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The dialkylcarbonate route to ionic liquids: purer, safer, greener?

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The synthesis of ionic liquids can generate large amounts of waste and use toxic or expensive raw materials. In this short review, we focused on one of the most promising pathways to large scale environment-friendly productions of ionic liquids. The "dialkylcarbonate route" has already allowed the preparation of more than one hundred original ion pairs, avoiding the use of pollutant alkylating agents and non-sustainable anion exchange materials, in a halide-free and water-free process.

1. Introduction

Ionic liquids are a unique class of salts composed of large and asymmetric ions making many of them liquid at room temperature.¹ The use of ionic liquids often leads to more sustainable chemical process, catalytic reactions or separations. This is linked with their unique properties, the most remarkable being their negligible volatility in a large temperature range and the possibility of tuning their liquid properties by combining different cations and anions. Because of these properties, ionic liquids can be recycled after their use thus minimising the waste of the overall process.

Sustainability of ionic liquids can still be improved, as far as their life cycle is concerned, by decreasing the environmental impact of their synthesis. In fact, researchers are becoming aware of environmental concerns regarding toxicity and persistence in the environment making reagent choice and control of the quantity and nature of waste generated when preparing the salts important issues if ionic liquids are to be considered as sustainable, green solvents.² This is particularly important as the scope of ionic liquids is already vast, with more than 17 000 patents using ionic liquids in applications having been filed, and almost 60 industrially implemented applications of ionic liquids (pilot or commercial) identified in March 2019.³

Although some efforts have been made towards improving the synthetic routes of ionic liquids, no real paradigm shift has been observed so far. In fact, incorporating sustainability into the selection of a chemical reaction or of a synthetic route

is a complex task. Thermodynamic, economic, and environmental issues need to be simultaneously considered in the design or the improvement of a chemical reaction. One simple way of conducting this multidimensional optimisation is to adopt different metric indexes, weighted by appropriate factors that allow to assess and compare reaction routes. Simple metrics such as *E*-factor, E_{fac} , atom economy, AE, mass efficiency, ME or yield, *Y*, are often used to quickly give insights into the potential environmental impact of a chemical reaction. The outcome of this simple analysis is, nevertheless, often misleading as it does not take into account, for example, of the different treatments required by distinct chemical wastes, of solvent use or of purification difficulties.

Life cycle assessment (LCA) is now recommended as the most accurate method to evaluate the environmental performance of any chemical process. LCA is a tool based on the identification of the environmental impact of each step and on considering the entire life cycle of the chemical process from 'cradle to grave'. This practice is not yet generalised for ionic liquids because they are not yet manufactured and used widely at an industrial scale. Some attempts to address this issue have been published⁴ as life cycle analysis was made for new ionic liquids for carbon dioxide capture thus contributing, amongst other factors, to aid in the synthesis process.

Some improvements towards more sustainable practices in the synthesis of ionic liquids, such as the use of microwave or ultrasound assisted reactions, have been recently highlighted.⁵ However, most synthetic pathways continue to make use of toxic or polluting alkylating agents (such as alkyl halides, and dialkyl sulfates) as well as waste-producing anion exchange processes. With this review, we aim to highlight the issues present with the current generally adopted two-step synthesis of ionic liquids, and discuss a more sustainable alkylation procedure, using dialkyl carbonates. We highlight the benefits of using such a route through the use of different simple metrics

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such as the E -factor (E_{fac}) that can be significantly reduced to values close to zero.

2. Ionic liquid synthesis

The first step for estimating the life cycle environmental impact of ionic liquids in novel processes or as replacement media in existing chemical unit operations, is the analysis of their preparation method. Because ionic liquids are a family of solvents still under development, *i.e.* prepared only at a laboratory scale, different routes should be considered to minimize negative environmental impacts. Different routes can differ on the starting materials, the nature of the waste generated or the reactions themselves. All should be considered to assess the environmental impact of ionic liquids.⁶ The most common synthesis paths of ionic liquids from commercially available reagents involves two steps (Fig. 1). Firstly, a neutral organic molecule is alkylated to form a salt as in the Menshutkin reaction shown as an example in Fig. 2. The salt contains the desired cation, the anion being then exchanged through metathesis to prepare the ionic liquid containing the appropriate ion pair.

2.1. Starting materials

Careful choice of starting materials can lead to a more sustainable preparation of ionic liquids, either by decreasing the impact of the reagents themselves, or by using chemicals leading to less harmful waste products. Common neutral

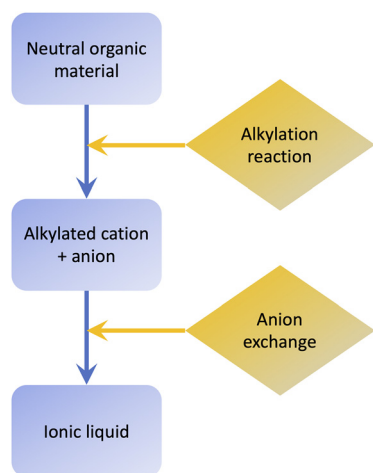


Fig. 1 Two-step synthesis path for the preparation of ionic liquids.

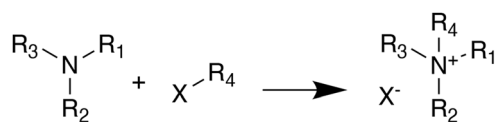


Fig. 2 Example of a Menshutkin reaction between a tertiary amine and a haloalkane to form a halide salt.

organic substrates used for the preparation of ionic liquids are tertiary amines, tertiary phosphines, and heterocyclic compounds (*e.g.* imidazoles, pyridines, alky pyrrolidines) leading, after alkylation, to the three major families of ionic liquids: quaternary ammoniums, phosphoniums or imidazoliums.

These starting compounds are generally commercially available with a high purity except for phosphines that might contain significant amounts of phosphine oxides, which must be removed by appropriate purification processes.⁶ Heterocycles often present a long-term toxicity to humans but have the advantage of not being flammable. Non-cyclic tertiary amines and tertiary phosphines on the other hand, are respectively slightly toxic and flammable, and corrosive and flammable. They are frequently considered as less harmful despite complexities in their handling.

The origin of these starting materials is varied. Tertiary organophosphines are commonly synthesised with a good yield ($Y > 80\%$) from the free-radical addition of phosphine, a highly toxic compound, to oil-derived unsaturated compounds in the presence of a free radical promoter. Most of the industrially significant tertiary amines are prepared by a chemical process, often regarded as green, that uses ammonia in an alkylation reaction with alcohols. More specific tertiary amines are produced by alternative routes, all presenting a relatively low environmental impact. Heterocyclic compounds that are used in the preparation of ionic liquids are frequently used as precursors in pharmaceutical industry and are prepared, often in low yield processes, by bio- or oil-based starting products. Depending on the properties sought, ionic liquids should preferably include cations prepared from starting materials with the lowest possible environmental impact.

2.2. Alkylation reaction

The most frequently used alkylating agents are alkyl halides. Although very efficient, these materials are also generally toxic, flammable, carcinogenic, and harmful to the environment. Commercially available alkyl halides are frequently not pure enough and so a purification is required. This step involves washing the alkyl halide with various acids and bases and is followed by multiple drying and distillation steps⁷ thus generating large amounts of harmful halogenated and aqueous waste.

Menshutkin reactions are robust coupling reactions commonly used to create a plethora of ionic liquids (Fig. 2). These reactions have a high atom economy (100%) and high yield (commonly $>95\%$), their main drawback being linked with the need of purification of the products as the alkyl halide used as a reactant is normally present in a slight excess (typically 10–20% mole fraction). Other impurities, such as possible by-products formed by elimination reactions of the alkyl halide, also need to be removed.⁸ As the prepared salts cannot be distilled, the usual purification steps consist in recrystallization, washing with solvents and using sorbent materials such as alumina or activated charcoal. These purification steps generate significant amounts of toxic, halogenated waste that has to be treated using expensive, and energy intensive procedures.

Dialkyl sulfates, dialkyl phosphates and alkyl triflates are alternative alkylating agents that are easier to purify than haloalkanes but more difficult to prepare and having comparable toxicities.^{8,9} These alkylating agents are preferred in the preparation of ionic liquids including alkyl sulfate, dialkyl phosphate or triflate anions that are then obtained in a single preparation step. It is however more difficult to use these alternative alkylating agents as a precursor to other ionic liquids as these anions are difficult to exchange.

2.3. Anion exchange

The salts prepared after the alkylation of the neutral organic reactants lead to salts that are solids near room temperature or viscous liquids that are not appropriate for most applications. Anion exchange is thus necessary to prepare ionic liquids with the required properties.

The three main methodologies are currently used to perform the anion exchange: acid/base neutralisation; the use of an ion exchange column; and ion exchange metathesis. They are schematically represented in Fig. 3.

In acid/base neutralisation, the initial salt must contain a basic anion that reacts with an added acid, its conjugate base being the anion of the final ionic liquid (scheme A, Fig. 3). This reaction is rarely used because the anions obtained after Menshutkin alkylations (halides, sulfates, phosphates, *etc.*) are typically not basic enough and because the removal of residual water from the final product is often difficult.

In the more commonly used ion exchange columns (scheme B, Fig. 3), the precursor salt of the ionic liquid is passed through an ion exchange resin containing the desired anion. This method presents several advantages including a

high conversion (often close to 100% when appropriately used) and the possibility of reusing or regenerating the resin. The drawback is the need of large quantities of solvent with the consequent increase of the E -factor E_{fac} for the preparation of the ionic liquid.

By far the most commonly used method is the anion exchange metathesis (scheme C, Fig. 3). This method involves mixing the precursor ionic liquid (AX) with a metal salt (MB) in a solvent, and collecting the desired ionic liquid (AB). Silver and lithium salts are commonly used for metathesis as they are insoluble in many solvents where ionic liquids are soluble, leading to precipitation of either the ionic liquid AB or the by-product MX that can then easily be separated by filtration, the ionic liquid product being washed to remove any impurities. Metathesis does not generate as much waste as the ion exchange method, however the waste generated from successive extractions can contain metal salts which can be toxic and harmful to the environment.

2.4. Drawbacks of actual ionic liquids preparation: a case study of ultra-pure ionic liquid preparation

As an example of the environmental impact of ionic liquid preparation, we analyse the synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$),¹⁰ a common and widely studied salt. E_{fac} is used as green metric. As the purification reported by Clark *et al.*¹⁰ was far more rigorous than usually required, we do not take into account the purification of starting materials, in order to make a more appropriate comparison with alternative methodologies. However, it should be noted that purification is often required for reagents in a Menshutkin reaction, and this will further increase the overall E_{fac} .

The first step consists in the synthesis of $[\text{C}_4\text{C}_1\text{im}][\text{Cl}]$ from *N*-methyl-imidazole and 1-chlorobutane. To synthesize 100 g of it, the Menshutkin reaction is carried out in 30 mL EtOAc, and subsequent purification of $[\text{C}_4\text{C}_1\text{im}][\text{Cl}]$ generate 245 g of waste (MeCN and EtOAc). Thus this step has an $E_{\text{fac}} \approx 2.75$.

