

## Supporting Information

# Novel Imidazolium-Based Poly(ionic liquid)s with Different Counter Ions for Self-Healing

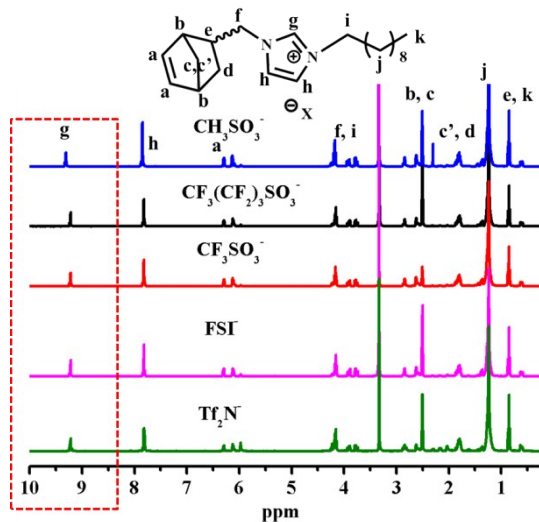
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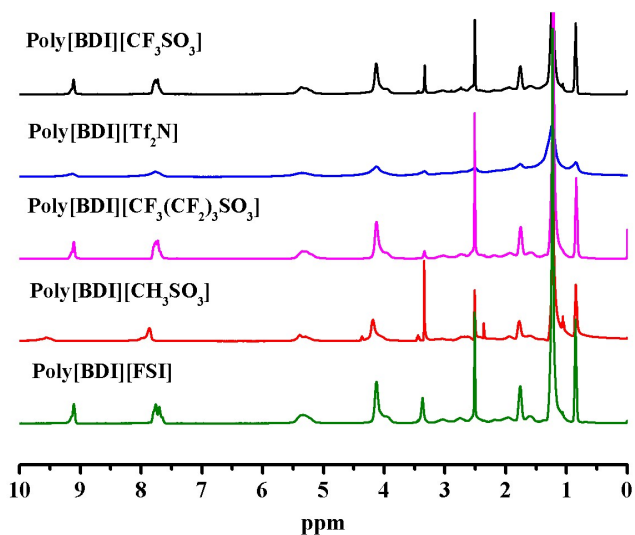
<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

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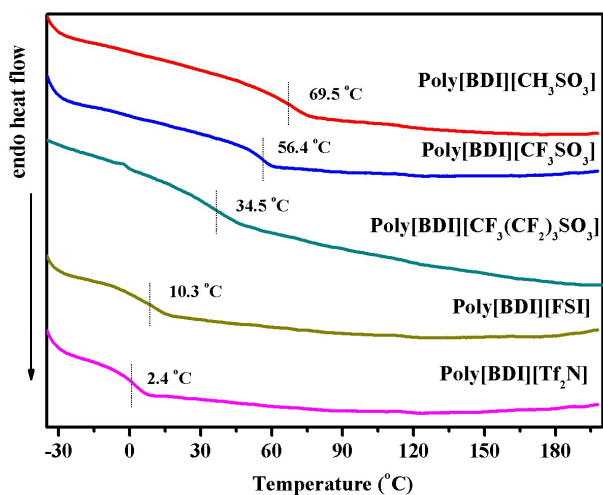
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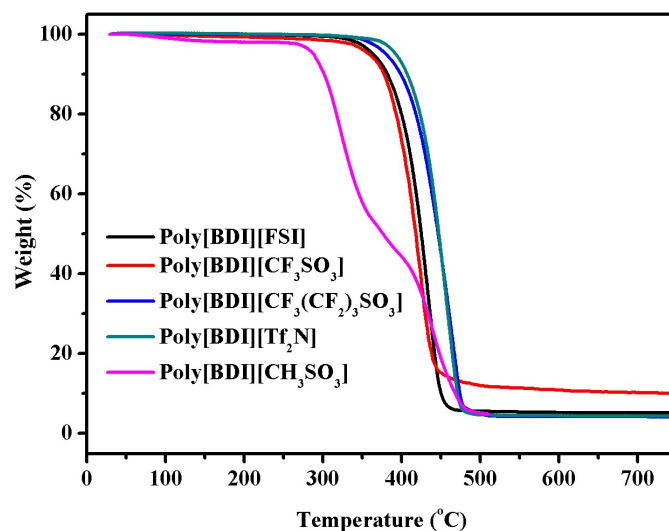
**Fig. S1.** The  $^1\text{H}$  NMR spectra of imidazolium-based norbornene derivatives with different counter ions (methyl sulfoxide- $d_6$ ).



