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A general environmentally friendly access to long chain fatty acid ionic liquids (LCFA-ILs)

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The development of bio-based ionic liquids (ILs) has attracted a great deal of interest in recent years. The so called long chain fatty acid ionic liquids (LCFA-ILs) represent a bio-based subfamily of the hydrophobic ionic liquids. Here, a new preparation of the three major classes of LCFA-ILs (phosphonium, ammonium, imidazolium) is presented with the aim to overcome previous environmental synthetic issues. The undeniable interesting properties and potential applications of the LCFA-ILs often led to the underestimation of the drawbacks related to their synthetic pathways.
Pure as well as cheaper mixture of LCFA-ILs have been obtained in a single step, in almost quantitative yields, and without production of waste water. The rheological and thermal stability properties of the prepared ILs have been analyzed.

Introduction

Ionic Liquids (ILs) are organic salts, generally composed of an organic cation and a wide range of different anions, which are liquid at or near room temperature.[1] They have attracted enormous interest in the last two decades due to their unique physicochemical properties comprising of negligible vapor pressure under ambient conditions, liquid state over a wide range of temperatures, low flammability, high ionic and thermal conductivity, wide electrochemical potential window, excellent thermal, chemical and radiochemical stability, and exceptional solvent power toward many substances. The virtually unlimited possible combinations of their constituents allow for the fine-tuning of these properties and for the tailoring of ILs to address specific problems. For all these reasons, the ILs research field is still expanding and encompasses, but is not limited to, their study as suitable green substitutes of volatile organic compounds (VOCs),[1] as exceptional media to dissolve and functionalize biopolymers (cellulose, chitin, lignin and so on)[2-7] or capture CO_2,[8,9] and as reagents or catalysts of some reactions. With regard to the latter, a new generation of ILs, characterized by at least an additional functional group either on the cation or on the anion directly involved in the reaction step, has been developed [task-specific ionic liquids (TSILs)].[10-12]
Despite the undeniable potential of ILs, from both an academic and an industrial perspective, there are some concerns about their use in large scale industrial processes or in health-related fields. These concerns originate from the petroleum-derived nature of the constituent building blocks of the majority of ILs, from the pollution implicated in their preparation, and from their possible intrinsic toxicity as final chemicals.[13]

A possible solution to these issues has been identified in the use of biomass-based materials to prepare bio-based ILs.[14] These should have the advantage of having a higher biodegradability than the conventional ILs and of an unlimited availability of the starting material, obtainable from renewable resources. Unfortunately, this research field is still a niche of the ILs investigations and most of the bio-based ILs' preparations require several synthetic steps to convert the natural compounds (e.g. amino acids or sugars)[15,16] into the desired anions or cations. However, it can be anticipated that significant research efforts will target an easier access to bio-based ILs in the foreseeable future, with issues such as water pollution, pollution-derived climate changes and oil depletion needing to be addressed.
One particular class of bio-based ionic liquids is the so called long chain fatty acid ionic liquids (LCFA-ILs). Some members of this class have been reported in the literature and are based on ammonium,[17-21] phosphonium[22,23] or imidazolium[24,25] cations as counterions of natural fatty acid carboxylates, which are in turn obtained from vegetable or algae-derived oils. LCFA-ILs belong to the larger family of hydrophobic ILs and represent their environmentally friendlier part. Usually, for petroleum-based hydrophobic ILs, the properties can be tuned by changing the cation substituent(s) and the anion identity: for example, highly fluorinated anions give hydrophobic salts with remarkable physico-chemical properties (low viscosity, high conductivity and so on).[26-29] For LCFA-ILs, the major effect comes from the fatty acid anion alkyl chain length and degree of saturation. LCFA-ILs have been tested as green alternatives to the conventional hydrophobic ILs in liquid-liquid extraction, demonstrating their capability to extract metals[18,23] and phenols[22] from aqueous solutions. Moreover, interesting results were obtained when their behavior as a lubricant, for low friction and wear, was investigated.[19] A report also highlighted how they possess antimicrobial properties.[17]
Therefore, LCFA-ILs are a class of ILs which are based on renewable biomaterial, don't require long synthetic pathways for the preparation of a ready-to-use anion like most bio-based ILs, don't present halogens in the anion like the majority of the hydrophobic

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ILs, and already show interesting applications. Based on these considerations, LCFA-ILs appear as a class of ILs which overcame the above mentioned ILs concerns and deserve further investigation to define new possible applications.

However, this analysis would be short-sighted and would not take into consideration a paramount aspect of the life-cycle of any new chemical. When a new chemical is proposed, as important as its potential applications are, the way it is prepared has to be carefully evaluated to determine whether, or to what extent, it respects the easy, efficient, inexpensive and green manufacture principles.[30] This analysis could completely counterbalance possible benefits of a new chemical, and render its synthesis and use ineffective in practice.

For the reported LCFA-ILs, each synthetic procedure, apart from being developed for a narrow window of ILs, presents specific drawbacks (e.g. need of a large amount of water to remove the excess of polluting reagents, need to use organic solvents during the reaction or at the end of it to extract the final LCFA-IL, need to use resins which is unpractical and not cost-effective at an industrial level, presence of halogen contaminants even on a small scale) which are underestimated when the benefits of the new chemicals are praised.

