

Significant Improvements in CO₂ Capture by Pyridine-Containing Anion-Functionalized Ionic Liquids through Multiple-Site Cooperative Interactions**

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Abstract: A strategy for improving CO₂ capture by new anion-functionalized ionic liquids (ILs) making use of multiple site cooperative interactions is reported. An extremely high capacity of up to 1.60 mol CO₂ per mol IL and excellent reversibility were achieved by introducing a nitrogen-based interacting site on the phenolate and imidazolate anion. Quantum-chemical calculations, spectroscopic investigations, and calorimetric data demonstrated that multiple-site cooperative interactions between two kinds of interacting sites in the anion and CO₂ resulted in superior CO₂ capacities, which originated from the π -electron delocalization in the pyridine ring.

Cooperative interactions can be seen in some chemical and biological systems, such as enzymes and receptors, and they occur when these structures contain multiple binding sites.^[1] Cooperative interactions play significant roles in nature, for example in determining molecular recognition, supramolecular self-assembly, protein folding, and gene transcription, which are the basis of enzyme control and many other vital biological processes.^[2] Moreover, they have been applied in some chemical fields, such as catalysis^[3] and gas separation.^[4] On the other hand, the problem of CO₂ capture is regarded as one of the grand challenges for the 21st century. Although a great deal of materials and processes have been developed for carbon capture, to our knowledge, efficient and reversible CO₂ absorption driven by cooperative interactions using ionic liquids (ILs) has not been reported to date.^[5] Herein, we report a novel strategy for improving the capture of CO₂ by an IL through cooperative interactions. We show that an extremely high capacity more than 1.5 mol CO₂ per mol IL and excellent reversibility can be achieved by pyridine-containing anion-functionalized ILs through multiple-site cooperation interactions.

The development of more efficient, reversible, and economical processes for capturing CO₂ from the burning of fossil fuels is critical for the reduction of the emission of greenhouse gas implicated in global warming. Currently available technology for CO₂ capture in industry is based on the chemisorption process by an aqueous alkanolamine solution, with some advantages, such as low cost, rapid kinetics, and high capacity.^[6] Unfortunately, this amine-based process has some intrinsic disadvantages, including the high energy demand required to regenerate the liquid, solvent loss, and degradation.^[7] ILs are promising in this regard because of their negligible vapor pressures, wide liquid ranges, high thermal stabilities, and virtually limitless chemical tunability.^[8] Taking a lead from the amine-based process, Davis and co-workers reported the first example for CO₂ chemisorption that employs an amino-functionalized IL, where about 0.5 mol CO₂ per mol IL can be absorbed under ambient pressure.^[9] Subsequently, some other functionalized ILs, including sulfone, acetate, and amino acid anions, were reported for the capture of CO₂.^[10] Recently, a novel method for the capture of CO₂ in a 1:1 manner by tunable azole-based ILs and phenol-based ILs was reported by making use of the reactivity of the anion.^[11] Generally, CO₂ chemisorptions by these functionalized ILs are based on the single-site interaction between the electronegative nitrogen (for example, imidazolate) or oxygen atom (phenolate) and CO₂, resulting in up to equimolar stoichiometry at low pressure.^[12] It now needs to be seen whether a new method for capturing CO₂ in more than 1:1 stoichiometry can be developed.

Herein, we present a new method for carbon capture by several pyridine-containing anion-functionalized ILs with two kinds of different interacting sites through cooperative interactions. The essence of our strategy is to introduce a nitrogen-based interacting site such as pyridine to the anion. The results show that an extremely high capacity up to 1.60 mol CO₂ per mol IL was achieved. Spectroscopic investigations, calorimetric methods, and quantum-chemical calculations demonstrate that such a high capacity originates from cooperative multiple site interactions between the electronegative oxygen and nitrogen atoms in the anion and CO₂.

These pyridine-containing anion-functionalized ILs (Figure 1) were prepared by neutralization of various hydroxypyridine or 4-azabenzimidazole compounds with an ethanol solution of trihexyl(tetradecyl)phosphonium hydroxide, which was obtained by the anion-exchange method.^[13] The

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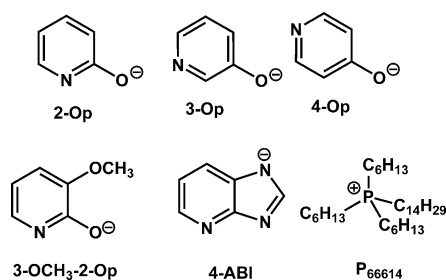


Figure 1. Structures of the anion and the cation in pyridine-containing anion-functionalized ionic liquids.

structures of these ILs were confirmed by NMR and IR spectroscopy and mass spectrometry (see the Supporting Information). Both thermal stability and water stability of these pyridine-containing ILs were investigated. The decomposition temperature of the ILs [P₆₆₆₁₄][2-Op] and [P₆₆₆₁₄][4-Op] was 240 and 278 °C, respectively (Supporting Information, Figure S1), indicating thermal stability of these pyridine-containing ILs are high. Furthermore, water stability of these ILs are also high (Supporting Information, Figure S2).

