

Fluoro-functionalized polymeric ionic liquids: highly efficient catalysts for CO₂ cycloaddition to cyclic carbonates under mild conditions

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1. General experimental methods

Materials

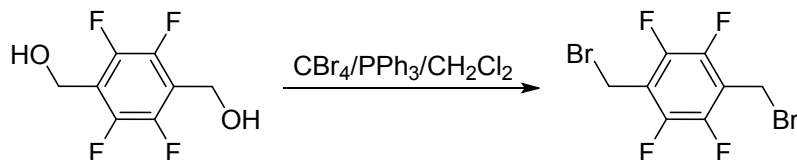
All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise.

Instrumentation

Liquid NMR spectra was recorded at Bruker 400 spectrometer. Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm^{-1} . The elemental analysis of the polymer was determined using a Flash EA1112 analyzer. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25 to 600 °C under air atmosphere with a heating rate of 20 °C/min. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV.

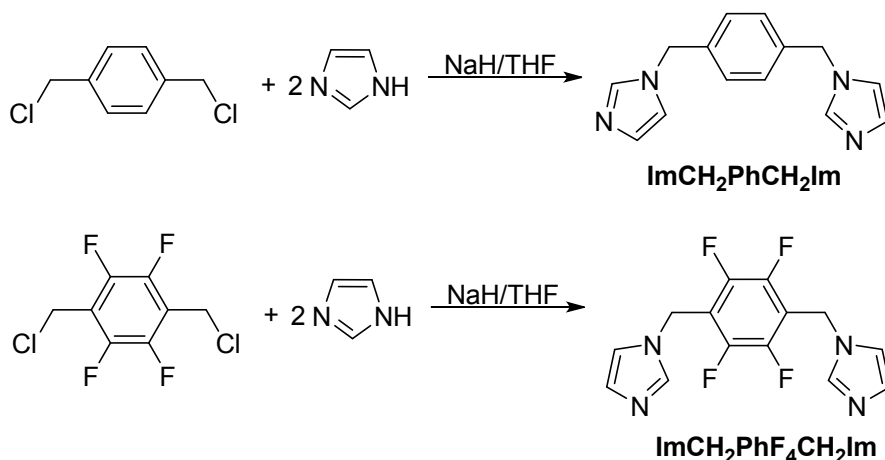
2. Synthetic procedures

(1) Synthesis of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene¹



1,4-Bis(hydroxymethyl)-2,3,5,6-tetrafluorobenzene (1 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. Carbon tetrabromide (2.5 mmol) and triphenylphosphine (2.5 mmol) were added to the reaction mixture. The reaction mixture was then warmed to room temperature and stirred for 16 h. The solvent was removed using a rotary evaporator, and the crude mixture was purified by flash chromatography (n-hexane). The product was obtained as a white crystalline solid. ^1H NMR (CDCl_3 , 400 MHz) δ 4.51 (s, 4H); EI-MS found $[\text{M}]$: 334 (336, 338), $[\text{M}-\text{Br}]$: 255 (257), $[\text{M}-2\text{Br}]$: 176.

(2) Synthesis of substituted imidazoles²



NaH (60% in oil, 11 mmol) was added to a THF solution of imidazole (10 mmol), and the resulting suspension was stirred at room temperature for 2 h. α, α' -dichloro-*p*-xylene (for $\text{ImCH}_2\text{PhCH}_2\text{Im}$, 5 mmol)/1,4-bis(chloromethyl)tetrafluorobenzene (for $\text{ImCH}_2\text{PhF}_4\text{CH}_2\text{Im}$, 5 mmol) was added to the residue. The resulting

solution was stirred at room temperature for another 4 h. The solvent was removed under vacuum. The product was extracted with dichloromethane, and **ImCH₂PhCH₂Im**/**ImCH₂PhF₄CH₂Im** was obtained in quantitative yield after removing the solvent.

