Supporting Information

Dual-Ionic Liquid system: an Efficient Catalyst for Chemical Fixation of CO_2 to Cyclic Carbonates under Mild Conditions

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1. General Information

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.99%. Epichlorohydrin (99%), epibromohydrin (97%), styrene oxide (97.5%), glycidyl phenyl ether (99%), 1,1,3,3-tetramethylguanidine (TMG) (99%), fumaric acid (99%) were purchased from J&K Scientific Ltd.. Methanol, petroleum ether, ethyl acetate were all analytical grade and purchased from Beijing Chemical Company. The chemicals above were used without further purification.

The ILs 1-carboxymethyl-3-methylimidazolium bromide ($[HO_2MMIm^+][Br^-]$) (99%), 1-carboxymethyl-3-methylimidazolium chloride ($[HO_2MMIm^+][Cl^-]$) (99%) were supplied by Lanzhou Yulu Fine Chemical Co., LTD. The ILs were used without further purification.

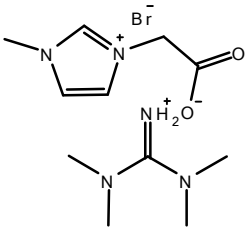
Standard column chromatography was performed on 20-40 μm silica gel using flash column chromatography. NMR spectra were recorded on a Bruker Fourier 300 MHz NMR spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C). Deuterated solvent dimethyl sulfoxide-d6 (D, 99.9%) was purchased from Cambridge Isotope Laboratories, Inc., and were used without further purification.

2. Experimental Section

2.1 The procedures for preparation of the dual-IL systems.

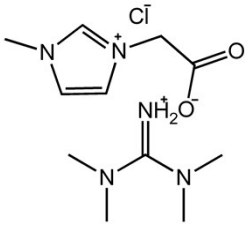
The dual-IL systems were synthesized by neutralization. As an example, the procedure for the preparation of [$TMGH^+$][$^-O_2MMIm^+$][Br^-] was described. In the experiments, methanol (10 mL), TMG (10 mmol, 1.1518 g) and [HO_2MMIm^+][Br^-] (10 mmol, 2.2105 g) were loaded into a 50 mL flask in a water bath of 25 ^oC and the neutralization reaction was allowed to proceed for 12 h. The solvent was removed by rotary evaporation under vacuum at 60 ^oC, and finally a white solid with more than 99% purity was obtained as target product.

2.1.1 NMR data of dual-IL systems.



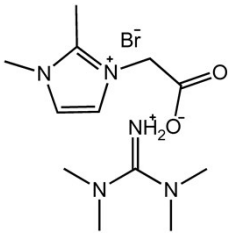
[$TMGH^+$][$^-O_2MMIm^+$][Br^-], White solid (Purity > 99%)

^1H NMR (300 MHz, MeOD) δ 8.89 (s, 1H), 7.54 (d, J = 1.3 Hz, 2H), 4.75 (s, 2H), 3.94 (s, 3H), 2.99 (s, 12H). ^{13}C NMR (75 MHz, MeOD) δ 169.95, 161.82, 137.46, 123.51, 122.66, 51.95, 38.64, 35.03.



[$TMGH^+$][$^-O_2MMIm^+$][Cl^-], White solid (Purity > 99%)

^1H NMR (300 MHz, MeOD) δ 8.88 (s, 1H), 7.54 (d, J = 1.0 Hz, 2H), 4.74 (s, 2H), 3.94 (s, 3H), 2.99 (s, 12H). ^{13}C NMR (75 MHz, MeOD) δ 169.97, 161.82, 137.46, 123.48, 122.64, 51.92, 38.59, 34.98.



[TMGH$^+$][$^-$O$_2$MMMIm$^+$][Br$^-$], White solid (Purity > 99%)

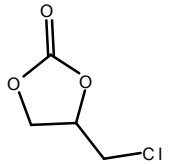
^{1}H NMR (400 MHz, MeOD) δ 7.46 (s, 1H), 7.44 (s, 1H), 4.70 (s, 2H), 3.84 (s, 3H), 3.00 (s, 12H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 169.74, 161.80, 145.24, 121.90, 121.61, 51.26, 38.73, 34.10, 8.44.

