DOI: 10.1002/chem.201103092

Tuning the Physicochemical Properties of Diverse Phenolic Ionic Liquids for Equimolar CO_2 Capture by the Substituent on the Anion

Congmin Wang,*[a, b] Huimin Luo,[d] Haoran Li,[a] Xiang Zhu,[c] Bo Yu,[d] and Sheng Dai*[b, c]

Abstract: Phenolic ionic liquids for the efficient and reversible capture of CO_2 were designed and prepared from phosphonium hydroxide and substituted phenols. The electron-withdrawing or electron-donating ability, position, and number of the substituents on the anion of these ionic liquids were correlated with the physicochemical properties of the ionic liquids. The results show that the stability, viscosity, and CO_2-capturing ability of these ionic liquids were significantly affected by the substituents. Furthermore, the relationship between the decomposition temperature, the CO_2-absorption capacity, and the basicity of these ionic liquids was quantitatively correlated and further rationalized by theoretical calculation. Indeed, these ionic liquids showed good stability, high absorption capacity, and low absorption enthalpy for CO_2 capture. This method, which tunes the physicochemical properties by making use of substituent effects in the anion of the ionic liquid, is important for the design of highly efficient and reversible methods for CO_2-capture. This CO_2 capture process using diverse phenolic ionic liquids is a promising potential method for CO_2 absorption with both high absorption capacity and good reversibility.

Keywords: absorption · carbon dioxide · ionic liquids · phenols · substituent effects

Introduction

Recently, ionic liquids (ILs) have attracted considerable attention as solvents,[1–3] catalysts,[4–7] sorbents,[8–10] materials,[11–13] etc., owing to their remarkable properties, including extremely low vapor pressure, high thermal stability, wide temperature range as liquids, and high ionic conductivity.[14–17] ILs are also recognized as designable liquids, because their physical and chemical properties are facilely tuned by different combinations of the cation and the anion. A great deal of attention has been paid to the study of the effects of cation structure on the physicochemical properties of ILs because the structure of the cation is easy to modify. However, investigations of the role played by the anion structure are few. In ILs, the anion generally plays a more-important role in the reaction than the cation, thus significantly affecting the conversion and selectivity of the reaction.[18,19] Therefore, modifying the structure of the anion may be very important in improving the reaction or separation of the products. The famous example is the effect that different amino acid anions have on physical properties such as ionic conductivity and glass transition temperature, as well as on chemical properties such as CO_2 absorption.[20–22] Herein, we report the effect of different substituents on phenol-based anions on the physical and chemical properties of the ILs. These results show that viscosity, thermal decomposition temperature, and CO_2 capture were easily tuned by the substituent on the anion, which originated from varying the charge on the oxygen atom in the anion. Thus, we can achieve desired physicochemical properties such as high stability, excellent absorption capacity, and low absorption enthalpy for CO_2 capture by conveniently tuning the anion structure of the ILs.

The emission of CO_2—the most significant greenhouse gas from the burning of fossil fuels—has received worldwide attention because of its connection to climate change and humanity's growing energy needs. One of the most commonly used technologies in industry for the capture of CO_2 is chemical absorption by an aqueous amine solution, with its advantages of low cost, high reactivity, and good absorption capacity.[23] However, this process for the capture of

---

[a] Prof. C. Wang, Prof. H. Li
Department of Chemistry
Zhejiang University
Hangzhou, 310027 (China)
Fax: (+86) 571-8795-1895
E-mail: chewcm@zju.edu.cn

[b] Prof. C. Wang, Dr. S. Dai
Chemical Sciences Divisions
Oak Ridge National Laboratory
Oak Ridge, TN, 37831 (USA)
Fax: (+1) 865-576-5235
E-mail: sdai@ornl.gov

[c] X. Zhu, Dr. S. Dai
Department of Chemistry, University of Tennessee
Knoxville, TN 37966 (USA)

[d] Dr. H. Luo, Dr. B. Yu
Nuclear Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN, 37831 (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103092.

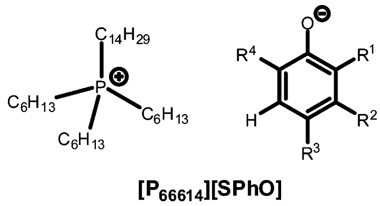
CO_2 has some serious inherent drawbacks, including solvent loss, corrosion, and high energy demands owing to the thermodynamic properties of water and high absorption enthalpy.[24,25] Currently, the goal is to design industrially attractive sorbent materials with high capacity and low absorption enthalpy for the capture of CO_2.

Ionic liquids offer a new opportunity for addressing this challenge to design and develop excellent CO_2-capture systems. Many research groups have conducted outstanding research on the physical absorption of CO_2 in ILs using both experimental and theoretical methods.[26–30] Their results have shown that CO_2 is very soluble in ILs, especially at high pressures. However, the physical absorption of CO_2 in ILs has some way to go because of their low capacity under atmospheric pressure. The Davis group[31] reported a method for the chemisorption of CO_2 that employs an amino-functionalized IL, where 0.5 mole CO_2 per mole IL could be captured under ambient pressure over 3 h. Subsequently, some other amino-functionalized ILs, including sulfone anions with ammonium cations, and amino acid anions with imidazolium or phosphonium cations, were reported for CO_2 capture.[32–34] Recently, a method was reported for the capture of CO_2 in a 1:1 manner by tunable azole-based basic ILs that makes use of the reactivity of the anion.[35,36] These investigations have made some significant advancements; however, alternative IL systems that are able to achieve efficient, reversible capture of CO_2 are still highly desired.

Herein, we prepared diverse phenolic ILs by neutralizing phosphonium hydroxide with various substituted phenols. We found that the physical and chemical properties of the ILs are facilely tunable by different substituents. Our investigation found that the electron-withdrawing or electron-donating ability, position, and the number of the substituents had significant effects on the capture of CO_2, which was explained by density functional theory (DFT) methods. Based on the relationship between CO_2 capture and substituted groups on the anion of the IL, a highly stable IL with high capacity and good reversibility for CO_2 capture was achieved.

Results and Discussion

A series of phenol-based ILs were prepared by neutralization of various substituted phenols, SPhOHs, with trihexyl(tetradecyl) phosphonium hydroxide, $[P_{66614}][OH]$, which was obtained by the anion-exchange method.[20] Electron-withdrawing groups, such as NO_2, Cl, and CF_3, and electron-donating groups, such as CH_3 and OCH_3, were selected to investigate the electronic push-pull effect on the properties of the ILs. ILs that had 2-Cl, 3-Cl, and 4-Cl groups, as well as 2,4-Cl and 2,4,6-Cl groups, on the phenolic anion were designed to assess the influence of the position and number of substituents on the properties of the ILs (Scheme 1). Phenolic ILs from 1-naphthol and 2-naphthol were also investigated.



R^1=H, Me or Cl; R^2=H, Me, Cl, MeO or NMe_2;
R^3=H, Me, MeO, Cl, *i*Pr or *t*Bu; R^4=H, Me or Cl

Scheme 1. Structures of the ionic liquids $[P_{66614}]$[SPhO] with various substituents. SPhO = substituted phenol.

Table 1. Physical properties of different phenolic ILs.

