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An Ionic Liquid Designed for Coordination Chemistry Revisited: Synthetic Routes and Safety Tests for 1-Ethyl-3-methylimidazolium Perchlorate ([emim][ClO_4])

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The colourless room-temperature ionic liquid 1-ethyl-3-methylimidazolium perchlorate, [emim][ClO_4], was revisited for reasons of its hydrophilic character and its weak coordinating ability. In this study, [emim][ClO_4] was synthesized from the cheaper ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate, [emim][$EtSO_4$], by way of direct and indirect membrane-assisted anion metathesis. Both synthetic methods, as alternatives to the metathesis of silver perchlorate and [emim] halides, are compared and discussed in detail. In addition, some physicochemical parameters were determined to characterize the ionic liquid. With respect to the hazardous nature of organic perchlorates, the thermal stability as well as the impact and friction sensitivity of [emim][ClO_4] were tested according to the UN Test Series 3a–3d.

Introduction

In recent years, room-temperature ionic liquids (RTILs) have extensively been discussed as alternative media in catalysis, synthesis, electrochemistry and separation techniques.[1] A primary motivation for many studies undertaken was to develop new and also environmental friendly chemical processes that take advantage of the unique properties of RTILs, such as their high conductivity and low volatility. The large range of possible cation and anion combinations allows a systematic tuning of the physicochemical properties of ionic liquids, and thereby enables the use of well-designed reaction media.[2] Therefore, some ionic liquids have already been adopted in new technologies.[3]

Since ionic liquids consist of cations and anions, they provide an exceptional chemical environment compared with that of conventional solvents.[4] Unfortunately, in many cases it is still unclear how substrates actually interact with this environment. In particular, applications that involve sensitive catalytically active metal complexes are considered to be influenced or controlled by interactions with the anionic or cationic components of an ionic liquid,[5] since some groups have reported an increase or decrease in reactivity, or even a complete inhibition of reactions, in ionic liquids.[6]

In terms of the effects of anions, the bis(trifluoromethylsulfonyl)imide anion (NTf_2^-) has emerged as one of the most suitable building blocks for ionic liquids because of its noncoordinating or at least weak-coordinating nature.[7] However, ionic liquids that consist of NTf_2^- have a low polarity and a significant hydrophobic character, with the result that organic substances in many cases show a good solubility, whereas inorganic compounds are usually poorly soluble. Although many crystal structures clearly reveal that the ClO_4^- ion can coordinate to various metal centres either as monodentate (η^1), bidentate (η^2) or bridging (μ) ligands, it is known from many kinetic and mechanistic studies that they behave mostly innocently in solution. Therefore, ClO_4^- salts are often applied to adjust the ionic strength of a solution that contains transition-metal complexes.[8]

In 1977, Chan et al. reported the synthesis and thermolysis of various imidazolium-based salts. Among others, they listed the substance 1-ethyl-3-methylimidazolium perchlorate, [emim][ClO_4] (**I**) (Scheme 1), which they found to be a liquid at room temperature.[9] At that point they were only interested in the thermolysis of their compounds, but from the present point of view they reported an exceptional RTIL that could be, due to the low coordinating ability of ClO_4^-, an interesting addition to other weakly coordinating RTILs. However, scientific publications that deal with this ionic liquid are rather scarce,[9,10] and a set of reliable fundamental data in terms of its physicochemical properties

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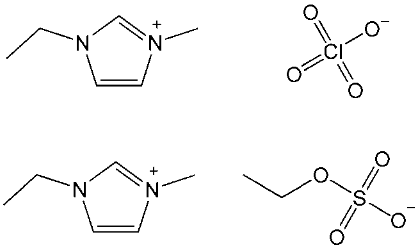
and the characterization of its stability are still missing even though [emim][ClO$_4$] recently became commercially available.[11]



Scheme 1. Schematic structures of the ionic liquids [emim][ClO$_4$] and [emim][EtSO$_4$].