The subsequent conversion of this to the final product is done through anion exchange metathesis with lithium bis(trifluoromethylsulfonyl)imide. The preparation of 60 g of pure 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$) generated 900 g of waste during the reaction and the subsequent purification (from the use of dichloromethane, water and *n*-hexane and the by-product LiCl). This second step has an E_{fac} of ≈ 15 . Comparing this to general E_{fac} values from other chemicals preparation processes,¹¹ one can see that this is very high, being comparable to 'fine chemicals'. As many of the proposed uses for ionic liquids are as solvents or bulk chemicals, it clearly appears that they compare very poorly to other bulk chemicals, which have systematically $E_{\text{fac}} < 5$.

Looking carefully at the breakdown of the E_{fac} above, one can see that the main production of the waste occurs during the anion exchange metathesis, and is due to the purification of the final ionic liquid when removing excess halide ionic liquid which is not easily separated from the final product.

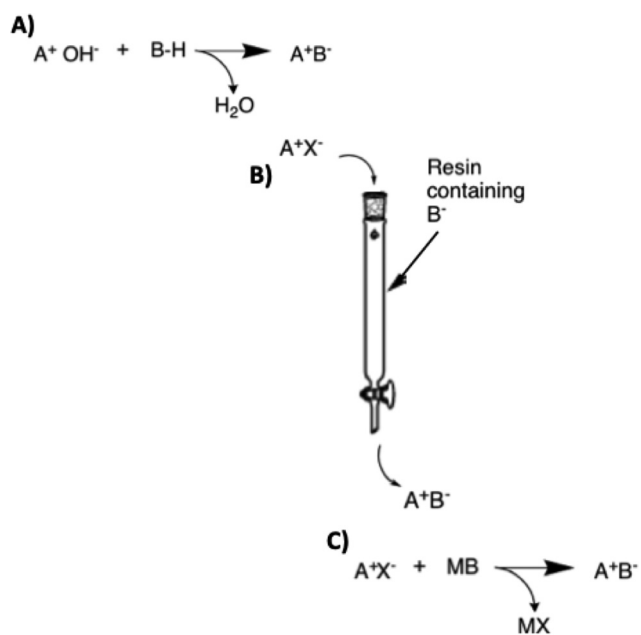


Fig. 3 Anion exchange methods: (A) Acid/base neutralisation, (B) ion exchange column, (C) ion exchange metathesis.

This case study highlights the issues using haloalkanes to synthesise ionic liquids. They are difficult and wasteful to purify, require less sustainable anion exchange methods, and cause purification problems in the alkylation and anion exchange steps.

3. Using the dialkyl carbonate route

A very general route to ionic liquids has emerged over the last twenty years, which involves the use of a dialkyl carbonate (DAC) as the alkylating agent. DACs, the most common being dimethyl carbonate (DMC), are widely used as solvents, alkoxy-carbonylating or alkylating agents, and are considered to be sustainable chemicals.¹² DMC is notably recommended as a sustainable solvent by the CHEM21 consortium on a set of safety, health and environment criteria.¹³

Selva and Perosa examined 33 published alkylation procedures using four alkylating agents: DMC, methyl iodide, dimethyl sulfate, and methanol. By comparing the AE and ME for each of these reactions, as well as considering the by-products, the toxicity of the agents, and the reaction conditions, they determined that DMC and methanol performed the best. Further comparing these two, they concluded that DMC was by far the less impactful solvent, due to its non toxicity, higher reactivity and easier recyclability of the catalytic medium.¹⁴

As early as 1988, Mori *et al.* used DMC as an alkylating agent to quaternize trialkylamine and trialkylphosphine and synthesized some ionic liquids, although they did not identify them as such.¹⁵ In 1999 Ue *et al.* also presented a similar synthesis in their patent on the synthesis of *N*-alkyl-*N*-methyl-imidazolium salts using DMC as the methylating agent.¹⁶ In 2002, the same research team used this route to synthesize 1-ethyl-3-methyl-imidazolium tantalumhexafluoride ($[\text{C}_2\text{C}_1\text{im}][\text{TaF}_6]$) and 1-ethyl-3-methylimidazolium niobiumhexafluoride ($[\text{C}_2\text{C}_1\text{im}][\text{NbF}_6]$).¹⁷

Finally, from 2000 to 2022, around 70 publications (articles and patents) reported studies on, or synthesis using the dialkyl carbonate route to ionic liquids, highlighting the interest in this more green synthesis of ionic liquids.

3.1. General mechanisms and experimental procedures

Nucleophiles can react with DAC *via* two distinct pathways: one of these leads to alkylation of the nucleophile ($\text{B}_{\text{AL}2}$ type mechanism, Fig. 4, pathway (1)), and the other to the alkoxy-

carbonylation of the nucleophile ($\text{B}_{\text{AL}2}$ type mechanism, Fig. 4, pathway (2)). In the case of the DAC route to ionic liquids, only the alkylation pathway is desired. It generally requires high temperatures ($>90\text{ }^\circ\text{C}$),¹² and leads to the formation of the DAC-alkylated cation and an alkylcarbonate anion (imidazole-based cations have an exception, which is discussed in section 3.2).

The experimental procedure followed in the alkylation using DMC (the most reactive DAC) involves heating the starting nucleophile with an excess of dimethyl carbonate in methanol in a sealed, high pressure vessel at temperatures between $80\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$ for 10 to 24 hours, depending on the substrates. Interestingly, even at relatively low temperatures ($\approx 80\text{ }^\circ\text{C}$), no competition with the methoxycarbonylation has been reported.¹⁸ Holbrey *et al.* have achieved, using microwave-assisted heating, the alkylation of phosphines, amines, and imidazoles with reduced reaction times, with excellent to quantitative yields.¹⁹ Kalb *et al.* investigated the industrial production of ionic liquids synthesized through the DMC route using a continuous flow method. The ionic liquid 1-ethyl-3-methylimidazolium methylcarbonate $[\text{C}_1\text{C}_1\text{im}][\text{MeOCO}_2]$ could be prepared with a productivity of 4.2 kg h^{-1} .²⁰ According to a recent kinetic study, the optimum productivity of continuous preparation of $[\text{N}_{10111}][\text{MeOCO}_2]$ *via* DMC route would be as high as $122\text{ kg h}^{-1}\text{ L}^{-1}$ ($T = 270\text{ }^\circ\text{C}$, residence time = 0.25 min, molar ratio 1 : 2.5 : 10 (*N*-dimethyldecylamine : DMC : MeOH)).²¹

After alkylation, the only purification step required is the evaporation of the solvent and of the excess of DMC, normally using a primary vacuum. The resulting alkyl carbonate ionic liquid can then be used as synthesized, or as an intermediate to prepare other ionic liquid, for example *via* the acid/base neutralisation as described in section 3. In these cases, a Brønsted acid (AH), a trimethylsilyl precursor ($\text{Me}_3\text{Si-A}$) or an ammonium salt (NH_4A) is added to react with the basic alkyl carbonate anion. The reaction proceeds with the alkyl carbonate anion being transformed in CO_2 and a volatile by-product (which depends upon the reagent added) leading to the formation of a new ion pair. Alternatively, the alkyl carbonate anion can also be converted into a hydrogen carbonate anion in the presence of air and water, further extending the scope of this methodology (Fig. 5).^{22,23} The experimental procedure would consist simply on the stoichiometric addition of a Brønsted acid into the alkyl carbonate salt, neat or in alcoholic solution (MeOH or EtOH as solvent), at room temperature. Effervescence of CO_2 can be used to monitor the progress of the anion metathesis, which is generally achieved in less than few hours.²² Again, no further purification is required except for the removal of side products *in vacuo*. These reactions are quantitative in yield.

3.2. The imidazolium case: formation of zwitterionic species

Attempts to synthesize imidazolium ionic liquids through the DAC route have faced difficulties, related to the formation of the zwitterionic species 1,3-dimethylimidazolium-4-carboxylate $[\text{C}_1\text{C}_1\text{im-4-CO}_2]$ and 1,3-dimethylimidazolium-2-carboxylate $[\text{C}_1\text{C}_1\text{im-2-CO}_2]$. Since 2001, several syntheses with similar experimental conditions were reported leading to the simul-

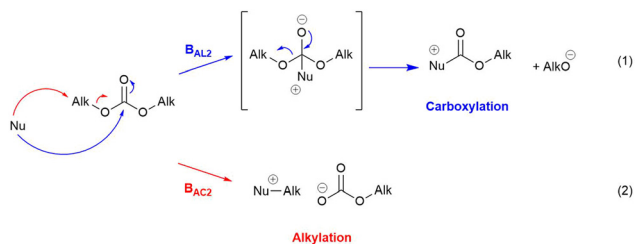


Fig. 4 Alkylation and alkoxy-carbonylation by dialkyl carbonate reagents.¹²

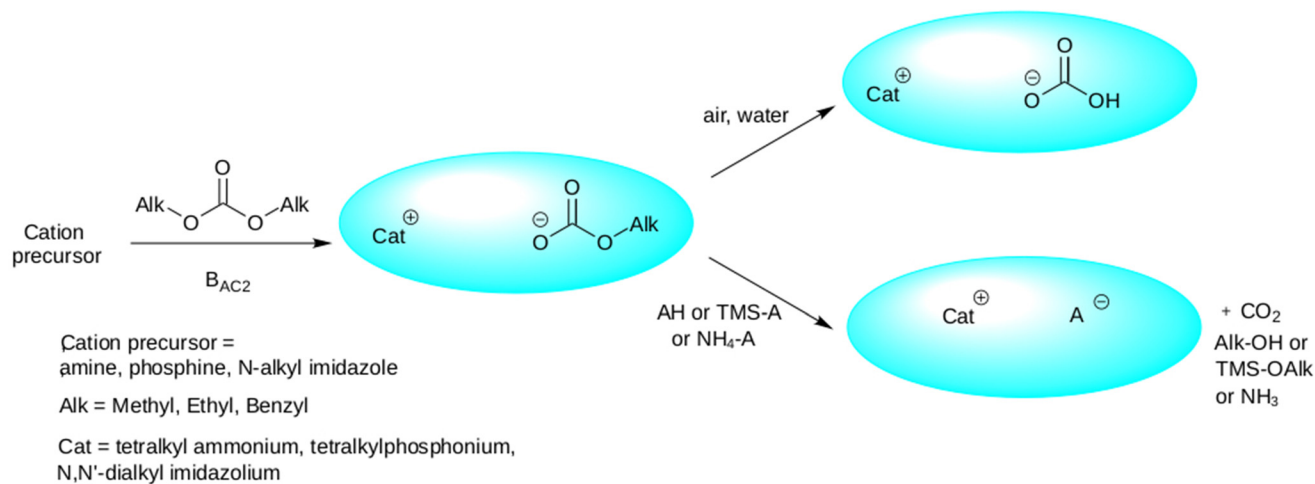


Fig. 5 Global scheme of the DAC route to ionic liquids.

taneous formation of these species, with or without the desired ion pair $[\text{dmim}][\text{MeOCO}_2]$.^{20,24–26}

The accepted mechanism consists of two steps: first, the *N*-methylation with DMC leads to the *N*-methyl-*N'*-alkylimidazolium methylcarbonate ionic liquid; second, the cation and the anion react leading to the carboxylation of the imidazolium and methanol. Smiglak *et al.* found that $[\text{C}_1\text{C}_1\text{im-4-CO}_2]$ is the thermodynamically favoured product, and can be formed from the kinetic compound $[\text{C}_1\text{C}_1\text{im-2-CO}_2]$ at high temperatures in the presence of a Brønsted acid (Fig. 6).²⁶ It has also been shown that using methanol as a solvent stabilizes the ionic liquid, $[\text{C}_1\text{C}_1\text{im}][\text{MeOCO}_2]$, due to hydrogen bonding between the anion and methanol, preventing proton abstraction from the imidazolium ring (Fig. 6).²⁷

The formation of a zwitterionic species should not be considered *a priori* as a limitation of this pathway, as the zwitterions can be readily converted into other ionic liquids using similar methodologies to those described to prepare alkylcarbonate ionic liquids. $[\text{C}_1\text{C}_1\text{im-2-CO}_2]$ can undergo a decarboxylation reaction in presence of a Brønsted acid to the ion pair $[\text{C}_1\text{C}_1\text{im}][\text{A}]$. Depending upon the nature of the acid, this decarboxylation can be spontaneous at room temperature, or require a catalytic amount of dimethylsulfoxide (DMSO). In the case of the more stable isomer $[\text{C}_1\text{C}_1\text{im-4-CO}_2]$,

a higher temperature is required for decarboxylation, which occurs at 140 °C.