Ionic liquid	η [cPa][a]	d [g cm^{-3}][a]	σ [s cm^{-1}][a]	T_d [°C][b]
$[P_{66614}]$[4-Me-PhO]	392.7	0.894	2.561	238
$[P_{66614}]$[4-MeO-PhO]	253.4	0.919	4.210	217
$[P_{66614}]$[4-H-PhO]	246.7	0.896	3.001	245
$[P_{66614}]$[4-Cl-PhO]	376.5	0.949	5.680	277
$[P_{66614}]$[4-CF_3-PhO]	286.4	0.968	3.800	259
$[P_{66614}]$[4-NO_2-PhO]	984.3	0.958	4.700	292
$[P_{66614}]$[3-Cl-PhO]	223.2	0.931	3.940	270
$[P_{66614}]$[2-Cl-PhO]	378.3	0.925	1.825	299
$[P_{66614}]$[2,4-Cl-PhO]	472.5	0.966	2.179	302
$[P_{66614}]$[2,4,6-Cl-PhO]	672.1	1.009	1.560	341
$[P_{66614}]$[3-Me-PhO]	335.1	0.893	2.951	221
$[P_{66614}]$[2-Me-PhO]	415.5	0.900	2.408	243
$[P_{66614}]$[2,4-Me-PhO]	334.1	0.901	1.653	205
$[P_{66614}]$[2,6-Me-PhO]	371.3	0.909	2.552	189
$[P_{66614}]$[4-*i*Pr-PhO]	388.2	0.906	1.612	250
$[P_{66614}]$[4-*t*Bu-PhO]	585.8	0.887	0.812	255
$[P_{66614}]$[3-MeO-PhO]	374.8	0.937	3.840	258
$[P_{66614}]$[3-NMe_2-PhO]	512.1	0.916	0.891	233
$[P_{66614}]$[1-Naph]	1077	0.929	1.019	294
$[P_{66614}]$[2-Naph]	878.4	0.930	1.010	284

[a] Determined at 23 °C. [b] Determined by TGA under a N_2 atmosphere.

The viscosity of an IL is an important physical property that significantly affects its kinetics of gas absorption. We investigated the effects of different substituents on the phenolic anion on viscosity (Table 1) and noticed several important trends: First, the presence of electron-withdrawing or electron-donating groups influenced the viscosity of the IL significantly. For example, the viscosities of $[P_{66614}]$[4-Cl-PhO], $[P_{66614}]$[4-CF_3-PhO], and $[P_{66614}]$[4-NO_2-PhO] (376.5 cP, 286.4 cP, and 984.3 cP, respectively) were all higher than $[P_{66614}]$[PhO] (246.7 cP). The viscosity also changed a little when a 4-MeO group was substituted on the anion. Second, the changing the position of the substituent had an obvious effect on viscosity. As shown in Table 1, the viscosity was reduced from 376.5 to 223.2 cP when $[P_{66614}]$[4-Cl-PhO] was replaced by $[P_{66614}]$[3-Cl-PhO]. Third, the number of substituents also had a significant effect on viscosity. For example, the viscosity of the IL increased with increasing amounts of Cl groups on the anion. Table 1 also shows the influence of the substituent on density. In general, the anions containing the Cl or MeO groups had higher densities.

The thermal-decomposition temperature of the ILs is another key physical property for gas absorption. High stabilities help ILs achieve good reversibility for CO_2 capture. In general, as shown in Table 1, placing electron-withdrawing groups on the phenolic anion is useful for increasing the stabilities of the ILs, whereas electron-donating groups decrease the stability. For example, the decomposition temperatures of [P_{66614}][4-Cl-PhO] and [P_{66614}][4-NO_2-PhO] were 277 and 292 °C, respectively, whereas that of [P_{66614}][4-MeO-PhO] was 217 °C. In comparison with [P_{66614}][4-H-PhO], ILs [P_{66614}][1-Naph] and [P_{66614}][1-Naph] showed higher stabilities. Furthermore, placing the substituents at different positions on the phenolic ring imparted different stabilities to the ILs. A comparison of 2-Cl- and 3-Cl-substituted anions showed that the anion of the 2-Cl substituent was more stable. Finally, the more Cl groups present on the ring, the higher was the stability of the ILs. We investigated whether there was a quantitative relationship between the stability of the IL and the substituents by considering the relationship between the decomposition temperature and the basicity of the anion. A roughly linear relationship between the pK_a value of the anion and the decomposition temperature was afforded, as shown in Figure 1. Clearly, the stability of the ILs increased as the pKa value of the anion decreased. Thus, we can facilely tune the stability of the ILs by making use of the basicity of the anion. After this discovery, we predominantly chose ILs with decomposition temperatures above 250 °C for our investigation of CO_2 capture.

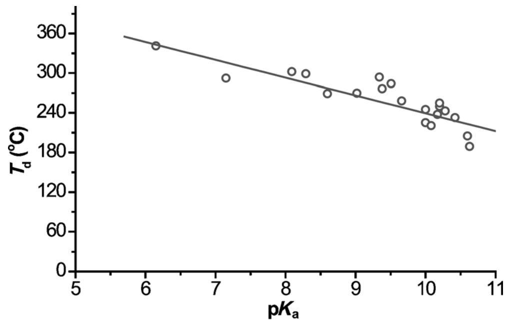


Figure 1. The relationship between the decomposition temperature (T_d) and the pK_a value of the anion in the ionic liquids; experimental values (○), fitted values (–).

Next, we investigated the effect on CO_2 capture when substituents such as NO_2, Cl, and Me were substituted at the 4-position on the phenolic anion (Table 2). The CO_2-absorption capacity was significantly affected by placing these substituents on the anion; the CO_2-absorption capacity decreased markedly from 0.85 mol CO_2 per mole IL to 0.61 and 0.30 mole CO_2 when CF_3 and NO_2 (both electron-withdrawing groups) replaced the H group at the 4-position on the anion, respectively. The stronger the electron-withdrawing group, the lower the CO_2-absorption capacity became. Conversely, placing an electron-donating group on the anion increased the CO_2-absorption capacity. These results indicated that the absorption capacity of CO_2 was easily tuned by electron-withdrawing and electron-donating substituents.

Table 2. The effect of the substituent at the 4-position of the phenolic anion on CO_2 capture.

Ionic liquid	t [min][a]	CO_2 absorption[b]
[P_{66614}][4-Me-PhO]	30	0.91
[P_{66614}][4-MeO-PhO]	30	0.92
[P_{66614}][4-H-PhO]	30	0.85
[P_{66614}][4-Cl-PhO]	30	0.82
[P_{66614}][4-CF_3-PhO]	30	0.61
[P_{66614}][4-NO_2-PhO]	20	0.30

[a] Determined at 30 °C. [b] Mole CO_2 per mole of ionic liquid.

Table 3 shows the effect of the location and number of Cl substituents on the capacity of CO_2 capture. Clearly, placing the Cl group at different positions around the phenol ring resulted in remarkable variations in the absorption capacity. For example, the absorption capacity decreased from 0.82 mol CO_2 per mole IL to 0.72 and 0.67 mol when [P_{66614}]-[3-Cl-PhO] and [P_{66614}][2-Cl-PhO] replaced [P_{66614}][4-Cl-PhO], respectively. Furthermore, we investigated the effect of the number of Cl substituents on CO_2 capture (Table 3). The CO_2-absorption capacity decreased when a higher number of Cl groups were substituted on the phenolic ring. Other phenolic ILs, such as [P_{66614}][1-Naph] and [[P_{66614}][2-Naph], also showed good CO_2 absorption. Next, the addition of specific amounts of water on the efficiency of CO_2 capture was investigated (Table 3). The results showed that the CO_2-absorption capacity increased when water was added to the IL, presumably because bicarbonate formation occurred. This result is in agreement with results obtained for other anion-functionalized ILs.[19,21]

Table 3. The effect of the position and number of substituents, temperature, and water on CO_2 capture.

