.0 path quartz cell. The transmittance of solutions was determined by a UV-vis spectrophotometer at 800 nm. The initial solution concentration was 100 mg/mL. The pH was adjusted by HCl or NaOH solution (3.0 M), and the pH value were detected through a pH meter.

### *Measurement of binodal curves of PIL-based ATPSs*

All the binodal curves of PIL-based ATPSs were determined through the cloud point titration method according to the procedures described in the literatures.<sup>[1]</sup> Typically, a known concentration of Fc-PIL-10 aqueous solution was added into a test tube at the room temperature (25 °C), and a known mass fraction of salting-out agent solution was added dropwise until the mixture became turbid. Then, a known mass of water was added to make the mixture clear again. These procedures were repeated to obtain sufficient data to construct a liquid–liquid equilibrium binodal curve. The binodal curve data were mathematically fitted according to Equation 1:<sup>[2]</sup>

$$[\text{PIL}] = A \exp(B \times [\text{salt}]^{0.5}) - (C \times [\text{salt}]^3) \quad (1)$$

in which [PIL] and [salt] indicate the mass fraction percentages of PIL and salting agent in the

mixture solution, respectively, and A, B and C are the fitting parameters obtained by the regression of the experimental binodal data.

#### *Dynamic light scattering (DLS)*

Dynamic light scattering (DLS) data were obtained by BeNano 90 Zeta (Dandong Bettersize, China) using a 1.0 path quartz cell. The temperature of solutions was set at 25 °C and the initial solution concentration was 150 mg mL<sup>-1</sup>. The pH was adjusted by adding the HCl solution or the NaOH solution (3.0 M), and the pH value were detected through a pH meter.

#### *Determination of phase composition of PIL-based ATPSs*

The solutions (1.0 mL) in the upper and lower phases of PIL-based ATPS were taken, and diluted to 10 mL using deionized water. Then, the diluent (3.0 mL) was measured by UV-vis absorption spectroscopy. The phase composition was calculated according to the work plot of Fc-PIL-10.

#### *Fabrication of pH-responsive PIL-based ATPSs*

Bn-PIL-x (0.30 g) and Fc-PIL-10 (0.30 g) was added into a vial, and deionized water (2.0 mL) was added to dissolve the polymers. After standing, PIL-based ATPSs were obtained. For the pH-response experiment, HCl (30 μL, 3.0 M) aqueous solution was added under stirring. After standing, the phenomenon was observed. After that, NaOH (30 μL, 3.0 M) aqueous solution was added. After the similar procedure, the phenomenon was observed and recorded.

#### *Cyclic voltammetry (CV) measurement*

CV measurements were conducted on a CHI660e electrochemical station. The electrochemical window was set from -1.6 V to 0.8 V, and the scanning rate was 0.02 V s<sup>-1</sup>. The concentration of Fc-PIL was 3.5 wt%.

#### *X-ray photoelectron spectroscopy (XPS) measurement*

XPS data were obtained using a Thermo ESCALAB 250 with Al K $\alpha$  irradiation with the X-ray source at  $\theta = 90^\circ$ . The C1s peak standard value (284.8 eV) was used as a reference for energy calibration, and the curve was fitted using XPSPEAK41 software with an energy background of "Linear".

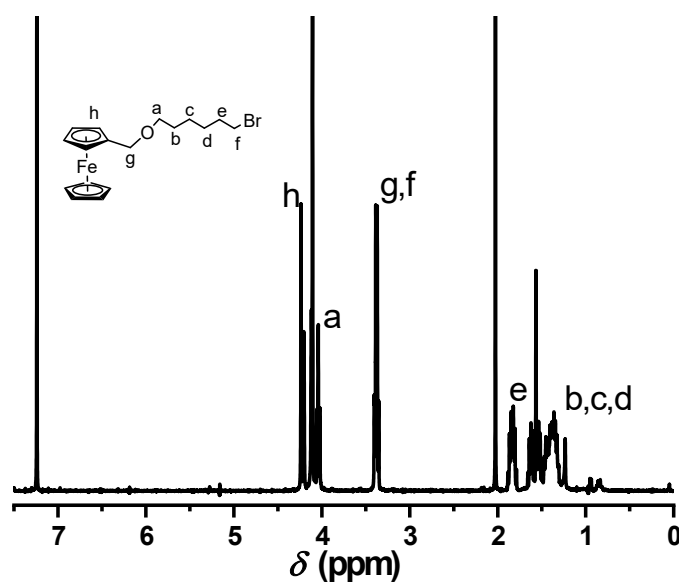
#### *Surface Tension ( $\gamma$ ) measurement*

The liquid surface tension through the free-hanging method was recorded on a ThermoCahn Radian series 300 dynamic contact angle analyzer (USA ).