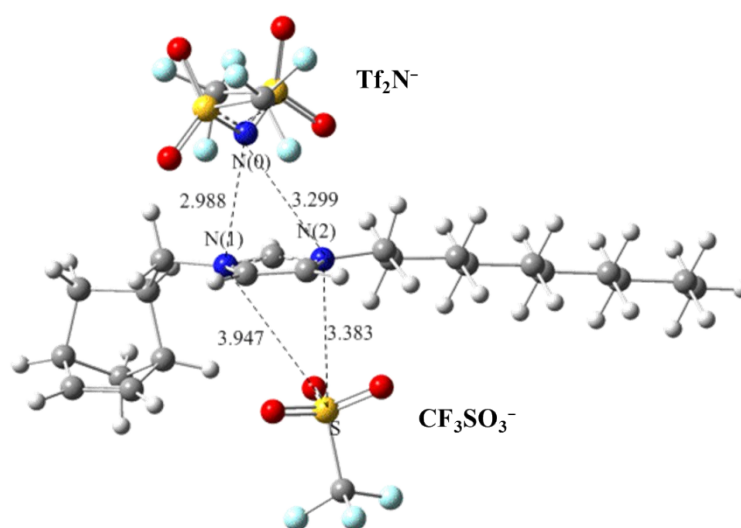
**Fig. S2.** The  $^1\text{H}$  NMR spectra of PILs (methyl sulfoxide- $d_6$ ).



**Fig. S3.** DSC curves of PILs.



**Fig. S4.** TGA curves of PILs.



**Fig. S5.** An optimized model for ion aggregation of an imidazolium cation surrounded by a  $\text{Tf}_2\text{N}^-$  counter ion and a  $\text{CF}_3\text{SO}_3^-$  counter ion.

**Table S1.** Interaction Energies <sup>a</sup> for 3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-decyl-3H-imidazolium ([BDI]) with two different counter ions ( $\text{Tf}_2\text{N}^-$  and  $\text{M}^-$ ) shown in Fig. S5.

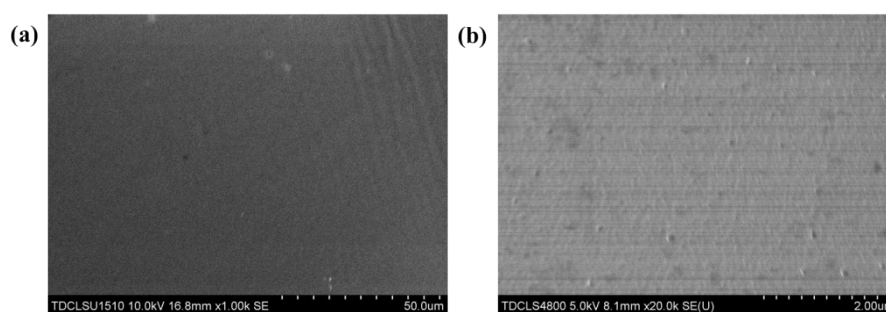
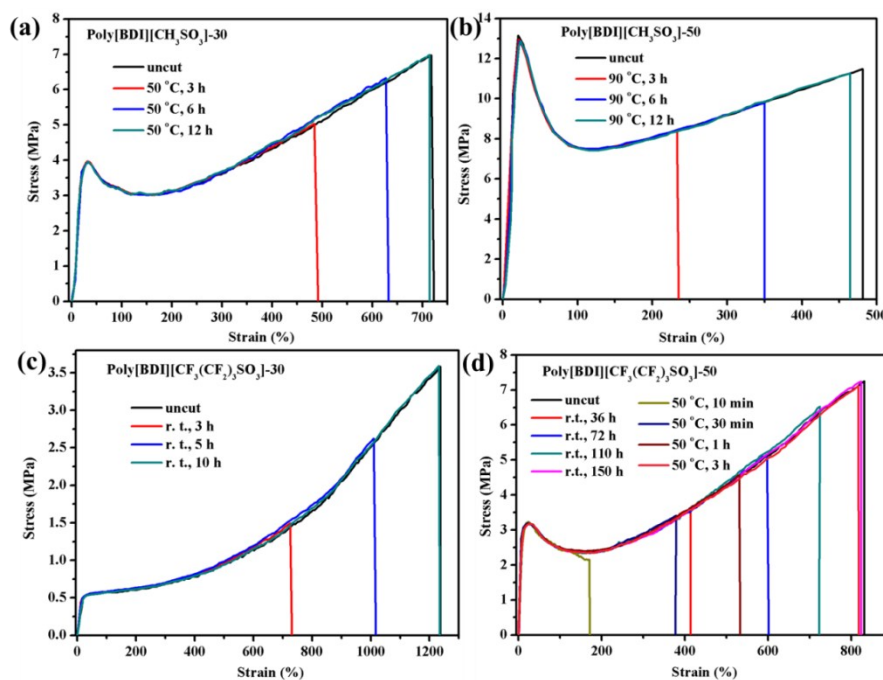
$\text{\AA}/(\text{kcal/mol})$	$\text{CH}_3\text{SO}_3^-$	$\text{CF}_3\text{SO}_3^-$	$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$
N(0)-N(1)	3.014	2.988	2.982
N(0)-N(2)	3.339	3.299	3.285
S-N(1)	3.973	3.947	3.963
S-N(2)	3.408	3.383	3.401
$\Delta E$	-114.4	-108.8	-107.7

