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Volume 18 | Number 7 | 7 April 2016 | Pages 1821–2242

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ISSN 1463-9262

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# Dimethyldioxirane (DMDO) as a valuable oxidant for the synthesis of polyfunctional aromatic imidazolium monomers bearing epoxides.

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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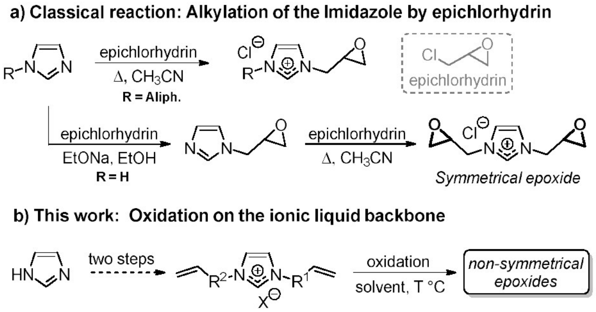
**Conventional organic salts represent a new paradigm in many areas of research. Despite their great potential, an improvement of their physicochemical properties requires the chemical modification of their intrinsic structure. Thus, an efficient pathway was developed for the preparation of polyfunctional imidazolium monomers incorporating aromatic rings and terminal epoxides which presented a real synthetic challenge. In this work, we describe the reactivity of various oxidizing agents to develop a strong, clean and powerful methodology to generate epoxidized salts. Various reactions conditions for the formation of the epoxides were investigated such as the role of the cation and the counterion as well as the influence of an aromatic and/or aliphatic linker chain. Finally, we have evaluated the thermal properties of these new polyfunctional salts by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).**

Versatile organic salts form a new fundamental class of compounds[1] with many applications in organic synthesis, analytical chemistry, electrochemistry, materials science and many other fields.[2] In all these areas, imidazolium skeleton represents the most interesting structure with several efficient and complementary physicochemical properties including a good conductivity, high thermal and electrochemical stability, low volatility and nonflammability.[3] However, discussing their chemical stability will depend on the functionalization (or not) of the whole pattern.[4] From conventional imidazolium salts ([Bmim][$PF_6$], [Emim][$NTf_2$],...), these particularly inert ionic liquids will be mainly used as reaction media and in some cases, they can be reused several times.[5] Depending on the imidazolium backbone, the ionic liquids can also influence positively during a process through different interactions. Thus, some ionic liquids which display stable mesophases over a wide temperature range[6] were used as anisotropic fluids.[7] To influence the stereochemical result of asymmetric syntheses, chiral ionic liquids were also used[8] either as a solvent and/or organocatalyst to induce the chirality.[9] In a recent past, while many ionic liquids were employed as catalysts or ligands,[10] only few efficient pathways to polyfunctional ionic liquids as starting materials were reported, and this despite the growing demand of the scientific community to use these new salts in drug synthesis or drug delivery systems[11] as well as monomers to access to polymerized ionic liquids.[12] In this sense, incorporating a terminal epoxide on ionic liquid skeleton represents a real challenge as they can provide access to new reactive imidazolium skeletons.[13]

To date, alkylation of the imidazole ring using highly toxic and carcinogen epichlorohydrin leads to the direct insertion of an epoxide close to the heterocycle, while a second alkylation affords a symmetrical diepoxide salt (scheme 1a).[14] In this work, we disclose an efficient and direct method to synthesize non-symmetrical diepoxides from polyfunctional ionic liquids under mild conditions using an oxidation reaction (scheme 1b).



***Scheme 1.*** Access to ionic liquids containing epoxides.

In the recent years, new epoxy monomers bearing a quaternary ammonium were designed and synthesized to introduce cationic groups covalently bonded into the polymer network.[15] In this way, the cationic moiety is attached onto the network and the counter anion is the only mobile ion. Unfortunately, there is no reliable and flexible methodology in the literature to prepare these organic salts carrying epoxides and poor knowledge regarding their use. Thus, polymerized ionic liquids are prepared from their corresponding monomers obtained by organic synthesis which constitutes crucial precursors for the development and processing of gelled electrolyte polymers. Indeed, the design of three-dimensional polymer

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of imidazoliums by $^1H$, $^{13}C$ and $^{19}F$ NMR, Mass spectrometry, DSC, TGA and IR. See DOI: 10.1039/x0xx00000x

