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COMMUNICATION

Highly efficient CO₂ 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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A strategy to improve CO₂ capture significantly through the non-covalent interaction strengthened by the anion was reported, which exhibits an extremely high capacity up to 1.24 mole CO₂ per mole ionic liquid and excellent reversibility due to the presence of the enhanced lewis acid-base and cooperative C-H...O hydrogen bonding interactions.

Non-covalent interactions including hydrogen bonds, electrostatic association, stacking, and Van der Waals forces have attracted more and more attention due to their important roles in chemistry, biology and material science.¹ Among them, C-H...O hydrogen bonding interaction as one of non-covalent interactions manifests itself in myriad ways in chemistry and biology such as protein folding,² crystals,³ and supramolecular chemistry.⁴ However, the effect of C-H...O hydrogen bonding interaction on gas absorption such CO₂ capture is very weak because this interaction is a kind of weak interaction.⁵ Therefore, it is very important to enhance this kind of weak interaction in order to achieve improved CO₂ capture. Herein, we report a novel strategy for improving the capture of CO₂ by carbonyl-containing anion-functionalized ionic liquids (ILs) through the enhanced C-H...O hydrogen bonding interaction. We show that how we can achieve an extremely high capacity up to 1.24 mole CO₂ per mole IL and excellent reversibility through this interaction strengthened by the anion.

ILs have recently attracted more and more attention owing to their remarkable properties,⁶ for instance, extremely low vapor pressure, high thermal stability, wide liquid temperature range, and excellent designable property, where their physical and chemical properties are facilely tuned by different combinations of the cation and the anion.⁷ A large number works have focused on CO₂ physical absorption in traditional ILs. However, the capacity of CO₂ by these ILs is up to 0.03 mole per mole IL

under room pressure due to the weak interaction.⁸ Another method for CO₂ capture is the chemisorptions by functionalized ILs. Davis group reported the first example of CO₂ capture using an amine-functionalized IL, where 0.5 mole CO₂ per mole IL can be achieved under atmospheric pressure.⁹ Subsequently, some anion-functionalized ILs with the anions such as amino acid anion,¹⁰ azolate,¹¹ and phenolate¹² have been reported for efficient CO₂ capture. However, only equimolar CO₂ capture can be obtained by these anion-functionalized ILs. So how to achieve higher CO₂ capacity with improved desorption by tuning the specific structure of the IL such as introducing the non-covalent interaction is still an urgent issue.

Herein, we present a new strategy for improving CO₂ capture by ILs through the enhanced Lewis acid-base and cooperative C-H...O hydrogen bonding interaction, where a carbonyl group was introduced to the anion such as phenolate and imidazolate. The essence of our strategy is to strengthen the weak interaction by the anion, which provides an adding interacting site with CO₂, leading to the enhanced capacity. Through a combination of absorption experiment, quantum chemical calculation, and spectroscopic investigation, we show that both enhanced CO₂ absorption and improved CO₂ desorption can be achieved due to the dual effect of carbonyl group on the anion.

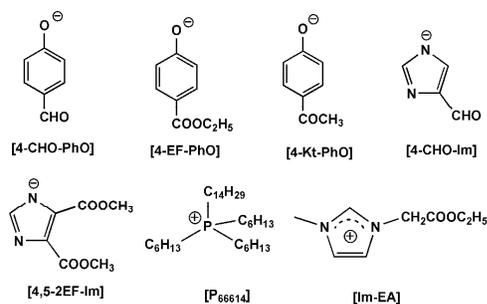
These carbonyl-containing anion-functionalized ILs were prepared by the acid-base neutralization between substituted phenols or substituted imidazole and a solution of phosphonium hydroxide in ethanol, which was obtained by the anion-exchange method.¹³ Among them, different carbonyl groups including aldehyde, ester, and ketone were selected to investigate that how the kind of group affects the capture of CO₂. Furthermore, a kind of IL with the ester-based cation and two kinds of ILs with the aldehyde-based anion were investigated to discuss the importance of the carbonyl group that introduced to the anion. Thus, several kinds of carbonyl-containing ILs including [P₆₆₆₁₄][4-CHO-Im], [P₆₆₆₁₄][4-CHO-PhO], [P₆₆₆₁₄][4-EF-PhO], [P₆₆₆₁₄][4-Kt-PhO], [P₆₆₆₁₄][4,5-2EF-Im], [Im-EA][Tf₂N] were designed and explored (Scheme 1). The structures of these ILs were confirmed by NMR and IR [see the Supporting Information (SI)].