Finally, the implementation of the DAC route for the synthesis of imidazolium-based ionic liquids is more delicate than for phosphonium- or ammonium-based salts. Several methylcarbonate imidazolium ion pairs are nevertheless commercially available in methanol solution by Proionic GMBH under the trademark CBIL.²⁸

3.3. DAC route with acidic ionic liquids precursors

A variant of this DAC route has been developed by Zheng *et al.* for phosphonium and ammonium quaternization,²⁹ and by Xiao *et al.* for the synthesis of imidazolium ionic liquids.³⁰ In their case, the first step consisted in the formation of a protic ionic liquids precursor, by reaction between the corresponding phosphine or amine or *N*-alkyl-imidazole and a Brønsted acid, to form an acidic ionic liquids precursor, which is subsequently used in a quaternization step with a DAC reagent (Fig. 7).

4. Scope, limitations, and greener synthesis

4.1. A safer, halide-free synthetic pathway

The dialkyl carbonate route presents an opportunity to greatly improve the greenness and sustainability of the synthesis of ionic liquids. Several major improvements compared to traditional synthesis can be summarized by: the use of safer and more sustainable reagents; and the absence of expensive and

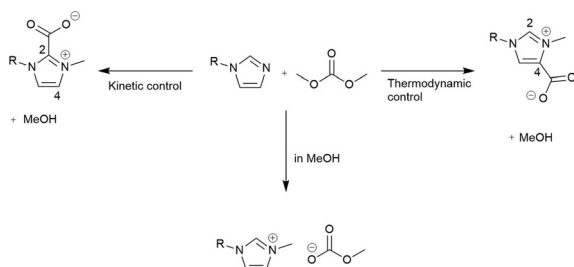


Fig. 6 Reaction products between DMC and *N*-alkyl imidazole.

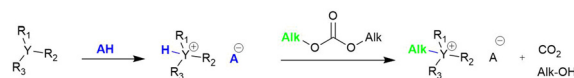


Fig. 7 Use of acidic ionic liquid precursors.^{29,30} Y = P or N.

polluting purification techniques as the only wastes are excess DAC and solvent (usually methanol), which can be easily removed by evaporation. With the exception of a recrystallization step needed when a zwitterionic intermediate species is formed,²⁴ the ionic liquids synthesized through this pathway have been used without any further purification. For example, the continuous flow process developed by Kalb *et al.* affords $[C_2C_1im][OAc]$ with a purity $\geq 99.9\%$, with no detectable starting material, without purification step.²⁰ Fabris *et al.* reported a conservative estimate of the purity greater than 95 %, based on 1H NMR of fourteen ionic liquids synthesized through the DAC route.²² Moreover, the ionic liquids made by this route are totally halide-free and metal free, as no halide-containing reactant, nor metal salts for ion exchanges are used. This constitutes a major advantage of this method when even traces of these impurities can interfere with the studied properties (see section 5.6).

4.2. Determining the E-factor of the DMC route to ionic liquids : the case study of $[C_4C_1Im][OAc]$

Clark, Bakis *et al.* used the DMC route to synthesize $[C_4C_1im][OAc]$.³¹ Firstly, for the formation of 380 g of $[C_4C_1im][MeOCO_2]$, 40 g of methanol were used as solvent and then extra 20 g for recrystallization. 16 g of DMC did not react, which corresponds to 76 g of waste. The E_{fac} is therefore 0.2 for the alkylation step. The conversion of this methylcarbonate ionic liquid to 300 g of the acetate ionic liquid generates 50 g of methanol waste from solvent, 5 g of excess acetic acid waste, 66 g of CO_2 , and 48 g of methanol are generated. Thus, for the anion metathesis step, E_{fac} is 0.56. Thus the whole synthesis of $[C_4C_1im][OAc]$ has an $E_{fac} \approx 0.76$, which is much lower than the halogenation method, and quite comparable to the greenest synthesis of bulk chemicals. In addition, it should be noted that the waste generated during this process are easily recyclable and does not cause environmental drawback, at the contrary of halide and/or metal containing solutions waste generated with the synthetic methods presented in section 2.

4.3. Nature of the cation

As previously discussed, the DMC route has been principally used to prepare phosphonium, ammonium and imidazolium based ionic liquids, with more than one hundred having already been synthesized by this pathway. The most common cations are methyl-trialkyl-phosphoniums ($[P_{8881}]$, $[P_{6661}]$, *etc.*) methyl-alkyl-imidazoliums ($[C_1C_1im]$, $[C_2C_1im]$, *etc.*), methyl-trialkyl-ammoniums ($[N_{4441}]$, $[N_{6661}]$, *etc.*), or cyclic ammoniums (methyl-alkyl-pyrrolidinium, methyl-alkyl-morpholinium cations). Oelkers and Sundermeyer have also reported the synthesis of 17 methyl-pentalkyl-guanidinium based ionic liquids through this pathway.²⁷ Kalb *et al.* found that degradation occurred during the attempts to methylate pyridinium-, pyrrolium- or sulfonium-based ionic liquid precursors, limiting the scope of this route.²⁰ However, Tintori *et al.* synthesized methylcarbonate and hydrogenocarbonate methyl-dimethylaminopyrididinium $[Me-DMAP][MeOCO_2]$ and $[Me-DMAP][HCO_3]$ ³² (Fig. 8).

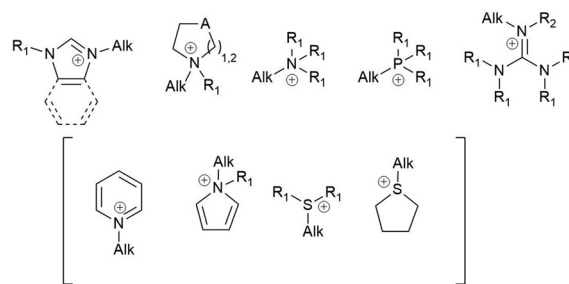


Fig. 8 Cations reached by DAC route. ADD Me-DMAP In brackets: non viable cations according to Kalb *et al.*³⁴

The nature of the dialkylcarbonate remains an important limiting element. Although the alkylation step with dimethylcarbonate and dibenzylcarbonate leads to excellent to quantitative yields, the yields with other reported dialkylcarbonates were low. Aresta *et al.* reported a 14% yield for the reaction between *N*-methylimidazole and diethylcarbonate.³³ Using the acidic ionic liquids precursors, Zheng *et al.* and Xiao *et al.* reported 2% to 54% yield for the ethylation of trialkylammonium chloride and 1*H*-3-alkyl-imidazolium respectively,^{29,30} For the authors, the major parameters are the reactivity of the carbonates, affected by the stability of carbon cations and the steric hindrance of the substituent groups in the carbonates.³⁰ To date, no other dialkylcarbonates have been employed in a DAC route to ionic liquids. Consequently, it should be noted that not all ionic liquids can be reached by this route: for those containing very specific functionalised alkyl chains, conventional Menshutkin reactions can still be more suitable.

4.4. Nature of the anion

After formation of the methylcarbonate ionic liquid, the anion metathesis has a very large scope. The anion precursor must be a Brønsted acid, for example a carboxylic acid, and the reaction between the alkyl carbonate anion leads to anion metathesis, with carbon dioxide and the alkyl alcohol as by-products. In order to introduce other non-basic anions, Ue *et al.* and Oelkers and Sundermeyer used ammonium salts as precursors. NH_4F was used to exchange the anion to a fluoride F^- ,¹⁷ and NH_4SCN and NH_4N_3 to introduce the thiocyanate anion SCN^- and azide anions N_3^- .²⁷ Finger *et al.* used bis(trimethylsilyl)chalcogenides (TMS_2E).³⁵ In all cases, the metathesis were quantitative, and led only to the reached pair ions and volatile by-products, CO_2 and ammonia in the first case, and CO_2 and methoxytrimethylsilane $MeO-TMS$ in the second one.

5. Potential uses of the dialkyl carbonate route

We report the use of the dialkyl carbonate route to prepare a wide range of ionic liquids and ion pairs. Some of the reported studies use commercial methylcarbonate and hydrogenocarbon-

nate ionic liquid solutions (in methanol, or in methanol/water mixtures) available from Proionic (Austria), Sigma-Aldrich (USA), Iolitec (Germany) or ABCR (Germany). These materials, often used as received, are reported for direct applications or for synthesis of other salts by acid/base neutralization.

5.1. Hydrogenocarbonate and methylcarbonate ionic liquids as organocatalysts

The catalytic properties of ionic liquids composed of a methylcarbonate or a bicarbonate anion and a tetralkylphosphonium or tetralkylammonium cation have been extensively investigated by Selva, Perosa and coworkers.³⁷ $[P_{8881}][MeOCO_2]$ and $[N_{8881}][MeOCO_2]$ salts were prepared with quantitative yields from trioctylphosphine and trioctylamine, respectively. When mixed with water in air at 40 °C for 2 hours, $[P_{8881}][HCO_3]$ and $[N_{8881}][HCO_3]$ salts are formed quantitatively. $[P_{8881}][MeOCO_2]$ can also be used to prepare halogenate, nitrate, tosylate, triflate, phenylalaninate, benzoate, and *p*-toluenesulfonate ionic liquids^{22,37,38} that were screened for catalysis of Michael, Henry, and trans-esterification reactions. The desired products were prepared with appropriate yields for trans-esterification of carbonates^{36,39} (Table 1, entries 4 and 6), excellent yields for Michael addition of several compounds to α - β unsaturated carbonyl compounds,²² and excellent yields for Henry-type reaction of addition of nitroethane onto carbonyl compounds⁴⁰ (Table 1, entries 1 and 2).

