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Stability of Divalent Europium in an Ionic Liquid: Spectroscopic Investigations in 1-Methyl-3-butylimidazolium Hexafluorophosphate

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Stability of divalent europium in an ionic liquid: Spectroscopic investigations in 1-Methyl-3-Butylimidazolium Hexafluorophosphate

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In this work, devoted to 1-methyl-3-butylimidazolium hexafluorophosphate ionic liquid (BumimPF$_6$), the importance of the purity of the solvent for spectroscopic investigations is highlighted. Results from small angle X-ray scattering indicate that the pure solvent exhibits a local organisation. Europium(II), which appears to be unusually stable in BumimPF$_6$, is characterised by spectroscopic techniques (absorption, luminescence). Solvation of Eu(II) in BumimPF$_6$ and complexation effects in the presence of the crown-ether 15C5 solubilised in the ionic liquid are discussed.

1. Introduction

The use of organic solvents in process operations leads to many problems, the main ones concerning their toxicity for both the process operator and the environment and their volatility and flammable nature, which are also of importance for their transport and storage.[1,2] Industrial processes, including nuclear waste management and nuclear fuel cycle processes, use organic phases, that emit Volatile Organic Compounds (VOC's) damaging the environment.

Recently, Room Temperature Ionic Liquids (RTIL's) have emerged and are gaining academic and industrial attention in catalysis, separation processes and electrochemistry due to their particular properties, especially with the emergence of the new N-N-dialkylimidazolium cation derivatives (Scheme 1).

Both the cationic and the anionic partners can be easily varied, so that these ionic liquid solvents can be designed for particular applications or for particular sets of properties. [3-

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[5] Whatever the alkyl length or the counter anion structure, they display very low vapour pressure and hence do not emit VOC's, are easy to transport and to store. They are air and moisture stable and, as a consequence, usable for biphasic systems such as in liquid liquid extraction. They are highly solvating for both ionic and molecular species, non coordinating, conductive and polar (equivalent to ethanol).[6-8] Their high thermal stability and their wide liquidus allow temperature variations to be used for process optimisation.

Moreover, RTIL's may also appear as an interesting alternative to pyrochemical processes because they present properties similar to the ones obtained in high temperature molten salts[9] such as a high solubilisation capacities and large electrochemical windows but at room temperature.

From the very specific viewpoint of nuclear industry, in which the actual processes mainly rely on specific oxidation states (such as Pu(III)/Pu(IV)) and variable acidic conditions (for reviews on the subject, see[10-13]), it is now understood that aqueous solutions in contact with the actual organic phases may not be the best system for partitioning actinides and lanthanides because water is a very good complexing agent that competes with other ligands even in the organic phase.[14,15] Two possible alternatives may be considered: i) liquid liquid extraction using water in contact with new solvents, in which complexation and solvation effects would be more favourable as compared to the present situation ii) new solvents that could stabilize unusual oxidation states in order to avoid liquid/liquid extraction, that would be replaced by direct metal electrodeposition. Recently, it has been shown that some ionic liquids present an interesting stability under alpha and gamma irradiation[16] and that the use of ionic liquids in actinide process flow sheets would significantly enhance the criticality safety of these processes[17]. Therefore, ionic liquids appear as promising media to investigate other routes than those used nowadays.

This work reports the first results on the spectroscopic characterisation of pure 1-methyl-3-butylimidazolium hexafluorophosphate ($BumimPF_6$) and of europium(II) salts dissolved in this ionic liquid. $BumimPF_6$ was chosen because it is particularly air and moisture stable, it is a good electrochemical conductor, has a ~~low~~ moderate viscosity as compared to other RTIL's and is usable in biphasic separation.[5] In order to improve our knowledge of the physicochemical properties of actinides and lanthanides dissolved in ionic liquids, we focussed on a spectroscopic characterisation through absorption and luminescence spectroscopy. Synthesised $BumimPF_6$ and commercially available $BumimPF_6$ (Solvent

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Innovation, Köln, Germany) were compared in terms of purity and stability under laser irradiation. Results obtained show that for spectroscopic purposes, $BumimPF_6$ must be purified until it is colourless. Spectroscopic data were obtained that allow the characterisation of $BumimPF_6$ and of Eu(II) dissolved in it.

2. Materials, chemicals and methods

2.1 Synthesis of $BumimPF_6$

The synthesis of $BumimPF_6$ is based on a method by Visser et al.[18] and is typically performed as described in the following :

All chemicals were of the best reagent grades (Aldrich) and were used without further purification. All aqueous solutions were prepared with deionized water that was purified with a Millipore deionization system (w = 18.3 MΩcm).

First step: *synthesis of BumimCl*. A three necked round bottomed flask under argon, equipped with a water refrigerant is charged with 1 mole (82.11 g) of methylimidazole and 1 mole (92.57 g) of n-chlorobutane. The mixture is stirred under argon for 48 hours at 70°C, until a pale yellow viscous mixture is obtained. It is then transferred into a flask and stored at 3-5°C under argon until the mixture precipitates quantitatively (≈ 12 hours). White crystals are obtained which are washed several times with ethyl acetate and filtered each time on a Buchner apparatus. These white crystals are then transferred into a dry box containing phosphorus pentoxide under vacuum. A fine white powder of BumimCl is obtained with typical yields of ≈80%.

Second step: synthesis of $BumimPF_6$. BumimCl crystals (125 g, 0.71 mole) are dissolved in deionized water (360 mL), stirred and cooled at 0°C in an ice bath. Hexafluorophosphoric acid (1.1 eq. of a 40% aqueous solution, 192 g, 0.78 mole) is slowly added (30-45 min) under vigorous stirring. After addition, the mixture is allowed to come to room temperature and stirred for 2 hours. Two phases are obtained and the upper one (acidic aqueous phase) is decanted. The bottom phase ($BumimPF_6$) is washed several times with deionized water (10x350 mL), until neutrality of the upper aqueous phase is ensured and no chloride ions are found in the aqueous phase transferred from the $BumimPF_6$ phase (silver nitrate test in the aqueous phase). $BumimPF_6$, as a pale yellow ~~slightly~~ viscous liquid, is transferred and stored in a dry box under vacuum containing phosphorus pentoxide. Typical yields of ≈80% were obtained. As our interest is to study $BumimPF_6$ in liquid liquid extraction conditions versus an aqueous phase, we did not try to dry the ionic liquid more than described in this section.

