

Electronic Supplementary Information

Highly Efficient and Reversible SO₂ Capture by Tunable Azole-based Ionic Liquids through Multiple-Site Chemical Absorption

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Experimental Section

Materials and general methods

Tetrazole (Tetz), imidazole (Im), and trihexyl(tetradecyl)phosphonium bromide ([P₆₆₆₁₄][Br]) were purchased from Adrich. An anion-exchange resin [DOWEX MONOSPHERE 550A (OH)] was obtained from Dow Chemical Company. All chemicals were obtained in the highest purity grade possible, and were used as received unless otherwise stated. All Ionic Liquids (ILs) samples were dried under vacuum at 60 °C for 24 h to reduce possible traces of water. ¹H NMR, ¹³C NMR, and ¹⁵N NMR spectra were recorded on a Bruker spectrometer (500MHz) in CDCl₃ or DMSO-d₆ with tetramethylsilane as the standard. FT-IR spectra were recorded on a Nicolet 470 FT-IR spectrometer, and in-situ IR spectra were recorded on a Bruker MATRIX-MF. Decomposition temperatures were measured with a TGA 2100 series of TA Instrument with a heating rate of 10°C/min.

Preparation of azole-based ILs

The ILs were prepared by neutralizing of trihexyl(tetradecyl)phosphonium hydroxide ([P₆₆₆₁₄][OH]) and weak proton donors such as tetrazole according to literature's method.^{1,2} A solution of [P₆₆₆₁₄][OH] in ethanol was prepared from [P₆₆₆₁₄][Br] using the anion-exchange resin method. Equimolar tetrazole was added to the [P₆₆₆₁₄][OH] solution in ethanol. The mixture was then stirred at room temperature for 12 h. Subsequently, ethanol and water were distilled off at 60 °C under reduced pressure. The obtained ILs was dried in high vacuum for 24 h at 60 °C. The structures of these azole-based ILs were confirmed by NMR and IR spectroscopy; no impurities were found by NMR. The water content of these ILs was determined with a Karl Fisher titration and found to be less than 0.1 wt%. The residual bromide content of these basic ILs was determined by a semi-quantitative Nessler cylinder method, which showed that the bromide content was lower than 0.15 wt%.

Absorption and desorption of SO₂

In a typical absorption of SO₂, SO₂ of atmospheric pressure was bubbled through about 1.0 g ILs in a glass container with an inner diameter of 10 mm, and the flow rate was about 60 ml min⁻¹. The glass container was partly immersed in a circulation water bath of desirable temperature. The amount of SO₂ absorbed was determined at regular intervals by the electronic balance with an accuracy of ± 0.1 mg. During the absorption of SO₂ under reduced pressure, SO₂ was diluted with N₂ in order to reduce the partial pressure of SO₂ passing through the system. The SO₂ partial pressure was controlled by changing the flow of SO₂ and N₂. The standard deviations of the absorption loadings under 1.0 and 0.1 bar are 0.07 and 0.05 mole SO₂ per mole IL, respectively.

The ILs were regenerated by heating or bubbling nitrogen through ILs. In a typical desorption of SO₂, N₂ of atmospheric pressure was bubbled through about 1.0 g captured ILs in a glass container, which was partly immersed in a circulation oil bath of desirable temperature, and the flow rate was about 60 ml min⁻¹. The release of SO₂ was determined at regular intervals by the electronic balance.

NMR and IR data of azole-based ILs

[P₆₆₆₁₄][Tetz]: ¹H NMR (CDCl₃): 0.81 (m, 12H, CH₃), 1.10-1.40 (m, 48H, CH₂), 2.10 (m, 8H, PCH₂), 8.28 ppm (s, 1H, Tetraz C5); ¹³C NMR (CDCl₃): 13.8, 14.0, 18.5, 18.9, 21.5, 22.2, 22.6, 28.8, 29.2, 29.4, 29.5, 30.2, 30.3, 30.5, 30.6, 30.9, 31.8, 149.7 ppm; ¹⁵N NMR (CDCl₃): 318.9; 388.9 ppm; IR: 2956, 2925, 2855, 1465, 1420, 1377, 1136, 1110, 1043, 1006, 979, 849, 805, 715, 704, 676, 665, 657, 650 cm⁻¹.

