



Effect of UV Irradiation on Structural Stability and Aggregation Behavior of Imidazolium Ionic Liquids

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Authors' contributions

This work was carried out in collaboration between all authors. Author LR designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors WW, ZX, FL and FY managed the analyses of the study. Author KZ managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Ionic liquids (ILs) have attracted great attention in both industry and academic researches. They usually exposed under ultraviolet light (UV) irradiation when they were used as solvents for photochemical reactions, additives of chromatographic separation medium with UV detection. However, the photostability of ILs still remained unexplored. Herein, the photostability of imidazolium IL was studied. We selected 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) as the model because of its wide applications and remarkable properties. After UV irradiation, with maximal absorption between 250-350 nm was dramatically enhanced. To clarify the underlying mechanism, nuclear magnetic resonance, UV-vis spectrum, fluorescence spectrum, high performance liquid chromatography equipped diode array detector and electrospray ionization mass spectrometry were intensively applied. The results showed that UV irradiation induced both chemical transformation

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and physical aggregation of the imidazolium cations. In addition, we found out that only protonated N-methylimidazolium underwent similar chemical transformation as imidazolium cations. This was indicative that all the imidazolium cation-based ILs were chemically and physically unstable under UV irradiation.

Keywords: Ionic liquids; imidazolium cation; chemical transformation; aggregation.

1. INTRODUCTION

Ionic liquids (ILs) are salts exhibiting melting points near room temperature. They exhibit many extraordinary chemical and physical properties such as negligible vapor pressure, low melting point, high ionic conductivity, and wide electrochemical active window [1-3]. A typical IL usually consists of an organic cation with delocalized charges and a small inorganic anion. They have been considered as environmentally benign replacements for industrial volatile organic solvents [4-6]. Especially, those imidazolium cation-based ILs (namely imidazolium ILs) have been applied in a wide range of processes such as organic synthesis, [7] multiphase bioprocess operations, [8] liquid-liquid separations, [9] high performance liquid chromatography (HPLC), [10] and capillary electrophoresis (CE) [11]. For the purpose of robust applications, the structural stability and physical properties (e.g. aggregation behaviors) of ILs under the appropriate conditions require thorough understanding.

Among various operation conditions, particular attention needs to be paid for the electromagnetic irradiation. As previously reported ILs underwent redox reaction and gradual degradation with diverse irradiations such as α , β , γ -rays, [12-14] electron beam [15] and pulsed laser [16]. Apart from these aforementioned high-energy and high-intensity electromagnetic irradiations, ILs are used under the normal photo-irradiations such as UV light more widely. For instance, ILs frequently were used as separation media of UV detection-coupled HPLC [17] or CE [18], and as solvents for UV-initiated photochemical reactions, involving photo-reduction, [19] photo-substitution, [20] photo-isomerization, [21] photo-addition, [22,23] photo-polymerization, [24] and photo-degradation [25]. However, although the importance has long been recognized, no specific attention was paid by using sensitive techniques to investigate ILs' UV-stability.

Considering the importance of physical and chemical properties of ILs to their application

efficiency, it is significant to investigate the effect of UV-irradiation on structural stability and aggregation behavior of ILs. Herein, by using an imidazolium IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]), as a model, we found out that UV irradiation can not only induce ILs degradation, but also cause its aggregation state variation. A series of sensitive chromatographic and spectroscopic techniques were peculiarly applied to discern the underline mechanism. In addition, a general insight into the UV-stability of imidazolium ILs was drawn.

2. MATERIALS AND METHODS

2.1 Materials

Imidazolium ILs ($\geq 99\%$) was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China) and was dried under vacuum at -55°C for 48 h. N-methylimidazole (MIM, $\geq 99\%$) was purchased from Aladdin (Shanghai China). Deuterium oxide (D₂O, 99.9%) was purchased from Cambridge Isotope Laboratories, Inc. Ultrapure water ($\geq 18.2 \text{ m}\Omega\cdot\text{cm}$) used throughout was prepared by an AKWL-IV-16 water purification system (Chengdu Tang's Kangning Science and Technology Development Co., Ltd., Chengdu, China).

2.2 Methods

A 300 W deuterium lamp (purchased from Beijing ShuGuang-Ming Electronic Lighting Instrument, Beijing, China) was used as the UV light source. The [Bmim][BF₄] was irradiated in a 4 mL cuvette with 4 cm² effective radiating area for 30 min. The radiant intensity is 240 mW \cdot cm⁻². A series of 10 mM MIM water solutions with pH 5.7-9.1 were prepared with the adjustment of HCl. The pH was measured by a Delta 320 pH meter (Mettler-Toledo Instruments, Shanghai). The MIM solutions were irradiated under the same conditions as that of [Bmim][BF₄].