BumimPF$_6$ was also purchased from Solvent Innovation (>98% purum) as a deep yellow viscous liquid. In order to avoid confusion, this chemical will be denoted as BumimPF$_6$-SI in the following.

2.2. Other chemicals and solutions with BumimPF$_6$ as a solvent

Europium(II) iodide (Aldrich), NaI (Prolabo), KI (Prolabo), K$_2$Cr$_2$O$_7$ (Prolabo) and the two crown-ethers 15C5 and 12C4 (Aldrich) were used as received.

2.3. Methods of characterisation

Elemental CHN microanalyses are performed by complete oxidation and detection is performed by gas chromatography (Perkin-Elmer).

Chloride ions were analysed by High Performance Ionic Chromatography (HPIC) using a Dionex 4500i Ion Chromatograph equipped with a conductivity detection, an AG 12A guard column, an AS12A column and an anion chemical suppressor AMMS. A CO_3^{2-}/HCO_3^- buffer (2,7 mM Na$_2$CO$_3$/0,3 mM NaHCO$_3$) at 1 mL.min^{-1} was used as eluent and 12,5 mM H$_2$SO$_4$ at 3-5 mL.min^{-1} as regenerant.

The water amount in BumimPF$_6$ is determined by the Karl Fischer technique using standard procedures. The apparatus is composed of a Metrohm 703TI Stand titrator and a Metrohm 756KF coulometer.

Absorption spectra in the range 190-900 nm are recorded on a Uvikon 930 (Kontron). In the case of highly absorbing samples (see below) quartz cuvettes of 2 mm path length are used. For other samples, 1 cm-path length quartz cuvettes are used. The former spectra are normalised to a 1 cm path length for the sake of comparison. For pure solvents, the reference is an empty quartz cuvette and for solutions, the reference is the pure solvent. Experiments are performed at a controlled temperature of 294 ± 1 K.

The XRD patterns (Small angle X-ray Scattering, SAXS) are obtained with the liquid being filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-Kα$_1$ beam (λ = 1.5405Å) is obtained using a Debye-Scherrer camera equipped with a bent quartz monochromator and an electric oven. The diffraction patterns are registered with a gas curved counter (Inel CPS 120) associated with a data acquisition computer system; periodicities up to 60 Å can be measured, and the sample temperature is controlled within ±0.05°C. Central diffusion experiments are carried out at room temperature with a small angle X-ray scattering spectrometer Nanostar, developed by Bruker-Anton Paar. The sample is held in calibrated mica cells of 1 mm thickness to avoid multiple scattering. The Nanostar spectrometer operates

with a pinhole collimator and a wire proportional gas detector. A monochromatic ($\lambda = 1.54$ Å) and almost parallel beam (divergence = 0.03°) is obtained through two Gobel crossed mirrors. The size of the incident beam on the sample is close to 300 μm. The sample-detector distance is set at 1 m (0.01 Å^{-1} < q < 0.2 Å^{-1}). The q resolutions are 0.003 Å^{-1}.

Emission spectra are recorded on a classical spectrofluorimeter (Photon Technology International) which does not allow time-resolved emission spectra. The Time-Resolved Emission Spectroscopy (TRES) apparatus is described in detail elsewhere.[19,20] Experiments are performed at a controlled temperature of 294 ± 1 K.

3. BumimPF$_6$ characterisation and purification
3.1 General characterisation

A structural characterisation of BumimPF$_6$ has been obtained by ^{1}H and ^{13}C NMR spectroscopy. Signals were attributed using the DEPT protocol. The major findings are reported in table 1 and are in agreement with the expected cationic structure. It can be observed that the resonances of proton and carbon (6) suffer an important downfield shift (δH_6=8.89 ppm, δC_6=136.37 ppm), confirming the quaternary structure of the proximate ammonium atom and the strong sp^2 hybridisation character of carbon (6). This effect also affects protons and carbons 4 and 5 (δH_4=4.3 ppm, δC_4=49.5 ppm, δH_5=4 ppm, δC_5=35.63 ppm) which are also relatively moved toward downfield shift.

Elemental analysis (C, H, N) is in agreement with the theoretical structure of BumimPF$_6$ (table 2).

The water content in BumimPF$_6$ of various origin is reported in table 2. As one of our final goals is to use ionic liquids in liquid liquid extraction versus an aqueous phase, BumimPF$_6$ is not dried further after synthesis (table 2). This also allows comparison with data from usual liquid/liquid extraction systems where the organic phase is not particularly dried either. From these results two major points can be highlighted: (1) the purification procedure as described in section 3.2 eliminates about half of the water present. (2) the presence of water in BumimPF$_6$ cannot be neglected considering its solvation capabilities for ionic species, a point to be discussed in section 5.

The large difference in colour between the two ionic liquids (synthesized and commercial) indicates the presence of impurities in variable amounts. This seems to be a common feature of commercial products of this kind.[8] The presence of impurities is

confirmed by High Performance Ionic Chromatography (table 2): BumimPF$_6$-SI (as received) contains large amounts of Cl$^-$ and additional SO$_4^{2-}$, PO$_4^{3-}$, NO$_3^-$ and F$^-$ ions, plus, at least, an additional anion which was not identified. In contrast, BumimPF$_6$ contains Cl$^-$ as the only anionic impurity, in smaller amounts. Most probably, Cl$^-$ anions come from the first synthesis step (see sect. 2.1). The chloride amount significantly differs from one synthesised batch to the other. These differences in impurity are also revealed in the absorption spectra (see fig. 1). The BumimPF$_6$-SI spectrum (2 mm-path length cuvette required) shows a significant absorption up to the visible region.

3.2. Purification procedures

Following the work of Cammarata and co-workers,[21] purification was attempted according to three different procedures: i) alumina alone (aluminium oxide, anhydrous – γ-alumina-, Merck), ii) activated charcoal alone (3 mm grain size), iii) activated charcoal plus alumina. The impact of each procedure onto raw BumimPF$_6$ has been evaluated by absorption spectroscopy and by HPIC. The last procedure is very efficient and is thus described in detail: 100 mL of BumimPF$_6$ is mixed with 5 g of activated charcoal (3 mm grain size or 100 mesh give similar results) and stirred for 12 hours. The resulting mixture is centrifuged (15 min, 6000 rpm) and the floating phase is transferred in a 4 cm height alumina column preequilibrated with BumimPF$_6$. A colourless liquid is obtained and stored in a dry box under vacuum containing P$_2$O$_5$. The yield of this purification procedure is very low (around 50%), mainly because the activated charcoal retains part of the liquid.

