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Supported Absorption of CO_2 by Tetrabutylphosphonium Amino Acid Ionic Liquids

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Abstract: A new type of "task specific ionic liquid", tetrabutylphosphonium amino acid $[P(C_4)_4][AA]$, was synthesized by the reaction of tetrabutylphosphonium hydroxide $[P(C_4)_4][OH]$ with amino acids, including glycine, L-alanine, L-β-alanine, L-serine, and L-lysine. The liquids produced were characterized by NMR, IR spectroscopies, and elemental analysis, and their thermal decomposition temperature, glass transition temperature, electrical conductivity, density, and viscosity were recorded in detail. The $[P(C_4)_4][AA]$ supported on porous silica gel effected fast and reversible CO_2 absorption when compared with bubbling CO_2 into the bulk of the ionic liquid. No changes in absorption capacity and kinetics were found after four cycles of absorption/desorption. The CO_2 absorption capacity at equilibrium was 50 mol % of the ionic liquids. In the presence of water (1 wt %), the ionic liquids could absorb equimolar amounts of CO_2. The CO_2 absorption mechanisms of the ionic liquids with and without water were different.

Keywords: absorption · amino acids · carbon dioxide fixation · ionic liquids · SiO_2

Introduction

In view of sustainable development and green chemistry, investigation of efficient methods for capturing CO_2 from flue gas, produced by combustion of fossil fuels in which CO_2 concentration varies from 3 to 14 %, is significant as it concerns both the conversion of CO_2 as C1 feedstocks into industrially useful compounds and environmental issues, such as the reduction of the greenhouse effect. During the past two decades, the chemical fixation and conversion of CO_2 have been attracting increasing interest. One of the most widely utilized processes for CO_2 recovery is chemical absorption of CO_2 by aqueous amines to form carbamates.[1–6] However, this process has many disadvantages: 1) The uptake of water into the gas stream requires an additional drying process. 2) The loss of volatile amines and the evaporation of water make the process energy and cost intensive. 3) The desorption of CO_2 by heating causes serious corrosion and other operational difficulties.

Ionic liquids are novel media composed of ions. The negligible volatility of these liquids results in a noncontaminated target gas, making them especially attractive for the absorption of gases. For example, Brennecke and co-workers studied CO_2 solubility in imidazolium-based ionic liquids[7–9] under high pressures. The high CO_2 solubility of ionic liquids when compared to methane provides them with the potential to be utilized in the separation of CO_2 from natural gas. The interaction between CO_2 and imidazolium-type ionic liquids, attributed to the activity of H-2 in the imidazolium ring, accounts for its higher solubility of CO_2.[10–11] Due to the unique "self-designable" character of ionic liquids, alkaline groups, such as $-NH_2$, can be attached to ionic liquids to give a zwitterion after absorption of CO_2.[12] This kind of "task specific ionic liquid" can help to overcome the limitations of aqueous amine. As another kind of useful adsorbent, the amidine structure was applied in the reversible absorption of CO_2.[13] The absorption of CO_2 can transform the substances that contain an amine group from molecular compounds to inner zwitterions.

Amino acids have been used as both anions and cations in ionic liquids. Shan and co-workers[14] reacted amino acids (AA) with equimolar amounts of H_2SO_4 and obtained $[AAH][HSO_4]$-type ionic liquids. If the amount of H_2SO_4

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was decreased by a half, $[AAH]_2[SO_4]$-type ionic liquids were obtained. This type of ionic liquid can not effectively absorb CO_2. Recently, ionic liquids with amino acids as anions were synthesized by neutralization between [emim][OH] and amino acids.[16] Optimistically, the H^+ in the new ionic liquid have been removed, resulting in an active -NH_2 group, which would be promising for CO_2 absorption.

Phosphonium $[PR^1R^2R^3R^4]^+$ is another type of cation used for room temperature ionic liquids (RTILs).[17–21] Phosphonium is more stable in a basic environment at high temperatures than nitrogen-containing cations, such as imidazolium.[22] In this work, a series of phosphonium ionic liquids with amino acids as anions $[P(C_4)_4][AA]$ were synthesized. The ionic liquids were further supported on porous silica gel and their CO_2 absorption was investigated. The rates of CO_2 absorption of the supported ionic liquids were much higher than those of the viscous ionic liquids themselves.

