Synthesis and Properties of Room-Temperature Choline Carboxylate Zwitterionic Ionic Liquids as Potential Electrolytes

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Dedicated to Professor Carlos A. M. Afonso on the occasion of his 50th birthday

Choline carboxylate zwitterions were prepared by two different synthetic routes through esterification of choline salts with a range of anhydrides. Their conjugation with lithium bis(trifluoromethylsulfonyl)imide resulted in the formation of stable room-temperature ionic liquids. In view of their use as potential electrolytes the physicochemical characterization of these attractive ionic liquids was performed. These compounds presented a glass transition temperature between -43 and $-34\,^{\circ}$C, good thermal stability up to $224\,^{\circ}$C, densities above $1.44\,\mathrm{g\,cm^{-3}}$ at $25\,^{\circ}$C, and viscosities between 3.56 and 12.27 Pa s at $25\,^{\circ}$C. In terms of conductivity the most promising ionic liquid showed an excellent conductivity between $8.66\times10^{-5}\,\mathrm{S\,cm^{-1}}$ at $25\,^{\circ}$C and $1.80\times10^{-3}\,\mathrm{S\,cm^{-1}}$ at $90\,^{\circ}$C. These zwitterionic ionic liquids maintained a liquid state, and no dissociation was observed even after six months of storage at room temperature.

Introduction

Over the last decades ionic liquids have been designed to enhance their already attractive physicochemical properties and fulfill the specific needs of many applications.[1] An example of this effort is the design of a new subclass of ionic liquids, called zwitterionic ionic liquids (ZILs). ZILs, like other zwitterionic compounds, are mainly characterized by having formal unit electrical charges of opposite sign.[2] Among the zwitterionic-type ionic liquids, imidazolium cations tethered with sulfonate anions are by far the most common and have been intensively studied as electrolytes for lithium batteries[3] or for fuel cells[4] (Scheme 1). These studies have shown that zwitterions are excellent ion dissociators and can promote target ion transport.[5]

Other less explored zwitterionic salts based on imidazolium cations are the compounds containing carboxylate anions. These have been used mainly as Brønsted acidic catalysts,[6] on desulfurization of fuels,[7] metal oxides solubilization,[8] and liquid crystals.[9] Concerning their synthesis, these zwitterionic carboxylates have been prepared by neutralization of the respective carboxylic acid with a base and subsequent dissociation of the halide salt from the zwitterion inner salt[6,9] or by hydrolysis of an ester derivative of the desired zwitterions through an anion-exchange resin.[5d]

In 1953, Phillips[10] reported the synthesis of a carboxylic ammonium salt (**1**) from the reaction between choline iodide (**2a**) and succinic anhydride (**3**), two cheap, readily available, and known low toxicity materials that caught our attention (Scheme 2). Despite the reported synthesis of **1**, to the best of our knowledge no choline zwitterionic inner salts of this type
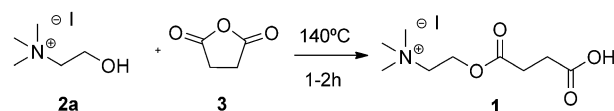
Scheme 2. Synthesis of carboxylic ammonium salt from the reaction between choline iodide and succinic anhydride.[10]
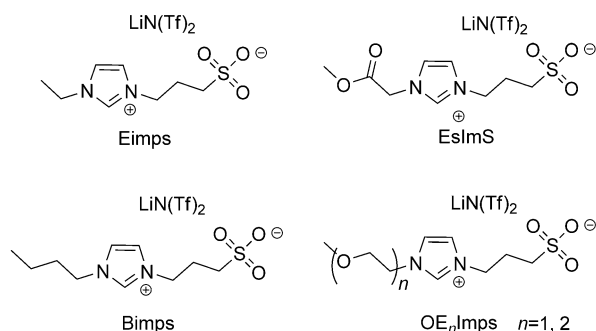
Scheme 1. Some examples of zwitterionic ionic liquids reported in the literature.[5]

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have been reported until now. These zwitterionic inner salts present some features that could be beneficial for its use as electrolytes. Particularly, concerning their structural features, the ester and the carboxylate group constitute added value in terms of ion transport.[5e] Additionally, in terms of biodegradability both groups facilitate the degradation of the compound at the end of its life cycle. Its primary degradation products are choline and dicarboxylic acid, biomaterials that can hardly be considered waste.[11]

However, owing to the presence of the ester moiety on these molecules, the common alkaline and anion-exchange methods cannot be used, because they result in the hydrolysis of the starting material. Accordingly, mild conditions needed to be developed to synthesize these new choline zwitterionic inner salts.

