Electronic Supplementary Information

Highly efficient CO$_2$ capture by carbonyl-containing ionic liquids through lewis acid-base and cooperative C-H···O hydrogen bonding interaction strengthened by the anion

Fang Ding,¹ Xi He,¹ Xiaoyan Luo,¹ Wenjun Lin,¹ Kiahong Chen,¹ Haoran Li,¹,² and Congmin Wang¹

¹Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou 310027, P. R. China
²State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, P. R. China

Email: chewcm@zju.edu.cn
Experimental Section

Materials and general methods

$^1$H-Imidazole-4-carbaldehyde (4-CHO-Im), 4-Hydroxyacetophenone (4-Kt-PhOH), 4-Hydroxybenzaldehyde (4-CHO-PhOH), and 4-Hydroxy-ethylbenzoate (4-EF-PhOH) were purchased from Sigma-Aldrich. Lithium bis (trifluoromethane sulfonyl)imide (LiTf$_2$N) was obtained from 3M company. N-methyl imidazole and Trihexyl(tetradecyl) phosphonium bromide ([P$_{66614}$][Br]) were bought from Nanjing Chemlin company. An anion-exchange resin -711(Cl) was obtained from Shanghai Huazhen Sci. & Tech. Co., Ltd. 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. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker spectrometer (600MHz) in CDCl$_3$ or DMSO with tetramethylsilane as the standard. FT-IR spectra were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer.

Preparation of carbonyl-containing anion-functionalized ILs

These carbonyl-containing anion-functionalized ILs were prepared by the neutralizing between substituted phenols or substituted imidazole and a solution of phosphonium hydroxide ([P$_{66614}$][OH]) in ethanol, which was obtained by the anion-exchange method from [P$_{66614}$] [Br].$^{[1-3]}$ In a typical synthesis of carbonyl-based IL [P$_{66614}$][4-CHO-Im], equimolar 4-CHO-PhOH was added to the [P$_{66614}$][OH] solution in ethanol. The mixture was then stirred at 30°C for 12 h. Subsequently, ethanol and water were distilled off at 60 °C under reduced pressure. The obtained IL [P$_{66614}$][4-CHO-Im] was dried in high vacuum for 12 h at 60°C to remove possible trace of water. The structures of these carbonyl-based anion-functionalized ILs were 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 CO$_2$

In a typical absorption of CO$_2$, CO$_2$ 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 metal heating jacket of desirable temperature. The amount of CO$_2$ 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 to reduce the partial pressure of CO₂ passing through the system. The CO₂ partial pressure was controlled by changing the flow rate ratio of CO₂ and N₂.

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 metal heating jacket 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.

Computational Section

All calculations were performed using the GAUSSIAN03 programs package. For each set of calculations, we calculated geometry optimization for each free anion, the free CO₂ molecule, the anion-CO₂ complex, and the anion-2CO₂ complex at the B3LYP/6-31G++(d,p) level.

1. NMR and IR data of carbonyl-containing anion-functionalized ILs

[boxed{P6614}|Im-4-CHO]: ¹H NMR (CDCl₃): 0.86 (m, 12H, CH₃), 1.22-1.43 (m, 48H, CH₂), 2.20 (m, 8H, PCH₂), 7.65 (s, 1H, Im C5), 7.83 (s, 1H, Im C2), 9.68 (s, 1H, CHO); ¹³C NMR (CDCl₃): 13.9, 14.1, 18.8, 19.1, 21.7, 22.3, 22.6, 28.9, 29.2, 29.3, 29.5, 29.6, 30.3, 30.4, 30.9, 31.8, 137.0, 141.8, 146.5, 183.2 ppm. IR: 2954, 2924, 2854, 2732, 2678, 1640, 1575, 1490, 1462, 1377, 1349, 1240, 1174, 1111, 984, 782, 762, 720, 655 cm⁻¹.

[boxed{P6614}|4-EF-PhO]: ¹H NMR (DMSO): 0.87 (m,12H,CH₃), 1.30-1.34 (t,3H,CH₃), 1.24-1.42 (m, 48H, CH₂), 2.18 (m, 8H, PCH₂), 4.22-4.28 (q, 2H, CH₂), 6.69-6.72 (d, 2H, Ph C3,5), 7.77-7.79 (d, 2H, Ph C2,6); ¹³C NMR (DMSO): 13.8, 17.2, 17.7, 20.6, 21.8, 22.1, 28.1, 28.7, 29.0, 29.1, 29.7, 29.8, 30.4, 31.3, 57.9, 106.2, 118.6, 131.4, 166.5, 177.0 ppm. IR: 2954, 2924, 2854, 1670, 1580, 1511, 1462, 1366, 1302, 1266, 1147, 1103, 1086, 985, 847, 776, 713, 619 cm⁻¹.

