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Highly Efficient Nitric Oxide Capture by Azole-Based Ionic Liquids through Multiple-Site Absorption

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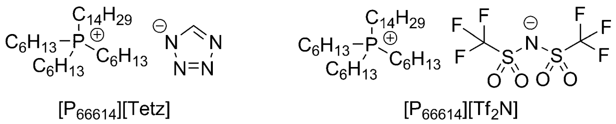
Abstract: *A novel method for highly efficient nitric oxide absorption by azole-based ionic liquid was reported. The NO absorption capacity reached up to 4.52 mol per mol ionic liquid and is significant higher than the capacity other traditional absorbents. Moreover, the absorption of NO by this ionic liquid was reversible. Through a combination of experimental absorption, quantum chemical calculation, NMR and FT-IR spectroscopic investigation, the results indicated that such high capacity originated from multiple-site interactions between NO and the anion through the formation of NONOate with the chemical formula* $R^1R^2N-(NO^-)-N{=}O$*, where* R^1 *and* R^2 *are alkyl groups. We believe that this highly efficient and reversible NO absorption by an azole-based ionic liquid paves a new way for gas capture and utilization.*

Nitric oxide, mainly generated from the burning of fossil fuel, is one of the suspects for smog and acid rain.[1] In industry, the major methods for post-combustion NO_x emission control are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).[2] These methods are challenging because of catalyst poisoning caused by sulfur compounds, the high working temperature and the corrosion by NH_3.[3] On the other hand, NO also plays a significant role in plenty of biological processes such as in the cardiovascular, nervous, and immune systems.[4] For the excellent work to identify NO as endothelium-derived relaxation factor (EDRF), Furchgott, Ignarro and Murad earned the Nobel Prize in 1998.[5] Therefore, the study on NO absorption and release is important in some fields such as chemistry, biology, and industry.

Ionic liquids (ILs) are the ideal absorbent for many gases because of their unique properties, such as negligible vapor pressure, wide liquid temperature range, high stability, and tunable properties.[6,7] In 2002, Davis group reported the first CO_2 chemisorption by an amino-functionalized IL, which could absorb about 0.5 mol CO_2 per mol IL at ambient pressure.[6a] After that, SO_2 chemisorption by tetramethylguanidinium lactate (TMGL) was firstly demonstrated by Han and co-workers, where the SO_2 absorption capacity was about 1 mol SO_2 per mol IL in a gas-mixture with less than 8% SO_2.[7a] Nowadays, a great deal of anion-functionalized ILs were developed as efficient absorbents for CO_2 or SO_2 absorption.[6c–j, 7b–f] Although NO is also one of the major constituents in fuel gas, there is little public research, as far as we know, reporting NO chemisorption by pure ILs.[8] NO, as a simple diatomic free radical, is susceptible to bind with transition metals.[9] Metal organic frameworks (MOF) and zeolites have been designed for NO adsorption.[10] However, these methods also bear numerous drawbacks such as being sensitive to the moisture and difficult to synthesis. Therefore, can we design a kind of functionalized IL that absorbs NO efficiently?

In biochemistry, first reported by Drago et al. in 1961, diazeniumdiolate ions (NONOates) is an interesting class of NO donors, which exhibited potential in treatment of cancer, cardiovascular disease, and inflammation.[11] NONOates are formed from the reaction between NO and primary or secondary amines in the presence of a strong base (NaOMe) and at a high NO pressure.[12] It can be viewed as the complex of Lewis base (B^-) and Lewis acid N_2O_2, where the B^- is used to stabilize the $N_2O_2^-$ anion. Azole-based anions as a new kind of Lewis base exhibited excellent CO_2 or SO_2 absorption performance.[6,7] Thus, can these ILs with azole-based anion capture NO efficiently?

Herein, we describe our result on NO absorption by azole-based ILs (Scheme 1). We showed that a high NO absorption capacity of 4.52 mol NO per mol IL can be achieved by an azole-based anion-functionalized IL through multiple-site interactions. Furthermore, the result was identified by quantum calculations, NMR and IR spectroscopy. To the best of our knowledge, this is the first example for NO chemisorption by pure ILs.



Scheme 1. Structures of ionic liquids used for NO absorption.