This study presents two alternative routes to synthesize [emim][ClO$_4$] by direct or indirect membrane-assisted anion metathesis by using the commercially available RTIL 1-ethyl-3-methylimidazolium ethyl sulfate, [emim][EtSO$_4$] (Scheme 1) as starting material. To gain further information, we additionally determined some physicochemical parameters of **I** and tested its thermal stability as well as its impact and friction sensitivity by the BAM (Bundesanstalt für Materialforschung und -prüfung) drop hammer and friction tester.

Results and Discussion

Direct Metathesis

In the case of direct metathesis, anion exchange is controlled by the polarity of the employed solvent. As known from the syntheses of other ionic liquids (e.g., [emim][NTf$_2$]), lithium ethyl sulfate (Li[EtSO$_4$]) is insoluble in organic solvents of low polarity.[12] On the other hand, LiClO$_4$ is one of the few inorganic perchlorate sources that is not only soluble in conventional polar solvents like water or methanol but also in nonpolar organic solvents like nitromethane or dichloromethane. Therefore, anion metathesis was performed according to Equation (1) using LiClO$_4$ and [emim][EtSO$_4$] as chemical precursors.

$$\mathrm{LiClO_4} + [\mathrm{emim}][\mathrm{EtSO_4}] \rightarrow [\mathrm{emim}][\mathrm{ClO_4}] + \mathrm{Li}[\mathrm{EtSO_4}](\downarrow) \qquad (1)$$

To achieve optimized conditions, a mixture of nitromethane and dichloromethane in a ratio of 3:1 was employed as reaction medium due to a higher solubility of LiClO$_4$ in nitromethane (Gutmann donor number, DN = 2.7 kcal mol^{-1}). Equimolar amounts of both precursors were dissolved separately, cooled to 0 °C and poured together. Within several seconds, Li[EtSO$_4$] began to precipitate as a bulky white solid, whereas the desired ionic liquid **I** remained in solution. After filtration of Li[EtSO$_4$] and removal of the solvent mixture by vacuum, **I** was isolated as a nearly colourless liquid in a yield of 94% (see Exp. Sect.). The water content of **I**, determined by Karl Fischer titration,[13] was found to be 0.01%. This value is low as expected for a water-free synthetic procedure. Due to an effective anion exchange in the metathesis process and the low water content, the elemental analysis of **I** is in good agreement with the expected values, which is also true for the analysis of the side product Li[EtSO$_4$] (see Table 1).

Table 1. Elemental analysis of **I** and Li[EtSO$_4$] synthesized by direct metathesis, and of **I** synthesized by membrane-assisted metathesis.

	Required [%]			Found [%]		
[emim][ClO$_4$] (direct metathesis)	N 13.30	C 34.22	H 5.26	N 13.15	C 34.22	H 5.50
Li[EtSO$_4$] (direct metathesis)	C 18.19	H 3.82	S 24.28	C 18.35	H 3.77	S 23.78
[emim][ClO$_4$] (membrane-assisted metathesis)	N 13.30	C 34.22	H 5.26	N 13.03	C 34.04	H 5.31

Indirect, Membrane-Assisted Metathesis

In this part of the work, **I** was produced by means of the hydroxide route. An aqueous solution of the free-base [emim][OH] was generated from [emim][EtSO$_4$] by electrodialysis with bipolar membranes (EDBM) as described elsewhere.[14] The membrane arrangement (all from FumaTech) consisted of bipolar (BM), anion-selective (AEM), cation-selective (CEM) and bipolar (BM) membranes (Figure 1). A feed concentration of 5 wt.-% was chosen as the [emim][OH] precursor solution shows increasing instability at higher concentrations. Afterwards, the aqueous solution of [emim][OH] was neutralized by adding an equimolar amount of perchloric acid, and water was removed at 40 °C under high vacuum.

