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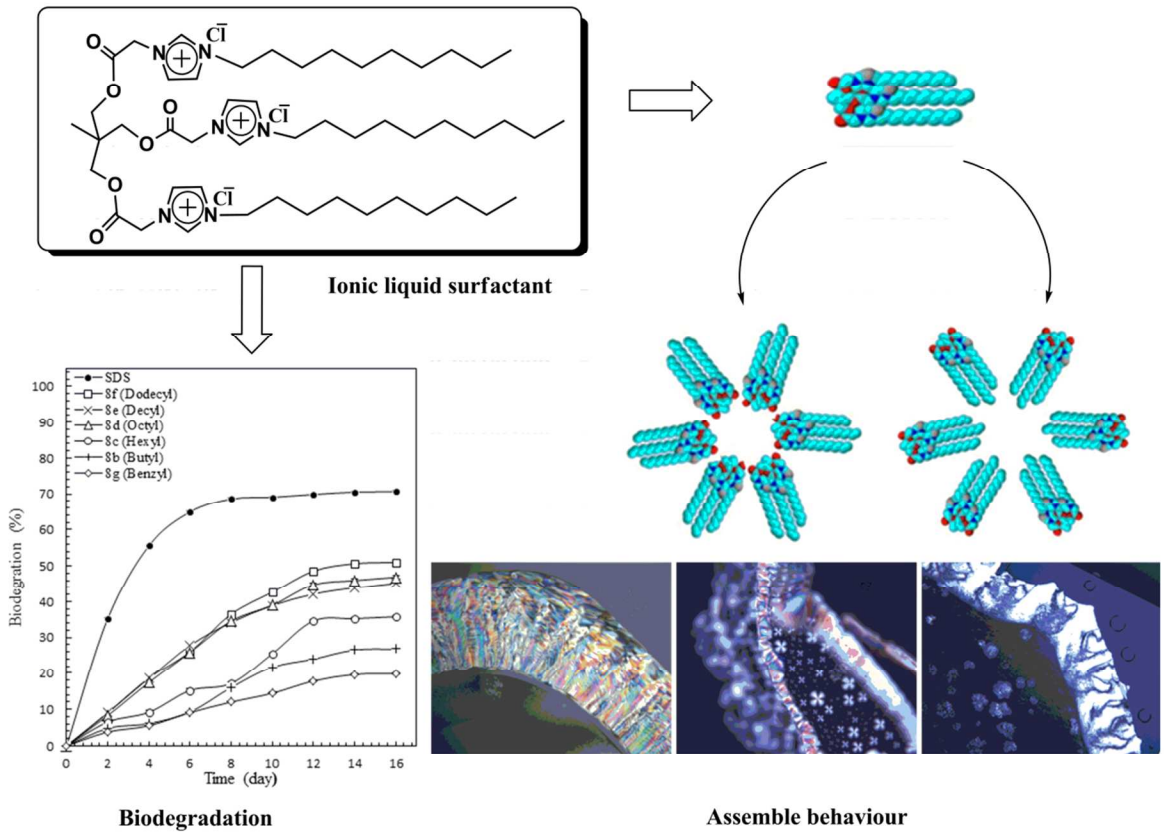

Factors that improved the biodegradation of surfactants have successfully used to prepare higher ordered biodegradable tris-imidazolium and benzimidazolium ionic liquids.

Tris-imidazolium and benzimidazolium ionic liquids: A new class of biodegradable surfactants

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Abstract

Based on imidazolium and benzimidazolium, series of novel tris-cationic ionic liquid surfactants containing ester groups synthesized simply from readily available starting materials in high yield. Biodegradability and surfactants properties of tris-imidazolium and tris-benzimidazolium ionic liquids were investigated. Some compounds showed assembly behaviour in pure form (*i.e.* absence of solvent) and in the presence of polar or nonpolar solvents. These surfactants are effectively reducing the surface tension of water in a range of 28-31 mN/m. Through using 'Closed-Bottle Test' OECD 301D, the incorporation of alkyl or phenyl side chains with ester groups in the same molecule significantly improved the biodegradation comparing to sodium *n*-dodecyl sulphate (SDS) as a reference. The aliphatic alkyl side chain, *i.e.*, butyl, hexyl, octyl, decyl and dodecyl, in both imidazolium and benzimidazolium ionic liquids have marked increasing biodegradation and phase behaviour results compared to aromatic side-chains.

Introduction

Ionic liquids (ILs) are organic salts melt below 100 °C and consist of bulky organic cation associated with either organic or inorganic anion.[1,2] Typically, most common organic cations are either imidazolium, pyridinium, or pyrrolidinium, with alkyl chain substituents[3,4] while anions such as halogen, $[AlCl_4]^-$, $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$, or $[n\text{-}C_8H_{17}OSO_3]^-$.[5] ILs have become increasingly attractive as ''green'' solvents (or environmental friendly) for a wide range of applications due to their low vapour pressure with recycling and catalytic ability.[6-12]

In principle, the physicochemical properties of IL solvents can be tailored for a given application by varying the cationic (or anionic) components. Thus, their properties including melting point, solubility, viscosity, thermal stability and hydrophobicity can be adjusted to suit a variety of wide applications. Some ILs also have surfactant behaviour; therefore, their assemblies can be tuneable by adjusting the solvent composition. Application of ILs as a solvent coupled with their liquid crystalline behaviour could be an advantage in anisotropic ion-conductors, templating and electrolytes in dye-sensitizer solar cells.[13,14]