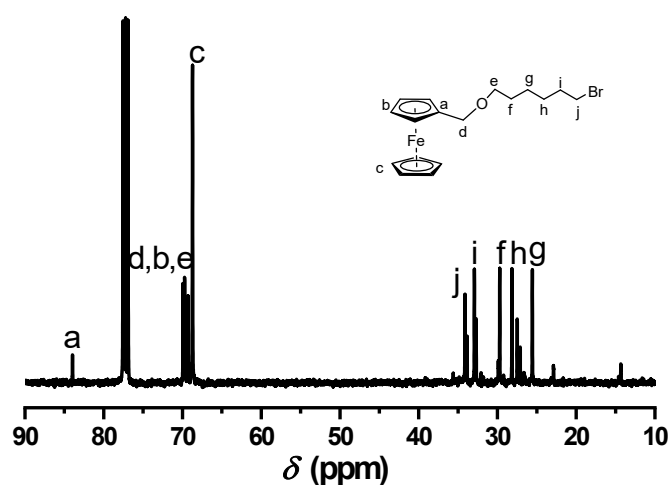
## Synthesis

### Synthesis of 6-bromohexyl-4-ferrocenyl ether ( $\text{FcC}_6\text{Br}$ )

$\text{FcC}_6\text{Br}$  was synthesized according to the reported methods in the literature.<sup>[3]</sup> Firstly,  $\text{FcCH}_2\text{OH}$  (0.9237 g, 4.27 mmol) was dissolved in  $\text{BrC}_6\text{H}_{12}\text{OH}$  (3.6002 g, 19.88 mmol) at room temperature. Then, the catalytic amount of glacial acetic acid was added. The solution was stirred at room temperature for 12 h in nitrogen atmosphere. Then, a small amount of triethylamine was added. The crude product was purified by silica gel column chromatography using PE/DCM mixed solvent (1 : 1, v/v) as the eluent. After dried at 30 °C overnight,  $\text{FcC}_6\text{Br}$  was obtained as red oil (Yield: 1.17 g, 69%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm, **Figure S1**): 4.25 (s, 2H), 4.22 (m, 2H), 4.12 (m, 7H), 3.41–3.36 (m, 4H), 2.05 (q, 2H), 1.54 (m, 2H), 1.37 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm, **Figure S2**): 83.51, 69.61, 69.34, 68.98, 68.32, 33.86, 32.61, 29.40, 27.85, 25.25 ppm.



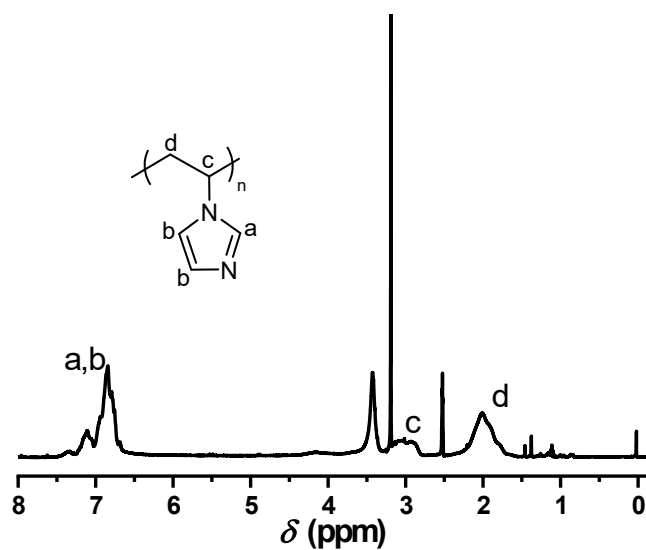
**Figure S1**  $^1\text{H}$  NMR spectrum of  $\text{FcC}_6\text{Br}$  in  $\text{CDCl}_3$ .