Liu *et al.* and Chen *et al.* used $[N_{2221}][MeOCO_2]$ as a catalyst for epoxide ring opening with methanol to obtain propylene glycol methyl ether with moderate to good yields (Table 1, entry 3).^{41,42} Coleman *et al.* and Atkins *et al.* used the ionic liquids $[P_{4441}][MeOCO_2]$ and *N*-butyl-*N*-methylpyrrolidinium methylcarbonate as catalysts for the preparation of glycidol from DMC and glycerol (Table 1, entry 5).^{43,44}

Ebel *et al.* patented the use of $[C_1C_1im][MeOCO_2]$ as a catalyst for the synthesis of bisoxazolidine structures from *N*-(hydroxy-alkyl)-oxazolidine and DMC (Table 1, entry 7).⁴⁵

Glasnov *et al.* on the other hand could perform the methylation of indole, phenol, thiophenol, and carboxylic acids using a continuous flow process using $[P_{4441}][MeOCO_2]$ as a catalyst (Table 1, entry 8).⁴⁶ Verma *et al.* used dimethylimidazolium hydrogenocarbonate as a catalyst for hydration of various nitriles in amides. Excellent yields were obtained at 80 °C in few hours for aromatic, aliphatic, alkenyl non protic nitriles (Table 1, entry 9).⁴⁷ Finally, Mishra *et al.* studied experimentally and *in silico* the catalytic properties of $[bmpyr][MeOCO_2]$ and $[N_{4441}][MeOCO_2]$ for the hydrogen release from ammonia borane and ethylene diamine bisborane. The best results were obtained with $[N_{4441}][MeOCO_2]$ at 105 °C (3.5 eq. of hydrogen released)⁴⁸ which are compatible with the use of amine boranes as a promising family of compounds for hydrogen storage requiring high temperatures. Mishra *et al.* studied experimentally and *in silico* the catalytic properties of $[bmpyr][MeOCO_2]$ and $[N_{4441}][MeOCO_2]$ for the hydrogen release of ammonia borane and ethylene diamine bisborane. The best results were obtained with $[N_{4441}][MeOCO_2]$ at 105 °C (3.5 eq. of hydrogen released).⁴⁸

5.2. Ionic liquids for selective extraction

One of the most promising applications of ionic liquids concerns the selective extraction of organic compounds or metal pollutants.^{49,50} The versatility and ease of the DMC route leads to the synthesis of large libraries of ionic liquids allowing large scale screening to discover interesting extraction properties.

Laredo *et al.* synthesized 17 ionic liquids through diverse methodologies including 5 triethylmethylammonium based ionic liquids by the DMC route. The authors showed that triethylmethylammonium butyrate or acetate can be used for the efficient removal of nitrogen compounds from gas oil feeds to produce diesel.⁵¹ Anderson *et al.* also studied extractions from crude oil, and found that $[N_{4441}][HCO_3]$, $[N_{4441}][MeOCO_2]$, $[N_{2221}][HCO_3]$, and $[N_{2221}][MeOCO_2]$ could be used to efficiently extract naphitic acids from crude oil.⁵²

Castillo-Cervantes *et al.* investigated the liquid-liquid extraction of the azo dye Reactive Orange 16 from aqueous solution. For that purpose, they synthesized trioctyl-methylammonium based ionic liquids, with dodecanoate ($[N_{8881}][Do]$), dodecanedioate ($[N_{8881}][Ddi]$), tartrate ($[N_{8881}][tar]$), and ethylenediaminetetraacetate ($[N_{8881}][EDTA]$) anions. Using UV-Vis, FTIR, and 2D-FTIR spectroscopy techniques, they studied the interactions between the dye and the ionic liquids at different pH and temperature. $[N_{8881}][tar]$ showed the best performances.⁵³ The same group showed that the extraction of betanin from beet root extract or fresh beet juice is effective using ionic liquids prepared using the DMC route.⁵⁴ $[N_{4441}][Hex]$, and $[N_{6661}]$ and $[N_{8881}]$ based ionic liquids with adipate [adi], fumarate [fum] salicylate [sal] tartrate [tar] mono-anions were used with the $[N_{4441}][Hex]/[N_{8881}][adi]$ mixture showing the best extraction yield, with 82 % of betanin extracted from fresh beet juice.⁵⁴

Other ionic liquids have been reported for selective extraction of metallic ions (Table 2). Vergara *et al.* investigated the extraction of nickel, copper, lead, zinc, and cobalt cations in aqueous solution by hydrophobic ammonium-based ionic liquids. The authors have prepared, from trioctylamine or trihexylamine, six ionic liquids by alkylation with DMC followed by an acid base neutralisation with adipic, oxalic, salicylic, azelaic, and dodecandioic acids, to form $[N_{xxx1}][adi]$, $[N_{xxx1}][oxa]$ $[N_{xxx1}][sal]$, $[N_{xxx1}][aze]$ and $[N_{xxx1}][DDi]$ ($x = 6$ or 8). The efficiencies of the extraction of metallic ions with a concentration of 25 ppm in solution were good to excellent, $[N_{8881}][oxa]$ showing the best performance (Table 2, entry 1).⁵⁵

The ionic liquids $[N_{8881}][MeOCO_2]$ and $[P_{8881}][MeOCO_2]$ were synthesized through acid-base neutralisation from the commercially available methylcarbonate salts and using a carboxylic acid precursor. The products were obtained with quantitative yields and no further purification. Platzner *et al.* and Herce-Sesa *et al.* used thioglycolate-based ionic liquids for heavy metal extractions from drinking water, sea water and hypersaline waters (Table 2 entries 2 and 3).^{56,57} Pirkwieser *et al.* successfully extracted seven heavy metals from aqueous

Table 1 Uses of ionic liquids made via the DMC route as catalysts

Entry	Reaction	Catalysts	Yields	Reference
1		$[P_{8881}][HCO_3]$ $[P_{8881}][MeOCO_2]$	35–99%, 8 examples	Fabris <i>et al.</i> ⁴⁰
2		$[P_{8881}][HCO_3]$ $[P_{8881}][MeOCO_2]$	55–95%, 8 examples	Fabris <i>et al.</i> ²²
Michael donor (Md)				
3		$[N_{2221}][MeOCO_2]$	54–81%	Liu <i>et al.</i> , ⁴¹ Chen <i>et al.</i> ⁴²
4		$[P_{8881}][HCO_3]$ $[P_{8881}][MeOCO_2]$	92%	Selva <i>et al.</i> ³⁶
5		$[P_{4441}][MeOCO_2]$ $[C_4C_1pyrr][MeOCO_2]$	35–90%	Coleman <i>et al.</i> , ⁴³ Atkins <i>et al.</i> ⁴⁴
6		$[P_{8881}][MeOCO_2]$	42–47%	Fiorani and Selva ³⁹
7		$[C_2C_1im][MeOCO_2]$	77%	Ebel <i>et al.</i> ⁴⁵
8		$[P_{4441}][MeOCO_2]$	52–98%	Glasnov <i>et al.</i> ⁴⁶
Aryl–OH + $\xrightarrow[Continuous\ flow]{IL\ Cat.}$ Aryl–O–				
Aryl–SH + $\xrightarrow[Continuous\ flow]{IL\ Cat.}$ Aryl–S–				
Aryl–COOH + $\xrightarrow[Continuous\ flow]{IL\ Cat.}$ Aryl–CO–				
9		$[C_1C_1im][HCO_3]$	87–99%	Verma <i>et al.</i> ⁴⁷
R = Ar, Et, Bn CH ₂ =CH				
10		$[N_{4441}][MeOCO_2]$ $[bmpyr][MeOCO_2]$	0.96–3.5 eq. H ₂	Mishra <i>et al.</i> ⁴⁸

solution with 3-hydroxy-napthoate based ionic liquids (Table 2, entry 4).^{58,59} Using benzoate-derived or thioglycolate anions, Scheiflinger *et al.* sought to remove radionuclides from aqueous solutions and found good yields for U and ²¹⁰Po, irrespective of the pH of the solutions, though low yields were reported for ²³⁴Th, ²²⁶Ra, and ²¹¹Pb (Table 2, entry 5).⁶⁰

5.3. Ionic liquids for solid materials

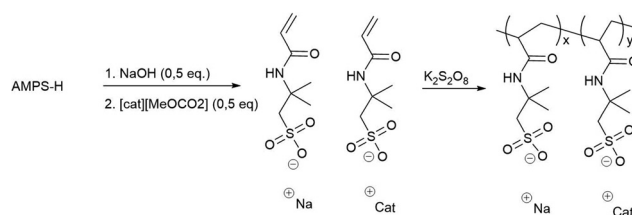
Ionic liquids prepared following the DMC route were also used for functionalising and synthesizing solids materials. Matsuno *et al.* and Talamatsu *et al.* recently used this route to synthesise new ionic liquids as monomers for the functionalisa-

Table 2 Ionic liquids made by DMC route for heavy metals extraction

Entry	Ionic liquid	Pollutant	Media	Reference
1	$[N_{6661}][adi]$, $[N_{6661}][sal]$, $[N_{6661}][adi]$, $[N_{6661}][aze]$, $[N_{8881}][DDi]$, $[N_{8881}][oxa]$	Ni, Cu, Pb, Zn, Co	Aqueous solution	Vergara <i>et al.</i> ⁵⁵
2	$[N_{8881}]^+$ or $[P_{8881}]^+$ $R = C_4H_9 - C_6H_{13}$ or Bn	Cu, Cd	Aqueous solution (sea water, drinking water)	Platzer <i>et al.</i> ⁵⁶
3	$[N_{8881}]^+$ or $[P_{8881}]^+$ $R = C_4H_9 - C_6H_{13}$	Ag, Cd, Co, Cu, Mn, Ni, Pb	hyper-saline waters	Herce-Sesa <i>et al.</i> ⁵⁷
4	$[N_{8881}]^+$ or $[P_{8881}]^+$	Ag, Cd, Co, Cu, Mn, Ni, Pb	Aqueous solutions	Pirkwieser <i>et al.</i> ^{58,59}
5	$[N_{8881}]^+$ or $[P_{8881}]^+$ $R_1 = OH, SH, NH_2$ $R_2 = H, NO_2, NH_2$ or $R = C_4H_9 - C_6H_{13}$	U, Po, Th, Ra, Pb	Aqueous solution	Scheiflinger <i>et al.</i> ⁶⁰