Through thorough studies against a wide range of organisms, the popular used ILs are proven as toxic in nature[15,16] where the both cationic and anionic components have influence on the toxicity.[17,18] Moreover, ILs that consist of a substituted cation with long linear hydrocarbon side chains ≥ 8 carbon atoms presented varying toxicity levels.[19,20] The positive head group of the cation plays essential role in IL toxicity[21] where the longer side chains have further biological serious influence on living cells.[22,23] At the same time, ILs demonstrated various levels of toxicity magnitude comparing to conventional organic solvents: acetone, acetonitrile, methanol, dichloromethane and methyl *t*-butyl ether.[24,25] First study related ILs toxic nature contributed by Jastorff and co-workers[26] in 2002 when reported theoretical multidimensional analysis of two ILs. They proposed environmental risk assessment of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-decyl-3-methylimidazolium tetrafluoro-

borate ILs with acetone as an organic solvent reference. Five ecotoxicological indicators were considered in this multidimensional analysis including: release, spatiotemporal range, bioaccumulation, biological activity and uncertainty. Further, the first comprehensive biological study by Ranke et al.[25] included effects of different *n*-alkyl chains for methyl- and ethyl-imidazolium ILs incorporated with variety of anions. The study revealed ILs toxicity increasing due to elongation in both alkyl chains length of imidazolium ring. Obviously, ILs may have greater potential to bioaccumulate (persist in the environment) and vice versa when not passing biodegradation tests. Further studies of biodegradation, mineralization and bioaccumulation are necessary to estimate the toxic hazards of ILs or their persisting in the environment. Although different studies on ILs, including toxicity, ecotoxicity and biodegradation have been reported in the literature,[15,27-31] biodegradation data are still seldom. Wells and Coombe[24] screened the biodegradation of ammonium, imidazolium, phosphonium and pyridinium ILs using Biochemical Oxygen Demand measurements in five days (BOD_5). Most of the investigated alkyl side chain ILs showed biodegradation resistant.

The first biodegradable compounds presented by Boethling[32,33] when highlighted the importance of biodegradable chemicals through biodegradable surfactants design for linear alkylbenzenesulfonates and dialkyl quaternaries. Furthermore, Boethling presented readily biodegradable compounds when introduced the long linear hydrocarbon side chain into an ester group. Generally, the biodegradable surfactants[32-34] have been developed based on: (i) the existence of potential sites of esters as an enzymatic hydrolysis, (ii) the introduction of oxygen in the form of hydroxyl, aldehyde or carboxylic acid groups, in addition to (iii) the existence of unsubstituted long linear alkyl chains or phenyl rings, which represent potential sites for attack by oxygenases. Hydrolysable bond (esters or amides) as functional groups introduced into the ILs cation side chain were required to synthesize early biodegradable ILs. The same principles were followed by Gathergood and co-workers[35,36] when evaluated the biodegradation for series of dialkylimidazolium ILs with ester or amide containing side chains using the closed bottle tests (OECD 301 B and D). Compounds with biodegradation levels of 60 % or higher are considered to be ‘‘readily biodegradable’’.[37,38]

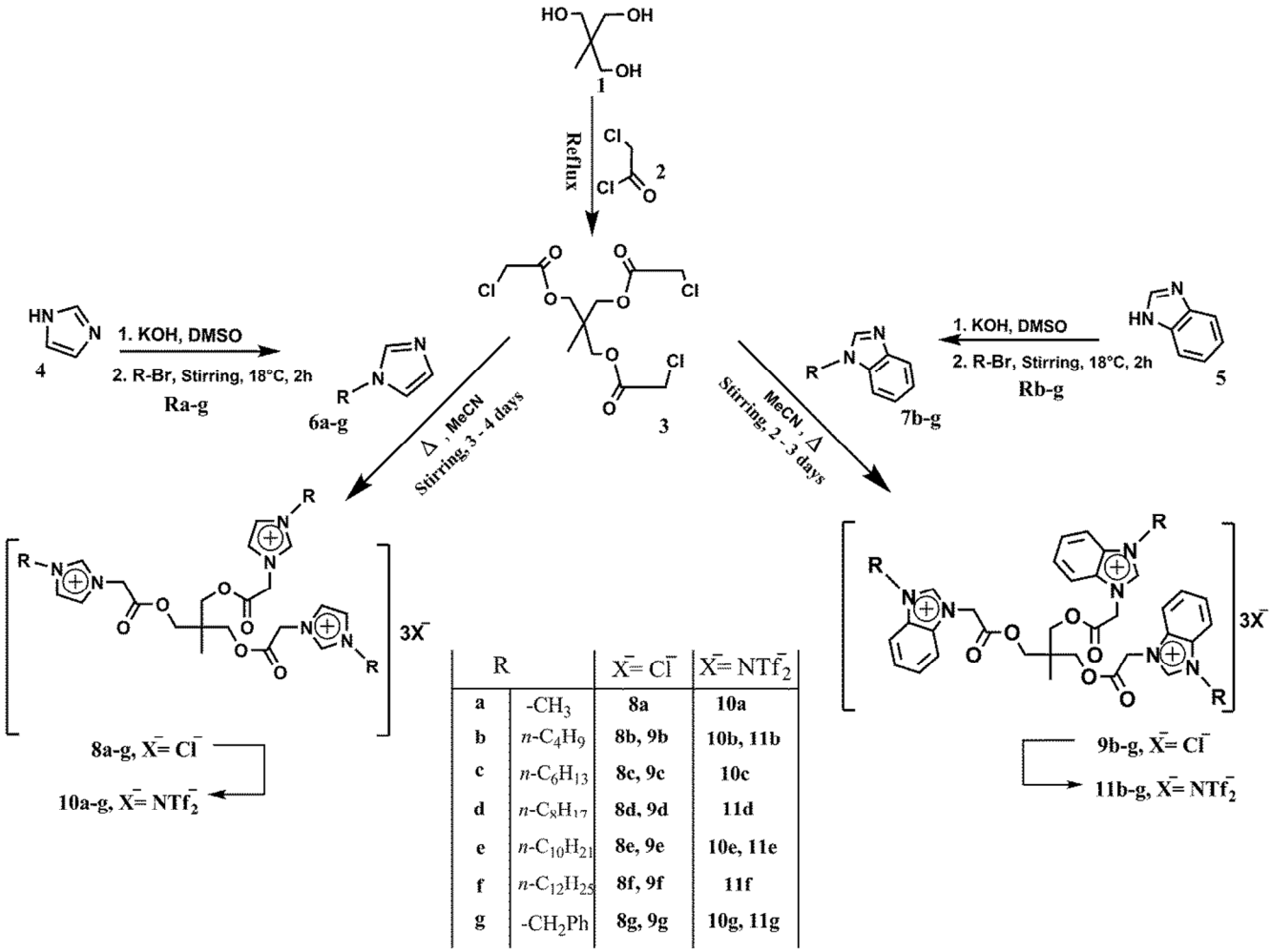
The design of potential biodegradable ILs affected by structure of the components that include most ILs: the cation core, cation side chain(s), and the anion. Imidazole such as the common amino acid; histidine is known to be degraded by microorganisms.[39] Further, imidazolium core has close structural relationship with surfactant like quaternary ammonium compounds[38]; therefore, imidazolium moieties were selected as the cation core. Thus, the factors that improved the biodegradation of surfactants could be applicable to design the ILs cation able to self-assemble with or without the presence of a solvent. In the surfactant’s point of view, rod-like molecules such as single-chain imidazole derivatives are generating nematic (N) and bilayer smectic A (SmA) phases[40,41] while triple-tails compounds have the tendency to form wedge-shape molecules. They have the affinity to form higher ordered molecular arrangements such as columnar (Col) or cubic (cub) phases.[42,43] Consequently, higher ordered phases are good candidates for application as anisotropic ion conductors.[13]