With this purification procedure, some anionic impurities remain in the BumimPF$_6$-SI (see table 2): this may be due to the high amounts of various anions present in the commercial product. After purification the commercial product is a pale yellow liquid, for which 1 cm path length cuvettes are usable for spectrophotometry (see fig. 1).

As for anions, the purification specifically eliminates the chloride ions from the synthesized BumimPF$_6$ (table 2), as has been checked with HPIC. Furthermore, by comparison of the various absorption spectra it can be deduced that the purification procedures suppresses the absorption band in the range 250 – 300 nm (fig. 2). The purification procedure has been tested for two aliquots of synthesized BumimPF$_6$ and the results appear reasonably reproducible in terms of absorption spectra. Starting from BumimPF$_6$ with a rather low amount of chloride ions (around the detection limit of HPIC, i.e. 0.1 ppm), the purification procedure leads to a further decrease of the absorbance in the 250 – 300 nm region (see fig. 2), which is attributed to an enhanced purification of the solvent. This improved purification cannot be followed by HPIC (below detection limit) and no attempts of

quantification have been made by use of the absorption spectra. However, the decrease in the chloride concentration (as measured by HPIC), the change in colour (from yellow to transparent by visual observation) and the change in the absorption spectrum are qualitatively correlated to the use of the purification procedure. Indeed, it is well known that activated charcoal is of great efficiency for the fixation of aromatic or heteroaromatic rings (including VOC's) by developing electrostatic interactions, such as Van Der Waals bonds. Moreover, the presence of an absorption band in the range 200-300 nm is often characteristic of the appearance of vibrational levels arising from a modification of the electron density repartition in an aromatic or heteroaromatic ring. In the case of $BumimPF_6$ several hypotheses can be evoked to explain both the retention on activated charcoal and alumina column and the absorption band: (1) an oxido-reduction reaction on the 5-membered ring, (2) an electrophilic addition on the ring, (3) a partial retrogradation of the addition of the butyl substituent. All these paths are known to be sensitive to the presence of chloride ions. Although there is no reason to assume that chloride ions are neither directly responsible for the colour of the raw $BumimPF_6$ nor for the band in the $250 - 300$ nm region, conversely, it is reasonable to assume that the presence of chloride ions, even in small amounts, has an indirect effect on these two aspects.

Therefore, it is our opinion that the purification procedure both eliminates chloride anions *and* some organic partners, which have not been studied further, chloride ions being mainly eliminated as a counter anion of the corresponding charged organic species.

As a whole, the absorption spectrum of purified $BumimPF_6$ as displayed in fig. 2 (batch #3) is considered to be the « true » absorption spectrum of the pure liquid. This spectrum is compared to the absorption spectra of 1-methyl-3-butylimidazolium, (introduced as its chloride salt) and PF_6^- (introduced as HPF_6) in water (fig. 2).

3.3. Influence of impurities on photostability

The stability of the solvents $BumimPF_6$ and $BumimPF_6$-SI (either raw or purified) towards laser irradiation has been investigated under the usual conditions of TRES.[19] This is necessary considering the non negligible absorption of some of the solvents at $\lambda_{exc} = 266$ nm (fig. 1).

Photodegradation is conveniently followed by spectrophotometry.[22-24] An aliquot of the solvent is irradiated at $\lambda_{exc} = 266$ nm at a constant beam average power for fixed short time durations (i.e. 2 min in average) and an absorption spectrum is recorded between each laser irradiation. Changes in the absorption spectrum monitor the photodegradation. Note that the samples were not shaken to enhance diffusion of the photodegradation products. Figure 3

presents a set of absorption spectra at increasing irradiation times for raw BumimPF$_6$ as a typical example. Assuming that photodegradation is a linear function of time (i. e. additive), a criteria has to be defined in order to set a limit to the irradiation duration below which the solvent is considered to be stable. It was decided that changes upon irradiation in the range 250 – 390 nm exceeding 0.1 in absorbance arbitrary units are indicative of photodegradation. On this basis, the duration for which the solvents are photostable have been determined and are reported in table 2. Again, impurities have a large impact onto the photostability: Emission spectra by TRES can be conveniently obtained solely for purified BumimPF$_6$. In the case of raw BumimPF$_6$-SI, above t = 8 min, a brown colored region is observed around the laser beam impact in the liquid. This is considered to be incompatible with photostability. In this respect, purification enhances the photostability of BumimPF$_6$-SI. It is most probable that the impurities present in BumimPF$_6$-SI have an impact onto other physico-chemical properties of this liquid as well and caution should be paid to this problem.

4. BumimPF$_6$ properties

4.1. First investigation of the structure of pure BumimPF$_6$

Small angle X-rays scattering provides insight about the structural inhomogeneity of the medium. It is mainly used to measure crystalline and amorphous structures on the atomic scale. Figure 4 presents the results obtained by this technique for purified BumimPF$_6$. Two peaks at $2\theta = 20°$ and $2\theta \approx 14°$ are observed, together with their first harmonics, which correspond to two structures with specific dimensions of 6.3 Å and 4.4 Å. Peak deconvolution and measurement of the full width at half maximum give the coherence distance which was estimated to be 15 Å for the 6.3 Å structure and should be of the same order of magnitude for the 4.4 Å structure. Complementary investigation with polarised light showed however that this solvent is not a liquid crystal (no birefringence observed). This is in line with previous studies on related ionic liquids, for which a liquid crystal behaviour was observed for cationic side chains containing more than 14 carbons for a PF$_6^-$ counter anion.[25,26] Further experiments (central diffusion) showed that no aggregates are present in BumimPF$_6$ (data not shown) : the liquid is purely monophasic, although it presents a local organisation.

