Supporting Information

Protic Ionic Liquid Units Constructed Ionic Framework for Improving Ammonia Uptake

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1. Experimental Section

Chemicals (Materials). In this work, NH₃ (99.999%) was supplied by Foushan Kodi Gas Chemical Industry Co., Ltd. 1,3,5-tri(1H-iMidazol-1-yl) (Ph3Im) (98%) was purchased from the Jinan Henghua technology Co., Ltd. 1-phenylimidazole (PhIm) (98%) was purchased from the Shanghai Aladdin biochemical technology Co., Ltd. Bistrifluoromethane-sulfonimide acid (HTf₂N) was obtained from Jiangxi state chemical industry Co., Ltd. Anhydrous Methanol was supplied by the Sinopharm Chemical Reagent Co., Ltd. All chemical reagents were used without further purification unless otherwise noted.

Preparations of the ionic network frameworks. $[Ph3ImH][Tf_2N]_2$ and $[PhImH][Tf_2N]$ were synthesized by the following methods. To obtain $[Ph3ImH][Tf_2N]_2$, 2.8g Ph-3Im (10.0mmol) was placed in a 50 mL beaker and dissolved in anhydrous methanol (10mL), which followed with the addition of 38.0mL HTf_2N aqueous solution (0.53mol/L) drop by drop. The solution was left for 2 days after being stirred 3 hours to get precipitated solid, which was filtered and washed with cold water several times, the gotten colourless needle-like crystal was placed into the vacuum oven at 80 °C for 24 h, the yield of $[Ph3ImH][Tf_2N]_2$ was 53.7 %. $[PhImH][Tf_2N]$ was synthesized according to the references (D. W. Shang, X. P. Zhang, S. J. Zeng, K. Jiang, H. S. Gao, H. F. Dong, Q. Y. Yang and S. J. Zhang, *Green Chem.*, 2017, **19**, 937-945).

Characterizations. The structure of $[Ph3ImH][Tf_2N]_2$ and $[PhImH][Tf_2N]$ were characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopies. FT-IR spectra were obtained using a Nicolet IS50 spectrometer recording in a range of 500-3900 cm⁻¹. ¹H NMR spectra were obtained using a 500 MHz Bruker Avance III spectrometer in deuterated dimethyl sulfoxide (d₆-DMSO) using tetramethylsilane as the standard. The melting point test was carried out by Tianjin Tianguang Optical YRT-3 melting point tester. Single crystal analysis (S-XRD) data for [Ph3ImH][Tf_2N]_2 was collected on a Aglient Gemini EGemini E. Thermogravimetric analysis (TGA) was carried out using the Shimadzu DTG-60H

under N_2 (99.999%) atmosphere with flow rate as 20 mL/min by a heating ratio of 10 °C /min from 25 to 600 °C. The sites of ammonia reaction were determined by PCA-1200 chemical adsorption instrument. N_2 adsorption isotherm measurements were performed on a micromeritics BAFLEX surface characterization measurement at 77K. Prior to the measurement, the samples were degassed in a vacuum at 90°C for 3 hours.

NH₃ uptake experiments

NH₃ uptake performance were measured by weighing method through open and sealed method as presented at Figure S8 and Figure S9. The open method was operated with controlled ammonia gas flow through the ionic framework until the weight of the sample keep steady within 5min. The sealed method was carried out in a stainless-steel seal pot (approximately 48 ml) under various ammonia concentration until the pressure of the gas in the seal pot maintained constant for at least an hour, and the final pressure was considered as the equilibrium pressure. The temperature of ammonia uptake through open and sealed method was controlled by a heating jacket and water bath, respectively. The effect of NH₃ partial pressure for open method was controlled by the aerated ammonia gas. The NH₃ release from the ionic networks were carried out under vacuum at 80 °C until the weight maintained constant. The coefficient of selectivity for NH₃/CO₂ and NH₃/N₂ were calculated according to the

equation , where 1 and 2 are two gas, $S_{1/2}$ is the capture selectivity of gas 1 over gas 2, c_1 and c_2 is the gas capacity of 1 and 2 (mmol/g, at 100 kPa and 298K), respectively.

