

## Supporting Information

### Degradation processes of protic ionic liquids for NH<sub>3</sub> separation

Huifang Duan,<sup>a,c,d</sup> Fan Liu,<sup>d</sup> Shahid Hussain,<sup>b</sup> Haifeng Dong,<sup>\*b,d</sup> Xiangping Zhang<sup>b,c</sup> and Zhiyu Cheng<sup>a</sup>

<sup>a</sup> College of Ecological Environment and Building Engineering, Dongguan University of Technology, Guangdong, 523808, China.

<sup>b</sup> CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex System, Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China.

<sup>c</sup> Advanced Energy Science and Technology Guangdong Laboratory, Huizhou, Guangdong, 529599, China.

<sup>d</sup> Huizhou Institute of Green Energy and Advanced Materials, Huizhou, Guangdong, 516003, China.

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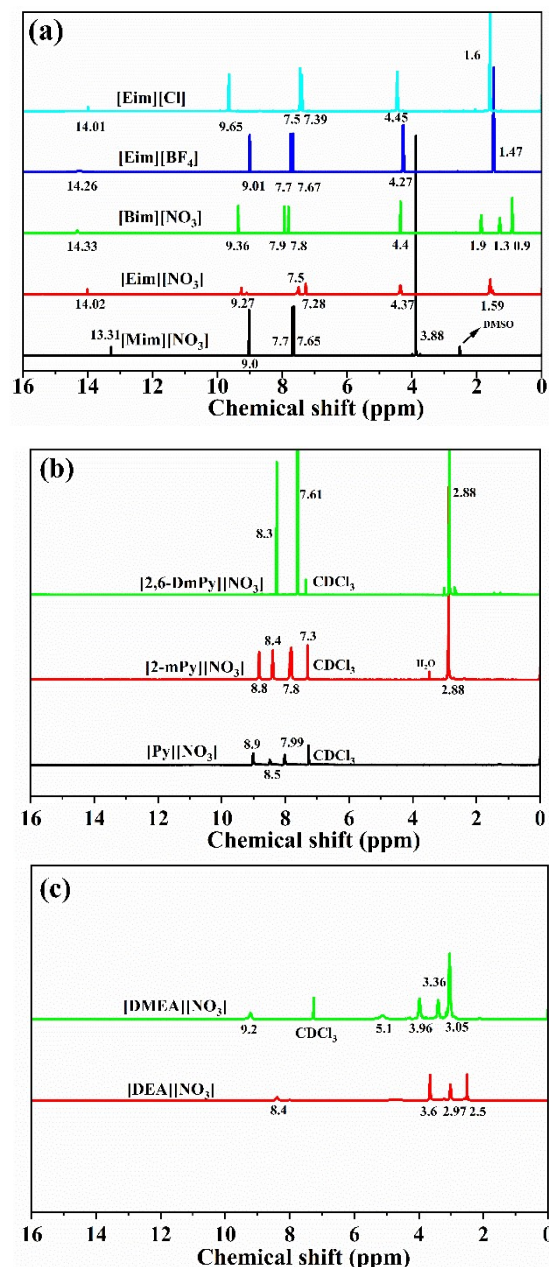
## **SI1. Typical procedure for the Synthesis of PILs.**

1-Ethylimidazole and nitric acid are mixed in an ice water bath, 1-Ethylimidazole: nitric acid=1: 1.05, the temperature of the mixing is maintained at 0-10 °C. After mixed well, mixture was stirred at room temperature for two hours, put in 75 °C rotary evaporator for 4 h to remove moisture, and then placed in a vacuum oven at 60 °C, dried for 48 h, [Eim][NO<sub>3</sub>] is synthesized.

In this paper, other imidazolium ionic liquids and alcohlamonium ionic liquids were synthesized using the same synthesis method as [Eim][NO<sub>3</sub>]. The synthesis of pyridinium protic ionic liquids is one more step than synthesis of imidazolium protic ionic liquids. Take 2-methylpyridine nitrate as an example, first dissolved 2-methylpyridine with ethanol, and then mix 2-methylpyridine with nitric acid in a ratio of 1mol: 1.05mol. The subsequent synthesis paths of pyridinium PILs are the same as synthesis of imidazolium PILs.

