

Supporting Information for

Polymers anchored with carboxyl-functionalized di-cation ionic liquids as efficient catalysts for the fixation of CO₂ into cyclic carbonates

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1. Materials

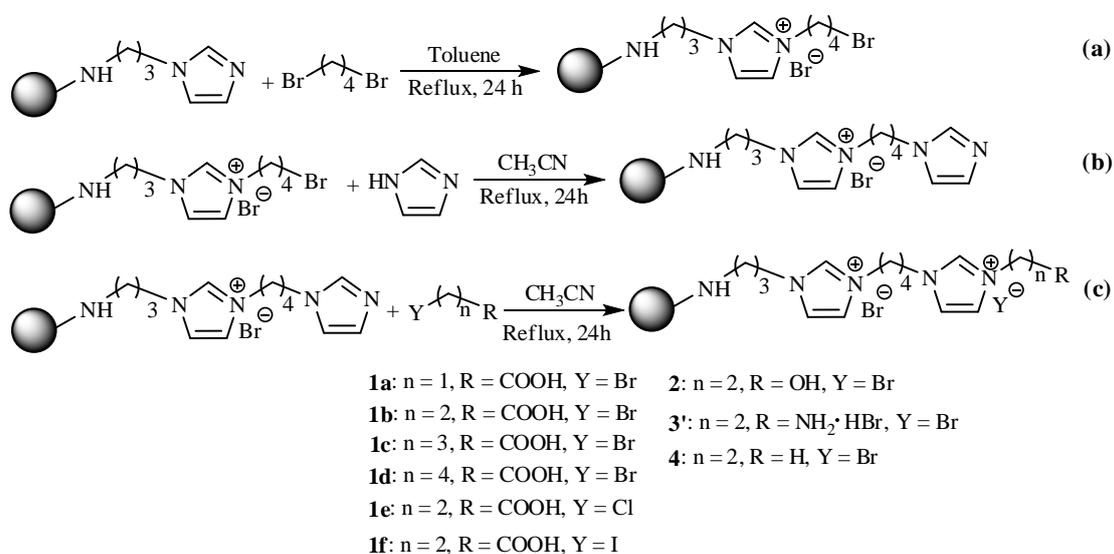
The polydivinylbenzene grafted with 1-(3-amino-propyl) imidazole (denoted as P-Im; QuadraPure IMDAZ, 100–400 μm particle size, content of labeling: 1.5 mmol/g loading, 1 % cross-linked with divinylbenzene), 2-bromoethanol, and 2-bromoethylamine hydrobromide, and 3-bromopropionic acid were purchased from Aldrich Chemical Co. Propylene oxide, bromoethane, imidazole, and 1,4-dibromobutane were purchased from Shanghai Jingchun Industry Co., Ltd. The other epoxides were purchased from Alfa Aesar China Co., Ltd. All chemicals were used as received. The CO₂ (99.9% purity) purchased from Nanchang Guoteng Gas Co. was used without any further treatment.

2. General procedures for the preparation of polymer anchored with dication imidazolium-based ILs (Scheme S1)

Step-1 Preparation of polymer that is grafted with 4-bromobutyl functionalized imidazolium (P-[ImBuBr]Br)

As shown in Scheme S1a, a mixture of P-Im (2.4 g, 3.6 mmol), 1,4-dibromobutane (7.2 mmol), and toluene (20 mL) was added to a round bottom flask (100 mL) and refluxed for 24 h. After the reaction, the resulting mixture was cooled to room temperature and subject to filtration. The obtained residue was washed three times

with ether, followed by drying at 60 °C for 12 h in vacuum to give the P-[ImBuBr]Br as intermediate product.



Scheme S1 Procedures for the preparation of polymer anchored with di-cation imidazolium-based ILs

Step-2 Preparation of polymer grafted with imidazole functionalized imidazolium (P-[ImBuIm]Br)

A mixture of P-[ImBuBr]Br (2.0 g), imidazole (4.5 mmol), and acetonitrile (20 mL) was refluxed for 24 h (Scheme S1b). The obtained solid was filtered out, washed three times with ethyl acetate, and dried at 60 °C for 12 h in vacuum to give the P-[ImBuIm]Br.