After the absorption of SO₂: ¹H NMR (CDCl₃): 0.87 (m, 12H, CH₃), 1.20-1.60 (m, 48H, CH₂), 2.24 (m, 8H, PCH₂), 8.92 ppm (s, 1H, Tetraz C5); ¹³C NMR (CDCl₃): 13.8, 14.0, 18.5, 18.9, 21.5, 22.2, 22.6, 28.7, 29.2, 29.4, 29.5, 30.1, 30.2, 30.5, 30.6, 30.8, 31.8, 142.9 ppm; ¹⁵N NMR (CDCl₃): 375.5, 280.9 ppm; IR: 2958, 2929, 2857, 1467, 1327, 1144, 1042, 989, 935, 868, 806, 706, 694, 683, 667, 648 cm⁻¹.

[P₆₆₆₁₄][Im]: ¹H NMR (d₆-DMSO): 0.87 (m, 12H, CH₃), 1.20-1.50 (m, 48H, CH₂), 2.17 (m, 8H, PCH₂), 6.66 (s, 2H, Im C4 and C5), 7.08 ppm (m, 1H, Im C2); ¹³C NMR (d₆-DMSO): 14.2, 14.3, 17.7, 18.1, 21.1, 22.3, 22.6, 28.7, 29.2, 29.5, 29.6, 30.2, 30.3, 30.4, 30.6, 30.9, 31.8, 124.6, 142.3 ppm; ¹⁵N NMR (CDCl₃): 250.9 ppm; IR: 2956, 2924,

2854, 2136, 1465, 1379, 1301, 1264, 1217, 1151, 1075, 1062, 1045, 916, 817, 756, 718.701, 686, 676, 667, 652 cm⁻¹.

After the absorption of SO₂: ¹H NMR (d6-DMSO): 0.85 (m, 12H, CH₃), 1.20-1.50 (m, 48H, CH₂), 2.19 (m, 8H, PCH₂), 7.26 (s, 2H, Im C4 and C5), 8.23 ppm (m, 1H, Im C2); ¹³C NMR (d6-DMSO): 14.3, 14.4, 17.8, 18.2, 21.2, 22.4, 22.7, 28.7, 29.3, 29.5, 29.6, 30.3, 30.4, 30.5, 30.6, 31.0, 31.9, 121.1, 135.2 ppm; ¹⁵N NMR (CDCl₃): 200.2 ppm; IR: 2956, 2927, 2856, 2126, 1748, 1466, 1325, 1143, 941, 693, 680, 664, 650 cm⁻¹.

Table S1. The comparison of SO₂ absorption by azole-based ILs with that by other typical ILs and solid phase adsorbent materials.

Ionic liquids	Temperature/	SO ₂ absorption	SO ₂ absorption	Reference
	°C	at 1 bar	at 0.1 bar	
[P ₆₆₆₁₄][Tetz]	20	3.72	1.54	this work
[P ₆₆₆₁₄][Im]	20	4.80	2.07	this work
[Bmim][BF ₄]	20	1.50	0.005	Riisager ³
[Bmim][Tf ₂ N]	20	1.33	0.007	Riisager ³
[TMGBu ₂][BF ₄]	20	1.60	0.080	Riisager ³
[TMG][Lac] ^a	40	1.70 ^c	0.978	Han ⁴
[E ₁ mim][MeSO ₃] ^b	30	2.30		Kim ⁵
[Bmim][MeSO ₄]	50	0.980		Jung ⁶
[Bmim][OAc]	25	1.91	0.664	Shiflett ⁷
[Hmim][Tf ₂ N]	25	0.916	0.005	Brennecke ⁸
Mg-MOF-74 ^d	25		1.560 ^e	Glover ⁹

^a[TMG][Lac], 1,1,3,3-tetramethylguanidinium lactate. ^b[E₁mim][MeSO₃], 1-ethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate. ^cAt 1.2 bar. ^dSO₂ concentration 1000 mg/m³ (~0.35 mba). ^e1.560 mol/kg.