Herein, we describe two synthetic routes based on the esterification of choline salts with anhydrides for the preparation of choline-based zwitterions, as well as the room-temperature ionic liquids obtained from their conjugation with lithium bis(trifluoromethylsulfonyl)imide (Scheme 3).

Results and Discussion

The first synthetic route (Scheme 3, route I) arose from the reaction of choline acetate (**2 c**) with glutaric anhydride (**4**). Under these conditions we observed the formation of the respective zwitterion inner salt **8** and acetic acid instead of the corresponding acetate salt. This interesting result can be explained by the different pK_a values of the involved compounds (pK_a values of glutaric acid and acetic acid are 4.34 and 4.76, respectively). The higher acidity of the zwitterion carboxylic group must be decisive to protonate the acetic acid, resulting in the formation of the zwitterion inner salt. This finding prompted us to use choline acetate for the synthesis of this type of zwitterions, where the acetic acid produced during reaction could be removed from the reaction medium by continuous distillation. Another important feature of this reaction is that no solvent is required. By performing the reaction at temperatures above the melting point of the anhydride, a liquid homogeneous reaction mixture is achieved allowing the reaction to proceed. The reaction was optimized with regard to the temperature, choline/anhydride ratio, and reaction time. The best experimental conditions were obtained under neat conditions at 75 °C in vacuum (0.5 mbar) with 1.5 equivalents of anhydride. Under these conditions complete esterification of the choline acetate was achieved after 2 hours (by NMR analysis; entry 1, Table 1). Over 76 % of the acetic acid was removed from the reaction mixture after 2 hours of vacuum, and less than 5 % remained after 12 hours. After the esterification reac-

Table 1. Synthesis of lithium bis(trifluoromethylsulfonyl)imide choline-based zwitterionic ionic liquids.[a]

Entry	Substrate	Anhydride (equiv)	T [°C]	t [h]	Conv. [%][b]	Product	Yield [%]
1	**2 c**	4 (1.5)	75	2	>98	**12**	73
2	**2 d**	4 (1.5)	75	2	>98	**12**	57
3	**2 c**	5 (2)	80	4	>98	**13**	74
4	**2 c**	3 (2)	145	4	90	**11**	—[c]
5	**2 c**	6 (2)	80	3	90	**14**	—[d]
6	**2 e**	4 (2)	75	3	>98	**12**	67
7	**2 e**	5 (2.5)	80	8	>98	**13**	63

[a] All reactions were performed between substrates (**2 c–e**) and anhydrides (**3–6**) under vacuum (0.5 mbar). [b] Determined by ¹H NMR spectroscopy for the zwitterionic compounds (**7–10**). [c] NMR data revealed partial cleavage of the ester bond. [d] NMR data revealed complete cleavage of the ester bond.
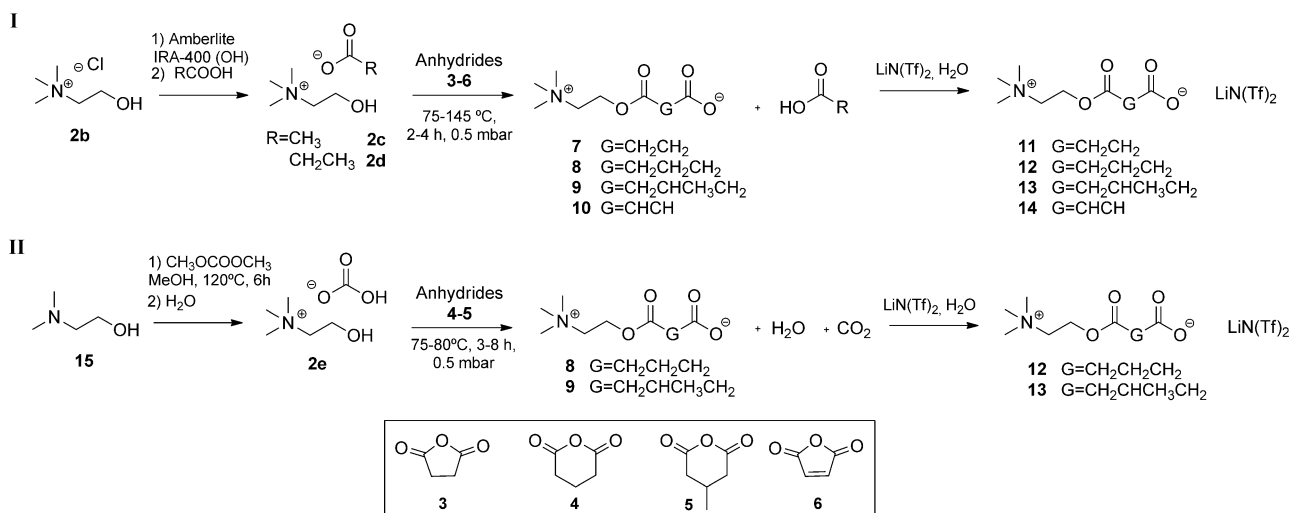
Scheme 3. Synthetic routes for the preparation of choline-based zwitterionic liquids.