Results and Discussion

The glass transition temperature and melting point are important physical properties of ionic liquids, and are determined by structural features of the anion and cation, such as hydrogen bonding, dipoles, and the distance between them. From Table 1, it can be seen that there is an order of $T_{g,[P(C4)4][Ser]} > T_{g,[P(C4)4][Lys]} > T_{g,[P(C4)4][Gly]} > T_{g,[P(C4)4][Ala]} > T_{g,[P(C4)4][\beta\text{-}Ala]}$. It is the distance between the anion and cation that plays the most important role in the order of $[P(C_4)_4][Gly] > [P(C_4)_4][Ala] > [P(C_4)_4][\beta\text{-}Ala]$. A shorter distance between the anion and cation leads to a higher attracting ability and a higher glass transition temperature. In the structure of $[P(C_4)_4][Ser]$, there is one additional OH compared to $[P(C_4)_4][Ala]$; therefore, it can be surmised that the additional hydrogen bond contributed to its higher glass transition temperature. This is in accord with $T_{g,[emim][Ser]} > T_{g,[emim][Ala]}$, reported earlier.[16] As for $[P(C_4)_4][Lys]$, there are two -NH_2 groups in its anion structure. Although $[Lys]^-$ is a larger anion compared to other amino acid anions, the hydrogen bond plays an important role in determining its melting point. The fact that all the glass transition temperatures of the phosphonium amino acids are lower than the [emim][AA]-type maybe due to the larger volume of the phosphonium cations.

From Table 1 it can be seen that the density of phosphonium amino acids follows a similar order to the glass transition temperature, that is, $\rho_{[P(C4)4][Ser]} > \rho_{[P(C4)4][Lys]} > \rho_{[P(C4)4][Gly]} > \rho_{[P(C4)4][\beta\text{-}Ala]} > \rho_{[P(C4)4][Ala]}$, suggesting that the micro interaction is determined by the same mechanism. The viscosity of the ionic liquids is strongly affected by the side alkyl chains of the amino acids anions. The anions with more complex structures, such as $[Lys]^-$ and $[Ser]^-$, have a greater viscosity. The electric conductivity is determined by viscosity. The larger the viscosity, the smaller the electric conductivity.

The absorption of CO_2 by $[P(C_4)_4][\beta\text{-}Ala]\text{-}SiO_2$, $[P(C_4)_4][Gly]\text{-}SiO_2$, and $[P(C_4)_4][Ala]\text{-}SiO_2$ were investigated and the results are presented in Figure 1. This data suggests that the absorption equilibriums can all be reached in less than 100 min. The absorbed CO_2 was released in a vacuum at room temperature over several hours. Due to the large surface area of silica gel (approximately $500\,m^2g^{-1}$), the absorption rate of CO_2 was significantly increased. Four cycles of absorption/desorption were repeated and no changes in the absorption capacity or the rates were observed. According to the mechanism proposed by James,[12] one mol of NH_2- can absorb half one mol of CO_2. In Figure 1, the greater than one half mol absorption of CO_2 may be a result of physical absorption. We also observed that the mass of the sample of $[P(C_4)_4][AA]\text{-}SiO_2$ saturated by CO_2 slightly but continuously decreased at room temperature and atmospheric pressure.

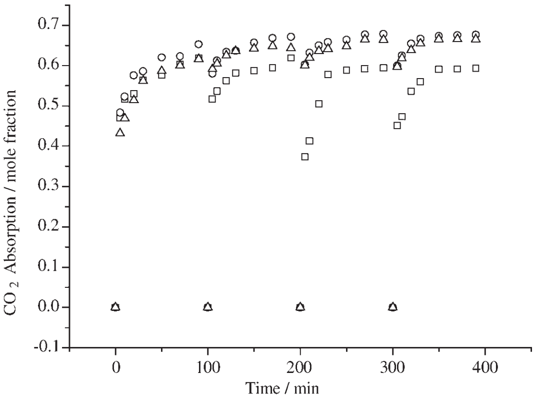


Figure 1. Cycles of CO_2 absorption of $[P(C_4)_4][AA]\text{-}SiO_2$. □ = $[P(C_4)_4][Gly]\text{-}SiO_2$, ○ = $[P(C_4)_4][Ala]\text{-}SiO_2$, and △ = $[P(C_4)_4][\beta\text{-}Ala]\text{-}SiO_2$.