Table S2. The effect of other flue gas constituents on SO₂ capture by [P₆₆₆₁₄][Tetz].^a

Gas	Temperature	Loading (mole/mole IL)
Water stream ^b	20	1.35

SO ₂ (dry)	20	3.72
SO ₂ (wet) ^b	20	3.86 ^d
CO ₂ ^c	20	0.08
90%SO ₂ +10%CO ₂ ^c	20	3.66

^aPerformed at 20 °C for 30 min. ^bRelative humidity is 100%. ^cAt 1 atm. ^dDoes not include mass of loaded water.

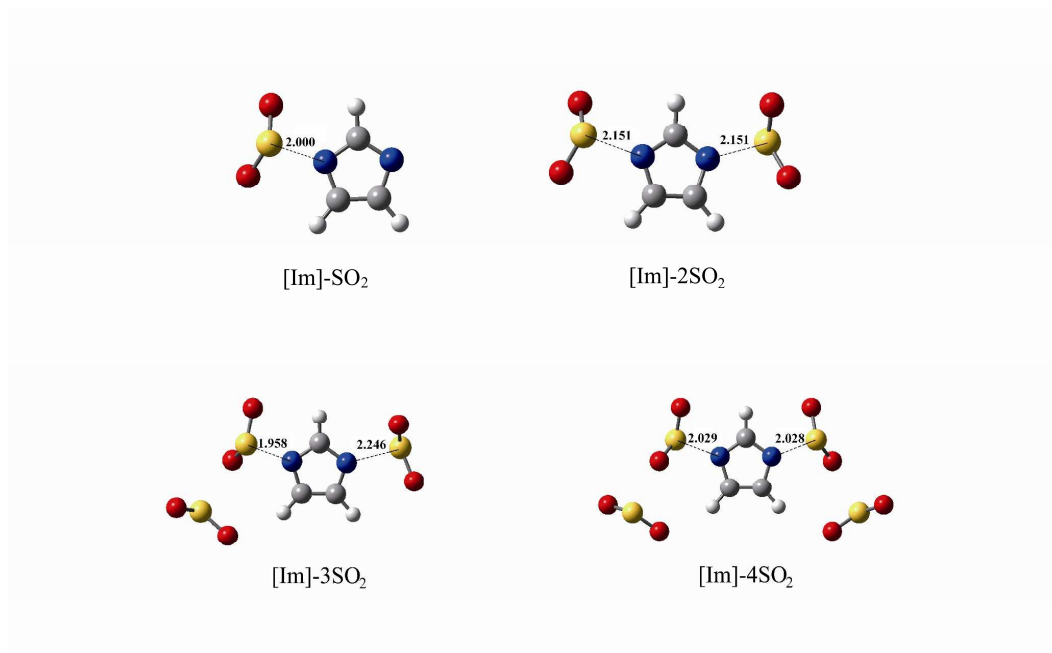


Figure S1. The optimized structure of [Im]-SO₂, [Im]-2SO₂, [Im]-3SO₂, and [Im]-4SO₂.

