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

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Dear editor,

I'm pleased to submit you in your journal our revised article with a new title: "**Study of imidazolium dicationic ionic liquids by Raman and FTIR spectroscopies: the effect of the nature of the anion.**" I send you an electronic version.

We brought the following corrections:

1)   The reviewer feels that there are too many line breaks in the introduction section.

We made the correction in the introduction.

2)   There are a few typos. For example, in the abstract, "bis-methyle" should be read as "bis-methyl"

We made the correction in the abstract (yellow highlight).

3)   Please cite the author's name in a unified way: in the introduction section, there are some scatterings, e.g., Sahu et al [11], Saeid Y. et al ….[10], K. Huangand et al [12]. So, I recommend that the authors carefully check these throughout the manuscript again.

We made the correction in page 2 (yellow highlight).

4)   Information on the measured temperature in the present study should be mentioned.

We made the correction in page 5 line 9 and line 19 (yellow highlight).

5)   If possible, can the authors put a little more science into

the results and discussion section, besides just a list of the frequency data, etc.?

The first stage of the characterization in Infrared spectroscopy and Raman is the identification of the modes and their assignments. Then, we proceeded to the comparison between our samples to characterize the influence of the anion type. Our experiments show the important sensibility of these experimental techniques in order to find the vibrational witnesses of these changes.

1-Some mistakes should be corrected such as 1) abstract 'were synthesized ", introduction ' ionic liquid' line 10, line 9: functionalize', line 16; synthesize, line 1, pag 3; were synthesized, line 1, pag. 3 ; diethyl ether, pag 3, line 9-line10; deionized water; deionizer; pag 3, line 15; characterization; line 27, pag 4; 70 °C, ionized, Pag 3, line 27; NTf2-, pag. 9, line 6 and in the Fig. 2-8.

We made the correction in the text (yellow highlight).

2-graphical abstract: structure of compound has mistake; positive charge on nitrogen and CH2 must be deleted.

We made the correction in the graphical abstract.

3- In Figure 1, structure of starting material and products have mistakes (1-methyl imidazole doesn't need to charge and product has two positive charges). In Figure 1, the raw materials and products are to be corrected. Also in Figure 1, the reaction conditions should be mentioned.

We made the correction in the Fig. 1.

4-The experimental methods have been developed for other ionic liquids.

We made the correction in page 4 line 1 to line 19 (yellow highlight).

5-References are not written according to guide for authors (10, 11, 13..,). eg: Reference to a journal publication: [1] J. van der Geer, J. A. J. Hanraads, R. A. Lupton, The art of writing a scientific article, J. Sci. Commun. 163 (2010) 51-59.

We made the correction in the text (yellow highlight).

6- Lines 8-12 (pag. 5) and lines 3-7 (pag. 7) should be corrected and rewritten.

We made the correction in the text (yellow highlight).

Yours sincerely,

Serge Bresson

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

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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 methylidene iodide $[M(CH_2)IM^{2+}][2I^-]$, bis-methyl imidazolium methylidene hexafluorophosphate $[M(CH_2)IM^{2+}][2PF_6^-]$, bis-methyl imidazolium methylidene 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.

Keywords

Dicationic ionic liquids; FT-RAMAN spectroscopy; FTIR/ATR spectroscopy; Imidazolium;

1. 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 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 P. K. Sahu *et al.* [11] wich discuss and compare structure-property relationships in monocationic and dicationic ionic liquids. Y. Saeid *et al.* present the effect of the anion type and the alkyle 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 K. Huangand *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.

2. Experimental

2.1. 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 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.

2.3. 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 C_1, and hexafluorophosphate, bis(trifluoromethylsulfonyl)imide as anions. A alkylene bis-methyl imidazolium iodide $[M(CH_2)IM^{2+}][2I^-]$ was prepared by reacting of $[(I(CH_2)I)]$ with two molar excess of 1-methylimidazole at 70°C during 7 hours [13]. In the Fig.1, we present the protocol of the synthesis.

2.3.1. Synthesis of bis-methyl imidazolium methylidene iodide $[M(CH_2)IM^{2+}][2I^-]$

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 hours. The reaction mixture was evaporated under vacuum and the product washed with diethyl ether (5×20 mL). bis-methyl imidazolium methylidene iodide yellowish solid (13.20 g, 31.86 mmol) was obtained in 73% yield.

2.3.2. Synthesis of bis-methyl imidazolium methylidene hexafluorophosphate [M(CH$_2$)IM^{2+}][2 PF$_6^-$]

Ammonium hexafluorophosphate (1.63 g, 10 mmol) dissolved in 15 mL of deionized water was added in a flask containing [M(CH$_2$)IM^{2+}][2I$^-$] (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 P$_2$O$_5$ to remove residual water.

2.3.3. Synthesis of bis-methyl imidazoliummethylidene bis(trifluoromethane-sulfonyl) imide [M(CH$_2$)IM^{2+}][2 NTf$_2^-$]

Following the similar procedure, [M(CH$_2$)IM^{2+}][2 NTf$_2^-$] was prepared by anion exchange reaction from iodide to bis(trifluoromethane-sulfonyl) imide which was carried out by mixing [M(CH$_2$)IM^{2+}][2I$^-$] and LiNTf$_2$ 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 ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR spectroscopy to confirm the absence of any major impurities and the spectra details are given below.

2.4. NMR results:

^{1}**H NMR** (CDCl$_3$) δ ppm *[M(CH$_2$)IM^{2+}][2I$^-$]*: 3.05 (s, 6H, 2×N*CH$_3$*), 6.09 (m, 2H, NC*H$_2$*N), 7.36 (m, 2H, N*CH*N), 7.73–7.49 (m, 4H, N*CHCH*N).

^{13}**C NMR** (CDCl$_3$) δ ppm *[M(CH$_2$)IM^{2+}][2I$^-$]* : 39.41, 51.66, 121.02, 123.23, 139.14, 139.96.

^{13}**C NMR** (CDCl$_3$) δ ppm *[M(CH$_2$)IM^{2+}][2NTf$_2^-$]* : 37.24, 54.01, 120.43, 121.09, 135.12, 149.08.

^{19}**F NMR** (CDCl$_3$) δ ppm *[M(CH$_2$)IM^{2+}][2NTf$_2^-$]* : -77.23 (s, *CF$_3$*SO$_2$)$_2$N).