2.3 Analytical Techniques

HPLC studies were performed with two modes of detection: EIS-MS and UV detection. HPLC/UV

experiments were carried out on an Agilent 1260 Series (Agilent Technologies, USA) liquid chromatograph system equipped with a diode array detector (DAD). HPLC/ESI-MS studies were performed on ACQUITY SQD single quadrupole LC/MS system (Waters, USA). The column was an Agilent Zobax SB-C18 column, 5 μm , 250/4.6 mm. The analyses were performed at the ambient temperature at a flow rate of 0.8 mL min^{-1} . Sample injections (10 μL) at 10 mM. The mobile phase was (A) water and (B) methanol under isocratic conditions (A/B 70/30). Following is the MS parameters: ionization mode, ES+; mass range of m/z from 100 to 500; scan rate, 1 scan/sec; and cone voltage, 20 eV. The absorption and fluorescence spectra were recorded on Shimadzu UV-vis spectrophotometer (UV-2450) and Shimadzu spectrofluorophotometer (RF-5301 PC), respectively. The $^1\text{H-NMR}$ spectra were measured by Bruker Avance 500 MHz NMR spectrometer.

3. RESULTS AND DISCUSSION

To investigate the effect of light irradiation, the neat $[\text{Bmim}][\text{BF}_4]$ in a quartz cuvette was first irradiated by a deuterium lamp (300 W) for 30 min. As compared in Fig. 1, the absorption 250-350 nm increased dramatically after lamp irradiation. In order to confirm the effect of UV-light, neat $[\text{Bmim}][\text{BF}_4]$ in a glass cuvette was irradiated by the deuterium lamp under the same conditions. Comparatively, the UV-vis spectra of $[\text{Bmim}][\text{BF}_4]$ were kept unchanged before and after irradiation. Comparing the light transmissivity between quartz cuvette and glass cuvette (Fig. S1), It was clear that the change of absorption spectra of $[\text{Bmim}][\text{BF}_4]$ was due to the interaction between the UV light and $[\text{Bmim}][\text{BF}_4]$. Then irradiation experiments were further conducted under the different wavelength. As shown in Fig. S2, only with the irradiation of UV light around 230 nm could induce the change of absorption spectra of $[\text{Bmim}][\text{BF}_4]$. Interestingly, energy of the UV light around 230 nm matched with the bandgap of $\pi-\pi^*$ transitions of the imidazolium ring. Consequently, we speculated that the UV-irradiation induced variation absorption spectra of $[\text{Bmim}][\text{BF}_4]$ should be due to two aspects, (1) chemical transformation of $[\text{Bmim}][\text{BF}_4]$, and /or (2) physical variation of aggregation state of imidazolium cation. To be mentioned, aggregation of imidazolium cation could induce overlap of π -orbitals and thus a result of red-shift absorption [26].

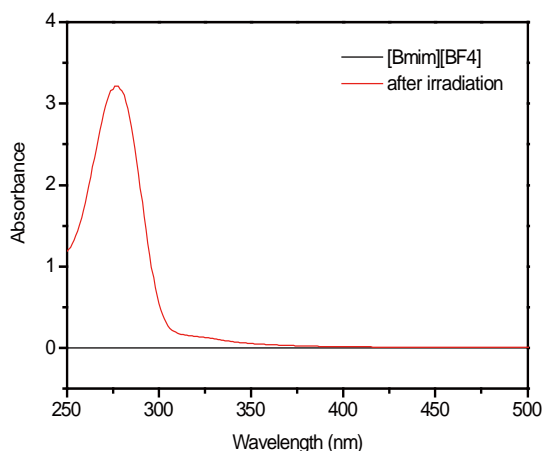


Fig. 1. Absorption spectra of $[\text{Bmim}][\text{BF}_4]$ before (black line) and after (red line) UV-light irradiation. For UV-vis measurements, the neat $[\text{Bmim}][\text{BF}_4]$ without and with UV irradiation were diluted with water to the same concentration of 100 mM

3.1 Structural Stability of $[\text{Bmim}][\text{BF}_4]$ under UV Irradiation

In order to confirm whether $[\text{Bmim}][\text{BF}_4]$ experienced chemical transformation under the irradiation of UV, HPLC/DAD analysis with dual wavelength (230 and 280 nm) detection was firstly carried out. The $[\text{Bmim}][\text{BF}_4]$ sample without UV-irradiation only displayed one peak at 6.68 min under 230 nm detection, and the peak was very weak under 280 nm (Fig. 2A). This was reasonable because $[\text{Bmim}][\text{BF}_4]$ possessed maximal absorption at 230 nm, and it was almost transparent to 280 nm (Fig. 2C). On the other hand, after 30 min irradiation, a new peak with elution time of 11.13 min was found under 280 nm detection (Fig. 2B). The UV-vis spectra of the component of 11.13 min peak was scanned online as well (Fig. 2D). It showed that, $[\text{Bmim}][\text{BF}_4]$ was induced to produce a new substance under UV irradiation with different absorption behaviors to pristine $[\text{Bmim}][\text{BF}_4]$.

