Electronic Supplementary Information

Highly Efficient SO_2 Capture through Tuning the Interaction between Anion-Functionalized Ionic Liquids and SO_2

Congmin Wang,[1] Junjie Zheng,[1] Guokai Cui,[1] Yanxiao Luo,[1] Guo Yan,[1] and Haoran Li[1,2]

[1]Department of Chemistry, Zhejiang University, Hangzhou 310027, China

[2]State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

Email: chewcm@zju.edu.cn; lihr@zju.edu.cn

Experimental Section

Materials and general methods

[Emim][SCN] and [Emim][C(CN)3] were purchased from Chengjie Chemical Co., Ltd. N_2 (99.99%) and SO_2 (99.9%) were purchased from Hangzhou Jingong Special Gas Co., Ltd. All chemicals were used as received unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (500 MHz) in DMSO-d6 with tetramethylsilane as the standard. FT-IR spectra were measured on a Nicolet 470 FT-IR spectrometer. Decomposition temperatures were measured with a TGA 2100 series of TA Instrument with a heating rate of 10 ^{o}C min^{-1}.

Absorption and desorption of SO_2

In a typical absorption of SO_2, SO_2 at atmospheric pressure was bubbled through about 1 g of IL in a glass container with an inner diameter of 10 mm at a flow rate of about 60 ml min^{-1}. The glass container was partly immersed in a water bath at 20 ^{o}C. The amount of SO_2 absorbed was determined at regular intervals by an electronic balance with an accuracy of ±0.1 mg. During 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 of SO_2 and N_2.

The IL was regenerated by bubbling N_2 at 80 ^{o}C through the IL. In a typical desorption of SO_2, N_2 of atmospheric pressure was bubbled though about 1.0 g IL that captured SO_2 in a glass container, which was partly immersed in a circulated oil bath at 80 ^{o}C, and the flow rate was about 60 ml min^{-1}. The desorption of SO_2 was determined at regular intervals by an electronic balance with an accuracy of ±0.1 mg.

Table S1 The comparison of SO_2 absorption by nitrile-containing anion-functionalized ILs with that by other typical ILs.

ILs [a]	Absorption temperature/^oC	Desorption [c] temperature/^oC	Available SO_2 absorption at 1 atm (g SO_2/g IL)	Reference
[Emim][SCN]	20	80	1.13	This work
[Emim][$C(CN)_3$]	20	80	0.74	This work
[P_{66614}][Tetz]	20	80	0.43	Wang[1]
[P_{66614}][Im]	20	80	0.48	Wang[1]
[Bmim][BF_4]	20	20 [e]	0.40	Riisager[2]
[Bmim][Tf_2N]	20	20 [e]	0.20	Riisager[2]
[$TMGB_2$][Tf_2N]	20	20 [e]	0.20	Riisager[2]
[TMG][Lactate]	40	100	0.42	Han,[3] Kim[4]
[E_1mim][$MeSO_3$]	30	100	0.62	Kim[4]
[Bmim][$MeSO_4$]	50	130 [d]	0.25	Jung[5]
[Bmim][OAc]	25	130 [d]	0.42	Shiflett,[6] Jung[5]
[TMG][TE]	20	100 [e]	0.87	Zhang[7]
[TMG][PhO]	20	100 [e]	0.55	Zhang[7]

[a][Emim][SCN], 1-ethyl-3-methylimidazolium thiocyanate; [Emim][$C(CN)_3$], 1-ethyl-3-methylimidazolium tricyanomethanide; [P_{66614}][Tetz], trihexyl(tetradecyl)phosphonium tetrazolate; [P_{66614}][Im], trihexyl(tetradecyl)phosphonium imidazolate; [Bmim][BF_4], 1-butyl-3-methylimidazolium tetrafluoroborate; [Bmim][Tf_2N], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [$TMGB_2$][Tf_2N], tetramethydibutylguandinium bis(trifluoromethylsulfonyl)imide; [TMG][Lactate], 1,1,3,3-tetramethyguandinium lactate; [E_1mim][$MeSO_3$], 1-ethyl-3-methoxyimidazolium methyl sulfate; [Bmim][OAc], 1-butyl-3-methylimidazolium acetate; [TMG][TE], 1,1,3,3-tetramethyguandinium trifluoroethoxylate; [TMG][PhO], 1,1,3,3-tetramethyguandinium phenolate. [b]Desorbed under bubbling N_2. [c]At 1.2 bar.[e] Desorbed under vacuum. [d]Desorbed by bubbling O_2.