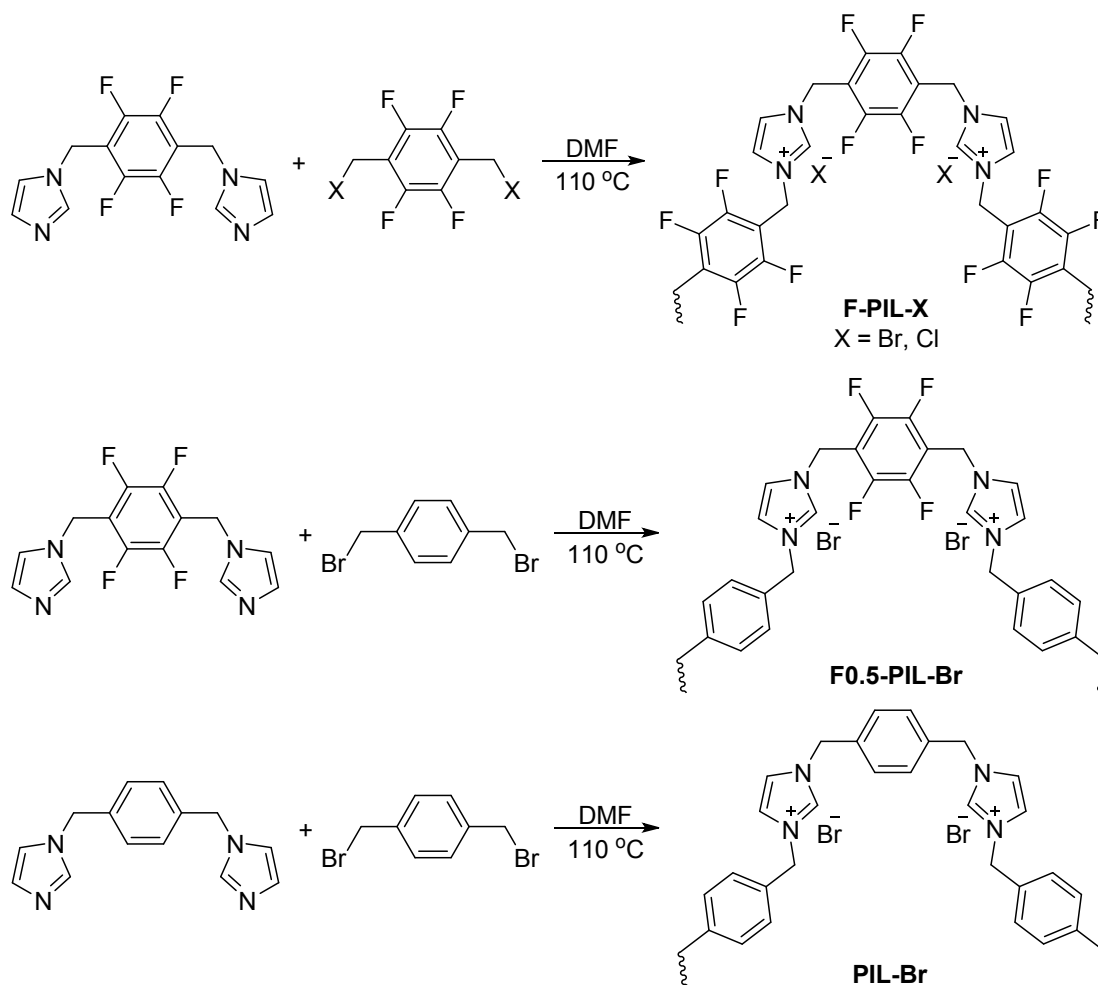
ImCH₂PhCH₂Im

¹H NMR (D₂O, 400 MHz) δ 5.21 (s, 4H), 7.04 (s, 2H), 7.11 (s, 2H), 7.24 (s, 4H), 7.80 (s, 2H); ESI-MS found [M+H]⁺: 239.1.

ImCH₂PhF₄CH₂Im

¹H NMR (D₂O, 400 MHz) δ 5.66 (s, 4H), 7.01-7.40 (m, 2H), 7.58 (s, 2H), 7.70-8.39 (m, 2H); ESI-MS found [M+H]⁺: 311.2.