Further investigation was carried out by HPLC/EIS-MS studies in order to characterize the new constituent separated from $[\text{Bmim}][\text{BF}_4]$ after UV irradiation. Fig. 3A is the mass spectrum of $[\text{Bmim}][\text{BF}_4]$ at 6.68 min retention time. It shows a peak at $m/z = 139.18$ corresponding to $[\text{Bmim}]^+$. Dimeric ions $[\text{Bmim}]_2[\text{BF}_4]^+$ ($m/z = 365.42$) were observed showing the molecular association between molecules.[12,27,28] The positive ionization mass spectrum of the new

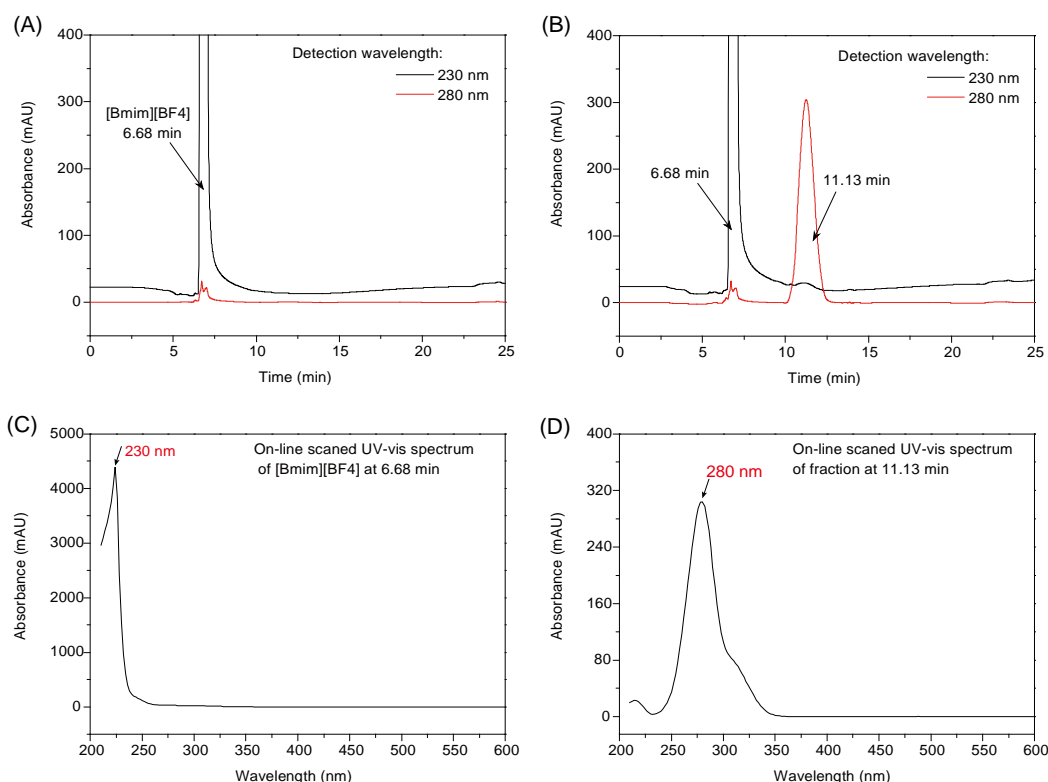


Fig. 2. Chromatograms of [Bmim][BF₄] before (A) and after (B) UV-light irradiation. The on-line scanned UV-vis spectra at 6.68 min (C) and 11.13 min (D) of chromatogram (B)

constituent at 11.13 min retention time is shown in Fig. 3B. The new peak at $m/z = 157.23$ is corresponding to $[\text{Bmim-F}]^+$.^[27] The peak at $m/z = 313.36$ is assigned to the dimer of $[\text{Bmim-F}]^+$. The results suggest that the chemical transformation of $[\text{Bmim}][\text{BF}_4]$ under UV irradiation are following: (a) $[\text{Bmim}\cdot]^+$ cation radical formed after the dissociation of the H-C2 bond of the imidazolium ring. (b) $\text{F}\cdot$ radicals from $[\text{BF}_4]^-$ anions. Then $[\text{Bmim-F}]^+$ cation formed by recombination of $\text{F}\cdot$ and $[\text{Bmim}\cdot]^+$ radicals. In addition, same low-intensity peaks such as at $m/z = 223.50$ for $[\text{mim}][\text{Bmim}]$, $m/z = 279.44$ for $[\text{Bmim}]_2$ and $m/z = 299.35$ for $[\text{Bmim-F}][\text{Bim-F}]^+$ were observed. This result shows that rupture of the methyl and butyl forms the photolysis products of the imidazolium cation. Therefore, the photolysis procedure of $[\text{Bmim}][\text{BF}_4]$ is proposed in Scheme 1. What's more, Comparison of ¹H-NMR spectra of $[\text{Bmim}][\text{BF}_4]$ before and after UV-light irradiation for 30 min indicated no detectable destruction or any other alteration of the molecular structure and bonding (Fig. S3). This result imply that less than 0.5% $[\text{Bmim}][\text{BF}_4]$ was photo-degenerated during the UV-light irradiation.

