

CO Capture

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Internationale Ausgabe: DOI: 10.1002/anie.201701919**Highly Efficient Carbon Monoxide Capture by Carbanion-Functionalized Ionic Liquids through C-Site Interactions**

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Abstract: A novel method for the highly efficient and reversible capture of CO in carbanion-functionalized ionic liquids (ILs) by a C-site interaction is reported. Because of its supernucleophilicity, the carbanion in ILs could absorb CO efficiently. As a result, a relatively high absorption capacity for CO (up to $0.046 \text{ mol mol}^{-1}$) was achieved under ambient conditions, compared with CO solubility in a commonly used IL [Bmim][Tf₂N] ($2 \times 10^{-3} \text{ mol mol}^{-1}$). The results of quantum mechanical calculations and spectroscopic investigation confirmed that the chemical interaction between the C-site in the carbanion and CO resulted in the superior CO absorption capacities. Furthermore, the subsequent conversion of captured CO into valuable chemicals with good reactivity was also realized through the alkoxycarbonylation reaction under mild conditions. Highly efficient CO absorption by carbanion-functionalized ILs provides a new way of separating and converting CO.

Carbon monoxide, which is mainly emitted from the exhaust of internal combustion engines, is a colorless, odorless, but very toxic gas for humans because of its high affinity for hemoglobin. An efficient CO elimination treatment is through the catalytic oxidation of CO into CO₂ using noble metals as catalysts.^[1] However, this process results in the increased emission of CO₂, a major greenhouse gas, and an additional process is required to treat the tail gas to reduce the emission of CO₂. On the other hand, CO is an important

industrial gas feedstock for the C₁ chemistry. Through the carbonylation process, CO can be transformed into various bulk chemicals, such as acetic acid, aldehydes, and esters.^[2] Therefore, research into the removal, purification, and utilization of CO is very important in fields such as environmental protection, chemistry, and industry.

Ionic liquids (ILs) are a class of state-of-the-art solvents owing to their unique properties, such as virtually unlimited tunability, negligible vapor pressure, excellent solubility, and high thermal stability.^[3–5] Thus, ILs have proved to be efficient absorbents and reaction media for many gases, such as CO₂,^[6] SO₂,^[7] H₂S,^[8] NO,^[9] and N₂O.^[10] However, it is difficult for ILs to capture CO, as a simple diatomic molecule, because it has the highest bond dissociation energy among all the diatomic molecules.^[11] There are a limited number of studies concerning the capture of CO by ILs.^[12] For example, Laurency's group reported the first example of CO capture by an IL ([Bmim][Tf₂N]) in 2004, in which a solubility of $1.25 \times 10^{-3} \text{ mol CO per mol of IL}$ was achieved at ambient pressure.^[12a] Thereafter, Peters et al. further investigated the absorption of CO by [Bmim][Tf₂N] at temperatures of up to 460 K and pressures of up to 10 MPa.^[12e] These findings show that the CO absorption capacities of ILs are very low; hence, it is highly desirable to develop IL systems that are able to efficiently capture CO at higher capacities.

CO can behave as a π -acid^[13] and readily coordinate with transition metals through CO-to-metal σ -donation.^[14] Taking advantage of this interaction, a CuCl/[hmim][Cl] mixture was found to be an efficient absorbent system that exhibits considerable CO capture capacity.^[15] However, this system is analogous to the conventional solution of ammoniacal cuprous chloride, which exhibits many drawbacks, such as water sensitivity and the instability of Cu⁺ ions owing to oxidation and disproportionation. Furthermore, CO is also susceptible to attack by a nucleophilic species through polarization of the CO triple bond.^[16] A nucleophile possessing strong nucleophilicity can react with CO efficiently. In light of the two distinctive types of interactions for CO, can we introduce these interactions into systems of CO capture by ILs, and design novel and stable functionalized ILs for efficient and reversible absorption of CO?