^{31}**P NMR** (DMSO-d$_6$) δ ppm *[M(CH$_2$)IM^{2+}][2PF$_6^-$]* : 141.01 (septet, **P**F$_6$). ^{19}F NMR (DMSO-d$_6$) δ ppm: -72.03, -73.54 (d, **P**F$_6$).

2.5. FTIR/ATR and FT-RAMAN measurements

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

2.5.1. 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.

2.5.2. 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 aluminium garnet crystal doped with triply ionized neodymium) with a wavelength for incident laser at 1064 nm (9398,5 cm^{-1}). The maximum of laser power is 1.5 W. The measurement accessory is pre-aligned, only the Z-axis of the scattered light is adjusted to set the sample in the appropriate position regarding the local point. The RAM II spectrometer is equipped with a liquid-nitrogen cooled Ge detector. FT-RAMAN spectra [4000-45cm^{-1}] were collected with resolution of 1 cm^{-1} by co-adding 128 scans for each spectrum at room temperature. The OPUS 6.0 software was used for the spectral acquisition manipulation and transformation.

3. Results and discussion

3.1. Comparison between FTIR / ATR spectra of ionic liquids ([M(CH$_2$)IM^{2+}][2I$^-$]), ([M(CH$_2$)IM^{2+}][2PF$_6$$^-$]) and ([M(CH$_2$)IM^{2+}][2NTf$_2$$^-$]).

The FTIR/ATR spectra [4000-600 cm^{-1}] of three dicationic ionic liquids are illustrated in Fig. 1- Fig.5, and the observed FTIR/ATR bands and their assignment are listed in Table 1.

3.1.1. Region 900-600 cm^{-1}

In this spectral region, we observed very different vibrational modes between ionic liquids according to the anion selected. According to the type of anion, the interaction anion - cation is translated by different intensities for the same vibrational mode, a frequency shift and appearance of modes specific to the anion.

In the region 700-600 cm^{-1}, there is a well-resolved triplet with a strong intensity (607, 613 and 622 cm^{-1}) for the anion I$^-$. For the anion PF$_6^-$, this less intense triplet seems to shift to the bigger frequencies (610, 619 and 626 cm^{-1} is a shift of $\sim +4$cm^{-1}), whereas for the anion NTf$_2^-$, we observe a doublet with an imposing peak at 605 cm^{-1}. Therefore, fewer changes for the mode at 681 cm-1 are observed; which is common between the three (just intensity more important for the anion I$^-$).

In the zone 900-700 cm^{-1}, the changes are more spectacular. In a first spectral zone 780-715 cm^{-1}, we observe for the anion I$^-$, a wide triplet with a dominant peak at 760 cm^{-1} with a shoulder at 741 cm^{-1} (729, 760 and 773 cm^{-1}). For the anion PF$_6^-$, we observe a quadruplet well defined and rather homogeneous in intensity at the following frequencies: 730, 740, 748 and 766 cm^{-1}, while for the anion NTf$_2^-$ we observe a quintuplet in the shape of roller coasters at the frequencies 733, 742, 755, 766 and 771 cm^{-1}. Then in the zone 900-780 cm^{-1}, each of 3 samples will particularise with its own vibrational mode: for the anion I$^-$ is noted a doublet at 845 and 852 cm^{-1}, for the anion PF$_6^-$ a wide peak centered at 810 cm^{-1} and for the anion NTf$_2^-$ a peak at 861 cm^{-1}. These isolated peaks are vibrational signatures of every sample.

3.1.2. Region 1700- 900 cm^{-1}

In this spectral zone, we observe a difference of peaks number between the 3 samples: we note a spectrum rich in peaks for the anions I$^-$ and especially for the anion NTf$_2^-$ while for the anion PF$_6^-$ we count few peaks. We notice two doublets of intensity that are important for the anion NTf$_2^-$ which do not intervene in the case of the two other anions: 1035, 1045 cm^{-1} and 1131, 1138 cm^{-1}, corresponding to the vibrational modes: SO str and SO$_2$ sym str respectively. These two doublets are two other important signatures in FTIR/ATR of this anion. The peak at 1170 cm^{-1} is common to the three samples with different intensities and with slight shifts in frequency: 1164 cm^{-1} for the anion I$^-$, 1172 cm^{-1} for the anion PF$_6^-$ and 1168 cm^{-1} for the anion NTf$_2^-$. There is also a peak at 1188 cm^{-1} assigned to CF$_3$ asym str only for the anion NTf$_2^-$. Once again, in the zone 1400-1300 cm^{-1}, the anion NTf$_2^-$ is distinguished by having a wide triplet of strong intensity (1324, 1344 and 1355 cm^{-1}) while for the anion I$^-$ we observe a peak imposing at 1327 cm^{-1} and a weak doublet at 1326 and 1338 cm^{-1} for the anion PF$_6^-$. On the other hand between 1700 and 1360 cm^{-1}, it is the anion I$^-$ which seems to interact best with its cation: we note five peaks at 1385, 1393, 1412, 1434 and 1457 cm^{-1} while we count two for the other anions in the same spectral zone. It is also the case in the zone of the 1500 cm^{-1} where for the anion I$^-$ we notice 5 rather impressive peaks while for the others we observe only three peaks with lesser intensities.

3.1.3. Region 4000-2800 cm^{-1}

In this spectral zone, we observe the assigned modes of the alkyl C-H stretch region. We observe that on these spectra every anion has its peculiarity: for the anion I$^-$ we have peaks with strong intensities in the zone 3050-2850 cm^{-1}, for the anion PF$_6^-$ instead it is in the region of 3200-3050 cm^{-1} that are the most intense modes and for the anion NTf$_2^-$ it is a little a mixture of both with a spectra much more supplied with peaks and with a wider zone 3200-3100 cm^{-1} than for the anion PF$_6^-$. It can be concluded that the spectral zone 4000-2800 cm^{-1} is very sensitive in FTIR/ATR depending on the choice of anion and cation coupled and it can serve as signature of such or such ionic liquid. In the 3 cases of anion, the $\square$(C-H) are the most intense in this spectral zone: 3048 cm^{-1} for the anion I$^-$; 3124, 3154 and 3174 cm^{-1} for the anion PF$_6^-$; and 3132 and 3150 cm^{-1} for the anion NTf$_2^-$. We can also note that the spectral zone 4000-2800 cm^{-1} is much less intense than the spectral zone 1700-600 cm^{-1} for the overall spectrum for NTf$_2^-$ and PF$_6^-$ anions while this is not the case for the anion I$^-$ if we compare these spectral regions.

