Acylamido-Based Anion-Functionalized Ionic Liquids for Efficient SO 2 Capture through Multiple-Site Interactions

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Acylamido-Based Anion-Functionalized Ionic Liquids for Efficient SO$_2$ Capture through Multiple-Site Interactions

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S *Supporting Information*

ABSTRACT: Acid gases such as SO$_2$ can be absorbed by ionic liquids (ILs) because of their unique properties. In this work, we developed a new approach for improving SO$_2$ absorption by novel acylamido-based anion-functionalized ILs. Several kinds of such ILs with different structures of acylamido group (anionic acylamide) were designed, prepared, and used for efficient capture of SO$_2$. It was shown that these acylamido-based ILs strongly interacted with SO$_2$, resulting in a very high SO$_2$ capacity up to ~4.5 mol SO$_2$ per mole of IL. The interactions between acylamido-based ILs and SO$_2$ were investigated by FT-IR, NMR, and quantum chemical calculations. It was found that the dramatic enhancement of SO$_2$ absorption capacity was originated from the multiple-site interactions such as N···S and C═O···S interactions between the anion and SO$_2$. Furthermore, the captured SO$_2$ was easy to release by heating or bubbling N$_2$ through the SO$_2$-saturated ILs. This novel strategy provides an excellent alternative to current SO$_2$ capture technologies.

KEYWORDS: *Ionic liquid, SO$_2$, Acylamide, Multiple-site interaction, Sulfur capture*
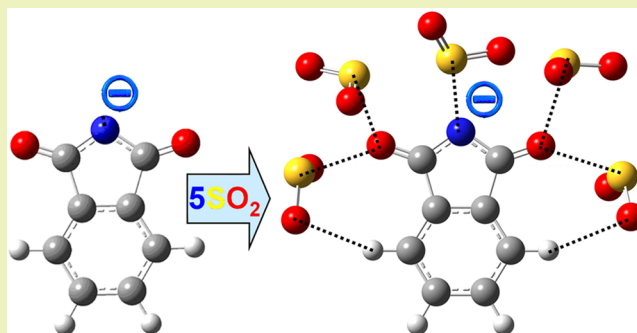
INTRODUCTION

Controlling and minimizing the emissions of such acid gas as SO$_2$ are highly important, because SO$_2$ is a significant source of atmospheric pollution that threatens environment and human health. Novel materials and processes for efficient, reversible and economical capture of SO$_2$ are highly desired to develop and are of critical importance for environmental protection. Although several conventional removal processes, such as limestone scrubbing and ammonia scrubbing, have been used for flue gas desulfurization (FGD), the inherent disadvantages of these technologies should not be ignored, including the production of large quantities of wastewater and useless byproducts.[1−3]

Recently, ionic liquids (ILs) have been proposed as better acid gas absorbents due to their unique properties, such as extremely low vapor pressure, wide liquid temperature range, nonflammability, chemical stability, and tunable structure and properties.[4−12] SO$_2$ has a high solubility in some ILs through physical interaction,[13−15] especially in ether-functionalized ILs.[16,17] However, effective capture of SO$_2$ from flue gas requires strong interaction between IL and SO$_2$ because of the relatively low SO$_2$ partial pressure in this stream. Han et al.[18] reported the first example for chemical absorption of SO$_2$ by 1,1,3,3-tetramethylguanidinium lactate ([TMG][L]), which absorbed about 1.0 mol SO$_2$ per mole of IL at 1 bar with 8% SO$_2$ in a gas mixture of SO$_2$ and N$_2$. Since then, other kinds of ILs, such as hydroxyl ammonium ILs,[19,20] imidazolium

ILs,[14,21−23] thiocyanate ILs,[24−26] phenolate ILs,[27,28] poly-(ILs),[29,30] and supported IL membranes (SILMs)[31,32] were used to capture and separate SO$_2$. Recently, Wang et al.[33−36] reported a new strategy for acid gas absorption by tunable azolate-ILs and found that trihexyl(tetradecyl) phosphonium tetrazolate ([P$_{66614}$][Tetz]) could capture 3.72 mol SO$_2$ per mole IL through multiple-site interactions between anion and SO$_2$.[33] Other groups studied the performance of carbon capture[37,38] or sulfur capture[39,40] by these functionalized ILs. Such azolate-ILs open a new door to achieving high gas capture capacity and rapid absorption kinetics. Nevertheless, development of alternative ILs that are able to achieve rapid and reversible SO$_2$ capture at high capacity is always highly desired. This requirement prompted us to investigate new anion-functionalized ILs for SO$_2$ capture.