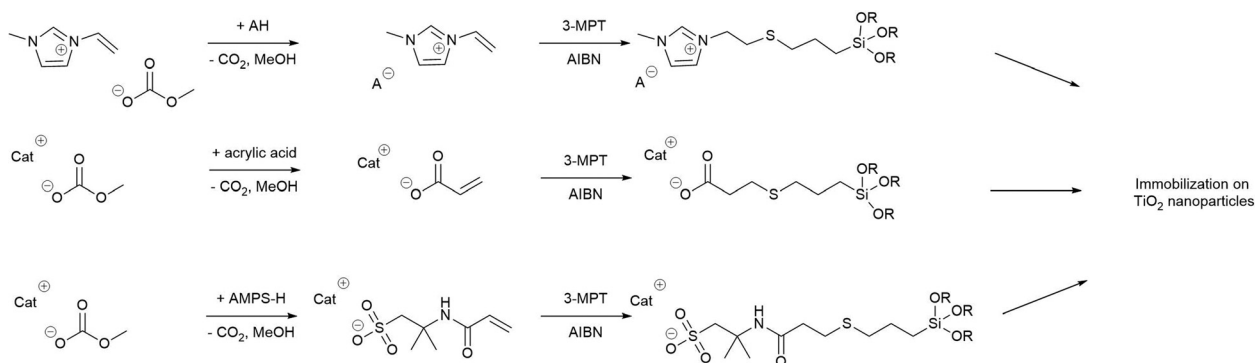
tion of TiO_2 nanoparticles.^{61,62} Commercially available methylvinyl-imidazolium hydrogenocarbonate and methylcarbonate were used to form ion pairs through acid/base neutralisation with benzenesulfonic, tosylic, triflic, methanesulfonic, and acetic acids. In addition, $[N_{4441}]$, $[P_{4441}]$, 1-butyl-1-methylpyrrolidinium $[C4C1pyr]$ and 4-ethyl-4-methylmorpholinium methylcarbonate were used to form 8 new ionic liquids with acrylate or 2-acrylamido-2-methylpropanesulfonate (AMPS) anions. Then, all of these ionic liquids were bonded to an alkoxy-siloxane linker *via* a thiol-ene reaction before being immobilized on the surface of TiO_2 nanoparticles (Fig. 9).^{61,62}

Noor *et al.* used the same ionic liquids, *i.e.* $[N_{4441}][AMPS]$ and $[N_{2221}][AMPS]$, to obtain new ionic monomers, in order to form polyelectrolytes through radical polymerization initiated with potassium persulfate (Fig. 10). The conductivities of poly-

**Fig. 10** Ionomer synthesis by Noor *et al.*⁶³ Cat^+ are $[N_{2221}]$, $[N_{4441}]$ or $[N_{14111}]$.

electrolytes, with or without the addition of a plasticizer were studied.⁶³

In their 2012 patent, Massonne *et al.* propose the reaction of $[C_2C_1im][MeOCO_2]$ with adipic acid and terephthalic acid to

**Fig. 9** Ion pair immobilization on TiO_2 nanoparticles.^{61,62} AH is benzenesulfonic, tosylic, triflic, methanesulfonic, or acetic acids. 3-MPT = 3-mercaptopropyltrimethoxysilane. Cat^+ are $[N_{4441}]$, $[P_{4441}]$, $[bmpyr]$ or $[emmorph]$ cations. AMPS-H is 2-acrylamido-2-methyl-1-propanesulfonic acid.

form di(1-ethyl-3-methylimidazolium) adipate $[\text{C}_2\text{C}_1\text{im}]_2[(\text{CH}_2)_4(\text{CO}_2)_2]$, and di(1-ethyl-3-methylimidazolium) terephthalate $[\text{C}_2\text{C}_1\text{im}]_2[\text{dbc}]$. These ionic liquids were successfully employed in esterification reactions with dichloroethane and 1,4-bis(chloromethyl)benzene, to form polyester-type polymers (Fig. 11).⁶⁴

Fischer *et al.* and Schwegler *et al.* used terephthalate based ionic liquids synthesized through the DMC route as precursors for the synthesis of an aluminium-based metal organic frameworks (MOF) using $[\text{C}_2\text{C}_1\text{im}]_2[\text{dbc}]$ and 1-ethyl-3-methylimidazolium hydrogen terephthalate, $[\text{C}_2\text{C}_1\text{im}]_2[\text{Hdbc}]$, this last synthesized by changing the stoichiometry during the anion exchange. By mixing aluminium nitrate and $[\text{C}_2\text{C}_1\text{im}]_2[\text{Hdbc}]$ (or $[\text{C}_2\text{C}_1\text{im}]_2[\text{dbc}]$) in DMF at 130 °C they managed to prepare in mild conditions a MIL-53(Al) type MOF (Fig. 12).^{65,66}

Husanu *et al.* assessed the use of citrate-based ionic liquids for the synthesis of colloidal silver and gold nanoparticles, as the citrate anion classically acts as a reducing agent and imidazolium and ammonium cations are good capping agents. Using $[\text{C}_4\text{C}_1\text{im}][\text{MeOCO}_2]$, $[\text{C}_2\text{C}_1\text{im}][\text{MeOCO}_2]$, and $[\text{N}_{8881}][\text{MeOCO}_2]$, the authors prepared $[\text{C}_4\text{C}_1\text{im}][\text{citrate}]$, $[\text{C}_2\text{C}_1\text{im}][\text{citrate}]$, and $[\text{N}_{8881}][\text{citrate}]$ ionic liquids. Silver and gold nanoparticles were synthesized by adding silver nitrate AgNO_3 at 70 °C, or by adding a hot aqueous solution of tetrachloroauric acid HAuCl_4 to an ethanol/citrate-based ionic liquid mixture.⁶⁷

Ionic liquids can play a prominent role as solvents for the dissolution of vegetal-based fibrous materials. For this application, Mezzetta *et al.* studied levulinate-based ionic liquids— $[\text{C}_2\text{C}_1\text{im}][\text{lev}]$, $[\text{C}_4\text{C}_1\text{im}][\text{lev}]$, $[\text{N}_{8881}][\text{lev}]$ and $[\text{P}_{8881}][\text{lev}]$ —prepared by the reaction of levulinic acid with the corresponding methylcarbonate precursors.⁶⁸ Levulinic acid is a particularly sustainable reactant as it can be directly obtained from cellulose⁶⁹ and allows for the preparation of ionic liquids with a good to remarkable capacity of dissolving polysaccharides, especially $[\text{C}_2\text{C}_1\text{im}][\text{lev}]$.⁶⁸

Lehmann *et al.* used carboxylate-based imidazolium ionic liquids obtained by the DMC route to dissolve vegetal polymers. Using 1-butyl-3-methylimidazolium cyclohexanecarboxy-

late $[\text{C}_4\text{C}_1\text{im}][\text{cyclohex}]$, they presented a new process to obtain lignocellulosic fibers from wood raw materials without the need to remove the other natural compounds nor any pre-treatment.⁷⁰ Heating a mixture of raw lignocellulose and $[\text{C}_4\text{C}_1\text{im}][\text{cyclohex}]$ at 130 °C for 5 h led to a homogeneous solution, from which they extruded filaments that could precipitate in an aqueous coagulation bath. The obtained fibers are similar in strength and quality to commercial cellulose fibres.⁷⁰

Jouannin *et al.* conceived poly(L-lactic acid) membranes containing ibuprofenate ionic liquids, *i.e.* lidocanium ibuprofenate and butyl-methylimidazolium ibuprofenate. This last one was synthesized *via* the DMC route, from a commercial solution of $[\text{C}_4\text{C}_1\text{im}][\text{HCO}_3]$ in water: methanol, and ibuprofenic acid. By mixing poly(L-lactic acid) and the ionic liquids in chloroform, followed by a controlled evaporation and drying, 42 μm -thick membranes could be prepared, with various concentrations of $[\text{C}_4\text{C}_1\text{im}][\text{Ibu}]$. The authors studied the influence of ionic liquid concentration on the crystallinity of the membrane, and the *in vitro* drug release kinetics in a standard pharmaceutical dissolution test.⁷¹

5.4. Ionic liquids for electrochemistry

Ionic liquids are excellent candidates as new non-aqueous electrolytes that can be used in fuel cells, capacitors and batteries.⁷² Since typical by-products of ionic liquid synthesis are halides and metal salts that interfere dramatically with the electrochemical properties of the molten salt,⁷³ the use of the halide-free and metal-free dialkylcarbonate route is particularly suited to the preparation of ionic liquids for these applications.

Ue *et al.* synthesized two new room-temperature molten salts, 1-ethyl-3-methylimidazolium hexafluorotantalate $[\text{C}_2\text{C}_1\text{im}][\text{TaF}_6]$ and hexafluoronioate $[\text{C}_2\text{C}_1\text{im}][\text{NbF}_6]$, in a two step procedure from $[\text{C}_2\text{C}_1\text{im}][\text{MeOCO}_2]$. First they introduced the fluoride anion F^- by reaction with ammonium fluoride, then solid tantalum pentafluoride (TaF_5) or niobium pentafluoride (NiF_5) were added at 0 °C, generating the final ionic liquids $[\text{C}_2\text{C}_1\text{im}][\text{NbF}_6]$ and $[\text{C}_2\text{C}_1\text{im}][\text{MeOCO}_2]$ with an overall yield of 98%. These ionic liquids were used as electrolytes for

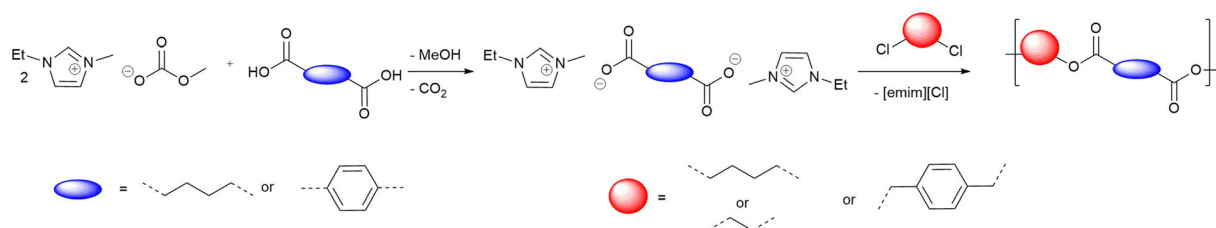


Fig. 11 Polycarbonate synthesis by Massonne *et al.*⁶⁴

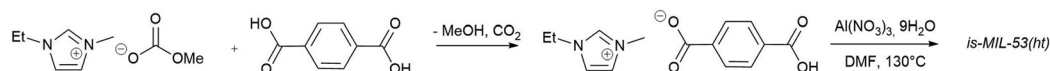


Fig. 12 Imidazolium salt is-MIL-53(Al) synthesis, by Fischer *et al.* and Schwegler *et al.*^{65,66}

double-layer capacitors, and showed similar performances to the commonly studied $[C_2C_1im][BF_4]$, with the added advantage of much lower melting points which allows for performances at low temperatures (Table 3, entry 1).¹⁶

Xu *et al.* prepared various phosphonium and ammonium based ionic liquids using dimethylcarbonate as the alkylating agent. The cations generated were triethylmethylammonium $[N_{2221}]$, tripropylmethylammonium $[N_{3331}]$, trimethyl-ethylammonium $[N_{112}]$, tributylmethylammonium $[N_{4441}]$, triethylmethylphosphonium $[P_{2221}]$, and tributylmethylphosphonium $[P_{4441}]$. The acids which were added to generate the final ionic liquids were hexafluorophosphoric acid (HPF₆), tetrafluoroboric acid (HBF₄), hydrogen hexafluoroarsenate(v) (HAsF₆), trifluoromethanesulfonic acid (HOTf), and bis(trifluoromethylsulfonyl)imic acid (HNTf₂).⁷⁴

