

Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis

Yuanyuan Cao and Tiancheng Mu*

Department of Chemistry, Renmin University of China, Beijing 100872, P. R. China

S Supporting Information

ABSTRACT: The thermal stabilities of 66 ionic liquids (ILs) were investigated using the thermogravimetric analysis (TGA) method. Isothermal TGA studies on the ILs showed that ILs exhibit decomposition at temperatures lower than the onset decomposition temperature (T_{onset}), which is determined from ramped temperature TGA experiments. Thermal decomposition kinetics of ILs was analyzed using pseudo-zero-order rate expression and their activation energy was obtained. Parameter $T_{0.01/10\text{h}}$, the temperature at which 1% mass loss occurs in 10 h, was used to evaluate the long-term thermal stability of ILs. The thermal stability of the ILs was classified to five levels according to T_{onset} . The ILs thermal stability is dependent on the structure of ILs, i.e., cation modification, cation and anion type. The correlations between the stability and the hydrophilicity of ILs were discussed. Finally, the thermal stabilities of acetate-based ILs, amino acid ILs, and dicyanamide ILs were analyzed.

1. INTRODUCTION

Ionic liquids (ILs), also known as room temperature molten salts, have many unique properties such as negligible vapor pressure, large liquid range, and high onset decomposition temperature (T_{onset}).^{1–5} In addition, there is a huge range of possible combinations between cation and anion, which contribute to the designability of ILs.⁶ They have been successively applied in many fields, and high temperature application may be one of the most wide application types: to name just a few, solvents for organic reactions at high temperature⁷ and biomass dissolution using acetate-based ILs (AcILs),^{8–11} amino acid ILs (AAILs),¹² and allyl-imidazolium-based ILs¹³ ([AMIM][Cl]) at elevated temperature for a period of time. Therefore, it is important to investigate the thermal stability of ILs.

Usually, the thermal stability of ILs is characterized by T_{onset} ¹⁴ which was obtained from the intersection of the baseline weight and the tangent of the weight dependence on the temperature curve as decomposition occurs. However, ILs were found to degrade at temperature significantly lower than the onset temperature. For example, decomposition temperature of ILs [bmpy][Tf₂N] and [BMIM][Tf₂N] were reported to be near 400 °C, while significant decomposition was observed at 250 °C.¹⁴ Therefore, a practical parameter $T_{0.01/x}$ (the temperature at which the decomposition of ILs reaches 1% for a given time x) was proposed to judge the long-term stability of ILs instead of T_{onset} . The difference between T_{onset} and $T_{0.01/10\text{h}}$ (the temperature at which 1% mass loss occurs in 10 h) was as large as 200 °C, which proved again that the thermal stability of ILs was complicated.^{15,16}

The thermal stability of ILs mainly depends on the ILs structure, i.e., cation/anion type, and cation modification (chain length, substituent number, C2 methylation and functionalization). The decomposition temperature could change from 200 to 400 °C by varying anion type, which indicates that anion plays the most important role on determining thermal stability.^{5,17–19} Thermal stabilities of ILs with different anions

have a good correlation with anion coordinating nature, nucleophilicity, and hydrophilicity.^{4,5,10,20,21} Imidazolium ILs are generally more stable than pyridinium, tetraalkyl ammonium, and piperidinium ILs.^{21,22} Besides the structure of ILs, contaminants (such as water, halide)^{23–28} and experimental conditions (such as sample mass, heating rate, atmosphere type, atmosphere flowing rate, sample pan material, and instrument type)^{17,24} could also have significant effects on the reported thermal stabilities of ILs.

The decomposition mechanism of ILs is another important issue. Several powerful analysis methods such as thermogravimetric analysis coupled with mass spectrometry (TGA-MS),^{29–32} pyrolysis-gas chromatography (pyrolysis-GC),^{33,34} and thermal desorption mass spectroscopy (TD-MS)¹⁹ have been successfully applied in measuring decomposition products and speculating the decomposition mechanisms of ILs. Previous studies show that most of the degradation processes of ILs are the substituent reaction, i.e., anion attack the cation, lead to the cleavage of C–N bond, and contained S_N2 and S_N1 pathways.^{19,29,35} Elimination or rearrangement reaction may occur when ILs comprising noncoordinative anions.^{29,33} In addition, quantum chemical calculations afford further information on the decomposition mechanisms.^{30,31,36}

In addition to this, some reviews have also been published on the thermal stability of ILs.^{17,18,37} However, the data were measured at different conditions. Hence thermal stability data from different literatures are not comparable.^{22,38,39} Meanwhile, studies on long-term stability are limited, and most investigations focus on conventional ILs, such as [BMIM][PF₆], [BMIM][Tf₂N], [BMIM][Cl], and so on.^{28,30,31,40–44} The thermal stabilities of functionalized ILs and some specific ILs, such as AcILs, AAILs, and cyano-based ILs, need to be

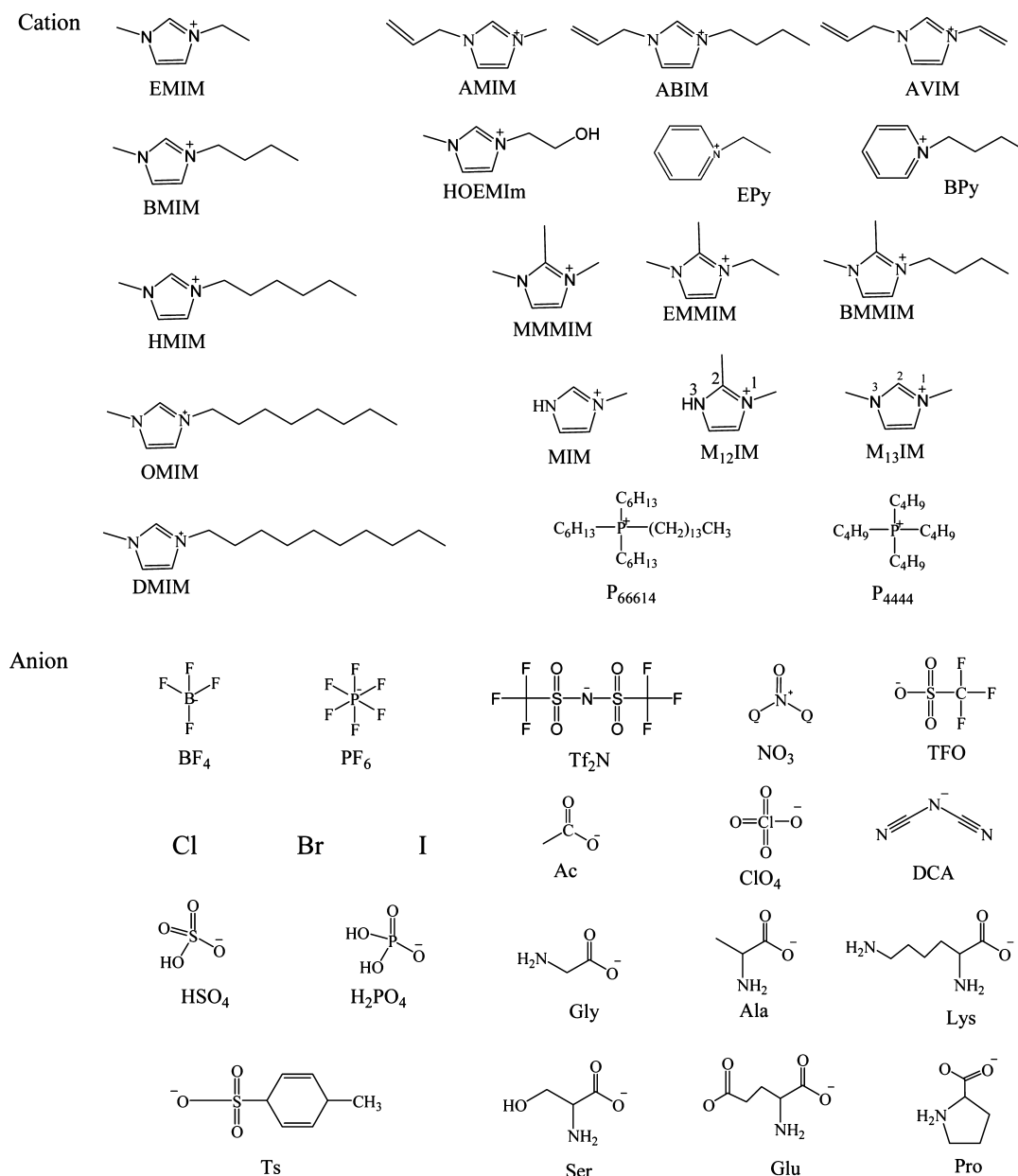
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Scheme 1. Structure and Notation of 66 ILs Composed of 19 Cations and 20 Anions



