

Electronic Supplementary Information

Highly Efficient CO₂ Capture by Tunable Alkanolamine -Based Ionic Liquids with Multidentate Cation Coordination

Congmin Wang,^{1,2} Guo Yan,¹ Xiang Zhu,^{3,4} Guokai Cui,¹ Haoran Li,¹ and Sheng Dai^{2,4}

¹Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China,

²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

³Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, P. R. China,

⁴Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

Email: chewcm@zju.edu.cn; dais@ornl.gov

Experimental Section

Materials and general methods

Ethanolamine, diethanolamine, 2-hydroxyethylene diamine, 2-(2-aminoethoxy)ethanol, and 2,2'-(ethylenedioxy)bis(ethylamine) were purchased from Adrich. Lithium bis(trifluoromethane sulfonyl)imide (LiTf₂N) was obtained from 3M company. All chemicals were obtained in the highest purity grade possible, and were used as received unless otherwise stated. All ionic liquids (ILs) samples were dried under vacuum at 60 °C for 24 h to reduce possible trace of water. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrometer (400MHz) in CDCl₃ or D₂O with tetramethylsilane as the standard. FT-IR spectra were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer. Decomposition temperature was measured with a TGA 2950 under N₂ of 60 ml min⁻¹ at 10°C min⁻¹ ramp rate.

Preparation of alkanolamine-based ILs

These novel ILs were prepared by simple mixing of alkanolamine such as diethanolamine and alkali metal salt.^{1,2} In a typical synthesis of alkanolamine-based ILs, equimolar diethanolamine was mixed with LiTf₂N, then stirred at 50 °C for 2 h. The obtained IL was dried in high vacuum for 24 h at 60 °C to remove possible trace of water. The structure of these alkanolamine-based ILs was confirmed by NMR and IR. No impurities were found by NMR spectroscopy. The water content of these ILs was determined with a Karl Fisher titration and found to be less than 0.1 wt%.

Absorption and desorption of CO₂

In a typical absorption of CO₂, CO₂ of atmospheric pressure was bubbled through about 1.0 g IL in a glass container with an inner diameter of 10 mm, and the flow rate was about 60 ml min⁻¹. The glass container was partly immersed in a circulation oil bath of desirable temperature. The amount of CO₂ absorbed was determined at regular intervals by the electronic balance with an accuracy of ± 0.1 mg. During the absorption of CO₂ under reduced pressure, CO₂ was diluted with N₂ in order to reduce the partial pressure of

CO₂ passing through the system. The CO₂ partial pressure was controlled by changing the flow of CO₂ and N₂. The standard deviation of the absorption capacity for [Li(DOBA)][Tf₂N] at 40 °C for 60 min is 0.02 mole CO₂ per mole IL.

The ILs including captured CO₂ were regenerated by heating or bubbling nitrogen through the ILs. In a typical desorption of CO₂, N₂ of atmospheric pressure was bubbled through about 1.0 g ILs containing captured CO₂ in a glass container, which was partly immersed in a circulation oil bath of desirable temperature, and the flow rate was about 60 ml min⁻¹. The release of CO₂ was determined at regular intervals by the electronic balance with an accuracy of ± 0.1 mg.

NMR and IR data of alkanolamine-based ILs

[Li(EA)][Tf₂N]: ¹H NMR (CDCl₃): 2.74 (s, 2H, NH₂), 2.93 (m, 2H, NCH₂), 3.61, (s, 1H, OH), 3.78 (m, 2H, NCH₂); ¹³C NMR (CDCl₃): 42.0, 62.6, 117.2, 121.6 ppm; IR: 3535, 3376, 3320, 2962, 2894, 1602, 1466, 1343, 1324, 1187, 1129, 1055, 970, 874, 851, 797, 745 cm⁻¹; MS: 68.0 for [Li(EA)]⁺; 280.0 for [Tf₂N]⁻.

[Li(DEA)][Tf₂N]: ¹H NMR (CDCl₃): 2.74 (s, 1H, NH), 2.87 (m, 4H, OCH₂), 3.70, (s, 2H, OH) 3.80 (m, 4H, NCH₂); ¹³C NMR (CDCl₃): 49.0, 60.6, 117.3, 121.6 ppm; IR: 3534, 2960, 2906, 2866, 1636, 1462, 1345, 1325, 1186, 1131, 1051, 931, 900, 795, 744 cm⁻¹; MS: 112.0 for [Li(DEA)]⁺; 280.0 for [Tf₂N]⁻.

