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Graphic Abstract

Novel pyridinium-based ionic liquids [NEt₂C₂Py][SCN], [C₄OPy][SCN] and [C₄CNPy][SCN] with high SO₂ gravimetric capacity were developed and the mechanism was discussed.
Improving SO₂ Capture by Tuning Functional Groups on the Cation of Pyridinium-based Ionic Liquids

Shaojuan Zeng a, b, Hongyan He a, Hongshuai Gao a, Xiangping Zhang *, a, Jian Wang a, b, Ying Huang a, b, Suojiang Zhang *, a

Abstract: In this work, three kinds of novel functionalized ionic liquids (ILs) [NEt₂C₂Py][SCN], [C₄OPy][SCN] and [C₄CNPy][SCN] were developed by introducing a tertiary amino group, ether group and nitrile group on the pyridinium cation to improve SO₂ absorption performances. Among the investigated ILs, [NEt₂C₂Py][SCN] showed the highest absorption capacity of 1.06 gSO₂·gIL⁻¹ under ambient conditions due to a combination of the chemical and physical absorption. By contrast, the enhancement in SO₂ capacity by [C₄CNPy][SCN] and [C₄OPy][SCN] is mainly ascribed to the stronger physical interaction between ILs and SO₂ than the conventional IL [C₄Py][SCN]. Meanwhile, higher SO₂/CO₂ selectivity was also obtained using these functionalized ILs, which was increased up to 41% comparing with that of [C₄Py][SCN]. Moreover, the effect of water on SO₂ capacity and the absorption mechanism were studied. The results indicated that the presence of water caused a slight decrease in SO₂ capacity of [C₄CNPy][SCN] and [C₄OPy][SCN] because of physical absorption, whereas a slight increase in SO₂ capacity by [NEt₂C₂Py][SCN] due to the formation of hydrogen sulfite salts through chemical absorption. In addition, three kinds of cation-functionalized ILs could remain the stable absorption performance after five cycles of absorption and desorption, implying these ILs show great potentials for SO₂ capture.

Keywords: pyridinium, ionic liquids, sulfur dioxide, separation, cation-functionalized
1. Introduction

The increasing emission of SO$_2$ from the combustion of fossil fuels has inevitably brought about very adverse influences on environmental issues and human health. Up to now, some traditional methods for flue gas desulfurization (FGD) have been developed, such as limestone scribbling, ammonia scribbling and organic amines scribbling$^{1-3}$. Among them, although limestone scribbling as one of the most attractive approaches has been applied widely in industries, this irreversible process usually results in huge amounts of byproducts and wastewater that doesn’t comply with the sustainable principles. For amine scrubbing that can efficiently minimize additional pollutants and recover SO$_2$, yet they also possess inherent drawbacks, such as the loss of solvents due to their high volatility and degradation as well as high energy consumption for regeneration$^{4-7}$. Therefore, the design and development of a proper absorbent for efficient and reversible capture of SO$_2$ is of critical importance in the absorption process.

Recently, ionic liquids (ILs) have drawn extensive attentions as competitive candidates in the field of acidic gases (CO$_2$$^{8-15}$, SO$_2$$^{16-23}$, and so on) capture and separation owing to their unique properties, such as extremely low vapour pressure, high thermal stability and tuneable properties$^{24-26}$. It was reported that in general SO$_2$ has optimistic physical solubility in conventional ILs, and compared with the cation of ILs the anion plays a primary role in SO$_2$ capture$^{27-29}$. Therefore, a great number of anion-functionalized ILs, such as azole-based ILs$^{30-33}$, benzoate and
phenolate-based ILs with halogen groups\textsuperscript{34}, dicarboxylic acid-based ILs\textsuperscript{35, 36}, lactate-based ILs\textsuperscript{37}, acetate-based ILs\textsuperscript{38}, phosphate-based ILs\textsuperscript{39}, were designed and synthesized for enhanced SO\textsubscript{2} capture by introducing different interaction sites on the anions. Among them, the phenyl-containing azole-based ILs showed the highest capacity of SO\textsubscript{2} absorption, which could reach 5.75 molSO\textsubscript{2}·molIL\textsuperscript{-1} (0.61 gSO\textsubscript{2}·gIL\textsuperscript{-1}) at 20°C and 0.1MPa. However, there are very few types of cation-functionalized ILs for SO\textsubscript{2} capture, which mainly focused on ether-functionalized ILs\textsuperscript{32, 40, 41} and the TMG-based ILs\textsuperscript{13, 42, 43}. For example, Hong et al\textsuperscript{41} developed the ether-functionalized imidazolium-based ILs as highly efficient SO\textsubscript{2} absorbents, which could exhibit very high capacity of up to 6.30 molSO\textsubscript{2}·molIL\textsuperscript{-1} (0.74 gSO\textsubscript{2}·gIL\textsuperscript{-1}) at 30°C and 0.1 MPa. Subsequently, Wang et al\textsuperscript{32} designed a new ether-functionalized IL with tetrazolate anion for SO\textsubscript{2} capture, and the absorption capacity could achieve as high as 5.00 molSO\textsubscript{2}·molIL\textsuperscript{-1} (0.76 gSO\textsubscript{2}·gIL\textsuperscript{-1}) at 20°C and 0.1MPa through chemical and physical absorption. Based on the above discussion, it was proved that in fact the functional groups on the cation also have a very positive effect on SO\textsubscript{2} absorption besides the anions. Meanwhile, although these functionalized ILs have extremely high molar capacity of SO\textsubscript{2} absorption comparing with conventional ILs, their gravimetric capacity of SO\textsubscript{2} is still relatively low.