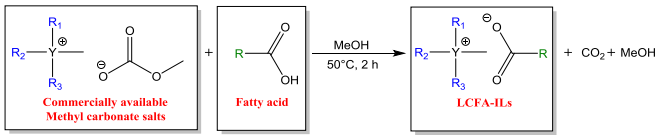
Herein, we report a new and green methodology to access LCFA-ILs, which overcomes all polluting drawbacks of the previous synthetic strategies. The proposed approach works well for all major classes of LCFA-ILs reported in the literature up to now, thus, representing a general way to prepare these bio-based ILs in an environmentally respectful manner. The new synthetized ILs were characterised and compared to known compounds in order to evaluate their rheological and thermal stability properties.

Results and discussion

Synthesis. The synthetic strategy explored here takes advantage of the commercial availability of the methyl carbonate salts of the three most used cations for the preparation of LCFA-ILs, namely imidazolium, ammonium, and phosphonium. In fact, 1-ethyl-3-methylimidazolium [EMIM], trioctylmethylammonium [N_{8881}], and trioctylmethylphosphonium [P_{8881}] methylcarbonate methanol solutions are prepared in multi-kilogram scale by Proionic GmbH. These reagents are in turn obtained employing dimethylcarbonate (DMC) as the methylating agent of 1-ethylimidazole, trioctylamine, and trioctylphosphine respectively. DMC has received growing attention after being exempted under the definition of volatile organic compounds by the United States Environmental Protection Agency in 2009. Nowadays, DMC is widely used as a fuel additive, as a green solvent, and, from a synthetic perspective, as either a carboxymethylating reagent (at temperatures around 90 °C) or a methylating agent (at temperatures above 120 °C).[31] Regarding the latter, it represents a green, safe, non-toxic, and biodegradable alternative to the classical methyl iodide and dimethysulfate. Its usefulness in the synthesis of ionic liquids has already been proved.[32]

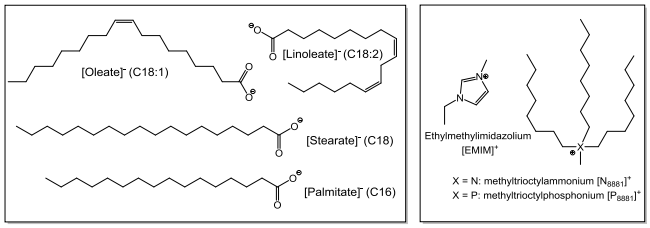
On these bases, a straightforward access to LCFA-ILs was investigated treating the commercial methyl carbonate salts with different fatty acids (Scheme 1).

The reaction was quick and clean giving the desired LCFA-ILs in almost quantitative yields by gently heating the reaction mixture at 50 °C for 2 hours. A careful titration of the carbonate salt with standard HCl solution was required before performing the reaction in order to add an equimolar amount of fatty acid and avoid the presence of unreacted reagents in the final compound. The different anions, which are present in the prepared LCFA-ILs, are reported in Figure 1.



Scheme 1. New synthesis of long chain fatty acid ionic liquids (LCFA-ILs).

Figure 1. Anions (left side) and cations (right side) components of the prepared LCFA-ILs.



In particular, palmitic acid, stearic acid, and linoleic acid were used as pure compounds while oleic acid was utilized as a mixture with either linoleic acid or minor amounts of other fatty acids. Information about the components of the latter mixture was obtained from the supplier.

Table 1. LCFA-ILs prepared in one step exploiting the commercial methyl carbonate salts.

LCFA-IL	Cation	Anion	Yield
1	[EMIM]	[C16]	>99%
2	[EMIM]	[C18]	>99%
3	[EMIM]	[C18:1 tested according to Ph.Eur.]	>99%
4	[EMIM]	[C18:2]	>99%
5	[EMIM]	[C18:1-C18:2 30%-70%]	>99%
6	[N_{8881}]	[C16]	>99%
7	[N_{8881}]	[C18]	>99%
8	[N_{8881}]	[C18:1 tested according to Ph.Eur.]	>99%
9	[N_{8881}]	[C18:2]	>99%
10	[N_{8881}]	[C18:1-C18:2 30%-70%]	>99%
11	[P_{8881}]	[C16]	>99%
12	[P_{8881}]	[C18]	>99%
13	[P_{8881}]	[C18:1 tested according to Ph.Eur.]	>99%
14	[P_{8881}]	[C18:2]	>99%
15	[P_{8881}]	[C18:1-C18:2 30%-70%]	>99%

The decision to use mixtures of fatty acids instead of pure compounds arises from the need to increase the appeal of these new

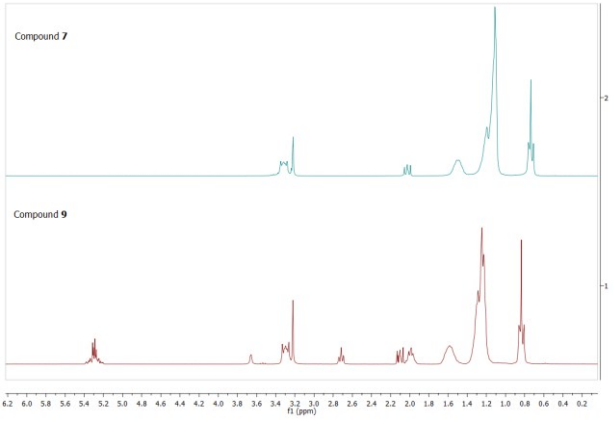
ionic liquids by decreasing their cost in view of an industrial use. For instance, the price of 99% pure oleic acid is over five hundred times higher than the price of the mixtures used in this work even on a lab scale. Therefore, the rheological properties of these mixtures of LCFA-ILs are of particular interest in order to evaluate their suitability as cheaper alternatives to pure LCFA-ILs. The different LCFA-ILs synthesized by reacting the commercial carbonate salts with the fatty acid counterparts are summarized in Table 1.