3.2 Aggregation Behavior of $[\text{Bmim}][\text{BF}_4]$ under UV-light Irradiation

Emission property of imidazolium ILs have been attributed to the imidazolium moiety and related to the presence of energetically different aggregates [29-31]. As shown in Fig. 4, when excited by shorter wavelength (< 300 nm), a normal emission peak appears at 355 nm which does not shift with the λ_{exc} (Fig. 4A). Interestingly, as the λ_{exc} increases, the emission peak shifts to the longer wavelength (Fig. 4B). It is speculated that the fluorescence spectrum of $[\text{Bmim}][\text{BF}_4]$ consists of two components: The maximum emission intensity ($\lambda_{\text{exc}} < 330$ nm) is ascribed to the isolated imidazolium-based structure, and the emission intensity at longer wavelengths, excited above 330 nm, is due to irradiative re-aggregation of associated structures [32,33]. The evidence from the effect of dilution on the fluorescence spectra (Fig. 5) shows that sufficient dilution of the ionic liquid results in complete disappearance of the long-wavelength emission band indicating the breaking of different kinds of associated structures of the ionic liquid. Even though the liquid state structure of the

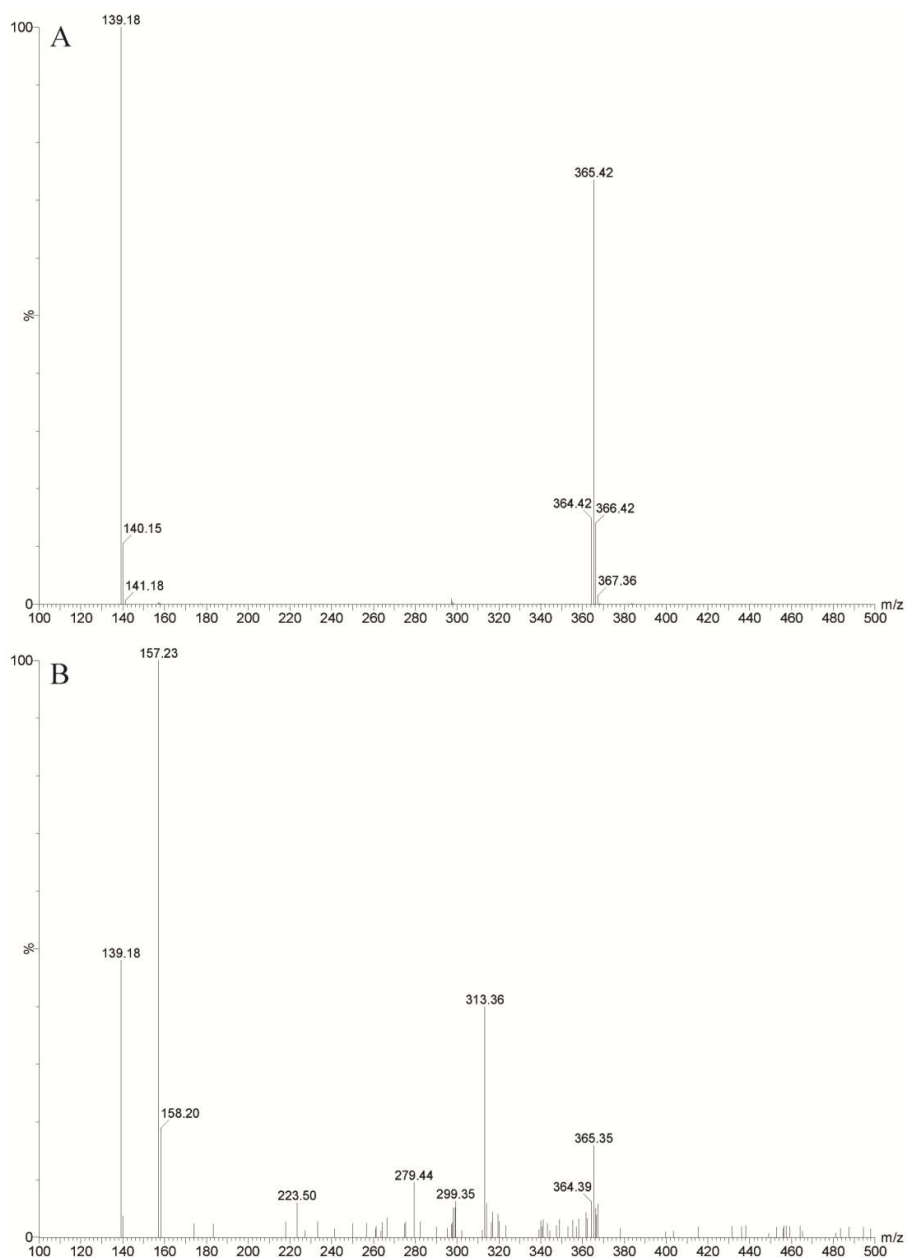


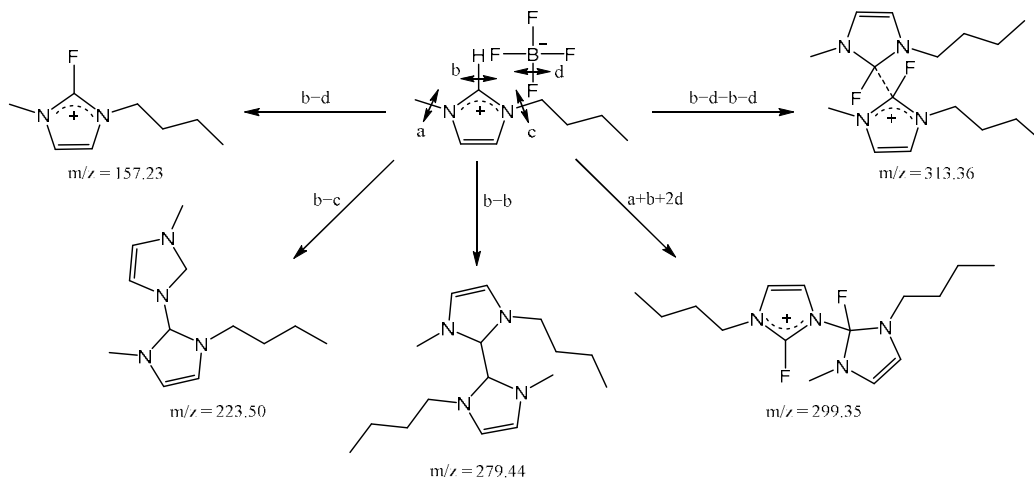
Fig. 3. The positive ionization mass spectra at 6.68 min (A) and 11.13 min (B) of irradiated sample chromatogram