tion the crude zwitterion inner salt **8** was dissolved in distilled water and mixed with a slight excess of LiN(Tf)$_2$. These two consecutive steps led to the formation of pure glutarylmonocholine/LiN(Tf)$_2$ salt (**12**; [gmch][LiN(Tf)$_2$]) as a colorless viscous liquid in 73% overall yield (entry 1, Table 1).

To understand the influence of the leaving group, the reaction was performed in the presence of choline propanoate (**2d**). Under similar conditions the esterification of choline propanoate was also complete after 2 hours but only about 50% of the acid was removed after this time (entry 2, Table 1).

Using choline acetate as substrate, this reaction was then extended to three other anhydrides: 3-methylglutaric (**5**), succinic (**4**), and maleic anhydride (**6**). Under the same conditions, 3-methylglutarylmonocholine/LiN(Tf)$_2$ (**13**; [mgmch][LiN(Tf)$_2$]) was obtained as a pale yellow viscous liquid in 74% yield (entry 3, Table 1). The other two zwitterionic ionic liquids (**11** and **14**) were found to be extremely delicate, with ester bond cleavage occurring during the purification/drying steps (entries 4 and 5, Table 1). Maleylmonocholine (**14**) with its rigid chain and oriented carboxylate group was extensively degraded, whereas succinylmonocholine (**11**) with a flexible chain revealed less degradation. An intramolecular attack of the carboxylate group to the ester group, and formation of a stable five-membered ring is the most probable mechanism for cleavage of the ester bond.[12]

On the other hand, the ZILs [gmch][LiN(Tf)$_2$] and [mgmch]-[LiN(Tf)$_2$] seem to be more stable, and no ester cleavage or color degradation was observed even after six months of storage at room temperature. In addition, during this period these zwitterionic ionic liquids maintained a liquid state and no dissociation was observed.

The second synthetic route (Scheme 3, route II) arose from the fact that route I is dependent on the zwitterions carboxylic acid pK_a values. With this in mind, a protocol for the synthesis of choline hydrogen carbonate (**2e**) from the reaction of dimethylaminoethanol (**15**) and dimethylcarbonate was developed. Because the hydrogen carbonate anion is essentially non-nucleophilic, this choline compound could also be esterified with anhydrides to prepare halogen-free zwitterions, CO$_2$ and water being the only by-products. Following the previous strategy, this reaction was performed to synthesize [gmch][LiN(Tf)$_2$] (**12**) and [mgmch][LiN(Tf)$_2$] (**13**), which were obtained as viscous liquids in 67% and 63% overall yields, respectively (entries 6 and 7, Table 1).

The structure of the compounds obtained by the two methods was confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis, after which they were characterized by differential scanning calorimetry (DSC), and their viscosities, densities, and conductivities measured (Table 2).