further investigated. Thus, in this work, the short-term thermal stability (by T_{onset}), decomposition kinetics (by rate constant k , activation energy E_a , and pre-exponential factor A), and long-term thermal stability (by $T_{0.01/10h}$) of 66 ILs composed of 19 kinds of cations and 20 kinds of anions were investigated. Cations investigated include 1-ethyl-3-methyl-imidazolium ([EMIM]), 1-butyl-3-methyl-imidazolium ([BMIM]), 1-hexyl-3-methyl-imidazolium ([HMIM]), 1-octyl-3-methyl-imidazolium ([OMIM]), 1-decyl-3-methyl-imidazolium ([DMIM]), 1-methyl-imidazolium ([MIM]), 1,2-dimethyl-imidazolium ([M₁₂IM]), 1,3-dimethyl-imidazolium ([M₁₃IM]), 1,2,3-trimethyl-imidazolium ([MMMIM]), 1-ethyl-2,3-dimethyl-imidazolium ([EMMIM]), 1-butyl-2,3-dimethyl-imidazolium ([BMMIM]), 1-allyl-3-methyl-imidazolium ([AMIM]), 1-allyl-3-butyl-imidazolium ([ABIM]), 1-allyl-3-vinyl-imidazolium ([AVIM]), 1-(2-hydroxyethyl)-3-methylimidazolium ([HOEMIM]), *N*-ethyl-pyridinium ([EPy]), *N*-butyl-pyridinium ([BPy]), tetradecyltriethylphosphonium ([P₆₆₆₁₄]), and tetra-

butylphosphonium ([P₄₄₄₄]). Anions investigated are tetrafluoroborate ([BF₄]), hexafluorophosphate ([PF₆]), bis(trifluoromethylsulfonyl)imide ([Tf₂N]), acetate ([Ac]), chloride ([Cl]), bromide ([Br]), iodide ([I]), nitrate ([NO₃]), trifluoromethanesulfonate ([TFO]), perchlorate ([ClO₄]), dicyanamide ([DCA]), hydrogen sulfate ([HSO₄]), dihydrogen phosphate ([H₂PO₄]), tosylate ([Ts]), glycinate ([Gly]), alaninate ([Ala]), serinate ([Ser]), glutamate ([Glu]), lysinate ([Lys]), and proline ([Pro]). The structure, notation, and cation–anion matrix are listed in Scheme 1 and Figure 1. On the basis of their structure diversity, the influence of cation chain length, cation substituent number, cation functionalization, C2 methylation, cation type, and anion type on the thermal stability of ILs was discussed. Finally, the thermal stability of AAILs, AAILs, and cyano-based ILs was analyzed in detail aiming to give guidance for their further application.

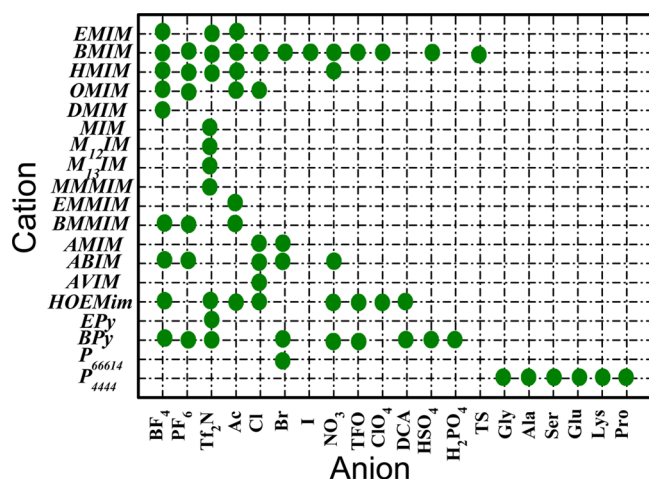


Figure 1. Cation-anion matrix of the studied 66 ILs.

2. EXPERIMENTAL SECTION

Six AAILs (Scheme 1 and Figure 1) were synthesized according to the literature.⁴⁵ The ¹H and ¹³C NMR analysis (Bruker AM 400 MHz spectrometer) indicated that no detectable impurities and degradants existed in the new synthesized ILs. All other ILs listed in Scheme 1 and Figure 1 were purchased from Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physical, Chinese Academy of Sciences, with purity >99%. Before experiment, the ILs were dried in vacuum for 96 h with the desiccant P₂O₅ nearby, with different dry temperature due to different ILs types. AAILs and AAILs were evacuated at 40 °C, while the other types of ILs were evacuated at 50 °C. Karl Fisher measurement ensured that the water content in the ILs was less than 220 ppm. Inductively coupled plasma optical emission spectrometry (ICP-OES) with a Varian Vista MPX measured the metal ion contents Li and Na (<30 ppm), and the content of Cl (<45 ppm) except for the ILs with Cl anion such as [BMIM][Cl], [OMIM][Cl], [AMIM][Cl], [AVIM][Cl], and [ABIM][Cl]. The nitrogen atmosphere with purity over 99.999% was supplied by Beiwen Gas Chemical Industry Co. Ltd.

Thermogravimetric Analyzer Q50 (TA Instrument company, America) was applied to investigate the thermal stability and decomposition kinetics of the ILs in nitrogen atmosphere. The short-term stability of ILs (about 18–20 mg with the mass precision ±0.1 μg) was measured at ramp mode (ramp 10 °C/min to 700 °C, N₂ flow 40 mL/min, Platinum pans). Meanwhile the long-term stability and decomposition kinetics were conducted at isothermal mode (heating 20 °C/min, from room temperature to specified isothermal temperature and then isothermal for 3 h, N₂ flow 40 mL/min, platinum pans, isothermal temperature interval 20 °C) at different isothermal temperature range for different types of ILs ([Ac], from 120 to 180 °C; [Cl], [Br], [I], [DCA], and [H₂PO₄], from 120 to 200 °C; AAILs (cation is [P₄₄₄₄] and anion is [Gly], [Val], [Ser], [Glu], [Lys] and [Pro], from 120 to 220 °C; [NO₃], [TFO], [HOEMim][ClO₄], and [BPy] [HSO₄], from 160 to 260 °C; and [BF₄], [PF₆], [Tf₂N], [TS], [BMIM][ClO₄], [BMIM][HSO₄], and [P₆₆₆₁₄][Br], from 200 to 300 °C). The decomposition of each ILs sample was performed three times with the deviations below 1.5%.

Three parameters, T_{onset} , T_{start} and T_{peak} could be obtained from fast scan TGA. T_{onset} is the intersection of the baseline weight and the tangent of the weight dependence on the

temperature curve as decomposition occurs. T_{start} is the temperature at which the decomposition of the sample just starts. Similarly, T_{peak} is the temperature at which the sample has maximum degradation, which could be obtained from the peak in the DTG curves. Note that if there are one more peaks in DTG curves, we only select one temperature corresponding to the highest peak and list them in Table 1.

3. RESULTS AND DISCUSSION

3.1. Two Measurement Methods for Evaluation of Thermal Stability. TGA is the most common used technique to investigate the thermal stability. Ramped temperature analysis and isothermal temperature analysis could be used to measure short-term and long-term stability of ILs. Both of them are important for comprehensive understanding of the stability.

3.1.1. Short-Term Thermal Stability. T_{onset} , T_{start} and T_{peak} the three parameters to characteristic ILs short-term thermal stability are shown in Table 1. Usually, they follow the order $T_{\text{start}} < T_{\text{onset}} < T_{\text{peak}}$ for the same IL. That is to say, ILs start to decompose at lower temperature than T_{onset} and the difference between them is about 100 °C. This indicates that the thermal stability would be overestimated using the T_{onset} value. Other reports also draw this conclusion.^{14,21,36} It is reasonable because the temperature increases rapidly at a fixed rate in the experiment, so it is easy to pass through the actual decomposition temperature without measuring mass loss, i.e., ILs may degrade at lower temperature within long period.³⁶ T_{peak} is another parameter to indicate ILs short-term thermal stability and the number of peaks obtained from DTG curves is significantly important. Unexpectedly, most of the 66 ILs have one peak in the DTG curves except (1) [ClO₄] anion with [BMIM] and [HOEMim] cation (Supporting Information Figure S2); (2) [DCA] anion with [HOEMim] and [BPy] cation (Supporting Information Figure S3); (3) [H₂PO₄] anion with [BPy] cation (Supporting Information Figure S4). This result is interesting and needs further investigation.

Literature reported T_{onset} values of ILs are also listed in Table 1. External experimental conditions,^{17,24} for example, sample mass, heating rate, atmosphere type, atmosphere flowing rate, sample pan material, and instrument type may lead to the inconsistent of experimental results obtained from different authors. Therefore, in this experimental process, we use similar experimental condition, mass at 18–20 mg, N₂ atmosphere with flowing rate 40 mL/min, platinum pans, and a heating rate 10 °C/min in the fast scan TGA experiment due to its optimum value.¹⁷

3.1.2. Long-Term Thermal Stability and Thermal Decomposition Kinetics. From industrial application point of view, ILs must endure certain high temperature for a period of time. In that case, T_{onset} is no longer applicable for judging the thermal stability. Therefore, long-term thermal stability is needed, which is measured isothermally at different temperature interval. The selection of temperature interval of ILs is based on the T_{onset} value (see details in the Experimental Section). After measuring the isothermal decomposition curves, pseudo-zero-order kinetics (eq 1) was used for analysis the kinetics because the mass loss against time is linear. The rate constant k is the slope of decomposition curves. Meanwhile, according to Arrhenius equation (eq 2), activation energy E_a and pre-exponential factor A can be obtained from linear fitting $\ln(k)$ vs $1/T$ (eq 3).