In this work, we describe a new strategy for significant improvement of the capture of SO$_2$ through acylamido-based anion-functionalized ILs. For this purpose, several kinds of acylamido-based ILs were prepared and applied to the capture of SO$_2$ (see Chart 1 for structures of the ILs). It was found that these ILs exhibited an extremely high capacity up to about 4.5 mol SO$_2$ per mole IL and excellent reversibility. The promoting role of acylamido group (anionic acylamide) for the enhance-

Chart 1. Structure and Abbreviations of the Cation and Acylamido-Based Anions Employed in This Work for SO$_2$ Capture
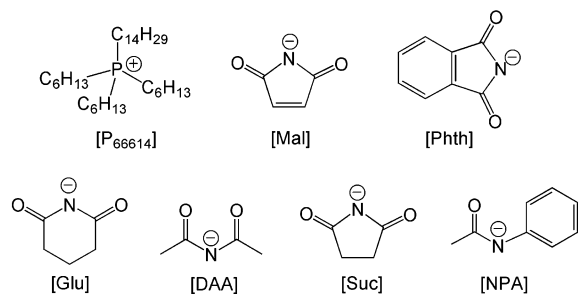
ment of SO$_2$ capture was studied through a combination of spectroscopic investigations and quantum chemical calculations, and the importance of the N···S interaction and the enhanced C=O···S interaction between acylamido-based anion and SO$_2$ was emphasized.

EXPERIMENTAL METHOD

Materials. Several kinds of different acylamides, such as maleimide (Mal), o-phthalimide (Phth), glutarimide (Glu), diacetamide (DAA), succinimide (Suc), and acetanilide (NPA), and carbonyl-free compounds, such as pyrrole (Pyro) and indole (Indo), were selected as proton donors and purchased from Sigma-Aldrich. Trihexyl-(tetradecyl)phosphonium bromide ([P$_{66614}$][Br]) was purchased from Strem Chemicals. A series of gases with different SO$_2$ partial pressure were prepared by mixing SO$_2$ (99.95%) and N$_2$ (99.9993%) which were obtained from Beijing Oxygen Plant Specialty Gases Institute Co., Ltd. An anion-exchange resin (Amersep 900 OH) was obtained from Alfa Aesar. All chemicals were in the highest purity grade possible and were used as received unless otherwise stated.

Preparation of ILs. In a typical synthesis of acylamido-based IL such as [P$_{66614}$][Phth], equimolar Phth was added to an ethanol solution of phosphonium hydroxide ([P$_{66614}$][OH]), which was prepared from [P$_{66614}$][Br] by the anion-exchange method.[41−43] The mixture was stirred at room temperature for 24 h. Then, ethanol and water were distilled off at 60 °C under reduced pressure. All the ILs obtained were dried with P$_2$O$_5$ under vacuum at 60 °C for 24 h to reduce possible traces of water.

Characterizations. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz) in DMSO-d_6 or CDCl$_3$ with tetramethylsilane (TMS) as the standard. FT-IR spectra were recorded on a Nicolet 4700 FT-IR spectrometer. The structures of these ILs were confirmed by NMR and FT-IR spectra measurements, and no impurities were found by NMR spectra. NMR and FT-IR spectra measurements were also performed to track SO$_2$ binding and release. The water content of these ILs was determined with a Karl Fisher titrator (Mettler Toledo DL32, Switzerland) and found to be less than 0.1 wt %. The residual bromide content of the ILs was determined by a semiquantitative Nessler cylinder method, which showed that bromide content was lower than 0.15 wt %. Viscosity was determined by a Brookfield DV2T viscometer at 25 °C.

SO$_2$ Capture and Release Experiments. In a typical absorption of SO$_2$, SO$_2$ of atmospheric pressure was bubbled through about 1.0 g IL in a glass container with an inner diameter of 10 mm, and the flow rate was about 40 mL min^{-1}. The glass container was partly immersed in a circulation water bath of desirable temperature. The amount of SO$_2$ absorbed was determined at regular intervals by the electronic balance with an accuracy of ±0.1 mg until the weight remained constant. The amount of SO$_2$ absorbed could be calculated by subtracting the amount of IL. For the absorption of SO$_2$ under reduced pressure, SO$_2$ was diluted with N$_2$ in order to reduce the partial pressure of SO$_2$ passing through the system. The SO$_2$ partial pressure was controlled by changing the flow rate ratio of SO$_2$ and N$_2$. The standard deviations of the absorption loadings under 1.0 bar is