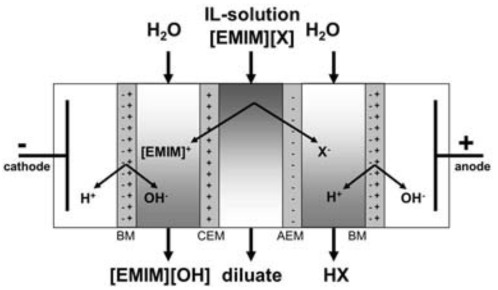


Figure 1. Production of [emim][OH] from [emim][X] by electrodialysis with bipolar membranes (see ref.[14]).

The water content of **I**, determined by Karl Fischer titration, was found to be 0.02%. This value is quite low for a water-miscible ionic liquid produced by an aqueous synthetic procedure. Elemental analysis of **I** produced by this procedure is again in good agreement with the expected values and shows that only very small amounts of undesired ions passed the membrane.

Discussion of Synthetic Methods

In contrast to Chan et al. who synthesized **I** from silver perchlorate and a 1-ethyl-3-methylimidazolium halide (no further information was given on the employed halide), both methods presented here start with notably cheaper components by using [emim][$EtSO_4$] and $LiClO_4$ or $HClO_4$. Furthermore, our earlier synthetic attempts to apply an ion exchange column failed, probably due to the fact that ClO_4^- does not interact strongly with the ion exchange resin.

The successful application of ionic liquids either as reaction media or as reagents depends strongly on their quality. Although many ionic liquids are already offered in a purity of 97–99%, further workup steps are often necessary to avoid unexpected complications.[15] Especially in the case of the direct metathesis, the quality of the resulting IL **I** mainly depends on the quality of the employed starting material [emim][$EtSO_4$]. Therefore, [emim][$EtSO_4$] has to be purified by extraction with various organic solvents prior to further application, as soluble contaminations are carried through the metathesis process and can later be detected in the resulting ionic liquid. In many cases, additional treatment with activated charcoal is necessary to eliminate or at least to reduce the yellow colour of the ionic liquid, which is caused by different decomposition products of the $[emim]^+$ cation.

By using membrane-assisted metathesis, problems caused by impurities are reduced right from the start. On the one hand, only a few uncharged molecules, which normally remain static in an electrical field, pass the ion-selective membranes very slowly by solution diffusion. On the other hand, only very small amounts of anionic contaminants pass the cationic-selective membrane as partner ions, since the major amount is retarded due to the negative charge. Thus, a time-consuming purification of the starting material [emim]-[$EtSO_4$] is not required. However, a small amount of sulfate from the electrode flushing solutions passes the bipolar membrane towards the product chamber, thereby resulting in a low (ppm) content of sulfate in the precursor solution of [emim][OH]. The concentration of the precursor is kept quite low at maximum 5 wt.-%. The free-base [emim][OH] in aqueous solution tends to be unstable on increasing concentration and temperature. Deprotonation at the C-2 position of the imidazolium ring leads to the formation of the corresponding carbene and dimerization, which contributes to the yellow colour of the aqueous solution and the resulting ionic liquid. This undesired subsequent reaction can be reduced by fast neutralization of the hydroxide precursor with an acid.

Properties of [emim][ClO_4]

The density of the ionic liquid **I** was measured with an oscillating U-tube transducer density meter (Anton Paar DMA5000) at temperatures of 20, 25 and 35 °C. To minimize inaccuracies, each measurement was repeated five times; the resulting mean values are listed in Table 2. Before and after the measurements, the water content of the ionic liquid was checked by Karl Fischer titration and found to be unchanged.

Table 2. Viscosity (η) and density (ρ) of **I** at various temperatures.

