Carbon Dioxide Capture by Superbase-Derived Protic Ionic Liquids**

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Emissions of carbon dioxide have received worldwide attention because of the environmental and economic threats posed by possible climate change. Accordingly, the development of sorbent materials that efficiently, reversibly, and economically capture CO_2 from burning of fossil fuels is essential in realizing practical carbon capture and sequestration. The traditional capture of CO_2 in industry is through a chemical adsorption by an aqueous solution of monoethanol-amine, which has some advantages, such as high reactivity, low cost, and a gravimetric capacity of about 7%. However, the use of monoethanolamine and water has the serious inherent drawbacks, including the solvent loss, corrosion, and high energy demand for regeneration.[1]

Ionic liquids (ILs) offer a new opportunity for developing novel capture systems that are capable of reversibly capturing CO_2 with a high capacity,[2] because of their unique properties, such as negligible vapor pressures, high thermal stabilities, excellent CO_2 solubilities, and tunable properties.[3] Davis and co-workers[4] reported the first example of the chemisorption of CO_2 that employs an amino-functionalized task-specific ionic liquid. Their results show that 0.5 mol CO_2 can be captured per mol of IL with a gravimetric capacity of about 7% for 3 h under ambient pressure. Subsequently, a number of research groups[5] have studied other amino-functionalized ILs for carbon capture, including functionalized sulfones and amino acid anions with imidazolium or phosphonium cations. Although these investigations have made important improvements, the maximum gravimetric absorption capacity is still limited to about 9%, and furthermore the sorption kinetic is very slow. This low capture efficiency associated with the capture system based on amino-functionalized ILs can be attributed to two factors: 1) the requirement of two amines to capture one CO_2, and 2) formation of solid or highly viscous gel products. More recently, Brennecke, Schneider, and their co-workers[6] reported new IL capture systems based on amino acid anions, which can capture about 0.9 mol CO_2 per mol of IL with a gravimetric capacity of about 6%. However, this gravimetric capacity is still low, and their carbon-capture kinetics are also expected to be slow because these IL systems are extremely viscous. Alternative IL strategies based on totally different classes of ILs that are able to achieve rapid, reversible CO_2 capture at higher sorption capacities are highly sought. This research need prompted us to investigate protic ionic liquids (PILs) for carbon capture.

Herein we describe an efficient carbon-capture system based on a diverse class of anion-functionalized PILs. The essence of our strategy to derive CO_2-reactive PILs is to use a very strong base (superbase or proton sponge) to directly deprotonate weak proton donors, such as fluorinated alcohols, imidazoles, pyrrolidinones, or phenols. We show that these superbase-derived PILs with low melting points are capable of reversibly capturing CO_2 with an extremely high capacity (more than 1 mol per mol IL). Furthermore, we also show that both polarities and basicities of these PILs can be easily tuned using CO_2 and N_2 as a switch, which opens up their potential applications in separation and catalysis.

PILs can be easily prepared by combining a Brønsted acid with a Brønsted base.[7] Although a number of PILs have been developed using a wide variety of anions, such as tetrafluoroborate, choride, carboxylate, and hexafluorophosphate, CO_2 capture by PILs has not been reported because of the low reactivity of the conventional PILs toward CO_2. Our approach was to design novel PILs from strong organic bases and a wide variety of weak proton donors by making use of their tunable chemical reactivity toward CO_2. Superbases, which are neutral organic bases with proton affinities so high that their protonated conjugate acids (BH^+) cannot be deprotonated by a hydroxide ion,[8] play a key role as strong proton acceptors, thereby providing a thermodynamic driving force for formation of reactive PILs. We have recently demonstrated that the PILs derived from organic superbases behave like aprotic ILs with considerably reduced vapor pressures.[8b] Scheme 1 shows the structures of two superbases and six weak proton donors used in our current investigation.

These novel PILs were synthesized in high yield (> 98%) by neutralization of superbases (MTBD or P_2-Et) with partially fluorinated alcohols (TFE, TFPA, or HFPD), imidazole (Im), pyrrolidone (Pyrr), or phenol (PhOH), where the pK_a values in DMSO of the proton donors are in the range of 18–24 (see Scheme 1).[9] The formation of these superbase-derived PILs was shown by both NMR spectroscopy and ion conductivity measurements. For example, a broad band that appeared at 4.07 ppm in the ^{1}H NMR