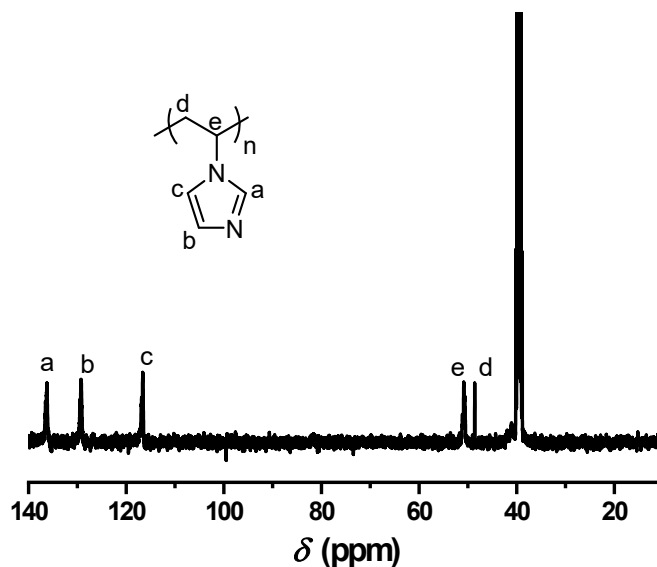
**Figure S2**  $^{13}\text{C}$  NMR spectrum of  $\text{FcC}_6\text{Br}$  in  $\text{CDCl}_3$ .

#### Synthesis of PVIm

According to the reported method,<sup>[4]</sup> VIm (10.01 g, 106.3 mmol) and AIBN (0.175 g, 1.063 mmol) were added into a flask containing methanol (20 mL). The mixture was refluxed for 60 h at 70 °C under nitrogen atmosphere. After cooled down to room temperature, the reaction solution was precipitated from ether. The crude product was purified by several dissolving-precipitation cycles. The polymer was dried 12 h under reduced pressure (Yield: 9.03 g, 90.30%).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz,  $\delta$  ppm, **Figure S3**): 7.58–6.45 (a, b), 3.21–2.71 (c), 2.34–1.53 (d).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 101 MHz,  $\delta$  ppm, **Figure S4**): 137.5–136.0, 131.0–128.5, 118.5–116.0, 51.9–50.6, 49.7–49.8.



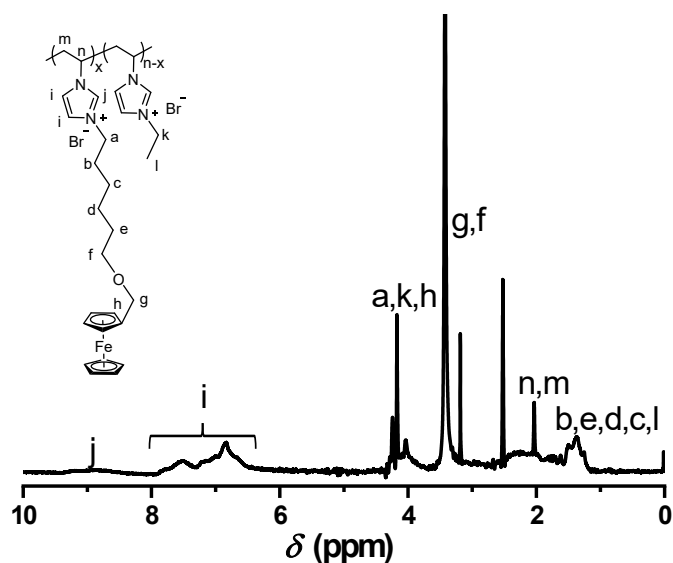
**Figure S3**  $^1\text{H}$  NMR spectrum of PVIm in  $\text{DMSO-}d_6$ .



**Figure S4**  $^{13}\text{C}$  NMR spectrum of PVIm in  $\text{DMSO-}d_6$ .

*Synthesis of Fc-grafted PIL with different  $GD_{Fc}$  (Fc-PIL- $x$ )<sup>[4]</sup>*