## SI2. <sup>1</sup>H NMR spectra of PILs.

The <sup>1</sup>H NMR spectra were measured to verify the structures of the PILs as shown in Fig. S1. <sup>1</sup>H NMR spectra of PILs were measured using the solvents deuterated dimethyl sulfoxide (d<sub>6</sub>-DMSO) or deuterated chloroform (CDCl<sub>3</sub>) (Bruker, 600MHz).



**Fig. S1.** <sup>1</sup>H NMR of PILs: (a) Imidazolium PILs. (b) Pyridinium PILs. (c) Alcoholammonium PILs.

There are five chemical shifts at 3.88, 7.65, 7.7, 9.0 and 13.31 ppm in the <sup>1</sup>H NMR spectra of [Mim][NO<sub>3</sub>], corresponding to hydrogen on -CH<sub>3</sub>, CH=CH-, -2H and -NH,

respectively. Similarly, there are six chemical shifts at 1.59, 4.37, 7.28, 7.5, 9.27 and 14.02 ppm in the  $^1\text{H}$  NMR spectra of  $[\text{Eim}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}=\text{CH}$ ,  $-\text{H}$  and  $-\text{NH}$ , respectively. For both  $[\text{Eim}][\text{BF}_4]$  and  $[\text{Eim}][\text{Cl}]$ , there are peaks at similar chemical shifts with  $[\text{Eim}][\text{NO}_3]$ . In addition, there are eight chemical shifts at 0.9, 1.3, 1.9, 4.37, 7.8, 7.9, 9.36 and 14.33 ppm in the  $^1\text{H}$  NMR spectra of  $[\text{Bim}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{CH}_3$ ,  $-\text{CH}_2$ ,  $-\text{CH}_2$ ,  $-\text{CH}_2$ ,  $\text{CH}=\text{CH}$ ,  $-\text{H}$  and  $-\text{NH}$ , respectively. The results indicated that these  $^1\text{H}$  NMR spectra are consistent with the structures of five imidazolium PILs.

There are three chemical shifts at 7.99, 8.57 and 8.9 ppm in the  $^1\text{H}$  NMR spectra of  $[\text{Py}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{H}$  in 3,5 position C of pyridine ring,  $-\text{H}$  in 4 position C and  $-\text{H}$  in 2,6 position C of pyridine ring, respectively. Similarly, there are five chemical shifts at 2.88, 7.3, 7.8, 8.4 and 8.8 ppm in the  $^1\text{H}$  NMR spectra of  $[2\text{-mPy}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{CH}_3$ ,  $-\text{H}$  in 5 position C,  $-\text{H}$  in 3 position C,  $-\text{H}$  in 4 position C, and  $-\text{H}$  in 6 position C of pyridine ring, respectively. In addition, there are three chemical shifts at 2.88, 7.61 and 8.3 ppm in the  $^1\text{H}$  NMR spectra of  $[2,6\text{-DmPy}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{CH}_3$  in 2,6 position C of pyridine ring,  $-\text{H}$  in 3,5 position C and  $-\text{H}$  in 4 position C, respectively. The results indicated that these  $^1\text{H}$  NMR spectra are consistent with the structures of three pyridinium PILs.

There are four chemical shifts at 2.5, 2.97, 3.6 and 8.4 ppm in the  $^1\text{H}$  NMR spectra of  $[\text{DEA}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{CH}_2$ ,  $-\text{CH}_2$ ,  $-\text{OH}$  and  $-\text{NH}_2$ , respectively. In addition, there are five chemical shifts at 3.05, 3.36, 3.96, 5.1 and 9.2 ppm in the  $^1\text{H}$  NMR spectra of  $[\text{DMEA}][\text{NO}_3]$ , corresponding to hydrogen on  $-\text{CH}_3$ ,  $-\text{CH}_2$ ,  $-\text{CH}_2$ ,  $-\text{OH}$  and  $-\text{NH}$ , respectively. The results indicated that these  $^1\text{H}$  NMR spectra are consistent with the structures of ammonium PILs.