3.2. Comparison between FT-RAMAN spectra of ionic liquids ([M(CH$_2$)IM^{2+}][2I$^-$]), ([M(CH$_2$)IM^{2+}][2PF$_6^-$]) and ([M(CH$_2$)IM^{2+}][2NTf$_2^-$]).

As shown in Fig.6 - Fig.8, the FT-RAMAN spectra [3500-45cm^{-1}] of studied dicationic ionic liquids are depicted; also, the observed FT-RAMAN bands and their assignment are summarized in table 2.

3.2.1. Region 200-45 cm^{-1}

The bands appearing in this zone correspond to inter and intramolecular vibrations with the anions I$^-$, PF$_6^-$ and NTf$_2^-$. On Raman spectra, we observe a strong interaction for the anion I$^-$ with the presence of the following vibrational modes: 52, 65 and 135 cm^{-1} assigned to intermolecular interactions and: 100 and 110 cm^{-1} assigned to intramolecular interactions. Some of these modes have important intensities compared to the other modes appearing on the complete spectra. We note that for this spectral zone for anions PF$_6^-$ and NTf$_2^-$ Raman spectra are similar with a slight shift in Raman frequency: 56 cm^{-1} for PF$_6^-$ against 57 cm^{-1} for NTf$_2^-$, 79 cm^{-1} against 84 cm^{-1} and 119 cm^{-1} for both anions. We have also noted between these two anions an inversion of intensity between the peaks at 80 cm^{-1} and 120 cm^{-1}: $\mathbf{I_{120}/I_{80}}=$ 1.09 for PF$_6^-$ against 0.86 for NTf$_2^-$. The peak at 175 cm^{-1} assigned to ω (N-C) seems much more intense for the anion I$^-$ than for the two other anions. In the zone 200-45 cm^{-1}, each anion has a particular vibration behavior indicating a high sensitivity in this spectral region related to the type of anion selected.

We note that the size of the anion adjacent imidazolium rings have an influence on the vibrational behavior of the modes situated in this spectral region. More the anion is bigger there is a significant Raman frequency shift for the intermolecular modes: 52 and 65 cm^{-1} for I$^-$ against 56; 79 and 57; 84 cm^{-1} for PF$_6^-$ and NTf$_2^-$ respectively; 135 cm^{-1} for I$^-$ against 151 cm^{-1} for NTf$_2^-$.

3.2.2. Region 1600-200 cm^{-1}

The bands appearing in this region are dominated by the contribution of different anions I$^-$, PF$_6^-$ and NTf$_2^-$. As for the mode at 175 cm^{-1}, a well-resolved Raman frequency doublet at 230 and 238 cm^{-1} are observed for the anion I$^-$ compared to other anions where the intensity of these peaks seems very low. On the other hand, in the spectral region 450-300 cm^{-1} is the anion NTf$_2^-$ that seems to have the best sensibility: We observed many peaks of average intensity at 276, 300, 316, 343 and 362 cm^{-1} while for the two other anions we note 3 peaks of very low intensities at 272, 310 and 365 cm^{-1}. We also noted a doublet at 399 and 410 cm^{-1} for the anion NTf$_2^-$ with an average intensity while for the anions I$^-$ and PF$_6^-$ we have a peak around 400 cm^{-1} with a very low intensity. Only the anion PF$_6^-$ has a peak at 471 cm^{-1} with an interesting intensity, which corresponds to a new signature of the anion PF$_6^-$.

In the region 900-500 cm^{-1}, there is an equivalent vibrational behaviour of the anions PF$_6^-$ and NTf$_2^-$. We count many common peaks having similar intensities: 567 cm^{-1} for the anion PF$_6^-$ against 571 cm^{-1} for the anion NTf$_2^-$, 609 and 624 cm^{-1} against 608 and 630 cm^{-1}, 743 cm^{-1} against 744 cm^{-1} (very intense peak assigned to ν(CF$_3$)) and 769 cm^{-1} against 771 cm^{-1}. The anion I$^-$ is distinguished compared to the two other anions by having a different vibrational behaviour: the presence of a quadruplet at 608, 615, 617 and 622 cm^{-1} of important intensity, the absence of the peak at 744 cm^{-1} and three doublets of average intensity at 776 and 786 cm^{-1}, 848 and 854 cm^{-1} and finally 876 and 880 cm^{-1}.

In the region 1600-900 cm^{-1}, we count fewer differences of vibrational behaviour between anions I$^-$, PF$_6^-$ and NTf$_2^-$. We observed new peaks for the anion NTf$_2^-$ at 1134 and 1242 cm^{-1}, a more intense doublet at 1288 and 1296 cm^{-1} for the anion I$^-$ and reports of intensity in the spectral zones 1100-1000 cm^{-1} and 1700-1400 cm^{-1}. In the zone 1100-1000 cm^{-1}, we find the same peaks for the three anions but with different intensities and with low shift in Raman frequencies: 1045, 1028, 1022 and 1016 cm^{-1}. In the table 3, we express the reports of intensities of these peaks by taking as reference the peak at 1045 cm^{-1}.

From these reports of intensity, it would seem that the peak at 1028 cm^{-1} is a vibrational behaviour identical between the three anions and that compared with anions PF_6^- and NTf_2^- peaks at 1022 and 1016 cm^{-1} have nearly reports of intensities. On the other hand, it seems clear that the anion I$^-$ has a singular vibrational behaviour for peaks at 1022 and 1016 cm^{-1} because we note reports I_{1022} / I_{1045} and I_{1016} / I_{1045} superior to 1,00.

In the region 1600-1400 cm^{-1}, only the peak at 1402 cm^{-1} for the anion I$^-$ seems to be distinguished by an important intensity compared with the nearly frequencies and compared with the other anions. We also observe only a peak of low intensity for the anion I$^-$ at 1451 cm^{-1} compared with the other anions.

3.2.3. Region 3500-2800 cm^{-1}

In this spectral region, we observed the modes assigned the alkyl C-H stretch region. We observed that for the anion I$^-$ we have numerous peaks with strong intensities in a wide spectral range zone 3200-2800 cm^{-1}. We count 13 peaks for the anion PF_6^-, the spectral zone of study is less wide from 3200 to 2980 cm^{-1} approximately with a peak dominating at 2982 cm^{-1}. For the anion NTF_2^-, it is approximately the same vibrational behavior that for the anion PF_6^-, but we observe more peaks with average intensities: 2967, 2993, 3045 and 3135 cm^{-1}.

