

STRUCTURE OF MATTER
AND QUANTUM CHEMISTRY

Synthesis, Characterization, Thermal Analyses,
and Spectroscopic Properties of Novel Naphthyl-Functionalized
Imidazolium Ionic Liquids¹

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Abstract—A series of novel ionic liquids based on naphthyl-functionalized imidazolium cation have been prepared. Their structure was characterized by NMR. The thermal stabilities of the prepared liquids were studied by thermal gravimetric analysis. The new ionic liquids containing NTf₂⁻ anion display significantly higher thermal stabilities (>400°C). Anion exchange to PF₆⁻, BF₄⁻, and Br⁻ decreases the thermal stabilities of such ionic liquids. Fluorescence and UV–Vis absorption spectroscopy were used to study the spectroscopic properties of the ionic liquids. Compared with common ionic liquids, the described ionic liquids provide robust fluorescence properties and remarkably increased UV–Vis absorption. This research may enrich the field of functionalized ionic liquids and provide a platform for extension of ionic liquid applications.

Keywords: ionic liquids, spectroscopy, naphthyl-functionalized, thermal analyses, fluorescence, UV–Vis absorption

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INTRODUCTION

In the past years, ionic liquids (ILs) have attracted numerous attention in many fields of chemistry and industry [1–7], due to their unique properties such as low melting point, negligible volatility, non-flammability and high thermal stability [8–13]. Recently, the appearance of functionalized ILs endows the ILs with huge diversity in properties, which makes the research of ILs has a greater space for further development. Generally, the chemical or physical characteristics of the ILs are modified by adding functional groups such as ethylene glycol [14, 15], nitrile [16, 17], sulfo acid [18, 19], amine [20, 21], aryl [22, 23], etc. Carlisle et al. [24] discovered that nitrile-functionalized ILs show good performance in gas separation. Wang et al. [25] reported that ethanolamine-based quaternary ammonium ILs display high activity and recyclability in palladium-catalyzed Heck reaction. Chaugule et al. [26] found that glycerol functionalized ILs exhibit excellent catalytic properties for 2-azidoalcohol synthesis. Besides, mixtures of ether-functionalized ILs and methyl perfluorobutyl ether as new safe electrolytes were also reported by Fang et al. [27]. Moreover, ILs

modified by functional groups have similar electron-donating properties with that of the major classes of organic molecules [28–30], which plays important role in exploring the potential applications of ILs in more fields.

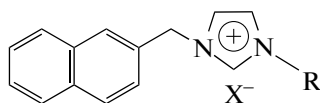
It has been a hot topic to develop new kinds of ILs with different properties in the field of current IL research. In this paper, we reported the preparation and properties of a series of ILs based on naphthyl-functionalized imidazolium with different alkyl chain lengths and anions (Br⁻, BF₄⁻, PF₆⁻, and NTf₂⁻), which adding a new family of functionalized ILs and providing a platform for extension of IL applications.

EXPERIMENTAL

Materials

2-(Bromomethyl)naphthalene 96% (Alfa Aesar) and lithium bis(trifluoromethylsulfonyl)imide 99% (Fluka) were used as received. 1-Bromobutane and 1-bromooctane were obtained from Shanghai Guangming Reagent Company. These reagents were first treated with concentrated sulfuric acid and then redistilled before use. 1-Methylimidazole was obtained

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[NMMIm]Br: R=CH₃, X=Br; [NMMIm]BF₄: R=CH₃, X=BF₄;
 [NMMIm]PF₆: R=CH₃, X=Br; [NMMIm]NTf₂: R=CH₃, X=N(CF₃SO₂)₂;
 [NMBIm]Br: R=C₄H₉, X=Br; [NMBIm]BF₄: R=C₄H₉, X=BF₄;
 [NMBIm]PF₆: R=C₄H₉, X=Br; [NMBIm]NTf₂: R=C₄H₉, X=N(CF₃SO₂)₂;
 [NMOIm]Br: R=C₈H₁₇, X=Br; [NMOIm]BF₄: R=C₈H₁₇, X=BF₄;
 [NMOIm]PF₆: R=C₈H₁₇, X=Br; [NMOIm]NTf₂: R=C₈H₁₇, X=N(CF₃SO₂)₂

Fig. 1. Molecular structures and abbreviations of the naphthyl-functionalized ILs.

from Shanghai Weite Regent Company and redistilled before use. All the other chemicals used in this work were of analytical grade.