Herein, we present a promising system with significantly enhanced CO capture by carbanion-functionalized ILs through C-site interaction. The essence of our strategy is to make use of the supernucleophilicity of carbanions to react with CO reversibly and thereby to enhance the interaction between ILs and CO. Thus, a high capacity for CO absorption (up to $0.046 \text{ mol CO per mol IL}$) could be achieved under ambient conditions. The interaction of carbanion-functional-

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ized ILs with CO was further identified by quantum mechanical calculations and by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. Furthermore, we demonstrated that the captured CO could be converted into valuable chemicals through the alkoxycarbonylation reaction under mild conditions.

The carbanion-functionalized ILs (Figure 1) were prepared by neutralization of various β -diketone compounds with an ethanol solution of tributyl(octyl)phosphonium hydroxide, which was obtained by the anion-exchange method.^[6h,17] The structures of these ILs were confirmed by NMR and IR spectroscopy, mass spectrometry, and elemental analysis. The physicochemical properties were characterized by densimeter, viscometer, thermogravimetric analysis, and differential scanning calorimetry. The characterization results are presented in the Supporting Information, Table S1.

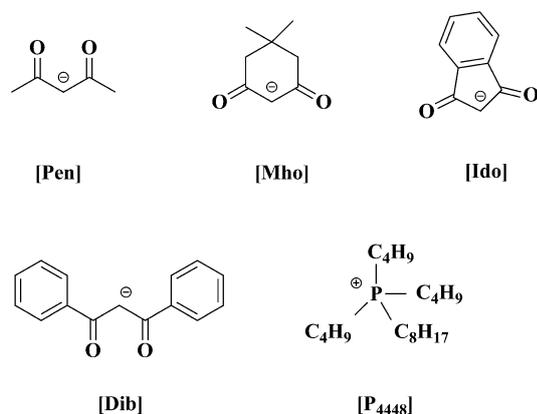


Figure 1. Structures of the anions and the cation in carbanion-functionalized ionic liquids.

First, we determined the solubilities of CO in these carbanion-functionalized ILs under ambient conditions (Table 1). To our surprise, the ILs showed a very high capacity for capturing CO at room temperature and atmospheric pressure. For example, absorption of 0.046 mol CO per mol IL was achieved in $[P_{4448}][Pen]$ at 25 °C and 1 bar. The other four carbanion-functionalized ILs also exhibited excellent CO capture capacities of up to 0.030 mol CO per mol IL. However, the solubility of CO in $[Bmim][Tf_2N]$ was as low as 2×10^{-3} mol mol⁻¹ (Supporting Information, Figure S1). Thus, compared to the data from previous studies, carbanion-functionalized ILs were found to be superior to most other ILs and traditional organic solvents in terms of CO uptake (Table 1). Moreover, the effects of pressure and the temperature on CO absorption were investigated (Supporting Information, Table S2). It is seen that the CO absorption capacity of $[P_{4448}][Pen]$ increased to 0.077 mol CO per mol IL when the partial pressure was increased to 3 bar, indicating that high pressure is favorable to CO capture. And it is also notable that the CO absorption capacity of $[P_{4448}][Pen]$ improved slightly, from 0.046 to 0.052 mol per mol IL, when the temperature increased from 25 °C to 50 °C. A similar behavior has also been observed in the absorption of CO in other ILs as reported by Maurer.^[12c] It is considered that the

Table 1: Absorption capacity of CO in carbanion-functionalized ILs compared with other ILs.^[a]

Absorbent	<i>T</i> [°C]	<i>p</i> [bar]	Solubility [mol mol ⁻¹]	Ref.
$[P_{4448}][Pen]$	25	1.0	0.046	–
$[P_{4448}][Mho]$	25	1.0	0.021	–
$[P_{4448}][Ido]$	25	1.0	0.011	–
$[P_{4448}][Dib]$	25	1.0	0.020	–
$[P_{4442}][Pen]$	25	1.0	0.030	–
toluene ^[a]	22	1.0	7.8×10^{-4}	[12a]
methano ^[a]	22	1.0	4.4×10^{-4}	[12a]
1-decene ^[a]	22	1.0	1.3×10^{-3}	[12a]
1-hexene ^[a]	22	1.0	2.1×10^{-3}	[12a]
$[Bmim][PF_6]$ ^[a]	22	1.0	3.0×10^{-3}	[12a]
$[Bmim][CF_3COO]$ ^[a]	22	1.0	5.2×10^{-3}	[12a]
$[Bmim][BF_4]$ ^[a]	22	1.0	2.9×10^{-3}	[12a]
$[Bmim][CH_3SO_4]$ ^[a]	20	1.0	2.6×10^{-3}	[12c]
$[Bmim][Tf_2N]$ ^[a]	30	1.0	1.5×10^{-3}	[12d]
$CuCl/[hmim][Cl]$	30	1.0	0.020	[15a]