In our previous work\textsuperscript{27}, considering the advantages of pyridinium-based ILs such as high thermal stability, lower cost and higher biodegradability, a series of conventional pyridinium-based ILs were synthesized and used for SO\textsubscript{2} capture. It was found that [C\textsubscript{4}Py][SCN] has very high gravimetric capacity of 0.84 gSO\textsubscript{2}·gIL\textsuperscript{-1} under ambient
conditions, which is much higher than that of most reported functionalized ILs. As a successive work towards further exploring more highly efficient ILs for reversible capture of SO₂, a new method was developed by introducing different active sites, such as the tertiary amino group, the nitrile group and the ether group onto the cation of pyridinium-based ILs with the thiocyanate anion. In this study, three kinds of novel cation-functionalized ILs [NEt₂C₂Py][SCN], [C₄OPy][SCN] and [C₄CNPy][SCN] with high gravimetric capacity of SO₂ absorption were synthesized. The effect of different functionalized groups on their physicochemical properties and the performances of SO₂ absorption were systematically investigated. Meanwhile, the effect of different conditions (such as temperature, partial pressure of SO₂ and the water contents in ILs) on the absorption performances, SO₂/CO₂ selectivity and the regeneration and recyclability of ILs were also studied. Moreover, the role of the tertiary amino group, nitrile group and ether group in SO₂ capture was well explained through both the experiments (FT-IR and NMR spectroscopy) and Quantum Chemical calculations.

2. Results and discussion

2.1 Physicochemical properties

The physicochemical properties of four pyridinium-based ILs with the same anion [SCN] including the tertiary amino-functionalized IL [NEt₂C₂Py][SCN]), the ether-functionalized IL ([C₄OPy][SCN]), the nitrile-functionalized IL ([C₄CNPy][SCN]) and the conventional IL ([C₄Py][SCN]) were studied. Density and
viscosity of the ILs in this work as a function of the temperature were shown in Fig.S1 and Fig.S2, and the effect of different substituent groups on the pyridinium cation on their physical properties were studied. Clearly, the groups on the cation of pyridinium-based ILs have an obvious effect on the density and viscosities of ILs. As seen in Fig.S1, Comparing with the conventional IL \([\text{C}_4\text{Py}][\text{SCN}]\), two kinds of cation-functionalized ILs, such as \([\text{C}_4\text{OPy}][\text{SCN}]\) and \([\text{C}_4\text{CNPy}][\text{SCN}]\), showed the higher density due to the introduction of ether and nitrile groups on the pyridinium cation, while there was only a slight decrease in the density of the amino-functionalized IL \([\text{NEt}_2\text{C}_2\text{Py}][\text{SCN}]\), which was very close to that of \([\text{C}_4\text{Py}][\text{SCN}]\)^27. Similarly, as shown in Fig.S2, the grafting of a tertiary amino group and a nitrile group onto the cation notably led to an increase in viscosity, while the incorporation of an ether group could effectively decrease the viscosity. For example, the viscosities of \([\text{NEt}_2\text{C}_2\text{Py}][\text{SCN}]\) and \([\text{C}_4\text{CNPy}][\text{SCN}]\) were 612.43 and 313.46 mPa·s at 20 °C, respectively, which exhibited higher viscosities than that of \([\text{C}_4\text{Py}][\text{SCN}]\) (107.34 mPa·s at 20°C) with only alkyl-based group on the cation. However, the viscosity of \([\text{C}_4\text{OPy}][\text{SCN}]\) as 94.07 mPa·s at 20°C was obviously lower than the that of alkyl-substituted one, which showed the same viscosity reduction trend as that for other ether-functionalized ILs based on different cations^44, 45.

In addition, the effect of different substituent groups on thermal stability was also studied. As shown in Fig.S3, the thermal decomposition temperatures of \([\text{NEt}_2\text{C}_2\text{Py}][\text{SCN}]\), \([\text{C}_4\text{OPy}][\text{SCN}]\) and \([\text{C}_4\text{CNPy}][\text{SCN}]\) were 160℃, 232℃ and 228℃,
respectively. Compared with the non-functionalized counterpart \([\text{C}_4\text{Py}][\text{SCN}]\) (220\(^\circ\)), the incorporation of ether group and nitrile group could improve slightly the thermal stability of \([\text{C}_4\text{OPy}][\text{SCN}]\) and \([\text{C}_4\text{CNPy}][\text{SCN}]\), while \([\text{NEt}_2\text{C}_2\text{Py}][\text{SCN}]\) exhibited a relatively lower thermal stability, which may be mainly attributed to the increased basicity due to the presence of a tertiary amino group\(^{31}\).