The DSC diagrams of the zwitterionic ionic liquids on their second heating trace (10 °C min^{-1}) showed that [gmch][LiN(Tf)$_2$] exhibits the lowest glass transition temperature (T_g) value of the two compounds, with a T_g of −43 °C, whereas [mgmch]-[LiN(Tf)$_2$] showed a T_g value of −34 °C (see the Supporting Information). These results seem to indicate that the introduc-

tion of an ester moiety is significant to obtain low T_g values, and is probably due to enhancement of motional freedom, as previously reported for the ether moiety.[5c, 13] As previously reported for the imidazolium cation,[5d] the addition of lithium salt to zwitterions results only in the observation of a glass transition temperature. No crystallization temperature or melting temperature was detected for these compounds. Evaluation of the thermal stability showed that [gmch][LiN(Tf)$_2$] and [mgmch][LiN(Tf)$_2$] are thermally stable up to 224 and 172 °C, respectively (see the Supporting Information). These decomposition temperatures are significantly lower than those observed for similar imidazolium compounds.[5c]

The conductivity measurements, displayed in Figure 1, revealed two distinct regions: the region of the electrode polarization on the low frequency side, and the region where a plateau is observed on the high frequency side. In the latter one, the conductivity is independent of frequency, that is, the direct conductivity.[14] The direct conductivity measurements at 25 °C showed that [gmch][LiN(Tf)$_2$] (**12**) and [mgmch][LiN(Tf)$_2$] (**13**) present an ionic conductivity of 8.66×10^{-5} and 3.30×10^{-5} S cm^{-1}, respectively. The higher conductivity of [gmch]-[LiN(Tf)$_2$] should be mainly attributed to the lowest T_g between the two compounds. The direct conductivity measurements at different temperatures were extended for [gmch][LiN(Tf)$_2$]

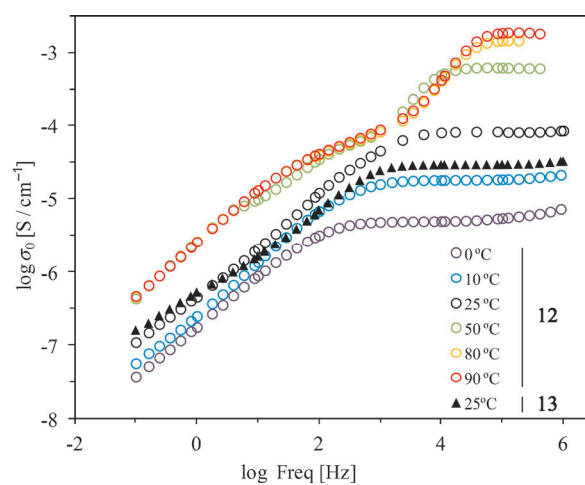**Table 2.** Data representative of the properties of new lithium bis(trifluoromethylsulfonyl)imide choline-based zwitterionic ionic liquids.

Entry	Product	Physical state[a]	Water content [%w/w]	T_g [°C][b]	T_{decomp} [°C][c]	Viscosity [Pa s][d]	Density [g cm^{-3}][d]	Direct conductivity [S cm^{-1}][d,e]
1	**12**	liquid	0.25	−43	224	3.56	1.4867	8.66×10^{-5}
2	**13**	liquid	0.23	−34	172	12.27	1.4487	3.30×10^{-5}

[a] Observed visual state at room temperature. [b] Determined as the onset temperature in the heating mode (10 °C min^{-1}). [c] Decomposition temperature is the temperature at which exothermic or endothermic behavior initiated after prolonged heating. [d] At 25 °C. [e] Conductivity independent of frequency.

Figure 1. Ionic conductivity as a function of frequency for [gmch][LiN(Tf)$_2$] (**12**) at temperatures between 0 and 100 °C (○), and for [mgmch] [LiN(Tf)$_2$] (**13**) at 25 °C (▲).

(Figure 1). At 80 °C a conductivity of 1.45×10^{-3} S cm^{-1} was obtained for [gmch][LiN(Tf)$_2$]. Pleasingly, these conductivities are about one fold higher than the ones reported so far for ZIL based on imidazolium salts.[5c] Furthermore, the viscosity of [gmch][LiN(Tf)$_2$] is three times lower than that of [mgmch]-[LiN(Tf)$_2$] (3.56 and 12.27 Pa s, respectively).

These results seem to be in line with the study of Tokuda et al.[15] that relates the behavior of the transport properties, viscosity, and diffusion to a ratio of ionic conductivities, which can be interpreted as a measure of ionic dissociation. These authors observed that the ionic dissociation is directly related to the diffusion coefficient, and inversely related to the viscosity, and they attribute this to a preponderance of the effect of the Van der Waals interactions over electrostatic terms. In addition, for these compounds we have observed that the viscosity remains constant with increasing shear rates (from 0 to 1000 s). This linear relationship between the shear stress and the shear rate indicates that these compounds present a Newtonian behavior (see the Supporting Information).