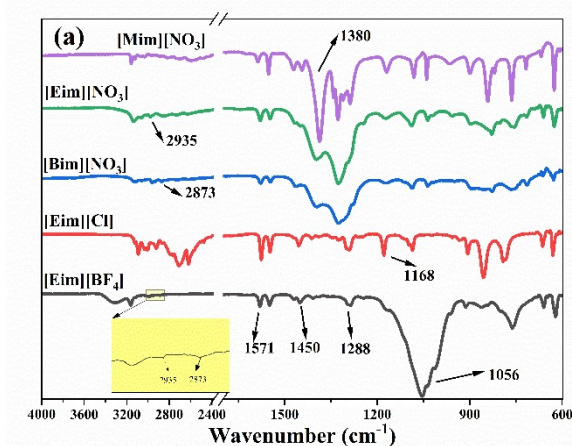
### SI3. The FTIR spectra of PILs.

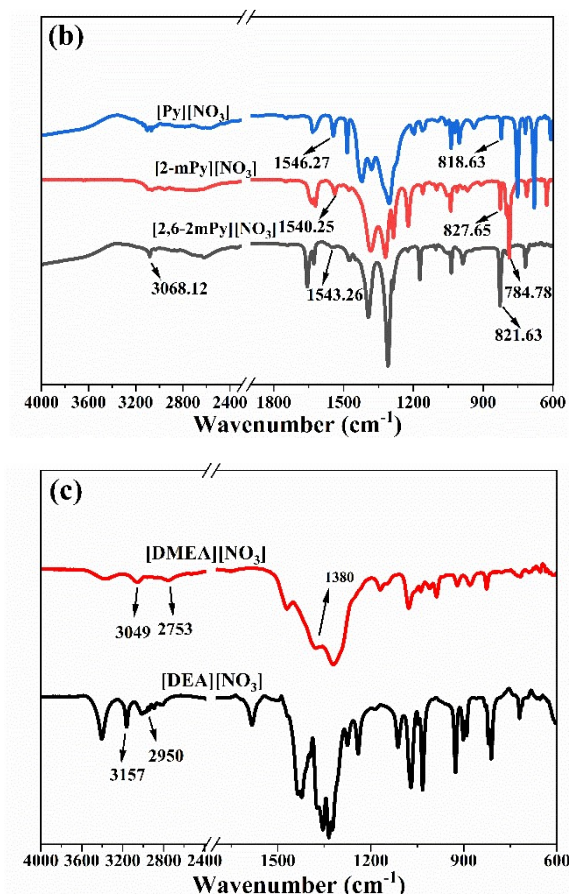
The FTIR spectra is used to determine whether the acid radical binds to the cation. FTIR spectra of these PILs were recorded in the range of 4000-400  $\text{cm}^{-1}$  (Thermo Fisher Scientific, Nicolet iS50).

The infrared spectrum results are shown in Fig. S2 below. The PILs with  $\text{NO}_3^-$  as anion has the absorption peak at 1380  $\text{cm}^{-1}$ , which is, attributed to telescopic vibration of N=O. The PIL containing  $\text{Cl}^-$  anion or  $\text{BF}_4^-$  anion has strong absorption peak of halogen at 1450  $\text{cm}^{-1}$ , 1288  $\text{cm}^{-1}$  and 1056  $\text{cm}^{-1}$ . Therefore, it demonstrated that  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{BF}_4^-$  are successfully combined with cations. The infrared absorption peak of each functional group in the cation appears in the figure.

It can be seen from the FTIR spectra of the imidazolium PILs that the peak of wavenumber at 1571  $\text{cm}^{-1}$  is assigned to C=N stretching vibration, the peaks of wavenumber at 2935, 2873 and 1168  $\text{cm}^{-1}$  attributed to bending vibrations of C-H of  $-\text{CH}_3$ , C-H of  $-\text{CH}_2-$  on alkyl chains and C-H on the imidazole ring, respectively. These peaks of FTIR spectra indicate that [Mim][ $\text{NO}_3$ ], [Eim][ $\text{NO}_3$ ], [Bim][ $\text{NO}_3$ ], [Eim][Cl] and [Eim][ $\text{BF}_4$ ] were all synthesized successfully.