$$\frac{dm}{dt} = k \quad (1)$$

Table 1. Decomposition Temperature and Activation Energy (E_a) Derived from TGA

no.	abbreviate name	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{onset}}(\text{lit})/^{\circ}\text{C}$	$T_{\text{start}}/^{\circ}\text{C}$	$T_{\text{peak}}/^{\circ}\text{C}$	$T_{0.01/10\text{h}}/^{\circ}\text{C}$	$\Delta T^{\circ}/^{\circ}\text{C}$	$E_a/\text{kJ/mol}$
1	[EMIM][BF ₄]	413	450 (Al ₂ O ₃ pan) ⁴ 445 ⁶⁸	333	455	217	196	110.9 ⁱ
2	[BMIM][BF ₄]	399	361, ²⁰ 380, ⁶⁹ 424, ⁶⁸ 315, ^{11,a} 403, ⁵ 360 ^{11,b}	316, 290 ²⁰	440	216	183	108.4 ⁱ 195 ^{44,j}
3	[HMIM][BF ₄]	420	425 ⁷⁰	332, 262 ⁷⁰	465	203	217	107.8 ⁱ
4	[OMIM][BF ₄]	397		313	438	199	198	116.0 ⁱ
5	[DMIM][BF ₄]	414		344	456	192	222	96.1 ⁱ
6	[BMIM][PF ₆]	421	349, ⁵ 370, ⁴⁴ 433 ⁷¹	329	461	248	173	137.8 ⁱ , 213 ^{44,j} 68 ⁴² (137–232 °C)
7	[HMIM][PF ₆]	422	454, ⁷⁰ 417, ⁵ 390	332, 320 ⁷⁰	460	252	170	135.6 ⁱ
8	[OMIM][PF ₆]	407	376 ⁵	334	443	254	153	136.0 ⁱ
9	[EMIM][Tf ₂ N]	419	439, ⁴⁹ 410, ¹⁹ 446 ⁴⁰ 419, ⁷² 455 ⁴	320	457, 479, ¹⁹ 487 ⁴⁰	222, 252 ⁴⁰ ($T_{0.02/10\text{h}}$)	197	131.6 ⁱ 131 ⁴⁰ (200–300 °C)
10	[BMIM][Tf ₂ N]	419	422, ²⁰ 439, ⁵ 427 ⁴⁹ 438, ⁴⁰ 409, ⁷² 365, ^{11,a} 401 ^{11,b}	336, 330 ²⁰	453	227, 250 ⁴⁰ ($T_{0.02/10\text{h}}$)	192	126.4 ⁱ 113 ⁴⁰ (200–300 °C) 255 ^{44,j}
11	[HMIM][Tf ₂ N]	411	461, ⁷⁰ 428 ⁴⁹	301, 302 ⁷⁰	447	218	193	119.6 ⁱ
12	[MIM][Tf ₂ N]	391		316	436	195	196	102.7 ⁱ
13	[M ₁₂ IM][Tf ₂ N]	403		323	444	205	198	119.5 ⁱ
14	[M ₁₃ IM][Tf ₂ N]	432	444 ⁴⁹	345	467	236	196	116.0 ⁱ
15	[MMMIM][Tf ₂ N]	437		327	467	235.7	201.3	116.6 ⁱ
16	[EMIM][Ac]	221	216, ³¹ 251.5, ¹⁰ 181, ^{11,a} 220 ^{11,b}	140	244	110.7, 102 ³¹	110.3	112.6 ^e 116 ³¹ (105–170 °C)
17	[BMIM][Ac]	216	179, ^{11,a} 224 ^{11,b}	139	242	112.8	103.2	115.9 ^e
18	[HMIM][Ac]	220		136	247	110.1	109.9	111.0 ^e
19	[OMIM][Ac]	216		121	241	112.7	103.3	115.4 ^e
20	[BMMIM][BF ₄]	430	380, ²⁰ 405, ¹⁹ 398 ²⁸	334, 285 ²⁰	469, 475, ¹⁹ 483 ²⁸	228	202	114.7 ⁱ , 182 ^{44,j} 88.4 ²⁸ (200–360 °C)
21	[BMMIM][PF ₆]	436	373, ²⁰ 425, ¹⁹ 425 ¹⁹	321, 235 ²⁰	474, 499 ¹⁹	224.2	211.8	101.7 ⁱ
22	[EMMIM][Ac]	228	221 ³¹	129	254	110.6, 99 ³¹	117.4	108.6 ^e 99.6 ³¹ (105–170 °C)
23	[BMMIM][Ac]	226		140	251	113.9	112.1	118.3 ^e
24	[BMIM][Cl]	257	264, ²⁰ 229, ^{11,a} 254, ⁵ 234, ¹⁹ 268, ⁶⁹ 270 ^{11,b}	208, 150 ²⁰	284, 285 ¹⁹	140.4	116.6	132.2 ^f , 127 ^{44,j} 121 ⁴³ (150–200 °C) 129 ³⁰ (150–190 °C)
25	[OMIM][Cl]	276	243 ⁵	165	249	131.8	144.2	129.9 ^f 128 ^{44,j}
26	[BMIM][Br]	272	273, ²⁰ 277.5 ⁴¹	224, 215 ²⁰	300	145.2	126.8	128.2 ^f 212.5 ⁴¹ (260–300 °C)
27	[BMIM][I]	278	265 ⁵	238	307	146.7	131.3	126.5 ^f
28	[BMIM][NO ₃]	290	285 ⁷³ ($T_{10\%}$)	246	315	182.9	107.1	120.7 ^h
29	[HMIM][NO ₃]	288	283 ⁷³ ($T_{10\%}$)	244	313	160.5	127.5	120.1 ^h
30	[BMIM][TFO]	393	392, ²⁰ 409 ⁷¹	354, 340 ²⁰	426	158.7	234.3	130.5 ^h
31	[BMIM][ClO ₄]	321		301	368	263.2	57.8	128.7 ⁱ
32	[BMIM][HSO ₄]	345		248	377	208.9	136.1	133.2 ⁱ
33	[BMIM][TS]	372		286	345	212.2	159.8	150.1 ⁱ
34	[AMIM][Cl]	254	249, ³⁰ 273 ⁷⁴	180	270	135.7	118.3	126.1 ^f

Table 1. continued

no.	abbreviate name	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{onset}}(\text{lit})/^{\circ}\text{C}$	$T_{\text{start}}/^{\circ}\text{C}$	$T_{\text{peak}}/^{\circ}\text{C}$	$T_{0.01/10\text{h}}/^{\circ}\text{C}$	$\Delta T^{\text{c}}/^{\circ}\text{C}$	$E_{\text{a}}/\text{kJ/mol}$
								125 ³⁰ (150–190 °C)
35	[AMIM][Br]	282		143	319	139.5	142.5	111.2 ^f
36	[AVIM][Cl]	263		145	292	105.5	157.5	92.8 ^f
37	[ABIM][BF ₄]	356		297	389	167.5	188.5	92.6 ⁱ
38	[ABIM][PF ₆]	349		313	390	195.7	153.3	110.3 ⁱ
39	[ABIM][Cl]	252		211	277	130.1	121.9	115.5 ^f
40	[ABIM][Br]	257		210	284	134.1	122.9	114.9 ^f
41	[ABIM][NO ₃]	264		223	296	164.9	99.1	148.5 ^h
42	[HOEMIm][BF ₄]	369		244	405	190.8	178.2	91.2 ⁱ
43	[HOEMIm][Tf ₂ N]	415	415 ⁵⁰ ($T_{5\%}$)	331	444	242	173	126.0 ⁱ
44	[HOEMIm][Ac]	238		137	264	126.2	111.8	132.8 ^e
45	[HOEMIm][Cl]	298		256	323	154.7	143.3	126.2 ^f
46	[HOEMIm][NO ₃]	296		262	320	159.2	136.8	126.2 ^h
47	[HOEMIm][TFO]	391		334	436	236.3	154.7	60.2 ^h
48	[HOEMIm][ClO ₄]	311		285	320	200.1	110.9	134.1 ^h
49	[HOEMIm][DCA]	227		183	274	88.3	138.7	69.1 ^f
50	[EPy][Tf ₂ N]	396		255	428	260.5	135.5	127.5 ⁱ
51	[BPy][BF ₄]	373		289	407	191.4	181.6	106.0 ⁱ , 134 ^{44,j}
52	[BPy][PF ₆]	392		307	426	211.6	180.4	127.1 ⁱ
53	[BPy][Tf ₂ N]	390	396 ²²	336	419	244.7	145.3	132.6 ⁱ
54	[BPy][Br]	239		207	265	137.6	101.4	161.9 ^f
55	[BPy][NO ₃]	263		235	288	162.4	100.6	147.9 ^h
56	[BPy][TFO]	362		302	391	226	136	108.8 ^h
57	[BPy][DCA]	252		226	267	141.1	110.9	115.3 ^f
58	[BPy][HSO ₄]	337		272	320	226	111	101.6 ^h
59	[BPy][H ₂ PO ₄]	242		162	268	117.7	124.3	81.6 ^f
60	[P ₆₆₆₁₄][Br]	356		380	319	221.1	134.9	143.6 ⁱ
61	[P ₄₄₄₄][Gly]	282	200, ⁴⁵ 293 ⁵⁹	163	317	109.5	172.5	15.04 ^g
62	[P ₄₄₄₄][Ala]	298	202, ⁴⁵ 286 ⁵⁹	210	319	30.7	267.3	33.02 ^g
63	[P ₄₄₄₄][Ser]	215	220, ⁴⁵ 243 ⁵⁹	118	268	<i>d</i>		14.94 ^g
64	[P ₄₄₄₄][Glu]	321	319 ⁵⁹	169	357	112	209	50.82 ^g
65	[P ₄₄₄₄][Lys]	245	225, ⁴⁵ 277 ⁵⁹	117	313	61.6	183.4	34.58 ^g
66	[P ₄₄₄₄][Pro]	305	314 ⁵⁹	208	338	54.5	250.5	42.78 ^g