In the beginning, DFT calculation was used to compare the reaction between -NONO and Et_2N or [Tetz].[13] As shown in Figure 1, the distance between N in Et_2N and N in -NONO was predicted as 1.438 Å in Et_2N-NONO, which was in agreement with previous reports (1.428 Å).[12b] As for [Tetz]-NONO, this distance was predicted as 1.420 Å, which was shorter than the distance in Et_2N-NONO, suggesting the stronger reaction between [Tetz] and -NONO. These results indicated that [Tetz] could react with NO through the

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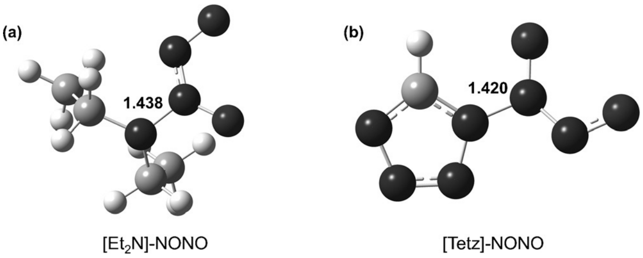


$[Et_2N]$-NONO $\quad$ [Tetz]-NONO

Figure 1. Optimized structures of a) Et_2N-NONO and b) [Tetz]-NONO.

formation of NONOate, indicating that this azole-based IL can capture NO efficiently.

First, to verify DFT calculations, NO absorption by the azole-based IL $[P_{66614}]$[Tetz] was investigated. As shown in entry 1 of Table 1, to our surprised, the molar ratio of NO to $[P_{66614}]$[Tetz] was as high as 4.52 and the viscosity of $[P_{66614}]$[Tetz] decreased after NO absorption (Table S1). Interesting, $[P_{66614}]$[Tetz] showed two kinds of absorption trend during NO absorption with the time. At first, NO absorption became slower within 5 h, when about 3 mol NO was captured by $[P_{66614}]$[Tetz]. As NO was kept bubbling, NO absorption showed a little acceleration. Thus, there probably was multiple-site interaction between the IL and NO (Figure 2). However, for traditional IL $[P_{66614}][Tf_2N]$, NO capacity is only 0.25 mol NO per mol IL because of the weak interaction between the IL and NO. The effect of temperature on NO absorption was investigated. Table 1 shows that the NO absorption capacity decreased significantly with the increase of the temperature. For instance, the molar ratio of NO to $[P_{66614}]$[Tetz] was reduced to 2.27, when the temperature increased to 90 °C. Furthermore, the effect of the pressure on NO absorption was also investigated. As seen in Table 1, the NO absorption capacity for $[P_{66614}]$[Tetz] was 3.26 mol NO per mol IL, when 0.1 bar NO was used, indicating the strong interaction between $[P_{66614}]$[Tetz] and NO. In addition, the effect of water on NO absorption capacity of $[P_{66614}]$[Tetz] was weak (Table S2).

Table 1: NO absorption using the azole-based ionic liquid.[a]

Entry	Ionic liquid	*T* [°C]	*t* [h]	Absorption capacity[b]
1	$[P_{66614}]$[Tetz]	30	11	4.52
2	$[P_{66614}]$[Tetz]	50	10	3.10
3	$[P_{66614}]$[Tetz]	70	8	2.56
4	$[P_{66614}]$[Tetz]	90	7	2.27
5[c]	$[P_{66614}]$[Tetz]	30	13	3.26
6	$[P_{66614}][Tf_2N]$	30	3	0.25

[a] The absorption was carried out by bubbling NO at 1 bar. [b] mol NO per mol ionic liquid. [c] 0.1 bar NO was used.

The reusability of IL is an important criterion to evaluate the potential of practical application. Thus, the reversibility of $[P_{66614}]$[Tetz] was investigated, which is shown in Figure 3. To our delight, NO absorption by $[P_{66614}]$[Tetz] was reversible and the NO absorption capacity could maintain for more than 5 times, where the desorption residue was about 2.79 mol NO per mol IL. Thermogravimetry (TG) analysis was further used to investigate NO desorption in this system. As presented in Figure S2, $[P_{66614}]$[Tetz]-NO complexes showed a weight loss of about 4.9 % (equal to 1.13 mol NO per mol IL) at low temperature (< 120 °C), which maybe mainly attributed to the loss of physical NO absorption. Furthermore, 7.7 % and 6.3 % mass losses (equal to 1.77 and 1.45 mol NO per mol IL, respectively) were observed at temperatures between 120–205 °C and 205–270 °C, which indicates that there are multiple-site interactions between the IL and NO.

