Supporting Information

Mesoporous Zwitterionic Poly(ionic liquid): Intrinsic Complexation and Efficient Catalytic Fixation of CO_2

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1. Chemicals

1-Vinylimidazole, tert-butyl-2-bromoacetate, trifluoroacetic acid (TFA) and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purchased from Sigma-Aldrich and used without further purification. All the solvents in this study were of analytic grade.

2. Characterization methods

^1H nuclear magnetic resonance (^1H-NMR) measurements were carried out at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz. DMSO-d_6 and D_2O were used as solvents.

Nitrogen (N_2) sorption experiments were performed on a Quantachrome Autosorb-1 or Quadrasorb at liquid nitrogen temperature, and data analysis was performed by Quantachrome software. The surface area and pore volume were calculated using the Brunaer–Emmett-Teller (BET) equation, and the Barrett-Joyner-Halenda (BJH) method, respectively. Samples for BET were degassed at 80 °C for 20 hours before measurements.

Scanning electron microscopy (SEM) was performed on a GEMINI LEO 1550 microscope at 3 kV, and samples were coated with a thin layer of gold before examination.

Elemental analysis was performed for carbon, hydrogen and nitrogen using a Vario EL Elementar.

3. Monomer synthesis

3-(2-(tert-butoxy)-2-oxoethyl)-1-vinylimidazolium bromide were prepared in the same manner according to the reference Macromolecules 2011, 44, 744-750. 1-vinylimidazole (9.41 g, 0.1 mol), tert-butyl-2-bromoacetate (19.40 g, 0.1 mol) and methanol (30 mL) were mixed at room temperature in a 100 mL reactor. The mixture was stirred at 60 °C for 15 h. After cooling down, the mixture was precipitated into 1 L of diethyl ether. The white solid was filtered off and dried by high vacuum at room temperature until constant weight. The chemical structure was confirmed by ^{1}H-NMR spectrum. Yield: 23 g (85%).

4. Polymerization step

5 g (0.017 mol) of 3-(2-(tert-butoxy)-2-oxoethyl)-1-vinylimidazolium bromide, 100 mg (0.6 mmol) of AIBN and 50 mL of DMSO were added in a 100 mL flask. After complete dissolution of the solid, the mixture was deoxygenated by four cycles of freeze-pump-thaw process. After being backfilled with argon, the flask was stirred in an oil bath thermostated at 80°C for 12 h. After cooling down, the reaction mixture was added dropwise into an excess of diethyl ether. The precipitate was redissolved in DMSO and precipitated again in diethyl ether. After filtering off, the product was dried under vacuum at 60°C till constant weight. The chemical structure were confirmed by ^{1}H-NMR spectrum.

5. Detaching of the tert-butyl protecting group

A mixture of 2 mL of trifluoroacitic acid and 1 mL of dichloromethane was added to of 0.5 g of poly(3-(2-(tert-butoxy)-2-oxoethyl)-1-vinylimidazolium bromide). After stirring for 24 h at room temperature solvent, the trifluoric acid was removed by high vacuum vacuum at 40°C.

6. Preparation of mesoporous PILC

In a typical run, PIL-COOH was dissolved in DMSO solvent at a designed concentration at room temperature to form a transparent solution. 30 mL of diethyl ether (complexing solvent) containing 0.5 wt% of NH_3 (prepared by using 3.5 g of 2M NH_3 in isopropanol as ammonia source) was placed in a glass beaker, into which 2 mL of polymer mixture solution was dropped (speed: 3 mL/min) under stirring rate of 900 rpm and sonication (40 % sonication amplitude of a Bandelin Electronics Sonorex RK 100 ultrasonic bath). The sonication was kept for 1 min after the addition was finished. The upper liquid phase was discarded and the solid content was collected, washed by diethyl ether four times, dried under vacuum at 50 ^{o}C for 12 h.

7. Catalytic capture of CO_2

Cycloaddition reactions were carried out under CO_2 (1MPa) in a teflon-lined stainless steel batch reactor. In a typical run, 3 mL of substrates and 50 mg of catalyst were loaded into the reactor (total volume: 100 mL). The reactor was sealed and purged with CO_2 to replace the air for 2 times. Afterwards the CO_2 pressure was increased to 1 MPa and the reactor was heated to 160 ^{o}C in 20 min. The reaction was carried out for 6-24 h under magnetic stirring (stirring rate: 1500 rpm). Afterwards the reaction was quenched by placing the reactor in ice water. The products were analyzed by GC.

8. Catalyst recycling test

After the reaction the reaction mixture was centrifuged at 4000 rpm for 10 min. The liquid layer was removed and the solid was first washed with ethanol and then centrifuged twice. After drying the catalyst in a vacuum oven at 50 ^{o}C for 24 h, the recovered catalyst was used in the subsequent reaction.

9. Supplementary data

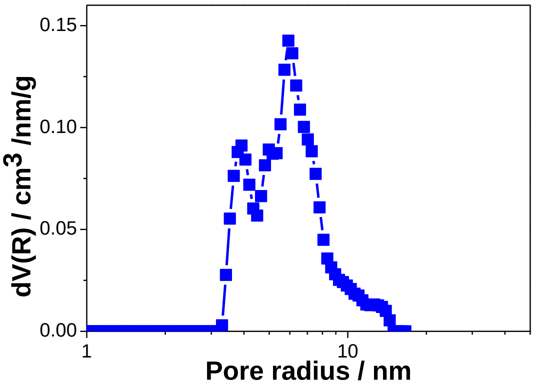

Figure S1. Pore size distribution curve of the PILC material prepared via precipitating 7 wt% of PIL-COOH solution into ammonia-containing diethyl ether solution. It was determined by quenched solid density functional theory, QSDFT (adsorption branch, cylindrical pores).

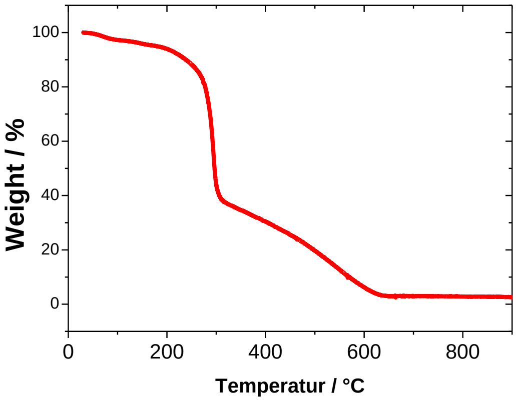

Figure S2. TGA (under nitrogen, 10 K/min) curve of the PILC material prepared via precipitating 7 wt% of PIL-COOH solution into ammonia-containing diethyl ether solution.