4. Conclusion

At the end of this study it can be concluded that when we compare the studied dicationic ionic liquids according to the nature of the anion, the spectral zone 4000-2800 cm^{-1} is very sensitive in FTIR/ATR and can serve as a signature for every ionic liquid. We observed very different vibrational modes between ionic liquids according to the anion selected. According to the type of anion, the interaction anion - cation is translated by different intensities for the same vibrational mode, by frequency shift and by appearance of modes specific to the anion.

In the zone 200-45 cm^{-1}, each anion has a particular vibrational behaviour indicating a high sensitivity in this spectral region related to the type of the selected anion.

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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
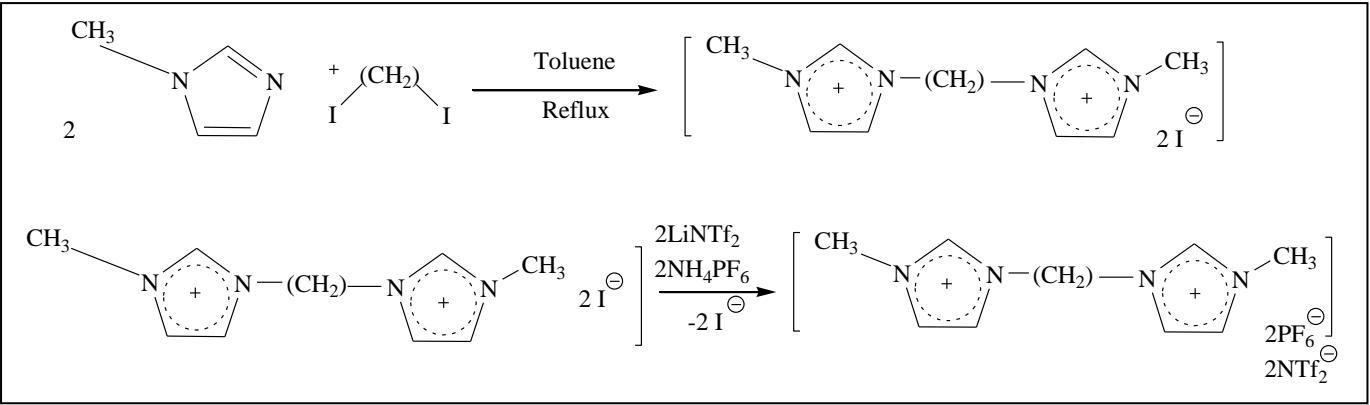- Each sample particularise with its own vibrational mode

