

Supplementary Information

Biodegradable betaine-based aprotic task-specific ionic liquids and their application in efficient SO₂ absorption

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Experimental Section

Details on synthesis and characterization of betaine-based ILs

Chemicals. All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise.

Synthetic details of the ILs:

Synthesis of [C₄bet][Br], [1O2][Br] and [2O2][Br]

Take the synthesis of [C₄bet][Br] as an example:

A mixture of betaine (35.145g, 0.30 mol) and 1-bromobutane (49.33g, 0.36 mol) in acetonitrile (100 mL) was vigorously stirred at 100°C for 24 h. After removal of the volatile components, the mixtures were washed with the absolute ethyl ether for three times to remove the unreacted 1-bromobutane. Then, the mixtures were dissolved in acetonitrile and filtration to remove the unreacted betaine. After evaporation under vacuum at 80°C, [C₄bet][Br] was obtained as a white solid.

Synthesis of [C₄bet][TFSI], [[1O2]][TFSI] and [2O2][TFSI]

Take the synthesis of [C₄bet][TFSI] as an example:

To a solution of the obtained [C₄bet][Br] (0.1 mol) in deionized water, the aqueous solution containing the LiNTf₂ (0.12 mol) was added under vigorous stirring at room temperature for 6 hours. The crude solid precipitates was separated from water, followed by thorough washing with deionized water until no residual bromine ion in the washed water detected by a Mettler–Toledo Seven Multi meter with a bromine ion selective electrode. The final product was dried under high vacuum at 100°C, and then stored in a desiccator under dry nitrogen.

Synthesis of [C₄bet][DCA], [[1O2]][DCA] and [2O2][DCA]

Take the synthesis of [C₄bet][DCA] as an example:

To a solution of the obtained [C₄bet][Br] (0.1 mol) in deionized water, the silver dicyanamide (0.12 mol) was added under vigorous stirring at room temperature for 12 h. After the reaction was finished, the crude liquid was extracted from water by adding CH₂Cl₂, and the combined extracts were washed with the deionized water until no residual bromine ion in the washed water detected by a Mettler–Toledo Seven Multi meter with a bromine ion selective electrode. The final product was dried under high vacuum at 80°C, and then stored in a desiccator under dry nitrogen.

Synthesis of [C₄bet][SCN]

To a solution of the obtained [C₄bet][Br] (0.1 mol) in deionized water, the aqueous solution containing the KPF₆ (0.12 mol) was added under vigorous stirring at room temperature for 6 hours. The crude solid precipitates was separated from water, followed by thorough washing with deionized water until no residual bromine ion in the washed water detected by a Mettler–Toledo Seven Multi meter with a bromine ion selective electrode. Then, to a solution of the obtained [C₄bet][PF₆] in CH₂Cl₂, the aqueous solution containing the KSCN (0.12 mol) was added under vigorous stirring at room temperature for 24 h. After removal of the CH₂Cl₂ and water, the mixtures were dissolved in CH₂Cl₂ and filtration to remove the KPF₆ and excessive KSCN. The collected mixtures were then dissolved in deionized water and washed with CH₂Cl₂ for three times to remove the unreacted [C₄bet][PF₆]. The final product was dried under high vacuum at 80°C, and then stored in a desiccator under dry nitrogen.

NMR and FT-IR

¹H and ¹³C NMR Spectra were measured by a Bruker AMX FT 400 MHz NMR spectrometer in the D₆-acetone solutions. Chemical shifts were reported downfield in parts per million (ppm, δ) from a tetramethylsilane reference. FT-IR spectra was recorded on a Thermo Nicolet 5700 FT-IR spectrophotometer.

Water content and content of the bromine ion

The water content in ILs was detected by means of a coulometric Karl–Fischer titration using a Mitsubishi CA-06 Moisturemeter, and each test was conducted in an anhydrous sealed chamber and was finished within 1 min. Duplicate measurements were performed on each sample with results agreeing to within 5%. Before the water content test, each sample were kept at 80°C and 10⁻²-10⁻³ mbar for 12 h, except for the ILs based on the [TFSI] anion, which were dried at 100°C. The content of bromide ion was determined by a Mettler–Toledo Seven Multi meter with a Br⁻ selective electrode.

Phase transitions and thermal stability

The DSC data were evaluated by using the Mettler–Toledo STARe software version 7.01. The samples were sealed in 40 μL aluminum pan and a pinhole at the top of the pan for the sake of the sample exposing to a flowing N₂ (50 mL min⁻¹) atmosphere using an empty pan as the reference.

DSC traces were typically scanned from 100 to -100 °C at speed of 10 °C min⁻¹, and then followed the heating process at the same speed.

The decomposition temperature (T_d) was recorded with 5% of mass loss by Pyris Diamond Perkin-Elmer TG/DTA at scan rate of 10 °C min⁻¹ under a N₂ atmosphere (flow rate = 100 mL min⁻¹) and each ILs was heated from room temperature to 800 °C.

Viscosity, density, conductivity and electrochemical stability

The viscosity of each ILs were measured on a Stabinger Viscosimeter SVM 3000/GR. The density was determined using a volume–mass method in a 10 mL volumetric flask calibrated with water. The ion conductivity was measured by a Mettler–Toledo Seven Multi meter. Cyclic voltammetry was conducted using a CHI 660A Electrochemical Work Station. The working electrode was a glassy carbon electrode (3 mm diameter), the auxiliary electrode was a platinum wire and a Ag/AgCl electrode was used as a reference.