0.05 mol SO$_2$ per mole IL. Desorption of SO$_2$ from saturated IL solutions was carried out and monitored in an analogous way as for the described absorption procedure. The ILs were regenerated by heating or bubbling N$_2$ through the SO$_2$-saturated ILs. In a typical desorption of SO$_2$, N$_2$ of atmospheric pressure was bubbled through about 1.0 g SO$_2$-saturated IL in a glass container, which was partly immersed in a circulation oil bath at 80 or 120 °C, and the flow rate was about 40 mL min^{-1}. The release of SO$_2$ was determined at regular intervals by gravimetric method.

Effect of Water on SO$_2$ Absorption. The effect of water in the ILs on the absorption of SO$_2$ was investigated at ambient pressure and 20 °C. First of all, N$_2$ was bubbled through water to form 100% humidity N$_2$, which was then bubbled through about 1.0 g IL in a glass container with an inner diameter of 10 mm, and the flow rate was about 40 mL min^{-1}. The amount of water absorbed was determined at regular intervals by an electronic balance with an accuracy of ±0.1 mg. The standard deviation of the absorption loadings is 0.03 g H$_2$O per g IL under 1.0 bar. Second, SO$_2$ was bubbled through water (to form 100% humidity SO$_2$) and then through about 1.0 g IL in a glass container with an inner diameter of 10 mm, and the flow rate was also about 40 mL min^{-1}. The amount of SO$_2$ and water absorbed was determined at regular intervals by the same electronic balance. The difference of the IL saturated with SO$_2$ and water relative to the IL saturated with N$_2$ and water could be calculated according to gravimetric method, which was the amount of SO$_2$ absorption capacities of ILs under the influence of water.

RESULTS AND DISCUSSION

Absorption of SO$_2$. In this work, acylamido-based ILs were easily prepared by acid−base neutralization reaction of different acylamides (Mal, Phth, Glu, DAA, Suc, and NPA) with a solution of [P$_{66614}$][OH] in ethanol, which was synthesized by anion-exchange method. In order to investigate the effect of the C=O group on the performance of SO$_2$ capture, we also prepared some carbonyl-free ILs using Pyro and Indo by the same method. The structures of these ILs were verified by NMR and FT-IR spectra (Supporting Information). Physical properties including viscosity and density of all these ILs were also determined, and the results were listed in Table S1. It can be seen that the density values of the ILs were in the range of 0.905−0.980 g cm^{-3}, while the viscosity values were in the range of 89.2−463.2 cP at 25 °C. In addition, although some of the functionalized ILs have higher viscosity values, the viscosity of ILs was decreased when SO$_2$ was absorbed in them.

The effect of chemical structure of the acylamido-based ILs on the absorption of SO$_2$ was investigated, and the results were shown in Figure 1. It can be seen that the absorption capacities of all these ILs were very high. For the ILs containing
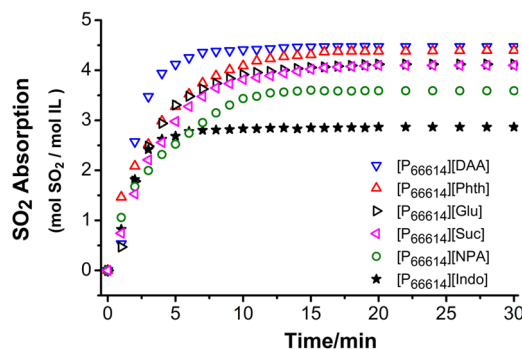

Figure 1. SO$_2$ absorption by typical acylamido-based anion-functionalized ILs as a function of time at 20 °C and 1 bar under SO$_2$ (40 mL min^{-1}).

acylamido functional group ($-N-C=O$) in their anions including $[P_{66614}][DAA]$, $[P_{66614}][Phth]$, $[P_{66614}][Glu]$, $[P_{66614}][Suc]$, $[P_{66614}][Mal]$, and $[P_{66614}][NPA]$, their absorption capacities at 20 °C and 1 bar were 4.47, 4.40, 4.12, 4.10, 4.15, and 3.59 mol SO_2 per mole IL, respectively. Compared with these acylamido-based ILs, carbonyl-free ILs $[P_{66614}]-[Pyro]$ and $[P_{66614}][Indo]$ only exhibited 2.52[44] and 2.86 mol SO_2 per mole IL. This indicates that SO_2 absorption capacities increased significantly due to the N···S interaction and the enhanced C=O···S interaction between the acylamido-based anions and SO_2. Therefore, it seems likely that the enhanced absorption performance of the acylamido-based anions for SO_2 than their carbonyl-free counterparts can only be ascribed to the C=O···S interaction. Another important feature on SO_2 capture by these acylamido-based ILs is that the absorption kinetics is very fast. As can be seen in Figure 1, SO_2 absorption by these acylamido-based ILs was almost complete within the first 10 min.