After removal of the solvent from the reaction mixtures by simply heating at 50 °C under vacuum, liquids of different viscosities were obtained for the [N_{8881}] and [P_{8881}] series (see next section for comments on viscosities), while the [EMIM] derived compounds appeared like waxy solids. For this latter series, the removal of methanol was not straightforward and significant quantities of residual solvent were observed even after repeating the drying procedure for longer periods as evidenced by NMR and thermal analysis.

The structures of the LCFA-ILs were confirmed by FTIR and NMR analysis (please refer to the Supporting information file). Integration of the peaks in the ^{1}H-NMR spectra ascertained the high purity of the LCFA-ILs and the 1:1 ratio between cation and anion. Signals for carbene derivatives, which have been observed before in the preparation of imidazolium carboxylates, were not found in the EMIM series.

For example, a comparison between two ammonium LCFA-ILs, compound **7** and **9**, is reported. In Figure 2, the top ^{1}H-NMR spectrum (stearate-ammonium **7**) shows five sets of signals.

Figure 2. Comparison between ^{1}H-NMR spectra of compound **7** and compound **9**.



The cationic and the anionic centers of the LCFA-ILs have deshielding effects. The methyl and the three methylene groups directly attached to the nitrogen atom exhibit the chemical shift in the range of 3,4-3,2 ppm, while the methylene adjacent to the carboxylate group exhibits the chemical shift in the range of 2,1-2.0 ppm. The deshielding effects decrease with the distance and therefore two separate sets of signals are found for the remaining methylene groups, both from the stearate and the octyl chains in the range of 1,6-1,4 ppm and 1,3-1,1 ppm. Terminal methyl groups show chemical shifts in the range of 0,8-0,7 ppm.

In the bottom spectrum (linoleate-ammonium **9**), the signals are practically identical apart from the peaks attributed to the presence of the 1,4-diene system in the linoleate anion, namely the four olefinic protons (5,4-5,2 ppm), the two *bis*-allylic protons (2,8-2,7 ppm), and the four allylic protons (2,0-1,9 ppm).

The FTIR spectra (Fig S37 for **7** and S39 for **9**) show the characteristic bending modes of methyl and methylene groups at 1465 cm^{-1} and 1380 cm^{-1} for **7**, and 1464 cm^{-1} and 1386 cm^{-1} for **9**. The distinguishing asymmetric stretches of the carboxylate group are also observed at 1573 cm^{-1} for **7** and 1570 cm^{-1} for **9**, which ensure the presence of the fatty acid anions. The vibrational mode of the =C-H stretching at 3005 cm^{-1} is only present for the unsaturated ionic liquid **9**.

The main drawback of the proposed approach comes from the side products obtained from the reaction: CO_2 and methanol (MeOH). CO_2 especially represents one of the main climate change-related concerns being involved in the greenhouse effect and in global warming. Its uncontrolled production is today absolutely forbidden and every new process which includes CO_2 formation has to be carefully evaluated.

However, interestingly enough, CO_2 and MeOH are the same reagents under investigation for the preparation of dimethyl carbonate through a metal catalysed step.[33-36] Thus, a completely environmentally friendly cycle for the LCFA-ILs preparation, where the side products (CO_2 and MeOH) are reused in the final DMC formation, can be envisaged.

Also, a comparison of the peculiar troublesome aspects of each different LCFA-ILs synthetic procedure reported in the literature up to now (Figure 3), highlights well the advantages of starting from commercially available methylcarbonate salts (bottom right).

From a practical point of view, only one synthetic step is required while no resins are needed to reach the final target. From an application point of view, halide free LCFA-ILs are obtained which means that no contamination of this type is possible in the final ILs. Otherwise, careful halide content control in each batch produced would be required to avoid halide-related viscosity variations and corrosion effects. Futhermore, no water is used in the synthesis. If a critical analysis of the previous preparations is performed, it can't be omitted that the production of waste water is an underestimated aspect. The amount of water saved by not requiring a) transformation of the fatty acid into its salt, b) activation of the resin, c) recovery of the ionic liquid from the resin, d) washing of the target IL to remove halide contamination, is the most relevant and environmentally beneficial aspect of the new LCFA-ILs synthesis. Finally, it is possible to envisage several economic benefits for a large scale industrial production following the proposed procedure, which arise both from the elimination of the waste water treatment, and the easy and fast removal of the solvent from the reaction mixtures by mild heating. This is an evident advantage in comparison to previous preparations where the emulsion formation determines a slow separation between the aqueous and the organic phases, which would increase the batch cycle time and, for a specific hourly production, the sizes of the equipment. Also, the possibility to use the side products obtained from the reaction, CO_2 and MeOH, once separated from the LCFA-IL, for the production of dimethylcarbonate, would lead to a highly-integrated process characterized by *in situ* production of the IL precursor.