2.2 Effect of different cations on \(\text{SO}_2\) absorption

Taking into account the high absorption capacity of \(\text{SO}_2\) and excellent reversibility for the pyridinium-based IL \([\text{C}_4\text{Py}][\text{SCN}]\) \(^{27}\), therefore, the anion \([\text{SCN}]\) was selected to pair with different cations containing a tertiary amino group, a nitrile group and an ether group on the pyridinium, and the effect of these groups on \(\text{SO}_2\) capture was investigated. As shown in Fig.1, the tertiary amino-functionalized IL \([\text{NEt}_2\text{C}_2\text{Py}][\text{SCN}]\) exhibited the highest absorption capacity of \(\text{SO}_2\) among the investigated ILs, which can capture 3.958 mol\(\text{SO}_2\)·mol\(\text{IL}^{-1}\) at 20\(^\circ\)C and 0.1 MPa. Under the same conditions, the capacity of \(\text{SO}_2\) absorption for \([\text{C}_4\text{OPy}][\text{SCN}]\) and \([\text{C}_4\text{CNPy}][\text{SCN}]\) could be as high as 2.956 and 2.917 mol\(\text{SO}_2\)·mol\(\text{IL}^{-1}\), respectively, whereas the capacity in \([\text{C}_4\text{Py}][\text{SCN}]\) was 2.553 mol\(\text{SO}_2\)·mol\(\text{IL}^{-1}\). Obviously, the cation-functionalized ILs exhibited enhanced absorption of \(\text{SO}_2\) in comparison with \([\text{C}_4\text{Py}][\text{SCN}]\) containing non-functionalized group on the cation, indicating these functionalized groups on the cation have a positive impact on improving \(\text{SO}_2\) capture.
2.2 Effect of temperature and pressure on SO$_2$ absorption

The effect of temperature and SO$_2$ partial pressure on SO$_2$ absorption by the cation-functionalized ILs were shown in Fig.2. As shown in Fig.2(a), the SO$_2$ absorption capacity of [NEt$_2$C$_2$Py][SCN], [C$_4$OPy][SCN] and [C$_4$CNPy][SCN] at 0.1MPa decreased continuously as the temperature increased. For instance, the molar ratios of SO$_2$ to IL for [NEt$_2$C$_2$Py][SCN], [C$_4$CNPy][SCN] and [C$_4$Py][SCN] decreased dramatically from 3.958, 2.917 and 2.553 to 1.411, 0.853 and 0.950 with an increase of temperature from 20 to 80°C, respectively. It was found that comparing with [C$_4$Py][SCN] the temperature has more great influence on SO$_2$ absorption for [C$_4$CNPy][SCN], which means that heating may be more favorable for SO$_2$ capture.
by [C₄CNPy][SCN] to be released completely due to the introduction of the nitrile group into the cation.

The pressure dependence of SO₂ absorption by [NEt₂C₂Py][SCN], [C₄OPy][SCN] and [C₄CNPy][SCN] at 20℃ was presented in Fig. 2(b). As expected, the SO₂ partial pressure also played a significant role in SO₂ absorption, and the SO₂ absorption capacity of [NEt₂C₂Py][SCN], [C₄CNPy][SCN] and [C₄Py][SCN] increased sharply with an increase of SO₂ partial pressure. For example, the molar ratios of SO₂ to [NEt₂C₂Py][SCN] and [C₄CNPy][SCN] increased from 1.363 to 3.958 and 0.652 to 2.917, respectively, when the SO₂ partial pressure changed from 0.01 to 0.1 MPa. Meanwhile, considering the low concentration of SO₂ in the real flue gas, the SO₂ absorption capacity for three kinds of cation-functionalized ILs at 5 kPa and 2 kPa of SO₂ partial pressure was also studied. The results showed that the absorption capacity of cation-functionalized ILs was less than 1 molSO₂·molIL⁻¹ as the partial pressure of SO₂ was lower than 5 kPa. For instance, the molar ratio of SO₂ to [NEt₂C₂Py][SCN] was 0.807 at 5 kPa and 0.126 at 2 kPa, respectively.
Fig. 2 Effect of temperature at 0.1MPa (a) and SO$_2$ partial pressure at 20°C (b) on SO$_2$ absorption by cation-functionalized ILs
2.3 SO$_2$/CO$_2$ Selectivity

As we know, there are usually other gases besides the low concentration of SO$_2$ in flue gas, such as CO$_2$, O$_2$ and N$_2$, so gas selectivity for judging the separation performance of a solvent becomes particularly important\textsuperscript{11}. As reported by Brennecke et al\textsuperscript{46} and our previous work\textsuperscript{27}, N$_2$ and O$_2$ solubility in ILs are generally much lower than CO$_2$ and SO$_2$ solubility, which suggests that the effective separation of two kinds of acid gases (SO$_2$ and CO$_2$) is the key procedure. Consequently, SO$_2$/CO$_2$ selectivity for [NEt$_2$C$_2$Py][SCN], [C$_4$OPy][SCN] and [C$_4$CNPy][SCN] was studied and the results were listed in Table 1. Comparing with [C$_4$Py][SCN], the remarkable improvement in SO$_2$/CO$_2$ selectivity for the three kinds of cation-functionalized ILs was achieved. Especially for [C$_4$OPy][SCN] and [C$_4$CNPy][SCN], SO$_2$/CO$_2$ selectivity substantially improved about 41% and 25%, respectively, which is more than 1.5 times that of [P$_{66614}$][Tetz]\textsuperscript{30}. The nature may be that the increase of the ILs’ polarity induced by an ether group and a nitrile group resulted in the enhanced absorption of polar SO$_2$ gas and slightly decreased absorption of non-polar CO$_2$ gas\textsuperscript{44,47,48}.