The IR spectra of $[P(C_4)_4][\beta\text{-}Ala]$, $[P(C_4)_4][Gly]$, and $[P(C_4)_4][Ala]$ contain only one peak at approximately $\tilde{\nu} = 1600\,cm^{-1}$, corresponding to the CO_2^- group in the AA anion structure (Figure 2). Upon exposure to CO_2, a new peak appeared at approximately $\tilde{\nu} = 1660\,cm^{-1}$, corresponding to the formation of a new CO_2H group (Figure 3). The -NH- absorption peak was overlapped with that of SiO_2 at $\tilde{\nu} = 3300\,cm^{-1}$. Thus, pure $[P(C_4)_4][\beta\text{-}Ala]$ was characterized by IR before and after absorption of CO_2 to increase the clarity of the peak change from NH_2- to -NH-. In addition, there was a new peak at $\tilde{\nu} = 1697\,cm^{-1}$

Table 1. Properties of the phosphonium amino acid ionic liquids.

	$[P(C_4)_4][Lys]$	$[P(C_4)_4][Ser]$	$[P(C_4)_4][Gly]$	$[P(C_4)_4][Ala]$	$[P(C_4)_4][\beta\text{-}Ala]$
T_g [K]	208.01	211.70	198.33	197.66	196.14
$T_{d\text{-}N2}$ [K]	498	493	473	475	476
ρ [$g\,cm^{-3}$]	0.9730	0.9910	0.9630	0.9500	0.9590
η [mPa s]	744.71	734.20	232.85	226.69	244.71
σ [$10^{-4}\,s\,cm^{-1}$]	1.04	1.68	4.85	4.18	4.04

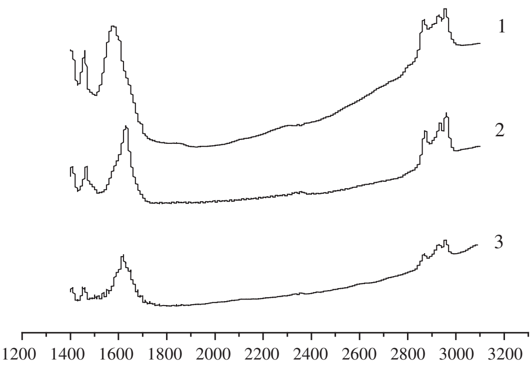


Figure 2. IR spectrum of ionic liquids supported on porous SiO_2 before absorption of CO_2. 1) $[P(C_4)_4][Ala]$-SiO_2, 2) $[P(C_4)_4][Gly]$-SiO_2, and 3) $[P(C_4)_4][\beta$-$Ala]$-SiO_2.

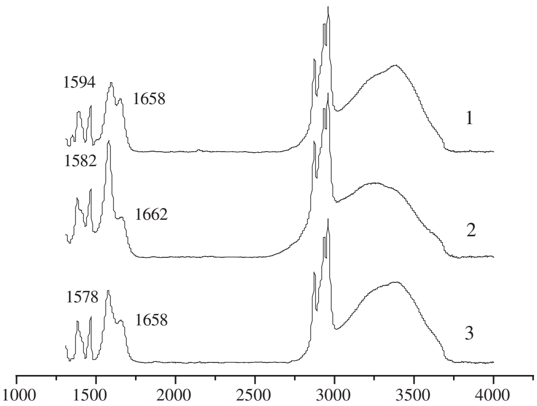


Figure 3. IR spectrum of ionic liquids supported on porous SiO_2 after absorption of CO_2. 1) $[P(C_4)_4][Ala]$-SiO_2, 2) $[P(C_4)_4][Gly]$-SiO_2, and 3) $[P(C_4)_4][\beta$-$Ala]$-SiO_2.