Ionic liquid	T [°C][a]	CO_2 absorption[b]
[P_{66614}][4-Cl-PhO]	30	0.82
[P_{66614}][3-Cl-PhO]	30	0.72
[P_{66614}][2-Cl-PhO]	30	0.67
[P_{66614}][2,4-Cl-PhO]	30	0.48
[P_{66614}][2,4,6-Cl-PhO]	30	0.07
[P_{66614}][4-Cl-PhO]	50	0.65
[P_{66614}][4-Cl-PhO]	70	0.50
[P_{66614}][4-Cl-PhO][c]	30	0.89
[P_{66614}][4-Cl-PhO][d]	30	0.88
[P_{66614}][3-NMe_2-PhO]	30	0.94
[P_{66614}][1-Naph]	30	0.89
[P_{66614}][2-Naph]	30	0.86

[a] Determined for 30 min. [b] Mole CO_2 per mole ionic liquid. [c] Addition of water (2 wt %) to the IL. [d] Addition of water (5 wt %) to the IL.

One important feature of the absorption by these phenolic ILs is that the absorption rate is rapid. Figure 2 shows some typical CO_2 absorptions by several phenolic ILs, such as [P_{66614}][4-Me-PhO] and [P_{66614}][4-Cl-PhO], as a function of time. The absorption of CO_2 was almost complete within the first 10 min. This rapid absorption is presumably related to the absence of strong hydrogen-bonded networks during the

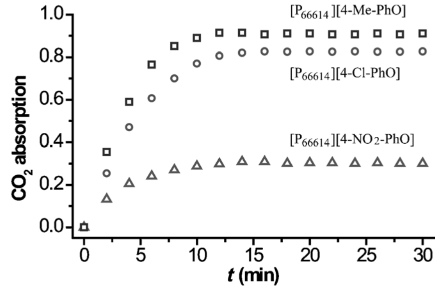


Figure 2. CO_2 absorption by three typical phenolic ionic liquids as a function of time at 30 °C: $[P_{66614}]$[4-Me-PhO] (□), $[P_{66614}]$[4-Cl-PhO] (○), and $[P_{66614}]$[4-NO$_2$-PhO] (△).

absorption of CO_2 by these phenolic ILs, which results in no obvious change in viscosity.[35] However, on the contrary, for traditional amino-functionalized ILs, molecular dynamics simulations have revealed that the viscosity increased drastically because strong hydrogen-bonding networks formed during the absorption of CO_2 by these ILs, thereby resulting in low absorption rates.[21,34,37]

To support our experimental results, the interaction of these phenolic ILs and CO_2 was investigated by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. During the absorption of CO_2 observed in this study, the phenolic ILs reacted with CO_2 to form liquid carbonate salts. The formation of the carbonate salt was verified by FTIR spectra of fresh IL $[P_{66614}]$[4-Cl-PhO] and of the corresponding carbonate salt $[P_{66614}]$[4-Cl-PhO]-CO_2 (Figure 3). A new peak at 1617 cm^{-1} in the FTIR spectrum of $[P_{66614}]$[4-Cl-PhO]-CO_2 can be assigned to carbonate (C=O) stretches after the absorption of CO_2 by $[P_{66614}]$[4-Cl-PhO]. Furthermore, the ^{13}C NMR spectrum of the product showed a new band at $\delta = 161$ ppm during the absorption of CO_2, thereby also indicating the formation of carbonate salt. On the basis of previous reports[35,38–40] and the observed reaction product, we present Scheme 2 as the absorption mechanism of CO_2 by these phenolic ILs. Thus, equimolar CO_2 capture can be achieved because these phenolic ILs react with CO_2 in a 1:1 manner.

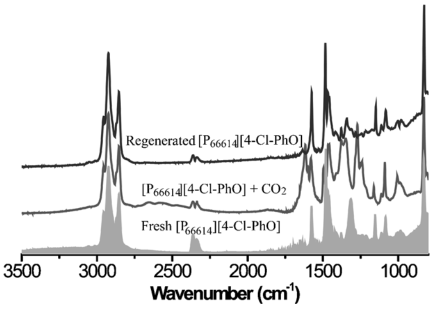


Figure 3. IR spectra of CO_2 capture by $[P_{66614}]$[4-Cl-PhO]. Top: IL formed from the desorption of CO_2; middle: carbonate salt resulting from the capture; bottom: fresh $[P_{66614}]$[4-Cl-PhO].

Next, we considered why the CO_2 capture was so significantly affected by different substituents, and whether there was a quantitative relationship between the CO_2-absorption capacity and the substituent. We investigated the relationship between CO_2-absorption capacity and the basicity of the phenolic ILs. As shown in Figure 4, the CO_2-absorption capacity decreased as the pK_a value of the anion decreased. This finding indicates that CO_2 absorption can be facilely tuned by varying the basicity of the ILs—a useful feature for the future design of ILs for CO_2 capture.

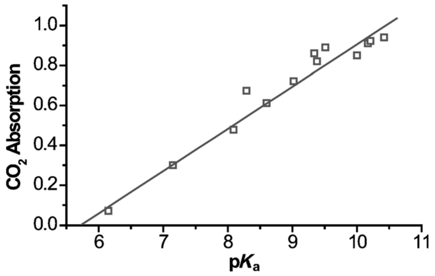
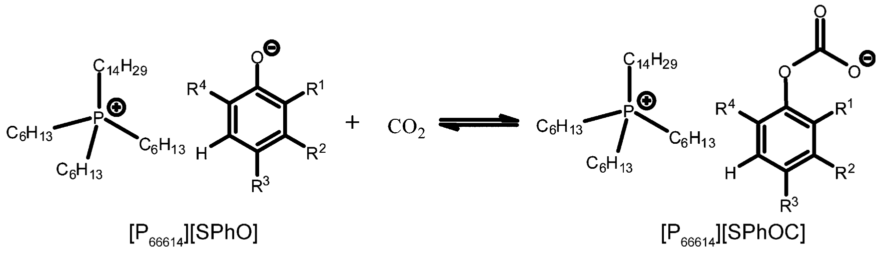
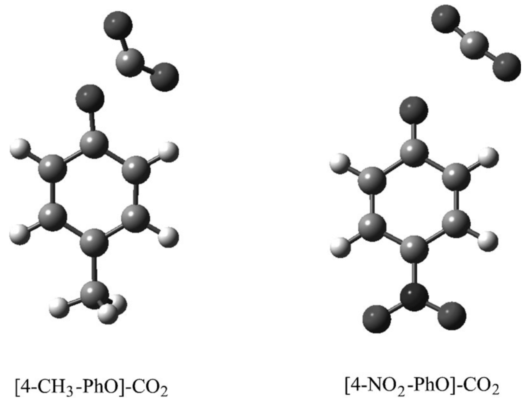


Figure 4. The relationship between CO_2-absorption capacity and pK_a value of the anion in the ionic liquids.