Synthesis

Twelve 1-naphthylmethyl-3-alkylimidazolium ILs were prepared according to the similar approach. Figure 1 gives the chemical structures and abbreviations of them. The synthetic process of 1-naphthylmethyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([NMBIm]NTf₂) as an example is given in the following and other naphthyl-functionalized ILs can be obtained analogously. Conventional IL 1-methyl-3-butylimidazolium hexafluorophosphate ([MBIm]PF₆) was also synthesized for comparison.

Synthesis of 1-Butylimidazole [2]

Under Ar atmosphere, 0.55 mol (12.65 g) Na was added in one portion to 250 mL absolute ethanol. The mixture was stirred until Na disappeared and the reaction temperature got back to room temperature. Then 0.5 mol (34.04 g) imidazole was added and the mixture was stirred for 1 h, followed by dropwise addition of freshly distilled 1-bromobutane (75.36 g, 0.55 mol) at room temperature. Then the mixture was refluxed for 3 h. The resulting mixture was filtered to remove the precipitated NaBr after cooling down to room temperature. After removal of solvent by rotary evaporation, the sample was refiltered to remove NaBr. The residual liquid was distilled under reduced pressure. Yield 45%, 27.94 g. ¹H NMR (CDCl₃, 400 MHz): 7.36 (1H, N=CH), 6.95 (1H, C=CH), 6.81 (1H, C=CH), 3.82 (2H, NCH₂), 1.67 (2H), 1.23 (2H), 0.85 (3H).

Synthesis of 1-Naphthylmethyl-3-butylimidazolium Bromide Ionic Liquid ([NMBIm]Br)

Under vigorous stirring, a solution of 2-(bromomethyl)naphthalene (13.27 g, 0.06 mol) and 1-butylimidazole (8.87 g, 0.072 mol) in 2-propanol (180 mL) was heated at 95°C for 72 h. After removal of

the upper organic phase, residual solvent was removed under reduced pressure. The bromide salt was dissolved in water and then washed with petroleum ether and ethyl acetate. After removal of the water under reduced pressure, the residue was purified by recrystallizing from acetone. 1-Naphthylmethyl-3-butylimidazolium bromide at 80% yield (16.57 g). ¹H NMR (DMSO-d₆, 400 MHz): 9.52 (1H, N=CH), 8.00–7.52 (9H), 5.64 (2H, NCH₂), 4.20 (2H), 1.77 (2H), 1.23 (2H), 0.87 (3H).

Synthesis of 1-Naphthylmethyl-3-butylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquid ([NMBIm]NTf₂)

Under vigorous stirring, 0.01 mol (3.45 g) [NMBIm]Br was dissolved in water, to the aqueous solution was added lithium bis(trifluoromethylsulfonyl)imide (3.45 g, 0.012 mol). The ion exchange proceeded for 12 h at room temperature. Two phases were formed in the mixture solution. The resulting solution was extracted with ethyl acetate and then washed with water. The organic phase was dried over anhydrous MgSO₄, filtered. Removal of solvent under reduced pressure afforded 1-naphthylmethyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide (yield 90%, 4.91 g). ¹H NMR (DMSO-d₆, 400MHz): 9.35 (1H, N=CH), 8.00–7.53 (9H), 5.62 (2H, NCH₂), 4.19 (2H), 1.78 (2H), 1.26 (2H), 0.90 (3H).

Instruments

¹H NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer. Thermal gravimetric analysis (TGA) was carried out on a STA 449 C Jupiter®–Simultaneous TG–DSC at a heating rate of 10°C/min in air atmosphere over temperature range from ambient to about 600°C. UV–Vis absorption spectra were conducted on an Agilent 8453 UV–Vis absorption spectrophotometer. Photoluminescence measurement was performed at room temperature using Hitachi Model F-4500 fluorescence spectrophotometer at a scan speed of 1200 nm/min.