Figure 1

Figure 1
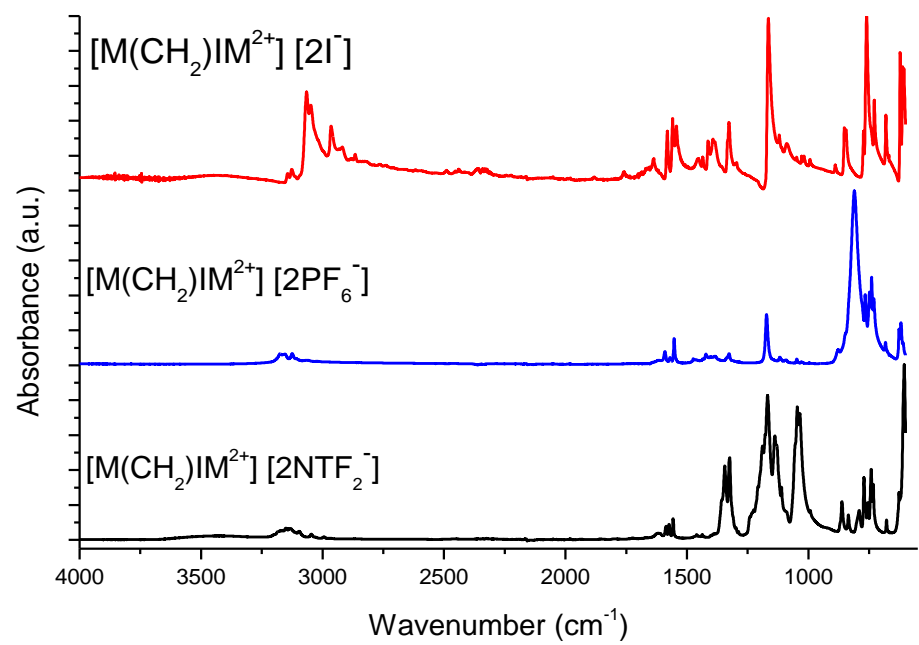

Fig.1. T. Moumene et al.
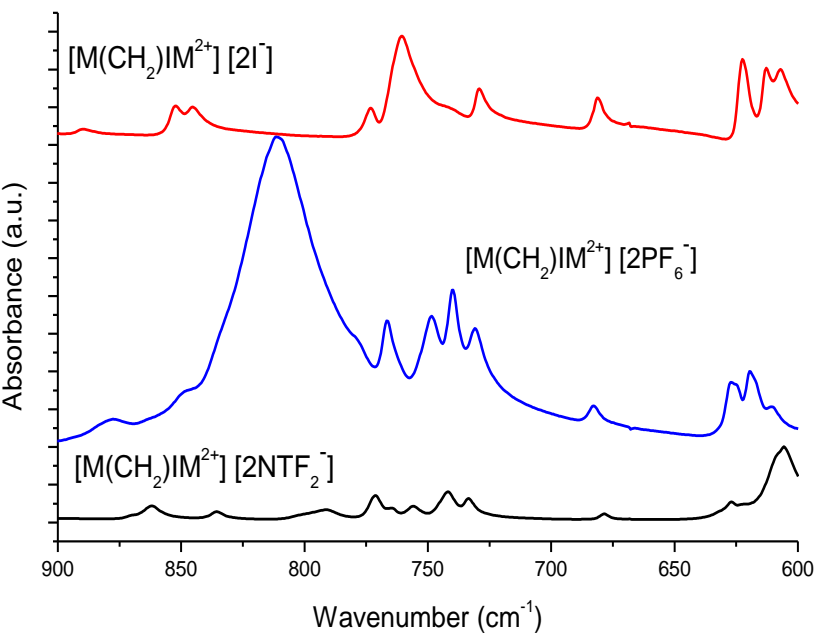
Figure 2

Fig.2. T. Moumene et al

Figure 3

Figure 3

Fig.3. T. Moumene et al

Figure 4
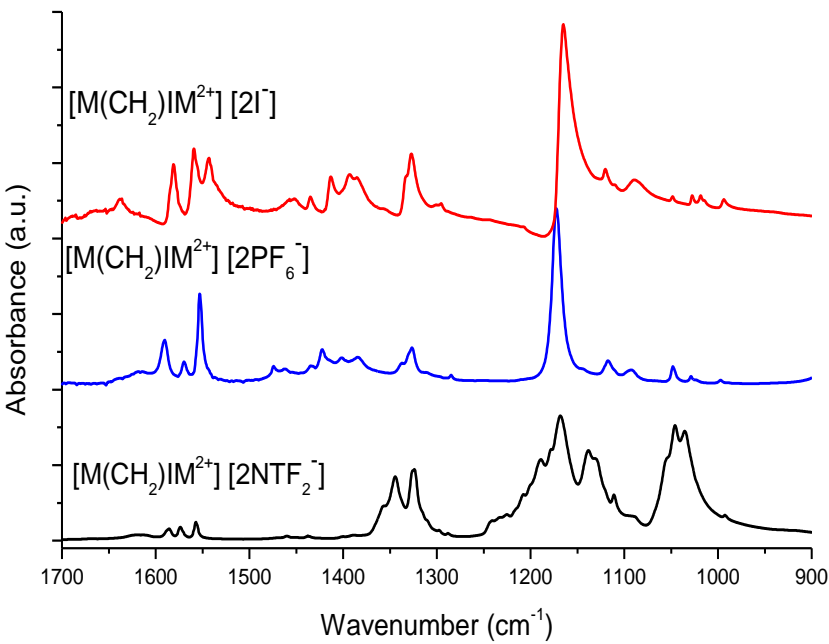
Figure 4

Fig.4. T. Moumene et al

Figure 5
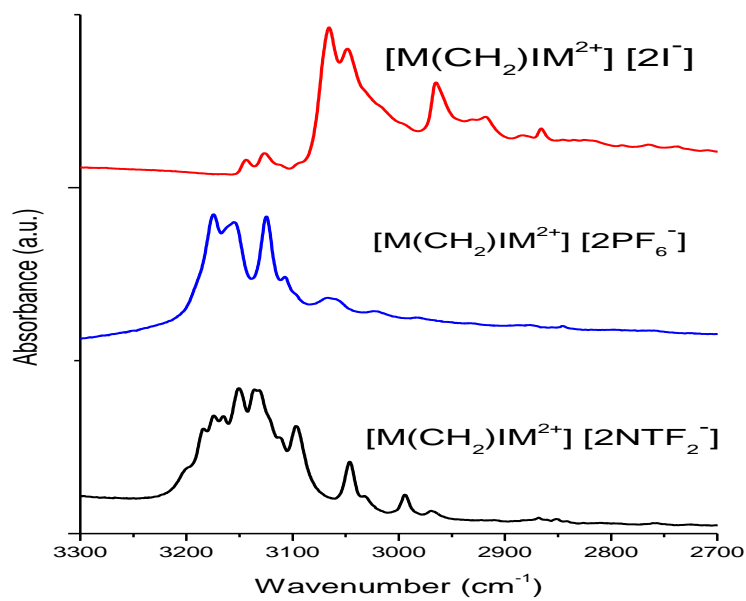
Figure 5

Fig.5. T. Moumene et al

Figure 6
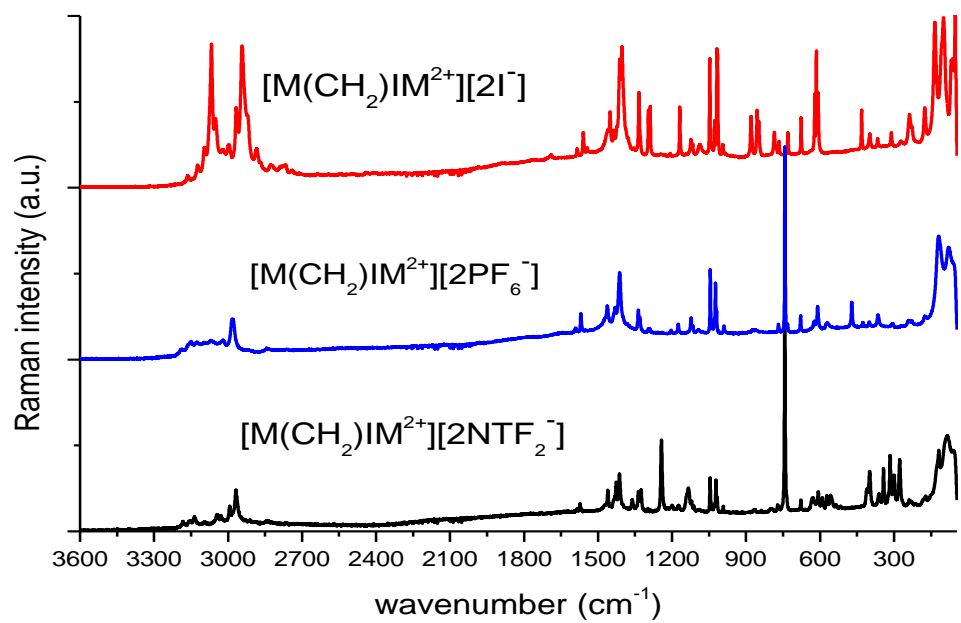
Figure 6

Fig.6. T. Moumene et al.