For the three pyridinium PILs, the peaks of wavenumber at 3068, 1540 and 820  $\text{cm}^{-1}$  attributed to stretching vibration of C-H, stretching vibrations of aromatic rings (skeletal spectral bands) and out-of-plane bending vibrations of C-H on aromatic rings, respectively, this indicates the presence of the pyridine ring. [2-mPy][ $\text{NO}_3$ ] and [2,6-DmPy][ $\text{NO}_3$ ] have stronger peak of stretching vibration at 1380  $\text{cm}^{-1}$  than [Py][ $\text{NO}_3$ ], this is due to the existence of  $-\text{CH}_3$  at 2 and 6 positions C on the pyridine ring. Therefore, [Py][ $\text{NO}_3$ ], [2-mPy][ $\text{NO}_3$ ] and [2,6-DmPy][ $\text{NO}_3$ ] were all synthesized successfully.





**Fig. S2** FT-IR spectra of PILs: (a) Imidazolium PILs. (b) Pyridinium PILs. (c) Alcohlonium PILs

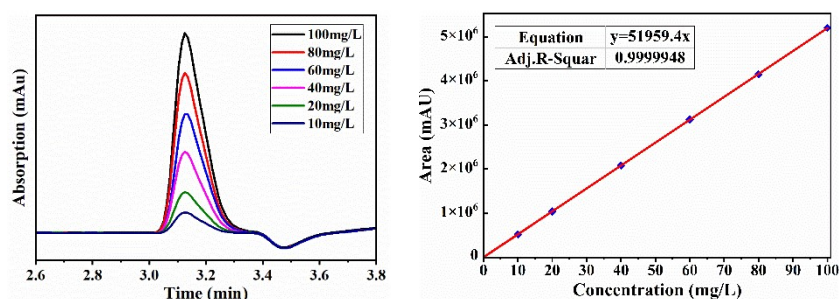
For the three alcohlonium PILs, the peak of wavenumber at 3398 cm<sup>-1</sup> is assigned to O-H stretching vibration; the peak of wavenumber at 3157 cm<sup>-1</sup> is assigned to N-H stretching vibration; the peak of wavenumber at 3049 cm<sup>-1</sup> is assigned to -CH<sub>3</sub> stretching vibration; the peaks of wavenumber at 2753 cm<sup>-1</sup> and 2950 cm<sup>-1</sup> attributed to -CH<sub>2</sub>. The presence of these characteristic peaks indicates the successful synthesis of [DEA][NO<sub>3</sub>] and [DMEA][NO<sub>3</sub>].

#### SI4. HPLC test conditions and Standard curves of PILs.

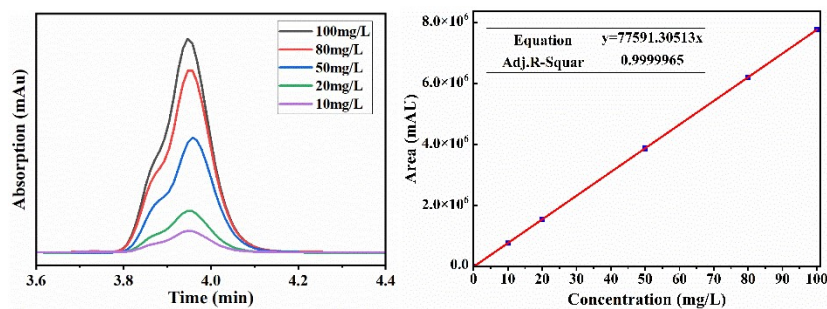
These Standard curves of PILs obtained by HPLC external standard method.