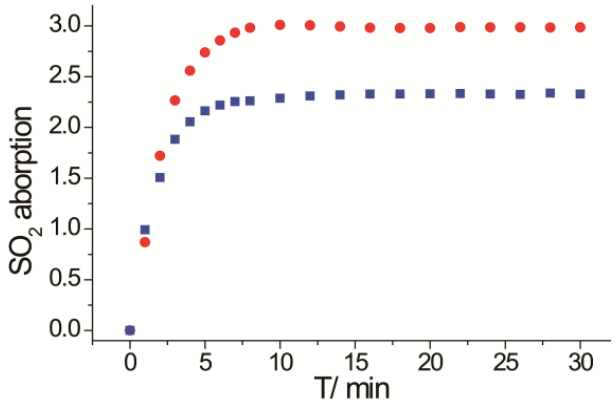

Figure S1 Absorption of SO_2 in [Emim][SCN] (●) and [Emim][$C(CN)_3$] (■) at 20°C and 1 atm.

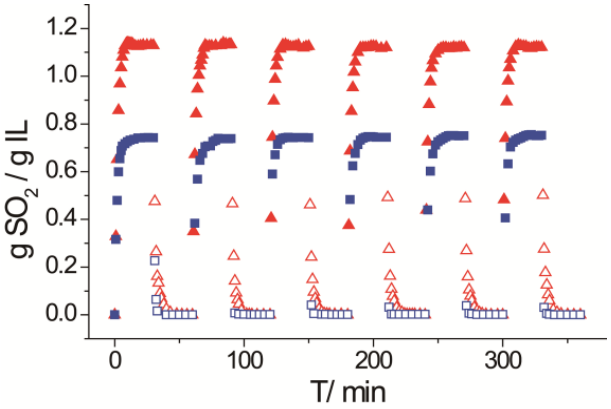

Figure S2 SO_2 absorption/desorption cycles of [Emim][SCN] and [Emim][$C(CN)_3$]. In each cycle, SO_2 is absorbed at 20 °C and 1 atm, and desorbed at 80 °C under N_2. [Emim][SCN], absorption (▲); desorption, (△). [Emim][C(CN)3], absorption, (■); desorption, (□).

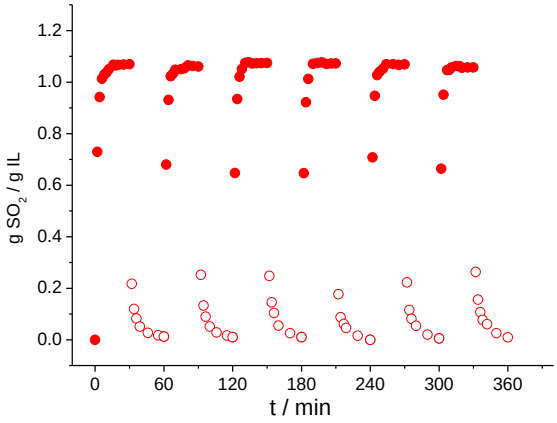

Figure S3 SO_2 absorption/desorption cycles of [Emim][SCN] under vacuum. In each cycle, SO_2 is absorbed at 20 ^oC and 1 atm, and desorbed at 80 ^oC under 0.1atm.

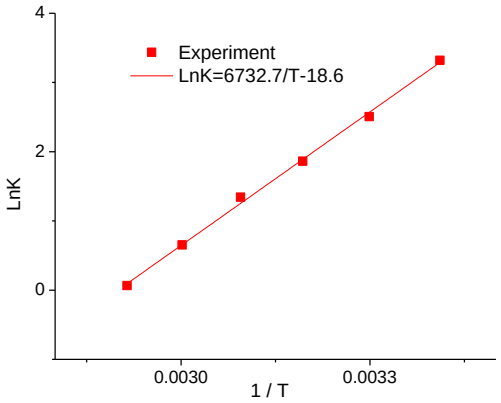

Figure S4 Variation in the natural logarithm equilibrium constant of [EMIM][SCN] with temperature.

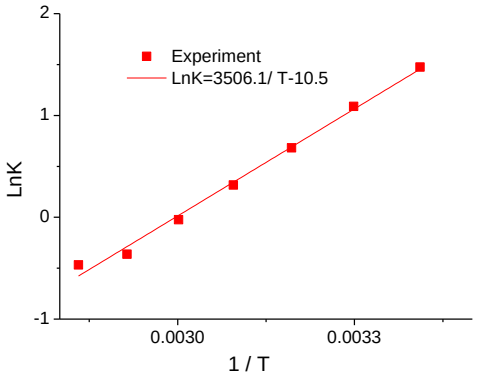

Figure S5 Variation in the natural logarithm equilibrium constant of [EMIM][$C(CN)_3$] with temperature.

