



Study of imidazolium dicationic ionic liquids by Raman and FTIR spectroscopies: The effect of the nature of the anion



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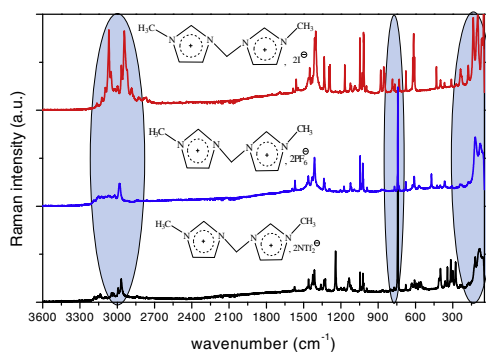
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HIGHLIGHTS

- Synthesis of dicationic ionic liquids $[M(CH_2)IM^{2+}][2I^-]$, $[M(CH_2)IM^{2+}][2PF_6^-]$, $[M(CH_2)IM^{2+}][2NTf_2^-]$.
- FTIR/ATR and FT-RAMAN spectroscopy study of the previous dicationic ionic liquids.
- Comparison between our liquids, effect of the nature of the anion.
- There are more active modes in FT-RAMAN than in FTIR/ATR spectroscopy.
- Each sample particularise with its own vibrational mode.

GRAPHICAL ABSTRACT



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ABSTRACT

In a previous paper, we investigated the comparison between monocationic and dicationic ionic liquids. In this study three new dicationic ionic liquids were synthesized, labeled: bis-methyl imidazolium methylenide iodide $[M(CH_2)IM^{2+}][2I^-]$, bis-methyl imidazolium methylenide hexafluorophosphate $[M(CH_2)IM^{2+}][2PF_6^-]$, bis-methyl imidazolium methylenide bis (trifluoromethanesulfonyl) imide $[M(CH_2)IM^{2+}][2NTf_2^-]$. In order to study the effect of the nature of the anion on the vibrational behaviors, their structures were identified by H, C, P, F NMR, FTIR/ATR and FT-RAMAN spectroscopies.

However, we observe very different vibrational modes between ionic liquids following the chosen anion. According to the type of anion, the interaction anion–cation is translated by different intensities for the same vibrational mode, by frequency shifts and by appearance of modes specific to the anion.

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Introduction

Ionic liquids have been considered as a new solvent. Most of them are molten salts at room temperature. They consist of an organic cation very often associated with an organic or inorganic

anion, and possible combinations of cations/anions are very numerous and constantly evolving. However, according to the intended applications, we found a number of ionic liquids more used than others. At the level of the cation, there is no doubt that the class of imidazolium is the most frequently used (form of ionic liquids with many anions and easiest to prepare and functionalize).

The advantages that ionic liquids present, compared with the other molecular liquids or molten salts, are due to the easiness of

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changing their intrinsic properties by varying the chemical nature of the combination of cation/anion. As reported previously, ionic liquids are widely developed because of their very interesting properties such as: their melting point which is lower than 100 °C, possession of a very low vapour pressure, the fact that they can be easily regenerated and recycled, their high chemical and thermal stability, are easy to synthesize and have a high conductivity [1]. In the same way, ionic liquids were developed in the field of the electrochemistry for the research for new systems of energy and electrolytes [2–5]. These new compounds are extensively applied in the field of organic synthesis and the catalysis. More recently, numerous researchers tried to highlight the interest of ionic liquids in the field of the processes of the analysis, the extraction and more particularly in the separation sciences [6–9].

Despite the studies on different generations of ionic liquids, there is still much to know about a wide variety of ionic liquids, especially in the case of dicationic ones. Dicationic ionic liquids are a new family of ionic liquids and consist of a doubly charged cation that is composed of two singly charged cations linked by an alkyl chain and paired with two singly charged anions [10]. Few results are reported on dicationic ionic liquids by Sahu et al. [11] which discuss and compare structure–property relationships in monocationic and dicationic ionic liquids. Yeganegi et al. present the effect of the anion type and the alkyl linkage length on the density and microscopic structure of liquid phase [10]. The application of new dicationic room-temperature ionic liquids as new Gas Chromatography stationary phases was studied by Huang et al. [12].

In a previous paper, we investigated the comparison between monocationic and dicationic ionic liquids [13]. In this work, new dicationic ionic liquids based on imidazolium were synthesized by varying the nature of the anion which also has an influence on the properties of these compounds. Their vibrational behaviors are studied by FT-RAMAN spectroscopy and FTIR/ATR spectroscopy for the first time.