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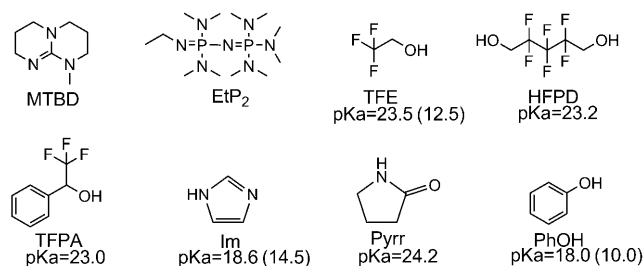
Scheme 1. Selected superbases, fluorinated alcohols, imidazole (Im), pyrrolidone (Pyrr), and phenol used as building blocks of superbase-derived PILs. pK_a values in DMSO (values given in brackets are in H$_2$O).

spectrum of a neat TFE disappeared in a spectrum of [MTBDH$^+$][TFE$^-$], suggesting the absence of free alcohol OH in [MTBDH$^+$][TFE$^-$]. Furthermore, the ^{1}H NMR peaks of [MTBDH$^+$][Im$^-$] agree well with those of [Im$^-$] in aprotic ILs [P$_{66614}$$^+$][Im$^-$] (see Supporting Information, Scheme S1, for its structure) and are very different with those of imidazole, clearly indicating the formation of ILs (Supporting Information, Table S1). The ionic conductivity of [MTBDH$^+$][TFE$^-$] and [MTBDH$^+$][Im$^-$] increased to 1.082 and 1.139 mS cm^{-1}, respectively, also suggesting that MTBD was the protonated species (Supporting Information, Table S2). All ten newly synthesized PILs showed low melting point and moderate ion conductivity. Coulombic interactions were critical to improving the thermal stability of PILs. For example, the decomposition temperature increased more than 80°C when the mixture of P$_2$-Et and ethanol was replaced by [(P$_2$-Et)H$^+$][TFE$^-$]. Clearly, the thermal stability of PILs could be significantly influenced by the combination of different superbases and proton donors.

The effect of different superbase-derived PILs on the capture of CO$_2$ was investigated (Table 1). Most of these PILs showed excellent CO$_2$ capture under atmospheric pressure. For example, a molar ratio of CO$_2$ to PILs of 1.13 could be achieved when [MTBDH$^+$][TFE$^-$] was used; [MTBDH$^+$]$_2$-[HFPD^{2-}] showed a higher CO$_2$ capacity of more than 2.0 mol per mol PIL because of the presence of two CO$_2$-reactive groups. For these PIL capture systems, a gravimetric capacity of more than 16% can be achieved, which is significantly

superior to the amount of CO$_2$ captured by traditional ILs (Supporting Information, Table S3).

The effect of different proton donors on the absorption of CO$_2$ is significant. It was clear that the absorption was almost complete within 5 min for [MTBDH$^+$][TFE$^-$], whereas that for [MTBDH$^+$][Im$^-$] it was about 30 min (Figure 1). In
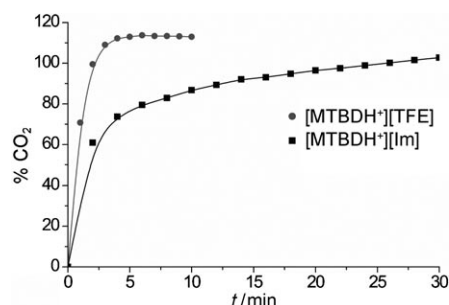
**Figure 1.** CO$_2$ absorption by typical superbase-derived PILs.

contrast, the chemically unreactive PILs, such as [MTBDH$^+$]-[Tf$_2$N$^-$], had a capacity of only 0.02 mol per mole PILs at atmospheric pressure. This rapid absorption, in the range of few minutes to tens of minutes, is related to their low viscosities. For example, the viscosity of [MTBDH$^+$][TFE$^-$] is 8.63 cP, and that of [MTBDH$^+$][Im$^-$] is 31.85 cP; these values are distinctly lower than that of amino-functionalized ILs.[5c,d]

During the capture of CO$_2$ observed in this study, CO$_2$ reacted with PILs to form a liquid carbonate, carbamate or phenolate salt. For example, the formation of carbamate is evident from NMR and IR spectra of [MTBDH$^+$][Im$^-$] and the corresponding carbamate [MTBDH$^+$][ImC$^-$]. After CO$_2$ bubbling, a new band for [MTBDH$^+$][ImC$^-$] at 1696.4 cm^{-1} produced, which can be assigned to carbamate stretches (Supporting Information, Figure S1). Based on previous reports[10] and the observed reaction product, the CO$_2$ absorption by our PILs can be straightforwardly described (Scheme 2). We computed the gas-phase energetics according to the reactions in Scheme 2 at the B3LYP/TZVP level of theory and obtained changes of energy at −116.8, −85.2, and −41.7 kJ mol^{-1} for TFE$^-$, Im$^-$, and PhO$^-$, respectively. This energetic trend indicates that the relatively weak driving force