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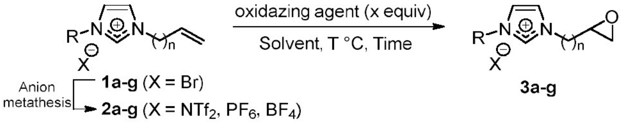
DOI: 10.1039/C7GC02372C

networks that combine excellent thermal stability, high mechanical performance as well as improved ionic conductivity depend on the structure of these monomer precursors.[16] For these reasons, we have focused this research on the development of a short and efficient access to new nitrogen heterocycles bearing epoxides by selective oxidation of ionic liquids. Nevertheless, depending on the conditions, an undesired ring opening reaction of the epoxide promoted by the ionic liquids[17] could occur during the oxidation process. This well-described reaction[18] will require investigation to overcome a possible disadvantage of this pathway.

In order to perform the epoxidation of salts on a several gram scale, the oxidizing agent must present an excellent reactivity and be easily accessible or available. Moreover, depending on the reaction conditions, the by-product of the oxidation must not decrease the stability of the epoxide and must be easily removed during the extraction and the purification of the product. In this work, we have examined the reactivity of five oxidants (oxidation rate, number of equivalents, temperature, alkene conversion, chemical kinetics) then we have isolated the product of the reaction in each cases and evaluated the issues related to the removal of the excess of oxidant, the formation of by-products resulting either from the reduction of the starting material or the ring opening of the epoxide.

Thus, in presence of meta-chloroperoxybenzoic acid (mCPBA, 1.4 to 3 equiv), the epoxidation of the model substrate **2a** gave a complete conversion after several days at room temperature (entries 1-2). A reasonable reaction time of 48 h was reached by heating the reaction at 40 ° C with 3 equiv of mCPBA (entries 3-4). Beyond this temperature, the formation of the ring opening by-product was noticed in NMR. Oxidation of **2a** in the presence of freshly prepared trifluoroperacetic acid (TFPAA, 1.4 equiv) was significantly more effective and afforded the corresponding epoxide in 100% conversion after 4 h (entry 5). However, the formation of a strong acid by-product (trifluoroacetic acid) caused partial ring opening of the epoxide during the concentration of the final product. To

***Table 1.*** Optimization of the epoxidation reaction



| Entry[a] | R | X | n | Oxidazing agent (equiv) | | Solvent | Temp | Time | Conv. (%)[b] | Yield (%)[c] | Salt |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | $NTf_2$ | 2 | mCPBA | 1.4 | $CH_3CN$ | rt | 12 d | 100 | 79 | **3a** |
| 2 | $CH_3$ | $NTf_2$ | 2 | mCPBA | 2.8 | $CH_3CN$ | rt | 6 d | 100 | 85 | **3a** |
| 3 | $CH_3$ | $NTf_2$ | 2 | mCPBA | 1.4 | $CH_3CN$ | 40 °C | 9 d | 100 | 84 | **3a** |
| 4 | $CH_3$ | $NTf_2$ | 2 | mCPBA | 3 | $CH_3CN$ | 40 °C | 48 h | 100 | 92 | **3a** |
| 5 | $CH_3$ | $NTf_2$ | 2 | TFPAA | 1.4 | $CH_2Cl_2$ | rt | 4 h | 100 | 85 | **3a** |
| 6 | $CH_3$ | $NTf_2$ | 2 | PAA | 2.8 | $CH_2Cl_2$ | rt | 48 h | 30 | / | **3a** |
| 7 | $CH_3$ | $NTf_2$ | 2 | UHP | 12 | $CH_3OH$ | rt | 48 h | 50 | / | **3a** |
| 8 | $CH_3$ | $NTf_2$ | 2 | DMDO | 1.4 | $(CH_3)_2CO$ | rt | 6 h | 100 | 99 | **3a** |
| 9 | $CH_3$ | $NTf_2$ | 5 | mCPBA | 1.4 | $CH_3CN$ | rt | 72 h | 100 | 70 | **3b** |
| 10 | $CH_3$ | $NTf_2$ | 5 | DMDO | 1.4 | $(CH_3)_2CO$ | rt | 2 h | 100 | 89 | **3b** |
| 11 | $CH_3$ | $NTf_2$ | 1 | mCPBA | 5 | $CH_3CN$ | 40 °C | 30 d | 100 | 56 | **3c** |
| 12 | $CH_3$ | $NTf_2$ | 1 | DMDO | 1.4 | $(CH_3)_2CO$ | rt | 6 h[d] | 54 | / | **3c** |
| 13 | $CH_3$ | $NTf_2$ | 1 | DMDO | 2.4 | $(CH_3)_2CO$ | rt | 12 h | 100 | 96 | **3c** |
| 14 | $C_6H_5$ | $NTf_2$ | 2 | mCPBA | 2.4 | $CH_3CN$ | rt | 10 d | 88 | / | **3d** |
| 15 | $C_6H_5$ | $NTf_2$ | 2 | DMDO | 2.4 | $(CH_3)_2CO$ | rt | 12 h | 100 | 87 | **3d** |
| 16 | $C_6H_5$ | $NTf_2$ | 1 | DMDO | 2.4 | $(CH_3)_2CO$ | rt | 12 h | 100 | 100 | **3e** |
| 17 | $CH_3$ | $BF_4$ | 2 | DMDO | 1.4 | $(CH_3)_2CO$ | rt | 6 h | 100 | 100 | **3f** |
| 18 | $CH_3$ | $PF_6$ | 2 | DMDO | 1.4 | $(CH_3)_2CO$ | rt | 6 h | 100 | 80 | **3g** |