2. Supporting figures



Figure S1 The comparison of ¹H NMR and IR spectra of $[Ph3ImH][Tf_2N]_2$ and $[PhImH][Tf_2N]$ with their non-protonated agents. (a) ¹H NMR spectra of $[Ph3ImH][Tf_2N]_2$. (b) ¹H NMR spectra of $[PhImH][Tf_2N]$. (c) ¹H NMR spectra of $[Ph3ImH][Tf_2N]_2$. (d) ¹H NMR spectra of $[PhImH][Tf_2N]$.



Figure S2 The crystal structure of [Ph-3ImH][Tf_2N]₂ confirmed by S-XRD. The red dash line represents hydrogen bond with bond length less than 2.8Å and bond angle larger than 140°.



Figure S3 The optimized structures of cations and the proposed NH₃ containing complexes and the corresponding calculated reaction enthalpies. (a) [PhImH], (b) [Ph3ImH]. Gray, C. blue, N. White, H.



Figure S4 Comparison of the IR spectra data of [PhImH][Tf₂N], its NH₃ saturated complexes, and the sample received after desorption at 80 °C and 1KPa for 30 min.



Figure S5 Comparison of the IR spectra data of the fresh [Ph3ImH][Tf₂N], the sample received after desorption at 80 °C and 1KPa for 30 min, and the sample after ion exchange.



Figure S6 The crystal structure of recovered [Ph-3ImH][Tf₂N]₂ confirmed by S-XRD



Figure S7 The PXRD pattern of the fresh and recovered $[Ph3ImH][Tf_2N]_2$ and the sample after few cycles of NH_3 uptake.



Figure S8 Dynamic ammonia capture device. 1, N_2 cylinder. 2, NH_3 cylinder. 3, buffer device. 4, incubator. 5, water bath. 6, exhaust gas treatment bottle. 7 and 8, needle valves. 9, temperature detector.



Figure S9 Apparatus for measurement of NH₃ capture. 1, NH₃ cylinder. 2, reservoir cell. 3, equilibrium cell. 4-6, needle valves. 7, digital displayer. 8, pump. 9, water bath and magnetic stirrer. 10 and 11, pressure transducers. 12, temperature detector.

3. Supporting tables

Table S1 The detail information about hydrogen bonds with bonds length less than 2.8Å and bonds angle larger than 140° of single crystal structure with six molecules of [Ph3ImH][Tf₂N]₂.

Hydrogen Bond	Hydrogen Bond length (Å)	Hydrogen Bond Angle (°)	Hydrogen Bond	Hydrogen Bond length (Å)	Hydrogen Bond Angle (°)
C_1 - H_1 ···O_1	2.6869	152.424	C_{22} - H_{25} ···· O_{10}	2.5039	163.062
C_2 - H_2 ··· O_3	2.5896	152.305	C_{16} - H_{17} ···· O_{12}	2.5039	163.062
C_3 - H_3 ··· N_1	2.7174	145.233	C_{18} - H_{19} ···O ₁₂	2.3576	165.926
C_4 - H_4 ···O_3	2.4333	153.623	C ₁₉ -H ₂₀ O ₈	1.9894	177.617
C_7 - H_8 ···O ₂	2.7044	144.757	C ₂₃ -H ₂₃ N ₆	2.7174	145.233
C_8 - H_7 ···O_4	2.5039	163.062	C ₂₁ -H ₂₁ O ₁₇	2.3289	151.956
C_{10} - H_{11} ···O ₄	2.3576	165.926	C ₂₆ -H ₂₇ O ₁₄	2.6869	152.424
C_5 - H_5 ··· O_5	2.3576	165.926	C_{29} - H_{30} O_{13}	2.3289	151.956
C_6 - H_6 ··· O_5	2.5039	163.062	C_{28} - H_{28} N_7	2.7174	145.233
N_2 - H_9 ··· N_4	1.8159	169.838	C ₂₅ -H ₂₆ O ₁₆	2.5896	152.305
N_2 - H_9 ··· C_{14}	2.7916	147.558	C ₂₇ -H ₂₉ O ₁₆	2.4333	153.623
C_{12} - H_{13} ··· N_3	2.7174	145.233	C ₂₄ -H ₂₄ O ₁₅	2.6869	152.424
C_{11} - H_{12} ··· O_9	2.3289	151.956	C ₃₆ -H ₃₄ O ₁₈	2.7044	144.757
C_{13} - H_{14} ···· O_{11}	2.6869	152.424	C ₃₀ -H ₃₁ O ₂₀	2.3576	165.926
C_9 - H_{10} ··· O_7	2.2291	160.167	C ₃₅ -H ₃₃ O ₁₉	2.5039	163.062
C_{14} - H_{15} ··· O_7	2.6869	152.424	C_{31} - H_{32} O_{20}	2.5039	163.062
C_{15} - H_{16} ···N ₅	2.7174	145.233	C ₃₂ -H ₃₅ O ₁₉	2.3576	165.926
C_{17} - H_{18} ···· O_6	2.3289	151.956	C_{34} - H_{36} N_8	2.7174	145.233
C_{20} - H_{22} ···O ₁₀	2.3576	165.926	C ₃₇ -H ₃₇ O ₂₁	2.6869	152.424