^a T_{onset} measured by reaction calorimetry. ^b T_{onset} measured by DSC. ^c $\Delta T = T_{\text{onset}} - T_{0.01/10\text{h}}$. ^d $T_{0.01/10\text{h}}$ of [P₄₄₄₄][Ser] is not available due to its low thermal stability. ^eIsothermal TGA temperature ranges: from 120 to 180 °C with anion [Ac]; ^ffrom 120 to 200 °C with anion [Cl], [Br], [I], [DCA], and [H₂PO₄]; ^gfrom 120 to 220 °C with anion [Gly], [Ala], [Ser], [Glu], [Lys], and [Pro]; ^hfrom 160 to 260 °C with anion [NO₃], [TFO], [HOEMIm][ClO₄], and [BPy] [HSO₄]; ⁱfrom 200 to 300 °C with anion [BF₄], [PF₆], [Tf₂N], [TS], [BMIM][ClO₄], [BMIM][HSO₄], and [P₆₆₆₁₄][Br]. ^jThe activation energy E_{a} was obtained from quantum chemistry calculation.

$$k = A \exp\left(\frac{-E_{\text{a}}}{RT}\right) \quad (2)$$

$$\ln(k) = \ln(A) - \frac{E_{\text{a}}}{RT} \quad (3)$$

Correspondingly, the time taken for 1% decomposition to occur ($t_{0.99}$) at each temperature can be calculated from eqs 4 and 5

$$t_{1-x} = \frac{100x}{k} \quad (4)$$

$$t_{0.99} = \frac{1}{k} \quad (5)$$

where x refers to the degree of decomposition, i.e., 1%. Then, the plot of $t_{0.99}$ vs T obeys an exponential fit equation (eq 6).

$$t_{0.99} = ae^{(-T/b)} \quad (6)$$

Extrapolation or interpolation this exponential curve could obtain a parameter $T_{z/y}$, which denotes the degree of decomposition z in a chosen time y . Scott et al.⁴⁶ chose 1% degradation in 10 h, $T_{0.01/10\text{h}}$; Liang et al.⁴⁷ used the 10% mass loss in 10 h, $T_{0.1/10\text{h}}$; meanwhile, Villanueva et al.⁴⁰ proposed the temperature at which 2% degradation occurs in 10 h, $T_{0.02/10\text{h}}$ to characterize the thermal stability of ILs. In addition to using $T_{z/y}$ to characterize the degradation level, Seeberger³⁶ and Navarro⁴⁸ et al. proposed the maximum operation

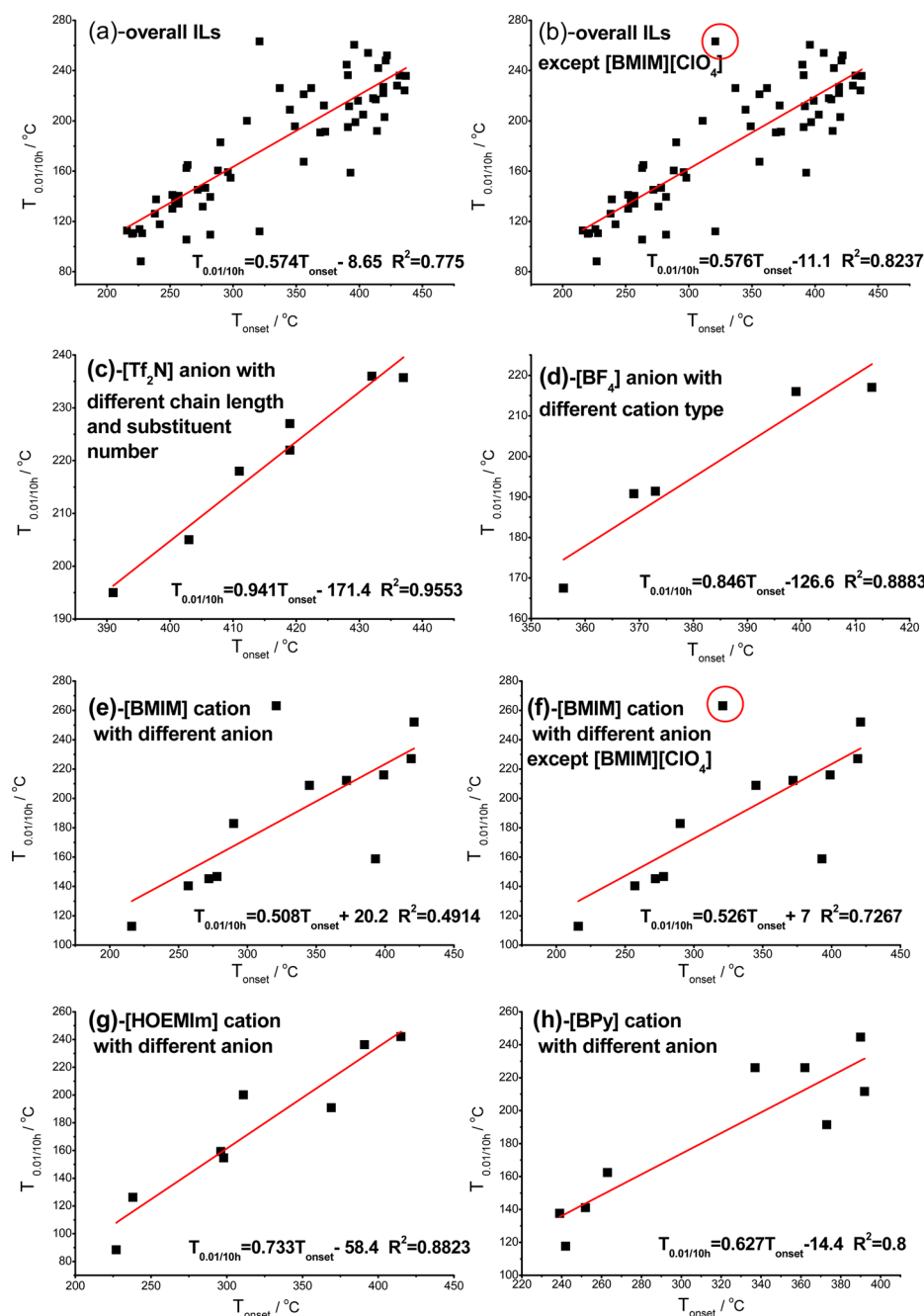


Figure 2. Correlation between T_{onset} and $T_{0.01/10h}$: (a) the overall correlation containing 60 ILs except from amino acid ILs; (b) the correlation except ILs [BMIM][ClO₄]; (c) the correlation containing [Tf₂N] anion with different chain length and substituent number; (d) the correlation containing [BF₄] anion with different cation type; (e) the correlation containing [BMIM] cation with different anion; (f) the correlation containing [BMIM] cation with different anion except ILs [BMIM][ClO₄]; (g) the correlation containing [HOEMIm] cation with different anion; (h) the correlation containing [BPy] cation with different anion. The linear fitted equation and adjusted R^2 are listed in the figures, respectively.

temperature (MOT) to estimate the long-term stability of ILs. In this work, we select the commonly used $T_{0.01/10h}$ for convenient comparison. Because $T_{0.01/10h}$ would be more appropriate when considering practical application, different degradation degrees and time periods. More importantly, the accuracy of $T_{0.01/10h}$ would reduce if extrapolating to very lengthy periods of time.⁴⁶

The values of E_a , A , and $T_{0.01/10h}$ for all the ILs are collected in Supporting Information Table S1. $T_{0.01/10h}$ was also listed in Table 1 to compare with T_{onset} . Results show that $T_{0.01/10h}$ is significantly lower than T_{onset} , the difference between $T_{0.01/10h}$

and T_{onset} is about 100–200 °C for different ILs. This proves again that there is overestimation on thermal stability by T_{onset} .

3.1.3. Relationship between T_{onset} and $T_{0.01/10h}$. An overview of the ILs thermal stability is shown in Supporting Information Figure S1. [MMMIM][Tf₂N] has the highest T_{onset} (437 °C), while [P₄₄₄₄][Ser] has the lowest (215 °C). The difference between them is 222 °C. That is to say, the thermal decomposition temperature of ILs covers a large temperature range. In addition, $T_{0.01/10h}$ is calculated from isothermal TGA method at different temperature for certain time, which is onerous and time-consuming to obtain it. Meanwhile, T_{onset} is