<table>
<thead>
<tr>
<th>ILs</th>
<th>molgas·molIL$^{-1}$</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NEt$_2$C$_2$Py][SCN]</td>
<td>3.958</td>
<td>0.061</td>
</tr>
<tr>
<td>[C$_4$CNPy][SCN]</td>
<td>2.917</td>
<td>0.037</td>
</tr>
<tr>
<td>[C$_4$OPy][SCN]</td>
<td>2.956</td>
<td>0.042</td>
</tr>
<tr>
<td>[C$_4$Py][SCN]$^{27}$</td>
<td>2.553</td>
<td>0.045</td>
</tr>
</tbody>
</table>
2.4 Effect of H$_2$O on SO$_2$ absorption

In practical applications, water is always accompanied with SO$_2$ in flue gas, and during SO$_2$ absorption the water can be also absorbed into absorbents. Therefore, the effect of water on SO$_2$ absorption by [NEt$_2$C$_2$Py][SCN], [C$_4$CNPy][SCN] and [C$_4$OPy][SCN] was investigated at 20°C and 0.1 MPa and the results were shown in Fig.3 and Fig.S4, respectively. It was demonstrated that the presence of water has a different impact on SO$_2$ absorption for the three kinds of cation-functionalized ILs. For [C$_4$CNPy][SCN] (Fig.3(a)) and [C$_4$OPy][SCN] (Fig.S4), SO$_2$ absorption capacity in the two ILs decreased slightly with an increase of water content, while SO$_2$ absorption capacity in [NEt$_2$C$_2$Py][SCN] (Fig.3(b)) increased a little after the addition of water. For example, when the water in ILs increased to about 1.0%, the molar ratio of SO$_2$ to [C$_4$CNPy][SCN] decreased from 2.917 to 2.851, while SO$_2$ absorption capacity in [NEt$_2$C$_2$Py][SCN] increased from 3.958 to 4.181 molSO$_2$·molIL$^{-1}$. The results indicated that the water present in [C$_4$CNPy][SCN] and [C$_4$OPy][SCN] plays a negative role in SO$_2$ absorption capacity, but is favorable for improving SO$_2$ absorption capacity in [NEt$_2$C$_2$Py][SCN]. The detail reason will be discussed in the section of the mechanism.
**Fig. 3** Effect of water on SO$_2$ absorption capacity by [C$_2$CNPy][SCN] (a) and [NEt$_2$C$_2$Py][SCN] (b) at 20°C and 0.1 MPa
2.5 Regeneration and recycle of ionic liquids

In order to examine the reversibility of SO$_2$ absorption, multiple consecutive cycles of SO$_2$ absorption and desorption for [NEt$_2$C$_2$Py][SCN], [C$_4$OPy][SCN] and [C$_4$CNPy][SCN] were studied. As shown in Fig.4, SO$_2$ captured by the three types of cation-functionalized ILs could be almost completely stripped out at 80$^\circ$C by bubbling N$_2$ through the ILs for 60 min, which was further proved by FT-IR spectra of [NEt$_2$C$_2$Py][SCN] (Fig.5), [C$_4$CNPy][SCN] (Fig.6) and [C$_4$OPy][SCN] (Fig.S5) before absorption and after desorption of SO$_2$. Comparing with [C$_4$Py][SCN], the residual capacity of SO$_2$ absorption by [C$_4$CNPy][SCN] decreased from 0.099 to 0.055 molSO$_2$·molIL$^{-1}$, implying that the desorption of SO$_2$ is enhanced owing to the presence of the nitrile group, which agrees well with the former results. Meanwhile, these cation-functionalized ILs can be repeatedly used and still remain the stable absorption performances after five cycles of absorption and desorption, which indicated that the process of SO$_2$ absorption and desorption by these cation-functionalized ILs is highly reversible and the ILs are recyclable.
Fig. 4 SO$_2$ absorption and desorption by cation-functionalized ILs. SO$_2$ absorption was carried out at 20°C, and SO$_2$ desorption at 80°C under N$_2$. [NE$_2$C$_2$Py][SCN], absorption ■, desorption □; [C$_4$OPy][SCN], absorption ●, desorption ○; [C$_4$CNPy][SCN], absorption ▲, desorption △.

2.6 Comparison with other ionic liquids

To our knowledge, the mass of SO$_2$ absorbed per unit mass of IL is of great importance in industrial separation processes$^{11,33}$. Therefore, in order to evaluate the potential of ILs for SO$_2$ capture, gravimetric absorption capacity of SO$_2$ for the three types of cation-functionalized ILs was compared with other ILs reported in literature in Table 2. It was clearly seen that although the molar absorption capacity of SO$_2$ in the investigated cation-functionalized ILs is slightly lower than some reported functionalized ILs, their corresponding gravimetric capacity of SO$_2$ is very high. Especially the tertiary amino-functionalized IL [NE$_2$C$_2$Py][SCN] exhibited the
highest absorption capacity of 1.06 gSO$_2$·gIL$^{-1}$ under atmospheric pressure in this work, which is very close to the maximum value (1.13 gSO$_2$·gIL$^{-1}$) reported to date$^{49}$, and even could absorb as high as 0.37 gSO$_2$·gIL$^{-1}$ under low SO$_2$ partial pressure of 0.01MPa. The results indicated the pyridinium-based IL [NEt$_2$C$_2$Py][SCN] will be a good candidate for SO$_2$ removal from flue gases.