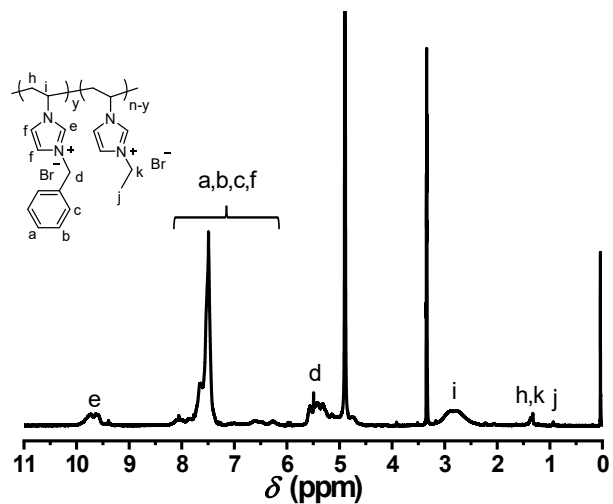
PVIm (2.4653 g, 26.2 mmol (imidazole monomer)) was dissolved in methanol (20 mL). Then,  $\text{FcC}_6\text{Br}$  (0.9821 g, 2.6 mmol) was added and the solution. The solution was refluxed at 70 °C. After 24 h, the solution was cooled down to room temperature and bromoethane (23.21 g, 213 mmol) was added. The reaction was further conducted at 70 °C for 24 h. After the reaction, the solution was poured into a great deal of ethyl acetate. The product was obtained as an orange solid through filtration (Yield: 78.70%, 3.90 g), and defined as Fc-PIL-10, in which the number '10' denoted the feeding molar ratio of  $\text{FcC}_6\text{Br}$  to the imidazolium units. Fc-PIL-5 (Yield: 3.99 g, 84.2%) and Fc-PIL-20 (Yield: 2.0 g, 40%) were synthesized according to the same procedure.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz,  $\delta$  ppm, **Figure S5**): 10.23–8.92 (N-CH=N), 8.64–7.01 (vinyl-N-CH, ethyl-N-CH, phenyl-H), 4.25 (s, 2H, Cp-CH<sub>2</sub>-O), 4.22 (m, 2H, CH of Cp-CH<sub>2</sub>O), 4.12 (m, 7H, CH of Cp-CH<sub>2</sub>O + CH of Cp), 3.41–3.36 (m, 4H, OCH<sub>2</sub> + CH<sub>2</sub>Br), 2.05 (quint, 2H, CH<sub>2</sub>), 1.54 (m, 2H, CH<sub>2</sub>), 1.37 (m, 4H, CH<sub>2</sub>) ppm. 2.90–2.09 (N-CH), 1.74–1.34 (N-C-CH<sub>2</sub>), 1.33–1.14 (N-C-CH<sub>3</sub>, CH<sub>2</sub>).



**Figure S5**  $^1\text{H}$  NMR spectrum of Fc-PIL-10 in  $\text{DMSO-}d_6$ .

*Synthesis of Bn-PIL with different  $\text{GD}_{\text{Bn}}$  (Bn-PIL- $x$ )*

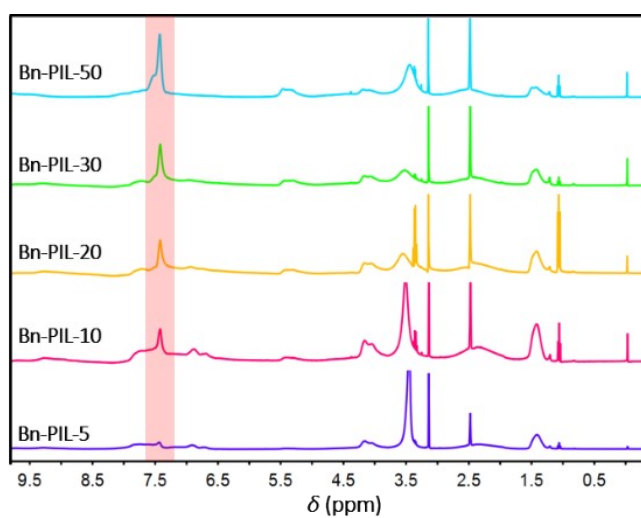
Bn-PIL was prepared by quaternization of PVI<sub>m</sub> using BnBr and bromoethane according to the method similar to Fc-PIL.<sup>[4]</sup> Specifically, PVI<sub>m</sub> (2.06 g, 21.89 mmol (imidazole unit)) was dissolved in methanol (20 mL). Then, BnBr (0.37 g, 2.19 mmol) was added and the solution was refluxed at 70 °C. After 24 h, the solution was cooled down to room temperature and bromoethane (11.75 g, 107.84 mmol) was added. The reaction was further conducted at 70 °C. After the reaction, the solution was poured into a great deal of ether. The product was obtained as a white solid through filtration (Yield: 3.45 g, 75.31%), and defined as Bn-PIL-10, in which the number '10' denoted the feeding molar ratio of BnBr to the imidazolium units.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz,  $\delta$  ppm, **Figure S6**): 10.33–8.53 (N-CH=N), 8.52–6.61 (vinyl-N-CH, ethyl-N-CH and phenyl-H), 4.96–5.85 (phenyl-CH<sub>2</sub>), 4.82–3.45 (N-CH<sub>2</sub>), 2.91–1.43 (N-CH), 1.42–1.07 (N-C-CH<sub>2</sub>), 1.07–0.95 (N-C-CH<sub>3</sub>). Bn-PIL-5 (Yield: 3.80 g, 85.70%), Bn-PIL-20 (Yield: 3.62 g, 77.68%), Bn-PIL-30 (Yield: 3.66 g, 74.95%), and Bn-PIL-50 (Yield: 3.68 g, 71.20%) were synthesized according to the similar procedure.