[Li(HDA)][Tf₂N]: ¹H NMR (CDCl₃): 2.00 (s, 1H, NH), 2.41 (s, 2H, NH₂), 2.70-2.82 (m, 6H, NCH₂), 3.69 (s, 1H, OH), 3.74 (m, 2H, OCH₂); ¹³C NMR (CDCl₃): 42.0, 49.5, 49.8, 62.6, 117.2, 121.3 ppm; IR: 3530, 3380, 3318, 2941, 2861, 1601, 1462, 1346, 1327, 1182, 1131, 1052, 972, 888, 793, 742 cm⁻¹; MS: 111.0 for [Li(HDA)]⁺; 280.0 for [Tf₂N]⁻.

[Li(AEE)][Tf₂N]: ¹H NMR (CDCl₃): 2.74 (s, 2H, NH₂), 2.87-2.96 (m, 4H, CH₂), 3.57-3.66 (m, 4H, CH₂), 3.80 (s, 1H, OH); ¹³C NMR (CDCl₃): 39.8, 60.0, 69.7, 70.1, 112.7, 117.0, 121.2, 125.5 ppm; IR: 3530, 3382, 2947, 2885, 1603, 1463, 1347, 1327, 1184, 1131, 1052, 974, 896, 795, 744 cm⁻¹; MS: 112.0 for [Li(AEE)]⁺; 280.0 for [Tf₂N]⁻.

[Li(DOBA)][Tf₂N]: ¹H NMR (CDCl₃): 1.55 (s, 4H, NH₂), 2.88 (m, 4H, NCH₂), 3.53 (m, 4H, OCH₂), 3.66 (s, 4H, OCH₂); ¹³C NMR (CDCl₃): 40.2, 67.9, 70.1, 113.3, 117.6, 121.8, 126.1 ppm; IR: 3383, 3322, 2928, 2884, 1604, 1462, 1349, 1330, 1180, 1133, 1095, 1053,

965, 866, 791, 741 cm⁻¹; MS: 155.1 for [Li(DOBA)]⁺; 280.0 for [Tf₂N]⁻.

Table S1. The comparison of CO₂ absorption by typical alkanolamine-based ILs with that by functionalized ILs and a solution of ILs and alkanolamine.

Ionic liquid ^a	Temperature (°C)	CO ₂ absorption ^b	Reference
[Li(DEA)][Tf ₂ N]	40	0.52	this work
[Li(DEA)][Tf ₂ N]	60	0.50	this work
[Li(EA)][Tf ₂ N]	40	0.54	this work
[Li(DOBA)][Tf ₂ N]	60	0.90	This work
DEA:[HOEmim][Tf ₂ N] (1:1)	40	0.29	Noble ³
EA:[Hmim][Tf ₂ N] (1:1)	40	0.50	Noble ³
EA:[HOPmim][BF ₄] (1:1)	60	0.27	Chen ⁴
EA:[HOPmim][BF ₄]: [HOPmim][Cl] (1:0.5:0.5)	60	0.31	Chen ⁴
[APBim][BF ₄]	25	~0.5	Davis ⁵
[AP ₄₄₄₃][Gly]	45	~1.1 ^c	Zhang ⁶
[P ₆₆₆₁₄][Pro]	25	0.91	Brennecke ⁷
[P ₆₆₆₁₄][Triz]	23	0.93	Wang ⁸
[Choline][Pro]	50	~0.5	Han ⁹

^a[HOEmim][Tf₂N], 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethane sulfonyl) imide; [HOPmim][BF₄], 1-hydroxypropyl-3-methylimidazolium tetrafluoroborate; [HOPmim][Cl], 1-hydroxypropyl-3-methylimidazolium chloride, [APBim][Tf₂N], 1-(3-aminopropyl)-3-butylimidazolium tetrafluoroborate; [AP₄₄₄₃][Gly], 3-(aminopropyl) tributyl phosphonium glycinate; [P₆₆₆₁₄][Pro], trihexyl(tetradecyl) phosphonium proline; [Choline][Pro], 2-(hydroxyethyl)-trimethylammonium proline; ^bMole CO₂ per mole IL. ^cILs on porous SiO₂.

Table S2. The effect of temperature, pressure and water on the absorption of CO₂ by typical alkanolamine-based ILs.^a

Ionic liquid	Temperature (°C)	Pressure (atm)	CO ₂ absorption ^b
[Li(DOBA)][Tf ₂ N]	60	1.0	0.90

[Li(DOBA)][Tf ₂ N]	70	1.0	0.85
[Li(DOBA)][Tf ₂ N]	80	1.0	0.81
[Li(DOBA)][Tf ₂ N]	100	1.0	0.71
[Li(DOBA)][Tf ₂ N]	60	0.1	0.81
[Li(DOBA)][Tf ₂ N] ^c	70	1.0	0.86

^aThe absorption was carried out for 30 min. ^bMole CO₂ per mole IL. ^cAddition of specific amounts of water to the IL is 2 wt%.