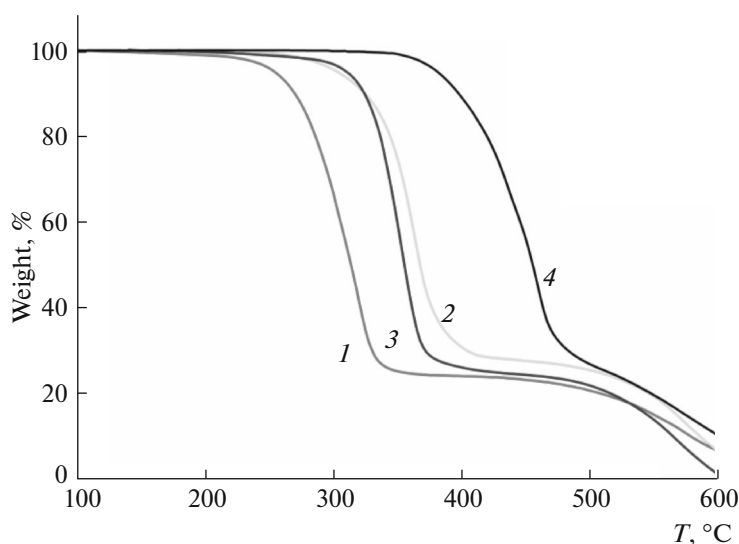


Fig. 2. TGA curves of 1-naphthylmethyl-3-butylimidazolium ILs with different anions: (1) Br^- , (2) BF_4^- , (3) PF_6^- , (4) NTf_2^- .

RESULTS AND DISCUSSION

Thermal Properties

Generally, thermal properties of ILs are affected by salt structure [3]. The effect of both anion and alkyl chain length on the thermal stabilities of the newly synthesized ILs were investigated. Figure 2 gives the TGA curves of 1-naphthylmethyl-3-butylimidazolium ILs with different anions (Br^- , BF_4^- , PF_6^- , NTf_2^-). We can see that anion greatly influences thermal stabilities of the ILs. A general trend of the thermal stabilities for the ILs is observed as follows: $\text{NTf}_2^- > \text{PF}_6^- \sim \text{BF}_4^- > \text{Br}^-$. IL with NTf_2^- anion is shown to be stable up to 400°C , whereas the one with Br^- anion decomposes at a temperature lower than 300°C . In order to study the effect of alkyl chain length on the thermal stabilities of the ILs, TGA curves of 1-naphthylmethyl-3-alkylimidazolium tetrafluoroborate ILs with methyl ($[\text{NMMIm}]\text{BF}_4$), butyl ($[\text{NMBIm}]\text{BF}_4$), and octyl group ($[\text{NMOIm}]\text{BF}_4$) on imidazolium cation are shown in Fig. 3. TGA curves of the three kind of ILs with different alkyl chain length are similar and almost flat up to nearly about 300°C . As the temperature increased, a slightly decrease of thermal stabilities has been detected by increasing length of the side alkyl chain.

The onset decomposition temperature (T_d) of the ILs is listed in Table 1. The T_d of the ILs with Br^- anion is in the range of $267\text{--}284^\circ\text{C}$. When BF_4^- or PF_6^- replaces Br^- anion, T_d of the ILs increases to $329\text{--}338^\circ\text{C}$ ranges. It is worthwhile to note that T_d of the ILs containing NTf_2^- anion is in the range of $405\text{--}417^\circ\text{C}$, which is significantly higher than others. Therefore anion plays a crucial role in determining the T_d of the ILs. In order to investigate length of alkyl

chain on the effect of T_d , ILs $[\text{NMOIm}]\text{Br}$, $[\text{NMBIm}]\text{Br}$, and $[\text{NMOIm}]\text{Br}$ with the same anion was studied. We can see that T_d of the ILs slightly reduced as the chain length increasing. The same trend was also found as for ILs with NTf_2^- , PF_6^- , and BF_4^- anion.

Spectroscopic Properties

The UV–Vis absorption spectra of the ILs with and without naphthyl group were investigated. Conventional IL 1-methyl-3-butylimidazolium hexafluorophosphate ($[\text{MBIm}]\text{PF}_6$) without naphthyl group was selected for comparison. Absorption spectra in the range $200\text{--}500\text{ nm}$ were recorded using a 1 cm path length quartz cuvette. All the ILs were diluted with ethanol in $1 : 12\,000$ weight ratio because of high absorbance of the naphthyl-functionalized ILs. Figure 4 gives UV–Vis absorption spectra of 1-naphthylmethyl-3-butylimidazolium ILs with different anions and IL $[\text{MBIm}]\text{PF}_6$ without naphthyl group. From the picture we can see that $[\text{MBIm}]\text{PF}_6$ only has a very weak and broad absorption band at about

Table 1. The onset decomposition temperature (T_d) of the naphthyl-functionalized ILs

ILs	$T_d, ^\circ\text{C}$	ILs	$T_d, ^\circ\text{C}$
$[\text{NMMIm}]\text{Br}$	284	$[\text{NMBIm}]\text{PF}_6$	331
$[\text{NMMIm}]\text{BF}_4$	338	$[\text{NMBIm}]\text{NTf}_2$	413
$[\text{NMMIm}]\text{PF}_6$	332	$[\text{NMOIm}]\text{Br}$	267
$[\text{NMMIm}]\text{NTf}_2$	417	$[\text{NMOIm}]\text{BF}_4$	332
$[\text{NMBIm}]\text{Br}$	275	$[\text{NMOIm}]\text{PF}_6$	329
$[\text{NMBIm}]\text{BF}_4$	335	$[\text{NMOIm}]\text{NTf}_2$	405