To further investigate the effect that different substituents on the phenolic anion have on CO_2 capture, theoretical calculations were performed using the Gaussian 03 program. For each set of calculations, we calculated the geometry and energy optimization of each free anion, free CO_2, and each anion–CO_2 complex at the B3LYP/6-31++G(p,d) level. The optimized structures of some typical anion–CO_2 complexes, including $[P_{66614}]$[4-Me-PhO]-CO_2 and $[P_{66614}]$[4-NO$_2$-PhO]-CO_2, are shown in Figure 5. We also calculated the gas-phase reaction energetics for CO_2 capture by different phenolic ILs according to Scheme 2. Table 4 shows that the absorption enthalpy decreased when electron-withdrawing groups (such as Cl) were present on the anion, and increased when electron-donating anions (such as Me) were used. Therefore, we can tune the absorption enthalpy of CO_2 by varying the electric push-pull properties of the substituents, thereby lowering the energy demand for regeneration. Furthermore, for these substituted phenolic ILs, the changes in the enthalpy of CO_2



Scheme 2. The CO_2-absorption mechanism for the phenolic ionic liquids used in this study.



[4-CH_3-PhO]-CO_2 [4-NO_2-PhO]-CO_2

Figure 5. The optimized structures of [P_{66614}][4-Me-PhO] and [P_{66614}][4-NO_2-PhO] with CO_2. The calculations were carried out at the B3LYP/6-31++G(p,d) level.

Table 4. The effect of the substituent on absorption enthalpy and charge on the oxygen atom.

Ionic liquid[a]	Absorption enthalpy [kJ mol^{-1}]	Charge on O atom
[P_{66614}][4-Me-PhO]	−49.2	−0.6932
[P_{66614}][4-MeO-PhO]	−51.4	−0.7062
[P_{66614}][4-H-PhO]	−46.8	−0.6873
[P_{66614}][4-Cl-PhO]	−38.1	−0.6833
[P_{66614}][4-CF_3-PhO]	−22.4	−0.6577
[P_{66614}][4-NO_2-PhO]	−17.1	−0.6187
P_{66614}][3-Cl-PhO]	−31.4	−0.6678
[P_{66614}][2-Cl-PhO]	−27.6	−0.6599
[P_{66614}][2,4-Cl-PhO]	−29.5	−0.6386
[P_{66614}][2,4,6-Cl-PhO]	−19.0	−0.6270
[P_{66614}][3-NMe_2-PhO]	−42.9	−0.6784
[P_{66614}][1-Naph]	−27.9	−0.6665
[P_{66614}][2-Naph]	−32.3	−0.6735

[a] Performed at the B3LYP/6-31++G(p,d) level.

absorption agree with the results of absorption capacity.

Next, we calculated the effect of the substituent on the Mulliken atomic charge of the oxygen atom in the phenolic anion (Table 4). The more-strongly electron-withdrawing the substituent is, the weaker the charge on the oxygen atom is. Conversely, more-electron-donating groups, such as MeO groups, caused the charge on the oxygen atom to increase. The charge on the oxygen atom in these phenolic ILs was also significantly affected by the position and the number of Cl groups. For example, the charge increased from −0.6833 in [4-Cl-PhO] to −0.6386 and −0.6270 with anions [2,4-Cl-PhO] and [2,4,6-Cl-PhO], respectively.

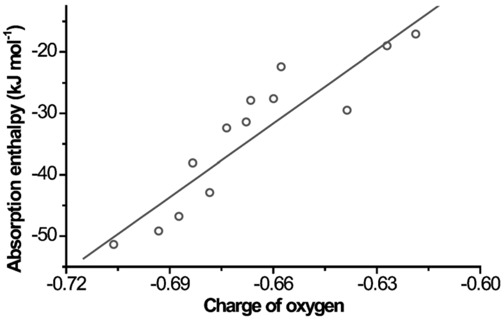


Figure 6. The relationship between CO_2-absorption enthalpy and the Mulliken charge on the oxygen atom for CO_2 capture; experimental values (○), fitted values (−).

Based on the results for oxygen charge, we investigated the relationship between CO_2-absorption enthalpy and the Mulliken charge of the oxygen atom. Figure 6 shows a roughly linear correlation between the CO_2-absorption enthalpy of the ILs and the Mulliken charge of the oxygen atom in the anion. The absorption enthalpy decreased with decreasing charge on the oxygen atom[41] as a result of the weaker interaction between the negative oxygen atom and the acidic CO_2. This relationship will be useful for designing ILs with lower energy demands during the desorption of CO_2.

Considering the high stability of the IL, the good absorption capacity, and the low absorption enthalpy, we believe that [P_{66614}][4-Cl-PhO] is an ideal sorbent for the capture of CO_2. When we investigated the effect of temperature on [P_{66614}][4-Cl-PhO] for CO_2 capture, we found that the CO_2-absorption capacity decreased as the temperature increased (Table 3). For example, the molar ratio of CO_2/IL decreased gradually from 0.82 to 0.50 as the temperature was increased from 30 to 70 °C. This outcome indicates that captured CO_2 is easy to release by heating the IL. We also investigated the absorption/desorption process using [P_{66614}][4-Cl-PhO] (Figure 7). Good capacity and rapid absorption rate persisted during the six recycles, thereby demonstrating the reversibility of CO_2 capture by [P_{66614}][4-Cl-PhO].

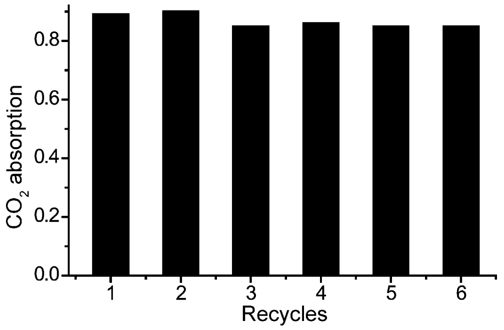


Figure 7. Six absorption/desorption cycles of [P_{66614}][4-Cl-PhO] during the capture of CO_2. The absorption of CO_2 (containing ca. 3.2 % H_2O) was carried out at 30 °C, and the desorption was performed at 80 °C under a N_2 atmosphere for 60 min.

Conclusions

We have developed a method for capturing CO_2 using diverse phenol-based ILs that were prepared from the neutralization of phosphonium hydroxide and substituted phenols. The results indicate that physical properties, such as decomposition temperature and viscosity, were significantly affected by the substituents on the phenolic ILs. These phenolic

ILs reacted with CO_2 to form a liquid carbonate salt, thereby resulting in equimolar CO_2-absorption capacity that was verified by theoretical calculations and spectroscopic analysis. CO_2 absorption was heavily affected by the electron-withdrawing or electron-donating ability, position, and quantity of substituents on the anion. Furthermore, a quantitative relationship existed between the stability, CO_2-absorption capacity, CO_2-absorption enthalpy, and basicity of the anion, which originated from variations in the Mulliken charge on the oxygen atom in different phenolic ILs. Therefore, we can achieve good absorption capacity as well as low absorption enthalpy by varying the substituents on the anion, which is useful in the future design of ILs for efficient and reversible CO_2 capture. Considering its diversity and tunability, we believe that this efficient and reversible process using phenolic ILs is a promising potential method for CO_2 absorption with both high absorption capacity and good reversibility.