Although many researchers[35,44-48] have studied degradable ILs, none have approached tri-cationic ILs in the literature up to authors’ knowledge. The current study concentrates on synthesis novel tris-imidazolium and tris-benzimidazolium degradable ILs surfactants, containing incorporated alkyl or phenyl side chains with tri-ester groups in same molecule. Towards degradable IL surfactants with higher ordered molecular arrangements phases, a unique evaluation of biodegradation, phase behaviour and their interaction with water of halogen ILs are investigated. Broad practical applications of industrial and medical applications are highly expected. The effects of anions on phase behaviour and biodegradation are beyond the scope of this study.

Results and discussion

Synthesis

ILs syntheses described in current study are based on a simple approach which was modified to prepare tris-imidazolium and tris-benzimidazolium ILs from readily available starting materials in high yield. This process involved alkylation of alkyl-imidazole and alkyl-benzimidazole with appropriate tri-ester halide that synthesized by simple esterification of 1,1,1-Tris (hydroxymethyl)ethane in net chloroacetyl chloride. Furthermore, the halides in the alpha position to carbonyl compound reflect excellent starting materials for high purity and excellent yield of ILs. The synthesis of different length chain of alkyl imidazoles and benzimidazoles was beneficial to obtain plenty of ILs derivatives. Thus, treatment of imidazole or benzimidazole with alkyl halides under basic conditions affords alkyl imidazoles (and benzimidazole) in optimum yield. Alkylation of the obtained alkyl imidazoles and benzimidazoles with active tri-ester halide in acetonitrile at 45-55 °C produced the quantitative yield of certain ILs as shown in (Scheme 1).



R		X= Cl	X= NTf_2
a	$-CH_3$	8a	10a
b	$n-C_4H_9$	8b, 9b	10b, 11b
c	$n-C_6H_{13}$	8c, 9c	10c
d	$n-C_8H_{17}$	8d, 9d	11d
e	$n-C_{10}H_{21}$	8e, 9e	10e, 11e
f	$n-C_{12}H_{25}$	8f, 9f	11f
g	$-CH_2Ph$	8g, 9g	10g, 11g

Scheme 1. Synthesis of tris-imidazolium and tris-benzimidazolium ILs

All the chloride ILs prepared in current work are semi-solid to syrup at room temperature which have been set as reference point to determine their classification as ILs.[1] Metathesis of halogen anion to NTf_2^- produced clear liquids at room temperature and clean samples were isolated after a simple workup. The process included mixing

an aqueous solution of chloride salt with $LiNTf_2$. The hydrophobic IL phase was then separated by simple extraction with ethyl acetate to produce pure ILs after organic layer evaporation under reduced pressure. Table 1 summarized the synthetic details of the prepared ILs.

Table 1: Structural and synthetic details of tris-imidazolium and tris-benzimidazolium ILs

IL	Cations	Alkyl chains	Counter ions	Status[c]	M.wt.	Yield (%)
8a	Im[a]	CH_3	Cl	Semi-solid	595.90	97
8b	Im[a]	*n*-C_4H_9	Cl	Syrup	722.14	98
8c	Im[a]	*n*-C_6H_{13}	Cl	Syrup	806.30	98
8d	Im[a]	*n*-C_8H_{17}	Cl	Syrup	890.46	97
8e	Im[a]	*n*-$C_{10}H_{21}$	Cl	Syrup	974.62	99
8f	Im[a]	*n*-$C_{12}H_{25}$	Cl	Syrup	1058.78	99
8g	Im[a]	-CH_2-Ph	Cl	Semi-solid	824.19	91
9b	BIm[b]	*n*-C_4H_9	Cl	Syrup	872.32	97
9c	BIm[b]	*n*-C_6H_{13}	Cl	Syrup	956.48	99
9d	BIm[b]	*n*-C_8H_{17}	Cl	Syrup	1040.64	98
9e	BIm[b]	*n*-$C_{10}H_{21}$	Cl	Syrup	1124.80	99
9f	BIm[b]	*n*-$C_{12}H_{25}$	Cl	Syrup	1208.96	99
9g	BIm[b]	-CH_2-Ph	Cl	Semi-solid	974.37	96
10a	Im[a]	-CH_3	NTf_2	liquid	1329.98	81
10b	Im[a]	*n*-C_4H_9	NTf_2	liquid	1456.22	84
10c	Im[a]	*n*-C_6H_{13}	NTf_2	liquid	1540.38	85
10e	Im[a]	*n*-$C_{10}H_{21}$	NTf_2	liquid	1708.70	94
10g	Im[a]	-CH_2-Ph	NTf_2	liquid	1558.27	91
11b	BIm[b]	*n*-C_4H_9	NTf_2	liquid	1606.39	84
11d	BIm[b]	*n*-C_8H_{17}	NTf_2	liquid	1774.71	90
11e	BIm[b]	*n*-$C_{10}H_{21}$	NTf_2	liquid	1858.88	90
11f	BIm[b]	*n*-$C_{12}H_{25}$	NTf_2	liquid	1943.04	96
11g	BIm[b]	-CH_2-Ph	NTf_2	liquid	1708.45	96