[boxed{P6614}|4-CHO-PhO]: ¹H NMR (CDCl₃): 0.89 (m,12H,CH₃), 1.26-1.44 (m,48H, CH₂), 2.18(m, 8H, PCH₂), 6.51-6.54 (d, 2H, Ph C3,5), 7.51-7.53 (d, 2H, Ph C2,6), 9.46 (s,1H,CHO); ¹³C NMR (CDCl₃): 13.8, 14.0, 18.5, 19.0, 21.6, 22.2, 22.6, 28.8, 29.2,
29.3, 29.4, 29.5, 29.6, 30.2, 30.4, 30.9, 31.8, 119.6, 121.0, 133.1, 177.3, 188.3 ppm. IR: 2954, 2924, 2854, 1670, 1580, 1511, 1462, 1366, 1302, 1266, 1147, 1103, 1086, 985, 847, 776, 713, 619 cm⁻¹.

\[ \text{[P}_{66614}\text{][4-Kt-PhO]} \]: \(^1\)H NMR (CDCl₃): 0.89 (m, 12H, CH₃), 1.26-1.43 (m, 48H, CH₂), 2.18 (m, 8H, PCH₂), 2.40 (s, 3H, COCH₃), 6.51-6.53 (d, 2H, Ph C3,5), 7.69-7.71 (d, 2H, Ph C2,6); \(^{13}\)C NMR (CDCl₃): 13.8, 14.0, 18.5, 19.0, 21.6, 21.7, 22.2, 22.6, 25.6, 28.8, 29.2, 29.3, 29.4, 29.6, 30.2, 30.4, 30.6, 30.7, 31.0, 31.8, 118.4, 130.5, 131.5, 174.8, 195.1 ppm. IR: 2954, 2924, 2854, 1670, 1580, 1511, 1462, 1366, 1302, 1266, 1147, 1103, 1086, 985, 847, 776, 713, 619 cm⁻¹.

\[ \text{[Im-EA][Tf}_2\text{N]} \]: \(^1\)H NMR (DMSO): 1.25-1.29 (t, 3H, CH₃), 3.94 (s, 3H, NCH₃), 4.21-4.26 (q, 2H, OCH₂), 5.25 (s, 2H, COCH₂), 7.73-7.74 (d, 2H, -CH=CH-), 9.09 (s, 1H, C2); \(^{13}\)C NMR (DMSO): 13.8, 35.9, 49.5, 61.8, 123.3, 137.7, 166.8 ppm. IR: 3163, 1751, 1574, 1347, 1176, 1135, 1053, 975, 845, 790, 741, 710, 653 cm⁻¹.

<table>
<thead>
<tr>
<th>Ionic liquid(^a)</th>
<th>Temperature (°C)</th>
<th>CO₂ absorption(^b)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{[P}_{66614}\text{][4-CHO-Im]}]</td>
<td>30</td>
<td>1.24</td>
<td>This work</td>
</tr>
<tr>
<td>[\text{[P}_{66614}\text{][Triz]}]</td>
<td>23</td>
<td>0.97</td>
<td>Wang(^4)</td>
</tr>
<tr>
<td>[\text{[P}_{66614}\text{][Pro]}]</td>
<td>25</td>
<td>0.91</td>
<td>Brennecke(^5)</td>
</tr>
<tr>
<td>[\text{[P}_{66614}\text{][2-CNpyr]}]</td>
<td>25</td>
<td>0.90</td>
<td>Brennecke(^6)</td>
</tr>
<tr>
<td>[\text{[MTBDH][Im]}]</td>
<td>30</td>
<td>1.03</td>
<td>Wang(^7)</td>
</tr>
<tr>
<td>[\text{[APBim][BF}_4\text{]}]</td>
<td>25</td>
<td>~0.5</td>
<td>Davis(^8)</td>
</tr>
<tr>
<td>[\text{[AP}_{4444}\text{][Gly]}]</td>
<td>45</td>
<td>~1.1(^c)</td>
<td>Zhang(^9)</td>
</tr>
<tr>
<td>[\text{[Choline][Pro]}]</td>
<td>50</td>
<td>~0.5</td>
<td>Han(^10)</td>
</tr>
</tbody>
</table>

\(^a\)[P\(_{66614}\)][Triz], trihexyl (tetradecyl)phosphonium trizolate; [P\(_{66614}\)][Pro], trihexyl (tetradecyl)phosphonium prolinate; [P\(_{66614}\)][2-CNpyr], trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide; [P\(_{4444}\)][Ala], tetrabutylphosphonium alanine; [APBim][BF\(_4\)], 1-(3-aminopropyl)-3-butylimidazolium tetrafluoroborate;
AP\textsubscript{4443}[Gly], 3-(aminopropyl)tributylphosphonium glycinate; [Choline][Pro], 2-(hydroxyethyl)trimethylammonium prolinate; \textsuperscript{b}Mole CO\textsubscript{2} per mole IL. \textsuperscript{c}ILs on porous SiO\textsubscript{2}.

**Figure S1.** The effect of (a) pressure and (b) temperature on CO\textsubscript{2} absorption by [P\textsubscript{66614}][Im-4-CHO].

**Figure S2.** The IR spectra of before and after the capture of CO\textsubscript{2} capture under reduced pressure (30\% CO\textsubscript{2}) and atmospheric pressure (100\% CO\textsubscript{2}) by [P\textsubscript{66614}][4-CHO-Im].
**Figure S3.** The IR spectra before and after the capture of CO$_2$ by [P$_{6614}$][4-CHO-PhO].

**References**