Experimental Section

General: Trihexyl(tetradecyl)phosphonium bromide, $[P_{66614}][Br]$, was purchased from Sigma-Aldrich. Anion-exchange resin Dowex Monosphere 550 A (OH) was obtained from Dow Chemical Company. Substituted phenols, including phenol (PhOH), *p*-methylphenol (4-Me-PhOH), *p*-methoxyphenol (4-MeO-PhOH), *p*-nitrophenol ($4\text{-}NO_2$-PhOH), *p*-trifluoromethylphenol ($4\text{-}CF_3$-PhOH), *p*-chlorophenol (4-Cl-PhOH), *m*-chlorophenol (3-Cl-PhOH), *o*-chlorophenol (2-Cl-PhOH), 2,4-dichlorophenol (2,4-Cl-PhOH), 2,4,6-trichlorophenol (2,4,6-Cl-PhOH), 2,4-dimethylphenol (2,4-Me-PhOH), 2,6-dimethylphenol (2,6-Me-PhOH), *p*-isopropylphenol (4-*i*Pr-PhOH), *p*-*tert*-butylphenol (4-*t*Bu-PhOH), *m*-methylphenol (3-Me-PhOH), *o*-methylphenol (2-Me-PhOH), and *m*-methoxyphenol (3-MeO-PhOH), *m*-dimethylaminophenol ($3\text{-}NMe_2$-PhOH), 1-naphthol (1-Naph), and 2-naphthol (2-Naph) were purchased from Sigma-Aldrich. All chemicals were obtained in the highest purity grade possible and used as received unless otherwise stated. All ILs were dried under high vacuum at 60 °C for 24 h to remove possible traces of water. The water content of the IL was determined by Karl Fischer titration, and was found to be less than 0.1 wt %. The residual chloride content was determined by a semi-quantitative Nessler cylinder method, which showed that the halide content was lower than 0.15 wt %.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 NMR spectrometer in $CDCl_3$ using tetramethylsilane as the standard. FTIR data were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer. Mass spectra (MS) were determined using a QSTAR elite mass spectrometer. Ionic conductivity was measured by an EC meter model 3084 from Amber Science Inc, and viscosity was determined by a Brookfield DV pro viscometer. Decomposition temperature was measured with a TGA 2950 under a N_2 atmosphere at a ramp rate of 10 °C min^{-1}.

Absorption of CO_2: In a typical absorption of CO_2, CO_2 at atmospheric pressure was bubbled through about 1.0 g of IL in a glass container with an inner diameter of 10 mm, where the flow rate of CO_2 was 60 mL min^{-1}. The glass container was partially immersed in a water bath at the desired temperature. The amount of CO_2 captured was obtained at regular intervals by an electronic balance with an accuracy of (±0.1) mg.

Desorption of CO_2: In a typical desorption of CO_2, N_2 at atmospheric pressure was bubbled through about 1.0 g of captured IL in a glass container that was partially immersed in a circulation oil bath at the desirable temperature; the flow rate was about 60 mL min^{-1}. The release of CO_2 was determined at regular intervals by an electronic balance.

Synthesis of phenolic ILs: These phenolic ILs were prepared from the neutralization of various substituted phenols with trihexyl(tetradecyl)phosphonium hydroxide, $[P_{66614}][OH]$, according to a literature procedure. For example, in a typical experiment, a solution of $[P_{66614}][OH]$ in EtOH was obtained from $[P_{66614}][Cl]$ using the anion-exchange resin, and equimolar *p*-chlorophenol was added to the EtOH solution of $[P_{66614}][OH]$. Then, the mixture was stirred at RT for 16 h. Subsequently, EtOH and water were distilled off at 70 °C under vacuum. The obtained ILs was dried under a high vacuum at 60 °C for 24 h.

Trihexyl(tetradecyl)phosphonium *p*-methylphenolate, $[P_{66614}]$[4-Me-PhO]: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.86$ (m, 12 H; $4\times CH_3$), 1.22–1.43 (m, 48 H; $24\times CH_2$), 2.21 (s, 3 H; C4H), 2.26 (m, 8 H; $4\times PH_2$), 6.86 (d, 2 H; C2H and C6H), 6.92 ppm (d, 2 H; C3H and C5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.7$, 18.4, 18.9, 20.2, 21.5, 22.1, 22.4, 29.1, 29.3, 29.4, 30.1, 30.2, 30.8, 31.7, 115.5, 126.6, 129.3, 156.0 ppm ; IR: $\tilde{\nu}=2956$, 2924, 2855, 1600, 1559, 1497, 1466, 1412, 1378, 1296, 1161, 1101, 826, 750, 719 cm^{-1}. MS (ESI): *m*/*z*: 483.5 $[P_{66614}]$, 107.1 [4-Me-PhO].

Trihexyl(tetradecyl)phosphonium *p*-methoxyphenolate ($[P_{66614}]$[4-MeO-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$ (m, 12 H; $4\times CH_3$), 1.21–1.44 (m, 48 H; $24\times CH_2$), 2.22 (m, 8 H; $4\times PH_2$), 3.67 (s, 3 H; OCH_3), 6.66 (d, 2 H; C2H and C5H), 6.85 ppm (d, 2 H; C3H and C4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.7$, 13.9 18.4, 18.9, 21.5, 22.1, 28.7, 29.1, 29.3, 29.4, 30.1, 30.2, 30.8, 31.7, 55.6, 114.3, 116.4, 151.1, 153.6 ppm; IR: $\tilde{\nu}=$ 2956, 2924, 2855, 1597, 1559, 1491, 1466, 1438, 1378, 1295, 1249, 1220, 1176, 1096, 1046, 993, 827, 738, 721 cm^{-1}.

Trihexyl(tetradecyl)phosphonium phenolate ($[P_{66614}]$[4-H-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$ (m, 12 H; $4\times CH_3$), 1.22–1.46 (m, 48 H; $24\times CH_2$), 2.29 (m, 8 H; $4\times PH_2$), 6.71 (m, 1 H; C4H), 7.01 (d, 2 H; C2H and C6H), 7.11 ppm (m, 2 H; C3H and C5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.7$, 13.9, 18.4, 19.1, 21.7, 22.2, 22.5, 28.8, 29.2, 29.5, 30.2, 30.3, 30.5, 30.9, 1.7, 115.9, 117.9 128.5, 158.5 ppm; IR: $\tilde{\nu}=2957$, 2924, 2855, 2364, 2341, 1581, 1559, 1485, 1467, 1306, 1156, 1105, 1054, 983, 859, 823, 754, 720 cm^{-1}. MS (ESI): *m*/*z*: 483.5 $[P_{66614}]$, 93.0 [4-H-PhO].

Trihexyl(tetradecyl)phosphonium *p*-chlorophenolate ($[P_{66614}]$[4-Cl-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.89$ (m, 12 H; $4\times CH_3$), 1.26–1.48 (m, 48 H; $24\times CH_2$), 2.29 (m, 8 H; $4\times PH_2$), 6.88 (d, 2 H; C2H and C6H), 7.01 ppm (d, 2 H; C3H and C5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 18.8, 19.1, 21.7, 22.2, 28.8, 29.2, 29.4, 29.5, 30.2, 30.4, 30.9, 31.7, 117.5, 127.9, 128.7, 158.8 ppm; IR (): $\tilde{\nu}=2955$, 2923, 2854, 2362, 2340, 1576, 1481, 1466, 1314, 1153, 1111, 1084, 985, 830, 720 cm^{-1}. MS (ESI): *m*/*z*: 483.5 $[P_{66614}]$, 127.0 [4-Cl-PhO].