RTILs is still not fully understood, the experimental studies, such as the neutron scattering, NMR, X-ray scattering and Raman spectroscopic measurements, clearly indicate several structures with both short- and long-range spatial correlations of the cation-anion and cation-cation pairs, [34,35,36,37] which be deemed as associated species to account for the long-wavelength emission band of ILs by Anunay

Samanta. After UV irradiation 30 min, the fluorescence spectra of [Bmim][BF₄] at various λ_{exc} were recorded. As can be seen (Fig. 4C), when the λ_{exc} is 290 nm, the emission peak intensity at 355 nm decreases from 91 mAU to 57 mAU. The fluorescence is lost approximate 40% during the UV-light irradiation, but less than 0.5% [Bmim][BF₄] was photo-degenerated as is mentioned above. It is reasonable that the UV

irradiation enhance the interaction among the isolated molecules. The emission peak intensity at 450 nm increases from 10 mAU to 16 mAU when the λ_{exc} is 360 nm (Fig. 4D). Fig. 6 reports the maximum emission intensity of [Bmim][BF₄] at different λ_{exc} (from 280 nm to 380 nm) before

and after UV irradiation, and the fluorescence peak position with different λ_{exc} is shown in the inset. The emission intensity decreases at shorter λ_{exc} and increases at longer λ_{exc} , which implies that imidazolium cations aggregate to associated forms under UV irradiation.