(Figure 4) and a N–H stretch at $\tilde{\nu}=3234\,cm^{-1}$ after absorption of CO_2, but the peak at $\tilde{\nu}=3359\,cm^{-1}$ disappeared, indicating that this N–H bond may react with a CO_2 molecule.

In addition, as the resonance of CO_2^- in the amino acid anion of the above three ionic liquids is at approximately $\delta=157$ ppm in the ^{13}C NMR spectrum (400 MHz, DMSO), a new resonance for CO_2H does not appear. However, the peak area at $\delta=157$ ppm increases in size after absorption of CO_2.

Absorption of CO_2 by using these ionic liquids with a small amount of water (1 %, mass fraction) was also investigated. The viscosity was low and the liquid was stirred with greater ease at the beginning of the absorption, but the viscosity gradually increased and finally became very high and the transparent liquid became cloudy. In Figure 5, it can be seen that $[P(C_4)_4][Gly]$ with water can absorb almost 13 wt % of CO_2, which is close to the theoretical absorption capacity (13.52 %, based on a 1:1 mol ratio between the ionic liquid and CO_2), in 200 mins. If more water is added, the ionic liquid saturated with CO_2 separates into a solid phase and a liquid phase. The residue liquid finally obtained, after drying in vacuum at 353.15 K for 12 h, is more viscous than pure $[P(C_4)_4][Gly]$. There was even trace of a white powder at the bottom of the glass container. As can be seen in Figure 6, the IR spectrum of CO_2 saturated

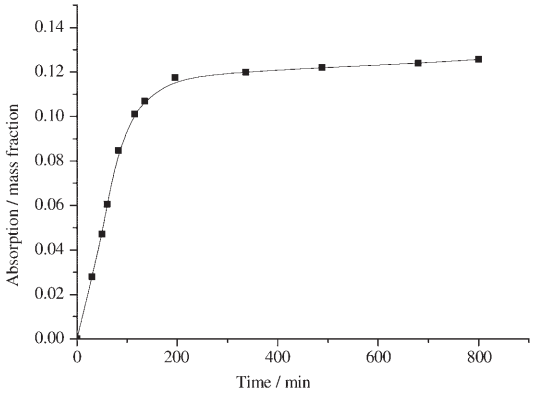


Figure 5. CO_2 absorption of $[P(C_4)_4][Gly]$ with water (1 % mass fraction).

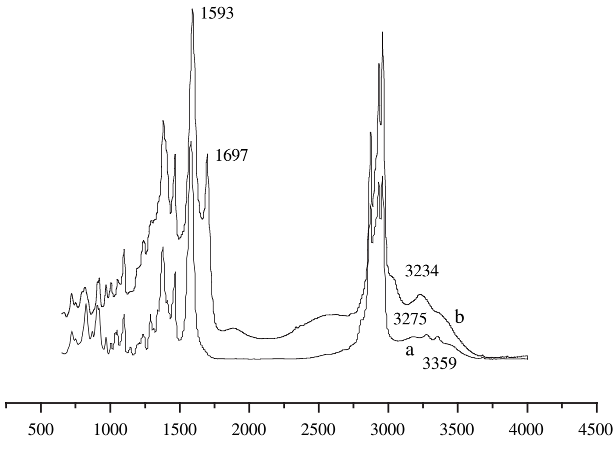


Figure 4. IR spectra of $[P(C_4)_4][\beta$-$Ala]$ a) before and b) after absorption of CO_2.

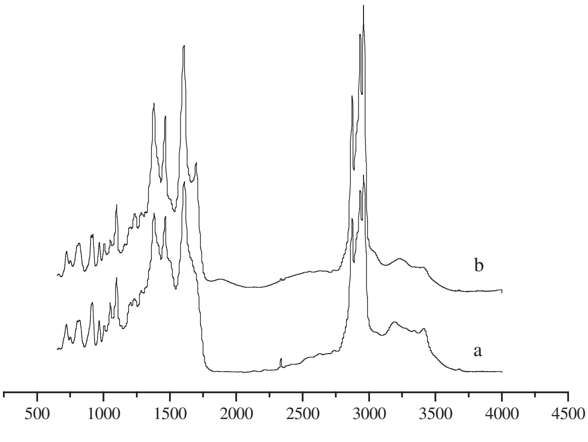
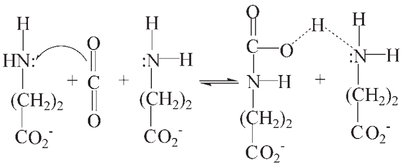