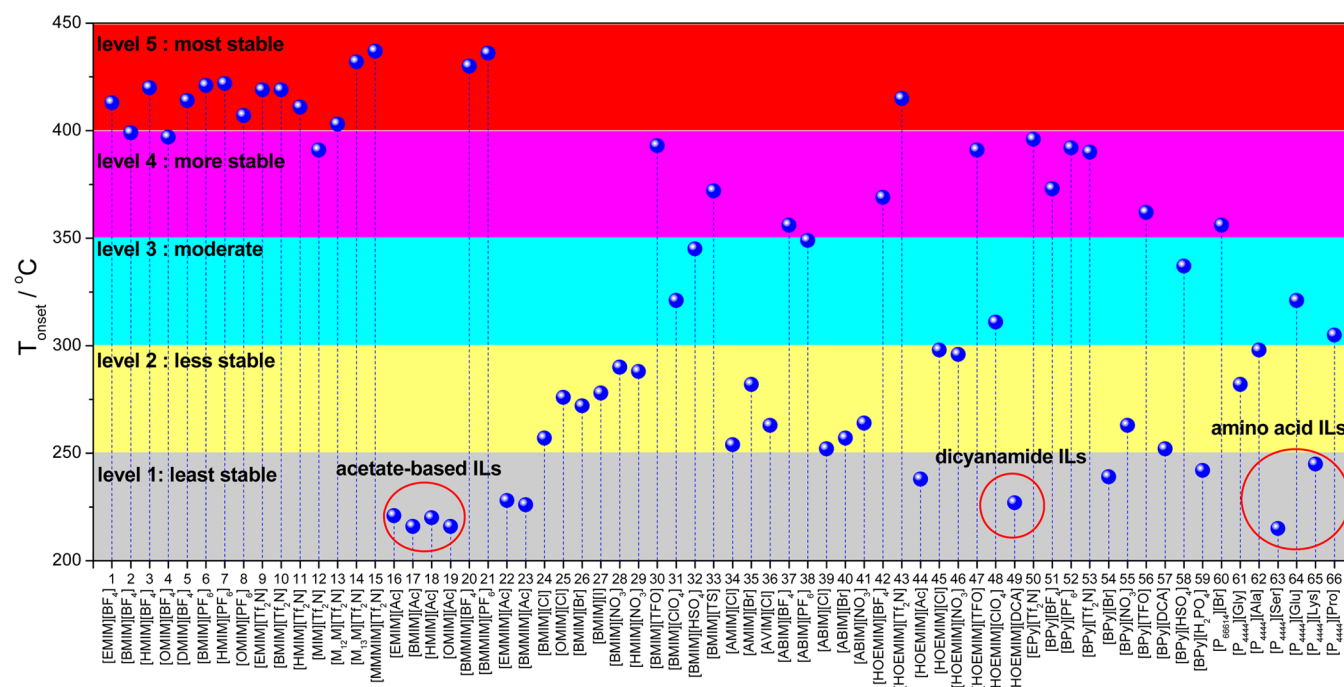


Figure 3. Five levels of the 66 ILs thermal stabilities based on their T_{onset} value.

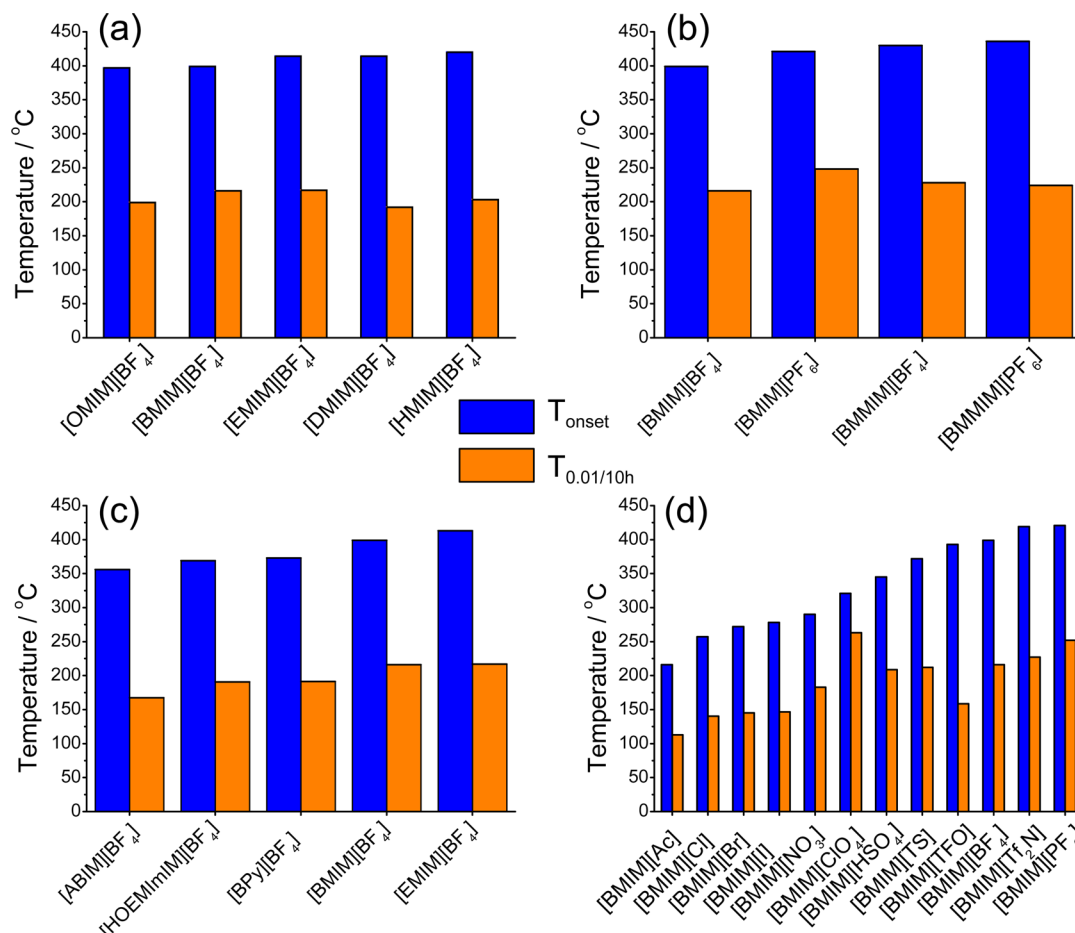


Figure 4. Effect of chain length (a), C2 methylation (b), cation type (c), and anion type (d) on thermal stability of ILs ordered as T_{onset} .

determined directly from ramped TGA and the measurement of it is relatively easy and fast. From this point of view, it would be important and desirable to estimate the relationship between

them. As illustrated in Figure 2a–g, it is indicated that T_{onset} and $T_{0.01/10h}$ of the 60 ILs (except six AAILs) have a moderate linear relationship with an adjusted R^2 value of 0.775; however,

the R^2 value increases to 0.8237 after excluding [BMIM]-[ClO₄]. When estimating the relationship between different chain length, substituent number, and cation and anion type, the relationship is more apparent and R^2 value are relatively high regardless of [Tf₂N] anion with different chain length and substituent number (Figure 2c, $R^2 = 0.9553$); [BF₄] anion with different cation type (Figure 2d, $R^2 = 0.8883$); [BMIM] cation with different anion except ILs [BMIM][ClO₄] (Figure 2f, $R^2 = 0.7267$); [HOEMIm] cation with different anion (Figure 2g, $R^2 = 0.8823$); [BPy] cation with different anion (Figure 2h, $R^2 = 0.8$). Through the above analysis, $T_{0.01/10h}$ could be estimated approximately by T_{onset} .

3.1.4. Classification of ILs' Thermal Stabilities. According to T_{onset} , the ILs' thermal stabilities could be classified into five levels, least stable ($T_{onset} < 250$ °C), less stable (250 °C $\leq T_{onset} < 300$ °C), moderately stable (300 °C $\leq T_{onset} < 350$ °C), more stable (350 °C $\leq T_{onset} < 400$ °C), and most stable (450 °C $\leq T_{onset}$) (Figure 3). Following this classification, all the acetate-based ILs, one dicyanamide IL [HOEMIm][DCA], two amino acid ILs [P₄₄₄₄][Ser] and [P₄₄₄₄][Lys], and two pyridinium ILs [BPy][Br] and [BPy][H₂PO₄] are the least stable ILs; all the halogen ILs ([Cl], [Br], and [I]) and all the [NO₃]-based ILs, [BPy][DCA], [P₄₄₄₄][Gly], and [P₄₄₄₄][Ala] are the less stable ILs; all the [ClO₄]- and [HSO₄]-based ILs, [P₄₄₄₄][Glu], and [P₄₄₄₄][Pro] are the moderately stable ILs; all the [TFO]-based ILs, pyridinium ILs containing [BF₄], [PF₆], and [Tf₂N] anion, and [P₆₆₆₁₄][Br] are the more stable ILs; and all the imidazolium ILs containing [BF₄], [PF₆], and [Tf₂N] anion are the most stable ILs. This is similar to the different isothermal temperature range for all the ILs primarily dependent on anion types, i.e., 120–180 °C for [Ac]; 120–200 °C for [DCA], [Cl], [Br], [I], and [H₂PO₄]; 120–220 °C for [Gly], [Ala], [Ser], [Glu], [Lys], and [Pro]; 160–260 °C for [NO₃], [TFO], [ClO₄], and [HSO₄]; and 200–300 °C for [TS], [BF₄], [PF₆], and [Tf₂N].

From the classification of the thermal stability, one can see that the thermal stable level varies from the least stable (i.e., [BMIM][Ac]) to the most stable (i.e., [BMIM][Tf₂N]) by altering the anion, regardless of imidazolium ILs or pyridinium ILs. Similarly, changing cation could also affect the thermal stable level to a large extent. Taking [BF₄]-, [PF₆]-, and [Tf₂N]-based ILs for example, when the cation is pyridinium, [BF₄]-, [PF₆]-, and [Tf₂N]-based ILs belong to the more stable ILs (level 4); however, if the cation is imidazolium, these ILs change to the most stable ILs (level 5). Of course, variations in the alkyl chain length, substituent number, and C2 methylation could also influence thermal stable level, but their effects are not as apparent as that of cation and anion type. Note that this classification is based on the short-term stability parameter T_{onset} not considering their long-term stability.