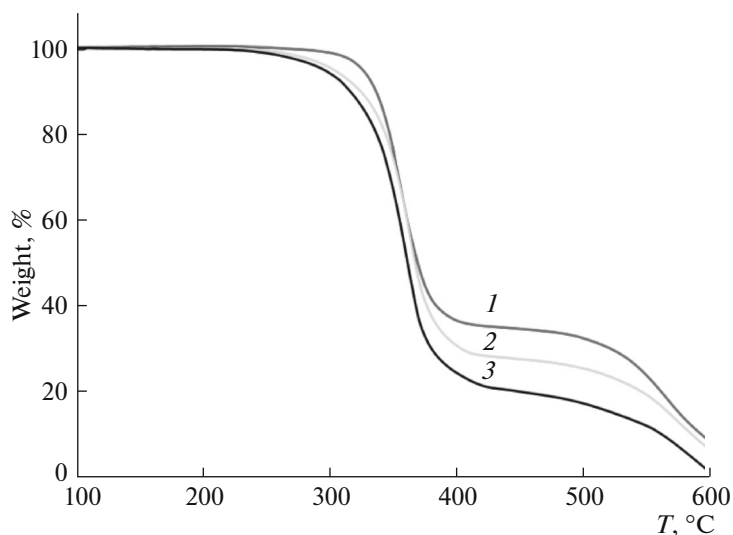


Fig. 3. TGA curves of 1-naphthylmethyl-3-alkylimidazolium tetrafluoroborate ILs with different length of the side alkyl chain: methyl (1), butyl (2), and octyl (3) group.

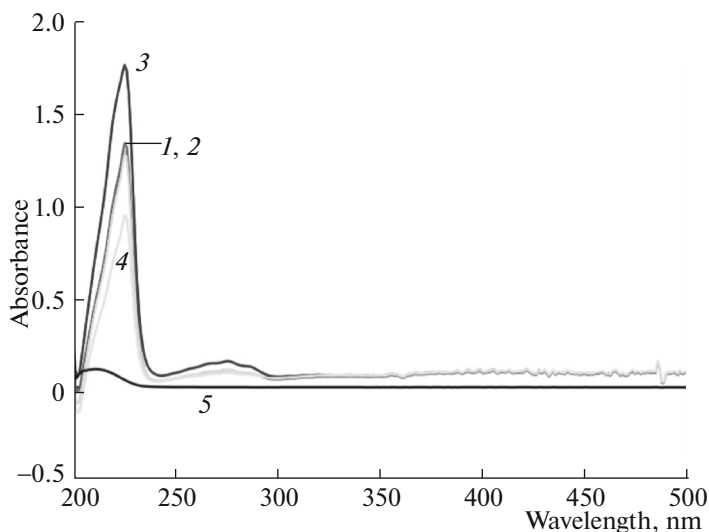


Fig. 4. UV-Vis absorption spectra of 1-naphthylmethyl-3-butylimidazolium ILs with different anions (1–4, see Fig. 2) and ionic liquid [MBIm]PF₆ (5) in ethanol.

211 nm. But for the 1-naphthylmethyl-3-butylimidazolium ILs, a strong peak at about 225 nm and a weak absorption band in the region 250–300 nm were observed. Besides, similar absorption characteristics were found in the spectra of 1-naphthylmethyl-3-butylimidazolium ILs with different anions, which indicates that anion has no obvious effect on the UV properties of ILs.

A comparative study was conducted by fluorescence between naphthyl-functionalized IL [NMBIm]PF₆ and the common IL [MBIm]PF₆, where the anion is same and the cation is similar. The fluorescence behavior of neat [NMBIm]PF₆ is illus-

trated in Fig. 5. As can be seen, when excited at wavelengths from 220 to 320 nm, a two-component emission spectrum is observed: a short-wavelength band around 335 nm and a long-wavelength band around 351 nm. With increase in the excitation wavelength, the emission gains intensity with no shift of the maximum. Then, with further increase in the excitation wavelength to 340 nm, the fluorescence disappeared immediately. In contrast, Fig. 6 depicts the fluorescence excitation spectra of [MBIm]PF₆. No fluorescence could be observed at excitation wavelengths below 250 nm. When excited between 250 and 350 nm, it exhibits weakly fluorescence and the spectral behavior dependent on the excitation wavelength. As the