The desorption of SO_2 by these functionalized ILs was also examined at 80 °C, 1.0 bar and 40 mL min^{-1} N_2, and the results were shown in Table S2. It can be seen that desorption of the SO_2-saturated ILs for 30 min was nearly complete under such a typical desorption condition, except for SO_2-saturated $[P_{66614}]-[Phth]$, $[P_{66614}][Mal]$, and $[P_{66614}][NPA]$, the desorption of which was not easy possibly because of the strong conjugated effect. However, desorption efficiency could be increased by treating the SO_2-saturated ILs at higher temperatures. For example, at 120 °C and keeping the other desorption condition unchanged, all the desorption was almost completed.

Figure 2a shows the effect of SO_2 partial pressure on its absorption by $[P_{66614}][Phth]$ (an acylamido-based IL) and
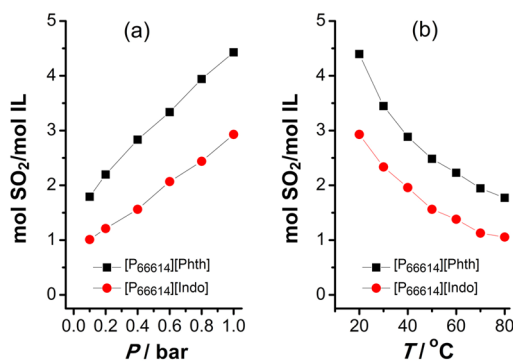

Figure 2. Effect of pressure (at 20 °C, a) and temperature (at 1.0 bar, b) on SO_2 absorption performance by acylamido-based IL $[P_{66614}]-[Phth]$ (■) compared with carbonyl-free IL $[P_{66614}][Indo]$ (●).
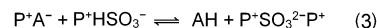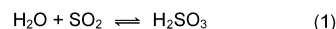
$[P_{66614}][Indo]$ (a carbonyl-free IL) at 20 °C. It was shown that as the pressure decreased from 1.0 to 0.1 bar, the molar ratios of SO_2 to $[P_{66614}][Phth]$ and $[P_{66614}][Indo]$ decreased from 4.40 and 2.86 to 1.80 and 1.00, respectively. Figure 2b shows the temperature dependence of the SO_2 absorption at 1.0 bar. It can be seen that when the temperature was increased from 20 to 80 °C, SO_2 absorption capacity by $[P_{66614}][Phth]$ and $[P_{66614}][Indo]$ decreased from 4.40 and 2.86 to 1.77 and 1.10 mol SO_2 per mole IL, respectively. It is known that the difference in chemical structure between $[P_{66614}][Phth]$ and $[P_{66614}][Indo]$ is the $-N-C=O$ unit in the [Phth] anion. Thus, we can deduce that it is $-N-C=O$ which enhances SO_2 capture. Additionally, it is also indicated that the captured SO_2 by $[P_{66614}][Phth]$ could be facilely stripped by heating or

bubbling N_2 through the IL. The effect of pressure (at 20 °C) and temperature (at 1.0 bar) on the absorption performance of the other acylamido-based ILs $[P_{66614}][DAA]$ and $[P_{66614}][NPA]$ was shown in Figure S1. Furthermore, the effect of low SO_2 partial pressure such as 10%, 1%, and 0.2% SO_2 on the absorption was also investigated (Table S3). As can be seen, the absorption capacity of SO_2 by ILs such as $[P_{66614}][Phth]$ was reduced to 1.09 and 1.03 mol SO_2 per mole IL when the content of SO_2 was decreased to 1% and 0.2%, respectively.