In terms of density [gmch][LiN(Tf)$_2$] and [mgmch][LiN(Tf)$_2$] showed very similar values, 1.4867 and 1.4487 g cm^{-3} at 25 °C, respectively (see the Supporting Information).

Another important aspect of the characterization of potential electrolytes is the illustration of the ionic conductivity as a function of the inverse of temperature. Since liquid electrolytes do not obey Arrhenius behavior above the glass transition temperature, a similar behavior should be expected. In fact, this behavior was observed for the tested compound, [gmch][LiN(Tf)$_2$] (**12**). One of the most common empirical forms used to describe ion transport in these systems is expressed by the Vogel–Fulcher–Tamman (VFT) equation.[16] The best fitting result is represented as the solid line in Figure 2, where we can conclude that the temperature dependence of the ionic conductivity for this compound (**12**) obeyed the VFT equation quite well. These results show that the ionic conductivity increases with increasing temperature, probably owing to the increase of the ionic dissociation and decrease of the viscosity at higher temperatures. The fitting parameters σ_∞, B, and T_0 for the VFT equation are described in Table 3.

Besides the zwitterionic ionic liquids reported in the literature, to the best of our knowledge, there is no published data concerning these parameters. However, if we compare these
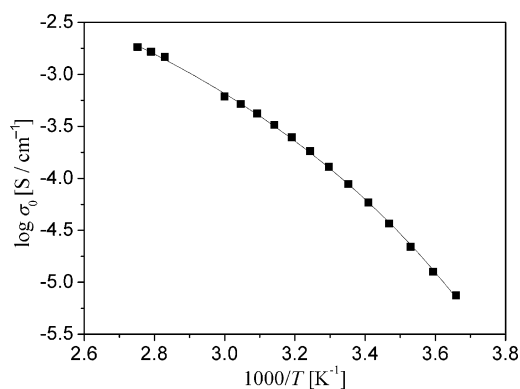
Table 3. Parameters for the VFT equation of ionic conductivity data.

$$\sigma_0(T) = \sigma_\infty \exp\left(-\frac{B}{T - T_0}\right)$$

Product	σ_∞ [S cm^{-1}]	B [K]	T_0 [K]
12	0.268 ± 0.048	837 ± 45	194 ± 3

parameters with the ones associated with the imidazolium ionic liquids,[15, 17] the value of σ_∞ is significantly lower, meaning that zwitterion has its lowest conductivity in the high temperature limit. Regarding the B value it is possible to conclude that the temperature dependence of zwitterion conductivity exhibits a relatively higher curvature, meaning that its conductivity changes more with the temperature while approaching the glass transition temperature (T_g). Concerning the value of T_0, it is possible to observe that it is in the same order of magnitude.

Conclusion

To conclude, two synthetic routes for the preparation of zwitterionic choline-based salts containing a carboxylate group were reported. In addition, one of the synthetic routes was developed as a halogen-free strategy. The addition of lithium salts, such as LiN(Tf)$_2$ to the zwitterionic salts produces room-temperature ionic liquids with low T_g values (−34 to −43 °C). Besides high viscosities (3.56–12.27 Pa s) the zwitterionic compounds showed high ionic conductivity between 3.30×10^{-5} and 8.66×10^{-5} S cm^{-1} at 25 °C and up to 1.80×10^{-3} S cm^{-1} at 90 °C. These compounds maintained a liquid state and no dissociation was observed even after six months of storage at room temperature. These encouraging results indicate that choline carboxylate zwitterionic ionic liquids are good candidates to be applied as matrixes for electrochemical applications.