Experimental

Reagents and materials

The reagents used in this study are, 1,2-diiodomethane, 1,3-dibromopropane (98 wt.%), 1-methylimidazole (99 wt.%), (Acros), lithium bis(trifluoromethylsulfonyl)imide, ammonium hexafluorophosphate (99.5 wt.%), diethyl ether and N,N-dimethylformamide, that were purchased from Fluka and used as received. Deionized H₂O was obtained with a Millipore ion-exchange resin deionizer.

NMR spectroscopy analysis

¹H NMR (400 MHz), ¹³C NMR, ¹⁹F (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 CFCl₃, respectively.

Synthesis and characterization of dicationic ionic liquids

In general, the synthesis of the three ionic liquids in the present study was based on a metathesis reaction of freshly prepared halide salts of the bis-methyl imidazolium alkylene cation with alkyl chain length C₁, and hexafluorophosphate, bis(trifluoromethylsulfonyl)imide as anions. A alkylene bis-methyl imidazolium iodide [M(CH₂)IM²⁺][I⁻] was prepared by reacting of [(I(CH₂)I)] with two molar excess of 1-methylimidazole at 70 °C during 7 h [13]. In the Fig. 1, we present the protocol of the synthesis.

Synthesis of bis-methyl imidazolium methyldene iodide [M(CH₂)IM²⁺][I⁻]

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 methyldene iodide yellowish solid (13.20 g, 31.86 mmol) was obtained in 73% yield.

Synthesis of bis-methyl imidazolium methyldene hexafluorophosphate [M(CH₂)IM²⁺][2 PF₆⁻]

Ammonium hexafluorophosphate (1.63 g, 10 mmol) dissolved in 15 mL of deionized water was added in a flask containing [M(CH₂)IM²⁺][I⁻] (2.07 g, 5 mmol) dissolved in 15 mL of deionized water. The mixture consisted of two separate phases: ionic liquid at the bottom and aqueous solution at the top. The former was separated from the latter by centrifugation (3000 rpm) for 60 s. After isolation, the ionic liquid was dried in a phosphorus pentoxide P₂O₅ to remove residual water.

Synthesis of bis-methyl imidazolium methyldene bis(trifluoromethane-sulfonyl) imide [M(CH₂)IM²⁺][2NTf₂⁻]

Following the similar procedure, [M(CH₂)IM²⁺][2NTf₂⁻] was prepared by anion exchange reaction from iodide to bis(trifluoromethane-sulfonyl) imide which was carried out by mixing [M(CH₂)IM²⁺][I⁻] and LiNTf₂ in water at room temperature for 2 h. Similar procedures were adopted for separation and isolation. Finally, a yellow solid was obtained.

The structures of obtained products were confirmed by using ¹H, ¹³C, ¹⁹F, ³¹P NMR spectroscopy to confirm the absence of any major impurities and the spectra details are given below.

NMR results

¹H NMR (CDCl₃) δ ppm [M(CH₂)IM²⁺][I⁻]: 3.05 (s, 6H, 2 × NCH₃), 6.09 (m, 2H, NCH₂N), 7.36 (m, 2H, NCHN), 7.73–7.49 (m, 4H, NCHCHN).

¹³C NMR (CDCl₃) δ ppm [M(CH₂)IM²⁺][I⁻]: 39.41, 51.66, 121.02, 123.23, 139.14, 139.96.

¹³C NMR (CDCl₃) δ ppm [M(CH₂)IM²⁺][2NTf₂⁻]: 37.24, 54.01, 120.43, 121.09, 135.12, 149.08.

¹⁹F NMR (CDCl₃) δ ppm [M(CH₂)IM²⁺][2NTf₂⁻]: -77.23 (s, CF₃SO₂)₂N).

³¹P NMR (DMSO-d₆) δ ppm [M(CH₂)IM²⁺][2PF₆⁻]: 141.01 (septet, PF₆). ¹⁹F NMR (DMSO-d₆) δ ppm: -72.03, -73.54 (d, PF₆).

FTIR/ATR and FT-RAMAN measurements

The measurements were realized in the Walloon Agricultural Research Center (Cra-w) Belgium.

FTIR/ATR measurements

All attenuated total reflectance Fourier transform mid-infrared (ATR/FTIR) spectra were acquired on a Vertex 70-RAM II Bruker spectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate TM diamond ATR accessory (Specac Ltd, Slough, UK).

FTIR/ATR spectra [4000–600 cm⁻¹] were collected with resolution of 1 cm⁻¹ by co-adding 64 scans for each spectrum at room temperature. The OPUS 6.0 software for windows of Bruker Instruments was used for instrument management.

FT-RAMAN measurements

FT-RAMAN spectra were acquired on a Vertex 70-RAM II Bruker FT-RAMAN spectrometer. This instrument is equipped with a Nd:YAG laser (yttrium aluminum garnet crystal doped with triply

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