The effect of water on SO_2 absorption by acylamido-based ILs was also investigated, and the result was shown in Table S4. As can be seen, the effect of water on the capture of SO_2 was very weak. For example, SO_2 absorption capacity of $[P_{66614}]-[Phth]$ was 4.32 mol SO_2 per mole IL at 20 °C and 1 bar under 100% humidity SO_2, which was very close to the value of 4.40 mol SO_2 per mole IL under dry SO_2. When water is present in the IL or in the gas, SO_2 reacts with water to form H_2SO_3. Taking $[P_{66614}][Phth]$ as an example, since Phth ($pK_a = 8.3$) is a weaker acid than H_2SO_3 ($pK_{a1} = 1.9$, $pK_{a2} = 7.21$), the conjugated base ([Phth]) would be favorable to existence as neutral Phth in the presence of H_2SO_3. As a result, $[P_{66614}][Phth]$ would react with H_2SO_3 to form $[P_{66614}]^+[HSO_3]^-$ and neutral Phth (Scheme 1).[45,46] However,

Scheme 1. Proposed Absorption Mechanism of SO_2 by Acylamido-Based ILs in the Presence of Water[a]

In the presence of water:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3 \quad (1)$$

$$P^+A^- + H_2SO_3 \rightleftharpoons AH + P^+HSO_3^- \quad (2)$$

$$P^+A^- + P^+HSO_3^- \rightleftharpoons AH + P^+SO_3{}^{2-}P^+ \quad (3)$$

[a]P^+ stands for phosphonium cation, A^- stands for acylamido-based anion, and AH stands for neutral acylamides.

only very little $[P_{66614}]_2{}^{2+}[SO_3]^{2-}$ was formed due to the formation of large amount of H_2SO_3. Thus, the theoretical results were further supported by FT-IR spectroscopy (Figure S2).

Multiple SO_2 absorption cycles were investigated by using $[P_{66614}][Phth]$ as an example (Figure 3). It is evident that the SO_2 absorption process could be recycled for more than six times without a loss of absorption capability, indicating that SO_2 absorption process by $[P_{66614}][Phth]$ was highly reversible.
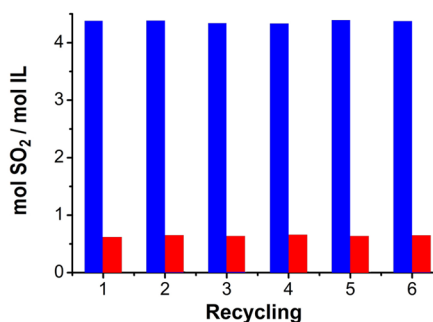

Figure 3. Six consecutive cycles of SO_2 absorption and release by the IL $[P_{66614}][Phth]$. SO_2 absorption (blue) was carried out at 20 °C and 1 bar under SO_2 (40 mL min^{-1}) for 30 min, and desorption (red) was performed at 80 °C and 1 bar under N_2 (40 mL min^{-1}) for 30 min.

Furthermore, the thermal stability of $[P_{66614}][Phth]$ was also investigated for 360 min under typical desorption condition (80 °C, 1.0 bar, 40 mL min^{-1} N_2), and the results were shown in Figure S3. It can be seen that no obvious loss of weight was found for $[P_{66614}][Phth]$ in 360 min, indicating high stability of the acylamido-based ILs.

Considering the fact of extremely high capacity, rapid rate, and excellent reversibility, we believe that these acylamido-based ILs provide a potential alternative for the capture of SO_2 (Table S5). At this stage, one may wonder why these ILs show such a high capacity for SO_2 capture. This is certainly resulted from the chemical structure of these interesting ILs. It can be seen from Chart 1 that there are two kinds of activate interaction sites including N atom and C=O group in the anions of these ILs, thus multiple-site interaction between the acylamido-based anion and SO_2 may be the reason.

Quantum Chemical Calculations. To investigate the interactions between the acylamido-based ILs and SO_2, we calculated the charge distribution of N and O atoms on the acylamido-based anion from natural bond orbital (NBO)[47] analysis at B3LYP/6-31++G(p,d) level[48−51] (Table 1). To our

Table 1. Effect of Chemical Structure of the Acylamido-Based Anions on Interaction Enthalpy and NBO Atomic Charge of N and O Atoms on the Acylamido Group

anion	$\Delta H^{a,b}$		NBO atomic charge^b	
	ΔH_1	ΔH_2	N	O on C=O
[Pyro]			−0.596	
[Mal]	−66.5	−48.4	−0.710	−0.666, −0.666
[Indo]			−0.594	
[Phth]	−55.8	−43.9	−0.675	−0.661, −0.661
[Glu]	−76.3	−55.2	−0.688	−0.700, −0.700
[DAA]	−82.0	−53.7	−0.716	−0.745, −0.699
[Suc]	−74.3	−54.8	−0.679	−0.701, −0.701
[NPA]	−84.6		−0.702	−0.750