[a] The solubilities at 1.0 bar were estimated according to Henry's law: $K_H = P_{CO}/x_{CO}$.

absorption of CO in carbanion ILs may be kinetically controlled owing to a high activation energy. In other words, increasing the temperature could reduce the kinetic barrier and promote this reaction efficiently. Furthermore, the solubilities of a binary mixture 50% CO + 50% N₂ and pure N₂ in $[P_{4448}][Pen]$ were measured at 25 °C and 1 bar, respectively. It is remarkable that $[P_{4448}][Pen]$ showed very low capacity for capturing pure N₂ (Supporting Information, Figure S2). In contrast, $[P_{4448}][Pen]$ retained a relatively high CO absorption capacity of 0.034 mol mol⁻¹ for the absorption of the mixture of CO and N₂ (Supporting Information, Table S2). Thus, it is demonstrated that carbanion-functionalized ILs can capture CO efficiently, even at a low CO concentration, showing great potential for selective separation of CO from N₂.

Why did $[P_{4448}][Pen]$ show such high CO absorption capacity? To illustrate the underlying mechanism, we first estimated CO solubility in various ILs based on pure physical interaction. With the COSMOtherm program,^[18] simulated CO solubilities of $[P_{4448}][Pen]$ and $[Bmim][Tf_2N]$ were 2.06×10^{-3} and 1.64×10^{-3} mol mol⁻¹, respectively. The latter value is in good agreement with experiment, while the former underestimated significantly. Thus there must be stronger interaction between $[Pen]$ anion and CO rather than the normal physical interaction. Subsequently, we employed density functional calculations at the M06-2x/6-311G++(d,p) level^[19] to investigate the interaction of $[Pen]$ and $[Tf_2N]$ with CO. The calculated binding ΔH between $[Tf_2N]$ and CO is -11.8 kJ mol⁻¹ (Figure 2b), implying physisorption, which is supported by the large CO–anion separation of 3.573 Å. Similarly, if $[Pen]$ attracts CO by non-bonded interaction only, ΔH is -13.6 kJ mol⁻¹, which is also close to that of $[Tf_2N]$ and in consistent with the result from COSMOtherm prediction but far away from the experimental data. Thus, considering the supernucleophilicity of carbanions, we propose the formation of a product consisting of an aldehyde group between $[Pen]$ -CO, as shown in Figure 2a, where CO is

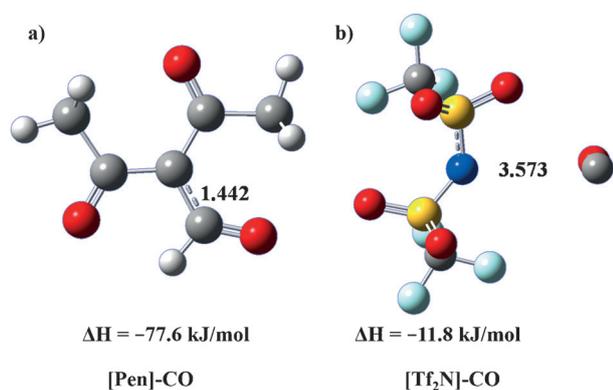


Figure 2. Optimized structures of a) [Pen]-CO and b) [Tf₂N]-CO. Anion-CO distances (in Å) and ΔH of interaction are also shown. C gray, O red, N blue, S yellow, H white, F blue.

inserted into the C-H bond at the carbanion site. The reaction energy between [Pen] and CO was calculated to be rather favorable, at $-77.6 \text{ kJ mol}^{-1}$, and the other three carbanion-functionalized ILs could also react with CO very favorably (Supporting Information, Figure S3). This carbanion-CO chemistry is very similar to the industrial synthesis of methyl formate, in which CH₃OH and CO are combined in the presence of a strong base (for example, potassium methoxide).^[20] Furthermore, we analyzed the atomic charges of the carbon atoms in the carbanion and the complex of the carbanion with CO by natural bond orbital (NBO) analysis (Supporting Information, Figure S4). After complexing with CO, the partial atomic charge on the C-site in [Pen] becomes less negative by $0.101 |e|$, which is close to the decreased positive charge on the carbon atom in CO ($0.095 |e|$). Hence, such strong chemical interactions made the capture of CO by carbanion-functionalized ILs more efficient than its capture by conventional ILs such as [Bmim][Tf₂N].