The effect of different carbonyl-containing ILs on the capture of CO₂ was investigated, which was shown in Table 1. It was clear that the capacity of CO₂ increased significantly when the CHO group was introduced to the anion. For example, the molar

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Scheme. 1 The structures of the cation and the anion in these carbonyl-containing anion-functionalized ionic liquids for CO₂ capture.

Table 1. The effect of different carbonyl-containing ionic liquids on CO₂ absorption, interaction enthalpies, and Mulliken atomic charges of oxygen or nitrogen in the anion, and oxygen atom in carbonyl-based groups.

Anions	Absorption capacities ^a	$\Delta H^{b,c}$	Mulliken charges ^c	
			O/N	carbonyl (O)
[PhO]	0.81	-	-0.687	-
[4-Kt-PhO]	1.04	-13.9	-0.636	-0.528
[4-EF-PhO]	1.03	-13.5	-0.639	-0.566
[4-CHO-PhO]	1.01	-17.6	-0.631	-0.485
[Im]	0.98	-	-0.398	-
[4-CHO-Im]	1.24	-18.9	-0.373	-0.499
[Im-EA] ^d	0.06	-2.7	-	-0.451
[4,5-2EF-Im]	0.85	-14.4	-0.386	-0.508

^a Reaction conditions: CO₂ absorbed at 30 °C and 1 bar, mole CO₂ per mole IL. ^b The interaction enthalpies of the complexes of carbonyl-based groups and CO₂, kJ mol⁻¹. ^c Carried out at B3LYP/6-31++G(d,p) level. ^d Carbonyl-based cation.

ratios of CO₂ to [P₆₆₆₁₄][4-CHO-PhO] and [P₆₆₆₁₄][PhO] are 1.01 and 0.81, respectively, which exhibits a gap of 0.20. Besides, other carbonyl groups such as ketone play the similar roles in CO₂ capture, where the molar ratios of CO₂ to [P₆₆₆₁₄][4-EF-PhO] and [P₆₆₆₁₄][4-Kt-PhO] are 1.03 and 1.04, respectively, indicating the enhanced capacity. It was emphasized that the carbonyl group that attached to the anion was very important. For the IL with the carbonyl-containing cation [Im-EA][Tf₂N], CO₂ capacity is only 0.06 mole per mole IL. However, for the carbonyl-containing IL with the stronger basicity [P₆₆₆₁₄][4-CHO-PhO], CO₂ capacity increased to 1.24 mole per mole IL from 0.98 mole per mole IL of [P₆₆₆₁₄][Im], which exhibits a bigger gap of 0.26. Furthermore, for the anion [4, 5-2EF-Im] which contains two ester group, CO₂ capacity is only 0.85 mole per mole IL.

The effect of pressure on the capture of CO₂ by the carbonyl-containing IL [P₆₆₆₁₄][4-CHO-Im] was investigated (Fig. S1a). It was seen that the molar ratio of CO₂ to the IL reduced from 1.24 to 0.96 when the pressure decreased from 1.0 to 0.2 bar. Fig. S1b shows the temperature dependence of CO₂ capture at 1.0 bar. It can be seen that CO₂ capacity reduced significantly when the temperature increased. Clearly, the captured CO₂ is readily released by heating or bubbling N₂ through the IL. Fig. 1 shows the CO₂ absorption/desorption recycling exhibited by [P₆₆₆₁₄][4-

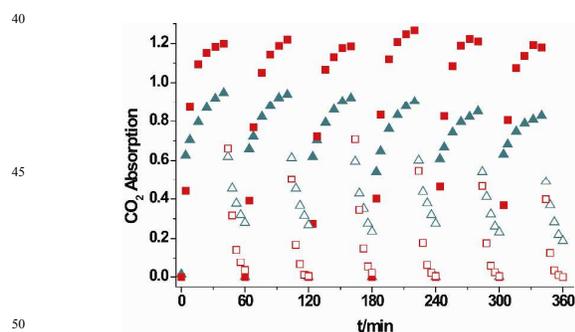


Fig. 1 Six cycles of CO₂ absorption and desorption using [P₆₆₆₁₄][4-CHO-Im] and [P₆₆₆₁₄][Im]. CO₂ absorption was carried out at 30 °C and 1 bar, and desorption was performed at 80 °C under N₂. For [P₆₆₆₁₄][4-CHO-Im]: ■, absorption; □, desorption. For [P₆₆₆₁₄][Im]: ▲, absorption; △, desorption.