Viscosity. Viscosity (η) was determined in a temperature range of 20 to 80 °C by applying 15 different shearing rates between 1 s^{-1} and 100 s^{-1}. The resulting average values are summarized in Table 2. Viscosity has not been measured for [EMIM] based ILs because they are solids at room temperature.

Careful drying procedures were carried out (stirring under high vacuum for at least 8 h at 50 °C) in order to remove residual reaction

solvent or water possibly absorbed during handling, which both affect (reduce) ionic liquids' viscosity.[37]

It is of interest to note that these ILs did not display an ideal Newtonian behaviour, and that the Casson regression gives better correlation coefficients. However, decrease of viscosity by increasing the shear rate in the temperature range under investigation, which is typical for a pseudo-plastic fluid, became more evident at high shear rates.

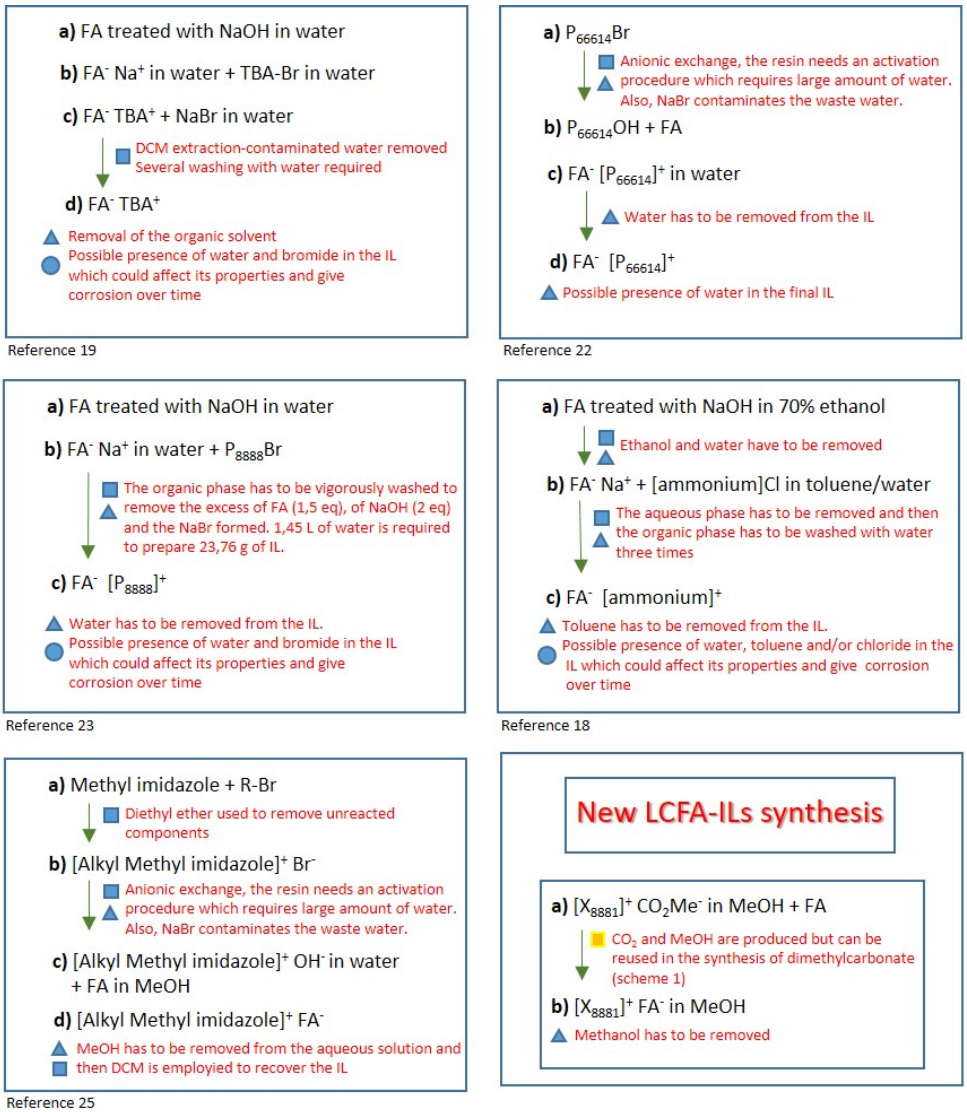
As generally observed for ILs, viscosity rapidly decreases on increasing temperature (Figure 4) and the temperature dependence of viscosity only approximately follows the Arrhenius equation (1),

$$\ln \eta = \ln \eta^{\infty} + E_{\eta}/RT \quad (1)$$

where E_{η} is the activation energy for viscous flows, and $\ln \eta^{\infty}$ is the natural logarithm of the viscosity at infinite temperature. The resulting parameters are listed in Table 2.

As usually observed, the experimental values (Table 2) show a dependence of ILs viscosity on the cation and anion's nature. In particular, ammonium ILs are characterized by a higher viscosity than corresponding phosphonium ILs, and viscosities decrease with the following order: $[N_{8881}][C16]>[N_{8881}][C18]>[N_{8881}][C18:2]>[N_{8881}][C18:1_{PhEur}]$, and $[P_{8881}][C16]>[P_{8881}][C18]>[P_{8881}][C18:1_{PhEur}]>[P_{8881}][C18:2]$. Two effects are generally considered in the analysis of these sequences, the one deriving from the extra van der Waals interactions when moving to longer aliphatic chains, which increase the viscosity values, and the converse effect related to the unsaturation degree. While this latter effect explains the last part of the series ($[P/N_{8881}][C18]>[P/N_{8881}][C18:2]$), the higher values for the palmitate ILs in comparison with the stearate ILs require an additional consideration. It has to be mentioned that this specific inversion has been reported before for a symmetrically alkylated phosphonium LCFA-IL where the viscosity for $[P_{4444}][C16]$ was higher than $[P_{4444}][C18]$.[22] A possible explanation is that in these

Figure 3. Exemplification of the previous LCFA-ILs synthetic approaches and the new proposed approach (bottom right), and related environmental (■), contamination derived (●), and practical (▲) issues.