Experimental Section

General methods

All reagents and solvents were obtained commercially, unless otherwise noted, and appropriately purified, if necessary. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AVANCE II 400 MHz NMR spectrometer, using [D$_6$]DMSO as solvent and the residual solvent peak as reference. Water content of all ionic liquids was measured by Karl Fisher titration with a Methrom 831 KF coulometer. Elemental analyses and DSC measurements were conducted by REQUIMTE-DQ-FCT (Portugal) and carried out with a Thermo Finnigan Flash EA 111 and Setaram DSC 131 calorimeter at a scanning rate of 10 °C min^{-1}, respectively. Viscosity measurements were performed on a Bohlin Gemini HRnano Rotational reometer. Density measurements were carried out with an Anton Paar DMA5000 density meter. The conductivity measurements were performed using dielectric relaxation spectroscopy. Two silica spacers of 0.05 mm thickness were used. The samples were placed between two stainless-steel plated electrodes (10 mm diameter) in a parallel plate capacitor, BDS 1200. The sample cell was mounted on a cryostat, BDS 1100, and exposed to a heated

Figure 2. Ionic conductivity as a function of the inverse temperature for [gmch][LiN(Tf)$_2$] (**12**).

gas stream being evaporated from liquid nitrogen in a Dewar. The temperature control was assured by the Quatro Cryosystem and performed within ±0.5 K (all modules supplied by Novocontrol). Measurements were carried out using an Alpha-N analyzer also from Novocontrol GmbH, covering a frequency range from 10⁻¹ Hz to 1 MHz.

General procedure for the synthesis of choline alkanoates 2c and 2d

Choline chloride **2b** (1.047 g, 7.5 mmol) dissolved in methanol (75 mL) was slowly passed through a column filled with resin AMBERLITE IRA-400(OH) (12.5 g). The dripping choline hydroxide solution was collected in an Erlenmeyer flask containing a slight excess of the desired carboxylic acid dissolved in methanol. The resulting solution was passed through a small column filled with Celite 577, activated basic aluminum oxide, and silica-gel, for removal of unreacted carboxylic acid and visible particles. After solvent removal by evaporation under reduced pressure, the resulting product was dried in vacuo at 50 °C overnight.

Choline acetate 2c: From acetic acid (0.430 mL, 7.5 mmol), compound **2c** was obtained as a white to pale yellow hygroscopic solid (1.06 g, 86%). ¹H NMR (400 MHz, 25 °C): $\delta = 3.83$ (m, 2H), 3.42 (m, 2H), 3.13 (s, 9H), 1.58 ppm (s, 3H); ¹³C NMR (100 MHz, 25 °C): $\delta = 173.6$, 67.3, 54.8, 53.0, 25.7 ppm.

Choline propanoate 2d: From propionic acid (0.560 mL, 7.5 mmol), compound **2d** was obtained as a yellow viscous liquid (1.10 g, 84%). ¹H NMR (400 MHz, 25 °C): $\delta = 3.84$ (m, 2H), 3.43 (m, 2H), 3.13 (s, 9H), 1.83 (q, 2H), 0.88 ppm (t, 3H); ¹³C NMR (100 MHz, 25 °C): $\delta = 176.6$, 67.4, 54.9, 53.1, 31.2, 11.4 ppm.

Synthesis of choline hydrogen carbonate 2e

A mixture of dimethylaminoethanol (DMAE) (8.1 mL, 80 mmol), dimethylcarbonate (DMC) (7.4 mL, 88 mmol), and methanol (5.5 mL) was heated at 120 °C in a Teflon-coated stainless-steel reactor (90 mL) for 6 h. The crude mixture was diluted with methanol (15 mL), mixed with an abundant amount of activated carbon, and left under vigorous stirring for 24 h. After filtration of solids and removal of unreacted materials and solvent by evaporation under reduced pressure, the product was dried in vacuo at RT until a pale yellow solid was obtained. This solid was decolorized by stirring it in a solution of acetonitrile/tetrahydrofuran (1:2) for 48 h, with renewal of the solution after 24 h. After filtration, the solid was dissolved in a minimum amount of ethanol and two equivalents of distilled water were added. The reaction was stirred overnight at RT, after which the solvent was removed by evaporation under reduced pressure. Choline hydrogen carbonate was obtained as a white to pale yellow hygroscopic powder (9.08 g, 69%). ¹H NMR (400 MHz, 25 °C): $\delta = 3.83$ (m, 2H), 3.42 (m, 2H), 3.11 ppm (s, 9H); ¹³C NMR (100 MHz, 25 °C): $\delta = 159.4$, 67.4, 55.4, 53.5 ppm.