Step-3 Preparation of polymer anchored with di-cation imidazolium-based ILs

A typical procedure for the preparation of polymer anchored with carboxymethyl functionalized dication imidazolium-based ILs (P-[Im-CMIm]Br₂, **1a**) is as follows: A mixture of P-[ImBuIm]Br (2.0 g), bromoacetic acid (4.2 mmol), and acetonitrile (20 mL) was refluxed for 24 h (Scheme S1c). The obtained solid was filtered out, washed three times with ether, and dried at 60 °C for 12 h in vacuum to give the catalyst, P-[Im-CMIm]Br₂.

Similarly, other polymers that were anchored with functionalized di-cation imidazolium-based ILs were fabricated as shown in Scheme 1c, including P-[Im-CEIm]Br₂ (**1b**), P-[Im-CPIIm]Br₂ (**1c**), P-[Im-CBuIm]Br₂ (**1d**), P-[Im-CEIm]BrCl (**1e**), P-[Im-CEIm]BrI (**1f**), P-[Im-HEIm]Br₂ (**2**), P-[Im-AEIm]Br₂·HBr (**3'**), and P-[Im-EIm]Br₂ (**4**).

Furthermore, polymer that was anchored with aminoethyl functionalized di-cation imidazolium-based ILs (P-[Im-AEIm]Br₂, **3**) was fabricated by additional procedure (Scheme S1d): **3'** (2.0 g), NaOH (8.0 mmol), and CH₃CN/H₂O (1:1, v/v) solution (5 mL) were added to a round bottom flask (100 mL) and stirred at room temperature for 24 h to neutralize hydrobromide. The as-obtained solid was filtered out, washed three times with CH₃CN/H₂O and ethyl acetate respectively, and dried at 60 °C for 12 h in vacuum for the generation of P-[Im-AEIm]Br₂.

3. Characterization

Scanning electron microscopic (SEM) observations were carried out over a Nova NanoSEM 450 microscope. Energy dispersive X-ray spectroscopy (EDS) was performed using the INCA 250 accessory of Nova NanoSEM 450. The FT-IR spectra were recorded using a Bruker vertex 70 FT-IR spectrophotometer. TG-DSC analysis was performed on a SDT Q600 (TA Instruments-Waters LLC) at a heating rate of 15 °C/min in a N₂ flow. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker 400 MHz spectrometer using CDCl₃ as solvent. The ¹³C solid-state NMR experiments were carried out at frequencies of 100.6 MHz on an AVANCE III 400 WB spectrometer equipped with a commercial 4.0 mm T3 HXY MAS probe. All NMR spectra were measured at room temperature under the following conditions: magic-angle spinning at 5 kHz; $\pi/2$ pulse, 7 μ s, and a repetition delay of 5 s; 1024 scans. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2200PC operating at 40 kV and 40 mA using Ni-filtered Cu K α radiation (λ = 1.542 Å). The diffractograms were recorded in the 2 θ range of 5° to 80°.

4. Typical procedure for the synthesis of cyclic carbonates

The cycloaddition reactions were conducted in a 50 mL high-pressure stainless-steel autoclave equipped with a magnetic stirring bar. In a typical run, the

reactor was charged with epoxide (35.7 mmol), catalyst (0.3 mol%, calculated according to the amount of ionic liquid), and an appropriate amount of biphenyl (as internal standard for GC analysis). After the reactor was fed with CO₂ to a desired pressure, the autoclave with its contents was heated to a selected temperature and stirred for a designated period of time. Then the reactor was cooled to 0 °C in an ice-water bath, and the remaining CO₂ was released. The resulting mixture was quantitatively analyzed using a GC (Agilent 7890A) that was equipped with a FID and a DB-wax capillary column (30 m × 0.53 mm × 1.0 μm). The products structures were also identified by GC-MS and NMR (TMS as internal standard) methods.