[a] Imidazolium
[b] Benzimidazolium
[c] at room temperature

Liquid crystalline behaviour

Optical polarizing microscope equipped with heating stage was used to investigate liquid crystalline properties of compounds **8b-f** and **9b-f** thermotropically and lyotropically as highlighted in the experimental section. In absence of solvents, compounds **8b**, **8c**, **8d** and **9b**, **9c**, **9d** appeared to be viscous fluids at room temperature with no birefringence, while compounds with ≥ C10 carbons chain length showed birefringent at room temperature. Tris-imidazolium series showed birefringent property with clearing points of 116 °C and 172 °C for compounds **8e** and **8f**, respectively. Both compounds expected to form smectic A phases (oily streaks) based on the textures shown in Fig. 1. While tris-benzimidazolium compound series showed relatively lower clearing point *i.e.* 37 °C for **9e** and 50 °C for **9f**. The benzanelation of the imidazole reduced the clearing point significantly and increased the molecules area of nonpolar domain; thus, the chains packed in a wedge-shaped molecule which favours the formation of columnar phase (Fig. 2). Precisely, ascending and descending trends was observed in clearing points of tris-imidazolium and benzimidazolium ILs, respectively, as a function of chains length increasing illustrated in Table 2. Clearing point[13,49] is the transition temperature between liquid

crystalline phase (mesophase) and isotropic liquid whereas the liquid crystal phase is completely converted to an isotropic liquid above the clearing point.

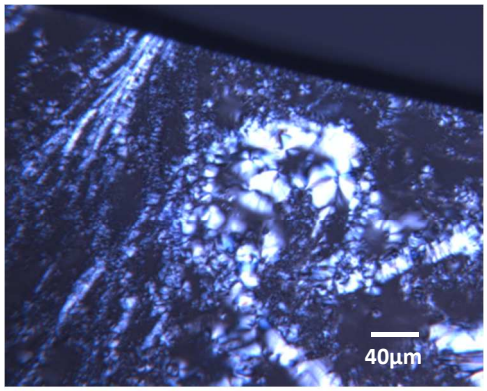


Fig. 1. The oily streaks texture observed under polarized microscope for compound **8f** at 25°C (50×).

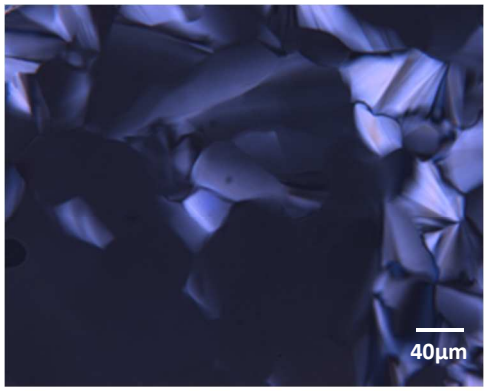


Fig. 2. The columnar texture observed under polarized microscope for compound **9e** at 25°C (50×).

Lyotropic investigation was performed using contact penetration scans method where the samples are sandwiched between two slides with or without adding solvent at the slide edge. The solvent diffused through the sample by capillary force then the liquid crystalline phase was formed when the solvent penetrated the sample with different concentration gradient. Water as polar solvent and 1-undecanol as nonpolar were used to investigate the polymorphism in different system. In water penetration study compounds **8b**, **8c**, **9b**, **9c**, and **9d** are very soluble; therefore, formation of micellar, L_1, solution was expected, while for compounds **8d**, **8e** and **8f**, a normal hexagonal phase, H_1, was observed with slowly dissolving into L_1 phase. In contrast, tris-benzimidazolium compounds series was less soluble and exhibited a cubic phase. The penetration profile of compound **8f** at room temperature is shown in Fig. 3 and the image for **9e** in contact with water is shown in Fig. 4.

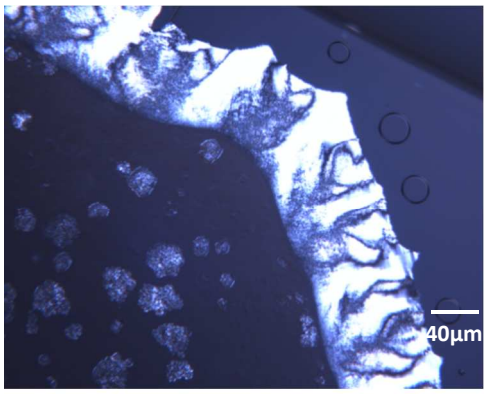


Fig.3. Water penetration scans observed under polarized microscope for compound **8f** at 25 °C (50×).