(3) Synthesis of the polymeric ionic liquids²



Take **F-PIL-Br** as an example: In a stainless steel autoclave, 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (1 mmol) and **ImCH₂PhF₄CH₂Im** were dissolved in 100 mL of DMF. The autoclave was capped and placed in an oven at 110 °C for 24 h. A white solid product was precipitated and filtered, washed with DMF and Et₂O, and dried under vacuum at 80 °C for 24 h. **F-PIL-Br** was obtained as white powder with 75% yield. Elemental analysis: C 40.40%, H 2.58%, N 8.67%.

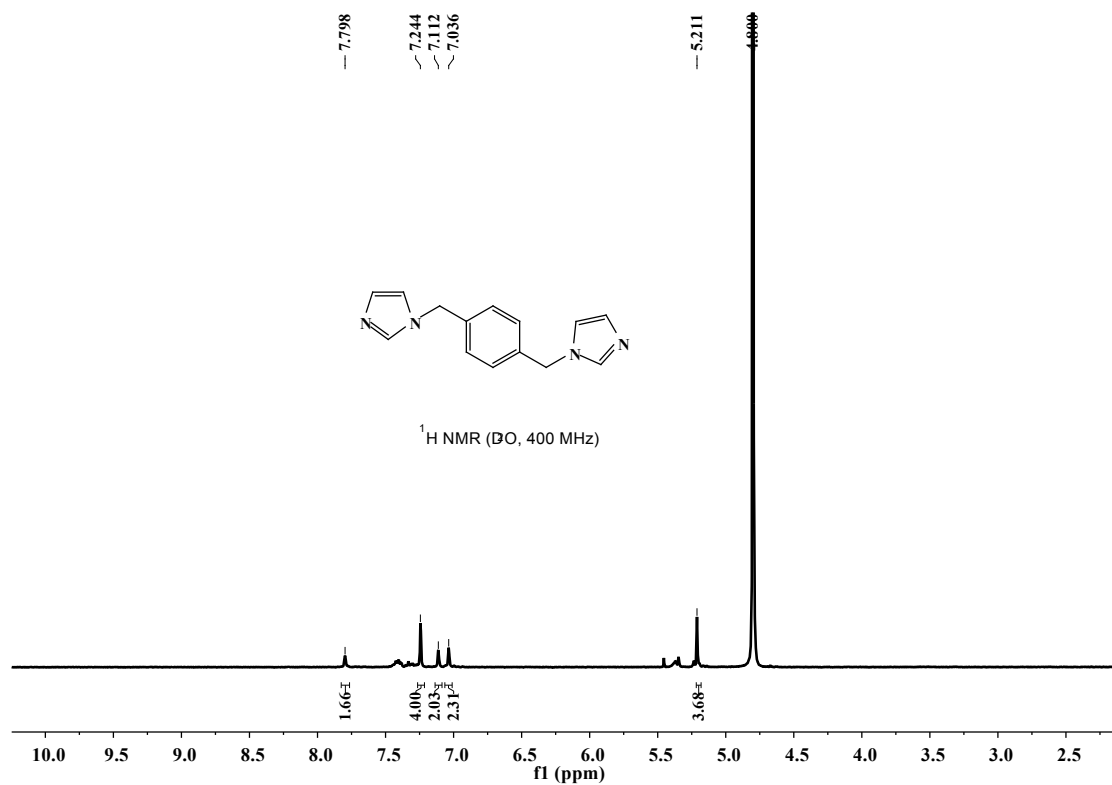
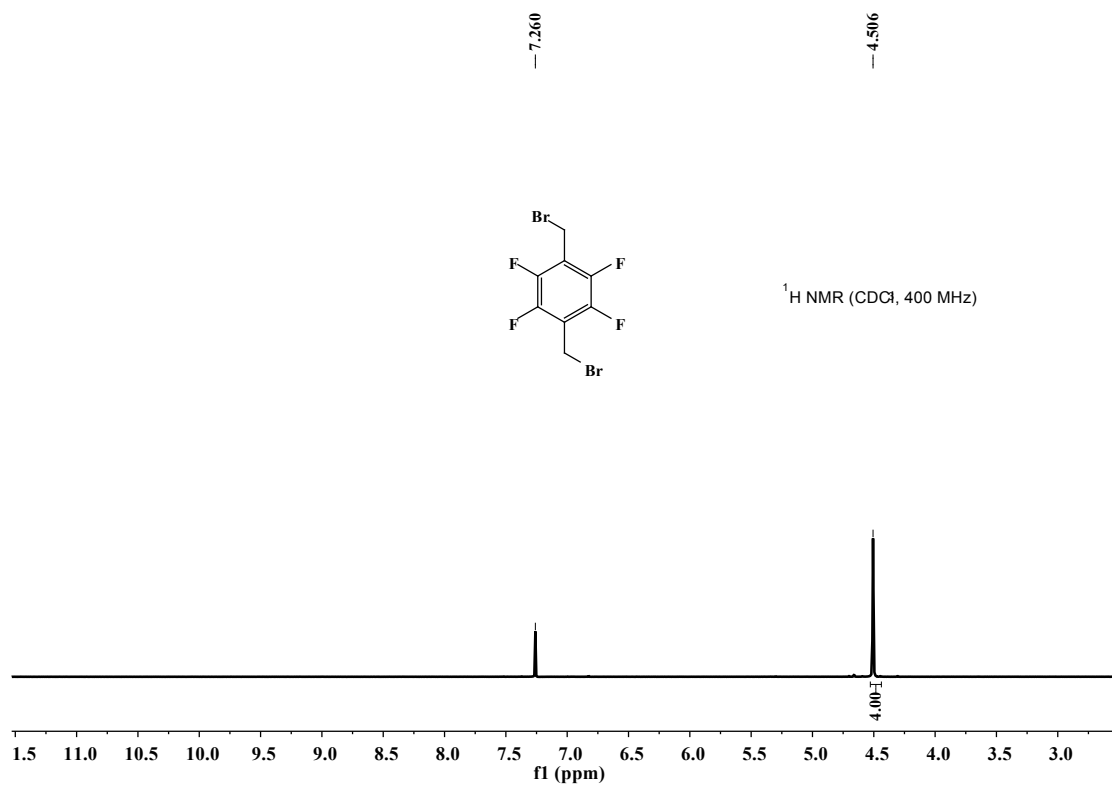
F-PIL-Cl: Raw materials were 1,4-bis(chloromethyl)-2,3,5,6-tetrafluorobenzene and **ImCH₂PhF₄CH₂Im**. Elemental analysis: C 45.98%, H 2.81%, N 9.93%.