The effect of different pyridine-containing anion-functionalized ILs on the capture of CO₂ was investigated (Table 1). As can be seen, the effect of the position of

Table 1: The effect of different pyridine-containing anion-functionalized ionic liquids on CO₂ capacity and the Mulliken atomic charges of the nitrogen and oxygen atoms in the anion.^[a]

Ionic liquids	Absorption capacity ^[c]	Mulliken atomic charges ^[d]	
		N charge	O charge
[P ₆₆₆₁₄][2-Op]	1.58	−0.323	−0.630
[P ₆₆₆₁₄][4-Op]	1.49	−0.285	−0.672
[P ₆₆₆₁₄][3-Op]	1.38	−0.235	−0.713
[P ₆₆₆₁₄][3-OMe ₃ -2-Op]	1.65	−0.362	−0.609
[P ₆₆₆₁₄][PhO] ^[b]	0.85	–	−0.687
[P ₆₆₆₁₄][4-ABI]	1.60	−0.312 (N in pyridine)	–
Pyridine	0.013	−0.161	–

[a] The absorption was carried out at 20 °C and 1.0 atm. [b] Trihexyl(tetradecyl)phosphonium phenolate; the absorption was carried out at 30 °C and 1.0 atm. [c] Mol CO₂ per mol IL. [d] Carried out at the B3LYP/6-31++G(p,d) level.

nitrogen atom in the anion on CO₂ absorption is significant. For example, for [P₆₆₆₁₄][2-Op], 1.58 mol CO₂ per mol IL was achieved at 20 °C under ambient pressure, while [P₆₆₆₁₄][3-Op] and [P₆₆₆₁₄][4-Op] exhibit a CO₂ capacity of 1.38 and 1.49 mol per mol IL, respectively. Clearly, these ILs show a high capacity for CO₂ capture, which is significantly greater than 1:1 stoichiometry.

The effect of the pressure on the capture of CO₂ by [P₆₆₆₁₄][2-Op] was investigated (Figure 2). It was seen that CO₂ capacity decreased from 1.58 to 1.28 mol per mol IL when the partial pressure decreased from 1 atm to 0.1 atm. The effect of the temperature on CO₂ capture by [P₆₆₆₁₄][2-Op] is shown in Figure 2 and the Supporting Information, Table S1. The mol ratio of CO₂ to IL decreased to 0.37 upon increasing the temperature to 120 °C. Thus, the captured CO₂

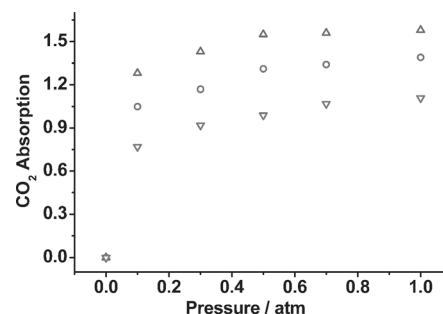


Figure 2. The effect of pressure and temperature on the capture of CO₂ by [P₆₆₆₁₄][2-Op]. Δ 20 °C; $\circ$ 40 °C; ∇ 60 °C.

was easy to release by heating or under reduced pressure. The multiple absorption/desorption cycles by [P₆₆₆₁₄][2-Op] at 80 °C were investigated (Supporting Information, Figure S3). As can be seen, all of the CO₂ capacities remained steady during six cycles, indicating that this capture process by [P₆₆₆₁₄][2-Op] was highly reversible. Furthermore, the effect of water on CO₂ capture by [P₆₆₆₁₄][2-Op] was investigated. It was seen (Supporting Information, Figure S4) that CO₂ capacity reduced about 0.1 mol per mol IL using moist CO₂, where water may be preferentially absorbed, and the absorption rate using moist CO₂ increased significantly because of the decrease in the viscosity during CO₂ absorption.^[14]

Clearly, these pyridine-containing anion-functionalized ILs exhibit very high capacity for CO₂ capture by functionalized ILs and some other adsorbent materials (Supporting Information, Table S2). Why do these ILs exhibit such high capacities for CO₂ capture? There are two kinds of interacting sites, including oxygen and nitrogen atoms in the anion. Thereby, we believe that it may be contributed to two site interactions between the electronegative nitrogen and oxygen atoms in this anion and CO₂, where the former can be viewed as the interaction between phenolate IL [P₆₆₆₁₄][PhO] and CO₂, while the latter can be looked as the interaction between pyridine and CO₂. Generally, the nitrogen atom in neutral pyridine has poor ability for CO₂ capture.^[15] As shown in Table 1, the mol ratios of CO₂ to [P₆₆₆₁₄][PhO] and pyridine are 0.85^[11c] and 0.013,^[16] respectively. Clearly, CO₂ capacities of these hydroxypyridine-based ILs, such as [P₆₆₆₁₄][2-Op], are significantly higher than the combination of that by phenolate IL and that by pyridine. Therefore, we believe there must lie in a positive cooperative interaction between two kinds of sites in the anion, resulting in the significant increase of CO₂ capacity.