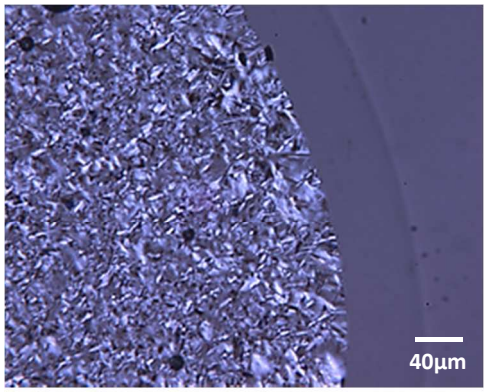


Fig.4. Water penetration scans observed under polarized microscope for compound **9e** at 25 °C (20×).

The behaviour of tris-imidazolium series in contact with nonpolar solvent showed that longer chain compound *i.e.* **8f** is very soluble to form an inverted micellar solution, L_2. Further, additional liquid crystalline phases were observed for **8b**, **8c**, **8d** and **8e** besides the L_2. E.g. inverted hexagonal (H_2), maltese crosses with H_2 and finally lamellar phases with H_2 for **8b**, **8c** and **8d** ILs, respectively, as depicted in Fig. 5.

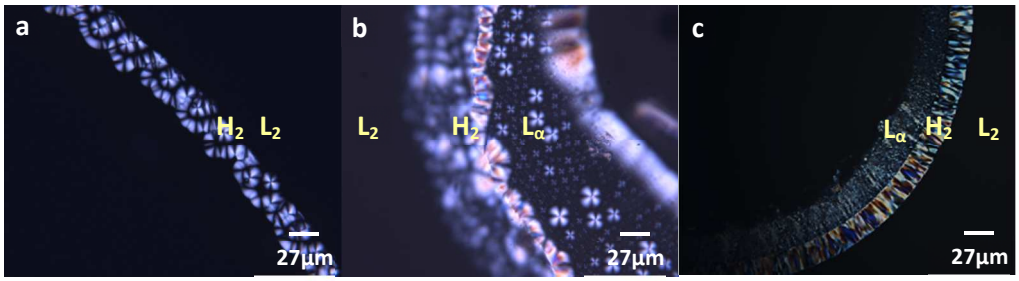


Fig.5. 1-Undecanol penetration scans for compounds (a) **8b** (b) **8c** (c) **8d** at 25 °C (50×).

Compounds **9b** and **9c** did not show any liquid crystal phase in contact with 1-undecanol, while compound **9d** exhibited inverted hexagonal and inverted cubic phases. Generally, longer chains length of tris-benzimidazolium compounds such as **9e** and **9f** displayed H_2 and lamellar phases as presented in Fig. 6.

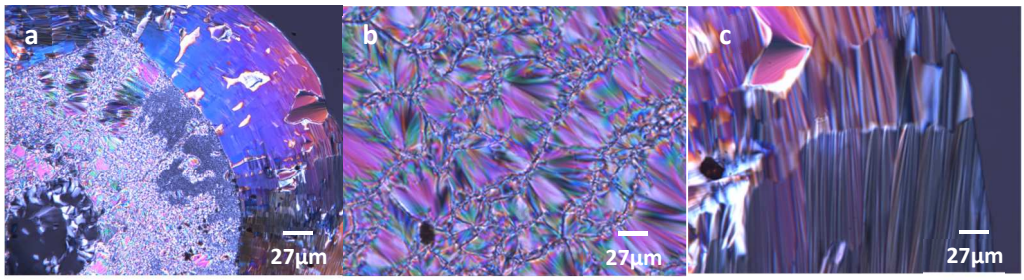


Fig.6. 1-Undecanol penetration scans at 25 °C for compound **9e** (a) overall scan penetration study taken at (10×) magnification, (b) zoom for the lamellar phase (50×), and (c) the outer penetration displays H_2 (50×).

For this type of mesogen in both tris-imidazolium and benzimidazolium ILs, compounds starting with 10 carbon alkyl chains showed a birefringent behaviour while shorter than 10 are most likely not flexible enough to align unisotropically. In present liquid crystal phase, the molecules are still ordered in some direction with flows like a liquid. According to literature, the same trend was noticed for 2-tridecylpyridine chloride[50] which melts at 52 °C and clears at 109 °C. Moreover, materials based on IL can self-assemble into a liquid crystal phase by solvent addition; for example, triethylammoniumdodecyloxycyanobiphenyl bromide[51] showed lamellar phase in contact with water. Thus, the phase behaviour of ILs can be produced in pure state (spontaneously) and during their interaction with polar and nonpolar solvents.

Prediction and cartoon molecular alignment of IL material in the liquid crystalline phase is illustrated in Fig. 7 where the micro-phase separation within the material is the driving force for its assembly. At the molecular level, all alkyl chains are aligned in parallel as depicted in Fig. 7 (a) for compound **8e**, while, at lower concentration of solvent, the material preferably arranged in a smectic A or lamellar phase as illustrated in Fig. 7 (b). Further, in contacting with solvent, the molecules tend to reassemble depending on the nature of solvents. Where in water, the chains arranged near each other with the polar part domain contacted to water as demonstrated in Fig. 7 (c). The reverse arrangement occurred in contact with 1-undecanol, where several discs assembled together to form hexagonal phase as shown in Fig. 7 (d). Phase behaviour summarization results of synthesized tris-imidazolium and bezimidazolium ILs are illustrated in Table 2.