General procedure for the synthesis of choline-based zwitterionic ionic liquids 11–14

A mixture of choline compound **2c–e** (2 mmol) and anhydride **3–6** (from 3–5 mmol) was heated (from 75–145 °C) in vacuo (0.5 mbar) for 2–8 h. After cooling at RT, the crude product was dissolved in distilled water (2 mL), mixed with lithium bis(trifluoromethylsulfonyl)imide (2.2 mmol), and vigorously stirred at RT for at least 14 h. Then the aqueous phase was removed and the ionic liquid phase washed 2–3 times with distilled water (0.5 mL). Finally the ionic liquid was dried in vacuo at RT for at least 48 h.

Succinylmonocholine lithium bis(trifluoromethylsulfonyl)imide (11): From choline acetate **2c** (0.325 g, 2 mmol) and freshly sublimated succinic anhydride **3** (0.400 g, 4 mmol). This mixture was heated at 145 °C in vacuo (0.5 mbar) for 4 h. Following the general procedure, the desired product was obtained with purity never above 90% owing to partial cleavage of the ester bond during the purification/drying steps.

Glutarylmonocholine lithium bis(trifluoromethylsulfonyl)imide (12): From choline acetate **2c** (0.324 g, 2 mmol) and glutaric anhydride **4** (0.346 g, 3 mmol). This mixture was heated at 75 °C in vacuo (0.5 mbar) for 2 h. Following the general procedure, the desired product was obtained as a colorless viscous liquid (0.73 g, 73%; water content (% w/w): 0.43).

From choline hydrogen carbonate **2e** (0.357 g, 2 mmol) and glutaric anhydride **4** (0.463 g, 4 mmol). This mixture was heated at 75 °C in vacuo (0.5 mbar) for 3 h. Following the general procedure, the desired product was obtained as a colorless viscous liquid (0.68 g, 67%; water content (% w/w): 0.25). ¹H NMR (400 MHz, 25 °C): $\delta = 4.44$ (m, 2H), 3.75 (m, 2H), 3.11 (s, 9H), 2.38 (t, 2H), 2.26 (t, 2H), 1.76 ppm (m, 2H); ¹³C NMR (100 MHz, 25 °C): $\delta = 174.1$, 172.0, 119.5 (q), 63.8, 57.8, 52.9, 32.8, 32.6, 19.8 ppm; elemental analysis calcd (%) for $C_{12}H_{19}F_6LiN_2O_8S_2$: C 28.58, H 3.80, N 5.55; found: C 28.26, H 3.80, N 5.38.

3-methyglutarylmonocholine lithium bis(trifluoromethylsulfonyl)imide (13): From choline acetate **2c** (0.326 g, 2 mmol) and 3-methylglutaric anhydride **5** (0.513 g, 4 mmol). This mixture was heated at 80 °C in vacuo (0.5 mbar) for 4 h. Following the general procedure, the desired product was obtained as a pale yellow viscous liquid (0.76 g, 74%; water content (% w/w): 0.53).

From choline hydrogen carbonate **2e** (0.358 g, 2 mmol) and 3-methylglutaric anhydride **5** (0.646 g, 5 mmol). This mixture was heated at 80 °C in vacuo (0.5 mbar) for 8 h. Following the general procedure, the desired product was obtained as a pale yellow viscous liquid (0.65 g, 63%; water content (% w/w): 0.23). ¹H NMR (400 MHz, 25 °C): $\delta = 4.44$ (m, 2H), 3.64 (m, 2H), 3.11 (s, 9H), 2.27 (m, 5H), 0.94 ppm (d, 3H); ¹³C NMR (100 MHz, 25 °C): $\delta = 173.6$, 171.4, 119.5 (q), 63.7, 57.8, 52.9, 40.4, 40.0, 26.9, 19.5 ppm; elemental analysis calcd (%) for $C_{13}H_{21}F_6LiN_2O_8S_2$: C 30.12, H 4.08, N 5.40; found: C 30.36, H 3.90, N 5.35.

Maleylmonocholine lithium bis(trifluoromethylsulfonyl)imide (14): From choline acetate **2c** (0.335 g, 2 mmol) and maleic anhydride **6** (0.401 g, 4 mmol). This mixture was heated at 80 °C in vacuo (0.5 mbar) for 3 h. Following the general procedure, extensive cleavage of the ester bond occurred, and the desired product could not be isolated.

Acknowledgements

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[18] By following the general procedure, extensive cleavage of the ester bond occurred and the desired product could not be isolated.