NMR data of 1-Bromobutane and betaine-based ILs

1-Bromobutane: ¹H NMR (Acetone-d₆): 0.94(t, 3H), 1.45(m, 2H), 1.83(m, 2H), 3.49(t, 2H); ¹³C NMR (Acetone-d₆): 12.50, 20.99, 33.51, 34.70.

[C₄bet][TFSI]: ¹H NMR (Acetone-d₆): 0.90(t, 3H), 1.37(m, 2H), 1.65(m, 2H), 3.53(s, 9H), 4.25(t, 2H), 4.57(s, 2H); ¹³C NMR (Acetone-d₆): 18.11, 23.87, 35.32, 59.27, 68.58, 71.39, 120.53, 123.73, 126.92, 130.11, 169.85.

[C₄bet][DCA]: ¹H NMR (Acetone-d₆): 0.91(t, 3H), 1.37(m, 2H), 1.65(m, 2H), 3.50(s, 9H), 4.25(t, 2H), 4.61(s, 2H); ¹³C NMR (Acetone-d₆): 18.22, 23.92, 35.37, 58.83, 68.35, 71.13, 124.96, 170.06.

[C₄bet][SCN]: ¹H NMR (Acetone-d₆): 0.93(t, 3H), 1.40(m, 2H), 1.65(m, 2H), 3.59(s, 9H), 4.27(t, 2H), 4.76(s, 2H); ¹³C NMR (Acetone-d₆): 13.05, 18.73, 30.20, 53.54, 63.04, 65.86, 131.69, 165.12.

[C₄bet][SCN]-SO₂: ¹H NMR (Acetone-d₆): 0.93(t, 3H), 1.40(m, 2H), 1.66(m, 2H), 3.59(s, 9H), 4.27(t, 2H), 4.76(s, 2H); ¹³C NMR (Acetone-d₆): 13.06, 18.74, 30.20, 53.56, 63.05, 65.88, 130.62, 165.01.

[C₄bet][SCN] with 5.1% water after SO₂ desorption: ¹H NMR (Acetone-d₆): 0.93(t, 3H), 1.40(m, 2H), 1.66(m, 2H), 3.59(s, 9H), 4.27(t, 2H), 4.76(s, 2H); ¹³C NMR (Acetone-d₆): 13.06, 18.74, 30.19, 53.54, 63.02, 65.86, 131.58, 165.02.

[1O2bet][TFSI]: ¹H NMR (Acetone-d₆): 3.30(s, 3H), 3.53(s, 9H), 3.60(t, 2H), 4.37(s, 2H), 4.58(s, 2H); ¹³C NMR (Acetone-d₆): 59.12, 63.04, 68.68, 70.34, 74.69, 120.53, 123.72, 126.92, 130.11,

169.72.

[1O2bet][DCA]: ^1H NMR (Acetone- d_6): 3.33(s, 3H), 3.53(s, 9H), 3.64(t, 2H), 4.40(s, 2H), 4.63(s, 2H); ^{13}C NMR (Acetone- d_6): 53.68, 57.94, 63.25, 65.14, 69.55, 119.75, 164.72.

[2O2bet][TFSI]: ^1H NMR (Acetone- d_6): 1.11(t, 3H), 3.47(m, 2H), 3.54(s, 9H), 3.65(t, 2H), 4.37(t, 2H), 4.58(s, 2H); ^{13}C NMR (Acetone- d_6): 19.71, 59.13, 68.74, 70.58, 71.12, 72.65, 120.53, 123.73, 126.92, 130.11, 169.71.

[2O2bet][DCA]: ^1H NMR (Acetone- d_6): 1.11(t, 3H), 3.46(m, 2H), 3.51(s, 9H), 3.65(t, 2H), 4.37(t, 2H), 4.62(s, 2H). ^{13}C NMR (Acetone- d_6): 19.81, 58.90, 68.50, 70.54, 71.16, 72.70, 124.97, 169.92.

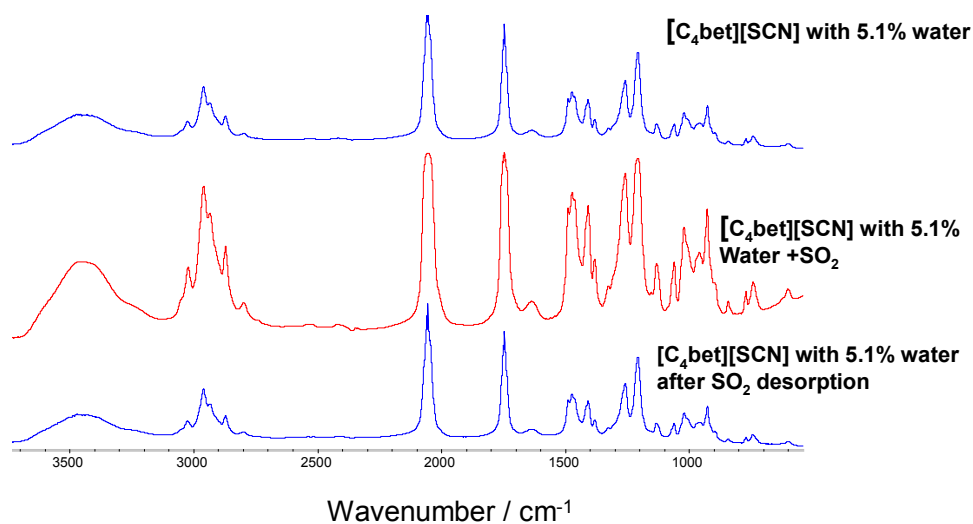


Fig. S1 FT-IR spectra of [C₄bet][SCN] with 5.1% water before and after absorption of SO₂.