

Supporting Information

Hydrophobic diamine-functionalized ionic liquid for effective transformation of CO₂: a bridge to achieve separation and recycle process in homogeneous system

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Experimental

Materials and instrumentation

CO₂ was supplied by Tianjin Feilin Gases Co., Ltd with a purity of 99.99%. 1,3-dibromopropan-2-ol (>99%), 1, 3-dichloropropan-2-ol (>99%), chloropropanol (>99%), bromopropanol (>99%) DMF (>99%) and KPF₆ were purchased by Aladdin Biochemical Technology Co., LTD. 1-methylimidazole (>99%) was purchased by Alfa Esha Chemical Co. LTD. 2-(Diethylamino)ethyl bromide hydrobromide (>98%), 2-bromoethyldimethylammonium bromide (>98%) and LiNTf₂ were purchased by Aichan (Shanghai) Chemical Technology Co., LTD. The ILs [AEMIm][NTf₂] and [AEMIm][PF₆] were supplied by Lanzhou Yulu Fine Chemical Co., LTD. Dimethyl sulfoxide-d₆ (99.9%) was supplied by Cambridge Isotope Laboratories, Inc. Other commonly used organic solvents were supplied by Sinopharm Chemical Reagent Co., Ltd. All of the reagents and solvents were used without further purification.

NMR spectra were recorded on a Bruker Fourier 400 MHz NMR spectrometer (400 MHz for ¹H and 100 MHz for ¹³C).

Synthesis of diamine-functionalized ionic liquid

The procedure for the synthesis of IL [MAMIm][PF₆] is as follows (Figure S1). Firstly, 1-methylimidazole (64.0 mmol, 5.2866 g) and 2-bromoethyldimethylammonium bromide (54.0 mmol, 12.5000 g) were dissolve completely in the acetonitrile (65 mL) and then stirred at 80 °C for 15 h under reflux conditions. After centrifugation, washing and drying, the white solid [MAMIm][Br][HBr] was obtained. Secondly, [MAMIm][Br][HBr] (64.0 mmol, 5.2866 g) was dissolved in 60 mL deionized water. Then, KOH was slowly added into this solution with continuous stirring in ice bath. After the KOH was completely dissolved, removed the ice bath and followed by stirring at room temperature for 2 h. Thirdly, KPF₆ (72 mmol, 13.2523 g) and dichloromethane (60 mL) were added to the above solution with stirring at room temperature for 2 h. The reaction mixture was divided into two phases. The organic phase containing IL [MAMIm][PF₆] was washed with deionized water (4×30 mL) and then dried with anhydrous sodium sulfate. At last, the dichloromethane was removed by evaporation and the light yellow IL [MAMIm][PF₆] was obtained.

The ¹H NMR and ¹³C NMR data of [MAMIm][PF₆] are as follows: ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.06 (s, 1H), 7.72 (s, 1H), 7.65 (s, 1H), 4.25 (t, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 2.62 (t,

$J = 5.8$ Hz, 2H), 2.17 (s, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 137.13, 123.69, 123.08, 58.16, 46.98, 45.32, 36.18.

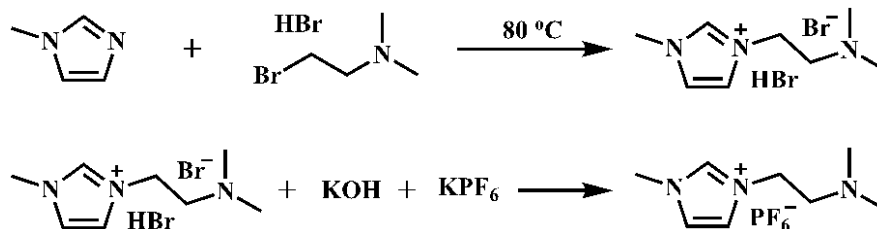


Figure S1. Synthesis procedure of the IL [MAMIm][PF₆].