^{a}Interaction enthalpies of the complexes of C=O group on the anion with the closest SO_2 molecule, kJ mol^{-1}. ^{b}Carried out at the B3LYP/6-31++G(d,p) level.

surprise, it was found that when the electro-withdrawing carbonyl group was added beside the basic N atom to form acylamido group on the anion, both the N and O atoms on the acylamido group showed increased NBO atomic charge compared with the N atom on carbonyl-free anion. For example, the NBO atomic charges of N and O atoms on the anion [Phth] were −0.675 and −0.661, respectively, while that of N atom on the anion [Indo] was only −0.594. Thus, the NBO atomic charge of N atom on carbonyl-free anion could be easily tuned through adding C=O group to form acylamido-based anion. Therefore, we believe there must lie in an enhanced cooperative interaction between the C=O group and N atom on the anion, which led to a negative C=O group and increased absorption capacity through the enhanced C=O···S interaction between C=O and SO_2. Clearly, this new strategy is useful for the design of new highly efficient ILs for gas separation.

In order to further investigate the role of acylamido group on the anion in SO_2 absorption, theoretical calculation was performed by using the Gaussian 09 program.[52] For each set calculations, we calculated the geometry and energy optimization for each free anion, free SO_2 molecule, and each anion-SO_2 complex at the B3LYP/6-31++G(p,d) level. The optimized structures reflecting the C=O···S interaction between C=O group and SO_2 were shown in Figures 4 and S4. It can be seen from Figure 4a and b that the intermolecular distance between S atom in SO_2 and O atom in C=O group of $[Phth]\cdot SO_2$ (C=O group of anion with the closest SO_2 molecule) and $[Phth]\cdot 2SO_2$ are predicted to be 2.342 and 2.445 Å, which corresponds to a reduction of approximately 29.4% and 26.4% of the sum of the van der Waals radii of the two interacting atoms O and S,[53] respectively. Hydrogen bond was formed between H of C−H bond of the phenyl on the anion and O of S=O bond of the SO_2. There are two S=O···H−C hydrogen bonds formed between SO_2 and [Phth] anion, and the bond distance was both predicted to be 2.347 Å (Figure 4b).[54] Additionally, the calculated enthalpies for $[Phth]\cdot SO_2$ and $[Phth]\cdot 2SO_2$ complexes were −55.8 and −43.9 kJ mol^{-1}, respectively. This indicates that the C=O···S interaction
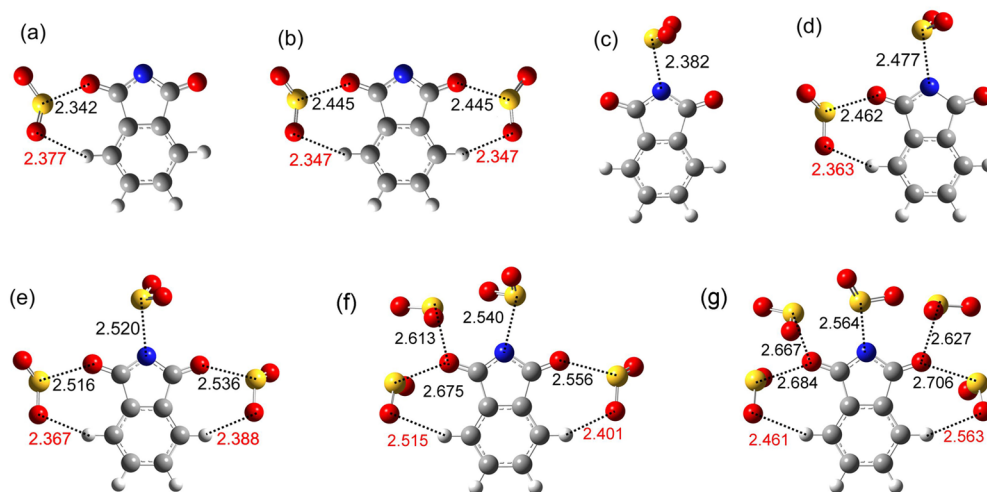