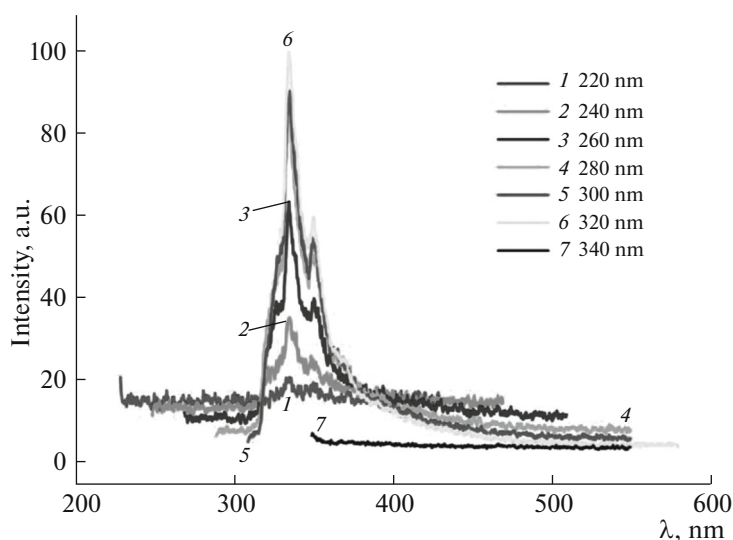


Fig. 5. Excitation wavelength-dependent emission behavior of neat [NMBIm]PF₆.

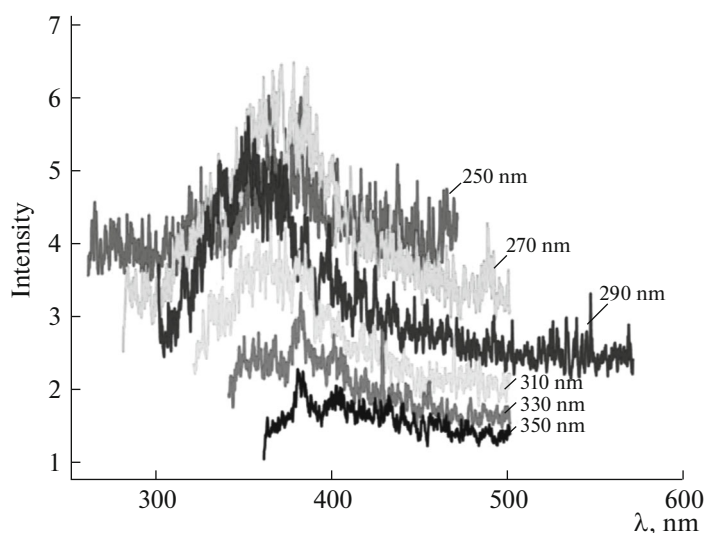


Fig. 6. Excitation wavelength-dependent emission behavior of neat [MBIm]PF₆.

excitation wavelength shifts from 250 to 350 nm, the fluorescence maximum shifts toward longer wavelength with decrease of the overall intensity. The fluorescence disappeared when excitation wavelength is above 350 nm. The unusual wavelength-dependent emission behaviors of [MBIm]PF₆ is attributed to the presence of different imidazolium associated forms [31, 32], whose position and intensity vary with excitation wavelength.

Compared with naphthyl-functionalized ILs and the common IL [MBIm]PF₆, we can see that the UV–Vis absorption spectra and fluorescence behavior of the naphthyl-functionalized ILs are quite different from that of the common one. The introduction of naphthyl group makes both a change in the peak posi-

tion and a remarkably increased luminescence intensity. The unusual spectroscopic properties of ILs may be attributed to the absorption of naphthyl group or the conformational changes in the imidazolium groups which caused by the interaction between the naphthyl group with other neighboring cations or anions.

CONCLUSIONS

A series of novel naphthyl-functionalized ILs have been synthesized and characterized in terms of their thermal and spectroscopic properties. Results of thermal gravimetric analysis suggested that ILs with NTf₂⁻ anion have good thermal stability, so they may be used in high temperature reactions or gas chromatography.

Additionally, the introduction of naphthyl group leads to a remarkable change in spectroscopic properties. These materials are expected to open new opportunities in a range of areas, such as fundamental photo-physical studies, optoelectronic materials, sensor materials, gas-liquid chromatography, etc.

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