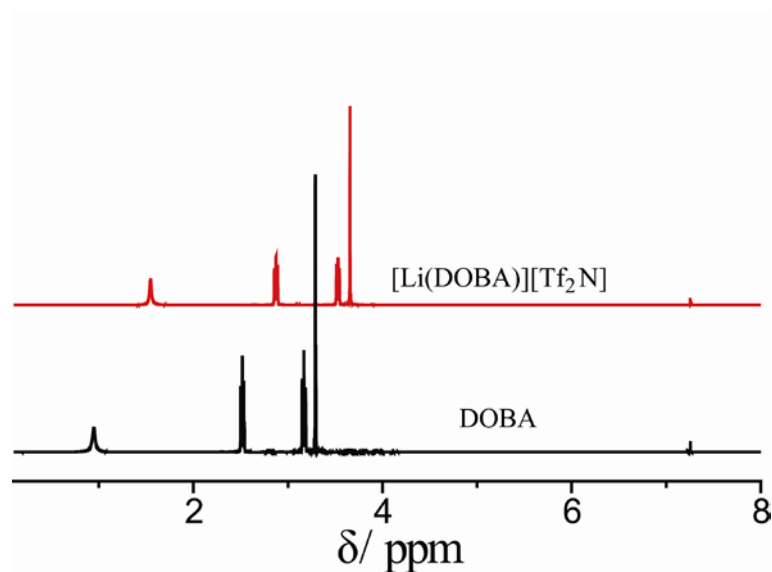


Figure S1. The comparison between ¹H NMR of [Li(DOBA)][Tf₂N] and that of DOBA.

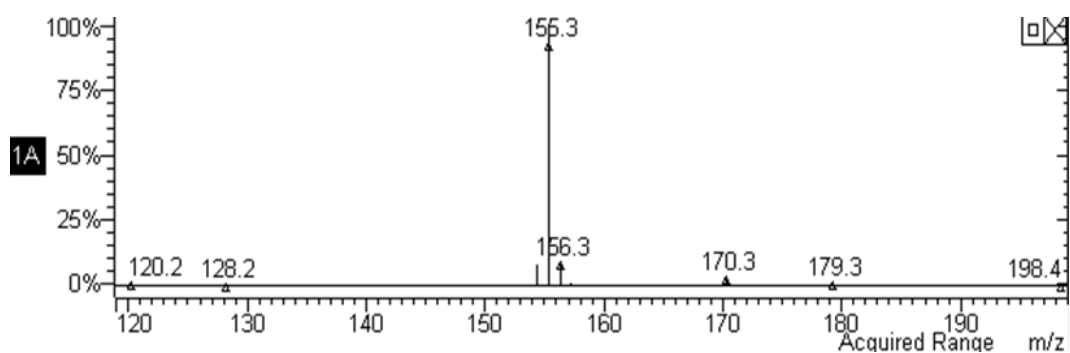


Figure S2 The Mass Spectrum of [Li(DOBA)]⁺.

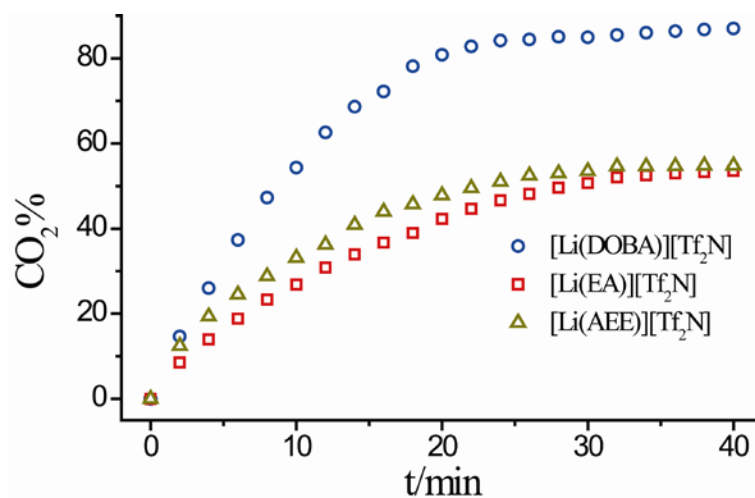


Figure S3. CO₂ absorption by typical alkanolamine-based ILs. ○, [Li(DOBA)] [Tf₂N]; □, [Li(EA)][Tf₂N]; △[Li(AEE)][Tf₂N].