3.2. Influence of Structure Factors on the Thermal Stability. Both experimental condition and ILs structure could influence the thermal stability of ILs. In this work, we only focus on the effect of ILs structure, i.e., cation modification (chain length, substituent number, C2 methylation, and functionalization), cation type (imidazolium ILs, pyridinium ILs, and phosphonium ILs), and anion type (as much as 20 kinds of anions). We will give detailed discussion on the structure effects below.

3.2.1. Chain Length. Effect of chain length on thermal stability of ILs is investigated with three types: imidazolium ILs with anion [BF₄], [PF₆], [Tf₂N], [Ac], [Cl], and [NO₃]; allyl-imidazolium ILs with anion [Cl] and [Br]; pyridinium ILs with

anion [Tf₂N] (Figure 4a and Supporting Information Figure S5). The effect of chain length on ILs thermal stability is relatively small for imidazolium, allyl-imidazolium, and pyridinium ILs. The difference between T_{onset} (highest) and T_{onset} (lowest) is around 30 °C for [BF₄] imidazolium ILs and 15 °C for [PF₆] imidazolium ILs, while it is only 5 °C for [Ac] imidazolium ILs and [Tf₂N] pyridinium ILs. Other experimental results and quantum chemical calculation results have drawn similar conclusions.^{4,5,21,44,49} In addition, shorter chain length results in higher thermal stability. For example, [OMIM][PF₆] < [BMIM][PF₆] \approx [HMIM][PF₆]; [OMIM][Ac] \approx [BMIM][Ac] < [HMIM][Ac] \approx [EMIM][Ac]; [HMIM][NO₃] < [BMIM][NO₃]; [ABIM][Cl] < [AMIM][Cl]; [ABIM][Br] < [AMIM][Br]; and [BPy][Tf₂N] < [EPy][Tf₂N]. However, there are exceptions. For [BF₄] imidazolium ILs, T_{onset} is ordered as [OMIM][BF₄] \approx [BMIM][BF₄] < [EMIM][BF₄] \approx [DMIM][BF₄] < [HMIM][BF₄], which are independent of chain length.

The influence of chain length on thermal stability with different cations and anions could be interpreted as follows.^{41,49–51} On one hand, a longer chain length results in greater van der Waals forces. Meanwhile, it could also decrease the intramolecular electrostatic interaction, which leads to an overall decrease interaction and the lower thermal stability.^{41,50} On the other hand, longer alkyl chain length may result in both the carbocation and carbon radicals being more stable, thus the decomposition reaction occurs more easily.⁵¹

3.2.2. Substituent Number and C2 Methylation and Functionalization. The effect of substituent number on thermal stability of ILs is investigated with [Tf₂N] anion (Supporting Information Figure S5b). Results show that T_{onset} increased with increasing substituent number, i.e., [MIM][Tf₂N] < [M₁₂IM][Tf₂N] < [M₁₃IM][Tf₂N] < [MMMIM][Tf₂N]. Similar results had been observed for [EMIM][PF₆] (375 °C), [DMPIM][PF₆] (399 °C), and [M₅IM][PF₆] (401 °C); the value in the brackets is T_{onset} .⁴ In addition, Crosthwaite et al. investigated a series of *N*-hexyl-pyridinium [Br] and [Tf₂N] salts with cations [C₆pyr], [C₆mpyr], and [C₆m₂pyr]. Results showed that for [Br] salts, the influence of substituent number is not obvious. However, for [Tf₂N] salts, the influence is apparent and the thermal stability increased with increasing degree of substitution.²¹

[EMMIM][Ac], [BMMIM][Ac], [BMMIM][BF₄], and [BMMIM][PF₆] are used to investigate the effect of C2 methylation (Figure 4b and Supporting Information Figure S5g). When compared to non-C2 methylation ILs, replacing hydrogen with methyl group at C2 position may increase thermal stability. The increase degree for different anion follows the order [Ac] (5 °C) < [PF₆] (15 °C) < [BF₄] (31 °C). Previous study also investigated the influence of C2 methylation on ILs thermal stability, including not only halide ILs, but also [BF₄], [PF₆], and [Tf₂N] based ILs.^{19,21,52}

The increase of decomposition temperature with increasing substituent number and C2 methylation may due to the removal of the ring hydrogen, and the removal of C2–H has the largest effect due to the high acidic character of C2–H.^{4,19} Methyl group substitution in the C2-position blocks the substitution nucleophilic decomposition mechanism, thus increasing the thermal stability.¹⁷ In addition, the replacement of ring hydrogen with a substituent group could increase the steric hindrance and van der Waals interactions, which is not favorable for the thermal degradation through the S_N1 or S_N2 mechanism, thus causing higher thermal degradation temper-

ature. Recent reports had explained the higher thermal stability of [EMMIM][Ac] than [EMIM][Ac] like this.³¹

Functionalization is also significantly important. Herein, the thermal stability of allyl and hydroxyl functionalization imidazolium ILs are investigated (Figure 4c and Supporting Information Figure S6a–h).

Allyl functionalization would decrease thermal stability, no matter for anion is [BF₄], [PF₆], [Cl], [Br], or [NO₃] (Figure 4c and Supporting Information Figure S6a and c–e), which coincides with previous study.³⁸ That is to say, replacing the saturated side chain of a cation with an unsaturated side chain (such as allyl) would generally decrease the decomposition temperature of ILs. This may be explained by the rigidity of the allyl group.³⁸ Quantum chemical calculation results also indicated that the average activation energy of [BMIM][Cl] was higher than [ABIM][Cl], as a result of the higher thermal stability of [BMIM][Cl] than [ABIM][Cl].³⁰

The effect of hydroxyl functionalization is a little complicated. For [BF₄] and [Tf₂N] anions, hydroxyl-functionalization would lower the thermal stability, i.e., [HOEMIm][BF₄] < [EMIM][BF₄], [HOEMIm][Tf₂N] < [EMIM][Tf₂N] (Figure 4c and Supporting Information Figure S6b); however, this is opposite for [Ac] anions (Figure S6b). This is an interesting finding, because previous research only indicated that replacing the alkyl group side with the hydroxyethyl group resulted a slightly lower thermal stability when anion is [Tf₂N], which could be attributed to the higher chemical activity and easier decomposition of the hydroxyethyl group.⁵⁰ Nevertheless, for the [Ac] anion, hydroxyethyl group substituent increases the thermal stability rather than decreases. The possible hydrogen bonding interaction between the hydroxyethyl group and [Ac] anion may result in this extraordinary trend, the higher intramolecular hydrogen bond interaction may stabilize ILs and block thermal decomposition reaction to some extent.

3.2.3. Cation Type. The cation effects on stability are summarized below (Figure 4c and Supporting Information Figure S6):

- [ABIM] < [HOEMIm] < [BPy] < [BMIM] < [EMIM] (anion is [BF₄], [PF₆])
- [BPy] < [HOEMIm] < [BMIM] < [EMIM] (anion is [Tf₂N])
- [BMIM] < [EMIM] < [HOEMIm] (anion is [Ac])
- [BPy] < [ABIM] < [BMIM] < [P₆₆₆₁₄] (anion is [Cl], [Br], [NO₃])
- [BPy] < [BMIM] (anion is [HSO₄] and only these two ILs are compared)
- [HOEMIm] < [BPy] (anion is [DCA] and only these two ILs are compared)

According to these results, some common trends could be found. Imidazolium ILs are generally more stable than pyridinium ILs, tetraalkyl ammonium, and piperidinium ILs, independent of anion type. While for imidazolium and phosphonium ILs, this trend may be different with different anion type. For [Br] anion in our investigation, [P₆₆₆₁₄][Br] is more thermally stable than [BMIM][Br]. Nevertheless, for [Tf₂N] anion, the onset temperature follows the order [EMIM][Tf₂N] > [P₆₆₆₁₄][Tf₂N].³⁸ Similarly, for imidazolium and pyrrolidinium ILs, this trend is not predictable due to different anion. Just taking [DCA] and [Tf₂N] anion for example, for the [DCA] anion, imidazolium salt is more

thermal stable than pyrrolidinium salt,³⁹ while this is opposite for the [Tf₂N] anion.²²

3.2.4. Anion Type. Anion type plays the major role on determining thermal stability, similar to determining the hydrophobicity of ILs.^{53–55} The influence of anion type has been investigated based on different cation types and several change trends have been obtained:

- [Ac] < [Cl] < [Br] < [I] < [NO₃] < [ClO₄] < [HSO₄] < [TS] < [TFO] < [BF₄] < [Tf₂N] < [PF₆] (for imidazolium cation) (Figure 4d and Supporting Information Figure S7a–d)
- [Cl] < [Br] < [NO₃] < [BF₄] < [PF₆] (when cation is allyl-functionalized, including [AMIM] and [ABIM]) (Figure S7e)
- [DCA] < [Ac] < [NO₃] < [Cl] < [ClO₄] < [BF₄] < [TFO] < [Tf₂N] (when cation is hydroxyl-functionalized, [HOEMIm]) (Figure S7f)
- [Br] < [H₂PO₄] < [DCA] < [NO₃] < [HSO₄] < [TFO] < [BF₄] < [PF₆] < [Tf₂N] (for pyridinium cation, [EPy] and [BPy]) (Figure S7g)
- [Ser] < [Lys] < [Ala] < [Gly] < [Pro] < [Glu] (for phosphonium cation, [P₄₄₄₄]) (Figure S7h)