Scheme 1. Proposed degradation scheme of [Bmim][BF₄] under UV-light irradiation

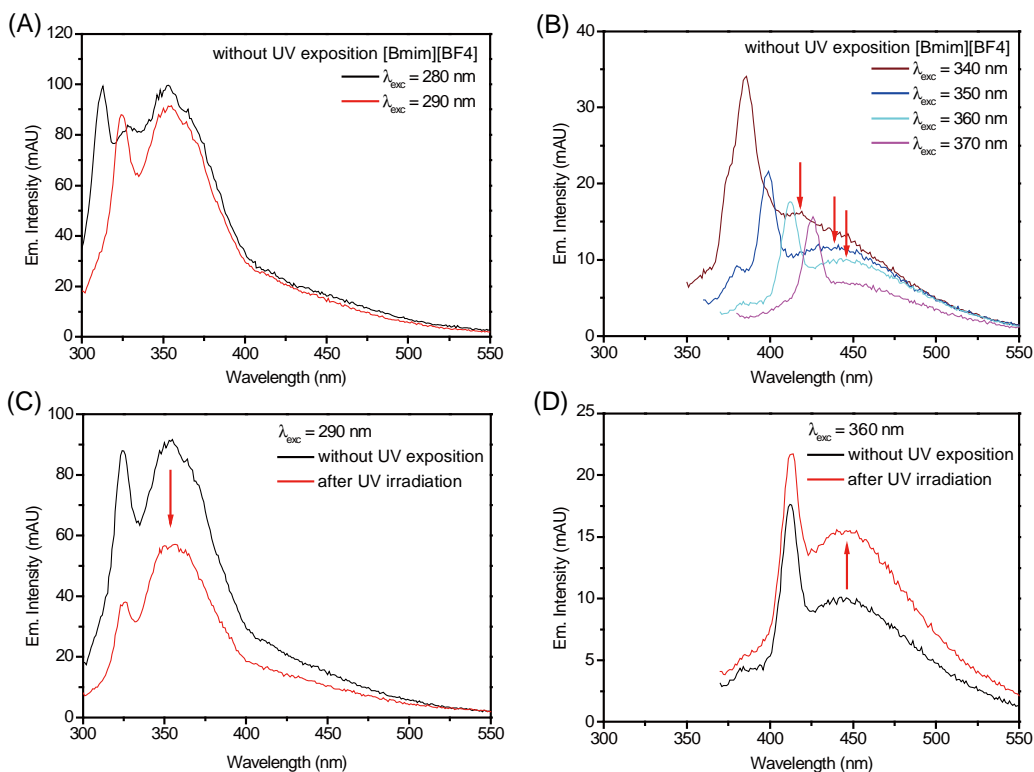


Fig. 4. Fluorescence emission spectra of [Bmim][BF₄] at shorter λ_{exc} (A) and (B) at longer λ_{exc} ; before and after UV-light irradiation at 290 nm λ_{exc} (C) and at 360 nm λ_{exc} (D). The sample diluted in water at 100 mM. The sharp peaks are Raman lines

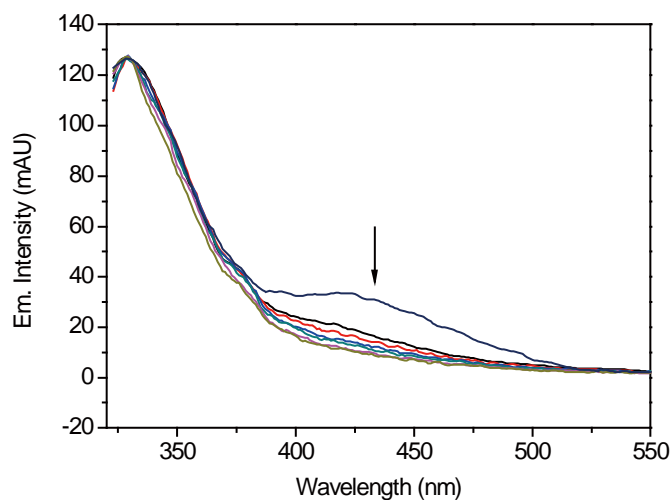


Fig. 5. Effect of dilution (using acetonitrile) on the fluorescence profile of [Bmim][BF₄]. λ_{exc} = 285 nm. The spectra are normalized at the lower wavelength emission maximum. The concentrations of [Bmim][BF₄] in decreasing order of the fluorescence intensity at 425 nm are 0.8, 0.4, 0.2, 0.1, 0.05, 0.025 and 0.0125 M

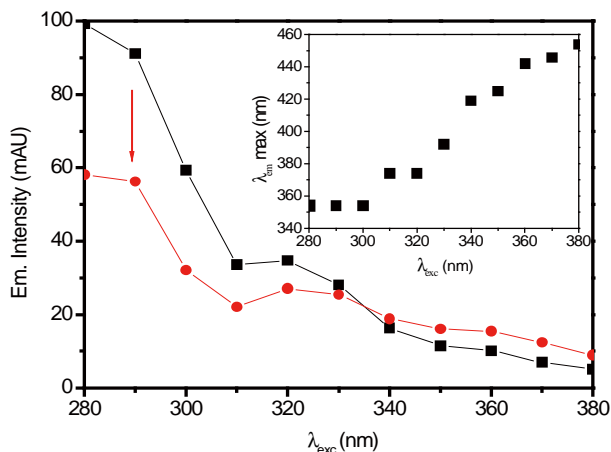


Fig. 6. The change of maximum emission intensity of irradiated [Bmim][BF₄]. The inset shows the variation of the fluorescence peak position with the λ_{exc}

Considering the case of fluorescence of dipolar molecular, in conventional molecular solvents, the dipolar solvent molecules undergo reorientation around the photoexcited solutes without moving from their original position. However, in ionic liquids, the ionic constituents of ionic liquids experience a net force when the dipole moment of the solute changes on photoexcitation [30]. In our case, we proposed that when part of the [Bmim][BF₄] been excited under UV irradiation, the ionic constituents of unexcited [Bmim][BF₄] around the photoexcited [Bmim] cation experience a net force. As a result, the imidazolium cation ions move from their initial

position to aggregate through π - π stacking interaction.

3.3 Implication to Photo-stability of Imidazolium ILs

The effect of UV irradiation on [Bmim][BF₄] is attributed to the imidazolium cation, which was proved by starting with N-methylimidazole (MIM), generating the corresponding imidazolium cation by protonation and then irradiated by deuterium lamp. Fig. 7A shows the absorption spectra of 10 mM MIM water solution before and after irradiated by deuterium lamp at different pH.