Trihexyl(tetradecyl)phosphonium *p*-trifluorophenolate ($[P_{66614}]$[$4\text{-}CF_3$-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$ (m, 12 H; $4\times CH_3$), 1.23–1.47 (m, 48 H; $24\times CH_2$), 2.32 (m, 8 H; $4\times PH_2$), 6.81 (d, 2 H; C2H and C6H), 7.22 ppm (d, 2 H; C3H and C5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.7$, 13.9, 18.6, 19.0, 21.6, 22.1, 28.7, 29.1, 29.4, 30.1, 30.3, 30.5, 30.6, 30.8, 57.4, 116.1, 126.3, 163.8 ppm; IR: $\tilde{\nu}=2957$, 2925, 2856, 1591, 1514, 1467, 1358, 1314, 1267, 1161, 1143, 1087, 1054, 880, 840, 750, 721 cm^{-1}. MS (ESI): *m*/*z*: 161.0 [$4\text{-}CF_3$-PhO].

Trihexyl(tetradecyl)phosphonium *p*-nitrophenolate ($[P_{66614}]$[$4\text{-}NO_2$-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.87$ (m, 12 H; $4\times CH_3$), 1.26–1.46 (m, 48 H; $24\times CH_2$), 2.17 (m, 8 H; $4\times PH_2$), 6.34 (d, 2 H; C2H and C5H), 7.96 ppm (d, 2 H; C3H and C4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 14.0, 18.4, 18.9, 21.5, 22.2, 28.7, 29.1, 29.2, 29.4, 29.5, 30.2, 30.3, 30.5, 30.8, 31.8, 119.1, 127.7, 131.0, 179.4; IR: $\tilde{\nu}=2955$, 2924, 2854, 1581, 1543, 1512, 1466, 1424, 1378, 1262, 1214, 1161, 1106, 1009, 986, 849, 819, 761, 718 cm^{-1}. MS (ESI): *m*/*z*: 138.0 [$4\text{-}NO_2$-PhO].

Trihexyl(tetradecyl)phosphonium *o*-chlorophenolate ($[P_{66614}]$[2-Cl-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$ (m, 12 H; $4\times CH_3$), 1.21–1.44 (m, 48 H; $24\times CH_2$), 2.23 (m, 8 H; $4\times PH_2$), 6.21(d, 1 H; C6H), 6.81 (m, 1 H; C5H), 6.88 (m, 1 H; C4H), 7.13 ppm (d, 1 H; C3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 14.0, 18.5, 19.0, 21.7, 22.2, 28.9, 29.2, 29.4, 29.5, 30.2, 30.3, 31.0, 33.9 111.9, 119.7, 127.5, 129.0, 162.6 ppm; IR : $\tilde{\nu}=2956$, 2924, 2855, 1573, 1475, 1435, 1378, 1337, 1279, 1105, 1053, 1019, 880, 848, 739, 717 cm^{-1}. MS (ESI): *m*/*z*: 127.0 [2-Cl-PhO].

Trihexyl(tetradecyl)phosphonium 2,4-dichlorophenolate ($[P_{66614}]$[2,4-Cl-PhO]): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$ (m, 12 H; $4\times CH_3$), 1.22–1.43 (m, 48 H; $24\times CH_2$), 2.20 (m, 8 H; $4\times PH_2$), 6.55 (m, 1 H; C6H), 6.77, (m, 1 H; C5H), 7.07 ppm (d, 1 H; C3H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ=13.8, 18.5, 18.9, 21.7, 22.2, 29.2, 29.4, 29.5, 30.2, 30.3, 30.5, 30.9, 120.2, 122.7, 127.3, 128.2, 163.4 ppm; IR: $\tilde{\nu}$=2956, 2924, 2855, 1569, 1493, 1476, 1394, 1338, 1245, 1100, 1032, 862, 809, 772, 715 cm^{-1}. MS (ESI): *m*/*z*: 160.9 [2,4-Cl-PhO].

Trihexyl(tetradecyl)phosphonium 2,4,6-trichlorophenolate ([P$_{66614}$][2,4,6-Cl-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.89 (m, 12H; 4×CH$_3$), 1.29–1.44 (m, 48H; 24×CH$_2$), 2.24 (m, 8H; 4×PH$_2$), 7.03 ppm (s, 2H; C3H and C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.8, 14.0, 18.4, 18.9, 21.7, 22.2, 22.6, 29.2, 29.4, 29.5, 30.2, 30.4, 30.5, 30.9, 108.9, 123.7, 126.9, 160.4 ppm; IR: $\tilde{\nu}$=2956, 2924, 2855, 2362, 2337, 1563, 1487, 1475, 1379, 1240, 1155, 855, 794, 774, 728 cm^{-1}. MS (ESI): *m*/*z*: 194.9 [2,4,6-Cl-PhO].

Trihexyl(tetradecyl)phosphonium *m*-methylphenolate ([P$_{66614}$][3-Me-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.88 (m, 12H; 4×CH$_3$), 1.21–1.43 (m, 48H; 24×CH$_2$), 2.22 (s, 3H; CH$_3$), 2.25 (m, 8H; 4×PH$_2$), 6.67 (m, 1H; C4H), 6.94, (m, 1H; C5H), 7.01 (d, 1H; C6H), 7.20 ppm (d, 1H; C3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.6, 13.8, 18.4, 18.8, 21.4, 22.0, 22.4, 28.7, 29.0, 29.2, 29.4, 30.0, 30.2, 30.8, 112.8, 116.4, 118.7, 128.6, 138.6, 158.3; IR: $\tilde{\nu}$=2956, 2924, 2855, 1581, 1559, 1468, 1416, 1378, 1319, 1303, 1255, 1164, 1150, 1104, 1054, 986, 860, 804, 767, 720 cm^{-1}. MS (ESI): *m*/*z*: 107.0 [3-Me-PhO].

Trihexyl(tetradecyl)phosphonium *o*-methylphenolate ([P$_{66614}$][2-Me-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.88 (m, 12H; 4×CH$_3$), 1.21–1.44 (m, 48H; 24×CH$_2$), 2.20 (s, 3H; CH$_3$), 2.24 (m, 8H; 4×PH$_2$), 6.52 (d, 1H; C6H), 6.78, (d, 1H; C4H), 6.80, (s, 1H; C2H), 7.20 ppm (m, 1H; C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.7, 13.9, 18.6, 19.0, 21.6, 22.1, 22.5, 29.2, 29.3, 29.5, 30.1, 30.3, 30.9, 31.7, 115.3, 118.3, 123.9, 126.3, 130.2, 155.8 ppm; IR: $\tilde{\nu}$=2956, 2924, 2855, 1585, 1468, 1378, 1299, 1104, 1054, 1038, 978, 879, 857, 751, 718 cm^{-1}. MS (ESI): *m*/*z*: 107.0 [2-Me-PhO].