5. Fig. S1-5

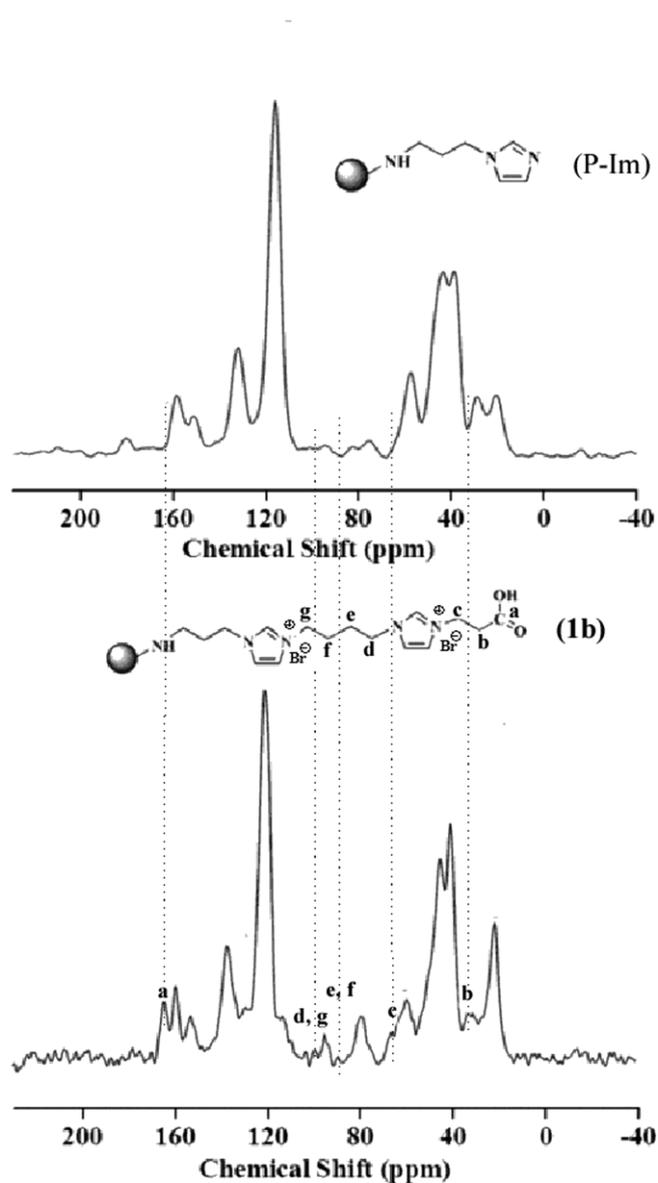


Fig. S1 Solid ¹³C NMR spectrum of P-Im and 1b.

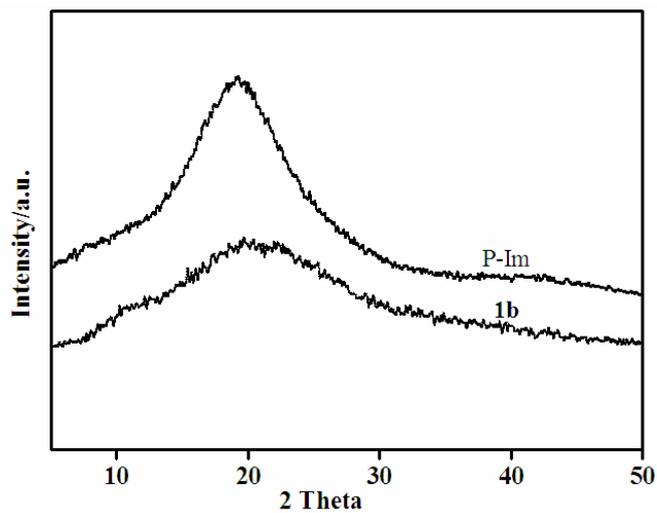


Fig. S2 XRD patterns of P-Im and **1b**.