Typical procedure for the synthesis of cyclic carbonates

As an example, the procedure using 1,3-dibromopropan-2-ol (**1a**) as the substrate is described, and those for other substrates were similar. **1a** (1 mmol, 0.2179 g), [MAMIm][PF₆] (1.5 mmol, 0.4488 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 CO₂ into the reactor. Then inflating 1.0 MPa pressure of CO₂ into the reactor. The reactor was placed in a 30 °C oil bath pan and the reaction mixture was stirred for a desired time. After the reaction, CO₂ was slowly released and the product was extracted by ethyl ether (3×2 mL). The yield of 4-(bromomethyl)-1,3-dioxolan-2-one (**2a**) was determined via ^1H NMR using DMF as an internal standard as the internal standard. In addition, the pure **2a** was obtained via a silica gel column chromatography (EtOAc: petroleum ether=1:20).

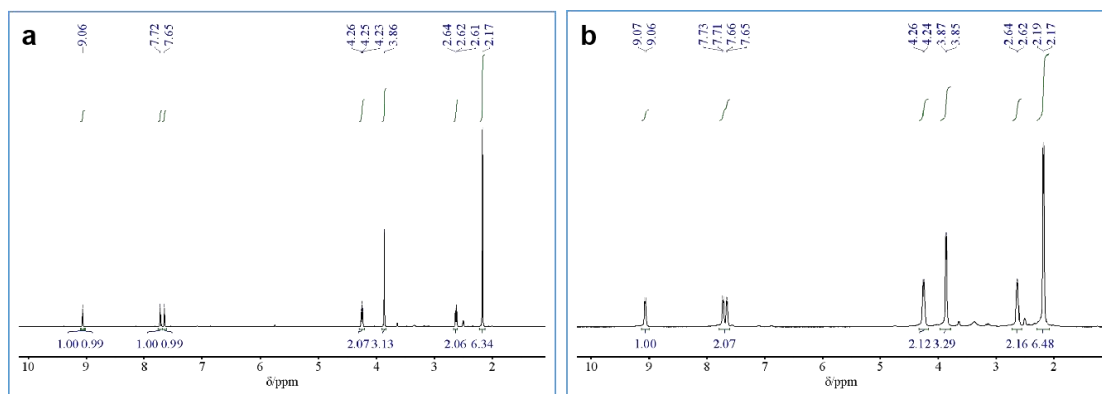
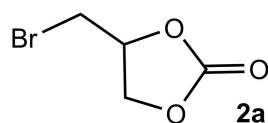


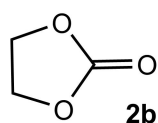
Figure S2 The ^1H NMR spectrum of IL [MAMIm][PF₆] before (a) and after used for five times (b).

NMR data of products



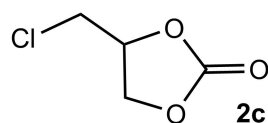
4-(bromomethyl)-1,3-dioxolan-2-one.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 5.13 – 5.05 (m, 1H), 4.60 (t, J = 8.6 Hz, 1H), 4.22 (dd, J = 8.7, 5.7 Hz, 1H), 3.91 – 3.77 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 154.84, 75.01, 68.45, 34.90.



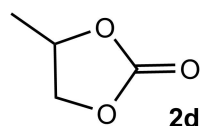
Ethylene carbonate.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 4.48 (s, 1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 156.03, 65.46.



4-(chloromethyl)-1,3-dioxolan-2-one.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 5.13 (dddd, J = 8.8, 5.6, 4.2, 3.3 Hz, 1H), 4.60 (t, J = 8.6 Hz, 1H), 4.28 (dd, J = 8.7, 5.6 Hz, 1H), 4.06 – 3.89 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 154.95, 75.41, 67.34, 45.79.



4-methyl-1,3-dioxolan-2-one.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 4.90 (ddt, J = 13.7, 7.5, 6.2 Hz, 1H), 4.57 (t, J = 8.0 Hz, 1H), 4.06 (dd, J = 8.3, 7.2 Hz, 1H), 1.37 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 155.38, 74.24, 70.94, 19.27.