Trihexyl(tetradecyl)phosphonium 2,4-dimethylphenolate ([P$_{66614}$][2,4-Me-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.87 (m, 12H; 4×CH$_3$), 1.21–1.46 (m, 48H; 24×CH$_2$), 2.16 (s, 6H; 2×CH$_3$), 2.36 (m, 8H; 4×PH$_2$), 6.74 (d, 1H; C6H), 6.83, (s, 1H; C3H), 7.02 ppm (d, 1H; C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.8, 14.0, 18.7, 19.2, 21.7, 22.2, 22.5, 28.8, 29.2, 29.4, 29.5, 30.2, 30.3, 30.9, 57.7, 115.7, 126.7, 130.9, 153.5 ppm; IR: $\tilde{\nu}$=2957, 2924, 2855, 1602, 1479, 1467, 1408, 1378, 1301, 1288, 1104, 1054, 873, 819, 785, 712 cm^{-1}. MS (ESI): *m*/*z*: 121.1 [2,4-Me-PhO].

Trihexyl(tetradecyl)phosphonium 2,6-dimethylphenolate ([P$_{66614}$][2,6-Me-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.89 (m, 12H; 4×CH$_3$), 1.24–1.51 (m, 48H; 24×CH$_2$), 2.28 (s, 6H; 2×CH$_3$), 2.43 (m, 8H; 4×PH$_2$), 6.72 (d, 1H; C4H), 6.95 ppm (d, 2H; C3H and C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.8, 18.8, 19.3, 21.7, 22.2, 28.8, 29.2, 29.4, 29.5, 30.3, 30.4, 31.0, 31.8, 57.8, 119.4, 126.5, 128.3 ppm; IR: $\tilde{\nu}$=957, 2924, 2855, 2364, 2339, 1584, 1559, 1462, 1420, 1369, 1328, 1294, 1102, 1086, 1053, 881, 843, 743, 720 cm^{-1}. MS (ESI): *m*/*z*: 121.1 [2,6-Me-PhO].

Trihexyl(tetradecyl)phosphonium *p*-isopropylphenolate ([P$_{66614}$][4-*i*Pr-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.88 (m, 12H; 4×CH$_3$), 1.19 (d, 6H; 2×CH$_3$), 1.28–1.45 (m, 48H; 24×CH$_2$), 2.29 (m, 8H; 4×PH$_2$), 2.85 (m, 1H; CH), 6.91 (d, 2H; C2H and C6H), 6.97 ppm (d, 2H; C3H and C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.7, 18.4, 18.9, 21.5, 22.1, 22.4, 24.1, 29.1, 29.4, 30.0, 30.2, 30.8, 31.6, 32.9, 115.3, 126.6, 138.2, 155.8 ppm; IR: $\tilde{\nu}$=2955, 2924, 2855, 1595, 1559, 1499, 1458, 1379, 1300, 1165, 1110, 1049, 833, 720 cm^{-1}. MS (ESI): *m*/*z*: 135.1 [4-*i*Pr-PhO].

Trihexyl(tetradecyl)phosphonium *p*-tertbutylphenolate ([P$_{66614}$][4-*t*Bu-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.89 (m, 12H; 4×CH$_3$), 1.21–1.46 (m, 48H; 24×CH$_2$), 1.23 (s, 9H; 3×CH$_3$), 2.34 (m, 8H; 4×PH$_2$), 6.93 (d, 2H; C2H and C6H), 7.14 ppm (d, 2H; C3H and C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.7, 18.6, 19.0, 21.6, 22.1, 29.1, 29.3, 29.5, 30.1, 30.3, 30.8, 31.4, 114.9, 125.6, 140.9, 155.1 ppm; IR: $\tilde{\nu}$=2956, 2924, 2855, 1595, 1501, 1460, 1413, 1390, 1360, 1301, 1264, 1173, 1105, 1054, 995, 833, 720 cm^{-1}. MS (ESI): *m*/*z*: 149.1 [4-*t*Bu-PhO].

Trihexyl(tetradecyl)phosphonium *m*-methoxyphenolate ([P$_{66614}$][3-MeO-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.87 (m, 12H; 4×CH$_3$), 1.25–1.42 (m, 48H; 24×CH$_2$), 2.20 (m, 8H; 4×PH$_2$), 3.68 (s, 3H; OCH$_3$), 6.19 (m, 1H; C6H), 6.46 (s, 1H; C2H), 6.47 (m, 1H; C4H), 6.95 (m, 1H; C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.7, 14.0, 18.4, 18.9, 21.6, 22.2, 28.8, 29.2, 29.4, 30.1, 30.3, 30.9, 31.7, 51.7, 102.2, 109.5, 129.2, 160.7, 162.6 ppm; IR: $\tilde{\nu}$=2955, 2924, 2855, 1590, 1558, 1467, 1323, 1297, 1258, 1205, 1147, 1112, 1044, 987, 842, 753, 720 cm^{-1}. MS (ESI): *m*/*z*: 123.0 [3-MeO-PhO].

Trihexyl(tetradecyl)phosphonium *m*-dimethylaminophenolate ([P$_{66614}$][3-NMe$_2$-PhO]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.87 (m, 12H; 4×CH$_3$), 1.25–1.41 (m, 48H; 24×CH$_2$), 2.21 (m, 8H; 4×PH$_2$), 2.84 (s, 6H; N-(CH$_3$)$_2$), 6.35 (m, 3H; C2H, C4H, and C6H), 6.94 (m, 1H; C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.8, 18.4, 18.9, 21.6, 22.2, 22.5, 28.0, 28.8, 29.0, 29.2, 29.5, 30.1, 30.3, 30.5, 30.6, 30.8, 31.1, 31.7, 40.6, 101.3, 102.5, 105.5, 129.1,152.0, 160.5 ppm; IR: $\tilde{\nu}$=2954, 2922, 2853, 1577, 1457, 1347, 1247, 1147, 1161, 1057, 978, 834, 749, 719 cm^{-1}.

Trihexyl(tetradecyl)phosphonium 1-naphtholate ([P$_{66614}$][1-Naph]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.87 (m, 12H; 4×CH$_3$), 1.18–1.27 (m, 48H; 24×CH$_2$), 1.75 (m, 8H; 4×PH$_2$), 6.78 (m, 2H; C2H and C3H), 7.55 (d, 1H; C5H), 7.13 (m, 2H; C4H and C6H), 7.24 (m, 1H; C7H), 8.35 (d, 1H; C8H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.8, 17.9 18.4, 18.9, 21.3, 22.2, 22.5, 28.8, 29.1, 29.2, 29.4, 29.5, 30.0, 30.1, 30.3, 30.4, 30.9, 31.8, 109.4, 112.3, 122.2, 123.9, 124.9, 126.9, 127.6, 128.2, 135.4, 161.2 ppm; IR: $\tilde{\nu}$=2956, 2923, 2854, 1554, 1443, 1410, 1315, 1080, 1012, 963, 885, 767 cm^{-1}. MS (ESI): *m*/*z*: 143.0 [1-Naph].

Trihexyl(tetradecyl)phosphonium 2-naphtholate [2-Naph]): ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.86 (m, 12H; 4×CH$_3$), 1.24–1.34 (m, 48H; 24×CH$_2$), 2.10 (m, 8H; 4×PH$_2$), 7.07 (m, 1H; C3H), 7.10 (m, 2H; C1H and C6H), 7.46 (m, 2H; C7H and C8H), 7.60 (m, 2H; C4H and C5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=13.8, 18.4, 18.8, 21.5, 22.2, 22.5, 28.1, 28.8, 29.1, 29.2, 29.4, 29.5, 30.1, 30.2, 30.4, 30.6, 30.9, 31.2, 31.8, 109.4, 120.3, 120.8, 124.8, 126.7, 127.3, 128.6, 135.6, 160.1 ppm; IR: $\tilde{\nu}$=2955, 2923, 2854, 1611, 1584, 1551, 1490, 1434, 1341, 1279, 1257, 1221, 1175, 1109, 1015, 981, 834, 811, 741, 724 cm^{-1}. MS (ESI): *m*/*z*: 143.0 [2-Naph].