The synthesis by the DMC route and the use of several new ionic liquids as electrolytes, including three ethyl-methyl-di (iso-propyl)ammonium-based salts made the object of a patent⁷⁵ (Table 3, entry 2).⁷⁵ Zhou *et al.* studied the electrolytic properties of per-fluoro-alkyl-tri-fluoro-borate based ionic liquids, made by reacting $[C_2C_1im][MeOCO_2]$ with $C_2F_5BF_3H$, $nC_3F_7BF_3H$, or $nC_4F_9BF_3H$. They presented a better low temperature conductivity than $[C_2C_1im][BF_4]$, but showed similar performances when used in capacitors (Table 3, entry 3).⁷⁶

Zhu *et al.* synthesized hydrogen phthalate [Hphthalate] and hydrogen maleate [Hmaleate]-based ionic liquids, by acid/base neutralisation with $[C_1C_1im][MeOCO_2]$, $[C_2C_1im][MeOCO_2]$, or $[C_1C_1pyrr][MeOCO_2]$, and phthalic acid or maleic acid. These salts were tested as electrolytes for capacitors when mixed with γ -butyrolactone (GBL) but with low performances.⁷⁷

Nishitani *et al.* synthesized 1,2,3,4-tetramethyl imidazolium methylcarbonate from DMC and 2,4-dimethyl-imidazoline, and used acid/base neutralisations to reach 1,2,3,4-tetramethyl-imidazolium dibutylphosphate [tmimn] $[(BuO)_2PO_2]$, [tmimn] $[(EtO)_2PO_2]$, and [tmimn][H-phthalate]. They patented the use of these liquids as electrolytes for aluminium capacitors when mixed with GBL and a borate ester (Table 3, entry 5).⁷⁸

Treskow *et al.* have developed several “anion amphiprotic ionic liquids” with an trifluoromethanesulfonamidate anion

$CF_3SO_2NH-(TFSAm)$, synthesized by anion metathesis with a methylcarbonate ionic liquid precursor. These ionic liquids showed good conductivity properties, even at low temperatures, and could be adapted for proton-exchange membrane fuel cells (PEMFC) (Table 3, entry 6).⁷⁹

Funabiki *et al.* prepared from a commercial solution of $[C_2C_1im][HCO_3]$ three tetrazole-thiolate imidazolium ionic liquids by acid/base neutralization to be used as electrolytes in dye-sensitizer solar cells DSSCs, after dilution in 3-methoxypropionitrile or an other ionic liquid (ethyl-methylimidazolium bis (fluorosulfonyl)amine) (Table 3, entry 7). A correct yield of 4.32% was obtained with n-hexyl tetrazole-thiolate ethyl-methylimidazolium based electrolytes.⁸⁰ Guglielmo *et al.* succeed to prepare original ionic liquids based on metal-EDTA complexes: starting from acidic trivalent metals EDTA complexes (M-EDTA-H), with (M = V, Cr, Mn, Fe, Co), they implemented the anion metathesis reaction with the commercially available $[P_{8881}][MeOCO_2]$ or $[C_4C_1im][MeOCO_2]$. The ten different new ionic liquids were studied for their electrochemical properties. The good thermal behavior and redox reversibility of the V and Mn based ionic liquids suggest that these compounds could be suitable electrolytes for redox flow batteries.⁸¹

Working on enantioselective electrochemistry, Grecchi *et al.* have developed and studied chiral ionic liquids derived from deoxycholic acid. Some of these were synthesized through anion metathesis from $[C_4C_1im][MeOCO_2]$, $[C_4C_1im][P_{4441}]$, $[C_4C_1im][P_{8881}]$ and $[C_4C_1im][N_{8881}]$ (Fig. 13).⁸²

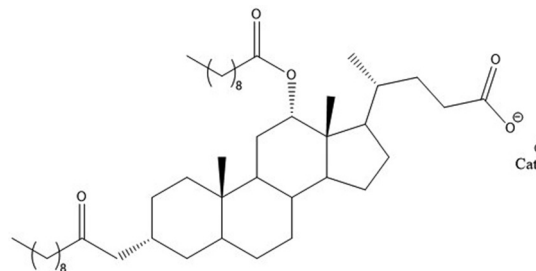
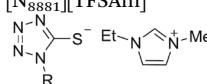


Fig. 13 Chiral ionic liquids developed by Grecchi *et al.* Cat = $[P_{4441}]$, $[P_{8881}]$, $[C_4C_1im]$, $[N_{8881}]$.⁸²

Table 3 Ionic liquid electrolytes

Entry	Ionic liquid	Application	References
1	$[C_2C_1im][TaF_6]$, $[C_2C_1im][NbF_6]$	Double-layer capacitors	Ue <i>et al.</i> ¹⁶
2	$[EtMe(iPr)_2N][NTf_2]$, $[EtMe(iPr)_2N][OTf]$, $[EtMe(iPr)_2N][PF_6]$	Double-layer capacitors	Xu <i>et al.</i> ⁷⁵
3	$[C_2C_1im][C_2F_5BF_3]$, $[C_2C_1im][nC_3F_7BF_3]$, $[C_2C_1im][C_4F_9BF_3]$	Capacitors	Zhou <i>et al.</i> ⁷⁶
4	$[C_1C_1im][H-phthalate]$, $[C_1C_1im][H-phthalate]$, $[C_2C_1im][H-phthalate]$, $[C_2C_1im][H-phthalate]$, $[C_1C_1pyrr][H-phthalate]$, $[C_1C_1pyrr][H-phthalate]$	Capacitors	Zhu <i>et al.</i> ⁷⁷
5	$[tmimn][((BuO)_2PO_2)]$, $[tmimn][((EtO)_2PO_2)]$, $[tmimn][H-phthalate]$	Aluminium capacitors	Nishitani <i>et al.</i> ⁷⁸
6	$[C_2C_1im][TFSAm]$, $[C_4C_1im][TFSAm]$, $[bmpyr][TFSAm]$, $[N_{4441}][TFSAm]$, $[N_{8881}][TFSAm]$	Proton-exchange membrane fuel cells	Treskow <i>et al.</i> ⁷⁹
7	 (R = n-Bu, n-Hex, n-Oct)	Dye-sensitized solar cells	Funabiki <i>et al.</i> ⁸⁰
8	$[P_{8881}][M-EDTA]$, $[C_4C_1im][M-EDTA]$ with M = V, Cr, Mn, Fe, Co	Redox flow batteries	Guglielmo <i>et al.</i> ⁸¹

Enantiodiscrimination tests were performed, showing significant potential differences in presence of chiral ferrocene derivatives in cyclic voltammetry experiments.

5.5. Carbon dioxide absorption and valorization

The challenge of carbon dioxide absorption, sequestration and valorization has led to the synthesis of various ionic liquids, which have then been used as absorbent media and as solvents for catalytic conversion of CO₂ into high added value chemicals.^{83,84}

Makino *et al.* studied the CO₂ absorption by ether-functionalized carboxylate ionic liquids synthesised through the DMC route. They showed that physical and chemical adsorption were affected in opposite ways as the length of the etherchain was varied, with longer ether chains favouring physisorption, and shorter ether chains favouring chemisorption⁸⁵ (Table 4, entry 1).

Stark *et al.* compared the use of eight commercial hydrogenocarbonate or methylcarbonate ionic liquids made *via* the DMC route and Dimcarb (dimethylamine–carbon dioxide (1.8 : 1) complex) as CO₂-source solvents for the microwave-assisted Kolbe–Schmitt carboxylation of resorcinol. [C₂C₁im][HCO₃] appeared to be the most reactive salt, although Dimcarb is much easier to synthesize from CO₂ (Table 4, entry 2).⁸⁶ After a life cycle assessment study, the same team concluded that the use of [C₂C₁im][HCO₃] in a continuous process is probably the most environmentally benign process.⁸⁷

Wuensch *et al.* examined the use of commercial hydrogenocarbonate-based ionic liquids [C₂C₁im][HCO₃], [C₂C₁im][HCO₃] and [C₄C₁im][HCO₃], as sources of CO₂ in an enzymatic alternative to the Kolbe–Schmitt carboxylation. A 46% conversion of resorcinol to 2,6-dihydroxycarboxylic acid was obtained with a suspension of 2,6-dihydroxycarboxylase in a mixture of [C₄C₁im][HCO₃] (20% v/v) with water when supplemented with potassium hydrogenocarbonate (conc. 3M), surpassing the other tested systems⁸⁸ (Table 4, entry 3).

Calmanti *et al.* synthesized original tungstate ionic liquids, including [N₈₈₈₁]₂[W₂O₃(O₂)₄] and [N₈₈₈₁]₂[WO₄] made by the DMC route from trioctylamine. The ionic liquids were used as catalysts for cyclic carbonate synthesis from styrene oxide and CO₂. Best results were obtained with *T* = 90 °C, *p*(CO₂) = 50 bar and 3 mol% catalyst (Table 4, entry 4).⁸⁹ The same group recently extended the scope of their study, by synthesizing [P₈₈₈₁]₂[WO₄] and [N₈₈₈₁]₃[PW₁₂O₄₀], and [C₄C₁im]₂[WO₄], used

as catalysts for a tandem carbonation reaction from unsaturated fatty acids, H₂O₂ and CO₂.⁹⁰

5.6. Luminescent ionic liquids

The DMC route was successfully implemented to synthesize luminescent ionic liquids, through two different approaches. Fiorani *et al.* developed a small library of dansyl-based ionic liquids by using aminoacids functionalised by a dansyl chromophore as anion precursors for acid/base neutralisation with [P₈₈₈₁][MeOCO₂], [P₄₄₄₁][MeOCO₂], and [N₈₈₈₁][MeOCO₂]. The anion exchanges were quantitative, leading to five intrinsically luminescent ionic liquids (Fig. 14).⁹¹

Malba *et al.* used the DMC route to synthesize phosphonium-based tetrakis dibenzoylmethane Eu(III) and Sm(III) complexes.⁹² Starting from [P₈₈₈₁][MeOCO₂], they obtained methyltrioctylphosphonium dibenzoylmethanate [P₈₈₈₁][dbm] by acid/base neutralisation with dibenzoylmethane. The ionic liquid-lanthanide complexes were directly generated from [P₈₈₈₁][dbm] by the addition of the corresponding lanthanide salt. The presence of the phosphonium cation means that these complexes have a high solubility in [P₈₈₈₁][NTf₂], making the ionic liquid luminescent. Using a similar method, Bortoluzzi *et al.* prepared europium and terbium-doped ionic liquids based on bromomalonaldehyde anion [BrMA] in dissolving EuCl₃ or TbCl₃ in [P₈₈₈₁][BrMA]⁹³ (Fig. 15).