CHO-Im], where [P₆₆₆₁₄][Im] was selected as a comparison to indicate the effect of the carbonyl group. As shown in Fig. 1, compared with CO₂ capture by [P₆₆₆₁₄][Im], [P₆₆₆₁₄][4-CHO-Im] exhibited higher CO₂ capacity and better stability during six recycles. Interestingly, [P₆₆₆₁₄][4-CHO-Im] also shows the improved desorption, where the release of CO₂ by [P₆₆₆₁₄][4-CHO-Im] is complete, while for [P₆₆₆₁₄][Im] about 0.25 mole CO₂ per mole IL remained. These results indicate that the CO₂ absorption by [P₆₆₆₁₄][4-CHO-Im] is highly reversible. It was mentioned that the aldehydes are easily oxidized, which possible limits the practical application of these formyl-containing ILs.

Considering both high absorption capacity and excellent reversibility, we believe that these carbonyl-containing anion-functionalized ILs provide an attractive alternative for CO₂ absorption, whose performance is superior to other ILs (Table S1). Why do these carbonyl-containing anion-functionalized ILs exhibit such a high capacity for CO₂ capture. We believe that there must lie in the C-H...O hydrogen bonding interaction between carbonyl group and CO₂, which was strengthened by the anion, providing an added interacting site to CO₂. Furthermore, the improved desorption maybe contributed to the role as an electron-withdrawing group of carbonyl group, leading to the reduced interaction between the anion and CO₂.

To seek the role of carbonyl group on the anion in CO₂ capture, theoretical calculations were carried out using the Gaussian 03 program. For each set of calculations, we performed geometry and energy optimizations at the B3LYP/6-31++(p,d) level.¹⁴ Fig. 2 shows the optimized structures that the anion [4-CHO-Im] and the neutral molecule [4-CHO-Im] interact with CO₂ separately. It can be seen that the C-H...O distance between the anion [4-CHO-Im] and CO₂ is predicted to be 2.641 Å, which is shorter than between the neutral [4-CHO-Im] and CO₂, indicating the stronger interaction between the former. The interaction enthalpy between the anion [4-CHO-Im] and CO₂ was also calculated, which is -18.9 kJ mol⁻¹, however, for that between the neutral [4-CHO-Im] and CO₂, the interaction enthalpy is only -5.87 kJ mol⁻¹, indicating that the interaction between the CHO group on the anion and CO₂ was strengthened by the anion significantly, leading to an increase in CO₂ absorption capacity. On the other hand, when the carbonyl-containing cation [Im-EA] was used, the interaction enthalpy is only -2.72 kJ mol⁻¹, leading to the weak

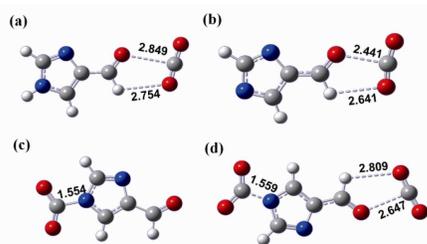


Fig. 2 Optimized structures of [4-CHO-Im]-CO₂ complexes at the B3LYP/6-31++G(d,p) level. a) the neutral [4-CHO-Im]-CO₂, $\Delta H = -5.87$ kJ mol⁻¹; b) the anion [4-CHO-Im]-CO₂(CHO), $\Delta H = -18.9$ kJ mol⁻¹; c) the anion [4-CHO-Im]-CO₂(N), $\Delta H = -51.0$ kJ mol⁻¹; d) the anion [4-CHO-Im]-2CO₂, $\Delta H = -18.9$ kJ mol⁻¹.

effect on CO₂ capture, which is in agreeable with the experimental result. Furthermore, the interaction between the N atom on the anion and CO₂ was also investigated, which was shown in Fig. 2c-d. It was seen that the absorption enthalpy decreased significantly from -89.9 kJ mol⁻¹ to -51.0 kJ mol⁻¹, when the CHO group was introduced to the anion, which is originated from the decrease in the Mulliken charges of the N atom in the anion because of the electron-withdrawing nature of CHO group, for example, the Mulliken charge of the N atom in [4-CHO-Im] is -0.373, while that in [Im] is -0.398. These results indicate that the interaction between the anion and CO₂ reduced, resulting in the improved desorption. Moreover, for the anion [4, 5-2EF-Im], the interaction enthalpy between CO₂ and the N atom of [P₆₆₆₁₄][4, 5-2EF-Im] reduced to -25.0 kJ mol⁻¹ due to the strong electron-withdrawing effect of two ester groups, leading to the decreased CO₂ capacity.