To explain the cooperative interactions of two kinds of sites in these ILs, we calculated the Mulliken atomic charge of the nitrogen and oxygen atoms in the anion using the Gaussian03 program.^[17] As can be seen in Table 1 that, compared with Mulliken atomic charge of the nitrogen atom in pyridine, in these ILs it increased significantly because of the π -electron delocalization in the pyridine ring, where the nitrogen atom shared the negative charge of the oxygen atom, thereby leading to the enhanced interaction between the nitrogen atom in the anion and CO₂. For example, the Mulliken atomic charges of the nitrogen atom in [P₆₆₆₁₄][2-

Op], $[P_{66614}][3\text{-Op}]$, and $[P_{66614}][4\text{-Op}]$ are -0.323 , -0.235 , and -0.285 , respectively, while that in pyridine is -0.161 . Clearly, the capacity for CO_2 capture increases with the increase of the charges of the nitrogen atom in these ILs.

It is well-known that a substituent in the anion has a significant effect on the electron-density distribution.^[11c,18] Therefore, to increase the negative charge of nitrogen atom, we introduced a strong electron-donating substituent, such as OCH_3 in the anion (Table 1). It was seen that Mulliken atomic charges of nitrogen atom in $[P_{66614}][3\text{-OCH}_3\text{-2-Op}]$ increased to -0.362 , resulting in the enhanced capacity of 1.65 mol CO_2 per mol IL. Interestingly, there lies in a linear relationship between CO_2 capacity and Mulliken atomic charge of nitrogen atom in the anion (Supporting Information, Figure S5). Thus, CO_2 capacity can be tuned quantitatively by changing Mulliken atomic charge of nitrogen atom in the anion, which is useful for the design of new highly efficient ILs for gas separation.

The multiple site interactions of these pyridine-containing anion-functionalized ILs such as $[P_{66614}][2\text{-Op}]$ with CO_2 were investigated by ^{13}C NMR and FTIR spectroscopy to support the experimental and theoretical results. In comparison with the IR spectrum of the fresh IL $[P_{66614}][2\text{-Op}]$ (Figure 3 a), the

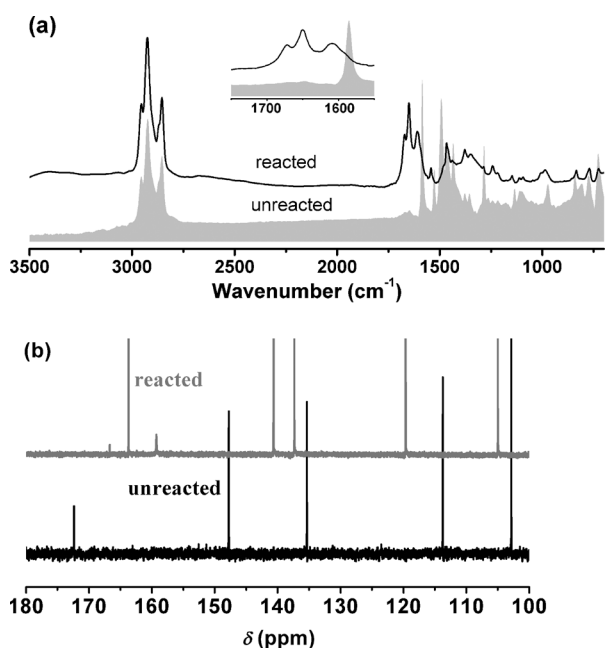


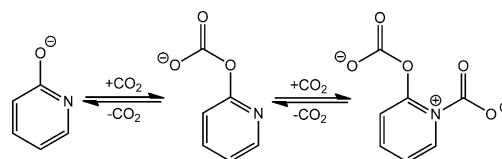
Figure 3. a) IR and b) ^{13}C NMR spectra of pyridine-containing anion-functionalized ionic liquids $[P_{66614}][2\text{-Op}]$ before and after the capture of CO_2 .

absorption band at 1587 cm^{-1} corresponding to C–O stretch shifted to 1607 cm^{-1} during the uptake of CO_2 , and two new peaks appeared in IR spectra at 1670 cm^{-1} and 1650 cm^{-1} , which can be assigned to the asymmetrical stretching vibration of carboxylate ion in N– CO_2 interaction and O– CO_2 interaction, respectively (Supporting Information, Table S3). In contrast, there is only one type of peak for CO_2 capture by $[P_{66614}][\text{PhO}]$, where the absorption of C–O

stretch at 1580 cm^{-1} moved to 1586 cm^{-1} , and one new peak appeared at 1620 cm^{-1} after CO_2 capture (Supporting Information, Figure S6). Similarly, it was seen in Figure 3 b that two new signals in the ^{13}C NMR spectra at 159.3 ppm and 166.6 ppm produced after the absorption of CO_2 , which can be attributed to carbonate and carbamate carbonyl carbon, respectively (Supporting Information, Table S4).