**Figure S6**  $^1\text{H}$  NMR spectrum of Bn-PIL-10 in  $\text{DMSO-}d_6$ .

#### Determination of actual $GD_{\text{Bn}}$ of Bn-PILs

In the  $^1\text{H}$  NMR spectrum of Bn-PILs, the signal of the methylene at 5.07–5.75 ppm and the signal of C-2 hydrogen of the imidazolium at 9.11–10.53 ppm were integrated to calculate  $GD_{\text{Bn}}$ . The results were summarized in **Table S1**.



**Figure S7**  $^1\text{H}$  NMR spectra of Fc-PILs with different  $GD_{\text{Fc}}$  in  $\text{DMSO-}d_6$ .

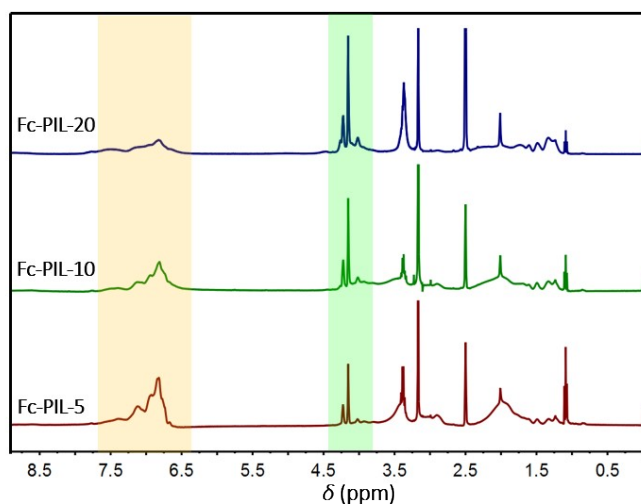


**Table S1** The actual benzyl grafting degree ( $GD_{Bn}$ ) of Bn-PIL-x

Bn-PIL-x	$GD_{abs}$ (%)	$GD_{act}$ (%)
Bn-PIL-5	5	4.7
Bn-PIL-10	10	9.8
Bn-PIL-20	20	19.3
Bn-PIL-30	30	29.9
Bn-PIL-50	50	49.0

*Determination of actual  $GD_{Fc}$  of Fc-PILs*

The signal of the ferrocene ring at 4.12–4.25 ppm and the signal imidazole ring at 9.11–10.53 ppm were used to calculate the actual  $GD_{Fc}$ . The results were summarized in **Table S2**.

**Figure S8**  $^1H$  NMR spectra of Fc-PILs with different  $GD_{Fc}$  ( $DMSO-d_6$ ).**Table S2** The actual benzyl grafting degree ( $GD_{Bn}$ ) of Fc-PIL-x

Fc-PIL-x	$GD_{abs}$ (%)	$GD_{act}$ (%)
Fc-PIL-5	5	4.6
Fc-PIL-10	10	9.9
Fc-PIL-20	20	17.7

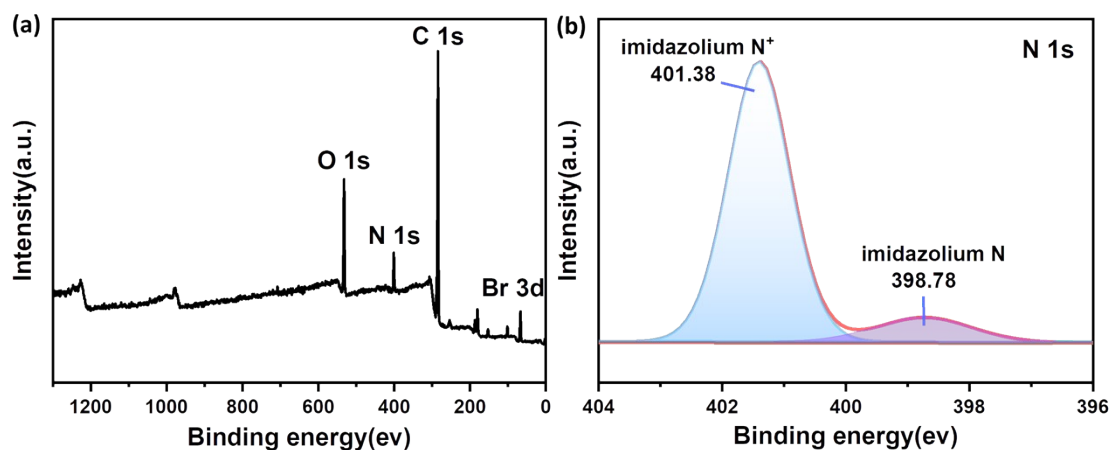


Figure S9 XPS spectra of Bn-PIL-20. (a) survey, (b) N 1s.