Table 1: CO$_2$ absorption by different superbase-derived PILs.[a]

| Ionic liquids	Time [min]	CO$_2$ absorption[b]	State
[MTBDH$^+$][TFE$^-$]	10	1.13	liquid
[(P$_2$-Et)H$^+$][TFE$^-$]	10	1.04	liquid
[MTBDH$^+$][TFPA$^-$]	60	0.93	liquid
[MTBDH$^+$]$_2$[HFPD^{2-}]	60	2.04	gel
[MTBDH$^+$][Im$^-$]	30	1.03	liquid
[(P$_2$-Et)H$^+$][Im$^-$]	10	0.96	liquid
[MTBDH$^+$][Pyrr$^-$]	30	0.92	liquid
[(P$_2$-Et)H$^+$][Pyrr$^-$]	30	0.86	liquid
[MTBDH$^+$][PhO$^-$]	300	0.49	gel
[(P$_2$-Et)H$^+$][PhO$^-$]	300	0.45	gel
[MTBDH$^+$][Tf$_2$N$^-$]	60	0.02	liquid

[a] The absorption was carried out at 23°C. [b] Mol CO$_2$ per mol PILs.
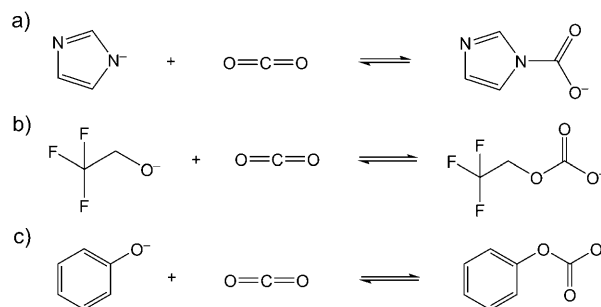
Scheme 2. CO$_2$ absorption by the anions of superbase-derived protic ionic liquids.

for reaction of CO_2 with PhO^- leads to a smaller CO_2 absorption capacity.

The stability of the CO_2 captured by these PILs was studied by thermogravimetric analysis (TGA), as shown in the Supporting Information, Figure S2. When the temperature reached 110°C, the weight losses for $[MTBDH^+][Im^-]$ and $[MTBDH^+][ImC^-]$ are 3% and 17%, respectively, indicating that the release of CO_2 was almost complete. The captured CO_2 was easy to strip out by heating or bubbling N_2 through the PILs. For example, the release of CO_2 by bubbling N_2 at 80°C for $[MTBDH^+][ImC^-]$ was fast, and almost complete in 10 min. The processes of CO_2 absorption by PILs are completely reversible, and the PILs show a slight loss in capacity after multiple absorption–desorption cycles (Figure 2). Thus, these PILs are good candidates as switchable solvents for the chemical reaction and separation.
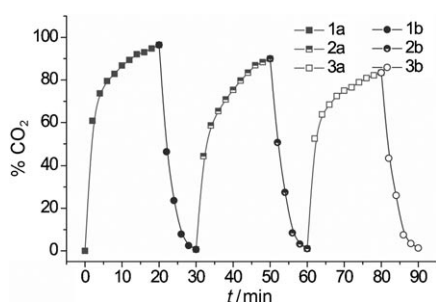
Figure 2. Three consecutive cycles of CO_2 absorption (1 a, 2 a, and 3 a, at 23°C) and release (1 b, 2 b, and 3 b, at 80°C under N_2) by $[MTBDH^+][Im^-]$.

Switchable solvents formed by mixing an amidine with an alcohol,[10] alkylamine,[10] or amino alcohol[11] have been reported. However, one key drawback associated with these switchable solvents is the volatile nature of their molecular constituents. The development of ILs with switchable chemical properties should be able to mitigate the evaporative loss of current switchable solvents. The study on switchable solvents based solely on ILs using CO_2 and N_2 as the switch is limited. This deficiency forms the rationale for us to explore ILs with switchable properties.

The switchable polarity of our superbase-derived PILs was investigated using $[MTBDH^+][TFPA^-]$ and $[MTBDH^+]$-$[Im^-]$ as examples and Nile Red as a solvatochromic probe. As shown in Table 2, $[MTBDH^+][HFPA^-]$ showed a λ_{max} increase of about 9 nm for the optical spectrum of Nile Red upon uptake of CO_2 to form the carbonate salt $[MTBDH^+]$-$[TFPAC^-]$. On the other hand, the formation of $[MTBDH^+]$-$[ImC^-]$ by reaction of $[MTBDH^+][Im^-]$ with CO_2 exhibited a λ_{max} increase of as large as 16 nm.[12] Accordingly, the polarity change of $[MTBDH^+][Im^-]$ upon uptake of CO_2 is more significant than that of $[MTBDH^+][TFPA^-]$. These results further underscore an important point that the degree of the polarity change associated with our PILs can be finely tuned through use of different proton donors.