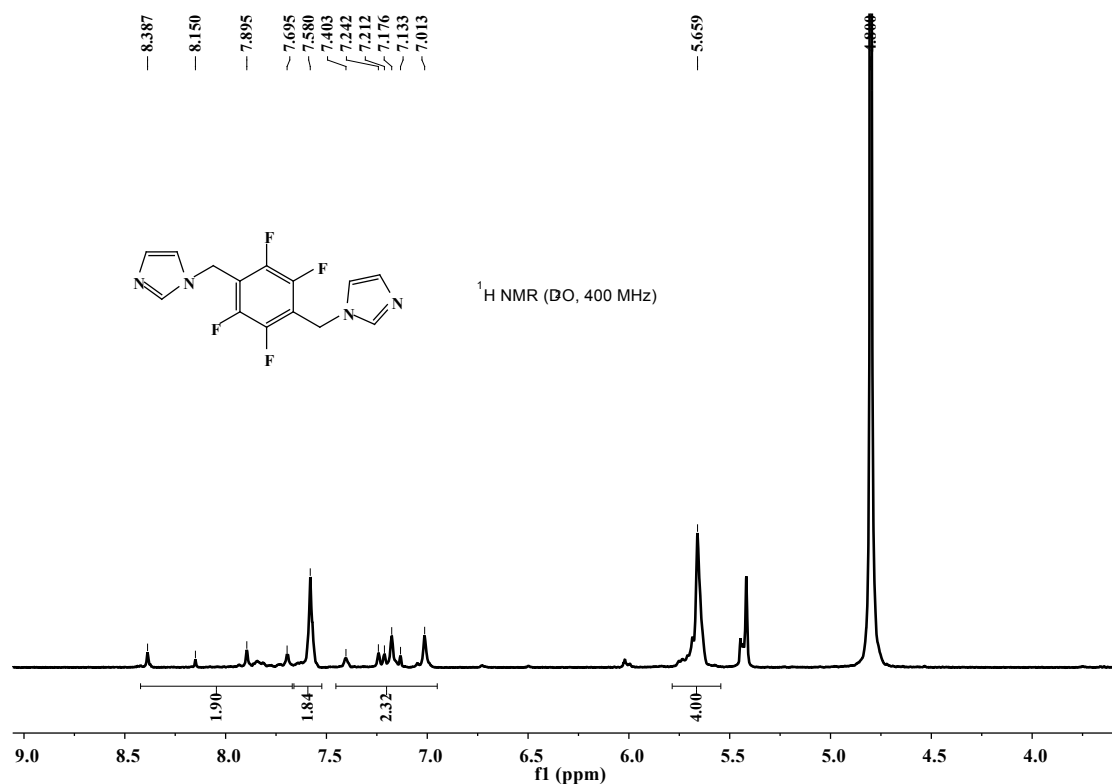
F0.5-PIL-Br: Raw materials were α,α' -dibromo-*p*-xylene and **ImCH₂PhF₄CH₂Im**. Elemental analysis: C 37.84%, H 2.98%, N 8.12%.