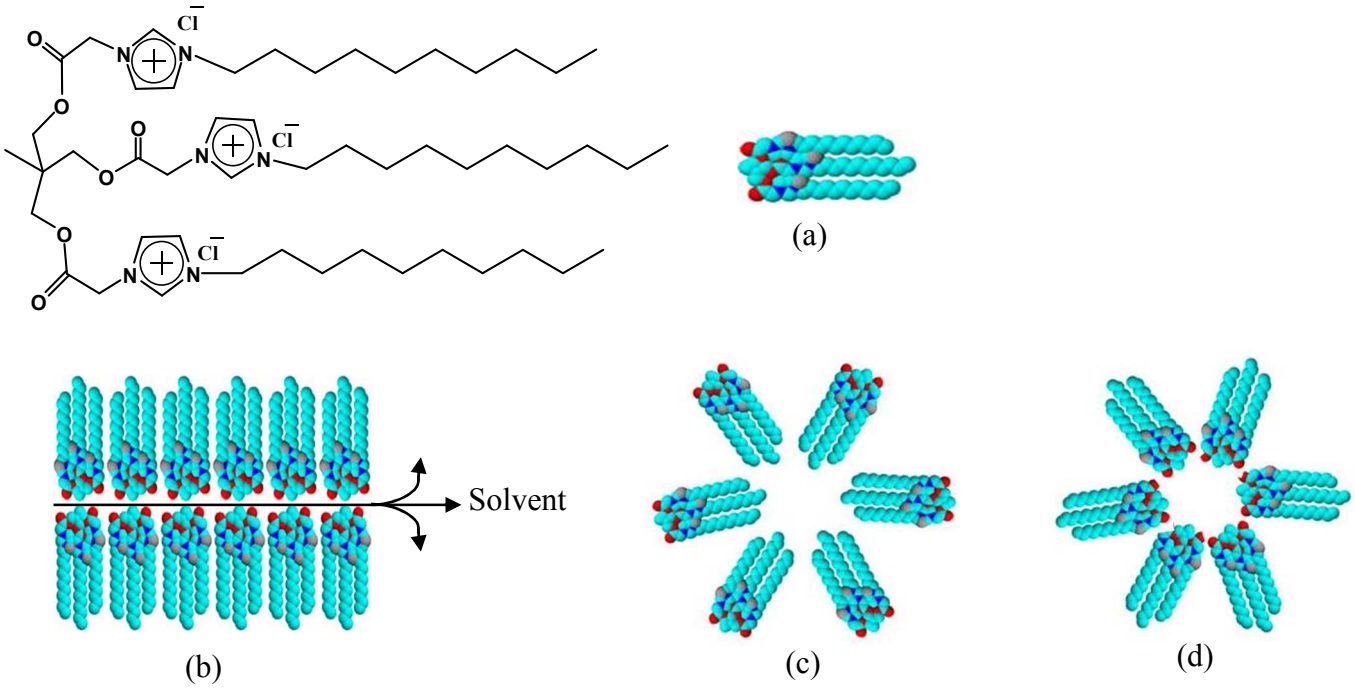


Fig. 7. Assembly illustration of (a) single molecule, (b) molecules arrangement in lamellar phase, (c) molecules arrangement in normal hexagonal, H_1 and (d) molecules arrangement in inverted hexagonal, H_2.

Table 2: Phase behaviours of the synthesized tris-imidazolium and bezimidazolium ILs as a function of alkyl chain length.

IL	Number of carbon atoms in side chains	Clearing point (°C)	Phase behaviour		
			In pure[b]	In water[c]	In 1-undecanol[d]
8b	4	ND[a]	Non-birefringent	Soluble	H_2
8c	6	ND[a]	Non-birefringent	Soluble	H_2, L_α
8d	8	ND[a]	Non-birefringent	I_1, H_1, V_1	H_2
8e	10	116	Smectic A	H_1	H_2
8f	12	172	Smectic A	H_1	H_2
9b	4	107	Non-birefringent	Soluble	I_2
9c	6	103	Non-birefringent	Soluble	I_2
9d	8	90	Non-birefringent	Soluble	H_2
9e	10	37	Columnar	I_1	H_2
9f	12	50	Columnar	H_1	H_2

[a] not detected
[b] is absence of solvent
[c] is contact with water
[d] is contact with 1-undecanol

Air-water interface behaviour

Results of surface properties; critical micelle concentration cmc, and surface tension γ_{cmc} beside Krafft temperature, T_K, are presented in Table 3. The values of T_K for all ILs solutions are below 10 °C. The surface tension measurements were recorded at 25 °C. The synthesized IL materials showed very low Krafft points indicating their solubility below room temperature and IL cmc results can be measured at room temperature. As

expected, cmc value of ILs (Table 3) decreased with increasing chain length, where, compounds with 4 carbons at chain length are very soluble in water and the cmc values are expected to be higher than 150 mM based on a preliminary investigation. Essentially, the compounds showed common trend for single chain non-ionic surfactant such as alkyl maltosides.[52] It is a decreasing by factor 10 upon addition of two methylene groups except compounds with 10 and 12 carbon atoms in side chains for both tris imidazolium and benzimidazolium ILs. The deviation from the trend may be attributed to multiple charges at high dilution of the IL, which destabilize the micellar assembly. Thus, the synthesized ILs materials lowered the water surface tension to 28-31 mN/m. Moreover, the hydrophobicity of ILs materials had very minor influence on the molecules packing at air/water interface. However, this only applied to the tris-imidazolium series. For the molecular shape a non-parallel alignment of the alkyl chains is assumed, figuring the shape of a tripod.