**Table 2** Comparison of SO$_2$ absorption capacity with other ILs

<table>
<thead>
<tr>
<th>ILs</th>
<th>Temperature</th>
<th>SO$_2$ absorption$^a$</th>
<th>Selectivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>0.1MPa</td>
<td>0.01MPa</td>
<td>SO$_2$/CO$_2$</td>
</tr>
<tr>
<td>[NEt$_2$C$_2$Py][SCN]</td>
<td>20</td>
<td>1.06 (3.958)</td>
<td>0.37 (1.411)</td>
<td>65</td>
</tr>
<tr>
<td>[C$_4$OPy][SCN]</td>
<td>20</td>
<td>0.90 (2.956)</td>
<td>0.23 (0.950)</td>
<td>70</td>
</tr>
<tr>
<td>[C$_4$CNPy][SCN]</td>
<td>20</td>
<td>0.85 (2.917)</td>
<td>0.20 (0.853)</td>
<td>79</td>
</tr>
<tr>
<td>[C$_4$Py][SCN]</td>
<td>20</td>
<td>0.84 (2.55)</td>
<td>0.16 (0.49)</td>
<td>56</td>
</tr>
<tr>
<td>[Emim][SCN]</td>
<td>20</td>
<td>1.13 (2.99)</td>
<td>0.37 (0.98)</td>
<td>-</td>
</tr>
<tr>
<td>[P$_{66614}$][SCN]</td>
<td>20</td>
<td>0.38 (3.24)</td>
<td>0.13 (1.06)</td>
<td>-</td>
</tr>
<tr>
<td>[P$_{66614}$][BenIm]</td>
<td>20</td>
<td>0.61 (5.75)</td>
<td>0.26 (2.59)</td>
<td>-</td>
</tr>
<tr>
<td>[P$_{66614}$][Tetz]</td>
<td>20</td>
<td>0.43 (3.72)</td>
<td>0.18 (1.54)</td>
<td>47</td>
</tr>
<tr>
<td>[P$_{66614}$][4-Br-pHCoo]</td>
<td>20</td>
<td>0.38 (4.12)</td>
<td>0.15 (1.66)</td>
<td>-</td>
</tr>
<tr>
<td>[P$_{444E3}$][Tetz]</td>
<td>20</td>
<td>0.76 (5.00)</td>
<td>0.29 (1.87)</td>
<td>-</td>
</tr>
<tr>
<td>[Emim][MeSO$_3$]</td>
<td>20</td>
<td>0.95 (4.43)</td>
<td>0.34 (1.58)</td>
<td>-</td>
</tr>
<tr>
<td>[Emim][BF$_4$]</td>
<td>30</td>
<td>0.74 (6.30)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Bmim][OAc]</td>
<td>20</td>
<td>0.62 (1.91)</td>
<td>0.21 (0.66)</td>
<td>-</td>
</tr>
<tr>
<td>[TMG]L</td>
<td>40</td>
<td>0.53 (1.70)</td>
<td>0.31 (0.98)</td>
<td>-</td>
</tr>
<tr>
<td>[TMG][BF$_4$]</td>
<td>20</td>
<td>0.40 (1.27)</td>
<td>0.02 (0.06)</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ gSO$_2$·gIL$^{-1}$ (molSO$_2$·molIL$^{-1}$)
2.7 The mechanism for SO$_2$ absorption

In order to understand the role of the different substituent groups on the cation in SO$_2$ absorption, FTIR and NMR spectroscopy were used to investigate the interaction between ILs and SO$_2$. The FT-IR spectra of fresh ILs, SO$_2$-absorbed ILs and ILs after desorption for [NEt$_2$C$_2$Py][SCN], [C$_4$CNPy][SCN] and [C$_4$OPy][SCN] were shown in Fig.5, Fig.6 and Fig.S5, respectively. As shown in Fig.5, compared with the FTIR spectrum of the fresh IL [NEt$_2$C$_2$Py][SCN], three new absorption bands centered at 1315, 1132 and 946 cm$^{-1}$ were observed in the FTIR spectrum of [NEt$_2$C$_2$Py][SCN] after uptake of SO$_2$. The peaks appearing at 1315 and 1132 cm$^{-1}$ could be assigned to the asymmetric and symmetric S=O stretches, and another new peak at 946 cm$^{-1}$ was attributed to the formation of S-O bonds as a result of SO$_2$ absorption, which indicated the chemical interaction exists between the amino-functionalized IL [NEt$_2$C$_2$Py][SCN] and SO$_2$ by the formation of a charge transfer complex$^{50,51}$ besides the physical interaction between the anion [SCN] and SO$_2^{30-32}$. 
Fig. 5 FT-IR spectra of [NEt$_2$C$_2$Py][SCN] before and after SO$_2$ absorption and after SO$_2$ desorption