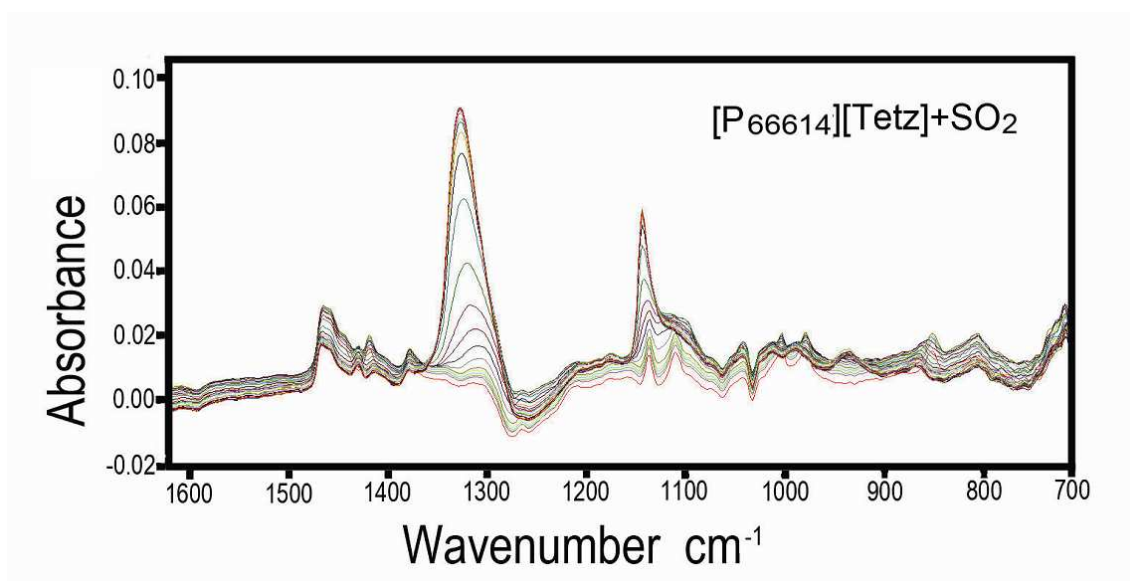
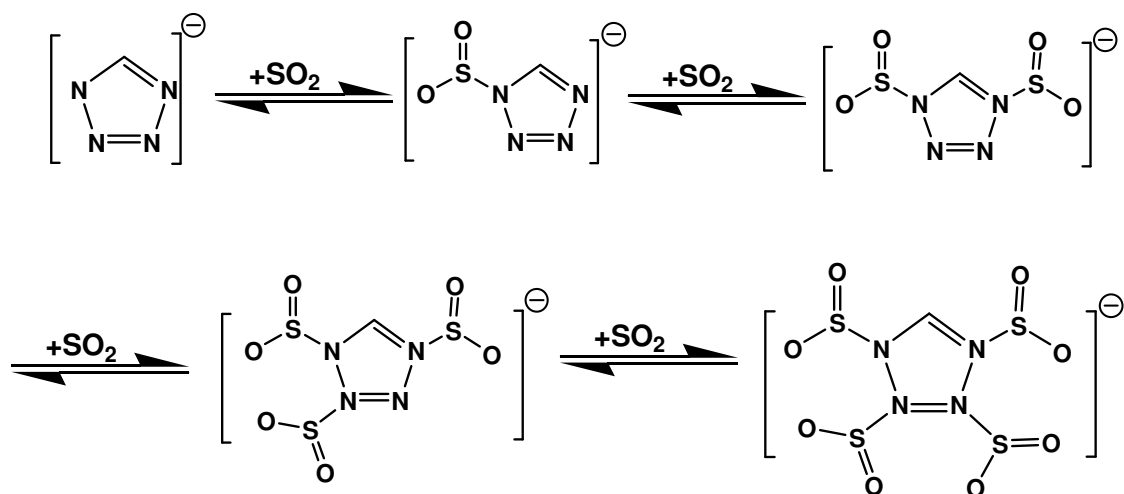


Figure S2. The stack plot of the in-situ FTIR spectra collected every 1 min for the SO₂

capture of [P₆₆₆₁₄][Tetz] in 30 min under 20 °C.



Scheme S1. The SO₂ absorption mechanism by the anion [Tetz] through multiple-site chemical absorption.

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