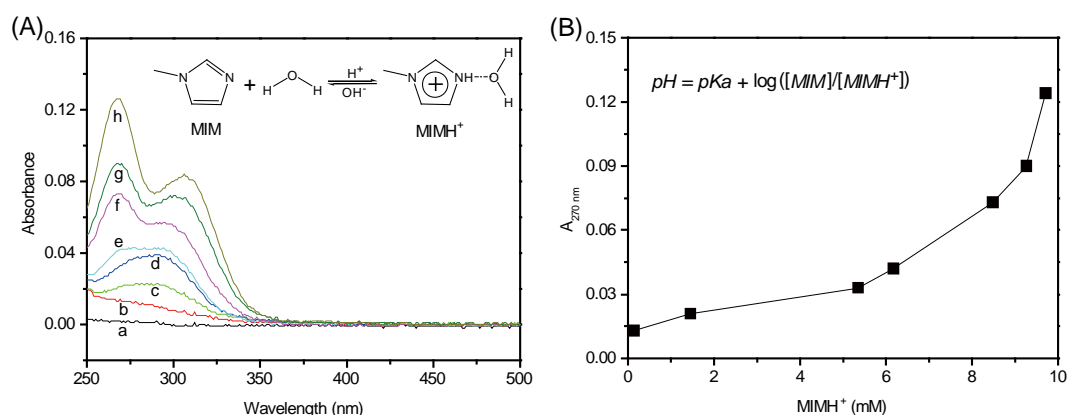


Fig. 7. (A) Effect of pH on the absorption spectrum of water solution of *N*-methylimidazole (10 mM) before and after UV-light irradiated. before irradiated, pH=9.13 (a), after irradiated, pH = 9.13 (b), pH = 8.03 (c), pH = 7.20 (d), pH = 7.05 (e), pH = 6.51 (f), pH = 6.17 (g), pH = 5.70 (h). (B) Effect of the concentration of MIMH⁺ on the absorbance at 270 nm

After irradiated for 10 min, the absorbance ($\lambda_{ab} > 250$ nm) increase obviously, and the amplification is related to the pH. At different pH, the concentration of protonated MIM (MIMH⁺) is defined by the Henderson-Hasselbalch equation. The Henderson-Hasselbalch function (pH) is defined as

$$pH = pK_a + \log\left(\frac{[MIM]}{[MIMH^+]}\right)$$

The pK_a is reported to be 7.2 for the protonation equilibrium of MIM.[38] [MIMH⁺] and [MIM] are the molar concentrations of the protonated and unprotonated forms in MIM/water solution, respectively. The absorbance at 270 nm of various concentrations of MIMH⁺ after UV-light irradiation 10 min is shown in Fig. 7B. The experiment results reveal that the electropositivity of imidazolium ring is the key factor to be influenced by UV-light. For imidazolium ionic liquids, the electropositivity in nature of the imidazolium ring, means all of them are sensitive under the UV-light irradiation. The absorption spectra of same other imidazolium ILs ([Bmim][PF₆], [Bmim]Br, [Bmim]Cl, [C₁₂mim][BF₄] and [Bmmim][BF₄]) before and after UV-light irradiation are shown in Fig. S4.

4. CONCLUSION

The effect of UV-light on [Bmim][BF₄] have been studied. The results suggested that the chemical structure and aggregation behavior of [Bmim][BF₄] influenced following UV-light irradiated. The formation of new substance is related to the photo-radiolysis of the imidazolium cation, and the isolated imidazolium cations aggregated

when it under UV-light irradiation. The photostability of imidazolium-based ILs is dependent on the positive charge density of imidazolium ring. Finally, these results extend the fundamental understanding of ILs. It is undoubted that more attentions should be paid for imidazolium ILs when they are used in photochemistry.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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APPENDIX

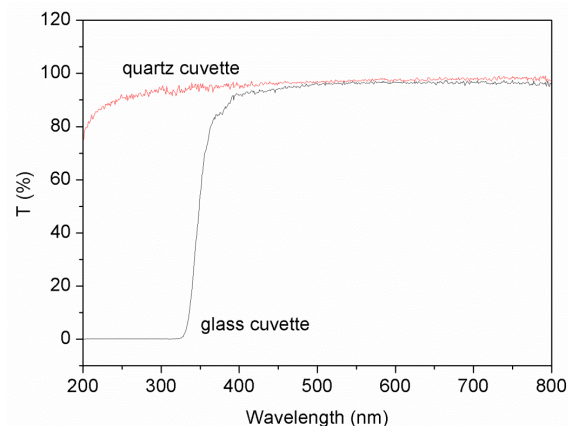


Fig. S1. The light transmissivity diagram of quartz cuvette and glass cuvette

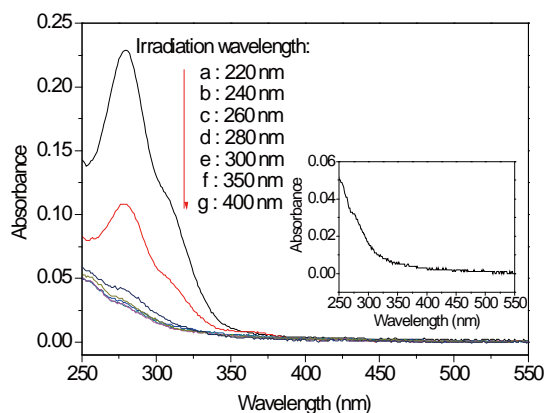


Fig. S2. The absorption spectra of 10 mM [Bmim][BF₄] water solution under different wavelength light irradiation for 10 min. The inset shows the absorption spectra of [Bmim][BF₄] before irradiated. 4 mL 10 mM [Bmim][BF₄] water solution was irradiated in a quartz cuvette by the excitation light of Shimadzu spectrofluorophotometer (RF-5301 PC) for 10 min. Set the excitation wavelength at 220, 240, 260, 280, 300, 350 and 400 nm with 20 nm slit width respectively. Then the absorption spectra were recorded on Shimadzu UV-vis spectrophotometer (UV-2450)