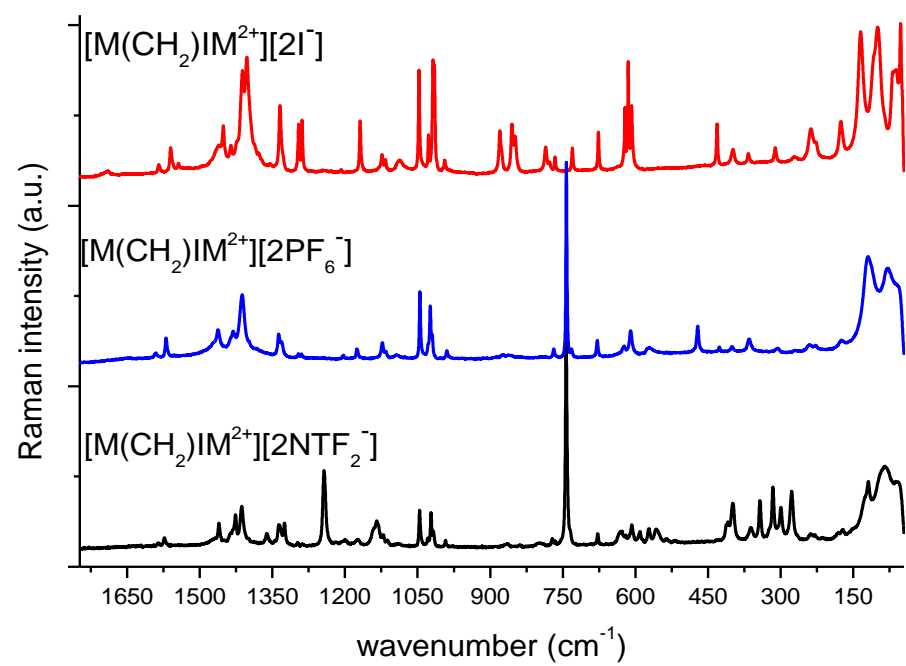**Figure 7**

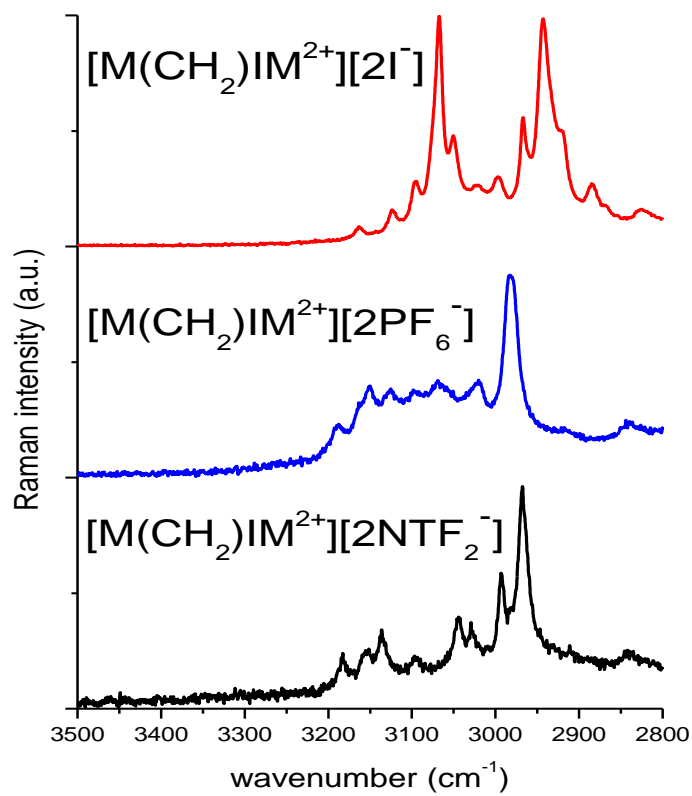**Figure 7**

Fig.7. T. Moumene et al.

Figure 8

Figure 8

Fig.8. T. Moumene et al.

Graphical abstract
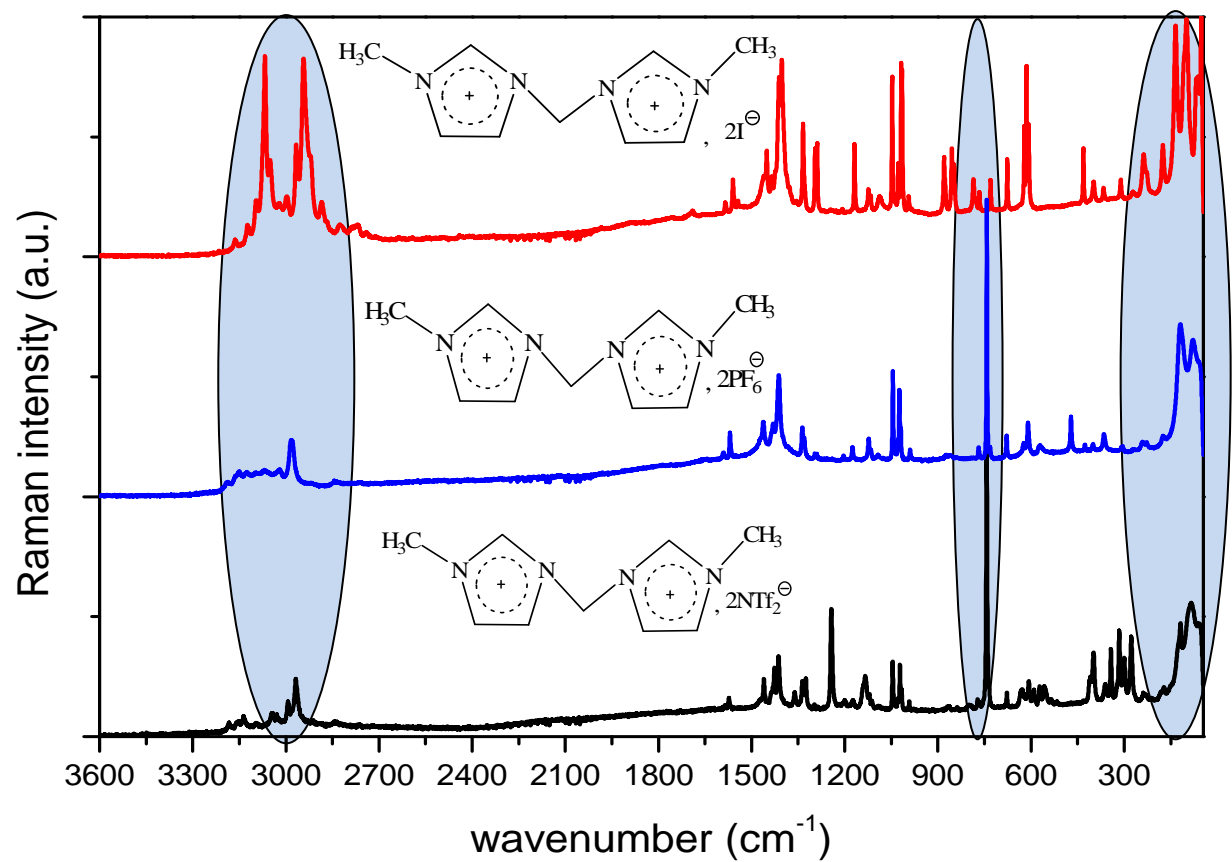
Table 1

Table 1. Observed FTIR / ATR bands and their assignment of ($[M(CH_2)IM^{2+}][2I^-]$), ($[M(CH_2)IM^{2+}][2PF_6^-]$) and ($[M(CH_2)IM^{2+}][2NTf_2^-]$). (vw = very weak; w = weak; m = medium, s = strong; sh = shoulder; ν = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; s = symmetric; as = antisymmetric)