**Table S1.** Test conditions of HPLC

PILs	Mobile phase	Flow rate (mL/min)	Ultraviolet wavelengths (nm)
[Bim][NO <sub>3</sub> ]	Acetonitrile:25mM/L potassium dihydrogen phosphate+ 0.5% triethylamine / phosphate buffer solution (pH=3)= 35:65	0.8	204
[2-mPy][NO <sub>3</sub> ]	Methanol:25mM potassium dihydrogen phosphate/ phosphate buffer solution (pH=3)	1.0	263
[Mim] [NO <sub>3</sub> ]	Methanol:25mM potassium dihydrogen phosphate/ phosphate buffer solution (pH=3)=30:70	1.0	254
[Eim] [NO <sub>3</sub> ]	Acetonitrile:25mM potassium dihydrogen phosphate/phosphate buffer solution (pH=3)=30:70	0.6	212
[Eim] [Cl]	Same as above	1.0	212
[Eim] [BF <sub>4</sub> ]	Same as above	1.0	212
[DMEA][NO <sub>3</sub> ]	Same as above	1.0	203



**Fig. S3 (a).** Standard curve of [Bim][NO<sub>3</sub>]



**Fig. S3 (b).** Standard curve of [Eim][NO<sub>3</sub>]



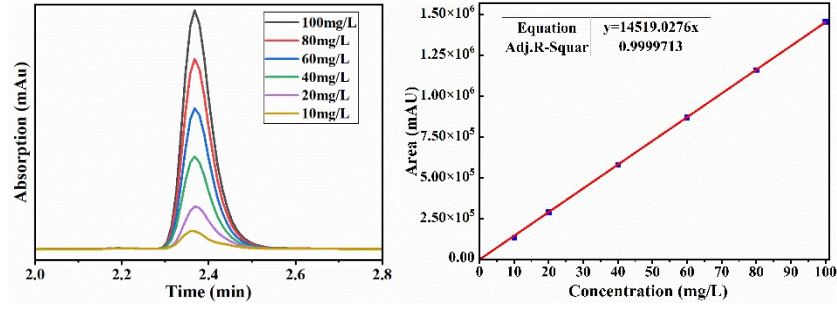


Fig. S3 (c). Standard curve of [Eim][Cl]

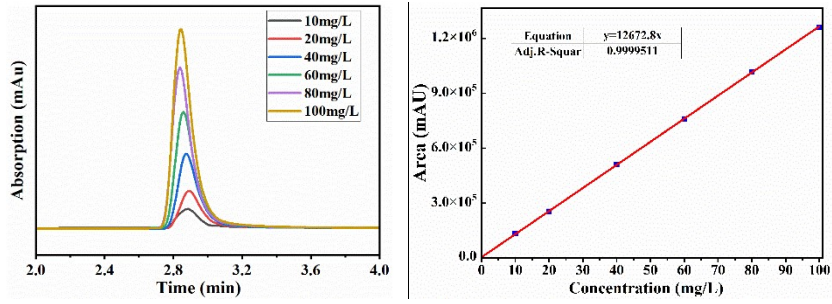


Fig.S3 (d). Standard curve of [Eim][BF<sub>4</sub>]

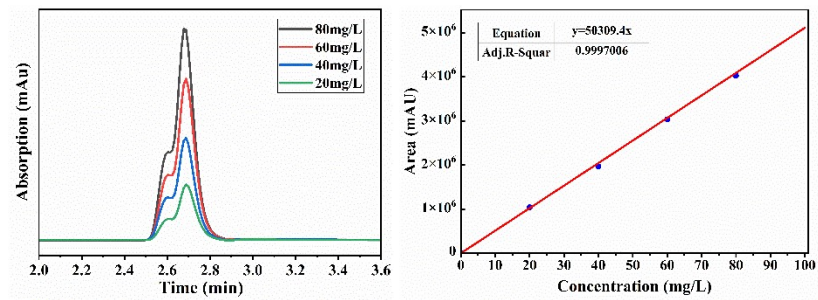


Fig. S3 (e) Standard curve of [Mim][NO<sub>3</sub>]