For the nitrile-functionalized IL [C$_4$CNPy][SCN], there were only two new bands at 1296 and 1124 cm$^{-1}$ for the asymmetric and symmetric S=O stretches in the FTIR spectrum of [C$_4$CNPy][SCN] saturated with SO$_2$ gas (Fig.6), which indicated that only physical absorption of SO$_2$ occurs in the nitrile-functionalized IL [C$_4$CNPy][SCN]. Similarly, the changes in the spectra of the ether-functionalized IL [C$_4$OPy][SCN] before and after SO$_2$ absorption showed the same results (Fig.S5), which is consistent with those previously reported by Hong et al$^{41}$ and Wang et al$^{32}$. 
Fig. 6 FT-IR spectra of [C₄CNPy][SCN] before and after SO₂ absorption and after SO₂ desorption

Furthermore, the FT-IR spectra of fresh ILs, SO₂-absorbed ILs and ILs after desorption for [NEt₂C₂Py][SCN], [C₄CNPy][SCN] and [C₄OPy][SCN] with water were shown in Fig.7, Fig.8 and Fig.S6, respectively. Compared with FT-IR spectra of [NEt₂C₂Py][SCN] without water after SO₂ absorption, a new peak at 1034 cm⁻¹ corresponding to S-OH were observed in FT-IR spectrum of [NEt₂C₂Py][SCN] with water after SO₂ absorption (Fig.7), which indicated that the enhanced absorption of SO₂ for [NEt₂C₂Py][SCN] in the presence of water could be ascribed to the formation of hydrogen sulfite salts. The results showed good agreements with that reported by Sayari et al.⁴, ⁵, ⁵², ⁵³. As shown in Fig.8 and Fig.S6, the results indicated that the presence of water does not change the physical absorption process between [C₄CNPy][SCN]/[C₄OPy][SCN] and SO₂, and the structure of
[C₄CNPy][SCN]/[C₄OPy][SCN] with water after absorption and desorption of SO₂ can also keep stable.

Fig. 7 FT-IR spectra of [NEt₂C₂Py][SCN] with water before and after absorption of SO₂ and after desorption.
The $^1$H NMR and $^{13}$C NMR spectra of [NEt$_2$C$_2$Py][SCN], [C$_4$CNPy][SCN] and [C$_4$OPy][SCN] before and after SO$_2$ absorption were further compared in Fig.9, Fig.10 and Fig.S7, respectively. As shown in Fig.9, after the absorption of SO$_2$, typical peaks in the $^1$H NMR spectrum of the cation in [NEt$_2$C$_2$Py][SCN] moved downfield from 2.44 and 2.86 ppm to 2.58 and 2.99 ppm, respectively. Meanwhile, the corresponding $^{13}$C NMR signals showed upfield shifting from 53.01 and 59.52 ppm to 52.53 and 58.72 ppm, respectively. These chemical shifts further proved that there exists the chemical interaction between the tertiary amino group on the pyridinium ring and SO$_2$. Additionally, neither new peaks or significant chemical shifts were observed after SO$_2$ absorption by the nitrile-functionalized IL.
[C₄CNPy][SCN] (Fig.10) and ether-functionalized IL [C₄OPy][SCN] (Fig.S7), which agrees well with the IR results.

![Fig.9](image1.png) **Fig.9** ¹H NMR and ¹³C NMR spectra of [NEt₂C₂Py][SCN] before and after SO₂ absorption

![Fig.10](image2.png) **Fig.10** ¹H NMR and ¹³C NMR spectra of [C₄CNPy][SCN] before and after SO₂ absorption
Moreover, the density functional theory calculations were performed using Gaussian 09 program to further investigate the interaction between ILs and SO$_2$. The optimized structures of IL-SO$_2$ systems for [NEt$_2$C$_2$Py][SCN], [C$_4$OPy][SCN], [C$_4$CNPy][SCN] and [C$_4$Py][SCN] were presented in Fig.11. As shown in Fig.11(a), 11(b) and 11(c), the interactions between SO$_2$ and these three pyridinium-based ILs are very different. Compared with that of [C$_4$Py][SCN]-SO$_2$, the intermolecular distance between the sulfur atom of SO$_2$ and the sulfur atom of SCN anion in [C$_4$OPy][SCN]-SO$_2$ and [C$_4$CNPy][SCN]-SO$_2$ became slightly shorter. Meanwhile, three hydrogen bonds formed between SO$_2$ molecule and the cations of [C$_4$CNPy][SCN] and [C$_4$OPy][SCN] whereas only two hydrogen bonds formed between SO$_2$ molecule and the cation of [C$_4$Py][SCN], suggesting the stronger interaction between SO$_2$ and [C$_4$OPy][SCN] or [C$_4$CNPy][SCN]. The results may further prove the higher absorption capacity of SO$_2$ using [C$_4$OPy][SCN] and [C$_4$CNPy][SCN] than [C$_4$Py][SCN], which is consistent with the experimental results. However, for [NEt$_2$C$_2$Py][SCN] that physically and chemically absorb SO$_2$, the optimized structures of IL-SO$_2$ in Fig.11(d) showed that the physical interaction of [NEt$_2$C$_2$Py][SCN] with SO$_2$ was almost similar to that of [C$_4$Py][SCN]-SO$_2$. Therefore, it was reasonably believed that the enhancement in SO$_2$ absorption for [NEt$_2$C$_2$Py][SCN] mainly originated from the strong chemical interaction between the tertiary amino group and SO$_2$. 
Fig. 11 Optimized structures showing the interactions of ILs with SO$_2$ molecules: (a) [C$_4$Py][SCN]-SO$_2$ (ΔH= -67.3 kJ·mol$^{-1}$), (b) [C$_4$OPy][SCN]-SO$_2$ (ΔH= -68.8 kJ·mol$^{-1}$), (c) [C$_4$CNPy][SCN]-SO$_2$ (ΔH= -62.8 kJ·mol$^{-1}$), (d) [NEt$_2$C$_2$Py][SCN]-SO$_2$ (ΔH= -63.9 kJ·mol$^{-1}$). H: light gray, C: gray, O: red, N: blue, S: yellow.