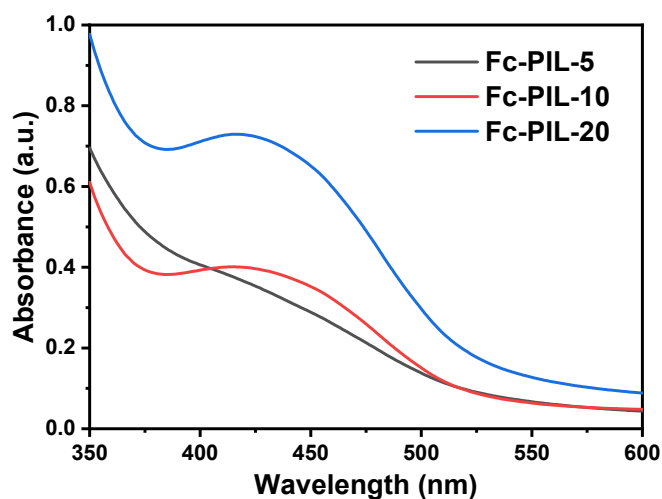
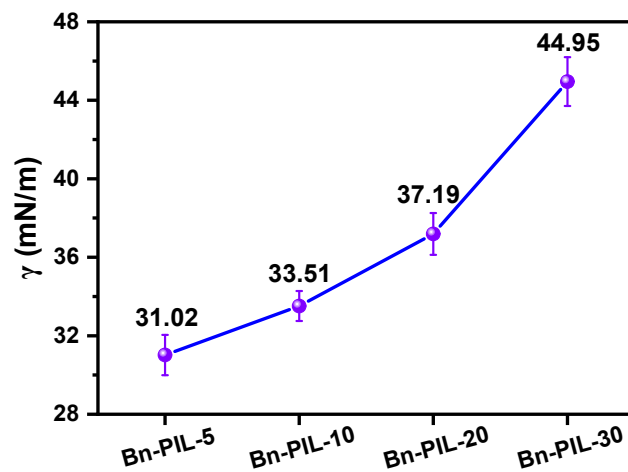


Figure S10 UV-vis absorption curves of Fc-PILs aqueous solution ( $7.5 \text{ g L}^{-1}$ ).

Table S3 Parameter data of CV curve of Fc-PIL-10 aqueous solution.\*

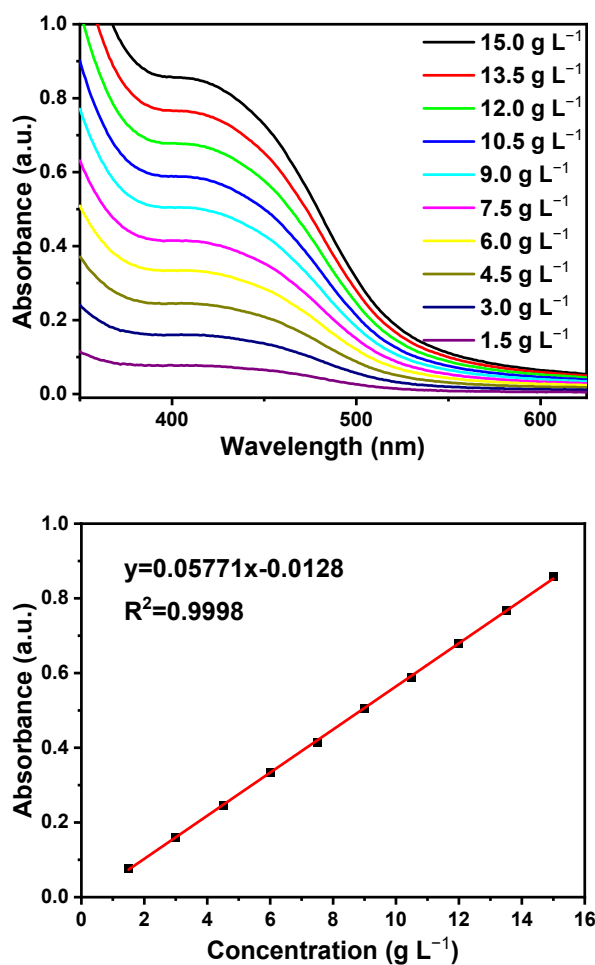
CV data									
substrate	$E_c$ (V)	$E_a$ (V)	$E_{Fc^+}$ (V)	$i_c$ ( $\mu\text{A}$ )	$i_a$ ( $\mu\text{A}$ )	$i_{Fc^+}$ ( $\mu\text{A}$ )	$E_{1/2}$ (V)	$\Delta E_p$ (V)	$i_c/i_a$
Fc-PIL-10	0.32	0.19	-0.65	7.61	7.01	-3.66	0.26	0.13	1.09