Law and Gannon[27,28] have investigated the molecular orientation at the surface of various ionic liquids, including BumimPF$_6$. In this liquid, they found that the surface is populated by both anions and cations, with no segregation, the cation ring being perpendicular to the surface. This is consistent with the hypothesis that the ions are associated as ion pairs in

the liquid state. A study of the structure of 1-methylimidazolium with $CF_3SO_3^-$ or NO_3^{-}[29] shows that the cations adopt a face to face orientation. In two previous works on solid 1-ethyl-3-methylimidazolium based ionic liquids, either with hexafluorophosphate[30] or NO_3^- counter-anions,[31] it was also shown that imidazolium cations are positioned in pairs, with a plane to plane separation of 4.5 Å. This value is not very different from the 4.4 Å value obtained in this work. It seems therefore reasonable to ascribe the 4.4 Å value observed in the liquid phase of $BumimPF_6$ to an interplanar distance between the imidazolium rings. Under this assumption, the coherence distance of 15 Å roughly corresponds to three repetitions of the pattern of parallel imidazolium rings. The presence of an alkyl chain involves a large parallel offset between the cations. Fuller *et al.*[30] found a centroid to centroid separation distance of 5.39 Å with 1-methyl-3-ethylimidazolium. Therefore, in the case of Bumim, we may attribute the 6.3 Å distance to this cation-cation separation.

4.2. Estimations of some solubilities

The solubilities of various salts in purified $BumimPF_6$ have been estimated by visual observation of the diffusion of He:Ne laser light (see table 3).[32] Salts that are not hygroscopic (such as EuI_2) could be easily dissolved in $BumimPF_6$.

5. Eu(II) solutions in $BumimPF_6$: a preliminary study

5.1. UV-Vis absorption spectra

The absorption spectrum of Eu(II) iodide salt in $BumimPF_6$ at a concentration of 10^{-4} M is displayed in fig. 5. To our knowledge, this is the first report on the solubility of Eu(II) in ionic liquids. Some publications already deal with the dissolution of Cd(II), Sr(II) or Co(II).[18,33,34] In these studies, the metals are assumed to exist as doubly charged cations in solution (Sr^{2+} for example in [33]) but it is not possible with the data of figure 5 alone to determine whether Eu(II) is in a molecular form, such as EuI_2, or in an ionic form, such as Eu^{2+}. Therefore, the notation Eu(II) will be used in the following.

The peak at $\lambda = 240$ nm is ascribed to iodine, by comparison with the absorption spectra of NaI and KI in $BumimPF_6$ (see fig. 5 for KI). The two absorption maxima at 290 and 355 nm are thus ascribed to Eu(II). The molar absorption coefficient of Eu(II) in $BumimPF_6$ at $\lambda = 290$ nm is equal to $\varepsilon = 10^4$ M^{-1} cm^{-1}, which is rather high *per se* and is approximatively one order of magnitude larger than the molar absorption coefficient of Eu^{2+} in water or in methanol.[35,36] The positions of the maxima are in line with what is known for Eu(II) or various Eu(II) crown-ether complexes in methanol. [37] In methanol, the presence of two absorption bands for Eu(II) is attributed to the 5d level splitting due to the coordination

properties of the surroundings (either methanol or a crown-ether ligand).[37] For all crown-ether complexes studied in methanol,[37] a red shift of the higher energy band and a blue shift of the lower energy band with respect to those of $EuCl_2$ in methanol are observed. In $BumimPF_6$, the two Eu(II) bands present a strong red shift as compared to the maxima ($\lambda = 248$ and 328 nm, from [37]) of $EuCl_2$ in methanol. In $BumimPF_6$, Eu(II) is most probably solvated but the exact nature of the first solvation sphere remains unclear.

5.2. Stability of divalent europium in BumimPF$_6$

Solutions of Eu(II) in $BumimPF_6$ appear to be perfectly stable, even without protecting them from natural light. It was attempted to oxidise Eu(II) into Eu(III) via three chemical methods, which all were unsuccessful: In a first trial, $K_2Cr_2O_7$ in excess was dissolved in a solution of Eu(II) in $BumimPF_6$. This salt has been chosen for its well-known oxidising properties in water but no changes in the absorption spectrum were observed even 18 hours after the introduction of $K_2Cr_2O_7$. Actually, $Cr_2O_7^{2-}$ is a strong oxidiser *in water* at pH below 2 and the oxidising/reducing couple requires the presence of H^+ ions: these chemical conditions are very different from those prevailing in $BumimPF_6$ solutions. As seen from table 2, the $BumimPF_6$ used in this work contains a non negligible amount of water but this water is unlikely to be very acidic as the pH of a water phase in contact with $BumimPF_6$ is around pH = 6. In a second trial, a solution of Eu(II) in $BumimPF_6$ was stirred for 18 hours with a large excess of $Ce(SO_4)_2$ (this salt does not dissolve significantly in $BumimPF_6$ but even a low solubility should be sufficient to obtain oxidation, the chemical equilibrium being then moved toward a low but continuous solubilisation of $Ce(SO_4)_2$ to obey the mass action law): After stirring, the solution was cloudy and centrifugation was of no help in this respect. Spectrophotometry could nevertheless be performed and it was observed that the relative absorbance ratio of the three peaks ascribed to iodine and Eu(II) were not significantly modified as compared to a solution without $Ce(SO_4)_2$. It is therefore concluded that no oxidation of Eu(II) occurred. Finally, O_2 was bubbled through a solution of Eu(II) for 50 min but again, no changes in the absorption spectrum could be detected. This is in line with the fact that O_2 is poorly soluble in $BumimPF_6$.[38]

Obviously, oxidation of Eu(II) is much more difficult in $BumimPF_6$ than in other solvents.[39] It has been noted previously that methanol should be carefully degassed to prevent oxidation of Eu(II) to Eu(III) and that Eu(II) polymers remain stable for a day or so.[39] In contrast, a Eu(II)/$BumimPF_6$ solution left in a container without special care is stable for months. This leads to the conclusion that solvation effects in $BumimPF_6$ are markedly different from what is known in an aqueous phase, as was discussed in a recent simulation

study.[40] It can be hypothesised that water does not significantly cluster around Eu(II) in BumimPF$_6$, otherwise Eu(II) would be readily oxidized to Eu(III). This offers interesting potential for the stabilisation of uncommon oxidation numbers, either for synthesis or for liquid/liquid extraction and requires in consequence extensive studies.