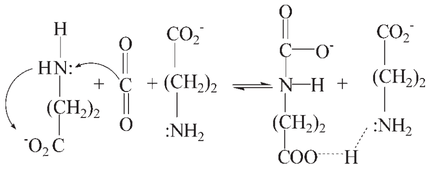
Figure 6. IR spectrum of $[P(C_4)_4][Gly]$ after absorption of CO_2 a) with and b) without water.

$[P(C_4)_4][Gly]$ (with small amount of water) does not contain a peak at approximately 1690 cm^{-1}, suggesting that the absorption mechanism is different. In the ^{13}C NMR (400 MHz, DMSO) spectrum of $[P(C_4)_4][Gly]$ (with small amount of water) after absorption, there is a new resonance at $\delta =$ 175.422 (markedly peaked, greater area) and 171.468 ppm (small peak and area), representing $[HCO_3]^-$ and $[CO_3]^{2-}$, respectively, in addition to the resonance at $\delta =$ 157.588 ppm, corresponding to the original CO_2^- group in the amino acid anion.

As for the micro absorption mechanism, it may be complicated with or without water. Possible mechanisms for the absorption processes for which the ionic liquids do not contain water are shown in Schemes 1 and 2. In the first mechanism (Scheme 1), CO_2 attacks the free electron pair of the N atom on the -NH_2 group and forms a hydrogen bond O–H···N with the NH_2 group of another AA^-. A second possibility is that one of the H atoms in the NH_2 group is taken as a proton by the original CO_2^- to form a new CO_2H group (Scheme 2).



Scheme 1. First proposed absorption mechanism between $[P(C_4)_4][\beta\text{-Ala}]$ and CO_2.



Scheme 2. Second proposed absorption mechanism between $[P(C_4)_4][\beta\text{-Ala}]$ and CO_2.

A different mechanism is proposed for absorption processes that used ionic liquids containing a small amount of water (Scheme 3, this mechanism is the same as that for the absorption of CO_2 by aqueous amines). When this mixture, saturated with CO_2, is heated in vacuum, another reaction may occur (Scheme 4) in which $2[HCO_3]^-$ decomposes into $1H_2O$, $1CO_2$, and $[CO_3]^{2-}$, possibly forming $[P(C_4)_4]_2[CO_3]$.

$$[H_2N\text{-}CH_2\text{-}COO^-] + [P(C_4)_4]^+ + CO_2 + H_2O \rightarrow {}^+H_3NCH_2COO^- + [HCO_3]^- + [P(C_4)_4]^+$$

Scheme 3. Proposed absorption mechanism between $[P(C_4)_4][Gly]\text{-}H_2O$ and CO_2.

$$2[HCO_3]^-[P(C_4)_4]^+ \xrightarrow[\text{vacuum}]{\text{heating}} H_2O + CO_2 + [P(C_4)_4]^+_2[CO_3]^{2-}$$

Scheme 4. Proposed CO_2-desorption mechanism of $[HCO_3][P(C_4)_4]$.

Conclusion

$[P(C_4)_4][Ser]$, $[P(C_4)_4][Gly]$, $[P(C_4)_4][Ala]$, $[P(C_4)_4][\beta\text{-Ala}]$, and $[P(C_4)_4][Lys]$ were synthesized from $[P(C_4)_4][Br]$ and the corresponding amino acids by the use of anion exchange resin and neutralization. The CO_2 absorption of the ionic liquids supported on porous SiO_2 is fast and reversible with a capacity of $1CO_2/2$ $[P(C_4)_4][AA]$. The proposed mechanism suggests that a CO_2 molecule attacks the N atom of the NH_2 group and results in -$NHCO_2^-$ formation, during which one H atom leaves and forms a new CO_2H with the $NHCO_2^-$ or the original CO_2^- in the amino acid anion. The CO_2H group formed a hydrogen bond with the electron pair of NH_2 in another amino acid anion for which the N atom was inert to reaction with CO_2. In the presence of water (1%, mass), the $[P(C_4)_4][AA]$ can absorb an equimolar amount of CO_2 by a different mechanism.