2.2 Typical procedure for the synthesis of cyclic carbonates.

As an example, the procedure using **1a** as the substrate was described, and those for other substrates were similar. **1a** (2 mmol, 0.1850 g), [TMGH$^+$][$^-$O$_2$MMIm$^+$][Br$^-$] (0.5 mmol, 0.1681 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO_2 into the reactor. Then the pressure of CO_2 was kept at 0.1 MPa using a balloon with CO_2. The reactor was placed in a constant temperature water bath and the reaction mixture was stirred for desired time. After the reaction, the reactor was placed in ice water for 20 minutes and the reaction mixture was passed through a plug of silica gel. The crude mixture was purified by silica gel column chromatography (EtOAc:petroleum ether = 1:5) to obtain the desired cyclic carbonate **2a**.

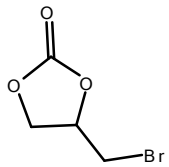
The procedures for reuse of the IL. 1a (2 mmol, 0.1850 g) and [TMGH$^+$][$^-$O$_2$MMIm$^+$][Br$^-$] (0.5 mmol, 0.1681 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO_2 into the reactor. Then the pressure of CO_2 was kept at 0.1 MPa using a balloon with CO_2. The reactor was placed in a water bath of 30 ^{o}C and the reaction mixture was stirred for 20 h. After the reaction, EtOAc (5 mL) were added in the reaction mixture and [TMGH$^+$][$^-$O$_2$MMIm$^+$][Br$^-$] in the mixture was separated by centrifugation. The product was in EtOAc phase and the yield was determined by ^{1}H NMR spectroscopy using fumaric acid as an internal standard. The IL separated was used directly for the next run after dried under vacuum at 50 ^{o}C for 24 h.

2.2.1 NMR data of cyclic carbonates.



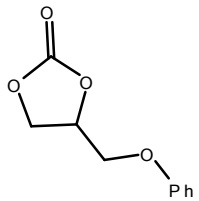
4-Chloromethyl-[1,3]dioxolan-2-one (2a), yellow liquid

^{1}H NMR (300 MHz, DMSO) δ 5.20-5.05 (m, 1H), 4.60 (t, J = 8.6 Hz, 1H), 4.27 (dd, J = 8.7, 5.6 Hz, 1H), 3.97 (qd, J = 12.3, 3.7 Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ 154.97, 75.43, 67.36, 45.82.



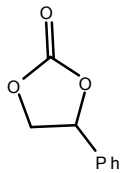
4-Bromomethyl-[1,3]dioxolan-2-one (2b), yellow liquid

^{1}H NMR (300 MHz, DMSO) δ 5.12-5.04 (m, 1H), 4.59 (t, J = 8.6 Hz, 1H), 4.21 (dd, J = 8.7, 5.8 Hz, 1H), 3.83 (qd, J = 11.4, 4.1 Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ 154.83, 74.99, 68.43, 34.87.



4-(Phenoxymethyl)-1,3-dioxolan-2-one (2c), white solid.

^{1}H NMR (300 MHz, DMSO) δ 7.43-7.21 (m, 2H), 7.00-6.95 (m, 3H), 5.24-5.06 (m, 1H), 4.64 (t, J = 8.5 Hz, 1H), 4.39 (dd, J = 8.4, 6.0 Hz, 1H), 4.24 (qd, J = 11.3, 3.6 Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ 158.41, 155.34, 130.08, 121.72, 115.08, 75.31, 67.86, 66.51.



4-Phenyl-1,3-dioxolan-2-one (2d), yellow liquid

^{1}H NMR (300 MHz, DMSO) δ 7.57-7.40 (m, 5H), 5.86 (t, J = 7.9 Hz, 1H), 4.88 (t, J = 8.3 Hz, 1H),

4.41 (t, J = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, DMSO) δ 155.23, 136.76, 129.83, 129.37, 127.14, 78.27, 71.31.