5.3. Evidence for Eu(II) complexation in BumimPF$_6$

Considering the high stability of Eu(II) in BumimPF$_6$, it is interesting to examine the possibility of complexation of Eu(II). In a first attempt, the complexing abilities of two crown-ethers (namely 15C5 and 12C4) were evaluated. These molecules have been chosen because the complexing ability of 15C5 towards Eu(II) in methanol has been already studied[37] and 12C4 was chosen for the sake of comparison.

Previous works have shown that various crown-ethers are highly soluble in ionic liquids[33] and whilst no attempt was made to determine the maximum solubilities, a concentration of 5×10^{-3} M of 15C5 (or 4×10^{-3} M of 12C4) dissolves readily in BumimPF$_6$. Figure 6 displays the absorption spectra of 15C5 and of 15C5 with Eu(II) in BumimPF$_6$ for a 3-fold and a 50-fold excess of crown-ether. As can be seen, the 15C5 affects the Eu(II) absorption bands: although the positions of the two maxima and their relative ratio remain unchanged, a global increase of the molar absorption coefficient is observed. This situation is very different from that prevailing in methanol. Finally, the absorption band of iodide is not affected, neither in shape nor in intensity. In contrast, 12C4, even at concentration as high as 4×10^{-3} M (as compared to Eu(II) at 10^{-4} M) does not modify the Eu(II) spectrum (data not shown).

These results are strong indications that europium is complexed as Eu^{2+} by 15C5 in BumimPF$_6$ while 12C4 does not significantly complex Eu(II). The equilibrium reaction rate constant of 15C5 towards Eu(II) is not very large, because complexation is not fully achieved for a 15C5 to Eu(II) ratio of 3 (see fig.6). The present data show that the determination of the value of the equilibrium reaction rate constant and the stoichiometry of the 15C5/Eu(II) system is *a priori* possible by use of spectrophotometry. Two possible reasons can be evoked to explain the presumably low complexation constant of the 15C5/Eu(II) system: (1) the viscosity of BumimPF$_6$ does not favor diffusion and (2) the solvation shell of Eu(II) and of the complex may also play an important role.

5.4 First investigation of the Eu(II) luminescence properties

Figure 7 displays the emission spectra of purified BumimPF$_6$ at excitation wavelengths of 266, 290 and 355 nm. The last two wavelengths correspond to the maxima of the Eu(II) absorption spectrum (see fig. 5) and $\lambda = 266$ nm corresponds to the fourth harmonic

of the Nd :YAG laser of the TRES setup. Again, the emission spectrum of purified and raw BumimPF$_6$ differ significantly (data not shown). In the region where Eu(II) luminesces (typically from 400 to 550 nm),[37] the signal provided by the pure solvent is obviously non negligible. These conditions are not the most favourable ones for a luminescence study, either by conventional spectrofluorimetry or TRES, but still allow for detection.

As a matter of fact, no luminescence was detected for a solution of EuI$_2$ in BumimPF$_6$ (C = 10^{-4} M). Such an absence of luminescence is similar to what is observed for Eu^{2+} in water.[35] Previous studies have shown that complexation with crown-ethers or cryptands strongly enhances the Eu^{2+} luminescence in methanol[37] and in water,[35] where Eu^{2+} encapsulated in a cryptand becomes luminescent. These results have been attributed to more or less efficient deactivation mechanisms due to the presence of OH bonds in the first solvation sphere of the excited Eu^{2+} ions: complexation is said to decrease the efficiency of these energy transfers, because the solvent molecules are not as close to Eu^{2+} in the complex as in the case of the free ion, thus allowing luminescence to be detected.[37] The luminescence enhancement of Eu^{3+} upon complexation in various solvents was interpreted along similar lines in [41,42] and was put in question, however in [43]. As is well-known, PF$_6$ based ionic liquids may contain water[8] and the BumimPF$_6$ solutions studied in this work do so (see table 2). Thus, water molecules might contribute to luminescence inhibition. On the other hand, it is not clear whether the solvation sphere of Eu(II) is constituted of H$_2$O or PF$_6^-$ species.

In order to gain insight into this question, the Eu(II) luminescence in BumimPF$_6$ was examined in the presence of the 15C5 crown-ether already studied. This crown-ether has been chosen because it appears to be very efficient in promoting Eu^{2+} luminescence in methanol (luminescence increase of a factor of 700).[37] In order to observe Eu(II) luminescence, if any, a compromise has to be found between the amount of complexed Eu(II) and the amount of free 15C5, the luminescence of which is non negligible. Despite the various experiments performed (different excitation wavelengths and 15C5/Eu(II) ratios) no significant luminescence ascribable to Eu(II) could be observed. No attempts were made with 12C4, as it does not complex Eu(II) (see sect. 5).

As no luminescence enhancement could be observed following the addition/complexation of 15C5, the aforementioned hypothesis of a deactivation mechanism via OH bonds only can be ruled out in the present case. The absence of luminescence should be therefore ascribed to global deactivation processes due to the solvent itself. In this respect, it has been shown that the CH and NH bonds of ligands have an important quenching effect onto Eu^{3+} luminescence in various solvents.[44] In BumimPF$_6$, it can be hypothesised that the

first solvation sphere of Eu(II) is composed solely of PF_6^- anions. The deactivation mechanism thus might occur at rather long distances, possibly via the CH bonds of the Bumim cation, and should be considered as a *bulk* effect.

6. Conclusion

This work has highlighted the great importance of chloride purification for selected physico-chemical properties of $BumimPF_6$. It should be understood that no reproducible and well-assessed results can be obtained with ionic liquids that are not perfectly characterised and, if possible, purified. In this respect, the purification procedure used in this work is very efficient. $BumimPF_6$ is an unusual liquid, as it presents a local order at short distances and as it stabilises Eu(II), which has been characterised by absorption spectroscopy. Some insight into the solvation sphere of Eu(II) in $BumimPF_6$ could be obtained. The preliminary results on complexation offer promising perspective for the chemistry of Eu(II). Moreover, these results are also interesting in the field of nuclear waste reprocessing, considering that actual aqueous processes are mainly based on the oxidation states of the species involved. Ionic liquids, allowing the stabilisation of unusual oxidation states may lead to a fresh look on these processes.
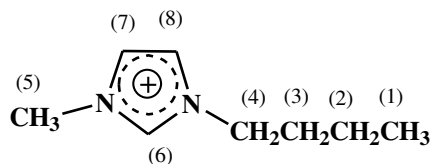
Tables

Table 1: [1]H and ^{13}C chemical shifts for $BumimPF_6$ in acetone-d_6 solvent from NMR spectroscopy

	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	$\delta_{7,8}$
[1]H	0.9	1.4	1.8	4.3	4	8.89	7.6 / 7.7
[13]C	12.6	19.2	31.89	49.5	35.63	136.37	122.37 / 123.71

δ in ppm relative to internal reference $SiMe_4$.