FA = generic fatty acid; TBA = tetrabutyl ammonium; DCM = dichloromethane

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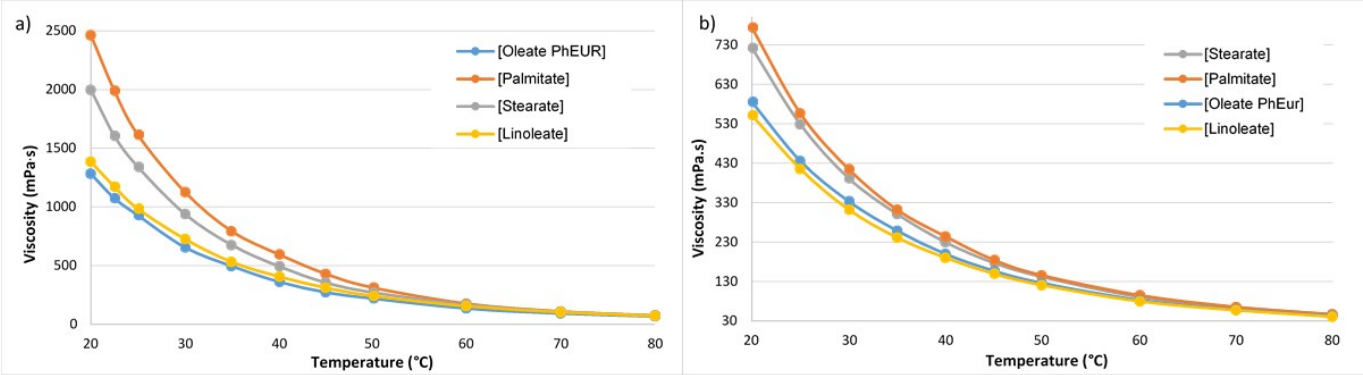
Figure 4. Dependence of ILs viscosity (mPa.s) on temperature of a) [N_{8881}] series and b) [P_{8881}] series.



cases the electrostatic interactions overcame the van der Waals interactions, and that an increase in the ions' size determines a decrease of the dominant interaction and the consecutive decrease of the viscosity. A similar result has been found comparing two LCFA-ILs characterized by the same anion and cations of different chain lengths ([N_{6666}][C18:1]>[N_{8888}][C18:1]).[20]

Table 2. Arrhenius equation fitting parameters

Cat.	Anion	ln η_∞ (mPa·s)	E_η (KJ·mol^{-1})	R^2
[N_{8881}]	[C16]	-13.02	50.58	0.9975
	[C18]	-12.03	47.62	0.9960
	[C18:1PhEur]	-10.49	42.83	0.9953
	[C18:2]	-10.33	42.65	0.9976
[P_{8881}]	[C16]	-9.992	40.38	0.9972
	[C18]	-9.721	39.56	0.9969
	[C18:1PhEur]	-9.175	37.76	0.9978
	[C18:2]	-9.061	37.33	0.9978

For the investigated phosphonium based ILs, the viscosity values, and the calculated E_η and ln $\eta\infty$ values are very close to each other, at least in comparison to the ammonium salts. The latter two parameters should give a quantitative evaluation of the ion difficulty to move past each other. The first is usually related to the ion physical size and to the presence of more or stronger interactions in the IL (hydrogen bond, dispersive and Coulombic interactions) whereas ln $\eta\infty$ is controlled solely by the geometric structure of the ions: consequently, the more attenuate effect of the anion structure on both these parameters for phosphonium ILs suggests a dominant role played by the large phosphonium cation. This dominant role could account also for the different viscosity values obtained when mixtures of fatty acids were used ([N_{8881}][C18:1$_{PhEur}$] vs [P_{8881}][C18:1$_{PhEur}$]). For the ammonium series the presence of a complex mixture of anions determines a lower viscosity than the pure linoleate compound **9**, a trend which is inverted in the phosphonium series.

Some differences between the data collected in this work and those reported in the literature for LCFA-ILs have been found. In case of **8**, the lower value of the viscosity compared to the pure LCFA-IL[20] plausibly arises from the presence of other fatty acids in the commercial oleic acid used. The higher discrepancy has instead been found for **9**, which is characterized by a higher viscosity value than the one previously reported.[18] This difference can be ascribed to different measurement methods and/or to the presence of impurities, deriving from synthetic contaminants (halogens, solvents, etc.) and water possibly adsorbed by contact with air (humidity) during manipulation.
As stated before, the presence of water has a huge effect on lowering the viscosity. This could sometimes be advantageous with high viscosity values often being one of the main hurdles for ILs practical applications. A previous study[23] showed that it is possible to tune the viscosity of phosphonium LCFA-ILs by carefully varying the amount of water uptake. A beneficial aspect of the synthetic approach here described is that water is not involved in any synthetic step and/or any purification/extraction procedure which gives access to reasonably dry ILs. This means that, if required, the viscosity can be adjusted for different applications by adding water up to the saturation level which has been estimated in around 11% wt.[23]