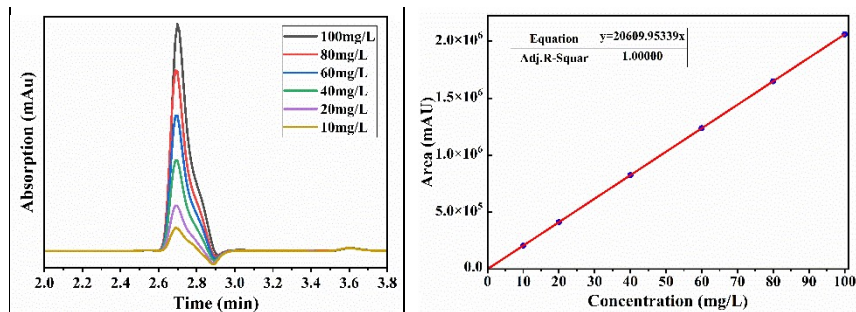
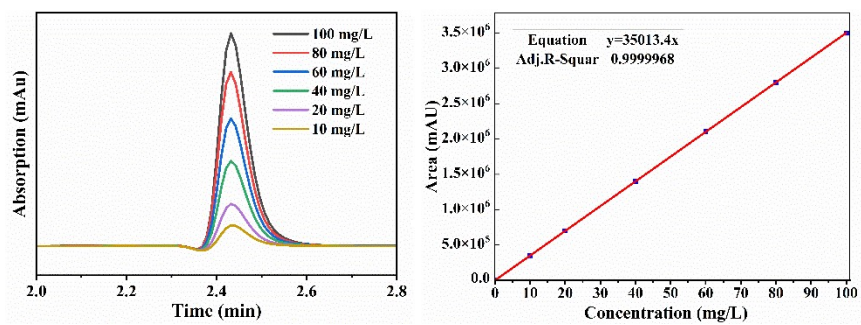


Fig. S3 (f). Standard curve of [2-mPy][NO<sub>3</sub>]



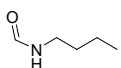

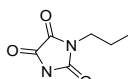
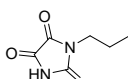
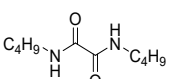


**Fig. S3 (g) Standard curve of [DMEA][NO<sub>3</sub>]**

## SI5. Main products after 600 h degradation of PILs.

Due to the content of products is small, products could not be measured by HPLC and be isolated for individual identification. Therefore, the area normalization method was used to roughly quantify the main products. These main products after 600 h degradation of imidazolium, pyridinium and alcoholmonium PILs were summarized in following Table S2-4.


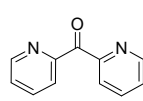
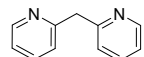
**Table S2.** Main degradation products of [Bim][NO<sub>3</sub>]

PILs	Main degradation products						
[Bim][NO <sub>3</sub> ]	1  <sup>a</sup> @25.63%	2  @1.55%	3  @1.68%	4  @14.39%	5  @ 4.61%	6  @ 13.76%	7  @ 18.53%

<sup>a</sup> denotes the products identified by the standa

@ denotes the proportion of relative area

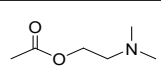

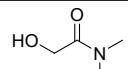
**Table S3.** Main degradation products of [2-mPy][NO<sub>3</sub>]

PILs	Main degradation products		
[2-mPy][NO <sub>3</sub> ]	1  @74.05%	2  <sup>a</sup> @6.92 %	3  @7.95%

<sup>a</sup> denotes the products identified by the standards

@ denotes the proportion of relative area

**Table S4.** Main degradation products of [DMEA][NO<sub>3</sub>]

PILs	Main degradation products		
[DMEA][NO <sub>3</sub> ]	 @50.31%	 @25.03%	 @22.73%