The interaction between these carbonyl-containing ILs and CO₂ was further investigated by FTIR and NMR spectroscopy to support the experimental and theoretical results, where [P₆₆₆₁₄][4-CHO-Im] was selected as a typical case, (Fig. 3). It was seen that a stretching vibration peak at 1640 cm⁻¹ moved to 1615 cm⁻¹ after the capture of CO₂ by [P₆₆₆₁₄][4-CHO-Im], which exhibits a red shift of carbonyl group in [4-CHO-Im], indicating the presence of C-H...O hydrogen bonding interaction between the anion [4-CHO-Im] and CO₂.¹⁵ At the same time, a stretching vibration peak of C-H in [4-CHO-Im] shifted from 2733 cm⁻¹ to 2743 cm⁻¹, which is a blue shift, also indicating the formation of C-H...O hydrogen bonding interaction.¹⁵ The IR spectrum under reduced pressure was also investigated to further verify the presence of C-H...O hydrogen bonding interaction (Fig. S2). As can be seen, the stretching vibration peak of carbonyl group at 1615 cm⁻¹ became weaker and that of C-H moved from 2743 cm⁻¹ to 2739 cm⁻¹ with the reduce of CO₂ pressure from 1.0 bar to 0.3 bar, illustrating the C-H...O hydrogen bonding interaction decreased when CO₂ partial pressure reduced. Furthermore, compared with the IR spectrum of the fresh IL [P₆₆₆₁₄][4-CHO-Im], a new peak at 1677 cm⁻¹ appeared, which can be attributed to a carbamate (C=O) stretch, formed by the absorption of CO₂. Similarly, after the absorption of CO₂ by [P₆₆₆₁₄][4-CHO-Im], a signal at 163.5 ppm produced, which was attributable to carbamate carbonyl carbon, while the peak at 185.8 ppm moved to 186.8 slightly as a result of the C-H...O hydrogen bonding interaction between the anion [4-CHO-Im] and CO₂. Based on previous reports and the observed results, the possible mechanism of CO₂ absorption by

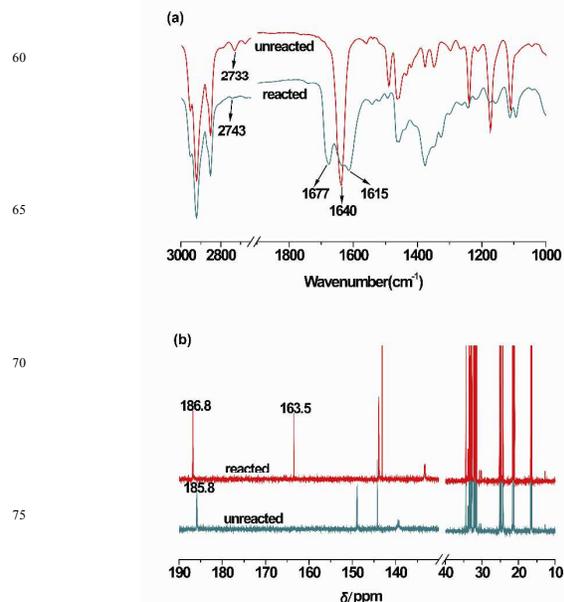


Fig. 3 The FT-IR a) and ¹³C NMR b) spectra of the IL [P₆₆₆₁₄][4-CHO-Im] before and after the absorption of CO₂.

[P₆₆₆₁₄][4-CHO-Im] can be proposed in Fig. 2, which shows two kinds of interactions including the interaction between acidic CO₂ and basic N atom as well as the enhanced C-H...O hydrogen bonding interaction between CO₂ and the CHO group.

In summary, a new method for improving the capture of CO₂ by anion-functionalized ILs was developed through introducing a carbonyl group on the anion. Several kinds of carbonyl-containing anion-functionalized ILs exhibited significant enhancements in CO₂ capacities, where up to 1.24 mole per mole IL were achieved. Quantum mechanical calculations and spectroscopic investigations show such a high CO₂ capacity was originated from the enhanced C-H...O hydrogen bonding interaction, where the anion plays a key role. Amazingly, the desorption was also improved due to the electron-withdrawing nature of carbonyl group, leading to excellent reversibility. This strategy strengthened the anion may be applied to other non-covalent interactions such as strong hydrogen bonds and stacking, which is promising in the field of gas separation as well as other fields. We believe that this efficient and reversible process by these ILs provides an attractive alternative for carbon capture.

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