[a]Reactions performed on 0.240 mmol scale at 0.03 M concentration. [b]Determined by $^1H$ NMR of crude mixture. [c]Isolated yields. [d]No reaction evolution after 6 h

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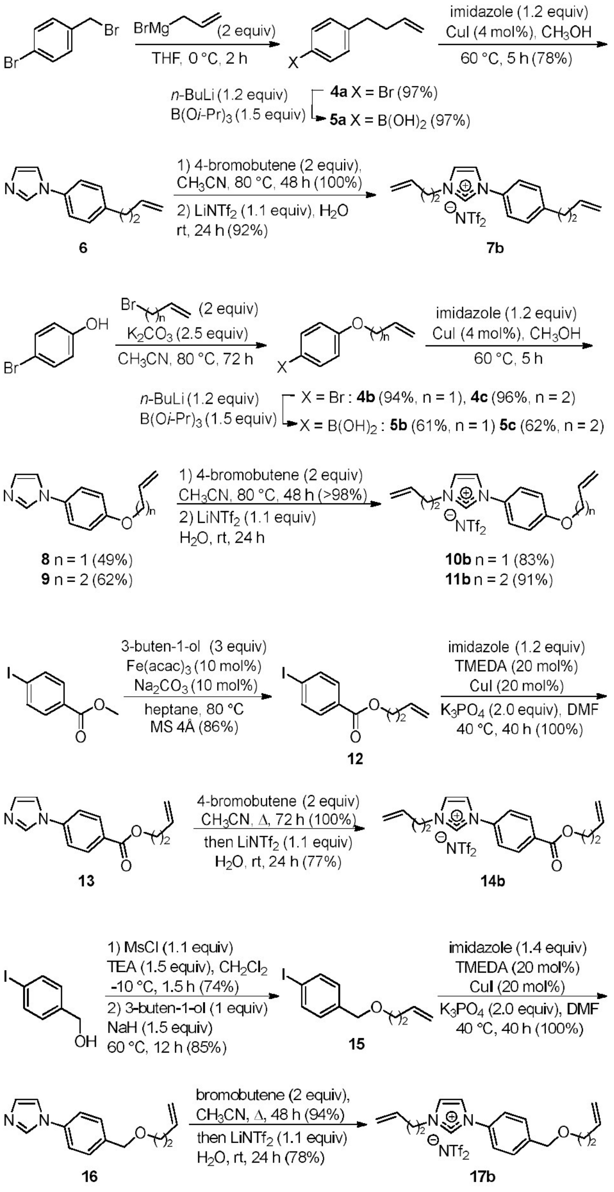
overcome this problem, the acid can be neutralized by filtration of the reaction mixture over $Na_2CO_3$. Worth of note, using the less oxidizing peracetic acid (PAA, 35% in acetic acid), the yield did not exceed 30% after 48 h despite a large excess of this reagent (entry 6). In the presence of 12 equiv of hydrogen peroxide-urea (activated by 2 equiv of DCC and 2 equiv of $Na_2CO_3$), the UHP was not effective enough to completely oxidize **2a** even after 48 h of reaction (entry 7). In order to circumvent the difficulties encountered previously, dimethyldioxirane was assessed thereafter. From a practical and feasible large-scale protocol[19a] containing acetone, oxone and sodium bicarbonate in distilled water, a solution of DMDO in acetone was prepared at a concentration of about 0.04-0.09 mol / L.[19] Oxidation of our model substrate **2a** with freshly distilled DMDO (1.4 equiv) provided complete conversion after 6 h at rt (entry 8) with acetone as a by-product that can be easily removed by evaporation (the slight excess of DMDO could be neutralized by addition of $Me_2S$). In order to confirm that DMDO was an efficient and clean oxidant at room temperature, we decided to modify the length of the chain between the imidazolium and the alkene moiety. Thus, salt **2b** (n = 5) was prepared and its oxidation was tried with mCPBA and DMDO in 72 h and 2 h respectively (entries 9-10). With the less reactive salt **2c** (n = 1), mCPBA could not completely oxidize the alkene (data not shown). In this case, 5 equiv of oxidizing reagent was required to give **3c** in 56% yield. On the opposite, a very clean oxidation was obtained when using 2.4 equiv of DMDO which afforded the epoxide **3c** in excellent yield (entries 12-13). When switching to aryl-imidazoliums, the salt **2d** was more difficult to oxidize when using mCPBA (entry 14) since 88% conversion was reached in the previously optimized conditions. Once again, DMDO (2.4 equiv) was required to obtain a full conversion and **3d** was isolated in 87% yield after 12 h at rt (entry 15). Similar result was obtained with **2e** and the corresponding oxidized salt **3e** was obtained in quantitative yield (entry 16). To note, the epoxidation of the $NTf_2$, $PF_6$ and $BF_4$ salts gave similar results (entries 8, 17 and 18). DMDO afforded the salts **3f** and **3g** after 6 h of reaction at rt. However, partial hydrolysis of **3f** was observed after several days which is in agreement with the known hygroscopic ionic liquids with $BF_4$ as counterion. Therefore, these anions have no influence on the oxidation step, whereas the ring opening by-product was observed on the epoxidation of the salt bromide **1a** which did not undergo metathesis of the anion (data not shown). From these results, we can confirm that DMDO represents an easy-to-use (N.B. safe storage at -20 °C for several month)[19a] and efficient reagent to prepare imidazolium epoxides in satisfactory yields although the protocol requires some adjustments depending on the nature of the salts. Compared with the other oxidizing reagents, the reaction rate is faster with a lower amount of DMDO to give a very clean product at room temperature after a simply evaporation of the volatile substances (extraction not required). A chemical kinetics of the epoxidation of **2a** is described in the supporting information.