Experimental Section

Glycine, L-serine, L-alanine, L-β-alanine, L-lysine, ethanol, and anion exchange resin −711(Cl) were of analytical grade and were produced by the Beijing Chemical Reagent Plant. Tetrabutylphosphonium bromide solution was provided by CYTEC CANADA INC. All aqueous solutions were prepared with deionized water. Anion exchange resin-711(Cl) was pretreated by hydrochloric acid (2 M) before use. Then, this resin was transformed from Cl-type into OH-type by passing NaOH solution (5 M, 10 $mL\,min^{-1}$) through the resin column ($l=100$ cm, $r=3$ cm) until Cl^- could not be detected with $AgNO_3/HNO_3$ solution. As the anion exchange resin (OH) is not stable at temperatures higher than 313.15 K, NaOH solution must be used after it is cooled. Excessive NaOH solution was washed by deionic water. Tetrabutylphosphoium bromide solution was diluted (2 M) and then transformed into tetrabutylphosphoium hydroxy solution, which was concentrated through rotation evaporation at 323.15 K (pure tetrabutylphosphoium hydroxy is not stable and its color may change from colorless to black after several days). The concentration of OH^- was determined by titration with HCl solution. Then, the tetrabutylphosphoium hydroxy solution reacted with a slight excess of amino acid (without further purification) solution through neutralization at room temperature for 24 h. After being dried at 323.15 K under vacuum, ethanol was added to the residue and the solution was agitated completely so that the excess amino acids were deposited. After filtration, the ethanol was removed by evaporation. The liquid product obtained was dried at 373.15 K under vacuum for 2 d. ^1H NMR, ^{13}C, ^{31}P, and IR spectroscopies were performed to determine the structure of the phosphonium amino acids. Due to the activity of the hydrogen atoms in -NH_2, its peak could not be easily observed by ^1H NMR spectroscopy; however, IR spectroscopic data indicated the existence of -NH_2. Further elemental analysis of C, H, N, and P (Elementar Vario EL, Germany) indicated that the elemental ratio of phosphonium amino acids agrees well with their predicted structure. Differential Scanning Calorimetry (DSC 2010, Thermal Analysis, USA) and TG-DTA (Netzsch STA 449, Germany) were performed to determine the melting points (glass transition temperature) and the decomposition temperature.

$[P(C_4)_4][Gly]$: ^1H NMR (400 MHz, DMSO, 25 °C, TMS): $\delta = 0.92$ (t, $J=$ 8.0 Hz, 12H; CH_3), 1.34–1.52 (m, 16H; $(CH_2)_2$), 2.13–2.23 (m, 8H; P-CH_2), 2.64 ppm (s, 2H; N-CH_2-CO_2); ^{13}C NMR (400 MHz, DMSO, 25°C): $\delta = 175.7$, 46.9, 23.9, 23.2, 18.0, 17.5, 13.8 ppm; ^{31}P NMR (400 MHz, DMSO, 25°C): $\delta = 33.88$ ppm; IR (KBr): $\tilde{\nu} = 3354$, 3276, 3182, 2958, 2931, 2873, 1577, 1465, 1409, 1379, 1341, 1312, 1290, 1237, 1099, 1051, 1037, 1006, 969, 918, 907, 871, 825, 750, 723, 650, 592 cm^{-1}; elemental analysis (%) calcd for: C 64.77, H 11.99, N 4.2, P 9.29; found: C 63.92, H 11.85, N 4.1, P 9.18.