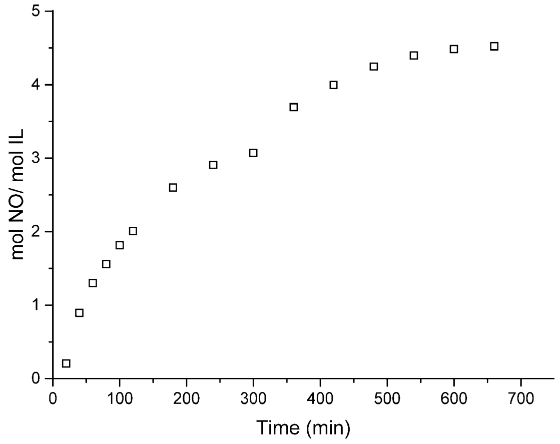


Figure 2. NO absorption by ionic liquid $[P_{66614}]$[Tetz].

Why did $[P_{66614}]$[Tetz] exhibit such high NO absorption capacity? As shown in Figure 2 and Figure S2, we first thought about multiple-site chemical absorption.[7b] To further investigate the reaction between [Tetz] and NO, the structures of [Tetz] with two -NONO and three -NONO were optimized (Figure 4) by a DFT method at B3LYP/6–31++(d,p) level. When [Tetz] was tethered with two -NONO, the bond length of the N in [Tetz] and the N in NONO- was a little longer than that reacted with one NONO-, which was predicted as 1.424 Å (Figure 4 a and b). However, the [Tetz]-2NONO complex had a weak interaction with the

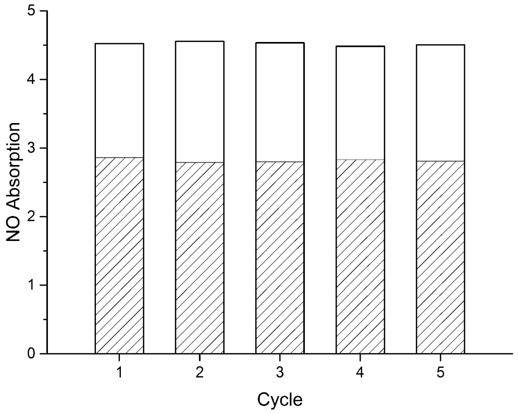


Figure 3. NO absorption by $[P_{66614}]$[Tetz] for five cycles. NO absorption was carried out at 30 °C for 11 h in the first time and 6 h in others, and the desorption was performed at 80 °C in N_2 for 1 h.

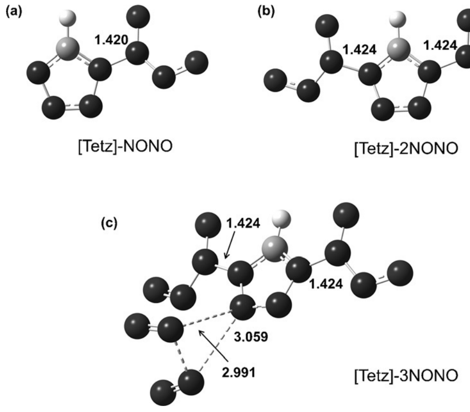


Figure 4. Optimized structures of a) [Tetz]-NONO, b) [Tetz]-2NONO, and c) [Tetz]-3NONO.

third -NONO. The distance of the N in [Tetz] and the third -NONO prolonged to 2.991 Å (Figure 4c). Therefore, the DFT calculation results were consistent with the absorption experiment, which showed that about 4 mol NO per mol IL could be chemical absorbed by [Tetz].