In addition, the interaction enthalpies ΔH between ILs and SO$_2$ were calculated as -67.3, -68.8, 63.9 and -62.8 kJ·mol$^{-1}$ for [C$_4$Py][SCN], [C$_4$OPy][SCN], [NEt$_2$C$_2$Py][SCN] and [C$_4$CNPy][SCN], respectively. It is clearly observed that ΔH of [C$_4$OPy][SCN]-SO$_2$ is comparable to that of [C$_4$Py][SCN]-SO$_2$, however, ΔH of [NEt$_2$C$_2$Py][SCN]-SO$_2$ and [C$_4$CNPy][SCN]-SO$_2$ is slightly lower than that of [C$_4$Py][SCN]-SO$_2$, which means that the cation-functionalized ILs may be more...
efficient for SO₂ absorption due to their higher SO₂ absorption capacity and comparable or lower interaction enthalpies.

3. Experimental

3.1 Materials

SO₂ gas (99.9%) was supplied by Beijing Beiwen Gas Factory. N, N-diethyl-2-amino-1-bromoethane hydrobromide (98%), 2-chloroethyl ethyl ether (98%), and 5-Chlorovaleronitrile (97%) were purchased from TCI. Other chemical reagents of analytical grade, including pyridine, 1-bromobutane, ethyl acetate, dichloromethane, acetone, ethanol, acetonitrile, methanol, diethyl ether and sodium thiocyanate were purchased from Beijing Chemical Company. All reagents were used for the synthesis of the ILs without further purification.

3.2 Synthesis and characterizations of ILs

Three types of cation-functionalized ILs with the same anion [SCN] including 1-(2-diethylaminoethyl)pyridinium thiocyanate ([NEt₂C₂Py][SCN]), 1-ethoxyethylpyridinium thiocyanate ([C₄OPy][SCN]) and 1-valeronitrilepyridinium thiocyanate ([C₄CNPy][SCN]) were synthesized in a two-step method, and the preparations of ILs were shown below. The structures of the ILs studied in this work were shown in Fig.12.
Synthesis of [NEt₂C₂Py][SCN]: The IL [NEt₂C₂Py][SCN] was synthesized following the preparation procedures of 1-(N,N-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoro-methanesulfonate ([mammim][TfO])\textsuperscript{54}. In the experiment, pyridine (7.62 g, 0.096 mol) and N,N-diethyl-2-amino-1-bromoethane hydrobromide (25.15 g, 0.096 mol) were dissolved in acetonitrile (200 mL) and heated under reflux at 80°C for 48 h. After cooling to room temperature, the mixture was filtered and the remaining solid was washed with acetone (3×40 ml). After drying at 60°C under vacuum for 48 h, [NEt₂C₂Py][Br][HBr] was obtained as white solid. [NEt₂C₂Py][Br][HBr] (29.65 g, 0.087 mol) and NaOH (3.49 g, 0.087 mol) were added in methanol (25 mL) at 0-5°C and stirred for 12 h at room temperature. Then equimolar NaSCN (7.069g, 0.087mol) was added and stirred for 24 h. After that time the methanol was removed by rotary evaporation, and the mixtures were washed with dichloromethane (200 ml). After filtration and removal of solvents from filtrate, the yellowish oil [NEt₂C₂Py][SCN] was finally obtained under vacuum at 50°C for 48 h.

Synthesis of [C₄CNPy][SCN]: Pyridine (10.614 g, 0.134 mol) and
5-Chlorovaleronitrile (Cl(CH\textsubscript{2})\textsubscript{4}CN, 15.778 g, 0.134 mol) were firstly mixed and stirred at 80°C for 8 h, then the reaction mixture was stirred at 110°C for 40 h. After cooling to room temperature, the reaction mixture was washed with diethyl ether (3×40 ml) and dried at 80°C under vacuum for 48 h to obtain the pale yellow solid \([\text{C}_4\text{CNPy}]\text{Cl}\). The anion exchange reaction was performed by mixing \([\text{C}_4\text{CNPy}]\text{Cl}\) (28.706 g, 0.146 mol) and equimolar NaSCN in acetone (200 ml). After stirring for 48 h at room temperature, the mixture was filtered and washed with acetone (3×100 ml). The organic layer was collected and concentrated by rotary evaporation to remove the solvent. The product \([\text{C}_4\text{CNPy}]\text{[SCN]}\) was finally obtained as the dark orange liquid under vacuum at 50°C for 48 h.

