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

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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 ($LiTf_2N$) 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 ^{o}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^{o}C for 12 h. Subsequently, ethanol and water were distilled off at 60 ^{o}C under reduced pressure. The obtained IL $[P_{66614}]$[4-CHO-Im] was dried in high vacuum for 12 h at 60^{o}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 $\pm$0.1 mg. During the absorption

of CO_2 under reduced pressure, CO_2 was diluted with N_2 to reduce the partial pressure of CO_2 passing through the system. The CO_2 partial pressure was controlled by changing the flow rate ratio of CO_2 and N_2.

In a typical desorption of CO_2, N_2 of atmospheric pressure was bubbled through about 1.0 g ILs containing captured CO_2 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 CO_2 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 CO_2 molecule, the anion-CO_2 complex, and the anion-$2CO_2$ complex at the B3LYP/6-31G++(d,p) level.

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

[P_{66614}][Im-4-CHO]: ^{1}H NMR ($CDCl_3$): 0.86 (m, 12H, CH_3), 1.22-1.43 (m, 48H, CH_2), 2.20 (m, 8H, PCH_2), 7.65 (s, 1H, Im C5), 7.83 (s, 1H, Im C2), 9.68 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$): 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}.

[P_{66614}][4-EF-PhO]: ^{1}H NMR (DMSO): 0.87 (m,12H,CH_3), 1.30-1.34 (t,3H,CH_3), 1.24-1.42 (m, 48H, CH_2), 2.18 (m, 8H, PCH_2), 4.22-4.28 (q, 2H, CH_2), 6.69-6.72 (d, 2H, Ph C3,5), 7.77-7.79 (d, 2H, Ph C2,6); ^{13}C 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}.

[P_{66614}][4-CHO-PhO]: ^{1}H NMR ($CDCl_3$): 0.89 (m,12H,CH_3), 1.26-1.44 (m,48H, CH_2), 2.18(m, 8H, PCH_2), 6.51-6.54 (d, 2H, Ph C3,5), 7.51-7.53 (d, 2H, Ph C2,6), 9.46 (s,1H,CHO); ^{13}C NMR ($CDCl_3$): 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}.

$[P_{66614}]$[4-Kt-PhO]: ^{1}H NMR ($CDCl_3$): 0.89 (m,12H,CH_3), 1.26-1.43 (m,48H,CH_2), 2.18 (m,8H,PCH_2), 2.40 (s, 3H, $COCH_3$), 6.51-6.53 (d, 2H, Ph C3,5), 7.69-7.71(d, 2H, Ph C2,6); ^{13}C NMR ($CDCl_3$): 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, 1634, 1568, 1513, 1462, 1438, 1360, 1281, 1155, 1104, 1065, 983, 948, 846, 719, 698cm^{-1}.

[Im-EA][Tf_2N]: ^{1}H NMR (DMSO): 1.25-1.29 (t,3H,CH_3), 3.94 (s,3H,NCH_3), 4.21-4.26 (q,2H,OCH_2), 5.25 (s, 2H, $COCH_2$), 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, 653cm^{-1}.

Table S1. The comparison of CO_2 absorption by typical carbonyl-containing ILs with that by other functionalized ILs.

Ionic liquid[a]	Temperature (^{o}C)	CO_2 absorption[b]	Reference
$[P_{66614}]$[4-CHO-Im]	30	1.24	This work
$[P_{66614}]$[Triz]	23	0.97	Wang[4]
$[P_{66614}]$[Pro]	25	0.91	Brennecke[5]
$[P_{66614}]$[2-CNpyr]	25	0.90	Brennecke[6]
[MTBDH][Im]	30	1.03	Wang[7]
[APBim][BF_4]	25	~0.5	Davis[8]
$[AP_{4443}]$[Gly]	45	~1.1[c]	Zhang[9]
[Choline][Pro]	50	~0.5	Han[10]

[a]$[P_{66614}]$[Triz], trihexyl (tetradecyl)phosphonium trizolate; $[P_{66614}]$[Pro], trihexyl (tetradecy)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_{4443}][Gly], 3-(aminopropyl)tributylphosphonium glycinate; [Choline][Pro], 2-(hydroxyethyl)trimethylammonium prolinate; [b]Mole CO_2 per mole IL. [c]ILs on porous SiO_2.