The C-site interaction between [Pen] and CO was verified by Fourier transform infrared (FTIR) and ¹³C NMR spectroscopy. In the FTIR spectra (Figure 3), two new character-

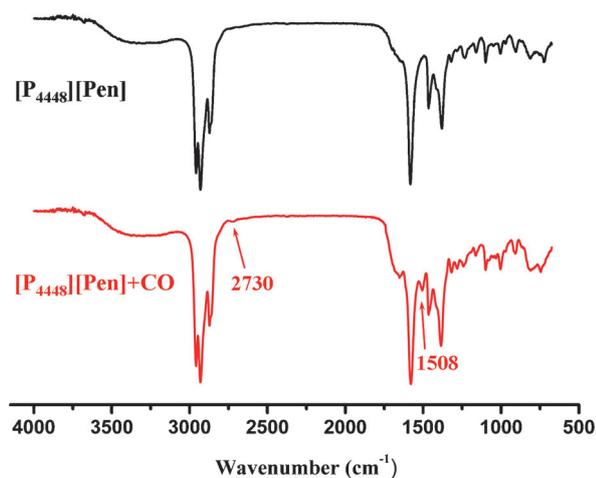


Figure 3. FTIR spectra of [P₄₄₄₈][Pen] before and after the capture of CO.

istic peaks were observed at 1508 cm^{-1} and 2730 cm^{-1} , which can be assigned to the stretching vibration of C-C and the stretching vibration of C-H in the [Pen]-CO interaction, respectively. However, the stretching vibration peak of the carbonyl group in captured CO was not clearly observed in Figure 3. Therefore, we then calculated the FTIR difference spectra of [P₄₄₄₈][Pen] and [P₄₄₄₈][Pen] + CO in the range of 1400 to 1800 cm^{-1} .^[21] As shown in Figure 4, the peak

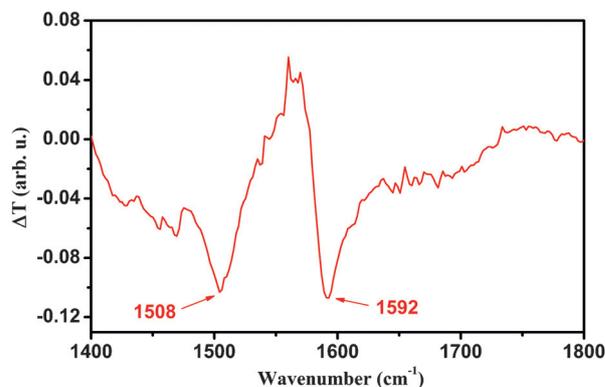


Figure 4. Comparison of FTIR difference spectra of [P₄₄₄₈][Pen] and [P₄₄₄₈][Pen] + CO in the range of 1400 to 1800 cm^{-1} .

appearing at 1592 cm^{-1} can be assigned to the stretching vibration of the carbonyl group in captured CO. Compared with free CO (2143 cm^{-1}),^[22] the vibrational frequency of captured CO was obviously red-shifted to 1592 cm^{-1} , demonstrating the strong chemical interaction of [Pen] with CO. Thus, on the basis of the FTIR spectra results, it is validated that CO was inserted into the C-H bond at the carbanion site and formed a product consisting of aldehyde group. Furthermore, it is seen in Figure 5 that a new signal at $\delta = 205.1 \text{ ppm}$ appeared in the ¹³C NMR after 0.046 mol CO uptake per mol IL, which is clearly attributable to the captured CO, further verifying the presence of aldehyde group in the [Pen]-CO chemical interaction. Meanwhile, the resonance of the carbonyl carbon atom in [Pen] showed a downfield shift