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20976151, 21176205, and 20704035) and by the Fundamental Research Funds of the Central Universities. The authors also gratefully acknowledge the support of the division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

---

[1] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789.

[2] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3691.

[3] C. A. Angell, N. Byrne, J. P. Belieres, *Acc. Chem. Res.* **2007**, *40*, 1228–1236.

[4] J. Y. Weng, C. M. Wang, H. R. Li, Y. Wang, *Green Chem.* **2006**, *8*, 96–99.

[5] Z. F. Zhang, E. Xie, W. J. Li, S. Q. Hu, J. L. Song, T. Jiang, B. X. Han, *Angew. Chem.* **2008**, *120*, 1143–1145; *Angew. Chem. Int. Ed.* **2008**, *47*, 1127–1129.

[6] H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597–1600.

[7] A. K. Chakraborti, S. R. Roy, *J. Am. Chem. Soc.* **2009**, *131*, 6902–6903.

[8] W. Z. Wu, B. X. Han, H. X. Gao, Z. M. Liu, T. Jiang, J. Huang, *Angew. Chem.* **2004**, *116*, 2469–2471; *Angew. Chem. Int. Ed.* **2004**, *43*, 2415–2417.

[9] J. E. Bara, T. K. Carlisle, C. J. Gabriel, D. Camper, A. Finotello, D. L. Gin, R. D. Noble, *Ind. Eng. Chem. Res.* **2009**, *48*, 2739–2751.

[10] D. J. Tempel, P. B. Henderson, J. R. Brzozowski, R. M. Pearlstein, H. S. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 400–401.

[11] J. S. Lee, X. Q. Wang, H. M. Luo, G. A. Baker, S. Dai, *J. Am. Chem. Soc.* **2009**, *131*, 4596–4597.

[12] J. F. Huang, H. M. Luo, C. D. Liang, I. W. Sun, G. A. Baker, S. Dai, *J. Am. Chem. Soc.* **2005**, *127*, 12784–12785.

[13] K. L. Ding, Z. J. Miao, Z. M. Liu, Z. F. Zhang, B. X. Han, G. M. An, S. D. Miao, Y. Xie, *J. Am. Chem. Soc.* **2007**, *129*, 6362–6363.
[14] T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083.
[15] D. Camper, J. E. Bara, D. L. Gin, R. D. Noble, *Ind. Eng. Chem. Res.* **2008**, *47*, 8496–8498.
[16] S. M. Chen, J. Zhang, T. Wu, P. Y. Feng, X. H. Bu, *J. Am. Chem. Soc.* **2009**, *131*, 16027–16028.
[17] A. J. Boydston, C. S. Pecinovsky, S. T. Chao, C. W. Bielawski, *J. Am. Chem. Soc.* **2007**, *129*, 14550–14551.
[18] Z. J. Lin, D. S. Wragg, J. E. Warren, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 10334–10335.
[19] C. M. Wang, G. K. Cui, X. Y. Luo, Y. J. Xu, H. R. Li, S. Dai, *J. Am. Chem. Soc.* **2011**, *133*, 11916–11919.
[20] K. Fukumoto, M. Yoshizawa, H. Ohno, *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399.
[21] Y. Q. Zhang, S. J. Zhang, X. M. Lu, Q. Zhou, W. Fan, X. P. Zhang, *Chem. Eur. J.* **2009**, *15*, 3003–3011.
[22] J. M. Zhang, S. J. Zhang, K. Dong, Y. Q. Zhang, Y. Q. Shen, X. M. Lv, *Chem. Eur. J.* **2006**, *12*, 4021–4026.
[23] J. Alejandre, J. L. Rivera, M. A. Mora, V. de La Garza, *J. Phys. Chem. B* **2000**, *104*, 1332–1337.
[24] D. J. Heldebrant, C. R. Yonker, P. G. Jessop, L. Phan, *Energy Environ. Sci.* **2008**, *1*, 487–493.
[25] J. E. Bara, D. E. Camper, D. L. Gin, R. D. Noble, *Acc. Chem. Res.* **2010**, *43*, 152–159.
[26] J. E. Bara, C. J. Gabriel, S. Lessmann, T. K. Carlisle, A. Finotello, D. L. Gin, R. D. Noble, *Ind. Eng. Chem. Res.* **2007**, *46*, 5380–5386.
[27] T. K. Carlisle, J. E. Bara, C. J. Gabriel, R. D. Noble, D. L. Gin, *Ind. Eng. Chem. Res.* **2008**, *47*, 7005–7012.
[28] Y. Wang, C. M. Wang, L. Q. Zhang, H. R. Li, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5976–5982.
[29] J. L. Anderson, J. K. Dixon, J. F. Brennecke, *Acc. Chem. Res.* **2007**, *40*, 1208–1216.
[30] X. C. Zhang, Z. P. Liu, W. C. Wang, *Aiche J.* **2008**, *54*, 2717–2728.
[31] E. D. Bates, R. D. Mayton, I. Ntai, J. H. Davis, *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
[32] M. D. Soutullo, C. I. Odom, B. F. Wicker, C. N. Henderson, A. C. Stenson, J. H. Davis, *Chem. Mater.* **2007**, *19*, 3581–3583.
[33] B. E. Gurkan, J. C. de La Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider, J. F. Brennecke, *J. Am. Chem. Soc.* **2010**, *132*, 2116–2117.
[34] X. Y. Li, M. Q. Hou, Z. F. Zhang, B. X. Han, G. Y. Yang, X. L. Wang, L. Z. Zou, *Green Chem.* **2008**, *10*, 879–884.
[35] C. M. Wang, X. Y. Luo, H. M. Luo, D. E. Jiang, H. R. Li, S. Dai, *Angew. Chem.* **2011**, *123*, 5020–5024; *Angew. Chem. Int. Ed.* **2011**, *50*, 4918–4922.
[36] C. M. Wang, H. M. Luo, D. E. Jiang, H. R. Li, S. Dai, *Angew. Chem.* **2010**, *122*, 6114–6117; *Angew. Chem. Int. Ed.* **2010**, *49*, 5978–5981.
[37] K. E. Gutowski, E. J. Maginn, *J. Am. Chem. Soc.* **2008**, *130*, 14690–14704.
[38] P. G. Jessop, D. J. Heldebrant, X. W. Li, C. A. Eckert, C. L. Liotta, *Nature* **2005**, *436*, 1102–1102.
[39] C. M. Wang, S. M. Mahurin, H. M. Luo, G. A. Baker, H. R. Li, S. Dai, *Green Chem.* **2010**, *12*, 870–874.
[40] D. J. Heldebrant, C. R. Yonker, P. G. Jessop, L. Phan, *Chem. Eur. J.* **2009**, *15*, 7619–7627.
[41] C. M. Teague, S. Dai, D. E. Jiang, *J. Phys. Chem. A* **2010**, *114*, 11761–11767.

Received: October 3, 2011