\*  $E_c$ ,  $E_a$  are the peak potential of cathode and anode;  $i_c$  and  $i_a$  are the peak current of cathode and anode;  $E_{1/2}$  is the half-wave potential;  $\Delta E_p$  is the potential difference of peak current.



**Figure S11** GD<sub>Bn</sub>-dependent surface tension ( $\gamma$ ) of Bn-PILs solution. The concentrations are 0.15 g/mL.

*Determination of upper and lower phase components*



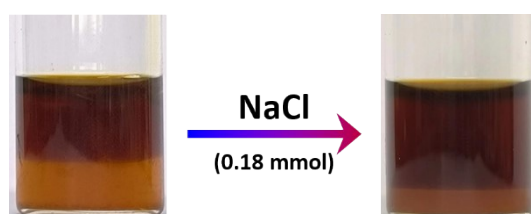
**Figure S12** The UV absorption curve and working curve of Fc-PIL-10 aqueous solution with different concentrations.

**Table S4** Binodal curve data of ATPSs composing of Fc-PIL-10 + Bn-PIL-x at 25 °C.

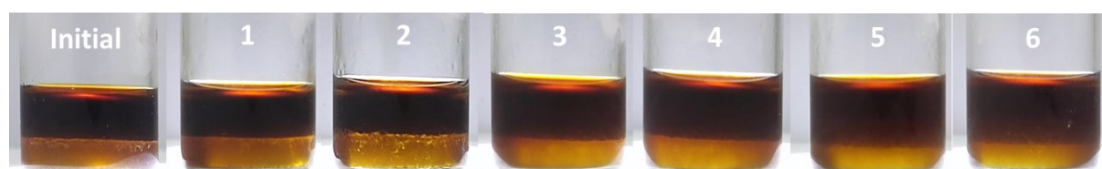
Bn-PIL-5		Bn-PIL-10		Bn-PIL-20		Bn-PIL-30		Bn-PIL-50	
$C_{Bn5}$ (wt %)	$C_{Fc}$ (wt %)	$C_{Bn10}$ (wt %)	$C_{Fc}$ (wt %)	$C_{Bn20}$ (wt %)	$C_{Fc}$ (wt %)	$C_{Bn30}$ (wt %)	$C_{Fc}$ (wt %)	$C_{Bn50}$ (wt %)	$C_{Fc}$ (wt %)
9.99	4.69	8.61	4.33	6.61	6.47	5.18	5.78	1.76	5.78
10.32	3.51	8.88	2.61	6.84	4.57	5.66	3.25	2.06	3.40
10.59	2.75	9	2.07	6.88	4.29	5.71	3.07	2.16	3.52
10.73	2.43	9.13	1.61	6.96	3.78	5.79	2.79	2.33	2.83
10.77	2.34	9.39	1.01	7.02	3.43	6.05	2.08	2.54	2.13
10.86	2.16	9.41	0.97	7.03	3.37	6.28	1.60	2.87	1.33
11.02	1.87	9.48	0.86	7.09	3.05	6.41	1.37	3.08	0.98
11.23	1.56	9.53	0.79	7.16	2.71	6.54	1.15	3.16	0.86
11.46	1.29	9.58	0.73	7.23	2.41	6.6	1.06	3.24	0.77
11.51	1.24	9.64	0.66	7.3	2.14	6.68	0.93	3.38	0.62
11.57	1.19	9.69	0.60	7.32	2.07	6.7	0.90	3.49	0.53
11.68	1.09	9.74	0.55	7.53	1.46	6.74	0.83	3.57	0.47
11.87	0.95	9.8	0.49	7.58	1.35	6.77	0.79	3.68	0.41
12.05	0.84	9.81	0.48	7.69	1.16	6.82	0.70	3.76	0.37
12.32	0.72	9.84	0.45	7.71	1.13	6.84	0.70	3.84	0.34
12.55	0.62	9.9	0.38	7.83	0.98	6.85	0.65	3.93	0.31
12.67	0.57			7.92	0.90	6.89	0.58	4.03	0.28
12.81	0.51			7.97	0.87	6.93	0.51		
12.98	0.44			8.11	0.82	6.94	0.50		