Table 2: Characterization of $BumimPF_6$ of different origin (see text). HPIC measurements show that all samples contain F^- anions.

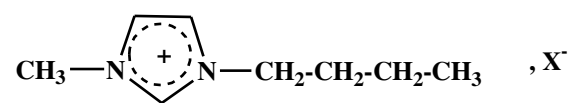|	Raw $BumimPF_6$	Purified $BumimPF_6$	Raw $BumimPF_6$-SI	Purified $BumimPF_6$-SI
elemental analysis exp.* (calc.) (%)	C: 33.66 (33.81) H: 5.37 (5.32) N: 9.70 (9.86)			
HPIC (ppm)	Cl^-: from (46 ± 5) to 0.1 (a)	Cl^-: <0.1	Cl^-: (80 ± 5) SO_4^{2-}, NO_3^- PO_4^{3-}	Cl^-: (14 ± 1) SO_4^{2-}, NO_3^- PO_4^{3-}
water content (ppm)	20000	9000	450	not determined
maximum time of irradiation (min)	17 (Cl^- = 46 ppm)	40	<8	<10

* : average of two determinations

(a) depending on the synthesized batch.

Table 3: Estimated solubilities of various salts in purified BumimPF$_6$.

Salt	EuI$_2$	NaI	KI	K$_2$Cr$_2$O$_7$
Estimated solubility (M)	2×10^{-3}	$> 1.1 \times 10^{-2}$	9×10^{-3}	$9.5 \ 10^{-3}$

Scheme

$$CH_3 - N \overset{+}{\underset{}{\diagup\diagup\diagdown}} N - CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad , X^-$$

Scheme 1

Figure captions

Figure 1: Absorption spectra of $BumimPF_6$ of various origin. (1): raw $BumimPF_6$-SI ; (2): raw $BumimPF_6$, (Cl^-) = 46 ± 5 ppm ; (3): purified $BumimPF_6$-SI ; (4): purified $BumimPF_6$.

Figure 2: Absorption spectra: (1) (batch #1): raw $BumimPF_6$, (Cl^-) = 46 ± 5 ppm ; (2) (batch #2): purified $BumimPF_6$ (starting from batch #1), (Cl^-) ≈ 0.1 ppm ; (3): best purified $BumimPF_6$ (starting from batch #2) ; (4): $BumimCl^-$ in water (1 M) ; (5): HPF_6 in water (1 M).

Figure 3: Absorption spectra of raw $BumimPF_6$ (with (Cl^-) ≈ 46 ppm) after various time of pulse laser irradiation. Average laser power 13 mW, repetition rate 10 Hz, λ_{exc} = 266 nm, t_{irr} = 0 min, 56 min and 93 min.
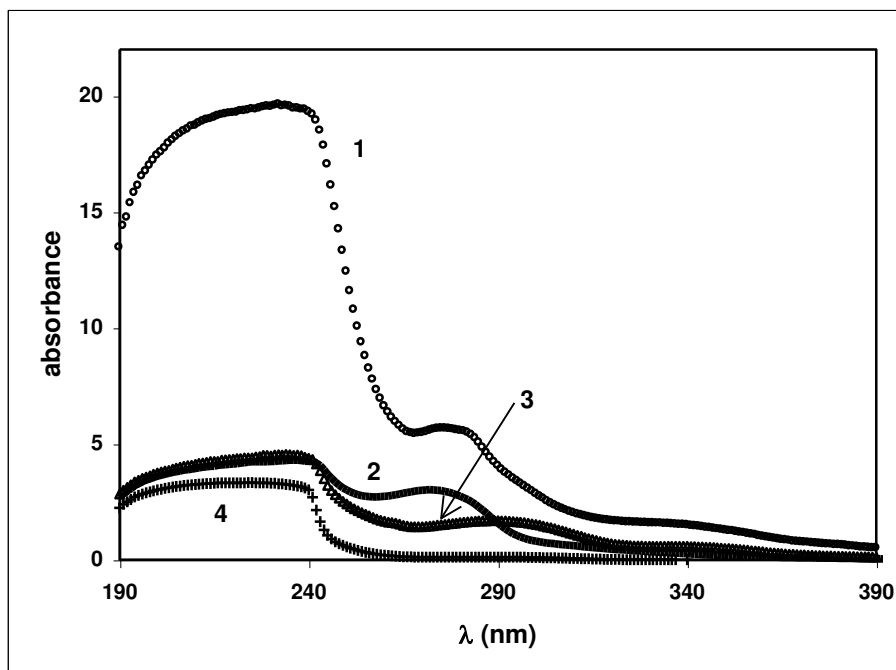
Figure 4: Small Angle X-Ray diffusion of $BumimPF_6$.