[P(C$_4$)$_4$][Ala]: ^{1}H NMR (400 MHz, DMSO, 25°C, TMS): $\delta = 0.92$ (t, J = 8.0 Hz, 12H; CH_3-C_3-P), 0.99 (d, J = 4.0 Hz, 3H; CH_3-C-N), 1.32–1.52 (m, 16H; $(CH_2)_2$), 2.12–2.27 (m, 8H; P-CH_2), 2.78 ppm (q, J = 10 Hz, 1H; CH); ^{13}C NMR (400 MHz, DMSO, 25°C): $\delta = 177.3$, 52.3, 23.8, 23.2, 18.0, 17.5, 13.9 ppm; ^{31}P NMR (400 MHz, DMSO, 25°C): $\delta = 33.92$ ppm; IR (KBr): $\tilde{\nu} = 3353$, 3278, 2958, 2932, 2873, 1591, 1465, 1382, 1346, 1315, 1234, 1099, 1072, 1006, 969, 921, 908, 828, 772, 723, 646, 528 cm^{-1}; elemental analysis (%) calcd for: C 65.61, H 12.09, N 4.03, P 8.91; found (%): C 65.45, H 12.11, N 4.02, P 8.89.

[P(C$_4$)$_4$][Ser]: ^{1}H NMR (400 MHz, DMSO, 25°C, TMS): $\delta = 0.92$ (t, J = 8.0 Hz, 12H; CH_3), 1.30–1.60 (m, 16H; $(CH_2)_2$), 2.12–2.26 (m, 8H; CH_2-P), 2.78 (q, J = 8.0 Hz, H; CH-O), 3.14 (t, J = 12 Hz, H; CH-N), 3.26 ppm (q, J = 4.0 Hz, H; CH-O); ^{13}C NMR (400 MHz, DMSO, 25°C): $\delta = 177.1$, 66.4, 55.5, 23.9, 17.7, 13.9 ppm; ^{31}P NMR (400 MHz, DMSO, 25°C): $\delta = 33.85$ ppm; IR (KBr): $\tilde{\nu} = 3354$, 3187, 2959, 2932, 2873, 1600, 1465, 1384, 1318, 1233, 1202, 1099, 1046, 1006, 969, 920, 909, 841, 766, 723, 559 cm^{-1}; elemental analysis (%) calcd for: C 62.72, H 11.55, N 3.85, P 8.52; found: C 62.60, H 11.58, N 3.84, P 8.51.

[P(C$_4$)$_4$][β-Ala]: ^{1}H NMR (400 MHz, DMSO, 25°C, TMS): $\delta = 0.91$ (t, J = 8.0 Hz, 12H; CH_3), 1.35–1.60 (m, 16H; $(CH_2)_2$), 1.86 (t, J = 8.0 Hz, 2H; CH_2-CO_2), 2.15–2.30 (m, 8H; CH_2-P), 2.52 ppm (t, J = 8.0 Hz, 2H; CH_2-N); ^{13}C NMR (400 MHz, DMSO, 25°C): $\delta = 175.4$, 42.5, 23.7, 17.6, 13.6 ppm; ^{31}P NMR (400 MHz, DMSO, 25°C): $\delta = 33.83$ ppm; IR (KBr): $\tilde{\nu} = 3354$, 3277, 3184, 2958, 2932, 2873, 1578, 1465, 1409, 1379, 1341, 1311, 1290, 1237, 1142, 1099, 1051, 1037, 1006, 969, 918, 907, 871, 825, 750, 723, 592 cm^{-1}; elemental analysis (%) calcd for: C 65.61, H 12.09, N 4.03, P 8.91; found: C 65.58, H 12.10, N 4.02, P 8.90.

[P(C$_4$)$_4$][Lys]: ^{1}H NMR (400 MHz, DMSO, 25°C, TMS): $\delta = 0.92$ (m, J = 8.0 Hz, 12H; CH_3), 1.12–1.32 (m, 6H; $CH_2CH_2CH_2$-N), 1.35–1.55 (m, 16H; CH_2CH_2-C-P), 2.13–2.24 (m, 8H; CH_2-P), 2.48 ppm (d, J = 8.0 Hz, 2H; CH-N), 2.69 (t, J = 8.0 Hz, 1H; CH-CO_2); ^{13}C NMR (400 MHz, DMSO, 25°C): $\delta = 177.8$, 56.9, 42.4, 36.9, 34.4, 24.0, 23.2, 17.8, 13.9 ppm; ^{31}P NMR (400 MHz, DMSO, 25°C): $\delta = 33.92$ ppm; IR (KBr): $\tilde{\nu} = 3357$, 3275, 3184, 2958, 2931, 2872, 1590, 1465, 1381, 1317, 1238, 1209, 1099, 1051, 1005, 969, 919, 908, 820, 725, 549 cm^{-1}; elemental analysis (%) calcd for: C 65.3, H 12.23, N 3.46, P 7.65; found: C 65.1, H 12.23, N 3.45, P 7.64.