<sup>a</sup> All calculations were carried out at the level of M05-2X/6-31+G(d) planted in Gaussian 09 program.

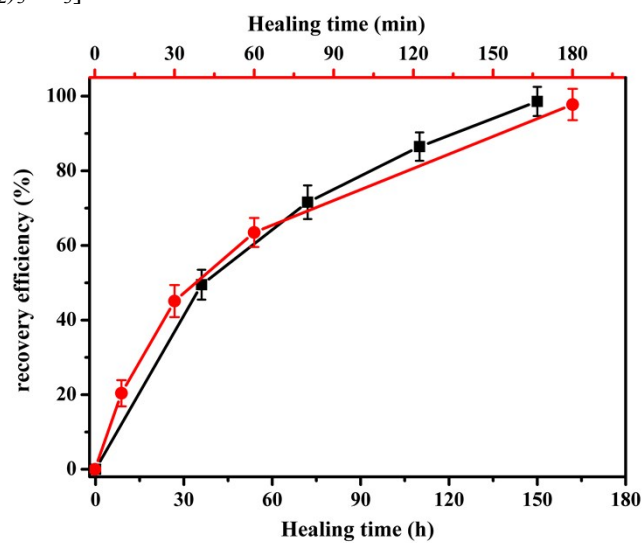
**Table S2.** Mechanical properties of polymer blends and Poly[BDI][FSI].<sup>a</sup>

Sample	Young's modulus (MPa) <sup>b</sup>	Yield stress (MPa)	Breaking stress (MPa)	Breaking strain (%)
Poly[BDI][FSI]	7.76±0.49	× <sup>c</sup>	3.98±0.25	1843±58
Poly[BDI][CH <sub>3</sub> SO <sub>3</sub> ]-30	42.20±3.62	3.90±0.08	6.97±0.44	722±25
Poly[BDI][CH <sub>3</sub> SO <sub>3</sub> ]-50	146.00±2.94	13.15±0.57	11.48±0.34	481±15
Poly[BDI][CF <sub>3</sub> SO <sub>3</sub> ]-30	14.68±1.80	×	4.49±0.13	1170±23
Poly[BDI][CF <sub>3</sub> SO <sub>3</sub> ]-50	49.00±2.16	4.60±0.21	7.12±0.16	705±33
Poly[BDI][CF <sub>3</sub> SO <sub>3</sub> ]-70	90.70±5.86	9.25±0.67	9.35±0.40	537±8
Poly[BDI][CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ]-30	13.78±1.06	×	3.58±0.15	1238±33
Poly[BDI][CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ]-50	43.05±2.05	3.41±0.01	6.24±0.19	707±27

<sup>a</sup> Strain rate = 100 mm min<sup>-1</sup>, room temperature; <sup>b</sup> Young's modulus, calculated from the initial slope of stress-strain curves (strain < 5%); <sup>c</sup> no detected.

**Fig. S6.** SEM photograph of Poly[BDI][Tf<sub>2</sub>N][CF<sub>3</sub>SO<sub>3</sub>]-50.**Fig. S7.** Stress-strain curves of the original and heated polymer blends. (a) Poly[BDI][CH<sub>3</sub>SO<sub>3</sub>]-30; (b) Poly[BDI][CH<sub>3</sub>SO<sub>3</sub>]-50; (c) Poly[BDI][CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>]-30; (d)

Poly[BDI][CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>]-50.



**Fig. S8.** Plots of the recovery efficiency of fracture strain as a function healing time for Poly[BDI][Tf<sub>2</sub>N][CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>]-50 at different temperatures, black plot represented room temperature and red plot represented 50 °C; Error bars denoted the standard deviations from at least five experiments