T [°C]	η [cP]	ρ [$g\,mL^{-1}$]
0	167.4	–
10	110.1	–
20	78.5	1.343
25	65.8	1.338
35	45.9	1.331

Viscosities were measured with a cone/plate viscosity meter (Physica MCR100) at shear rates from 0 to 1000 s^{-1} and temperatures between 0 and 35 °C. To avoid air humidity that could falsify the results, Argon was used as inert gas during the measurements. The determined values are between 167.4 cP at 0 °C down to 45.9 at 35 °C (see also Table 2). No dependence of the viscosity on shear rates could be observed within the range from 0 to 1000 s^{-1} and the ionic liquid appears to be a Newtonian fluid.

The chloride and ethyl sulfate content of the produced IL was determined by anion chromatography (IC25 with EG40, DIONEX; column set GC11-HC/AS11-HC, DIONEX). The IL produced by both methods has a chloride content lower than 5 ppm and $[EtSO_4]^-$ content lower than 10 ppm. The crystallization behaviour of **I** was also studied. The ionic liquid (1 mL) was filled into a glass vial. On storing this sample at –85 °C for one week, no crystallization occurred and only a glass transition could be observed. When the glassy IL sample was dipped into liquid nitrogen for ten minutes and then heated to –25 °C, it crystallized as a white solid within several minutes and stayed crystalline over several days at temperatures between –25 and 10 °C. On increasing the temperature, the sample melted slowly and again became a colourless liquid at 25 °C.

Differential scanning calorimetric (DSC) analysis (Netzsch Maja, –120 to 50 °C with 10 K min^{-1}) was performed on a precooled sample, which was stored at –85 °C for 24 h and then transferred immediately to the precooled DSC. On heating the sample from –120 to 50 °C, a glass transition with an onset at –90.7 °C could be observed. The exothermic heat effect at –54.4 °C is related to the crystallization of the sample. Upon cooling, no crystallization was observable and the sample froze in a glassy state. On heating the sample, the IL starts to crystallize at a temperature at which the thermal energy and the kinetics of crystallization are sufficiently high. These phenomena are quite common and known from the DSC analysis of other ILs.[16] On further heating, the sample melts and becomes com-

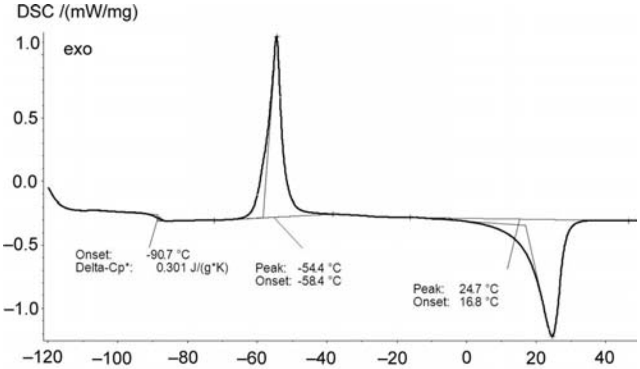


Figure 2. DSC of **I**: precooled sample showing glass transition, crystallization and melting upon heating.

pletely liquid at temperatures above 24.7 °C (Figure 2). The results of the DSC analysis are consistent with the visually observed crystallization behaviour of [emim][ClO$_4$]. The melting point of the neat IL with low water content is around room temperature, but due to kinetic reasons, quite strong subcooling can be observed.

Miscibility of [emim][ClO$_4$] with Other Solvents

Since several applications not only require pure ionic liquids as reaction media but also mixtures of ionic liquids with other solvents,[17] we also studied the miscibility of **I** with a selection of common solvents. Compound **I** and the selected solvents were mixed in a volume ratio of 1:1 and the possible occurrence of phase separation was observed.

In general solvents with a very high polarity tend to be better miscible with **I** than solvents with a very low polarity. As shown in Table 3, alkanes like *n*-heptane, *n*-hexane and *n*-pentane are not soluble, nor are the homocyclic aromates benzene or toluene. The same observation was made in terms of ethers. Both ethyl ether and its cyclic analogue tetrahydrofurane are not miscible with **I**, though tetrahydrofurane exhibits a higher polarity than ethyl ether.[18] Chloroform and dichloromethane were found to be soluble in **I** despite its lower polarity than tetrahydrofuran. This can be attributed to a smaller molecular size, which enables better interactions between solvent and solute.