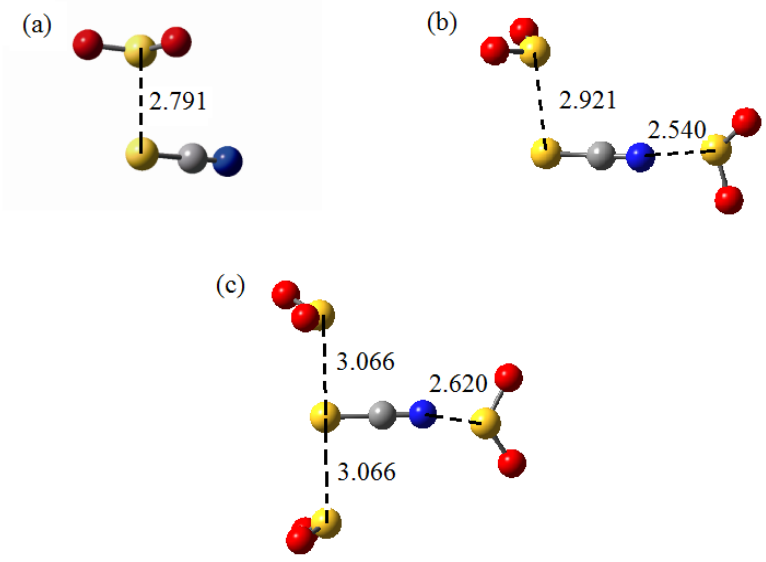

Figure S6 Optimized structures of [SCN]-SO_2, [SCN]-$2SO_2$, [SCN]-$3SO_2$ complexes. (a), [SCN]-SO_2, △H=-73.0 kJ mol^{-1}; (b) [SCN]-$2SO_2$, △H=-45.7 kJ mol^{-1}; (c) [SCN]-$3SO_2$, △H=-26.7 kJ mol^{-1}.

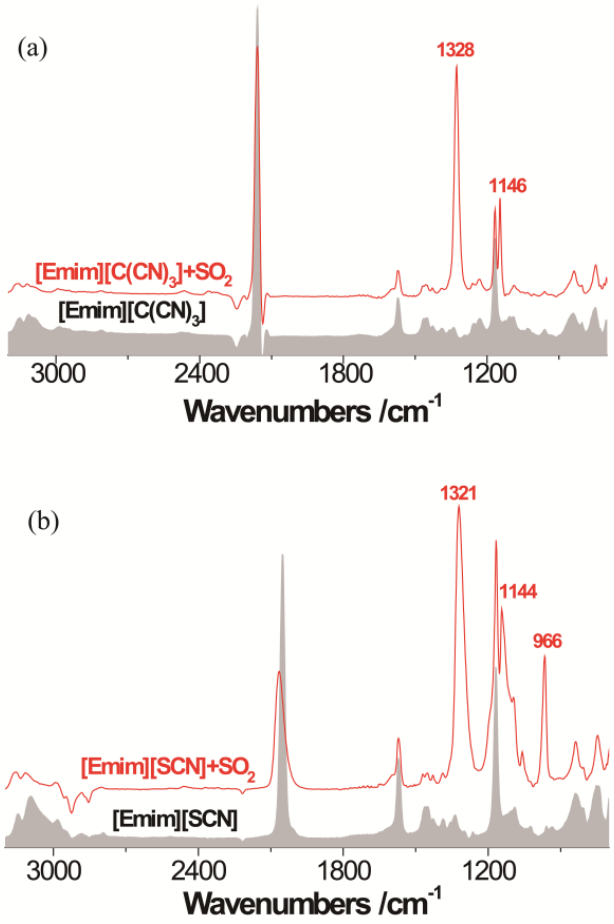

Figure S7 IR spectra of [Emim][SCN] and [Emim][$C(CN)_3$] before and after the absorption of SO_2.

References:

1 C. M. Wang, G. K. Cui, X. Y. Luo, Y. J. Xu, H. R. Li, S. Dai, *J. Am. Chem. Soc.* **2011**, *133*, 11916.

2 J. Huang, A. Riisager, P. Wasserscheid, R. Fehrmann, *Chem. Commun.* **2006**, 4027.

3 W. Z. Wu, B. X. Han, H. X. Gao, Z. M. Liu, T. Jiang, J. Huang, *Angew. Chem., Int. Ed.* **2004**, *43*, 2415.

4. S. Y. Hong, J. Im, J. Palgunadi, S. D. Lee, J. S. Lee, H. S. Kim, M. Cheong, K. D. Jung, *Energy Environ. Sci.* **2011**, *4*, 1802.

5 K. Y. Lee, G. T. Gong, K. H. Song, H. Kim, K. D. Jung, C. S. Kim, *Int. J. Hydrogen Energy*, **2008**, 33, 6031.

6 M. B. Shiflett, A. Yokozeki, *Ind. Eng. Chem. Res.* **2010**, *49*, 1370; (b) K. Y. Lee, H. S. Kim, C. S. Kim, K. D. Jung, *Int. J. Hydrogen Energy.* **2010**, *35*, 10173.

7 Y. Shang, H. P. Li, S. J. Zhang, H. Xu, Z. X. Wang, L. Zhang, J. M. Zhang, *Chem. Eng. J.* **2011**, *175*, 324.