Thermal stability and phase behavior. The thermal stabilities of the synthesized ILs were compared by the ramped or 'scanning' TGA that allows for a rapid comparison between compounds in a series. In Figure 5, the temperature-ramped TGA thermographs of selected ILs are reported. From these TG curves, three characteristic temperatures of the ILs short-term thermal stability were evaluated, T_{start}, T_{onset}, and T_{peak}. Note that if there are more peaks in DTG curves, only the decomposition temperature corresponding to the highest peak was considered. Usually, $T_{start} < T_{onset} < T_{peak}$ for the same IL. Experimental conditions such as sample mass, heating rate, atmosphere type, atmosphere flowing rate, sample pan material, and instrument type may lead to the inconsistency of the experimental results obtained from different authors.[38,39] Therefore, in this work, similar experimental conditions were used: mass at 15–18 mg, N_2 atmosphere with flowing rate 100 mL/min, platinum pans, and a 5 °C/min heating rate. The temperature-ramped TGA experiments were performed in triplicate for each IL, in order to assess the reproducibility of the measurement. For all ionic liquids in this investigation, T_{start}, T_{onset}, and T_{peak} values were reproducible to within ± 2 °C. The average values for each synthesized ionic liquid are reported in Table 3.

Figure 5. Temperature-ramped TGA thermographs for selected ionic liquids with heating rate of 5 °C/min.

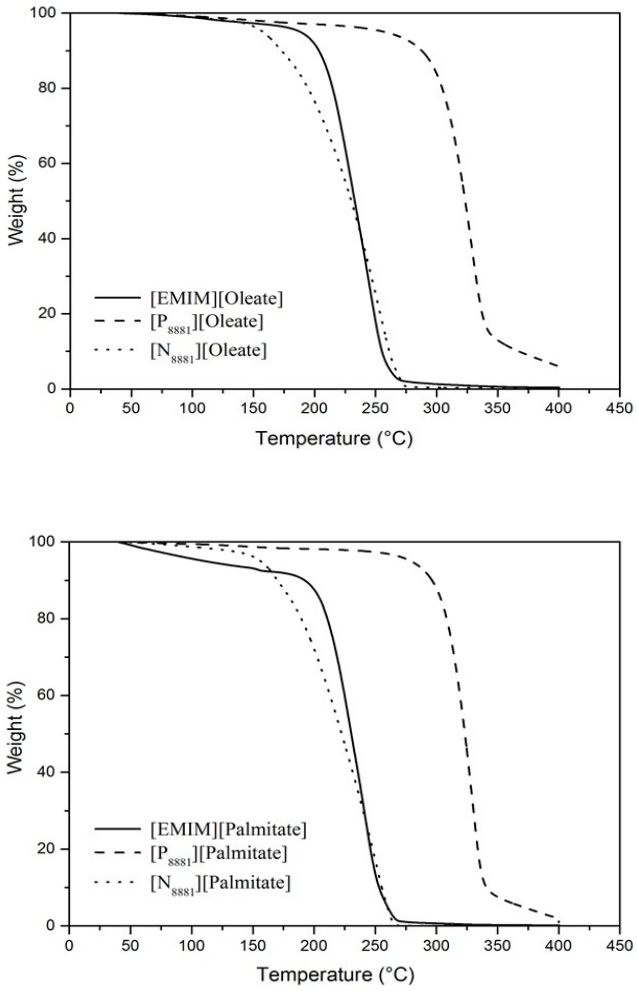
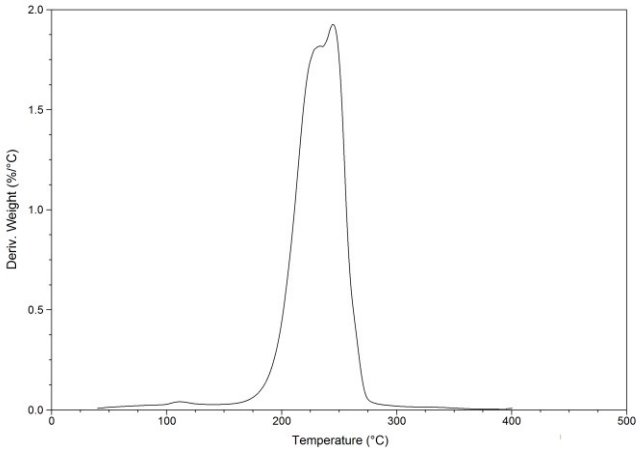


Figure 6. DTG curve for LCFA-IL **3**.