Table 3. Miscibility of **I** with various solvents at 25 °C.

Solvent	Miscible	Immiscible
Water	×	
Methanol	×	
Ethanol		×
2-Propanol		×
1-Pentanol		×
Acetonitrile	×	
Dimethyl sulfoxide	×	
Acetone	×	
Dichloromethane	×	
Chloroform	×	
Tetrahydrofuran		×
Diethyl ether		×
Toluene		×
Benzene		×
n-Pentane		×
n-Hexane		×
n-Heptane		×

On increasing the polarity, solvents become miscible with **I**. Some remarkable effects were found for the miscibility of **I** with water and short-chain alcohols. Usually, hydrophilic ionic liquids show strong hydrogen bonding between water molecules and their cations and anions. Although **I** is miscible with water in any ratio, water can quite easily be removed from this ionic liquid under high vacuum at 40 °C (see the section on membrane-assisted metathesis above). This observation can be ascribed to a chaotropic effect caused by the perchlorate anions, which disturb hydrogen bonding of water molecules and therefore simplify the removal of water under vacuum.[19]

For some technical applications, a controllable miscibility of ionic liquids with other solvents could be useful. Especially in the case of homogeneous two-phase catalysis and separation techniques, a temperature-dependent miscibility can be a special feature.[20] In terms of the solubility of alcohols, it was found that methanol as the alcohol with the shortest carbon chain is completely miscible with **I**, but phase separation occurs on cooling this mixture to a temperature of –10 °C. On the contrary, the next longer alcohol, ethanol, is not soluble in **I** at room temperature, but becomes miscible on heating up to 60 °C. This leads to the conclusion that the miscibility of alcohols with **I** is strongly controlled by the chain length and resulting molecular size of the applied alcohol. Therefore, 2-propanol and 1-pentanol were found not to be soluble in **I**. On the contrary, the small molecular size and high dipole moment of acetone, dimethyl sulfoxide and acetonitrile facilitate interactions between solvent and solute, and these solvents were found to be very miscible with **I** despite its lower polarity than water and short-chain alcohols.

Coordinating Ability of [emim][ClO$_4$]

Due to a complete delocalization of the negative charge over four oxygen atoms, perchlorate anions exhibit a perfect tetrahedral structure (Cl–O bond length: 146 pm) and a low polarizability. Consequently, they behave as poor nucleophiles with a low coordinating ability, similar to tetrafluoroborate (BF_4^-) anions. The interaction between anions and cations being surrounded by a solvation shell of water molecules in aqueous solution differs significantly from that in ionic liquids in which cations are surrounded by anions, and vice versa.[21]

We recently demonstrated by NMR spectroscopic studies and DFT calculations that the strength of the cation–anion interaction within the ionic liquid correlates with the chemical shift of the C and H atom in the C-2 position of the imidazole ring. This correlation can be used as a measure of the ability of the ionic-liquid anion to coordinate to other cations, for example, positively charged metal centres of catalytic active complexes.[22] To predict this tendency for **I** and to achieve a more detailed understanding at a molecular level, similar DFT calculations (B3LYP/LANl2DZp) were performed.[23–25] The resulting ion-pair stabilization energy of –318.6 kJ mol^{-1}, along with the measured NMR spectroscopic shifts of $\delta(^1H)$ = 7.76 ppm and $\delta(^{13}C)$ = 136.4 ppm (see Figures S1 and S2 in the Supporting Information), correlate well with the earlier published data and suggest a low coordinating ability for **I**.