Based on the results obtained above, this methodology was then applied to the synthesis of polyfunctional salts containing an aryl-imidazolium backbone. For this purpose, we have employed a copper-catalyzed arylation to create our carbon-nitrogen bond.[20] Recent advances with heterocycles[21] allow unprecedented exploitation of this coupling reaction to synthesize new aryl-imidazolium salts bearing functionalities. Thus, we have prepared several aryl-imidazolium salts such as compound **7b** without functional groups, compounds **10b, 11b** and **14b** which respectively have an ether and ester function directly attached on the aromatic ring and compound **17b** with a short aliphatic spacer. All the sequences described in scheme 2 are reproductive and feasible on large scale (several grams). These aryl-imidazolium salts were then subjected to previously optimized epoxidation reaction with either mCPBA or DMDO as oxidant.



***Scheme 2.*** Syntheses of functionalized aryl-imidazolium salts **7b**, **10b**, **11b**, **14b** and **17b**.

In the presence of an excess of mCPBA (4 equiv), the diepoxide **18** was isolated in 89% after 24 h at 40 °C from dialkene **7b** (table 2, entry 1). The same reaction performed at room temperature with 2.8 equiv of DMDO afforded the corresponding salt **18** quantitatively after only 12 h (entry 2). With electron donating group on the aromatic ring, an oxygen effect on the epoxidation was observed when mCPBA was used since imidazolium salt **19** was obtained in 65% yield after 5 days at 40 °C (entry 3). This effect was reduced when the oxidation was performed on the salt **11b** (entry 5). Swapping to 2.8 equiv of DMDO, the corresponding diepoxides of salts **10b** and **11b** were obtained quantitatively (entry 4) and in 92% yield (entry 6) respectively. The salt **14b** containing an ester reacted slower under the oxidation condition with mCPBA. In this case, 5