5.7. Other uses of DAC route

5.7.1. Halide or metal-free ionic liquids. The DMC route allows for the synthesis of halide-free and metal-free ionic

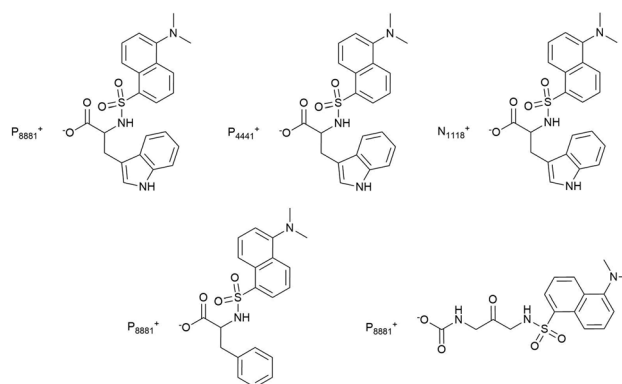


Fig. 14 Luminescent dansyl-aminocarboxylate-based ionic liquids.⁹¹

Table 4 Ionic liquid made by DMC route for CO₂ capture or valorization

Entry	Ionic liquid	Application	References
1	[C ₂ C ₁ im][MeO(CH ₂) ₂ OCH ₂ CO ₂], [C ₂ C ₁ im][MeO(CH ₂) ₂ O(CH ₂) ₂ CO ₂]	CO ₂ absorbent liquid	Makino <i>et al.</i> ⁸⁵
2	[C ₂ C ₁ im][HCO ₃], [C ₁ C ₁ im][HCO ₃], [N ₂₂₂₁][MeOCO ₂], [N ₄₄₄₁][MeOCO ₂], [P ₄₄₄₁][MeOCO ₂], [bmpyr][MeOCO ₂], [emmorph][MeOCO ₂], [empip][MeOCO ₂]	CO ₂ source (Kolbe-schmitt carboxylation)	Stark <i>et al.</i> ⁸⁶
3	[C ₂ C ₁ im][HCO ₃], [C ₂ C ₁ im][HCO ₃], [C ₄ C ₁ im][HCO ₃]	CO ₂ source (enzymatic carboxylation)	Wuensch <i>et al.</i> ⁸⁸
4	[N ₈₈₈₁] ₂ [W ₂ O ₃ (O ₂) ₄], [N ₈₈₈₁] ₂ [WO ₄], [P ₈₈₈₁] ₂ [WO ₄], [N ₈₈₈₁] ₃ [PW ₁₂ O ₄₀], [C ₄ C ₁ im] ₂ [WO ₄]	Carbonate synthesis	Calmanti <i>et al.</i> , ^{89, 90}

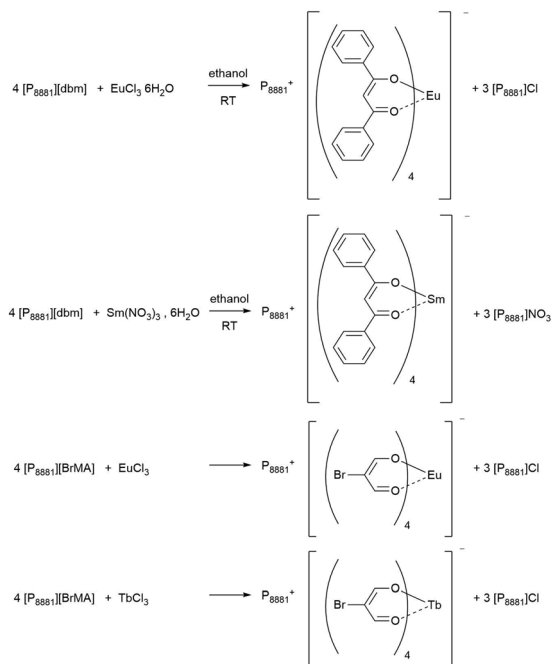


Fig. 15 Synthesis of phosphonium-based Eu(III), Sm(III), and Tb(III) complexes.^{92,93}

liquids. Vander Hoogerstraete *et al.* proposed a method to detect halide impurities calibrated using 1-butyl-3-methylimidazolium acetate ($[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$), 1-butyl-3-methylimidazolium trifluoromethane sulfonate ($[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$), and 1-butyl-3-methylimidazolium nitrate ($[\text{C}_4\text{C}_1\text{im}][\text{NO}_3]$) prepared from 1-butyl-3-methylimidazolium methylcarbonate ($[\text{C}_4\text{C}_1\text{im}][\text{MeOCO}_2]$). In all cases, the reaction was carried out by adding acid (HOAc, HNTf₂, HOTf, HNO₃ respectively) in methanol at room temperature for 1 hour, and purification consisted only of drying *in vacuo* for 48 h at 60 °C to produce halide-free ionic liquids.⁹⁴

Manini *et al.* studied antioxidant and radical properties of an allomelanin using ionic liquids as a tunable solvent. They used $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$, $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$, $[\text{C}_4\text{C}_1\text{im}][\text{DCA}]$ and two other less common ionic liquids, 1-butyl-3-methylimidazolium 2-aminoethanesulfonate and 1-butyl-3-methylimidazolium mandelate, all synthesized *via* the DMC route to avoid the use of silver salts for anion exchange, that can generate metallic by-products which can interfere with antioxidant properties.⁹⁵

Stolarska *et al.* studied the eutectic properties of various ionic liquids, one of which was the very hygroscopic 1-ethyl-3-methylimidazolium nitrate ($[\text{C}_2\text{C}_1\text{im}][\text{NO}_3]$) synthesised from 1-ethyl-3-methylimidazolium methylcarbonate ($[\text{C}_2\text{C}_1\text{im}][\text{MeOCO}_2]$) and a concentrated solution of nitric acid in methanol.⁹⁶

Harloff *et al.* explored the DMC route to synthesize ammonium pseudo-halide ionic liquids $[\text{N}_{2221}][\text{X}]$ and $[\text{N}_{4441}][\text{X}]$, where X = cyanide, azide, cyanate, or thiocyanate. $[\text{N}_{2221}][\text{MeOCO}_2]$ and $[\text{N}_{4441}][\text{MeOCO}_2]$ were obtained in a

modest (50–70%) yield (after three washes with diethyl ether and drying). The methylcarbonate ionic liquids were then reacted with trimethylsilyl-X compounds to give $[\text{N}_{2221}][\text{X}]$ and $[\text{N}_{4441}][\text{X}]$ ionic liquids in a quantitative yield, avoiding residual water and halide.^{97,98}

5.7.2. Others. Other original ionic liquids made by the DAC route were described for other applications, or for fundamental studies. Several studies concern new, original carboxylate-based ionic liquids. If the strategy is based on the same type of anion metathesis reaction between the corresponding carboxylic acid and the corresponding methylcarbonate ionic liquid, the applications differ from one structure to another.

Berger *et al.* used the DMC route to synthesize 1-ethyl-2,3-dimethylimidazolium acetate, which was used as solvent for the RuCl₃ catalyzed decomposition of formic acid to hydrogen and carbon dioxide (Table 5, entry 1).⁹⁹

Wilfred and Mustafa described the synthesis of several thiosalicylate based ionic liquids. Among them, tributylmethylammonium thiosalicylate and *N,N*-butyl-methyl-pyrrolidone thiosalicylate were prepared thanks to the DMC route, without requiring the subsequent removal of halides (Table 5, entry 2).¹⁰⁰

While working on the solubility of cellulose in carboxylate or dicarboxylate-based ionic liquids, Zhao *et al.* synthesized 27 ionic liquids through the normal DMC route (for dimethylimidazolium and ethyl-methylimidazolium ionic liquids), or with an acidic ionic liquids precursor (for diethyl dimethylammonium ionic liquids, see section 3.3). In $[\text{C}_2\text{C}_1\text{im}][\text{C}_2\text{H}_5\text{CO}_2]$, at $T = 373$ K, the solubility of cellulose reaches 18 wt%. They also proved that regenerated ionic liquids have the same performance, and studied the influence of water and halides impurities on the solubility (Table 5, entry 3).¹⁰¹ More recently, Xia *et al.*, Holding *et al.* studied the dissolution and the regeneration of cellulose in organic electrolyte solutions (OESs), that are binary mixtures of $[\text{P4441}][\text{OAc}]$ made by the DMC route and a polar aprotic co-solvent (DMSO or γ -valerolactone). They noticed that the quality of the regenerated cellulose (crystallinity and size and stability of cellulose particles) strongly depends on interdependent parameters, *i.e.* cellulose concentration, solvent composition, temperature and cooling rate, *etc.*^{102,103}

Guglielmero *et al.* synthesized and studied the thermal properties of several dicarboxylate ionic liquids. Although the majority of them were made from halide-based ionic liquid precursors, with an expensive anion exchange step (based on silver salt, or ion exchange resin), those with a butylmethylimidazolium cation were reached thanks to the DMC route. These were malonate, succinate, and glutarate butylmethylimidazolium salts that were synthesised without any purification steps (Table 5, entry 4).¹⁰⁴

Mezzetta *et al.* synthesized 14 long chain fatty acid ionic liquids (LCFA-ILs) in quantitative yields, starting from the commercially available solution of $[\text{C}_2\text{C}_1\text{im}][\text{MeOCO}_2]$, $[\text{N}_{8881}][\text{MeOCO}_2]$, and $[\text{P}_{8881}][\text{MeOCO}_2]$ in methanol, and the following fatty acids: oleic, palmitic, stearic, lineic, and myristic acids (Table 5, entry 5).^{68,105} The same group also studied

Table 5 Miscellaneous ionic pairs synthesized by DMC route

Entry	Ionic liquid	References
1		Berger <i>et al.</i> ⁹⁹
2		Wilfred and Mustafa ¹⁰⁰
3	Cat = [N ₄₄₄₁], [mbpyr] cat = [C ₂ C ₁ im], [C ₂ C ₁ im], [N ₂₂₁₁]; anion = [HCO ₂], [OAc], [EtCO ₂], [nPrCO ₂], [iPrCO ₂], [H-phtalate], [H-succ], [maleate], [succ]	Zhao <i>et al.</i> ¹⁰¹
4		Guglielmo <i>et al.</i> ¹⁰⁴
5		Mezzetta <i>et al.</i> ^{68,105}
6	Cat = [C ₁ C ₂ Im], [N ₈₈₈₁], [P ₈₈₈₁] 	Mezzetta <i>et al.</i> ¹⁰⁶
7	cat = [C ₁ C ₂ Im], [P ₄₄₄₁], [P ₈₈₈₁] R = H, NHAc [N ₆₁₁₁][C ₉ H ₁₉ CO ₂], [N ₈₁₁₁][nC ₉ H ₁₉ CO ₂], [N ₁₀₁₁₁][nC ₉ H ₁₉ CO ₂], [N ₈₁₁₁][nC ₇ H ₁₅ CO ₂], [N ₁₀₁₁₁][nC ₇ H ₁₅ CO ₂], [N ₁₀₁₁₁][nC ₇ H ₁₅ CO ₂], [N ₁₀₁₁₁][nC ₅ H ₁₁ CO ₂]	Medoš <i>et al.</i> ¹⁰⁷
8	[N ₁₀₁₁₁][RC ₆ H ₄ SO ₃]	Ju <i>et al.</i> ¹⁰⁸
9		Smiglak <i>et al.</i> ¹⁰⁹
10	Cat = [mmpyr], [C ₁ C ₁ Im], [1,2,3-trimethylimidazolium] 	Finger <i>et al.</i> ¹¹¹
11	[C ₄ C ₁ pyrr][TMSE], [C ₁ C ₁ pyrr][TMSE], [N ₁₁₁₁][TMSE], [P ₄₄₄₁][TMSE], [C ₄ C ₁ pyrr] ₂ [S ₆], [C ₁ C ₁ pyrr] ₂ [S ₆], [C ₄ C ₁ pyrr] ₂ [Se ₃], [C ₄ C ₁ pyrr] ₄ [Te ₁₂] where E = S or Se or Te	Finger <i>et al.</i> ^{35,110}

the synthesis and the stability of thiol-functionalised carboxylate ionic liquids, made through acid/base neutralisation of imidazolium and phosphonium methylcarbonates, with 3-mercapto propionic acid or *N*-acetyl-cysteine (Table 5, entry 6).¹⁰⁶ Depending on the conditions (bubbling air or inert atmosphere), they obtained the expected carboxylate ionic

liquids, or a dicarboxylate disulfide anion. It was also discovered that, even at moderate temperature (90 °C), the imidazolium ionic liquids decomposed to sulfide-based ionic liquid and imidazole 2-thione.¹⁰⁶