As shown by the TG curves (Figure 5), all ionic liquids tend to lose weight already at 50 °C, especially the [EMIM] series. The initial weight loss in the 50-120 °C range, accompanied by a small peak in the relative DTG curve (exemplified for LCFA-IL **3** in Figure 6), is mainly due to residual methanol and, secondarily, to the humidity absorbed (2-3wt.%) from the environment during handling. This is supported also by the NMR spectra as reported above. After this initial weight loss, the thermal decomposition of ILs occurs. On the basis of the T_{start}, T_{peak}, and T_{onset} values, the thermal stability of ILs seems to depend mainly on the cation, whereas the anion seems to have low influence on this property. The relative cation stabilities observed are $[P_{8881}]$>[EMIM]>$[N_{8881}]$. On the basis of the T_{onset} evaluated at a heating rate of 10 °C/min by ramped TGA experiments, Cao and Mu[40] classified the thermal stabilities of 66 ILs into five levels: least stable (T_{onset} < 250 °C), less stable (250 °C ≤ T_{onset} < 300 °C), moderately stable (300 °C ≤ T_{onset} < 350 °C), more stable (350 °C ≤ T_{onset} < 400 °C), and most stable (T_{onset} ≥ 400 °C). Following this classification and considering an increase of about 30-35 °C of the onset temperature when the heating rate increases from 5 °C/min (value used in this work) to 10 °C/min,[39] all the synthesized [EMIM] and $[N_{8881}]$ ILs can be classified as least stable ILs, and all the $[P_{8881}]$ ILs as moderately stable ILs.

Table 3. T_{start}, T_{onset} and T_{peak} values for the synthesized ILs measured under a nitrogen atmosphere and with a heating rate of 5 °C/min.

Cation	Anion	T_{start} (°C)	T_{onset} (°C)	T_{peak} (°C)
[EMIM]	[C16]	169	207	229
	[C18]	169	209	233
	[C18:1$_{PhEur}$]	172	208	236
	[C18:2]	168	206	223
	[C18:2 tec.]	169	205	228
[N_{8881}]	[C16]	123	189	251
	[C18]	124	195	247
	[C18:1$_{PhEur}$]	126	195	254
	[C18:2]	131	197	244
	[C18:2 tec.]	129	196	246
[P_{8881}]	[C16]	258	307	325
	[C18]	249	300	330
	[C18:1$_{PhEur}$]	248	304	331
	[C18:2]	234	306	327
	[C18:2 tec.]	242	301	331

The average DSC results in terms of crystallization temperature (T_c), glass transition temperature (T_g), cold crystallization temperature, (T_{cc}), melting temperature (T_m), and the relative heat fluxes are listed in Table 4 for the investigated ILs. T_c was taken as the onset temperature of the exothermic peak on the cooling run. T_g was obtained by taking the midpoint of the heat capacity change on heating from a glass to a liquid. T_{cc} was determined as the onset temperature of the exothermic peak on heating from subcooled liquid to a crystalline solid. T_m was taken as the onset temperature of the endothermic peak on heating run. The onset temperatures were chosen instead of the peak temperatures because they are more

suitable to characterize each transition due to their relative dependence of the experimental procedure. [41]

The DSC thermograms of the investigated ILs are reported in the Supporting Information.

As can be observed, all the synthetized ILs formed crystals upon cooling at 5 K/min, and, upon heating, presented one or more cold crystallization temperatures followed by the melting transition. The presence of two cold crystallization temperatures was also observed by Rocha et al. [20] for $[N_{8881}][18:1]$ using the same heat scanning rate of 5 K/min.

In the investigated temperature range (193 – 393 K), Tg was detected only for [EMIM][C16] (216 K), [EMIM][C18] (212 K) and $[N_{8881}][18:2]$ (211 K), because the ILs typically show glass transitions at very low temperatures, around 173-217 K. [20, 41]

Only the samples [EMIM][C16] and [EMIM][C18] presented melting temperatures above 298 K, being solid at room temperature.

Table 4. Crystallization (Tc), glass transition (Tg), cold crystallization (Tcc) and melting (T_m) temperatures for the synthesized ILs.

		Cooling		Heating				
Cation	**Anion**	**T_c (K)**	**ΔH_c (J/g)**	**T_g (K)**	**T_{cc} (°C)**	**ΔH_{cc} (J/g)**	**T_m (K)**	**ΔH_m (J/g)**
[EMIM]	[C16]	314.5	52.1	216.4	270.1	34.2	300.9 313.6	40.3 47.8
	[C18]	326.5	56.9	212.5	-	-	325.4	60.1
	[C18:2]	256.3	1.1	-	242.2	4.3	263.1	6.2
$[N_{8881}]$	[C16]	233.6	5.8	-	219.0 235.7 256.2	1.1 29.1 8.8	270.6	51.8
	[C18]	239.7	13.6	-	222.5 244.6 251.9	6.9 6.5 11.2	267.0	52.5
	[C18:2]	225.6	3.0	211.1	229.4 252.7	22.6 4.4	261.9	32.2
$[P_{8881}]$	[C16]	222.8	16.8	-	226.3 235.4	20.4 6.2	270.6	59.1
	[C18]	263.5 255.1	9.8 30.0		241.2 250.0	4.1 6.6	263.2	53.3
	$[C18:1_{PhEur}]$	240.9	14.4	-	218.7 238.4	4.5 3.5	252.9	24.9
	[C18:2]	233.4	9.1	-	218.5	6.4	242.1	16.7

For each series, ranging from unsaturated to saturated anion, a decrease of the T_m was observed, attributable to a lower packing efficiency in the crystal cell. The two endothermic peaks observed for the sample [EMIM][C16] are difficult to interpret. They may have been caused by the melting of different crystals or by a solid-solid transition followed by melting. In order to assign these peaks to their corresponding transitions with certain reliability, further experimentation should be conducted.