Synthesis of \([\text{C}_4\text{OPy}]\text{[SCN]}\): 2-Chloroethyl ethyl ether (20.524 g, 0.185 mol) was added to pyridine (14.654 g, 0.185 mol) while stirring at 100°C for 48 h. After the reaction, ethanol (150 mL) and activated carbon (8 g) were added into the reaction solution at room temperature, and the mixture kept stirring for 3 h. After filtration and removal of the solvents by rotary evaporation, the resulting product was washed with ethyl acetate (3×40 ml), and dried under vacuum at 75°C for 48 h to afford \([\text{C}_4\text{OPy}]\text{Cl}\) as the brown solid. The IL \([\text{C}_4\text{OPy}]\text{[SCN]}\) was synthesized following the same procedures described above for \([\text{C}_4\text{CNPy}]\text{[SCN]}\), except for the use of \([\text{C}_4\text{OPy}]\text{Cl}\) instead of \([\text{C}_4\text{CNPy}]\text{Cl}\). The final product \([\text{C}_4\text{OPy}]\text{[SCN]}\) was obtained as the brown liquid under vacuum at 50°C for 48 h.

All the ILs were dried under vacuum at 50°C for 48 h before use. The structures of these ILs were confirmed by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy with Bruker 600
spectrometer and FT-IR spectroscopy by a Thermo Nicolet 380 Spectrometer. The water content in the ILs after drying were determined with volumetric Karl Fischer Titration (Metrohm, 787 KF Titrino) and found to be less than 0.1 wt%. The residual halide contents in the ILs were measured using PXSJ-226 Series Ion meter (INESA Scientific Instrument Co. Ltd), and found to be less than 0.3 wt%. Decomposition temperature was measured with a Thermogravimetric Analysis (TGA) 2050 meter. Densities and viscosities were measured on Paar DMA 5000 density and Paar AMVN viscosity meters, respectively.

### 3.3 Absorption and desorption of SO\(_2\)

The experiments for SO\(_2\) absorption and desorption followed the same procedures of our previous work\(^{27}\). In a typical absorption of SO\(_2\), the pure SO\(_2\) was bubbled through about 5 g IL in the glass container with an inner diameter of 3.0 cm and a height of 12.0 cm at a flow rate of 140 ml min\(^{-1}\). The temperature of the glass container was controlled at the desired temperature within ± 0.1°C by a circulated water bath. The amount of SO\(_2\) absorbed in the IL was measured using an electronic balance with an accuracy of ± 0.1 mg and was finally determined according to the increase of the weight. For the absorption of SO\(_2\) under reduced pressure, the gases of different SO\(_2\) partial pressure were obtained by changing the flow of SO\(_2\) and N\(_2\).

SO\(_2\) desorption from saturated IL solutions was carried out in a similar way to the absorption method mentioned above. The pure N\(_2\) with the same flow rate was bubbled through the IL that absorbed SO\(_2\) in the glass container at 80°C, the amount
of SO₂ desorption was determined at regular intervals by an electronic balance until the weight kept unchanged. The reproducibility of the absorption and desorption experiments was less than ± 3%, and it was estimated that the experimental error involved in the method was at the level of ± 5%.

4. Conclusions

In this work, three kinds of novel cation-functionalized ILs [NEt₂C₂Py][SCN], [C₄OPy][SCN] and [C₄CNPy][SCN] were synthesized, and the effect of different functional groups on their physicochemical properties and the performances of SO₂ absorption were systematically investigated. The results demonstrated that these cation-functionalized ILs exhibited much better absorption capacity and SO₂/CO₂ selectivity than the conventional IL [C₄Py][SCN]. Among the investigated ILs, [NEt₂C₂Py][SCN] exhibited the highest absorption capacity of 1.06 gSO₂·gIL⁻¹ under ambient conditions. Meanwhile, SO₂/CO₂ selectivity was greatly improved up to 41% through the incorporation of these groups on the cation of ILs. The present of water causes a slight decrease in SO₂ capacity by [C₄CNPy][SCN] and [C₄OPy][SCN], whereas a slight increase in SO₂ capacity by [NEt₂C₂Py][SCN]. Moreover, spectroscopic characterizations and Quantum Chemical calculation results indicated that only physical absorption of SO₂ occurs in [C₄CNPy][SCN] and [C₄OPy][SCN], but a combination of the chemical and physical interaction coexists between [NEt₂C₂Py][SCN] and SO₂. The great enhancement in SO₂ absorption by [NEt₂C₂Py][SCN] mainly originates from the strong chemical interaction between the
tertiary amino group and SO$_2$ besides the physical interaction of [SCN]-SO$_2$. In addition, the three kinds of cation-functionalized ILs could also keep the stable absorption performance after five cycles of absorption and desorption, implying these ILs show great potentials for the applications of SO$_2$ capture.

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**Notes and references**

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Electronic Supplementary Information (ESI) available: NMR data, FTIR and NMR spectra of the investigated ILs before and after SO$_2$ absorption, Densities and viscosities at different temperatures and TGA results of the ILs, and the effect of water on SO$_2$ absorption for [C$_4$OPy][SCN].