**Table S5** Fitting parameters of Bn-PIL-x + Fc-PIL-10 + H<sub>2</sub>O double knotted line equation.

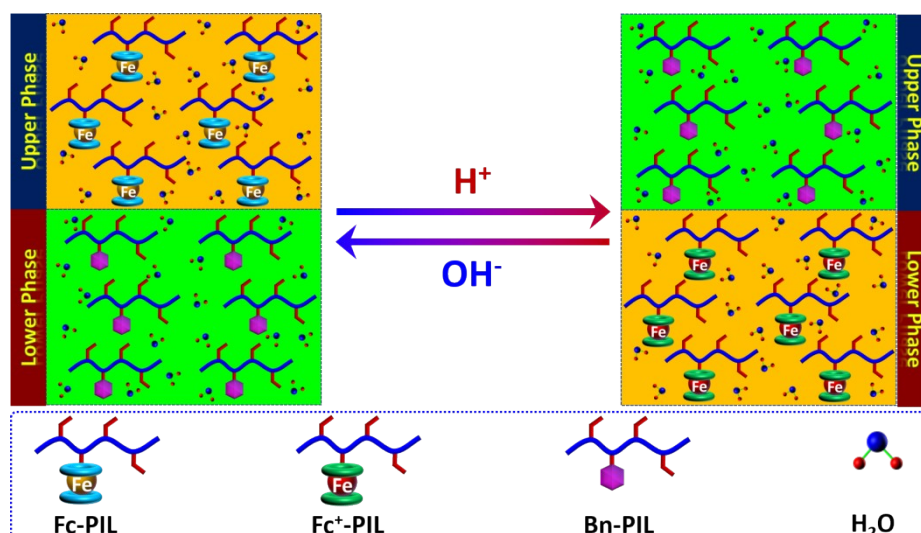
GD <sub>Bn</sub>	A ± σ	B ± σ	C ± σ	D ± σ	R <sup>2</sup>
5%	73±17	-88±28	30±12	-1±0.02	0.99224
10%	9641±1419	-8240±1244	1982±306	-34±5	0.99689
20%	2351±479	-2126±472	541±130	-10±0.004	0.99818
30%	1227±127	-1259±137	365±42	-9±0.003	0.99859
50%	67±19	-77±31	25±14	-0.7±0.8	0.99044



**Figure S13** Photographs of ATPS composing of Fc-PIL-10/Bn-PIL-30 before and after the addition of sodium chloride (0.18 mmol).



**Figure S14** The stability of ATPS composing of Fc-PIL-10 and Bn-PIL-30 under adding water (62 μL water was added each time). The concentration of ATPS is 0.15 mg/mL, and the volume is 1.0 mL.



**Scheme S1** A proposed mechanism for the pH-regulated reversible phase inversion behaviors of ATPSs composing of Fc-PILs and Bn-PILs.

## Reference

- [1] Z. Y. Li, Y. Feng, X. M. Liu, H. Y. Wang, Y. C. Pei, H. Q. Nimal Gunaratne, J. J. Wang, Light-triggered switchable ionic liquid aqueous two-phase systems. *ACS Sustainable Chem. Eng.*, **2020**, *8*, 15327–15335.
- [2] K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski, J. D. Holbrey, R. D. Rogers, Controlling the aqueous miscibility of ionic liquids: Aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations. *J. Am. Chem. Soc.*, **2003**, *125*, 6632–6633.
- [3] Y. Tang, P. Cao, W. Li, M. He, Z. Dai, Y. Xiong, Redox-responsive poly(ionic liquid) microgels explored as the building blocks for supramolecular assembly, *Polymer*, **2021**, *220*, 123575.
- [4] Y. Tang, Y. Zhang, X. Chen, X. Xie, N. Zhou, Z. Dai, Y. Xiong, Up/Down tuning of poly(ionic liquid)s in aqueous two-phase systems. *Angew. Chem. Int. Ed.*, **2023**, *62*, e202215722.