Figure 5: Absorption spectrum of: (1) EuI_2 (C = 10^{-4} M) in $BumimPF_6$ and (2) KI (C = 2.4 10^{-3} M) in $BumimPF_6$.
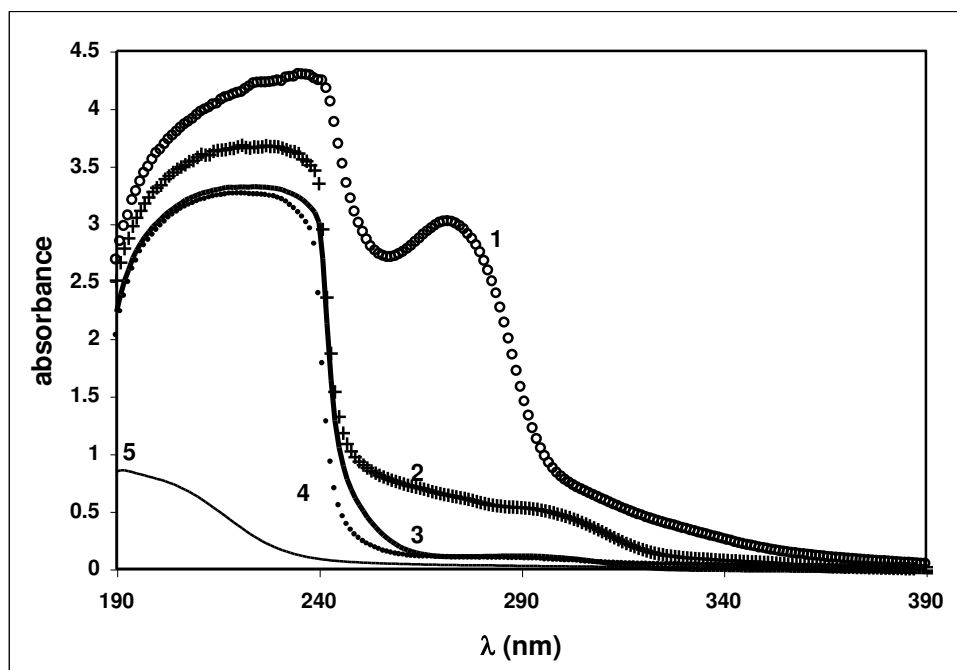
Figure 6: Absorption spectra in $BumimPF_6$. (1): 15C5 alone (C = $5x10^{-3}$ M) ; (2): EuI_2 alone (C = 10^{-4} M) ; (3): EuI_2 (C = 10^{-4} M) and 15C5 (C = $3x10^{-4}$ M) ; (4): EuI_2 (C = 10^{-4} M) and 15C5 (C = $5x10^{-3}$ M).

Figure 7: Emission spectra of purified $BumimPF_6$ at (1): λ_{exc} = 266 nm ; (2): λ_{exc} = 288 nm ; (3): λ_{exc} = 355 nm. The intense peaks at 532 nm and 576 nm correspond to the second harmonics of the excitation light.
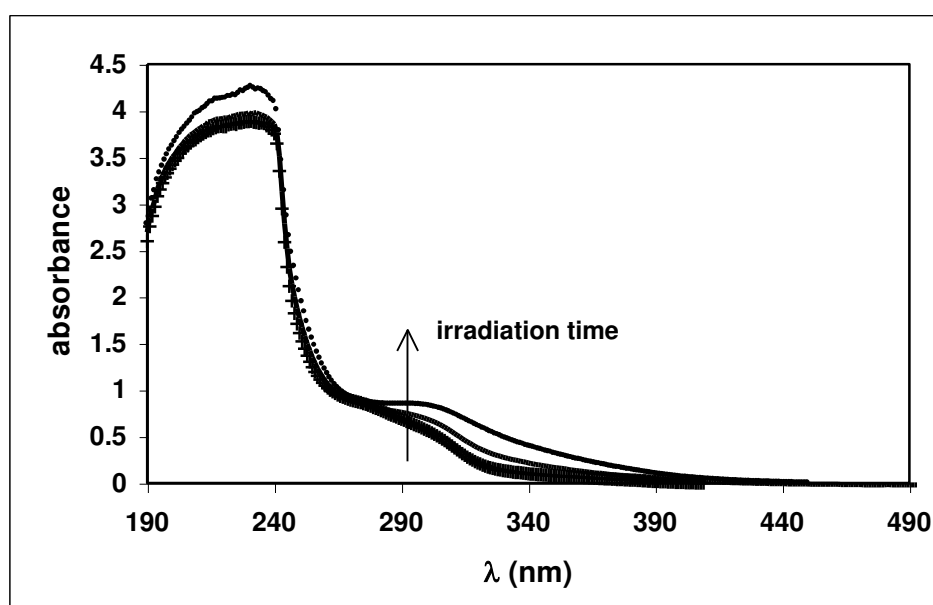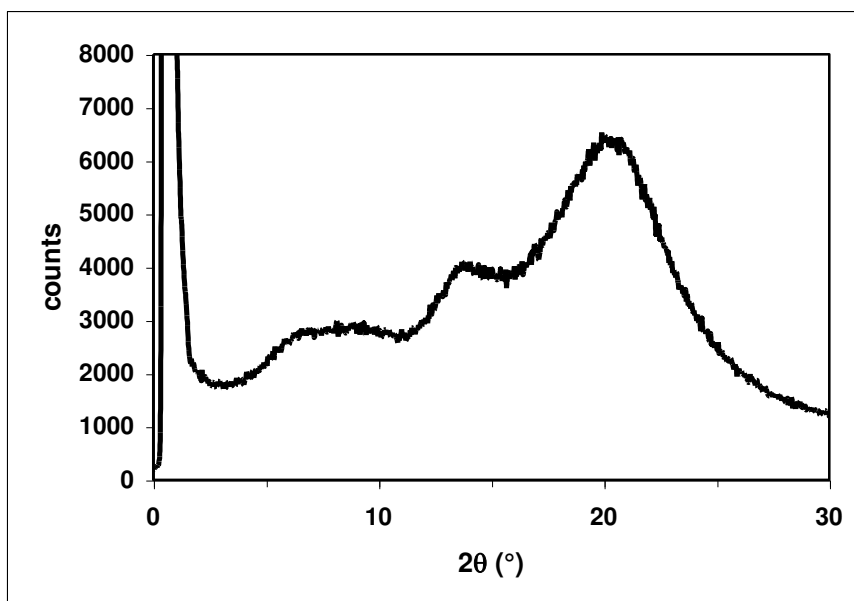
Figures