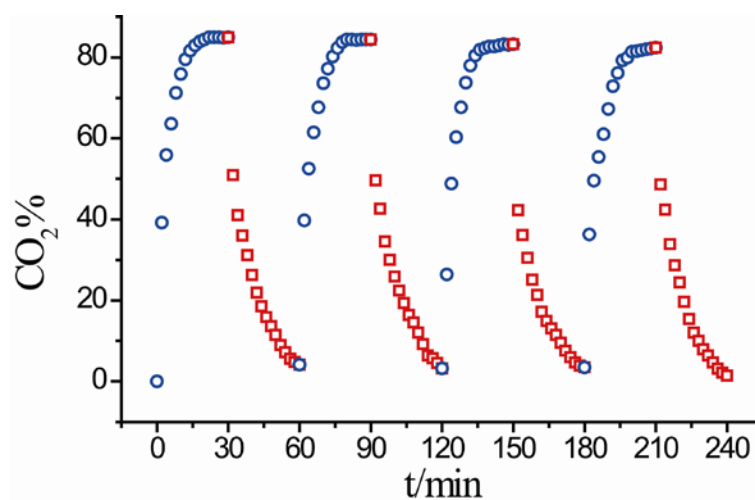


Figure S4. Four cycles of CO₂ absorption/desorption processes by the IL [Li(DOBA)][Tf₂N]. CO₂ absorption was carried out at 70 °C, and desorption was performed at 120 °C under N₂. ○, absorption; □, desorption.

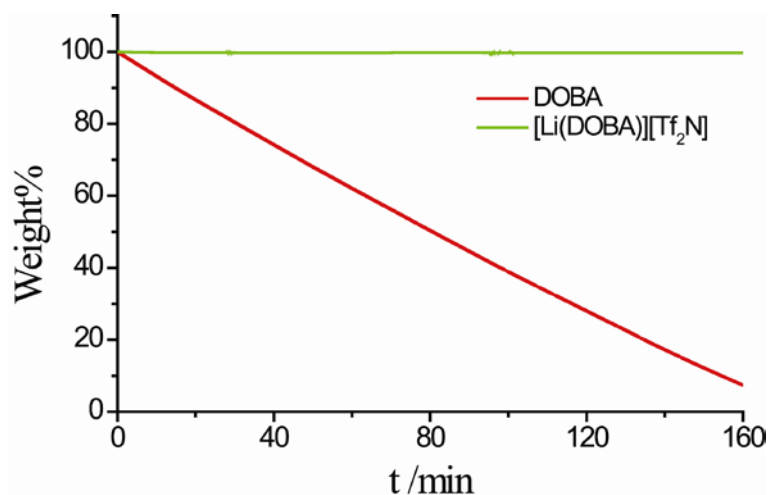


Figure S5. The comparison of the stability between typical alkanolamine-based ILs [Li(DOBA)][Tf₂N] and the corresponding alkanolamine DOBA. The loss of weight was determined at 120 °C under bubbling N₂.

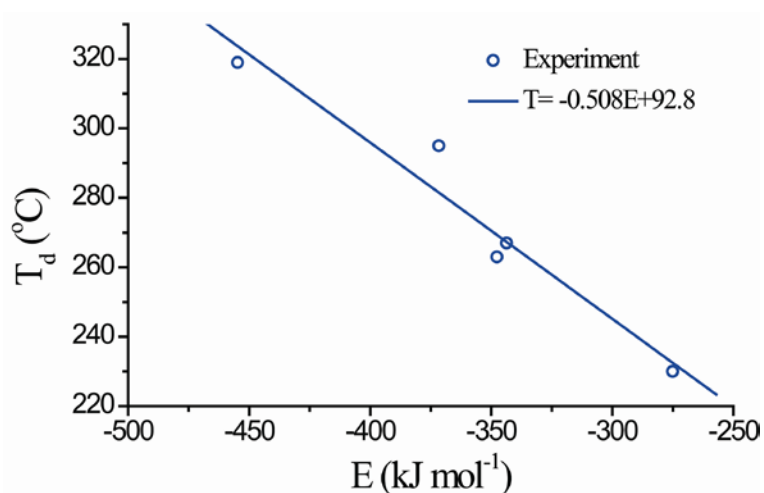


Figure S6. The relationship between decomposition temperature T_d and energy of the gas phase reaction E . \circ , experimental value. -, fitted line, where $T_d = -0.508E + 92.8$.

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