Figure 4. Optimized structures of $[Phth]−SO_2$ complexes at B3LYP/6-31++G(d,p) level. (a and b) C=O groups in [Phth] anion with the closest SO_2 molecules: (a) $[Phth]\cdot SO_2$, $\Delta H = -55.8$ kJ mol^{-1}; (b) $[Phth]\cdot 2SO_2$, $\Delta H = -43.9$ kJ mol^{-1}; (c−g) multiple-site interactions between the anion [Phth] and SO_2 molecules; (c) $[Phth]−SO_2$, $\Delta H = -68.7$ kJ mol^{-1}; (d) $[Phth]−2SO_2$, $\Delta H = -42.3$ kJ mol^{-1}; (e), $[Phth]−3SO_2$, $\Delta H = -39.5$ kJ mol^{-1}; (f) $[Phth]−4SO_2$, $\Delta H = -34.4$ kJ mol^{-1}; (g) $[Phth]−5SO_2$, $\Delta H = -30.9$ kJ mol^{-1}. Note that van der Waals radii (Å) are 1.70 (C), 1.20 (H), 1.52 (O), 1.55 (N), and 1.80 (S), repectively.[53] O, red; S, yellow; N, blue; C, gray.

between C=O group on the anion and the closest SO_2 was significantly enhanced (Table 1). Considering the fact that the cation in the IL would influence the gas capture and the effect of the chain length in the cation on absorption enthalpy was weak,[55] the optimized structures and energetics for $[P_{1111}]$-$[Phth]-SO_2$ complexes were also calculated (Figure S5). Taking $[P_{1111}][Phth]\cdot SO_2$ as an example, it can be seen that the intermolecular distance between S of SO_2 and O of $[P_{1111}][Phth]$ is predicted to be 2.517 Å, while O of SO_2 and H of $[Phth]$ in $[P_{1111}][Phth]\cdot SO_2$ would have a weak hydrogen bond interaction (the distance between them is 2.550 Å). In addition, the calculated absorption enthalpies for $[P_{1111}][Phth]\cdot$ SO_2 and $[P_{1111}][Phth]\cdot 2SO_2$ were −30.3 and −26.1 kJ mol^{-1}, which were lower than those for $[Phth]\cdot SO_2$ and $[Phth]\cdot 2SO_2$ (−55.8 and −43.9 kJ mol^{-1}), respectively. These results indicate that the interactions between $[Phth]$ and SO_2 becomes weaker when $[P_{1111}]^+$ is introduced in the calculation. However, the calculated enthalpies for neutral $Phth\cdot SO_2$ and $Phth\cdot 2SO_2$ complexes were only −15.1 and −14.4 kJ mol^{-1}, respectively, indicating that the acylamido-based anions result in strong C=O⋯S interactions.

Furthermore, we calculated the gas-phase reaction energetics between the acylamido-based anion and SO_2 (Table S6). The gas-phase reaction energetics and the geometry optimization of the complexes of $[Phth]$ and SO_2 were shown in Figure 4c−g. As can be seen, the calculated absorption enthalpies for $[Phth]-SO_2$, $[Phth]-2SO_2$, $[Phth]-3SO_2$, $[Phth]-4SO_2$, and $[Phth]-5SO_2$ complexes were −68.7, − 42.3, − 39.5, − 34.4, and −30.9 kJ mol^{-1}, respectively, while that for $[DAA]-SO_2$, $[DAA]-2SO_2$, $[DAA]-3SO_2$, $[DAA]-4SO_2$, and $[DAA]-5SO_2$ complexes were −94.7, − 53.8, − 38.1, − 26.3, and −29.8 kJ mol^{-1}, respectively (Figure S4), indicating that as an interaction site added, C=O groups on the anions led to the increase of absorption capacities. At the same time, the absorption enthalpies for $[Phth]-SO_2$ was found to be lower than that for $[Indo]-SO_2$ due to the electron-withdrawing nature of C=O group (Table S6).

Spectroscopic Investigations. The interaction of acylamido-based ILs with SO_2 was further investigated by FT-IR and NMR spectroscopy (Supporting Information) to support the experimental and theoretical results. FT-IR, ^{1}H NMR, and ^{13}C NMR spectra of $[P_{66614}][Phth]$ before and after the absorption of SO_2 were shown in Figure 5.