Based on the above results, some similar rules could be concluded. First, [Ac], [DCA], amino acid ([Gly], [Ala], [Ser], [Glu], [Lys], and [Pro]) and halogen ([Cl], [Br], and [I]) anion-based ILs are the less stable ILs (including level 1 and level 2); meanwhile for [BF₄], [PF₆], and [Tf₂N] ILs, if the cation is pyridinium, they are more stable ILs (level 4). If the cation is imidazolium, they are the most stable ILs (level 5). The rest of the anions are scattered in level 2 (less stable), level 3 (moderately stable), and level 4 (more stable), which is dependent on cation type. Second, the thermal stability caused by different anions is about 200 °C, greater than the influence of cation modification and cation type. This is consistent with other conclusions that the thermal stability of ILs is highly anion dependent.¹⁷

The previous investigations reported that the thermal stability of ILs with different anions decreases with the increase of coordinating nature, nucleophilicity, and hydrophilicity of the corresponding anion.^{4,5,10,20,21} Since we have carried out investigations on the hydrophilicity of many ILs,^{53–56} the correlations between the hydrophilicity and the stability of the ILs were investigated in this study (Figure 5). The maximum saturated water sorption capacity W_{∞} was proposed to evaluate the hydrophilicity of the ILs (HPI).⁵³ Interestingly, for

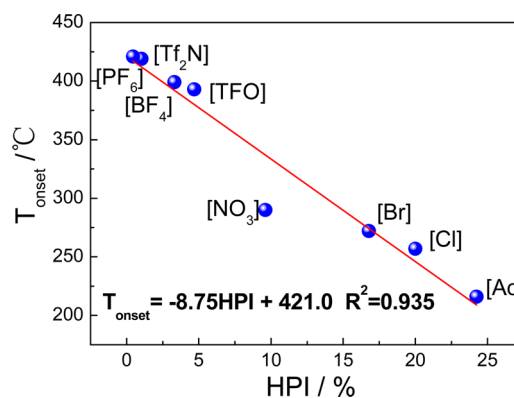


Figure 5. Relationship between T_{onset} and HPI value ($100W_{\infty}$) with the same cation [BMIM].

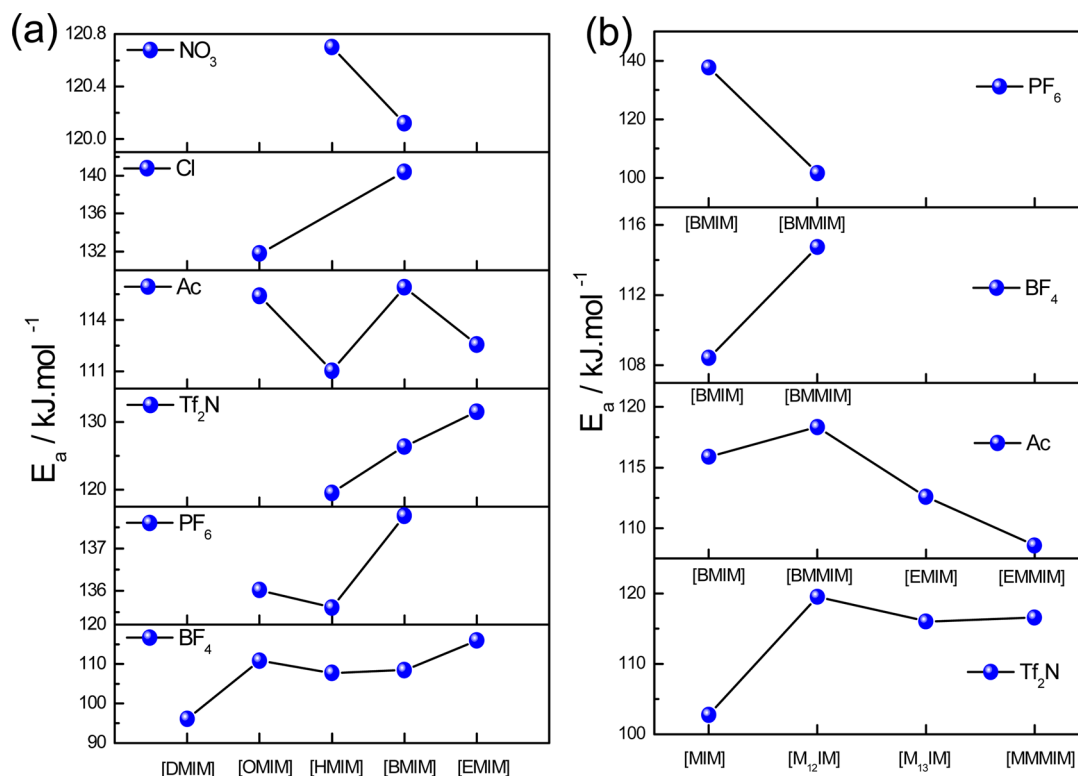


Figure 6. Comparison the change trend between E_a and T_{onset} , where the x axis is an ascending sort ordered as T_{onset} . (a) Change trend of E_a along with shortening chain length. (b) Change trend of E_a along with increasing substituent number and replacing C2-H with methyl group.

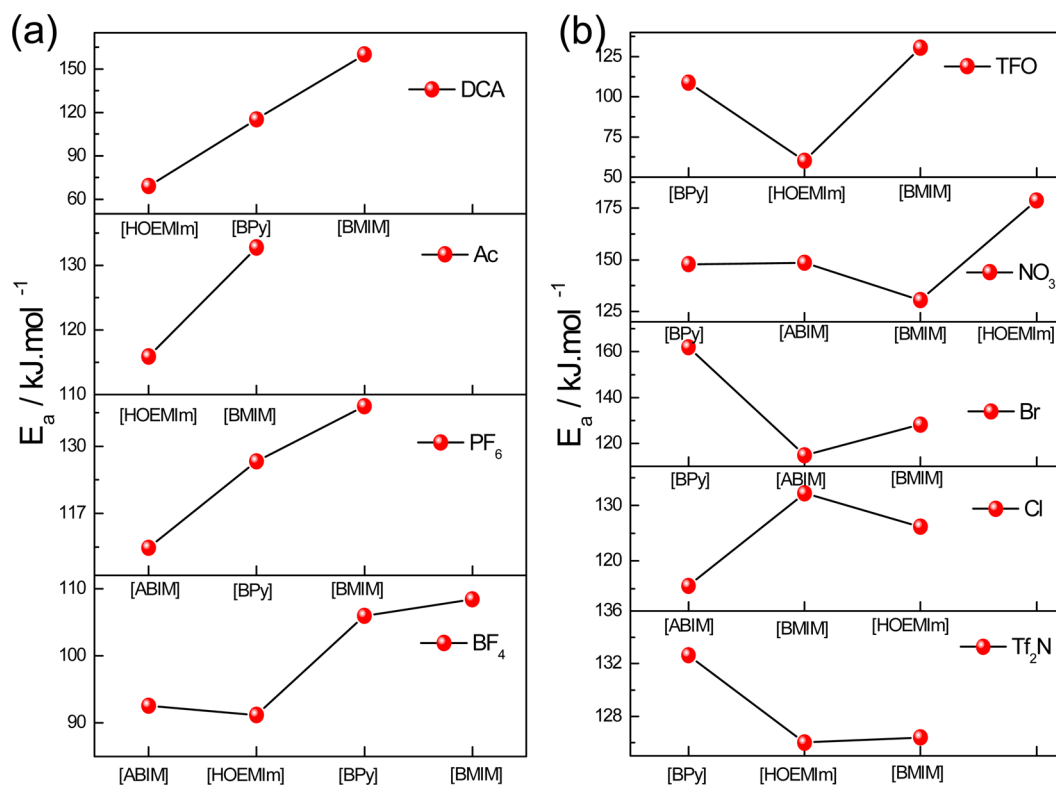


Figure 7. Comparison of the change trend between E_a and T_{onset} , where the x axis is an ascending sort ordered as T_{onset} . (a) Change trend is consistent between E_a and T_{onset} with cation influence. (b) Change trend is inconsistent between E_a and T_{onset} with cation influence.

[BMIM] based ILs varying in anion, the ILs thermal stability performs a negative correlation with HPI value, which is expressed as $T_{\text{onset}} = -8.75\text{HPI} + 421.0$ ($R^2 = 0.935$). The

thermal stability decreases with increasing the hydrophilicity as a sequence of $[\text{PF}_6] > [\text{Tf}_2\text{N}] > [\text{BF}_4] > [\text{TFO}] > [\text{NO}_3] > [\text{Br}] > [\text{Cl}] > [\text{Ac}]$.

3.3. General Evaluation of ILs' Thermal Stabilities by $T_{0.01/10h}$ and Activation Energy E_a . Note that all the above discussion on ILs thermal stability is mainly depended on T_{onset} value due to its popularity and conveniences. Apart from T_{onset} , the long-term stability parameter $T_{0.01/10h}$ and activation energy E_a are also important and useful to evaluate ILs' thermal stabilities. Next we will discuss them, respectively.

The influence of cation modification (chain length, substituent number, allyl and hydroxyl functionalization, and C2 methylation), cation type, and anion type on thermal stability obtained from $T_{0.01/10h}$ would be a little different from T_{onset} . For example, the effect of cation modification and cation type on ILs' thermal stabilities ordered as $T_{0.01/10h}$ is basically the same as the T_{onset} sequence, while for the effect of anion type, it is largely different. All of this can be seen from Figure 4 and Supporting Information Figures S5–S7. Therefore, it is necessary to consider T_{onset} and $T_{0.01/10h}$ comprehensively when estimating ILs' thermal stabilities.