PIL-Br: Raw materials were α,α' -dibromo-*p*-xylene and **ImCH₂PhCH₂Im**. Elemental analysis: C 50.86%, H

4.64%, N 10.66%.

(4) ¹H NMR spectra of the raw materials



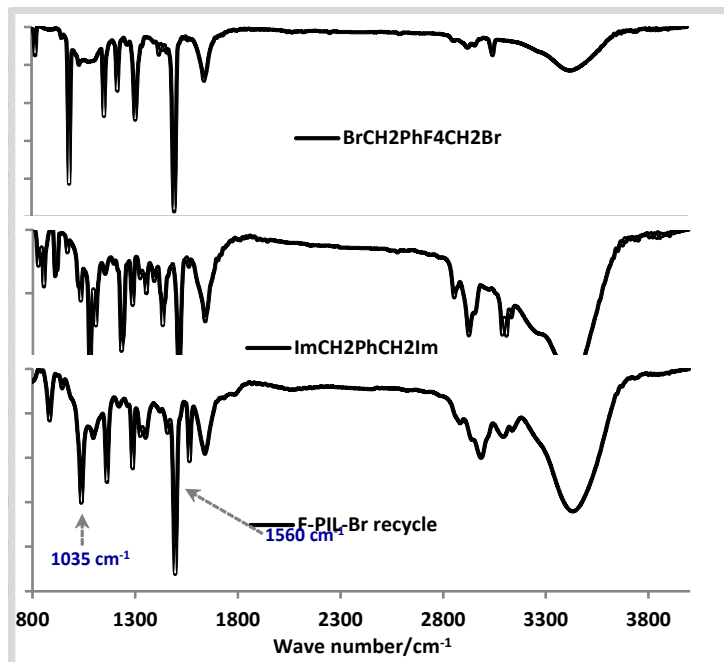
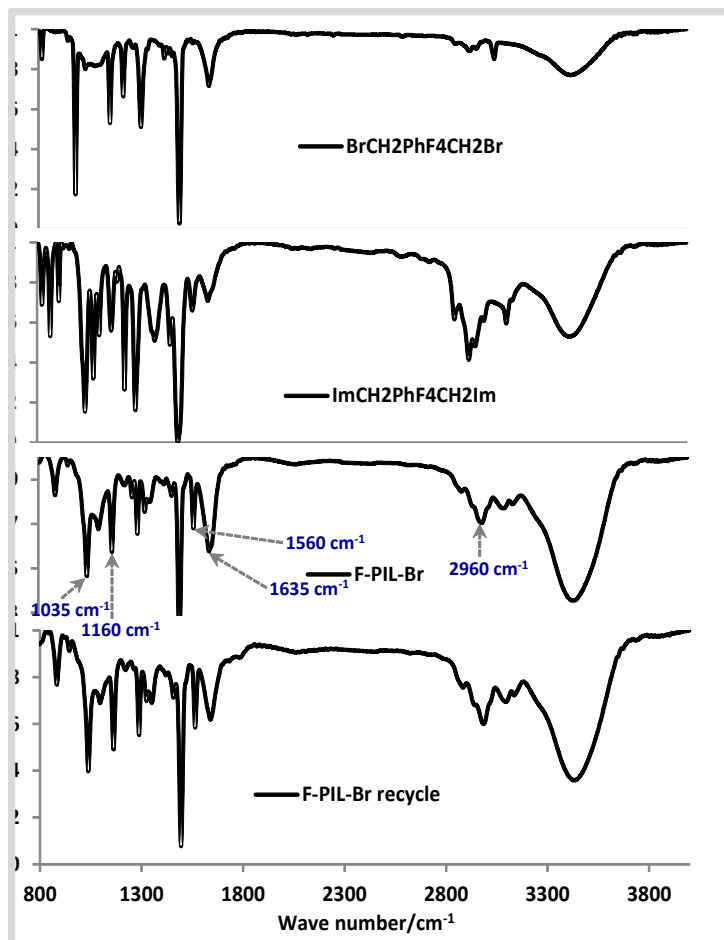