Moreover, NO absorption through multiple-site interaction by [P$_{66614}$][Tetz] was investigated by ^{1}H NMR spectroscopy (Figure 5). After treatment with NO for 1 h, a small ^{1}H NMR peak in [Tetz] moved from 7.99 ppm to 8.13 ppm, indicating that [Tetz] reacted with NO to form [Tetz]-NONO and 1.30 mol NO was absorbed by [P$_{66614}$][Tetz] (Figure 5a and b). Therefore, some NO was physically absorbed by [P$_{66614}$][Tetz] at this time. When [Tetz] reacted with NO for 6 h, the ^{1}H NMR peak of [Tetz]-NONO moved downfield to 9.05 ppm and a new peak appeared at 9.41 ppm (Figure 5c), because [Tetz]-NONO and [Tetz]-2NONO coexisted in this system. The ^{1}H NMR peak at 9.41 ppm appeared and another ^{1}H NMR peak disappeared, indicating the presence of only [Tetz]-2NONO when the reaction time prolonged to 11 h (Figure 5d). To get deep insight into this matter, ^{1}H NMR spectra were predicted by DFT calculation (Table S3).[13] When [P$_{1111}$][Tetz] was tethered with one -NONO, the ^{1}H NMR peak of [Tetz] moved downfield 0.87 ppm, which was less than that reacted with two -NONO groups (moved downfield 2.01 ppm). Obviously, the DFT calculation was consistent with our experiments.

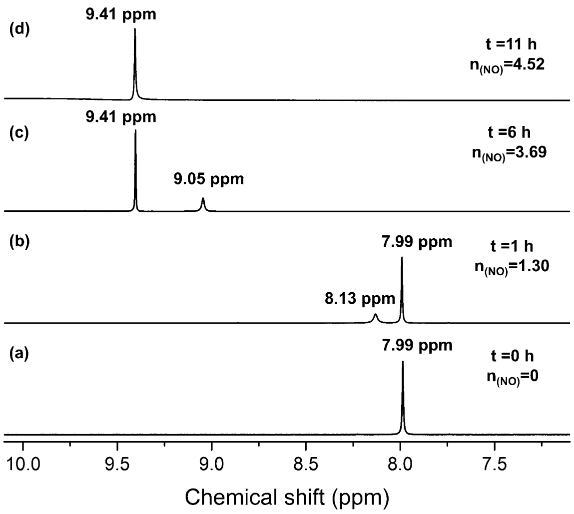


Figure 5. ^{1}H NMR spectra of a) [P$_{66614}$][Tetz], b) [P$_{66614}$][Tetz] with bubbling NO for 1 h, c) [P$_{66614}$][Tetz] with bubbling NO for 6 h, and d) [P$_{66614}$][Tetz] with bubbling NO for 11 h.

In order to further investigate multiple-site interaction of NO absorption by [P$_{66614}$][Tetz], FT-IR was used (Figure 6 and Figure S3). In FT-IR spectrum, four new peaks at 823, 872, 1313, and 1411 cm^{-1} appeared after NO absorption. Through comparison with DFT calculations[13] and a previous report,[12b] the new peaks at 823 and 872 cm^{-1} were mainly caused by ν(N-N) in -NONO, while additional peaks at 1313 and 1411 cm^{-1} should be assigned to ν(N−O) in -NONO. In the DFT calculation, these peaks were predicted at 869, 881, 1360 and 1404 cm^{-1}, respectively, which were close to the observed ones (Figure S5). As for the new peak at 1645 cm^{-1}, it should be attributable to ν(N−O) in NO, which was dissolved in the IL. The NO absorption by [P$_{66614}$][Tetz] can be analyzed step by step. First, after absorbing NO for 1 h, the new peak appeared at 1641 cm^{-1}, while the peaks corresponding to ν(N−O) in -NONO showed only little enhancement and the peak at 850 cm^{-1} moved only to 855 cm^{-1}, indicating that most of the NO was dissolved in [P$_{66614}$][Tetz] and some NO was absorbed by [P$_{66614}$][Tetz] as NONOate. Second, the peaks attributed to NONOate appeared after 6 h and increased until the reaction completed. Therefore, most of NO was chemical absorbed by [P$_{66614}$][Tetz] at 6 h where NO absorption capacity was 3.69 mol NO per mol IL. After NO desorption, most of NO, dissolved in [P$_{66614}$][Tetz], was released, because the peak at 1641 cm^{-1} became weaker (Figure S3). As for [P$_{66614}$][Tf$_2$N], the absorption capacity for NO was 0.25 mol NO per mol IL, NO was physically