According to thermal decomposition kinetics, the activation energy E_a and pre-exponential factor A of the ILs were obtained by a pseudo-zero-order rate expression. Note that, since the thermal stabilities of ILs are very different, different isothermal temperature ranges were used. Therefore, it is reasonable to compare E_a and A only in the same isothermal temperature range. E_a values of the ILs are listed in Supporting Information Table S1 and Table 1 together with literature values. The difference between the E_a values of same IL obtained from this work and the literature can be partly attributed to the different isothermal temperature ranges used. In addition, E_a values obtained from quantum chemistry calculation are significantly greater than experimental results.

The E_a values of ILs with different alkyl chain length, substituent number, and replacing C2–H with a methyl group are compared (Figure 6). Similar to the sequence ordered as T_{onset} , the difference among different ILs' E_a values caused by chain length is very small; for [Ac], [Tf₂N], [PF₆], and [NO₃] ILs, the difference is about 4, 4, 2, and 0.5 kJ/mol, respectively. This is consistent with the experimental and quantum chemical calculation results.^{43,44} In addition, even though the general trend is that E_a value increases with shortening chain length, increasing substituent number, and replacing C2–H with methyl group, some ILs have the opposite change trend. For example, T_{onset} increases from [OMIM][PF₆] to [BMIM][PF₆], but E_a ([HMIM][PF₆]) < E_a ([OMIM][PF₆]), also E_a ([BMIM][NO₃]) < E_a ([HMIM][NO₃]). Related to C2 methylation, T_{onset} increases from [BMIM][PF₆] to [BMMIM][PF₆] and [EMIM][Ac] to [EMMIM][Ac], but E_a ([BMMIM][PF₆]) < E_a ([BMIM][PF₆]); also E_a ([EMMIM][Ac]) < E_a ([EMIM][Ac]).

Analogous to this, the E_a change trend of some ILs with cation type, i.e., [BF₄][−], [PF₆][−], [Ac][−], and [DCA][−]-based ILs, is consistent with the T_{onset} change trend (Figure 7a), where the E_a of [BMIM][DCA] was obtained from literature.⁴⁷ While for other ILs, such as [Tf₂N], [Cl], [Br], [TFO], and [NO₃], this change trend is inconsistent (Figure 7b). The change trend between T_{onset} and E_a is not always the same might because T_{onset} is determined by ramped TGA directly while E_a is calculated from the Arrhenius equation. Therefore, T_{onset} may be the direct and determining parameter to characterize thermal stability.

3.4. Thermal Stability of Some Typical ILs. Table 1, Supporting Information Table S1 and Figure 3 show that AcILs, AAILs, and dicyanamide ILs are least stable. These ILs

have some particular applications developed rapidly in recent years, such as biomass dissolution, gas purification, extraction of aromatic compounds, etc. During the operation process, high temperature for a period of time is necessary. Therefore, the thermal stabilities are important and discussed in detail.

3.4.1. Acetate-Based ILs. AcILs are particularly focused on due to their dissolution of biomass (e.g., cellulose).^{8,9,57} Reports on thermal stability of AcILs are scarce and limited. Only recently has the stability of [EMIM][Ac] and [BMIM][Ac]^{10,11} and the decomposition mechanism of carboxylate ILs been reported.³¹

In this work, the stabilities of [EMIM][Ac], [BMIM][Ac], [HMIM][Ac], [OMIM][Ac], [EMMIM][Ac], and [BMMIM][Ac] were investigated (Supporting Information Figure S5c and g). Results indicate that AcILs are the least stable ILs and their T_{onset} is around 210 °C. The chain length does not influence T_{onset} and C2 methylation results in a higher T_{onset} . Recently, ILs' thermal stabilities have been reported to have strong correlation with their ability to dissolve cellulose.¹⁰ Thermal stability has negative correlation with the ILs' basicities, while the ability of ILs to chemically react with cellulose (cellulose dissolution in ILs) has a positive correlation with the ILs' basicities. The two aspects result in a correlation between cellulose dissolution in ILs and the ILs' thermal stabilities. In a word, the relative inherent reactivities of ILs could be predicted from T_{onset} and TGA experiments could in turn provide guidance for selection of optimal AcILs for biomass dissolution.

3.4.2. Amino Acid ILs. AAILs refer to ILs containing amino acids as anions,^{58,59} cations,⁶⁰ or both. They demonstrate biodegradability and biocompatibility.⁵⁹ AAILs have been applied in gas purification (e.g., CO₂, SO₂),^{45,61} biomass dissolution (e.g., cellulose, chitosan),¹² and so on. The cation could be imidazolium,^{62,63} ammonium,⁵⁸ phosphonium,^{59,64} and cholinium.⁶⁵ Phosphonium-based AAILs were more thermal stable than other AAILs.^{58,59}

T_{onset} of [P₄₄₄₄] AAILs with different anions follows the order [Ser] < [Lys] < [Ala] < [Gly] < [Pro] < [Glu] (Supporting Information Figure S7h), which is in agreement with Ohno's results.⁵⁹ However, for imidazolium and cholinium-based AAILs, the effect of anion follows the order [Gly] < [Ala] < [Ser] < [Pro].^{62,65} The difference indicated that cation type also have a certain effect on thermal stability of AAILs. $T_{0.01/10h}$ is not available for [P₄₄₄₄][Ser], and the $T_{0.01/10h}$ of [P₄₄₄₄][Ala] is only 30.7 °C. The E_a values of AAILs are also significantly lower than other ILs. In conclusion, the AAILs perform lower thermal stability.

3.4.3. Dicyanamide ILs. Dicyanamide (DCA) based ILs have excellent physical properties, such as low melting temperatures, significantly low viscosities, and hygroscopy, completely miscible with water.^{39,66} They have been used in many fields, i.e., biorefinery processes.⁶⁷

DCA ILs were not as stable as [Tf₂N] and [BF₄] ILs, they have similar thermal stable as halide ILs.³⁹ Also, thermal stabilities of cyano-containing ILs increase with increasing the number of cyano group (T_{onset} ordered as [SCN] < [DCA] < [TCM]).⁴⁸ The T_{onset} of DCA ILs with different cation type follow the order: quaternary ammonium (230 °C,⁴⁸ [N₆₂₂₂][DCA]) ≈ hydroxyl-functionalized (227 °C, this work, [HOEMIm][DCA]) < pyridinium (252 °C, this work, [BPy][DCA]) < pyrrolidinium (283 °C,⁴⁶ [P₁₄][DCA]) < imidazolium (296 °C,⁴⁸ [BMIM][DCA]) < phosphonium (396 °C,⁴⁶ [P₆₆₆₁₄][DCA]).

4. CONCLUSION

A general investigation on the thermal stability of 66 ILs by TGA shows that decomposition of ILs occurs at temperature significantly lower than T_{onset} . A pseudo-zero-order rate expression is suitable to analyze the thermal decomposition kinetics based on isothermal TGA curves. The parameter for evaluation of the long-term stability of ILs is characterized by $T_{0.01/10\text{h}}$, which refers to the temperature at which 1% mass loss occurs in 10 h. There are positive correlations between T_{onset} and $T_{0.01/10\text{h}}$, while between T_{onset} and E_a , the relationship is not apparent. Based on T_{onset} values, the ILs' thermal stabilities can be classified into five levels (least stable, less stable, moderately stable, more stable, and most stable).

The effects of structure factors on the thermal stability of ILs are analyzed based on our investigation and previous reports, and some conclusions could be drawn. (1) Anion type plays the major role on the thermal stability of ILs, and then cation type, while cation modification has the least effect. The thermal stability of ILs increases with shorter chain length, greater substituent number, and replacing C2–H with a methyl group. (2) Allyl-functionalization would decrease the thermal stability of ILs. While for hydroxyl-functionalization, the thermal stability depends on anion type. (3) Imidazolium based ILs are generally more stable than tetraalkyl ammonium-, piperidinium-, and pyridinium-based ILs, independent of anion; while for imidazolium-, phosphonium-, and pyrrolidinium-based ILs, the thermal stability is dependent on anion. (4) The thermal stabilities of ILs varying in anions have a close relationship with anion coordinating nature, nucleophilicity, and hydrophilicity. The thermal stability of [BMIM]-based ILs varying in an anion has a good negative correlation with the hydrophilicity of ILs.

Finally, the discussion on the thermal stability of AAILs, AAILs, and dicyanamide ILs may provide guidance for their high temperature applications, such as biomass dissolution, gas purification, and extraction of aromatic compounds.

■ ASSOCIATED CONTENT

■ Supporting Information

Overview of 66 ILs' short-term thermal stabilities (Figure S1) and decomposition kinetics (Table S1). TG and DTG curves of [BMIM][ClO₄] and [HOEMIm][ClO₄] (Figure S2), [HOEMIm][DCA] and [BPy][DCA] (Figure S3), and [BMIM][H₂PO₄] (Figure S4) with two peaks in the DTG curves. Effects of cation modification (Figure S5), cation type (Figure S6), and anion type (Figure S7) on the thermal stabilities of ILs ordered as T_{onset} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-10-62514925. Fax: +86-10-62516444. E-mail: tcmu@chem.ruc.edu.cn.

Notes

The authors declare no competing financial interest.

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