

Vibrational spectroscopic study of ionic liquids: Comparison between monocationic and dicationic imidazolium ionic liquids



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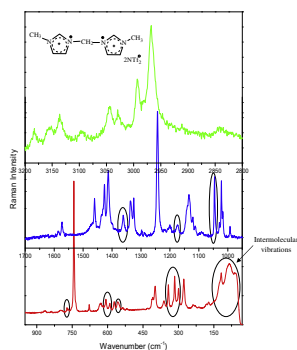
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HIGHLIGHTS

- Synthesis of dicationic ionic liquid **[M(CH₂)IM²⁺][2NTf₂]**.
- FTIR/ATR and FT-RAMAN spectroscopy study of the previous dicationic ionic liquid.
- Comparison between our dicationic ionic liquid and a monocationic ionic liquid.
- There are more active modes in FT-Raman than in FTIR/ATR spectroscopy.
- The passage from mono to dicationic is responsible of important vibrational changes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 December 2013

Received in revised form 6 February 2014

Accepted 11 February 2014

Available online 24 February 2014

Keywords:

Monocationic and dicationic ionic liquids

Imidazolium

Raman spectroscopy

FTIR/ATR spectroscopy

ABSTRACT

In this study, we synthesised a dicationic ionic liquids labeled bis-methyl imidazolium methylenide bis (trifluoromethanesulfonyl) imide (**[M(CH₂)IM²⁺][2NTf₂]**). The structure was identified by NMR. In order to characterise this ionic liquid, vibrational spectroscopy studies were performed by FTIR/ATR and FT-Raman spectroscopies. A comparative study was introduced by FTIR/ATR and FT-Raman spectroscopies, between our synthesised dicationic ionic liquid and a monocationic ionic liquid (**[EMIM⁺][NTf₂]**), where the anion and the cation are similar.

FTIR/ATR spectra of dicationic ionic liquid are richer in modes especially in the spectral range of 3000 cm⁻¹. In the 1400–900 cm⁻¹ spectral region, the mode corresponding to the vibration of the NTf₂⁻ anion at 1040, 1140 and 1340 cm⁻¹ is very sensitive by the number of cation change. It was also the case for the peak at 1575 cm⁻¹ assigned to ring in-plane symmetric/anti-symmetric stretch CH₂(N) and CH₃(N)CN stretch. In the 4000–2800 cm⁻¹ spectral region, we observed few new peaks for **[M(CH₂)IM²⁺]** comparatively with **[EMIM⁺]**; a splitting for the peak at 3105 cm⁻¹ and some wavenumber shifts for various modes.

For the FT-Raman spectroscopy study, we realised our study in the spectral region 4000–0 cm⁻¹ while that of the monocationique sample is realised in the spectral region 1700–200 cm⁻¹. We observe in the common region 19 new peaks with the passage from the mono to dicationic, what is consequent. The impact of the passage from mono to dicationic is more important for the anion contribution spectral

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range (1400–300 cm^{-1}) than in the FTIR/ATR spectroscopy study. Other markers of differentiation between $[\text{M}(\text{CH}_2)\text{IM}^{2+}]$ and $[\text{EMIM}^+]$ are observed for vibrational modes assigned to $\text{CH}_2(\text{N})$ and $\text{CH}_3(\text{N})\text{CN}$ stretch. We can also notice a contrast between the two spectroscopies: there are more active modes in FT-Raman than in FTIR/ATR spectroscopy.

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1. Introduction

Room temperature ionic liquids (RTILs) are molten salts at room temperature. They represent a new generation of solvents. Many researches have been developed the last years on these products because of their interesting properties such as: low melting temperature ($T_f < 100$), low vapour pressure, the easiness in regenerating and to recycling them, a very high chemical and thermal stability, and the easiness to synthesise them and obtain a very high conductivity. The advantage that the ionic liquids present is the possibility of changing their properties by varying the nature of the couple cation/anion [2,3].

Despite the studies on different generations of monocationic ionic liquids, there is still much to know about a wide variety of ionic liquids, especially in the case of dicationic ones.

Ionic liquids contain two head groups and two aliphatic chains linked by either a rigid or flexible connection. In addition to the combination of cation–anion, simple changes in the length of the bond or in the aliphatic chains of the cation are used to modify the physical properties of ionic liquids [4].

Dicationic ionic liquids are suitable candidates as advanced electrolyte materials in lithium ion batteries, fuel cells, dye-sensitised solar cells, and super capacitors [5–8,3]. In dicationic ionic liquids studied today, every dication is associated with two identical anions, which are either hydrophobic or hydrophilic. These ionic liquids are further classified as symmetric (the monocations that form the dication are the same) or asymmetrical (the monocations are different). There has been no report on the synthesis of dicationic ionic liquid, in which each dication is associated with two different anions, one hydrophobic and the other hydrophilic. By incorporating both hydrophilic and hydrophobic anions in dication, a further series of ionic liquid with properties that are different from existing ones are expected [9].