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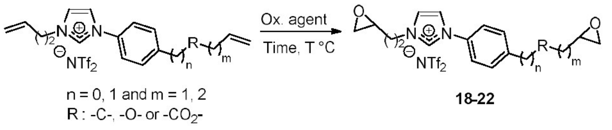
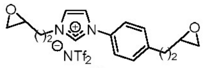
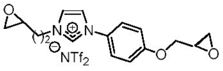
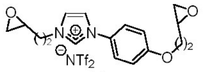
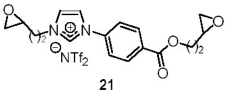
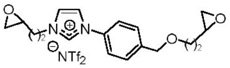
equiv of oxidizing reagent was required to give **21** in 88% yield and no difference was observed with DMDO (entries 7 and 8). Finally, the oxidized salt **22** with a short aliphatic spacer between the ether and the aromatic ring was isolated in 76% yield with mCPBA (entry 9). Once again, DMDO displayed a better result to afford this salt with a very high yield of 92% (entry 10).

***Table 2.*** Synthesis of polyfunctional imidazoliums diepoxides[a]



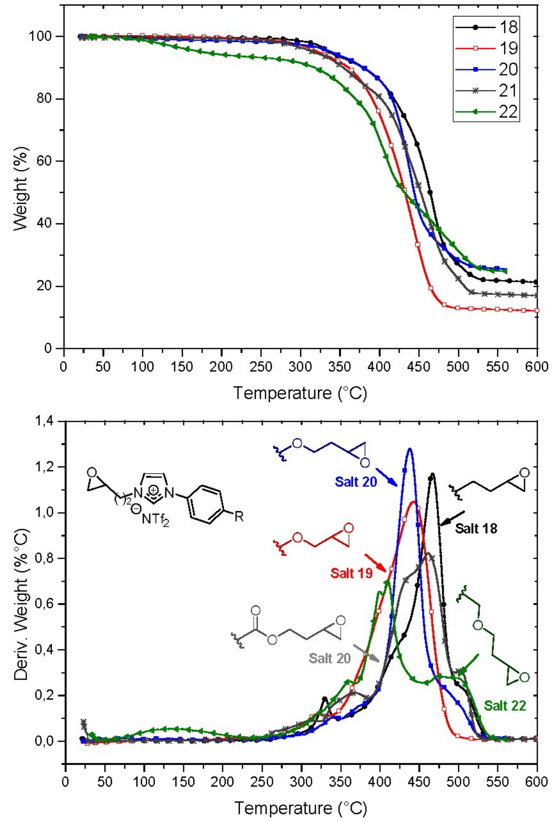
| entry | Ox. agent | Time<br>Temp. | Yield (%) | Salt |
|---|---|---|---|---|
| 1 | mCPBA | 24 h/40 °C | 89 |  18 |
| 2 | DMDO | 12 h/rt | 100 | |
| 3 | mCPBA | 5 d/40 °C | 65 |  19 |
| 4 | DMDO | 12 h/rt | 100 | |
| 5 | mCPBA | 24 h/40 °C | 89 |  20 |
| 6 | DMDO | 12 h/rt | 92 | |
| 7 | mCPBA[b] | 24 h/40 °C | 88 |  21 |
| 8 | DMDO | 5 h/rt | 92 | |
| 9 | mCPBA | 24 h/40 °C | 76 |  22 |
| 10 | DMDO | 12 h/rt | 92 | |

[a]Reactions performed with 2.8 equiv of DMDO or 4 equiv of mCPBA. [b]5 equiv of mCPBA was used. [c]Isolated yield

The thermal stability of the epoxy monomers **18**-**22** was then investigated by thermogravimetric analysis (TGA) using a Q500 (TA instruments) from 30 to 600 °C with a heating rate of 10 K.min$^{-1}$ under nitrogen atmosphere. The evolution of the weight loss in function of the temperature is presented in Figure 1. The decomposition temperatures and the percentage of degradation were measured and summarized in Table 3.