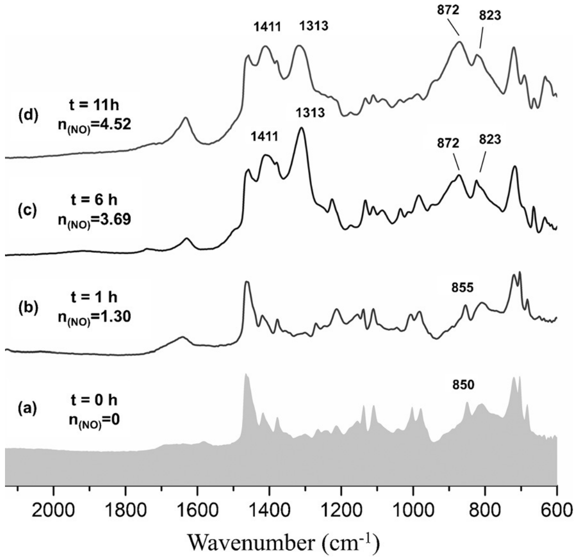
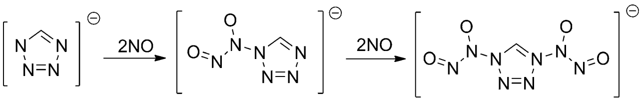


Figure 6. IR spectra of a) [P$_{66614}$][Tetz], b) [P$_{66614}$][Tetz] with bubbling NO for 1 h, c) [P$_{66614}$][Tetz] with bubbling NO for 6 h, and d) [P$_{66614}$]-[Tetz] with bubbling NO for 11 h.

absorbed, and the peak at 1640 was weak (Figure S4). This peak disappeared after desorption, indicating the weak interaction between NO and [P_{66614}][Tf_2N].

When taking the results of the ^{1}H NMR spectra and IR spectra into comparison, the outcome was interesting. There was only about 30 % of [P_{66614}][Tetz] in form of [P_{66614}][Tetz]-NONO in 1 h according to the NMR method (Figure 5 b). Therefore, the variation in FT-IR spectra (Figure 6 b) was also weak where the vibration strength of [P_{66614}][Tetz]-NONO was predicted to be much weaker than that of [P_{66614}][Tetz]-2NONO. When the reaction time prolonged to 6 h, most of [P_{66614}][Tetz] had captured 4NO (Figure 5 c), and the strength of the peaks assigned to -NONO were stronger (Figure 6 c). When the reaction completed, the strength of peaks at 823, 872, and 1411 cm^{-1} were stronger. However, the peak at 1313 cm^{-1} showed a little change (Figure 6 d). According to the DFT calculation, the peak assigned to ν(N−O) in [P_{66614}]-[Tetz]-NONO showed a red shift to that of [P_{66614}][Tetz]-2NONO, which was the strongest in [P_{66614}][Tetz]-NONO. So, the peak at 1313 cm^{-1} exhibited a little change during 6–11 h. Besides, these results also indicated a difference before and after 6 h, which is shown in the NO absorption kinetics curve (Figure 2).

At this point, a possible NO absorption mechanism can be presented in Scheme 2: [Tetz] reacted with NO to form [Tetz]-NONO at first, then [Tetz]-NONO could further absorb NO and [Tetz]-2NONO was formed.



Scheme 2. Possible NO absorption mechanism by [P_{66614}][Tetz].

In conclusion, we reported a novel model for gas absorption, where NO was chemical absorbed as NONOate in azole-functionalized ILs efficient. First, this model was predicted by DFT calculation and compared with Et_2N-NONO. Second, absorption experiments showed that [P_{66614}]-[Tetz] could absorb a high capacity of 4.52 mol NO per mol IL, which is significantly higher than the capacity of other materials for NO capture. Finally, through a combination of quantum chemical calculations, FTIR, and NMR investigations, it was shown that the high NO capacity originated from multiple-site interactions between the anion and NO through the formation of NONOate. To the best of our knowledge, this is the first example of NO chemical absorption by pure ILs. We believe this work paves a way to design new materials in NO absorption and utilization.

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