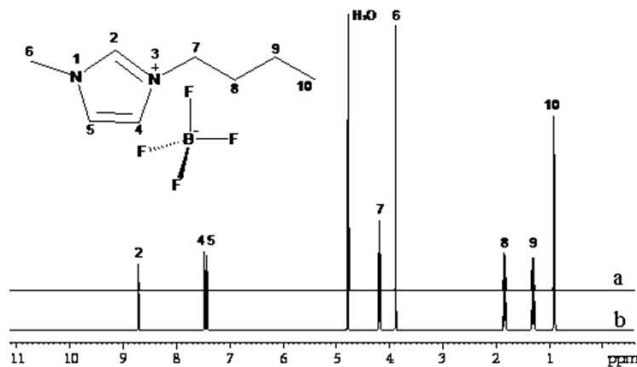


Fig. S3. H-NMR spectra of [Bmim][BF₄] before (a) and after (b) deuterium lamp irradiation. H-NMR was carried out on a Bruker Avance 500 MHz NMR spectrometer using D₂O as solvent

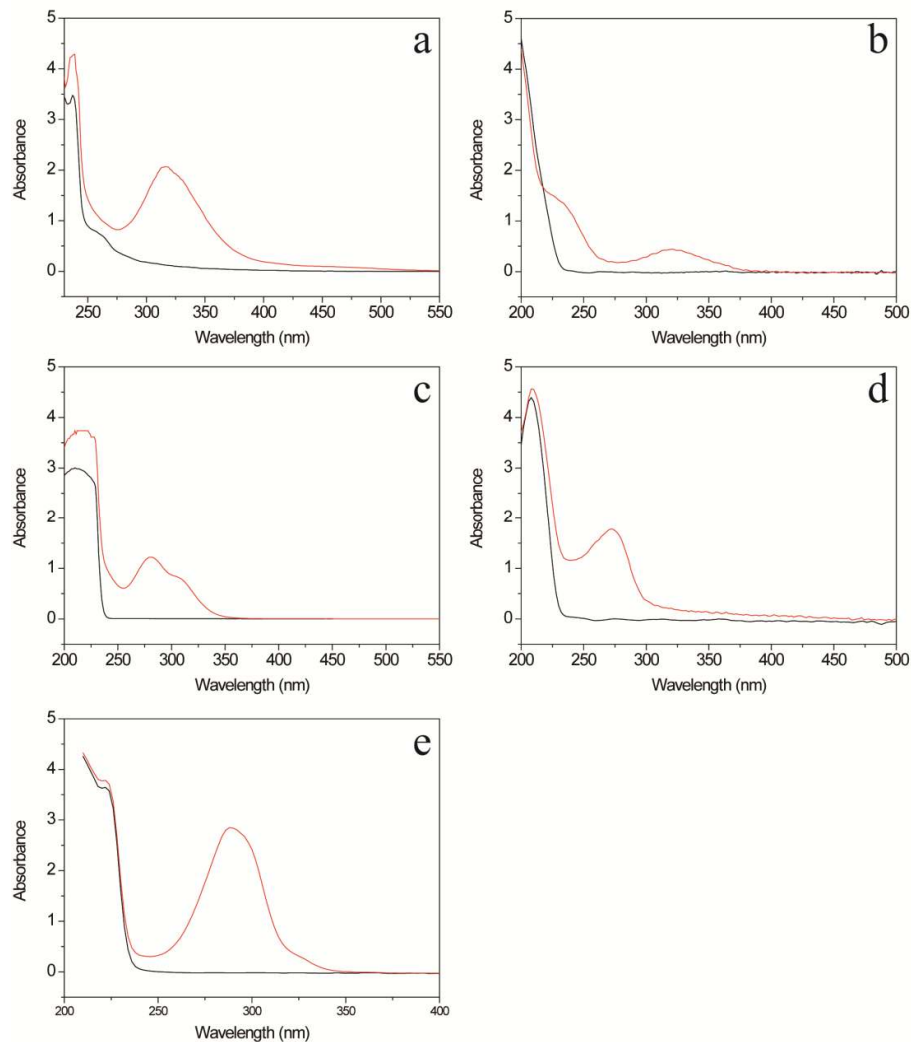


Fig. S4. Absorption spectra of [Bmim][PF₆] (a), [Bmim]Br (b), [Bmim]Cl (c), [C₁₂mim][BF₄] (d) and [Bmmim][BF₄] (e) before (black line) and after (red line) UV-light irradiation 30 min

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