Figure 3 demonstrates a specific application of this switchable polarity associated with our PILs in controlling solubil-

Table 2: Polarities of selected solvents and PILs as indicated by solvatochromic dyes.[a]

Solvents or PILs	λ_{max} (Nile Red) [nm][b]
DMF	541.2
$[MTBDH^+][TFPA^-]$	543[c]
Methanol	549.6
$[Bmim^+][BF_4^-]$	550.8[d]
$[MTBDH^+][Im^-]$	551[c]
$[MTBDH^+][TFPAC^-]$	552[c]
Ethylene glycol	565.2
$[MTBDH^+][ImC^-]$	567[c]

[a] Data were determined using Nile Red at 23°C. [b] Data as published in Ref. [12] except as indicated. [c] This work. [d] Ref. [13].
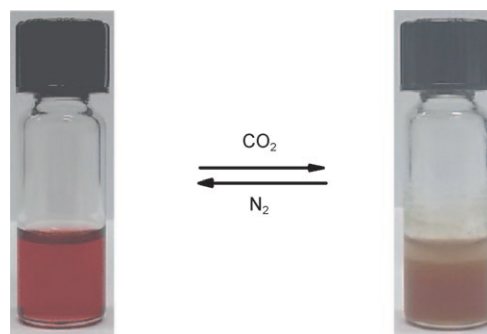
Figure 3. Photographs of the switchable polarity and basicity of $[MTBDH^+][Im^-]$ by CO_2 and N_2 as the triggers. The solutions were colored with a basicity indicator (2,4-dinitroaniline). Left: the miscibility and basicity of 2:1 (v/v) mixture of $[MTBDH^+][Im^-]$ and fatty acid methyl esters in the presence of 2,4-dinitroaniline under N_2. Right: the immiscibility and neutrality of 2:1 (v/v) mixture of $[MTBDH^+][ImC^-]$ and fatty acid methyl esters in the presence of 2,4-dinitroaniline under CO_2.

ities of organic species in ILs. Fatty acid methyl ester is miscible with $[MTBDH^+][Im^-]$, whereas two phases form upon uptake of CO_2. This phase separation was triggered by the formation of the more polar $[MTBDH^+][ImC^-]$. The switchable basicity of our superbase-derived PILs was investigated using $[MTBDH^+][Im^-]$ as an example and 2,4-dinitroaniline as a basicity indicator. As seen in Figure 3, $[MTBDH^+][Im^-]$ is strongly basic and can readily change the color of 2,4-dinitroaniline from yellow to purple, whereas $[MTBDH^+][ImC^-]$ derived from uptake of CO_2 is neutral.[14] The switchabilities associated with our PILs in both polarity and basicity can be exploited in catalyzing the transesterification of soybean oil to produce biodiesel. These switchable PILs provide an ideal reaction medium for efficient recycling of base catalysts and potential simplification of product separation (Supporting Information, Figure S3).

In summary, the properties of superbase-based PILs, which were prepared by the proton-transfer reaction between an organic superbase and a partially fluorinated alcohol, imidazole, pyrrolinone, or phenol, are easy to tune because of the diversity of organic superbases and weak proton donors that are available. We have shown that these anion-functionalized PILs are excellent systems for the rapid and reversible capture of CO_2 with equimolar CO_2 absorption by the anions

of PILs. Furthermore, to the best of our knowledge, these tunable anion-functionalized PILs are the first switchable PILs, which can be used in organic reactions to simplify separation processes. The method developed in this study opens a way to prepare novel switchable ionic liquids as well as to develop a potential method for the capture of CO_2 by totally different anion-functionalized ILs in industry.

Experimental Section

The superbase-derived PILs were synthesized according to methods detailed in the literature.[9] These PILs samples were dried in vacuum at 60°C for 24 h to reduce possible traces of water. The water contents of these PILs were measured by Karl Fischer titration and were found to be less than 0.1%. ^1H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 NMR spectrometer with tetramethylsilane as the standard. FTIR data were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer at room temperature. Viscosity was measured on a Grabner Minivis micro-viscometer. Glass-transition and decomposition temperatures were measured with a TGA 2950 and DSC Q 100 meter, respectively.

Absorption of CO_2: In a typical run, CO_2 at atmospheric pressure was bubbled through about 1.0 g PILs 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 an oil bath 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. The PILs were regenerated by heating or bubbling nitrogen through PILs.

Computations: Turbomole V5.10 was used for parallel density functional theory calculations[15] at the B3LYP level. The def2-TZVP orbital and auxiliary basis sets[16] were used for all atoms for structural optimization. Convergence criterion for self-consistent-field energy was 10^{-6} a.u.; convergence criterion for forces was 10^{-3} a.u.

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