Medoš *et al.* studied the preparation of surfactant ionic liquids and the possibility of scaling up their synthesis. They compared the DMC route to the classical synthesis using alkyl halides to reach hexanoate [hex], octanoate [oct], and decanoate [dec] ammonium carboxylates. They found that the synthesis of most of these ionic liquids gave much higher yields and purities using dimethyl carbonate as the alkylating agent (with the exception of [N₈₁₁₁][oct]). They also highlighted that the low cost of reagents and benign by-products also mean that the reaction scales up much better using the dimethylcarbonate synthetic method (Table 5, entry 7).¹⁰⁷ Following the same approach, Ju *et al.* used the DMC route to synthesize several alkylbenzenesulfonate from dimethylcarbonate, dodecyldimethylamine, and alkylbenzenesulfonic acid (RC₆H₄SO₃H) (Table 5, entry 8).¹⁰⁸

The DMC route was also implemented for the synthesis of ionic liquids with nitrogen aromatic heterocyclic anions. Smiglak *et al.* used this method to prepare 18 imidazolate, triazolate or tetrazolate based ionic liquids. Although their melting points are often high, around 100 °C, the authors used their study as a new approach towards the halide-free synthesis of new ionic liquids (Table 5, entry 9).¹⁰⁹

In their study of diverse 5,5' bis-tetrazolate salts, Finger *et al.* also used [C₂C₁im][MeOCO₂] as a starting material to reach a bis-tetrazolate imidazolium salts with a melting point of 95 °C (Table 5, entry 10).¹¹⁰

Finger *et al.* studied the formation of hydrochalcogenide and (trimethylsilyl)-chalcogenolate based ionic liquids. From a series of imidazolium and dialkylpyrrolidinium methylcarbonates, (synthesized by them or commercially available), four hydrosulfide and one hydroselenide solid salts were formed, and purified by recrystallization or sublimation. It was found that under reduce pressure (10⁻² bar), sublimation quantitatively occurred at temperatures below 100 °C (Table 5, entry 11).¹¹¹ In an other study, they proposed the synthesis of organic (trimethylsilyl)chalcogenolate salts, starting from methylcarbonate ionic liquids, and di(trimethylsilyl)chalcogenate (TMS)₂S, (TMS)₂Se, and (TMS)₂Te. These salts were then converted in hexasulfide, triselenide, and dodecatelluride salts (Table 5, entry 12).³⁵ Jost *et al.* studied the same synthetic methodology, with the use of E(SiMe₃)₃ (E = P or Sb) as anion precursors and 7 methylcarbonate-based ionic liquids as cation precursors. During the anion exchange, P(SiMe₃)₃ also reacted with the by-product CO₂ to form phosphanethylenate anion PCO⁻, and they obtained 7 new [cat][PCO] ionic pairs. With Sb(SiMe₃)₃ They also synthesize an original organic salt [P₄₄₄₁][Sb₁₁³⁻] (Table 5, entry 13).

Rijksen and Rogers proposed a solventless route to ethylmethylimidazolium fluoride hydrofluoride [C₂C₁im][F]·xH₂O in three steps from unsubstituted imidazole, which utilises the methylation with DMC and acid/baseneutralization of the zwitterionic intermediary by hydrofluoric acid (Table 5, entry 14).¹¹³

Table 6 Miscellaneous ionic pairs synthesized by DMC route (continue)

Entry	Ionic liquid	References
12	[C ₂ C ₁ im][HS], [C ₂ C ₁ im][HSe], [C ₂ C ₁ C ₁ im][HS], [C ₄ C ₁ im][HS], [C ₄ C ₁ pyrr][HS]	Finger <i>et al.</i> ¹¹¹
13	[P ₁₁₁₁][PCO], [P ₄₄₄₁][PCO], [bmpyr][PCO], [dmpyr][PCO], [N ₁₁₁₁][PCO], [C(NMe ₂) ₃][PCO], [EMIm][PCO], [P ₄₄₄₁] ₃ [Sb ₁₁ ³⁻]	Jost <i>et al.</i> ¹¹²
14	[C ₂ C ₁ im][F]·xH ₂ O	Rijksen and Rogers ¹¹³
15	[Me-DMAP][MeOCO ₂], [Me-DMAP][HOCO ₂]	Tintori <i>et al.</i> ³²
16	[N _{xxx1}] ₂ [SiF ₆], [N _{xxx}] ₂ [SiF(CN) ₅], [N _{xxx1}] ₂ [Si(CN) ₆] (x = 2,3,4)	Harloff <i>et al.</i> ¹¹⁴
17	[N ₄₄₄₁][NCS] [N ₄₄₄₁][PCO]	Beer <i>et al.</i> ¹¹⁵
18	[N ₈₈₈₁][RCO ₂] (R = C ₄ to C ₈ alkyl chain)	De Feo <i>et al.</i> ¹¹⁶

In their study about generation of organic electron-donors from air-stable precursors, Tintori *et al.* synthesized the zwitterionic structure [C₁C₁-4-CO₂] (see section 3.2) but also dimethylamino-methylpyridinium methylcarbonate [Me-DMAP][MeOCO₂] ionic liquid, made by nearly quantitative methylation of DMAP with DMC. They also obtained [Me-DMAP][HOCO₂] in heating [Me-DMAP][MeOCO₂] in a water : ethanol mixture (Table 5, entry 15).³²

Harloff *et al.* used the commercial salts [N₂₂₂₁][MeOCO₃], [N₃₃₃₁][MeOCO₃], and [N₄₄₄₁][MeOCO₃] to produce new ion pairs based on fluorosilicate SiF₆²⁻ and cyanosilicates anions SiF(CN)₅²⁻ and Si(CN)₆²⁻.¹¹⁴ [N_{xxx1}]₂[SiF₆] (x = 2,3, or 4) were obtained by acid/base neutralization of [N_{xxx1}][MeOCO₂] with the hexafluorosilicic acid H₂SiF₆ in a 90% yield. Then these new salts react with TMS-CN at room temperature (respectively at 100 °C) to form [N_{xxx1}]₂[SiF(CN)₅] (respectively [N_{xxx1}]₂[Si(CN)₆] (Table 5, entry 16).

Aith the aim of trapping hydrogen pseudo-halides (*i.e.* HCN, HN₃, HNCO, HNCS, HPCO), Beer *et al.* prepared with excellent yields [N₄₄₄₁][NCS] and [N₄₄₄₁][PCO], using commercial solution of [N₄₄₄₁][MeOCO₂] and trimethylsilyl-thiocyanate TMS-SCN, and trimethylsilyl phosphine TMS₃P (Table 5, entry 17).¹¹⁵

De Feo *et al.* patented the use of [N₈₈₈₁][RCO₂] ionic liquids (R is an alkyl chain (4 to 8 carbons)) made by anion exchange with commercial [N₈₈₈₁][MeOCO₂], as the major compound of lubricants (Table 6, entry 18).¹¹⁶

6. Conclusion

The development of truly sustainable solvents and liquid materials is a long quest, and requires the analysis of the product's life cycle. The synthesis of ionic liquids is a critical step when considering their environmental impact, as the most implemented synthetic routes use harmful reagents and can produce large amounts of harmful waste. The dialkylcarbonate route to ionic liquids meets sustainable environmental requirements, with the use of safe and non-toxic alkylating agents, a limited number of purification steps, and an anion exchange not requiring harmful by-products nor the use of large amount of solvents.

Since the first synthesis of ionic liquids *via* the DAC route in the late 1990s, more than 100 different ion pairs have been

synthesised in this way, taking advantage of the ease of anion metathesis from methylcarbonate ionic liquids, the safety of the chemicals used, and the absence of halides or water during the process. In this tutorial review, we presented the synthesis of existing and new ionic liquids, highlighting how large the scope of this pathway is to provide a wide variety of ion pairs. Certainly, the nature of the cations is limited by the alkylation step, but the most common cations (phosphonium, ammonium, imidazolium) can be reached. On the contrary, the scope of the anion metathesis seems to have very few limitations, as the numerous examples listed herein demonstrate.

Abbreviations

AIBN	Azobisisobutyronitrile
AE	Atom Economy
AMPS	2-Acrylamido-2-methylpropanesulfonate anion
bmpyr	<i>N,N</i> -Butyl-methylpyrrolidinium cation
bmmorph	<i>N,N</i> -Butyl-methylmorpholinium cation
CBILs	Carbonate-Based Ionic Liquids
dmpyr	<i>N,N</i> -Dimethylpyrrolodinium cation
dbm	Dibenzoylmethanate anion
DMC	Dimethylcarbonate
DAC	Dialkylcarbonate
DMAP	Dimethylaminopyridine
DMSO	Dimethylsulfoxide
dbc	Terephthalate (benzene-1,4-dicarboxylate) anion
DMF	Dimethylformamide
EC	Ethylene carbonate
<i>E</i> _{fac}	<i>E</i> -Factor
EMIm	1-Ethyl-2,3-dimethylimidazolium
empip	<i>N,N</i> -Ethyl-methylpiperidinium cation
emmorph	<i>N,N</i> -Ethyl-methylmorpholinium cation
GBL	γ -Butyro-lactone
ibu	Ibuprofenate anion
C _x C _y im	Dialkyl imidazolium cation
is-MIL-53 (Al)	imidazolium salt MIL-53(Al) type MOF
LCFA-ILs	Long chain fatty acid ionic liquids
lev	Levulinate anion
ME	Mass efficiency
Me-DMAP	Dimethylamino- <i>N</i> -methylpyridinium

MOF	Metal–organic framework
3-MPT	3-mercaptopropyltrimethoxysilane
N_{xyz}	Tetralkylammonium cation
NTf_2	Bis(trifluoromethane)sulfonimide anion
OAc	Acetate anion
OESs	Organic electrolyte solutions
P_{xyz}	Tetralkylphosphonium cation
PMI	Process Mass Intensity
succ	Succinate anion
TMS	Trimethylsilyl
tmimn	1,2,3,4-Tetramethyl-imidazolium cation
TFSAm	Trifluoromethanesulfonamide anion

Conflicts of interest

The authors have no conflicts to declare.

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