@ denotes the proportion of relative area

## SI6. TIC of PILs in GC-MS after 600 h degradation at 120 °C.

Variations in content of main degradation products from GC-MS

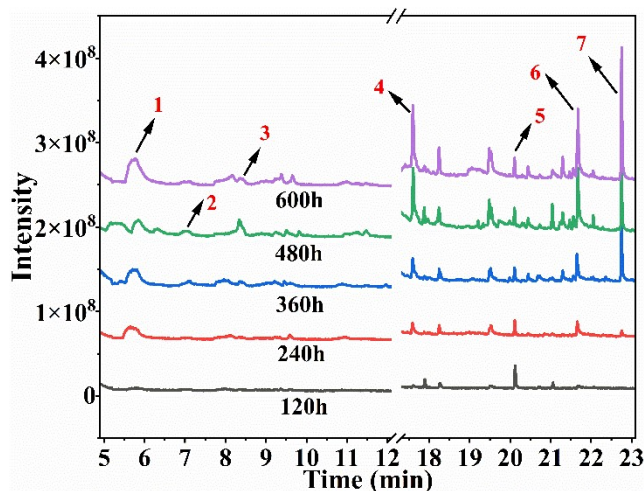


Fig. S4 TIC in GC-MS of [Bim][NO<sub>3</sub>] at 120 °C

The variations of the content of these main products of [Bim][NO<sub>3</sub>], summarized in Table S2, are shown in Fig. S4.

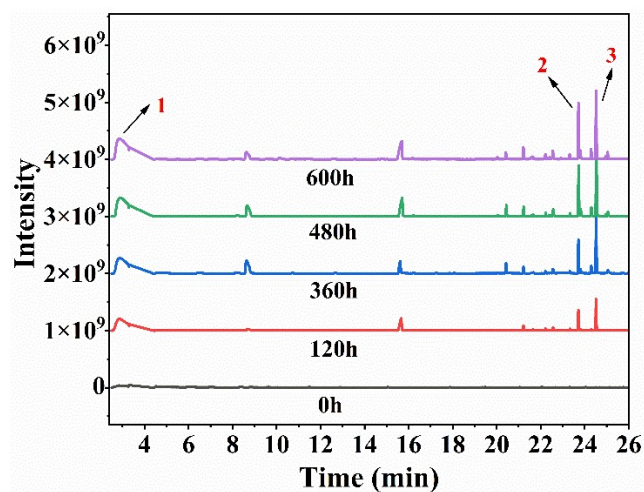
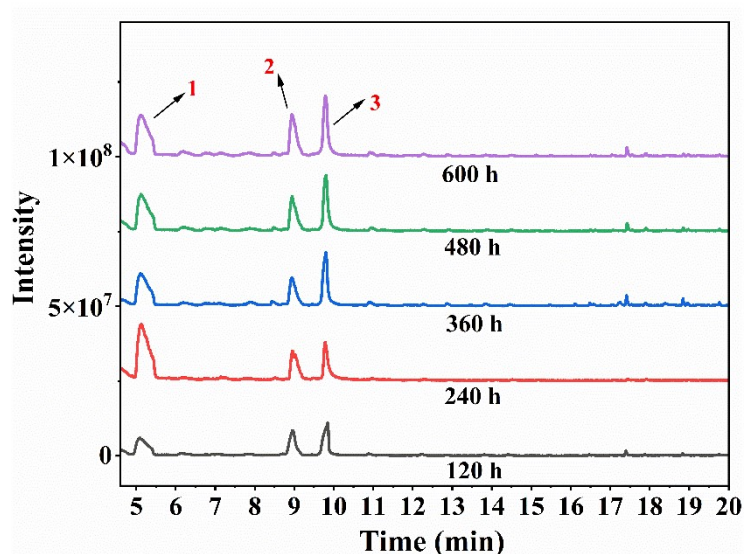


Fig. S5 TIC in GC-MS of [2-mPy][NO<sub>3</sub>] at 120 °C

The variations in the content of the primary products of [2-mPy][NO<sub>3</sub>] with increasing degradation time are shown in Fig. S5. The content of three main products of [2-mPy][NO<sub>3</sub>] showed an increasing trend. Especially products 1 and 3 significantly increased in content. The content of product 2 is less than 3 due to the transformation from product 2 to product 3.