Densities of pure ionic liquids were determined by using a pycnometer, calibrated by water. The uncertainty of the densities was estimated $<0.0001\ g\,cm^{-3}$. Dynamic viscosities were measured by an Ubbelohde viscometer, which was calibrated against the efflux time of a standard viscosity liquid 13609 (293.15 K, $\nu = 1094.8\ mm^2 s^{-1}$, $\eta = 1065.9$ mPa s) produced by Chinese National Standard Research Centre. The uncertainty of the dynamic viscosities was estimated to be $<0.1\%$. The electric conductivity was determined by an electric conductivity meter (DDS-307, Shanghai Leici Company) with a conductivity electrode (DJS-1C, Shanghai Jingke Company). The uncertainty of the electric conductivities was estimated to be $\pm 0.1\%$. The constant-temperature water bath for density, viscosity, and electric conductivity measurements was controlled by a special temperature controller and the temperature was determined by accurate mercury thermometers with an accuracy of ± 0.1 K.

Experiments were performed by using ultra high purity CO_2 (purity of 99.995%) purchased from Beijing Analytical Instrument Factory. [P(C$_4$)$_4$][AA] was placed in a special glass container and agitated with a magnetic bar at room temperature. CO_2, dried by P_2O_5, was then let into the container by PTFE pipeline at atmospheric pressure. Parafilm was used to prevent the humid atmosphere from entering the system. The viscosity of the [P(C$_4$)$_4$][AA] increases markedly as CO_2 absorption increases, making the agitation difficult, and eventually the diffusion of CO_2 becomes so slow that the absorption equilibrium is hard to reach.

To enhance the absorption rate, [P(C$_4$)$_4$][AA] was loaded on the porous silica gel (SiO_2, Qingdao Silica Gel Factory) by the dipping method. The porous silica gel was pretreated at 773.15 K for two hours. [P(C$_4$)$_4$][AA] was then dissolved in ethanol and mixed with the above silica gel in a mol ratio of 1:8, followed by evaporation of the ethanol at 343.15 K. The silica gel sample containing [P(C$_4$)$_4$][AA] was then further dried at 353.15 K in a vacuum for 48 h. Similar equipment was used to investigate the absorption behavior of [P(C$_4$)$_4$][AA] supported on porous silica gel. After a selected amount of time, the amount of CO_2 absorbed was determined by an Analytical Balance within an accuracy of ± 0.0001 g. As silica gel is porous and has a large surface area, it is necessary to distinguish the physical absorption from chemical absorption. The mass of the sample with [P(C$_4$)$_4$][AA] supported on silica gel after absorption equilibrium of CO_2 decreased when it was placed in a dry atmosphere at room temperature. When its mass appeared constant, the loss of mass, regarded as the amount of CO_2 physically adsorbed, was determined. The residue CO_2 was considered as chemisorption. Absorption/desorption was determined by several cycles of repeated experiments. The IR spectra of [P(C$_4$)$_4$][β-Ala]-SiO_2, [P(C$_4$)$_4$][Gly]-SiO_2, and [P(C$_4$)$_4$][Ala]-SiO_2 were taken after absorption to help determine the detailed mechanism of the absorption. Unfortunately, the peak of SiO_2 at approximately $\tilde{\nu} = 3300\ cm^{-1}$ overlaps with the peak of -NH_2, therefore the IR spectrum of [P(C$_4$)$_4$][β-Ala] without SiO_2 carrier before and after absorption of CO_2 was taken to provide auxiliary information. [P(C$_4$)$_4$][Gly] with water was also investigated and its IR spectrum was taken after absorption of CO_2.

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