At the same time, the peak at 172.4 ppm moved upfield to 163.9 ppm during the absorption of CO_2 , also indicating the interaction between $[2\text{-Op}]$ and CO_2 . Furthermore, calorimetric data was further investigated to verify multiple site interaction between the anion and CO_2 (Figure S7). As can be seen, two exothermic peak appeared after the absorption of CO_2 by $[2\text{-Op}]$, also indicating the presence of multiple-site interactions between the oxygen atom and nitrogen atom in $[2\text{-Op}]$ with CO_2 .

During CO_2 capture by $[P_{66614}][2\text{-Op}]$ through multiple-site cooperative interactions between the oxygen and nitrogen atoms in the anion with CO_2 , which one binds first? In situ IR spectroscopy with the aid of two-dimensional (2D) correlation analysis of $[P_{66614}][2\text{-Op}]$ in the region from 1590 cm^{-1} to 1690 cm^{-1} with the time was carried out (Supporting Information, Figure S8). It was seen that the comparison with the intensity of synchronous 2D correlation spectrum $\phi(v_1, v_2)$ and the asynchronous spectrum $\psi(v_1, v_2)$ indicated that the change of the peak at 1586 cm^{-1} and 1650 cm^{-1} preceded 1670 cm^{-1} according to the so-called Noda's rule.^[19] It was suggested the first CO_2 binds the O atom causing the movement of 1586 cm^{-1} and the appearance of 1650 cm^{-1} , and closely follow the appearance of 1670 cm^{-1} , which belongs to the second CO_2 . Furthermore, ^{13}C NMR spectra of $[P_{66614}][2\text{-Op}]$ with different captured CO_2 also verified the result that the O atom binds CO_2 first. One signal at 158.6 ppm and 159.3 ppm was produced (Supporting Information, Figure S9) when $[P_{66614}][2\text{-Op}]$ captured 0.3 and 0.8 mol CO_2 per mol IL, respectively, which was attributed to the interaction between the O atom and CO_2 . Based on previous reports^[11,20] and the observed product, a plausible mechanism of CO_2 absorption by $[P_{66614}][2\text{-Op}]$ can be proposed (Scheme 1), which exhibits two-site interaction between the electronegative oxygen and nitrogen atoms in the anion with CO_2 .



Scheme 1. The plausible mechanism of CO_2 absorption by $[P_{66614}][2\text{-Op}]$ through multiple-site cooperative interactions.

On the basis of the above results, we conclude that multiple-site cooperative interactions between these pyridine-containing anion-functionalized ILs and CO_2 result in such a high capacity. Thus, a kind of new 4-azabenzimidazole-based IL $[P_{66614}][4\text{-ABI}]$, which contains a pyridine group on the imidazolate anion, were designed, synthesized, and

applied for CO₂ capture. The results showed that high capacity of 1.60 mol CO₂ per mol IL can be achieved by [P₆₆₆₁₄][4-ABI] at 20°C, where the Mulliken atomic charge of the N atom in pyridine group is −0.312, which is also much higher than in pyridine. The studies on quantum-chemical calculations, IR, and ¹³C NMR spectra show that multiple-site cooperative interactions lead to such a high capacity, which is similar with the results in [P₆₆₆₁₄][Op] (Supporting Information, Figure S10).

In summary, we have developed a new method for capturing CO₂ using several pyridine-containing anion-functionalized ILs, which include two kinds of interacting sites, by cooperative interactions. These ILs show extremely high CO₂ capacities (up to 1.60 mol of CO₂ per mol of IL) owing to the presence of multiple-site cooperative interactions. Quantum-chemical calculations, spectroscopic investigations, and calorimetric data show that multiple site cooperative interaction between two kinds of interacting sites in the anion resulted in superior CO₂ capacities, which originated from the π -electron delocalization that increased Mulliken atomic charge of the nitrogen atom. We believe that this highly efficient and reversible process by pyridine-containing anion-functionalized ILs can provide a potential alternative for CO₂ capture. The use of cooperative interactions in gas separation promises to provide a general strategy for enhancing the capacity for other acid gases as well as for other adsorbent materials.

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