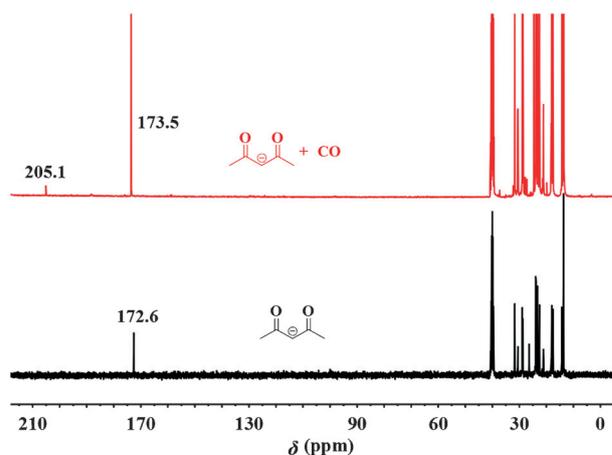
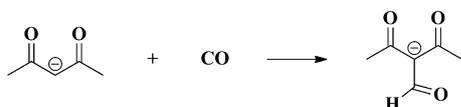


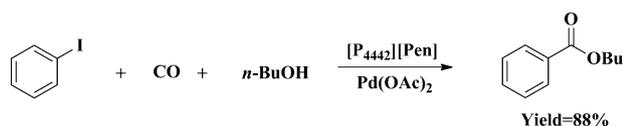
Figure 5. ¹³C NMR spectra of [P₄₄₄₈][Pen] before and after the capture of CO.

from $\delta = 172.6$ ppm to $\delta = 173.5$ ppm because of the change in the partial atomic charge on the C-site. Therefore, on the basis of observed results, a plausible mechanism of CO absorption by [Pen] can be proposed (Scheme 1), which exhibits a C-site chemical interaction between [Pen] and CO.



Scheme 1. The proposed mechanism of CO absorption by [P₄₄₄₈][Pen] through C-site interaction.

Multiple cycles of CO absorption/desorption in [P₄₄₄₈]-[Pen] at 25 °C were then investigated (Supporting Information, Figure S5). It was illustrated that the CO absorption capacity could remain steady during five cycles, showing that this CO capture process by [P₄₄₄₈][Pen] is highly reversible. Also, there was no obvious change in the characteristic bands of IR and NMR spectra between the fresh and reused [P₄₄₄₈][Pen] ILs (Supporting Information, Figures S6, S7), demonstrating that [P₄₄₄₈][Pen] is stable enough to be recycled. Furthermore, it is believed that captured CO could be more reactive than free CO and undergo subsequent conversion to produce valuable chemicals through the carbonylation reaction.^[23] Thus, the strategy for CO capture and utilization was examined for the catalytic synthesis of benzoate using iodobenzene, alcohol, and CO as raw materials (Scheme 2). We found that the captured CO in [P₄₄₄₂][Pen] could react with iodobenzene and *n*-butanol effortlessly to produce butyl benzoate with a yield of 88% under room temperature and atmospheric pressure. Alkoxy carbonylation reactions of captured CO with other alcohols were also conducted to obtain various benzoate products with good yields (Supporting Information, Table S3).



Scheme 2. The subsequent reaction of *n*-butanol with captured CO in [P₄₄₄₂][Pen] to synthesize *n*-butyl benzoate.

In summary, we developed a novel strategy for the capture of CO by carbanion-functionalized ILs through C-site interaction. It was illustrated that the carbanion in the ILs could interact with CO very efficiently and high CO absorption capacities (up to 0.046 mol CO per mol IL under ambient conditions) were thus achieved. Quantum mechanical calculations and spectroscopic investigations show that the C-site chemical interaction takes place between the carbanion and CO, and the CO absorption enthalpy is as high as -77.6 kJ mol⁻¹. Furthermore, the captured CO in carbanion-functionalized ILs could be utilized for the synthesis of benzoates at high yields under mild conditions. We believe that this highly efficient and reversible process using carban-

ion-based ILs has great potential for CO separation and conversion.

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Conflict of interest

The authors declare no conflict of interest.

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