(5) Reference

1. B. Radaram, J. Potvin and M. Levine, *Chem. Commun.*, 2013, **49**, 8259-8261.
2. Y. Zhang, L. Zhao, P. K. Patra, D. Hu and J. Y. Ying, *Nano Today*, 2009, **4**, 13-20.

3. Typical procedures for the synthesis of styrene carbonate from styrene oxide and CO₂

A stainless steel autoclave (25 mL inner volume) was purged with CO₂ to evacuate air, and then **F-PIL-Br** (1 mol%) (mol% of imidazolium salt moieties to epoxide) and styrene oxide (10 mmol) were added successively. CO₂ (1 MPa) was charged in the reactor at room temperature. The autoclave was heated at 120 °C for 9 h. After reaction, the autoclave was allowed to be cooled, and then the excess of CO₂ was vented. The product yield was determined by ¹H NMR (CDCl₃, 400 MHz) using mesitylene (1 mmol) as an internal standard. The products was also isolated by column chromatography on silica gel and identified by NMR spectra.



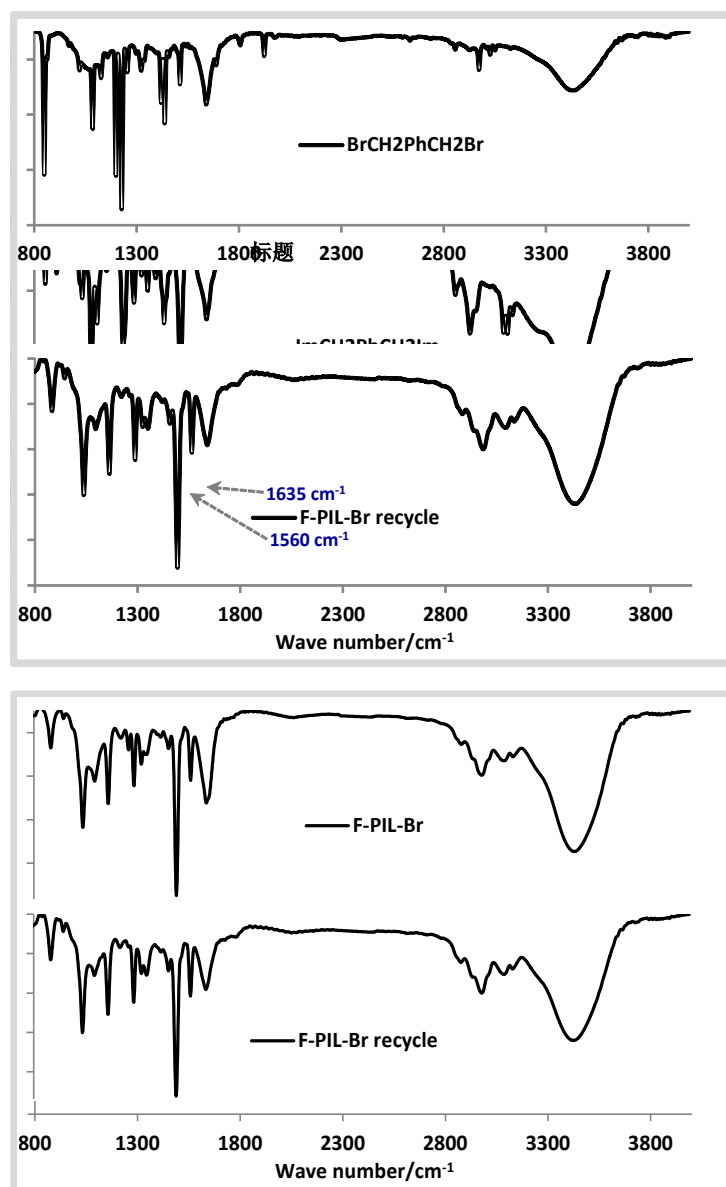
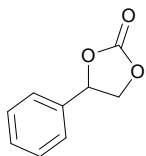