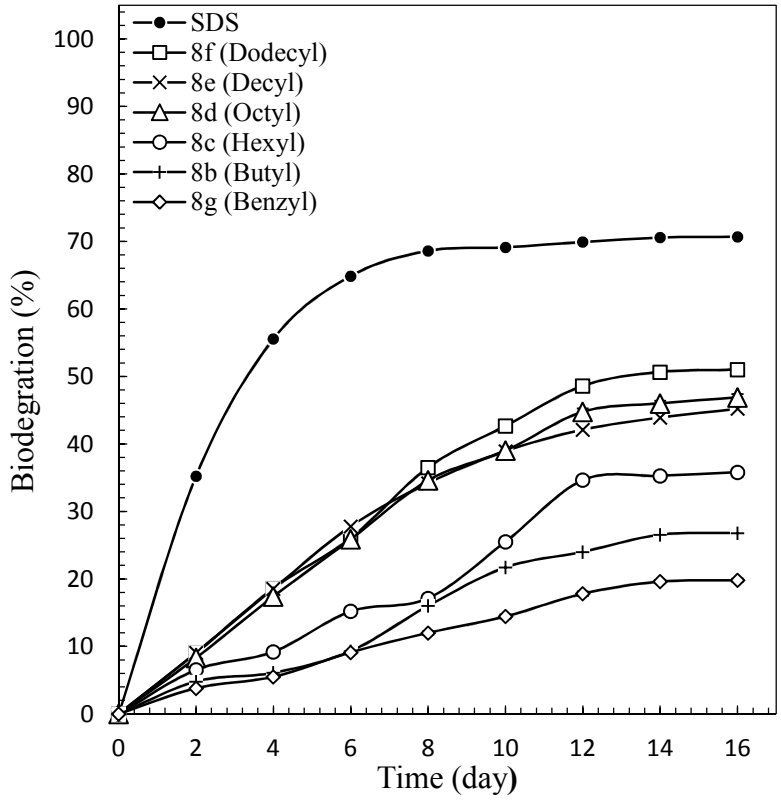
Table 3: CMC, surface properties and Krafft temperature of ILs/water systems at 25 °C

IL	Carbon atoms in side-chains	Cmc (mM)	γ_{cmc} (mN/m)	T_K (°C)
8b	4	–	–	–
8c	6	62.0	29	<10
8d	8	6.5	28	<10
8e	10	1.3	28	<10
8f	12	0.89	29	<10
8g	Benzyl	–	–	–
9b	4	–	–	–
9c	6	40.8	29	<10
9d	8	3.8	31	<10
9e	10	0.9	30	<10
9f	12	0.3	31	<10
9g	Benzyl	–	–	–

Biodegradation results

'Closed bottle' OECD 301D test was used to evaluate the biodegradability of synthesized ILs as highlighted in the experimental section. ILs with only imidazolium cations revealed higher degradation than those based on benzimidazolium moieties as shown in Fig. 8 and 9. Further, the biodegradation was improved to highest percent of 51% in **8f** (dodecyl side chain) due to alkyl side chain length increment[53] as illustrated in Fig. 8. The presence of fused aromatic rings increased the stability of the ILs towards microbial degradation, therefore, changing the cationic part to benzimidazolium compound **9f** (dodecyl side chain) has reduced the IL degradation to 45% as revealed in Fig 9.

Moreover, the tri-ester linkages improved the biodegradation progression of the synthesized ILs; and upon concordance, it was agreed that microbial enzymatic hydrolysis of the ester bonds could be the possible initiation stage in degradation enhancement. As a result, separation of imidazolium-alkyl chain fragment and corresponding primary alcohol that would consider as readily metabolized *via* fatty acid β-oxidation was achieved.[15,36,54] The ILs biodegradation was promoted due to reasonable solubility for both of the produced fragments in water. Similar trend in degradation percentage have previously reported in literature[36] for ILs with mono-imidazolium cation containing ester groups.



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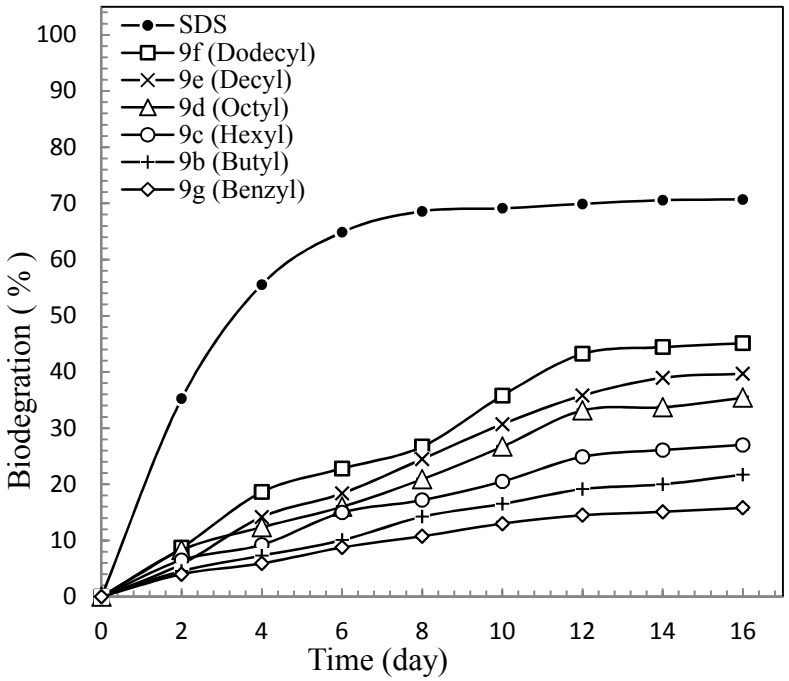
222 **Fig 8.** Biodegradation curves of tris-imidazolium ILs series using closed-bottle test.



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224 **Fig 9.** Biodegradation curves of tris-benzimidazolium ILs series using closed-bottle test.

For the purpose of starting and end test identification based on standard SDS samples results[38,55] and current ILs biodegradation curves, 16 days test duration was considered due to attain a plateau from the last three measurements of these curves as shown in Fig. 8 and 9. Moreover, obvious difference in biodegradation values was notified in 10 days comparing to 16 days of the test duration as shown in Fig. 10 and 11.