In all cases, an excellent thermal behavior of the epoxy monomers (> 390-400 °C corresponding to the maximal degradation temperature $T_{max}$) was noticed from the TGA curves. These results confirmed the thermal stability of the heterocycle imidazolium before the decomposition process[22] although the chemical nature of the fluorinated anion playing a key role on the thermal stability.[22,23] In the case of salts **18**-**22**, only the cation influenced the thermal stability since the same counter anion was used, *i.e.* $NTf_2$. Thus, the presence of a flexible spacer linked between the oxygen and the epoxide group (**20** vs **19**) or between the phenyl group and the oxygen (**22** vs **20**) led to an increase of the degradation temperature (figure 1). Indeed, for compound **20**, a weight loss of 11% was observed instead of 22% for compound **19** at 400 °C. Between compounds **22** and **20**, the difference was slightly lower with a maximum degradation temperature at 461 °C for **22** and 437 °C for **20**, respectively. Finally, the absence of ether or ester groups on the epoxy monomer induced a better thermal stability (salt **18**). In summary, the thermal stability of these new functional and reactive monomers can be classified as follow: **21**<**19**<**20**<**22**<**18**.

***Figure 1.*** Evolution of weight loss in function of temperature (TGA) and derivative of TGA curves (DTG).



The influence of the chemical nature of the salts on the polymer physical characteristics was then investigated. The glass transition temperature ($T_g$) of the epoxy monomers **18** to **22** are summarized in Table 3.

***Table 3.*** Thermal properties of the salts **18**-**22** (TGA/DSC).

| Salts | $T_g$ (°C) | $T_{max}$ (°C) | Weight loss (%) | |
|---|---|---|---|---|
| | | | at 300 °C | at 400 °C |
| **18** | -46 | 421-470 | 1.5 | 13 |
| **19** | -30 | 442 | 2.8 | 22 |
| **20** | -38 | 437-490 | 2.3 | 11 |
| **21** | -52 | 399-409 | 8.5 | 25 |
| **22** | -46 | 461-503 | 2.9 | 12 |

During the first heating at a rate of 10 K.min$^{-1}$ under nitrogen flow of 50 mL.min$^{-1}$, the DSC thermograms (see ESI) showed a heat capacity change corresponding to the glass transition temperature of all the epoxy monomer based-ILs. Thus, we obtained a $T_g$ between -30 °C and -52 °C depending on the functionalization of the imidazolium cation. Salts **19** and **20** having an electron donating on

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the aromatic presented a higher glass transition temperature of -30 °C and -38 °C, respectively. On the opposite, lower $T_g$ from -46 °C to -52 °C were observed for salts **18**, **21** and **22**. These results are in agreement with the ones known of imidazolium monomers having vinyl group (Tg between -65 °C and -81 °C).[24] In addition, no melting temperatures ($T_m$) characterized by the presence of an endothermic peak was observed for the different organic salts. This phenomenon is commonly described and reported in the literature of ionic liquids.[25]

## Conclusions

In conclusion, an efficient, versatile and clean methodology for the oxidation of preformed ionic liquids has been successfully developed. In this study, the potential of various readily available oxidizing agents was investigated and compared to establish the best conditions. According to the anion, the length of the aliphatic chain and the substituents on the imidazolium, we have shown that DMDO is the most efficient oxidizing agent to prepare imidazolium epoxides in excellent yields and forming acetone as inert and volatile by-product. Compared to mCPBA, DMDO is particularly reactive at room temperature, the reaction rate is faster when using a lower amount and the methodology does not require extraction of the product at the end respecting several principles of the green chemistry with especially the use of less hazardous chemicals (3) with a reduction of solvents used (5) while avoiding waste (1). This methodology also leads to increased energy efficiency (6) with only acetone as environmentally friendly by-product (10). In a second part, we have applied this strategy to develop new pathways to polyfunctional aryl-imidazoliums bearing two epoxides in multi-grams scale. Despite their complexity, all diepoxides were obtained in excellent yields. In addition, DSC and ATG analyses confirm the high purity and thermal stability of these new salts. Finally, the influence of the chemical nature of the cation on the thermal properties was investigated by the presence of a functional group and/or a spacer between the polymerizable group and the ionic part. All these data will play a key role on the ionic conductivity of the future polymer electrolytes.[26]

## Acknowledgements

The Ministery of Higher Education and Research, the “Region Basse Normandie” (fellowships to C.C.), CNRS, and the European Union (FEDER) are greatly acknowledged for funding this work. We thank the LABEX SynOrg (ANR-11-LABX-0029) for financial support and Dr Majdouline Roudias for helpful discussions.

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View Article Online
DOI: 10.1039/C7GC02372C

Graphical abstract :