Experimental

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Materials. 1-Ethyl-3-methylimidazolium [EMIM] (98%), trioctylmethylammonium [N8881] (98%) and trioctylmethylphosphonium [P8881] (98%) methylcarbonate methanol solutions (30%, 43%, and 54% respectively) were purchased from Proionic GmbH. Palmitic acid (≥99%), stearic acid (95%), linoleic acid (99%), and technical linoleic acid (60-74%) were obtained from Sigma-Aldrich. Oleic acid was purchased from Fluka, product number 75096, tested according to Ph. Eur. All reagents were used as received, without further purification.

Methods. *Preparation of LCFA-ILs*. Accurate concentrations of methylcarbonate ILs in the commercial methanol solutions were determined by titration using a 1M HCl solution (pH Meter EUTECH pH 700, calibrated with three standard buffer solutions at pH 4.01, 7.00, and 10.00). An equimolar amount of the desired fatty acid was added to the commercial methylcarbonate IL (1-ethyl-3-methylimidazolium [EMIM], trioctylmethylammonium $[N_{8881}]$ or trioctylmethylphosphonium $[P_{8881}]$) methanol solution at room temperature. The mixture was gently heated to 50 °C. After 2h at 50 °C, the mixture was concentrated in vacuo at 50 °C to remove the methanol and then was dried under high vacuum and continuous stirring at 50 °C for 8 h. Both saturated acids (palmitic acid and stearic acid) and unsaturated acids (oleic acid and linolenic acid) were used. When the unsaturated acids were used, the reaction was performed under nitrogen atmosphere. For the unsaturated fatty acid and its mixtures, which are liquid at room temperature, CO_2 evolution was observed even before heating. In the case of palmitic acid and stearic acid, CO_2 evolution was instead noticed during the dissolution of the solid saturated fatty acids. The reactions have been performed on three different scales (1g, 10g, and 20g of fatty acid) without noticing differences in terms of time, conversion, and purity.

Unsaturated LCFA-ILs became darker if stored under light at room temperature. Viscosity of the prepared LCFA-ILs greatly influences the methanol removal, which became increasingly difficult in the following order: trioctylmethylphosphonium $[P_{8881}]$> trioctylmethylammonium $[N_{8881}]$> 1-ethyl-3-methylimidazolium [EMIM].

The chemical structure of synthesized ILs was confirmed by ^{1}H- and ^{13}C-NMR spectra and ATR FT-IR analysis (Supporting Information).

Characterizations. NMR spectra were recorded at room temperature using a Bruker Instrument at 250 MHz (^{1}H) and 75.7 MHz (^{13}C) using deuterated chloroform as solvent. Infrared spectra were registered using an ATR-FTIR Agilent 660 (Agilent Technologies, Santa Clara, CA, USA). The thermal stability of the synthesized ILs was investigated by thermal gravimetric analysis (TGA), conducted in a TA Instruments Q500 TGA. IL (15-18 mg) was heated in a platinum crucible. First, the heating mode was set to isothermal at 40 °C in N2 (100 mL/min) for 5 min. Then, IL was heated from 40 to 400 °C with a heating rate of 5 °C min−1 under nitrogen (100 mL/min) and maintained at 400 °C for 5 min. Mass change was recorded as a function of temperature and time. TGA experiments were carried out in triplicate. The thermal behaviour of the ionic liquids was analysed by a differential scanning calorimeter (TA DSC, Q200, USA). About 10 mg of sample was loaded in aluminium crucibles and the phase behaviour was explored under nitrogen atmosphere in the temperature range of 193–393 K. In

order to allow volatile degradations to escape and to avoid the risk of the pan bursting under pressure, a small incision was made in the top of both the sample and the reference pan. The sample was heated from room temperature to 343K and maintained at 343K for 10 minutes. Then, it was cooled from 343 K to 193 K at a rate of 5K/min and maintained at 193 K for 10 minutes (cooling run). Finally, the sample was heated to 393 K at a rate of 5 K/min to ensure the complete sample melting (heating run). DSC experiments were carried out in duplicate. The viscosities of ILs as a function of temperature were measured by Brookfield DV-II+Pro (Brookfield AMETEK, Inc., Middleboro, MA, USA) programmable viscometer, with an uncertainty of ±2%. The measurements were carried out in the temperature range from 20 to 80 °C which is controlled by Brookfield TC-502 thermostat with an accuracy of ± 0.1°C.

Conclusions

A general approach to access the three major classes of LCFA-ILs, namely imidazolium, ammonium, and phosphonium ILs, has been proposed. This takes advantage of the commercial availability of the methylcarbonate precursors which allow for the preparation of the target compounds in a single easy step. The practical feasibility is not the only improvement of the reported strategy, even more interesting are the environmental benefits. The synthesis doesn't require any halide-containing intermediate, which means that none will be detected as contaminants in the final products, as is often found for ILs. Also, it doesn't involve the use of water, thus avoiding the production of waste water, the real drawback of previous preparations. The viscosity values, as well as the thermal stabilities, are in good agreement with the previously reported data for LCFA-ILs.

Overall, a new synthetic procedure of this biobased class of hydrophobic ionic liquids has been presented which will permit us to choose the proper LCFA-ILs depending on the required properties and characteristics (viscosity, thermal stability, and phase behavior), and further investigate their potential applications without having to be concerned about their innate environmental impact. Furthermore, the possibility to employ cheaper mixtures of fatty acids in the preparation of LCFA-ILs has been proven, and the related cost reduction represents a further step toward their real industrial use.

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