$[M(CH_2)IM^{2+}]$ $[2I^-]$	$[M(CH_2)IM^{2+}]$ $[2PF_6^-]$	$[M(CH_2)IM^{2+}]$ $[2NTf_2^-]$	ASSIGNEMENT	Ref.
607 (s)	610 (m)	605 (s)	ω(N-H) / CH$_3$(N)CN Str	[15,16]
613 (s)	619 (m)		ω(N-H) / CH$_3$(N)CN Str	[15,16]
622 (s)	626 (m)	626 (w)	ω(N-H) / CH$_3$(N)CN Str /ν(PF$_6^-$)	[15,16]
668 (vw)			ω(N-H) / CH$_3$(N)CN Str	[15,16]
681 (m)	682 (w)	678 (w)	ω(C-H)+ ω(N-H)	[15]
729 (m)	730 (m)	733 (m)	anion interaction	
741 (sh)	740 (m)	742 (m)	CH$_2$(N)/CH$_3$(N)CN bend/CF$_3$ sym bend ring/ν(PF$_6^-$)	
	748 (w)	755 (w)	w(C-H) / SNS sym Str	[15,17]
760 (s)	766 (w)	766 (w)	δHCCH / Ring HCCH asym bend	[18,17]
773 (w)		771 (m)	ν(N-C)	[15]
		791 (w)	Ring HCCH asym bend/CS Str	[17]
	810 (s)		ν(PF$_6^-$)	
		835 (w)	NC(H)Nbend/CCHbend	[16]
845 (m)	848 (sh)		NC(H)Nbend/CCHbend	[16]
852 (m)			NC(H)Nbend/CCHbend	[16]
		861 (w)	ω(C-H) +ρ_{as}(CH2)	[15]
	879 (vw)	871 (w)	ρ_{as}(CH2)	[19]
889 (w)			ρ_{as}(CH2)	[19]
993 (vw)	997 (vw)	992 (w)	ρ_{as}(CH2)	[19]
1014+1018 (vw)			ν(C-C)	[15]
1027 (vw)	1028 (vw)		ν(C-C)	[15]
1048 (vw)	1048 (vw)	1035(m)+1045(m)	CH$_3$N Str/CH$_2$N Str, SO str	[17]
		1053 (sh)	Ring ip asym str, CC str, NCH3 twist, SNS asym str	
1089 (vw)	1091 (vw)	1090 (sh)	CC Str	[16]
1109 (vw)	1110 (vw)	1110 (sh)	CC Str / δCH	[16,18]
1119 (w)	1117 (w)		CC Str / δCH	[16,18]
		1131(m)+1138(m)	SO$_2$ sym Str	
1164 (s)	1172 (s)	1168 (s)	Ring asym Str CH$_2$(N) and CH$_3$(N)CN Str/CC Str	[17]
		1188 (m)	Ring sym Str CH$_2$(N) and CH$_3$(N)CN Str/CF$_3$ asym Str	[17]
		1225 (w)	ν(N-C) /CF3sym Str	[15]
		1242 (w)	Ring ip asym str str, butyl chain str	[17]
	1284 (vw)	1288 (vw)	ρ(C-H)	[15]
1295 (vw)		1297 (vw)	ν(C-C)	[15]
1327(m)+1332(sh)			SO$_2$ asym str, ring ip sym str, CH$_2$(N) and CH$_3$(N) CN str	
	1326(vw)+1338(vw)	1324(m)+1344(m)	SO$_2$ asym str, ring ip sym str, CH$_2$(N) and CH$_3$(N) CN str	
		1355 (sh)		
1385 (w)	1384(vw)+1401(vw)		ρ(N-H)	[15]
1393 (w)			ρ(N-H)	[15]
1412 (w)			ρ(N-H)	[15]
1434 (w)			CH$_3$(N)Str/CH$_3$(N)HCH sym bend/NC(CH$_3$)N HCH bend	[17]
	1434 (vw)	1437 (vw)		
1457 (vw)		1460 (vw)	δ(CH2) /CCH HCH asym bend	[20,16]
1543 (m)			ν(N=C)	[15]
1555(sh)+1559(m)	1552 (m)	1557 (w)	ν(N=C)	[15]
1577(w)+1580(w)+1590(w)	1569(vw)+1590 (w)	1573 (w)+1585(w)	asym Str CH2(N)/CH3(N)CN Str	[17]
1637 (w)			ν(C=C)	[20]
1665 (w)			ν(C=C)	[20]
1690 (vw)			ν(C=C)	[20]
1759 (vw)			ν(C=O)	[20]
2864 (w)			ν_s(CH$_2$)	[20]
2883 (w)			ν_{as}(CH$_2$)	[20]
2918 (w)+2925 (w)			ν_{as}(CH$_2$)	[20]
2963 (m)		2967 (vw)	CH$_2$HCH asym Str	[17]
		2994 (vw)	CH$_3$(N)HCH asym Str	[17]
3023 (sh)	3019 (vw)	3028 (sh)	ν(C-H)	[15]
3048 (s)		3046 (w)	ν(C-H)	[15]
	3062 (w)		ν(C-H)	[15]
3095 (sh)+3108 (sh)	3107 (w)	3096(w)+ 3110(w)	ν(C-H) /νCH	[15,18]
3126 (w)	3124 (m)		ν(C-H)	[15]
		3132 (w)	Ring NC(H)NCH Str	[16]
3144 (w)	3154 (m)	3150 (w)	C-H Str	[17]

	3165 (w)	C-H Str	[17]
3174 (m)	3173(w)	C-H Str	[17]
	3185(sh)	C-H Str	[17]
	3201 (sh)	v(C-H)	[15]

Table 2

Table 2. Observed FT-RAMAN bands and their assignment of ($[M(CH_2)IM^{2+}][2I^-]$), ($[M(CH_2)IM^{2+}][2PF_6^-]$) and ($[M(CH_2)IM^{2+}][2NTf_2^-]$).(vw = very weak; w = weak; m = medium, s = strong; sh = shoulder; ν = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; s = symmetric; as = antisymmetric).