Dicationic ionic liquids are promising catalysts for the esterification reaction [10]. They have also been widely used in various fields of science because of their high thermal stability, a wide temperature range of the liquid state, and the biological activities such as antiviral, antifungal and anticancer activities. The ability of fictionalisation of dicationic ionic liquids gives the possibility of designing structures with respect to cations, anions and the length of the chain linking two cations, to achieve significant properties based on specific chemical tasks. In particular, the dicationic ionic liquids based on imidazolium and pyrrolidinium showed a variety of promising physicochemical properties in many applications [11].

FTIR/ATR and Raman spectroscopies are a vibrational spectroscopies technique that can provide a sensitive, relatively quick, non-destructive means of probing molecular structure in solid and liquid phases. It is also convenient for analysis of conformational dependence, and intra- and inter-chain interactions [12–16]. Numerous studies were performed on monocationic ionic liquids by FTIR/ATR and FT-Raman spectroscopies [1,17–21], but to the authors' knowledge, there does not exist at present a published FTIR and Raman spectroscopy study of dicationic ionic liquid behavior.

In this work, we present a comparative study by vibrational spectroscopies (FTIR/ATR and FT-Raman) between two ionic

liquids; the first one is a dicationic ionic liquids that we have synthesised and characterised, and the second one is a monocationic ionic liquid, cited in the literature in the work of Noack et al. [1].

In this paper we use the $[\text{EMIM}^+][\text{NTf}_2^-]$ notation instead of $[\text{C}_2\text{C}_1\text{IM}^+][\text{NTf}_2^-]$ used in the previous Ref. [1].

2. Materials and methods

2.1. Reagents and materials

The reagents used in this study are, 1,2-diiodomethane, 1-methylimidazole (99 wt.%), (Acros), lithium bis(trifluoromethylsulfonyl)imide, diethylether and N,N-dimethylformamide, that were purchased from Fluka and used as received. Deionized H_2O was obtained with a Millipore ion-exchange resin deionizer.

2.2. NMR, spectroscopy analysis

^1H NMR (400 MHz), ^{13}C NMR, ^{19}F (100.6 MHz) spectra were recorded on DRX 400 MHz spectrometer. The chemical shifts (δ) are given in ppm and referenced to the internal solvent signal, TMS (Tetramethylsilane), and CFCl_3 , respectively.

2.2.1. Synthesis and characterisation of bis-methyl imidazolium methylenidene bis (trifluoromethanesulfonyl) imide

The synthesis of bis-methyl imidazolium methylenidene bis (trifluoromethanesulfonyl) imide ionic liquid in the present study was based on a metathesis reaction of freshly prepared halide salts of the bis-methyl imidazolium alkylene cation and bis (trifluoromethylsulfonyl) imide as anions. An methylenidene bis-methyl imidazolium iodide $[\text{M}(\text{CH}_2)\text{IM}^{2+}][\text{I}_2\text{I}^-]$ was prepared by reacting of $[\text{I}(\text{CH}_2)\text{I}]$ with two molar excess of 1-methylimidazole at 70 °C during 7 h.

In a round bottom flask, 1-methylimidazole (9.07 mL, 100 mmol) and 1,2-diiodomethane (5.07 mL, 50 mmol) were dissolved in toluene (15 mL) and the mixture was stirred at 70 °C for 5 h. The reaction mixture was evaporated under vacuum and the product washed with diethyl ether (5×20 mL). Bis-methyl imidazolium methylenidene iodide yellowish solid (13.20 g, 31.86 mmol) was obtained in 73% yield. In Fig. 1, we present the protocole of the synthesis.

The reaction mixture was condensed by evaporation and the resultant solid was washed with diethylether to remove unreacted reagents. The ionic liquid was also subjected to anion exchange from iodide to bis (trifluoromethane-sulfonyl) imide.

2.2.2. NMR results

The spectra details are given below,

^1H NMR (CDCl_3) δ ppm $[\text{M}(\text{CH}_2)\text{IM}^{2+}][\text{I}_2\text{I}^-]$: 3.05 (s, 6H, $2 \times \text{NCH}_3$), 6.09 (m, 2H, NCH_2N), 7.36 (m, 2H, NCHN), 7.73–7.49 (m, 4H, NCHCHN).

^{13}C NMR (CDCl_3) δ ppm $[\text{M}(\text{CH}_2)\text{IM}^{2+}][\text{I}_2\text{I}^-]$: 39.41, 51.66, 121.02, 123.23, 139.14, 139.96.

^{13}C NMR (CDCl_3) δ ppm $[\text{M}(\text{CH}_2)\text{IM}^{2+}][\text{2NTf}_2^-]$: 37.24, 54.01, 120.43, 121.09, 135.12, 149.08.

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