Entri es	Capture Agent	NH ₃ capacity	Desorption condition	Refs	
1	[Ph3ImH][Tf ₂ N] ₂	15.65 mmol/g (266 mg/g) at 298 K and 1bar	353 K and 1kPa, 1 h	This work	
2	KUF-1a	6.67 mmol/g (11.3 wt%) at 298 K and 1bar	room temperature and vacuum	Hong C.S. ¹	
3	M ₂ Cl ₂ BTDD (M= Mn, Co, Ni)	15.47-12.00 mmol/g (26.3- 20.4 wt%) at 298 K and 1bar	473 K and vacuum	Dinca M. ²	
4	M ₂ Cl ₂ BBTA (M= Co, Ni, Cu)	19.79-14.68 mmol/g (33.6-25.0 wt%) at 298K and 1bar	473 K and vacuum	Dinca M. ³	
5	COF-10	15 mmol/g (25.5 wt%) at 298K and 1bar	473 K and vacuum	Yaghi O.M. ⁴	
6	[MOOC] ₁₇ -COFs (M= Sr)	14.3 mmol/g (24.3 wt%) at 298 K and 1bar	473 K and vacuum	Zhu G.S. ⁵	
7	HKUST-1	7.4 mol/kg (12.6 wt%) at 293K with 2000 mg/m ³ NH ₃ mixure	-	Cohen S.M. ⁶	
8	BPP-5	17.7 mmol/g (30.1 wt%) at 273K and 1 bar	5.3 mmol/g residue at 203 ppm	1 ID 7	
9	BPP-7	16.1 mmol/g (23.4 wt%) at 273K and 1 bar	4.5 mmol/g residue at 204 ppm	Long J.R.'	
10	[Bim][Tf ₂ N]	2.69 mol NH ₃ /mol IL (11.7 wt%) at 313 K and 100 kPa	353 K and 1kPa, 2 h	Zhang S.J. ⁸	
11	[BzAm][Tf ₂ N]	2.8 mol NH ₃ /mol IL (11.9 wt%) at 303 K and 1 bar	303 K and 1 kPa, 2 h, or 323 K and 1 kPa,30 min	Lin J.Q. ⁹	
12	[2-mPy][Tf ₂ N]	3.078 mol NH ₃ /mol IL (14.0wt%) at 313.1 K and 0.10 MPa	353.1 K and 0.10 MPa	Zhang X.P. ¹⁰	
13	SBA-46 wt% [mimC ₃ SO ₃ H][Tf O]	1.53 mmol/g (2.6 wt%) at 0.01 kPa and 293 K	5-10 micron vacuum and 393 K, overnight	Glover T.G. ¹¹	
14	ChCl+PhOH +EG (1:7:4)	9.619 mmol/g (16.4 wt%) at 298.2 K and 101.3 kPa	333.2 K and 0.1 kPa, 2 h	Huang K. ¹²	
15	ChCl + urea (1:2.0)	2.213 mmol/g (3.8 wt%) at 298 K and 95.0 kPa		Peng H.L. ¹³	

 Table S2 Comparison of NH₃ capture and desorption properties for different agents.

4. Reference

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