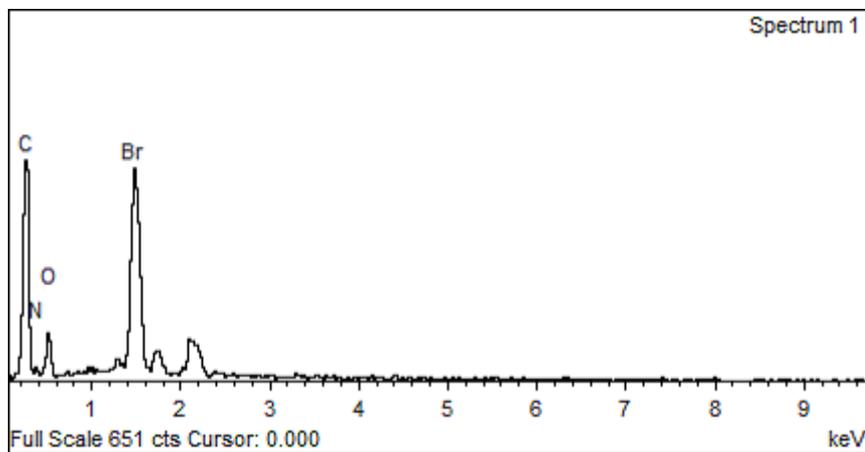


Fig. S3 EDS spectra of **1b**

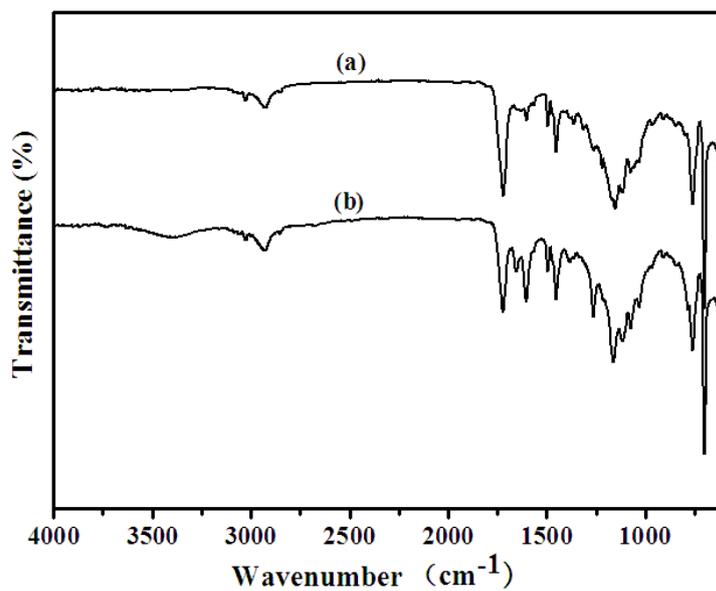


Fig. S4 FT-IR spectra of **1b**: (a) fresh, (b) recovered.

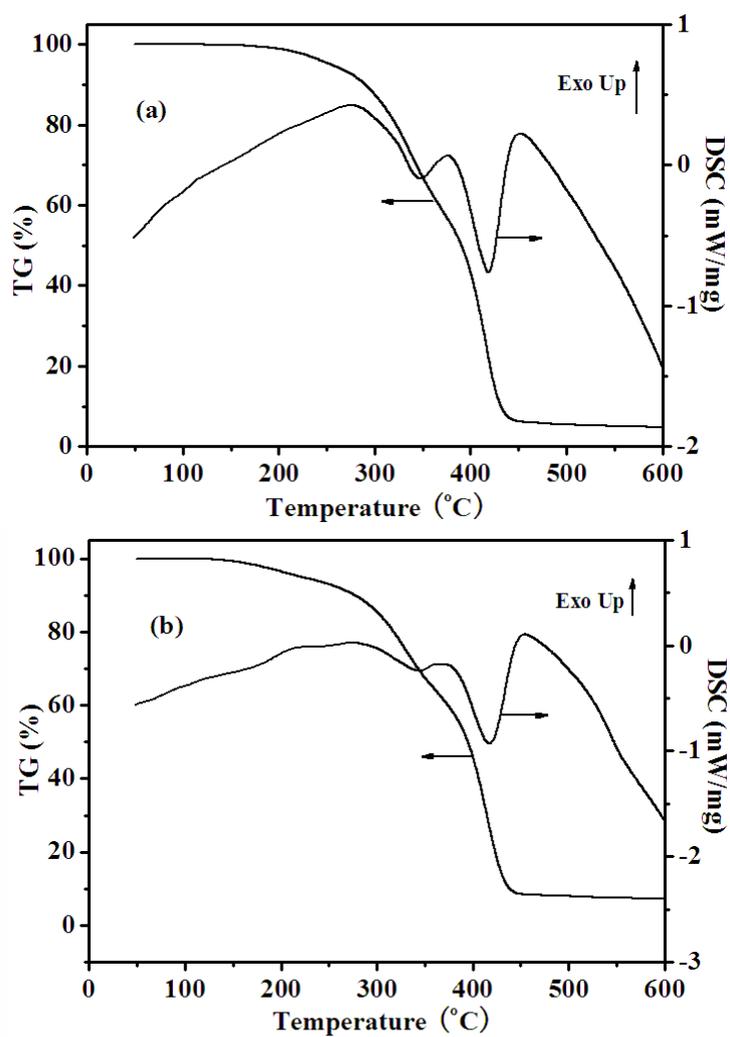


Fig. S5 TG and DSC curves of **1b**: (a) fresh, (b) recovered.