A more accurate way to predict the coordination behaviour of an ionic liquid is to use the Gutmann donor numbers (*DN*).[26] Although originally introduced for conventional organic solvents, we found that this parameter can quite reliably be transferred to ionic liquids.[27] If the *DN* of a solvent is higher than that of a particular ligand of a metal complex, the anion of the ionic liquid is expected to displace the ligand. These *DN*s can easily be obtained by applying the concept of Ehrlich and Popov, who used the chemical shift of the ^{23}Na signal (abundance = 100%) of $NaClO_4$, dissolved in the appropriate solvent to determine this value.[28] We found a *DN* value of 31.8 kJ mol^{-1} for **I**, which is low compared to other imidazolium-based ionic liquids, located between that for the fluorinated ionic liquids [emim][NTf_2] (*DN* = 46.9 kJ mol^{-1}) and [emim][BF_4] (*DN* = 30.6 kJ mol^{-1}), and clearly suggests a weak coordinating ability for **I**.

Stability of [emim][ClO_4]

With respect to the hazardous nature of organic perchlorates, we tested the stability of **I** according to the UN Test Series UN 3a to UN 3d.[29] This series includes tests on mechanical stimuli (impact and friction sensitivity) as well as its thermal stability (heat and flames). The impact and friction sensitivity were determined with a drop hammer or friction-test apparatus (Reichel & Partner GmbH) in agreement with standard procedures of BAM (Bundesanstalt für Materialforschung und -prüfung).[30] In terms of the impact sensitivity, a weight of 5 kg fell from a height of 0.8 m onto a sample of **I**. An explosion was not observed and **I** seems to be insensitive to impacts with an energy up to 39 J. To determine its friction sensitivity, the ionic liquid was subjected to a static vertical compression force while being moved in horizontal direction on a sliding anvil. Up to a force of 360 N, **I** did not explode but decomposed accompanied by hushed crackling noises and decolouration. Therefore, **I** has to be categorized as less friction sensitive.[31] Prior to a long-time test of the thermal stability, DSC curves (Linseis PT 10, 35 to 340 °C, 5 K min^{-1}) were recorded to estimate its stability at elevated temperature. As shown in Figure 3, the onset of exothermic decomposition was observed at 186 °C. However, in agreement with the DSC measurements, **I** was found to be stable under the conditions of a long time test (i.e., a constant heating at 75 °C for 48 h).

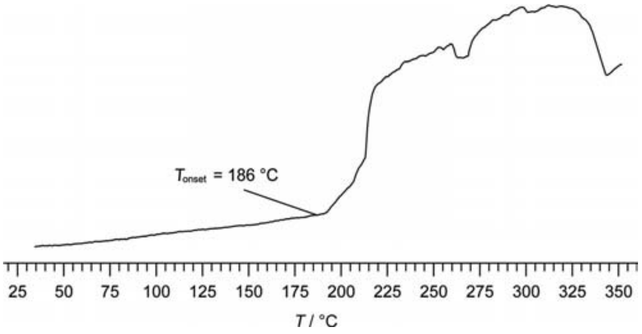


Figure 3. DSC of **I**. The onset of exothermic decomposition is observed at 186 °C.

A small-scale fast-cook-off test (FCO) was used to determine a transition from deflagration to detonation for unconfined substance quantities. Therefore, an open plastic beaker was filled with the substance (25 g). It was placed in a bed of kerosene-soaked sawdust and ignited electrically. About 2 min after ignition, **I** heavily deflagrated accompanied by loud crackling noises; an explosion or detonation did not occur.

According to the requirements for an interim hazard classification (IHC), **I** passed the appropriate tests (UN 3a–3d). Therefore, it would be likely that any US authority would issue an interim hazard classification.