Compared with the FT-IR spectra of the fresh IL $[P_{66614}][Phth]$ (Figure 5a), the new bands at 1326 and 1144 cm^{-1} formed in the absorption of SO_2 could be assigned to asymmetric stretching and symmetric vibration of S=O bonds, respectively, and the new band at 936 cm^{-1} was attributable to S−O stretches,[18,33] indicating the presence of SO_2 chemisorption. Also, the wavenumber at 1698 cm^{-1} corresponding to C=O stretch increased to 1725 cm^{-1} during the uptake of SO_2, suggesting the presence of C=O⋯S interaction. Meanwhile, another new band at 1044 cm^{-1} should be assigned to the vibration of O−S stretching mode of − OSO_2^-,[56] indicating the strong CO⋯SO_2 interactions between carboxyl group on the anion and SO_2. Furthermore, new band at 2461 cm^{-1} would be assigned to the C−H⋯O hydrogen bonding between C−H bond of the anion and O atom of SO_2.[56−58]

Similarly, compared with the fresh $[P_{66614}][Phth]$, typical peaks in ^{1}H NMR spectra of the anion moved downfield from 7.30 (2H) and 7.36 (2H) ppm to 7.82 (4H) ppm after the absorption of SO_2 (Figure 5b). The changed peak position and peak shape of H atom was probably resulted from the
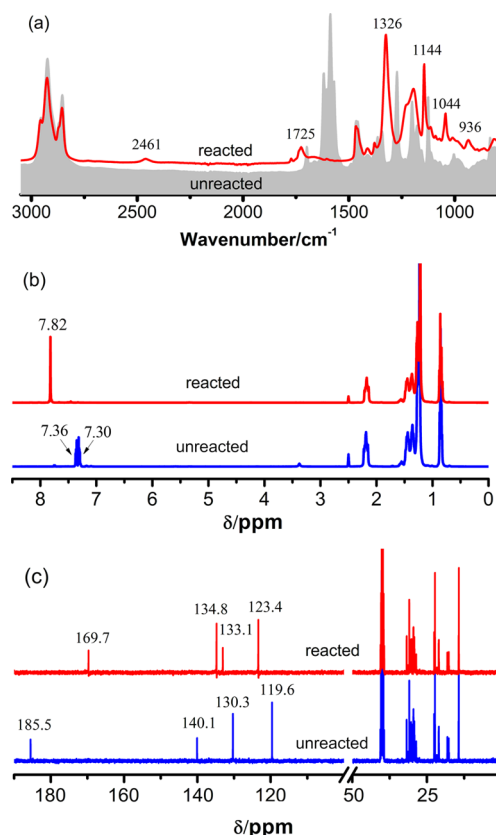

Figure 5. FT-IR (a), ^{1}H NMR (b), and ^{13}C NMR (c) spectra of the fresh IL $[P_{66614}][Phth]$ and $[P_{66614}][Phth]$ after the absorption of SO_2. The NMR data were measured at 20 °C in DMSO-d_6.

formation of C−H⋯O hydrogen bonds of C−H on the anion with S=O in both SO_2 and DMSO-d_6.[59] Furthermore, the peaks of C=O group and C adjacent to the C=O on the $[Phth]$ anion in the ^{13}C NMR spectra shifted upfield from 185.5 and 140.1 ppm to 169.7 and 133.1 ppm, respectively, appeared as a result of the interaction between C=O group and SO_2, while that on phenyl group moved downfield from 130.3 and 119.6 ppm to 134.8 and 123.4 ppm, respectively (Figure 5c).

On the basis of previous reports[18,33] and the observed products, the mechanism of SO_2 absorption by $[P_{66614}][Phth]$ and $[P_{66614}][DAA]$ can be proposed as described in Figure 4 and Figure S5, respectively, which exhibits two kinds of interaction sites of the electronegative O atoms and N atom on the anion to which SO_2 was interacted.

■ CONCLUSIONS

In summary, we have developed a new method for highly efficient capture of SO_2 by acylamido-based anion-functionalized ILs. These ILs reacted with SO_2 through multiple-site interactions between acylamido-based anion and SO_2. Thus, an extremely high SO_2 capacity up to ∼4.5 mol per mole IL was achieved. On the other hand, the captured SO_2 could be easily released by heating or bubbling N_2 through the ILs. Spectroscopic investigations and quantum chemical calculations showed that dramatic enhancement in SO_2 capacity was originated from the strong N⋯S interaction and enhanced C=O⋯S interactions between acylamido-based anion and SO_2. This method using the reactivity of carbonyl group to achieve highly efficient and reversible capture of SO_2 by acylamido-

based ILs provides a potential alternative for acid gas capture and separation such as SO_2, CO_2, and H_2S.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00526.

> NMR and IR data of ionic liquids before and after the absorption of SO_2, Figures S1−S5, Tables S1−S6 (PDF)

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Notes

The authors declare no competing financial interest.

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