Figure 1: Absorption spectra of BumimPF$_6$ of various origin. (1): raw BumimPF$_6$-SI ; (2): raw BumimPF$_6$, (Cl$^-$) = 46 $\pm$ 5 ppm ; (3): purified BumimPF$_6$-SI ; (4): purified BumimPF$_6$.
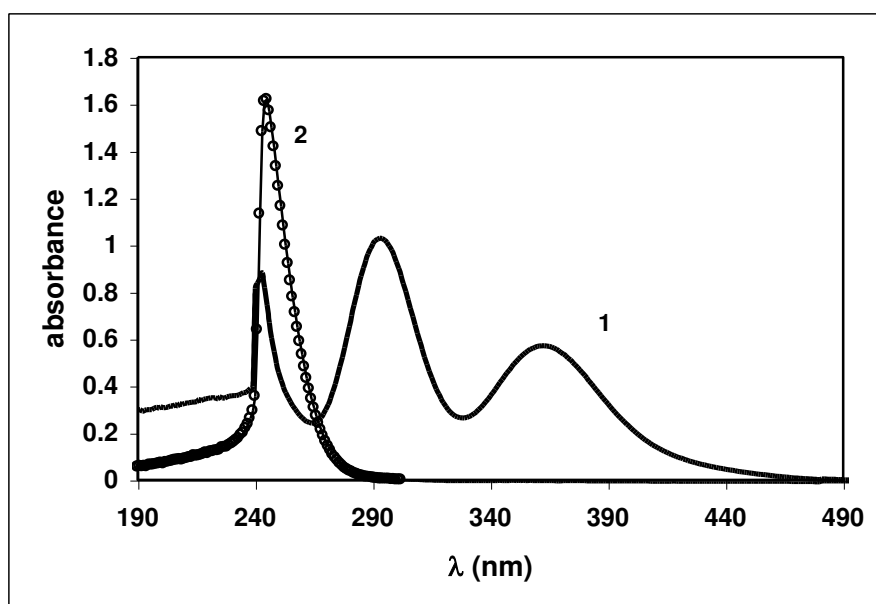
Figure 2: Absorption spectra: (1) (batch #1): raw BumimPF$_6$, (Cl$^-$) = 46 ± 5 ppm ; (2) (batch #2): purified BumimPF$_6$ (starting from batch #1), (Cl$^-$) ≈ 0.1 ppm ; (3): best purified BumimPF$_6$ (starting from batch #2) ; (4): BumimCl$^-$ in water (1 M) ; (5): HPF$_6$ in water (1 M).
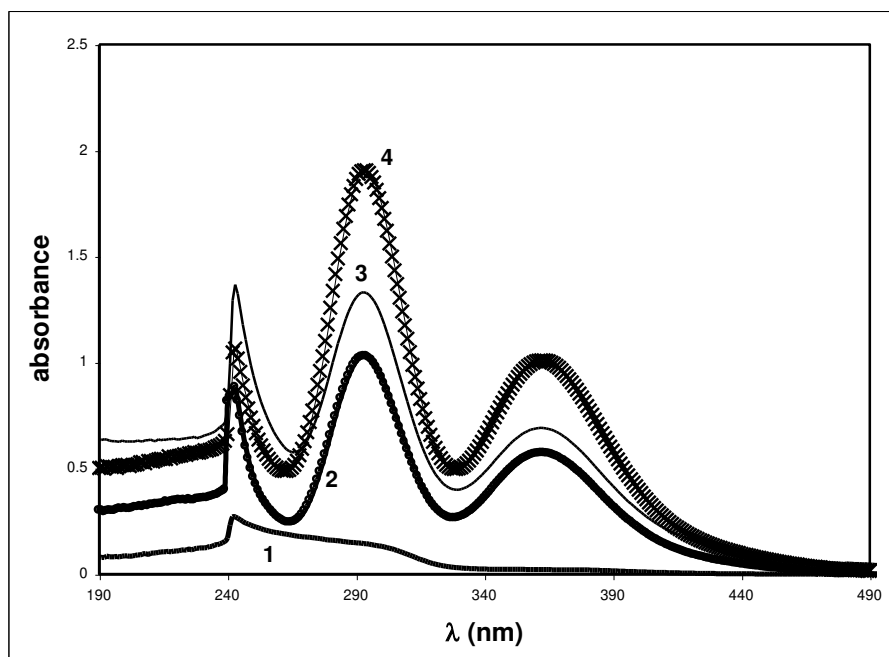

Figure 3: Absorption spectra of raw BumimPF$_6$ (with (Cl$^-$) ≈ 46 ppm) after various time of pulse laser irradiation. Average laser power 13 mW, repetition rate 10 Hz, λ_{exc} = 266 nm, t_{irr} = 0 min, 56 min and 93 min.
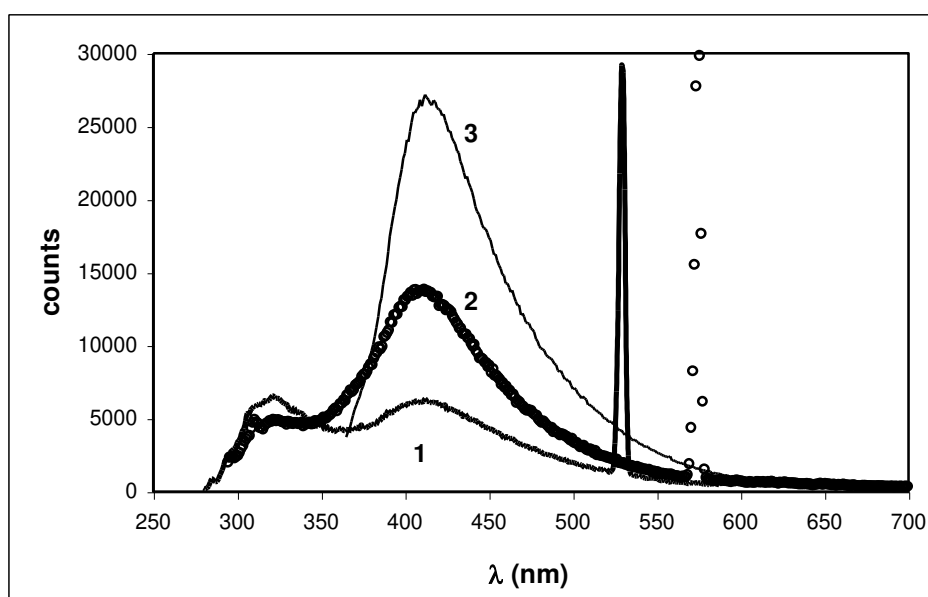
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Figure 6: Absorption spectra in BumimPF$_6$. (1): 15C5 alone (C = 5x10^{-3} M) ; (2): EuI$_2$ alone (C = 10^{-4} M) ; (3): EuI$_2$ (C = 10^{-4} M) and 15C5 (C = 3x10^{-4} M) ; (4): EuI$_2$ (C = 10^{-4} M) and 15C5 (C = 5x10^{-3} M).

Figure 7: Emission spectra of purified BumimPF$_6$ at (1): λ_{exc} = 266 nm ; (2): λ_{exc} = 288 nm ; (3): λ_{exc} = 355 nm. The intense peaks at 532 nm and 576 nm correspond to the second harmonics of the excitation light.

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