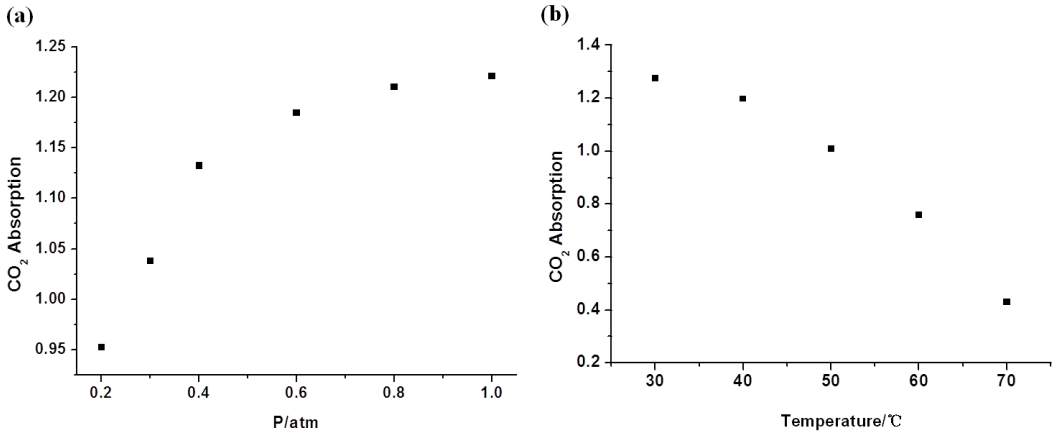

Figure S1. The effect of (a) pressure and (b) temperature on CO_2 absorption by [P_{66614}][Im-4-CHO].

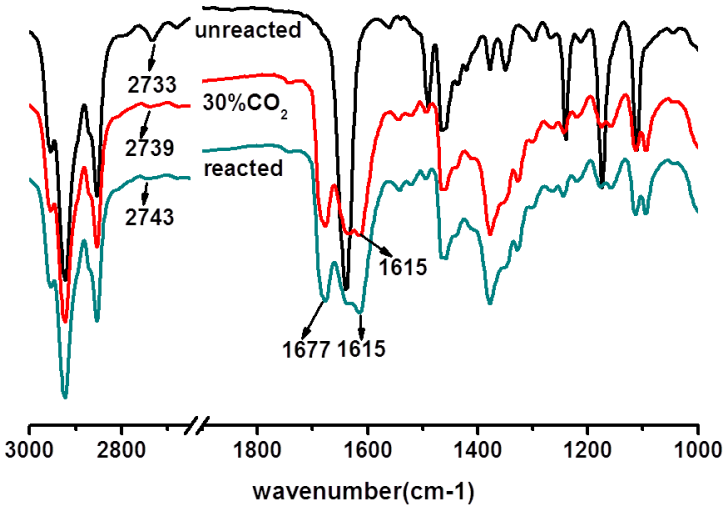

Figure S2. The IR spectra of before and after the capture of CO_2 capture under reduced pressure (30% CO_2) and atmospheric pressure (100% CO_2) by [P_{66614}] [4-CHO-Im].

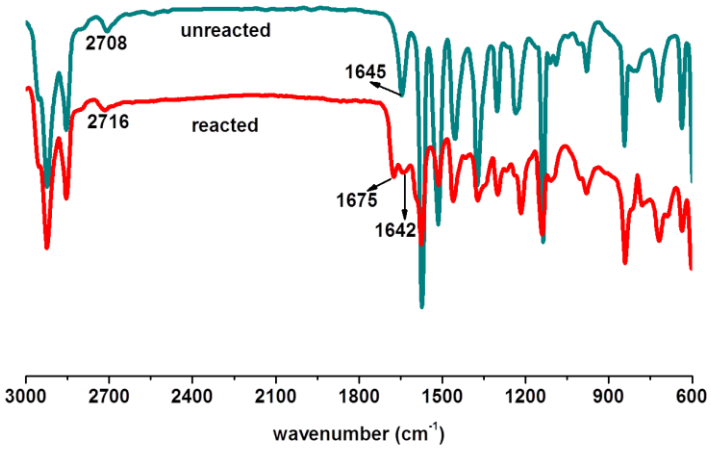

Figure S3. The IR spectra before and after the capture of CO_2 by $[P_{66614}][4\text{-CHO-PhO}]$.

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