$[M(CH_2)IM^{2+}]$ $[2I^-]$	$[M(CH_2)IM^{2+}]$ $[2PF_6^-]$	$[M(CH_2)IM^{2+}]$ $[2NTf_2^-]$	ASSIGNEMENT	Ref.
52 (s)	56 (m)	57 (m)	Intermolecular vibration	[14]
65 (m)			Intermolecular vibration	[14]
	79 (m)	84 (m)	Intermolecular vibration	[14]
100(m)+110(sh)			Intramolecular vibration	[14]
	119 (m)	119 (m)	Intramolecular vibration	[14]
135 (w)			Intermolecular vibration	[14]
		151 (vw)	Intermolecular vibration	[14]
175 (w)	174 (vw)	171 (vw)	ω(N-C)	[15]
		181 (vw)	ω(N-C)	[15]
230 (w)	228 (vw)	230 (vw)	ω(N-C)	[15]
238 (w)	241 (vw)	238 (vw)	ω(N-C)	[15]
272 (vw)	271 (vw)	276 (m)	CF_3 sym bending	[17]
311 (vw)	307 (vw)	300 (w)	CH_2(N)/CH_3(N)CH bend	[17]
		316 (m)	SC Str	[17]
		343 (w)	SC Str	[17]
366 (w)	365 (w)	362 (vw)	SC Str	[17]
398 (vw)	400 (vw)	399(m) + 410(w)	CH_2(N) and CH_3(N) CH bond, CH3 bend	[17]
431 (w)	427 (vw)		CH_2(N) and CH_3(N) CH bond, CH3 bend	[17]
	471 (w)		$\nu(PF_6^-)$	
	534 (vw)	534 (vw)	SO_2 sym bending	[17]
		556 (vw)	SO_2 sym bending	[17]
	567 (vw)	571 (w)	CH_2(N)/CH_3(N)CN Str/$\nu(PF_6^-)$	
		590 (w)	CH_2(N)/CH_3(N)CN Str	
608(m)+615(m)+617(sh)+622(m)	609 (w)+624(vw)	608 (vw)+630(vw)	w(N-H)/ν_{ip}(N-CH3) /$\nu(PF_6^-)$	[15,21]
677 (w)	679 (vw)	677 (vw)	CH_2(N)/CH_3(N)CN Str	[17]
730 (m)				
	732 (w)+743 (vs)	744 (vs)	CF_3 sym str, $\nu(PF_6^-)$	
766 (vw)	769 (vw)	771 (vw)	ω(CH2)rocking	[22]
776 (vw)+786 (w)			ν(N-C)	[15]
848 (w)+854 (w)			NC(H)Nbend/CCHbend	[16]
876(sh) +880(w)			NC(H)Nbend/CCHbend	[16]
994 (vw)	990 (vw)	992 (vw)	ρ_{as}(CH₂) e	[19]
1015 (m)+1018 (m)	1020 (w)+1023(w)	1016(w) + 1022(m)	ν(C-C)	[15]
1027 (w)	1028 (vw)	1029(w)	ν(C-C)	[15]
1047 (w)	1045 (w)	1046 (m)	ν(C-C)	[15]
1116(w) + 1124 (w)	1115 (w)+1122(w)	1111(w) + 1120(w) +1134(m)	SO_2 sym str, CC Str	[16]
1168 (w)			Ring asym Str CH_2(N) and CH_3(N)CN Str	
	1175 (vw)	1174 (vw)	SO_2 asym Str , CC Str	[16]
		1242 (s)	SO_2 asym Str/CF3 sym Str	[16]
1288 (w)+1296 (w)	1289 (vw)+1296 (vw)		ρ(C-H)	[15]
1334 (w)			CH_3(N)CN Str	
	1331 (w)+1337 (w)	1324(w) + 1335(w)	SO_2 asym Str, CH_2(N)/CH_3(N)CN Str	
		1361 (vw)	ν(SO2)	[23]
1402 (m)+1412 (m)+1425 (w)	1412 (w)+1431(vw)	1399(sh)+1413(w)+1426(w)	CH_2(N)/CH_3(N)CN Str	
1436 (w)			δ(CH2)	[20]
1451 (vw)			δ(CH2)	[20]
1461 (sh)	1462 (w)	1461 (w)	CH3(N)HCH sym bend	[17]
1543 (vw)			ν(N=C)	[15]
1560 (vw)			ν(N=C)	[15]
1585 (vw)	1569 (vw)+1585 (vw)	1572 (vw)+1585 (vw)	CH_2(N)/CH_3(N)CN Str	
2825 (vw)	2840 (vw)	2838 (vw)	ν_s(CH₂)	[24]
2863 (sh)			ν_{as}(CH₂)	[20]
2884 (w)			ν_{as}(CH₂)	[20]
2920 (m)			ν_{as}(CH₂)	[20]
2943 (s)			ν_s(CH₃)	[19]
2967 (m)		2967 (m)	ν_{as}(CH₃)	[19]
	2982 (m)		ν_{as}(CH₃)	[19]
2995 (w)		2993 (w)	ν_{as}(CH₃)	[10]
3023 (vw)	3031(vw)	3028 (vw)	C-H Str / ν(C-H)	[22,15]
3050 (m)		3045 (w)	ν(C-H)	[15]
3068 (s)	3066 (vw)		C-H Str	[17]
3095 (vw)	3097 (vw)	3096 (vw)	CH3(N)HCH asym Str	[16]
3124 (vw)	3126 (vw)		C-H Str	[17]

	3135 (w)	Ring NC(H)NCH Str	[16]
3151 (vw)	3155 (vw)	Ring HCCH asym Str / v(C-H)	[16,15]
3162 (vw)		C-H Str	[17]
3189 (vw)	3183 (vw)	v(C-H)	[15]

Table 3

Table 3. Reports of intensity of many peaks of ($[M(CH_2)IM^{2+}][2I^-]$), ($[M(CH_2)IM^{2+}][2PF_6^-]$) and ($[M(CH_2)IM^{2+}][2NTf_2^-]$) in the spectral range 1100-1000 cm^{-1}.

Anion	I_{1028}/I_{1045}	I_{1022}/I_{1045}	I_{1016}/I_{1045}
I^-	0.54± 0.02	1.07± 0.02	1.02± 0.02
PF_6^-	0.50± 0.02	0.86± 0.02	0.59± 0.02
NTf_2^-	0.51± 0.02	0.93± 0.02	0.62± 0.02