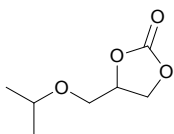
Fig. S1 FTIR spectra of the polymeric ionic liquids and the corresponding monomers.

4. Characterization (NMR) of the cyclic carbonates



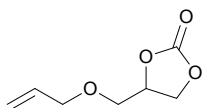
styrene carbonate

White solid; ¹H NMR (400 MHz, CDCl₃) δ 4.35 (t, ³J = 8.4 Hz, 1H), 4.80 (t, ³J = 8.4 Hz, 1H), 5.68 (t, ³J = 8 Hz, 1H), 7.35-7.38 (m, 2H), 7.42-7.47 (m, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 71.1, 77.9, 125.8, 129.2, 129.7, 135.8, 154.8.

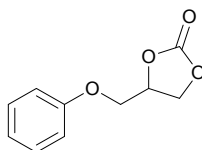


4-(isopropoxymethyl)-1,3-dioxolan-2-one:

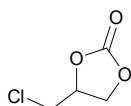
Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 4.77-4.80 (m, 1 H), 4.48 (t, $^3J = 8.4$ Hz, 1 H), 4.37-4.40 (m, 1 H) 3.59-3.67 (m, 3 H), 1.56 (d, $^3J = 5.6$ Hz, 6 H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 155.0, 75.2, 72.6, 66.9, 66.2, 21.7, 21.6.

**4-((allyloxy)methyl)-1,3-dioxolan-2-one:**

Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 5.82-5.92 (m, 1H), 5.22-5.31 (m, 2H), 4.79-4.85 (m, 1H), 4.50 (t, $^3J = 8.4$ MHz, 1H), 4.39-4.22 (m, 1H), 4.05-4.07 (m, 2H), 3.60-3.71 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 154.9, 133.6, 117.8, 75.0, 72.5, 68.8, 66.2.

**4-(phenoxymethyl)-1,3-dioxolan-2-one**

White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 4.04-4.17 (m, 2H), 4.43-4.46 (m, 1H), 4.52 (t, $^3J = 8.4$ Hz, 1H), 4.91-4.98 (m, 1H), 6.83 (d, $^3J = 8$ Hz, 2H), 6.93 (t, $^3J = 7.6$ Hz, 1H), 7.23 (t, $^3J = 7.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 66.2, 66.8, 74.1, 114.6, 121.9, 129.6, 154.6, 157.7.

**4-(chloromethyl)-1,3-dioxolan-2-one:**

Light Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 4.93-4.99 (m, 1 H), 4.59 (t, $^3J = 8.4$ Hz, 1 H), 4.40-4.44 (m, 1 H), 3.71-3.80(m, 2 H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 154.0, 74.2, 67.0, 43.5.

5. NMR spectra of the cyclic carbonates