Conclusion

The experimental studies clearly revealed that both synthetic methods employed are suitable for the synthesis of [emim][ClO_4]. Compared to the classical metathesis procedure used by Chan et al., both methods reported here start with notably cheaper material. Besides the available laboratory equipment, other factors that determine which method to select include the required amount and quality of the IL. Though both synthetic routes result in a good elemental analysis, membrane-assisted synthesis achieved a higher optical purity (see Figure S3 in the Supporting Information). For applications that require **I** to be of a high (optical) purity (e.g., analytical applications), membrane-assisted metathesis is preferred, otherwise many time-consuming workup steps are necessary. On the contrary, larger quantities can be synthesized more easily with standard laboratory equipment using the direct metathesis process. According to the performed UN Test series on the stability of **I**, this IL is not an explosive substance. In a subsequent computational study we calculated several detonation parameters.[32] The obtained values for the detonation velocity and pressure are significantly lower than those of TNT. Despite being relatively stable against mechanical stress, the friction test leads to the conclusion that **I** has to be categorized as a hazardous explosive material. Therefore, **I** would not become a commonplace ionic liquid like [emim][NTf_2]. Due to the fact that most ionic liquids with a weak coordinating ability exhibit a low polarity and therefore a hydrophobic character, **I** can be an interesting addition to this group of ionic liquids, since it exhibits a hydrophilic character despite its low *DN*. On the basis of its properties and the low viscosity (65.8 cP at 25 °C), interesting applications for **I** are feasible, especially for studies in coordination chemistry. To which extent these can be realized is the subject of current and future investigations.

Experimental Section

General: All chemicals used in this study were of analytical reagent grade or of the highest purity commercially available. Nitromethane, dichloromethane, $LiClO_4$ and perchloric acid (70% solution in water) were purchased from Acros Organics, and nitromethane was distilled twice before use. The ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate, [emim][$EtSO_4$], was purchased from Solvent Innovation/Merck.

Direct Metathesis: [emim][$EtSO_4$] was purified from traces of other chemicals by repeated extraction with a mixture of dichloromethane and water in a 1:1 ratio. To achieve a colourless ionic liquid,

[emim][EtSO$_4$] was stirred for one week with activated charcoal (Acros Organics: Norit A SUPRA) under high vacuum at a temperature of 55 °C. After filtration with a Millipore filter, Ø = 0.2 µm, the water content was determined by Karl Fischer titration and found to be 0.03 %. All the subsequent operations were performed under nitrogen atmosphere.

A solution of [emim][EtSO$_4$] (70 mL, 0.36 mol) in a solvent mixture (150 mL; dichloromethane and nitromethane, 1:3) was added to a solution of LiClO$_4$ (38.3 g, 0.36 mol) dissolved in the solvent mixture (400 mL) at 0 °C. Within several seconds Li[EtSO$_4$] began to precipitate as a bulky white solid. After stirring constantly for 3 h, the precipitate was filtered and washed two times with dichloromethane. After removal of the solvent mixture under vacuum and drying under high vacuum, [emim][ClO$_4$] was obtained as a clear, colourless liquid in a yield of 71.6 g (94 %).

Membrane-Assisted Metathesis: [emim][EtSO$_4$] was used without any purification. A solution (300 mL) of [emim][EtSO$_4$] (5 wt.-%) in deionized water was circulated through the feed chamber. Deionized water (300 mL) was circulated in both the product and coproduct chambers, in which [emim][OH] and HEtSO$_4$ are enriched during the experiment. Electrode chambers were flushed with an aqueous solution of NaSO$_4$ (5 wt.-%). A constant current of 2.1 A was applied and the production was stopped when the voltage was raised 5 V above its minimum plateau (15 V). The concentration of the [emim][OH] solution (330 mL, 0.114 mol L^{-1}) was then determined by titration with 0.1 M HCl to pH 7. An equimolar amount of perchloric acid (0.92 mol L^{-1}, 41 mL) was added and the water was removed under high vacuum.

Supporting Information (see footnote on the first page of this article): Figures S1 and S2 show ^{1}H and ^{13}C NMR spectra of [emim]-[ClO$_4$]; Figure S3 shows UV/Vis spectra of [emim][ClO$_4$], comparing the applied synthetic procedures.

Acknowledgments

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