**Fig. S6** TIC in GC-MS of [DMEA][NO<sub>3</sub>] at 120 °C

As shown in Fig. S6, three major products were produced in the degradation of [DMEA][NO<sub>3</sub>]. The content of these three products was high. The content of product 1 increased and then decreased, reaching the highest content at 240 h and then decreased, while the content of products 2 and 3 showed an upward trend with increasing degradation time.

SI7. Mass spectrum of main degradants and standard identification.

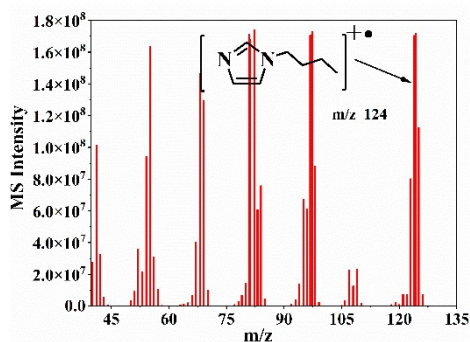


Fig. S7 Mass spectrum of 1-butylimidazole

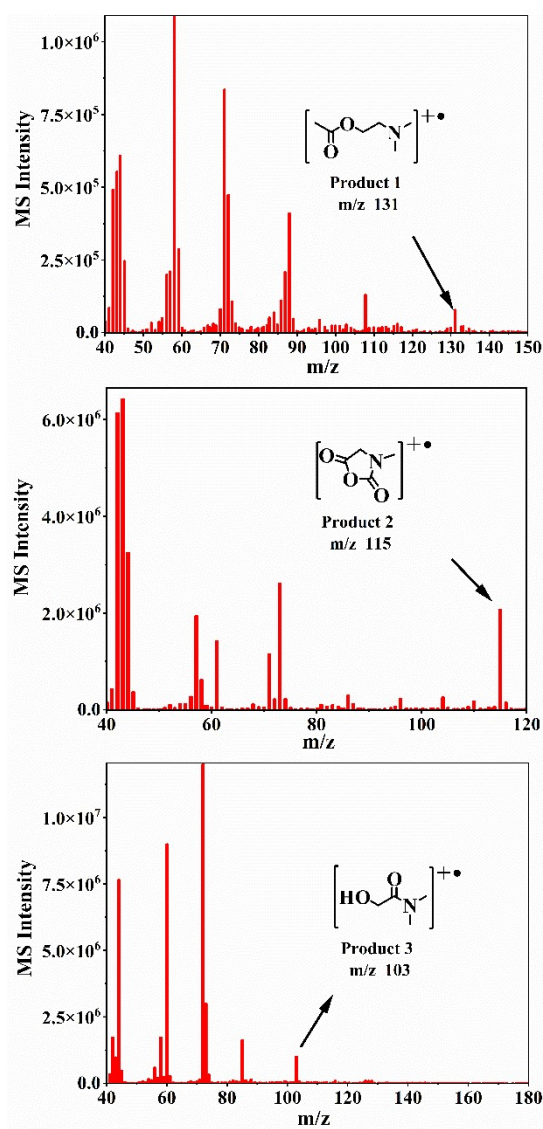
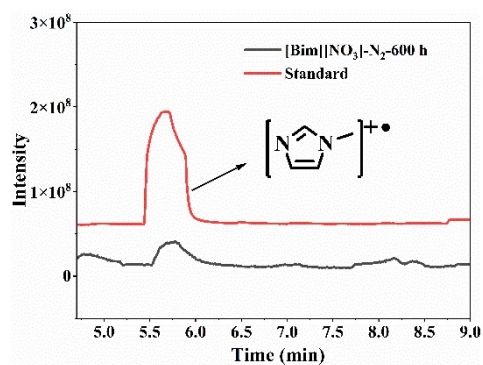


Fig. S8 Mass spectrum of three main degradants in the degradation of [DMEA][NO<sub>3</sub>]

at 120 °C for 600h



**Fig. S9** Comparison of times of peaks in TIC between product 1 (1-methyl imidazole) of [Bim][NO<sub>3</sub>] and standard.