Furthermore, the presence of aliphatic alkyl side chain altered the hydrophobicity of mono-cationic ILs and subsequently enhanced their biodegradation.[53] In comparison to mono-cationic ILs,[36,56,57] current tris-cationic ILs showed a higher degradation percentage within shorter test duration in the presence of long linear alkyl side chains. Moreover, changing the side chains from aliphatic groups (butyl- dodecyl) to aromatic chains (benzyl) demonstrated a significant decreasing in degradation; 20 % and 16% in both **8g** and **9g**, respectively, as shown in Fig. 10 and Fig. 11. The summarized biodegradation results of synthesized tris-imidazolium and bezimidazolium ILs are illustrated in Table 4.

Table 4: Biodegradation results of synthesized tris-imidazolium and bezimidazolium ILs as a function of alkyl chains length.

IL	Carbon atoms in side-chains	Biodegradation (%)	
		10 day	*16 day*
8b	4	22	27
8c	6	25.5	36
8d	8	39	47
8e	10	39	45
8f	12	43	51
8g	Benzyl	14.5	20
9b	4	16.5	22
9c	6	20.5	27
9d	8	27	35.5
9e	10	31	40
9f	12	36	45
9g	Benzyl	13	16

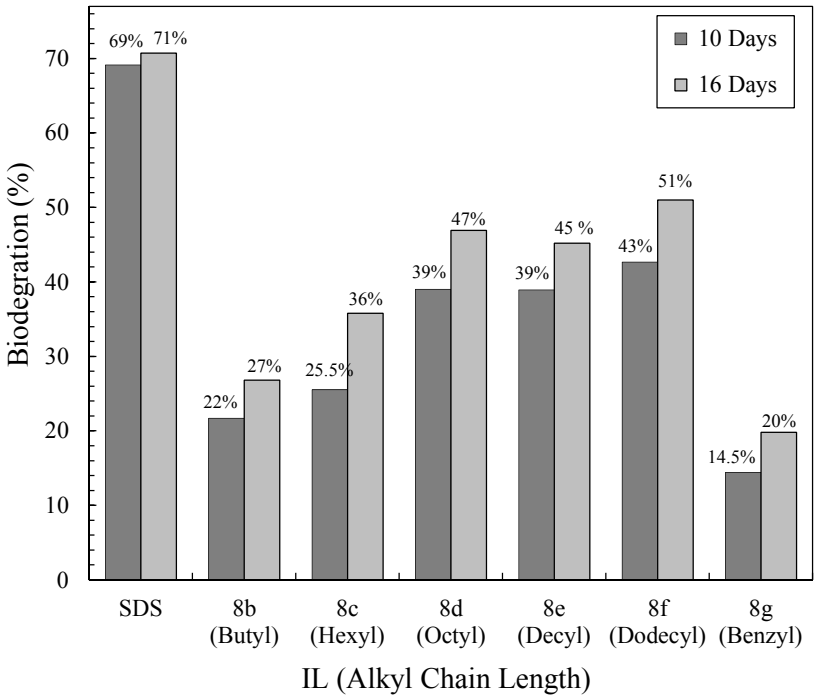

Fig 10. Biodegradation of tris-imidazolium ILs series as a function of aliphatic or aromatic side chains on 10 and 16 days.

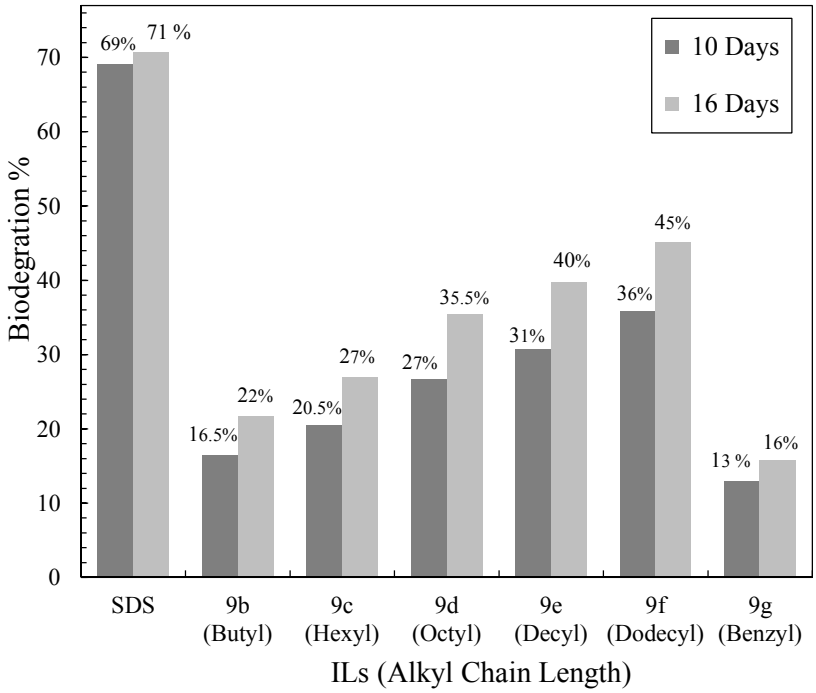

Fig 11. Biodegradation of tris-benzimidazolium ILs series as a function of aliphatic or aromatic side chains on 10 and 16 days.

Generally, the tested ILs displayed significant levels of biodegradation, where ILs (**8d**, **8e**, **8f** and **9f**) showed distinctive biodegradability values of 47%, 45%, 51%, and 45%, respectively, after 16 days period from test evaluation. The results indicated that these ILs are on the border of 60% pass level of readily biodegradation.[35,37,53]

Conclusions

Tris-imidazolium and tris-benzimidazolium ILs contain incorporation of alkyl or phenyl side chains with tri-ester groups was generally found semi-solid to syrup at room temperature. Metathesis of chloride anion to NTf_2 was tuned it to liquids in excellent yield and purity. In absence of solvent, only compounds with ≥ 10 carbon atoms at their hydrocarbon chains shows assembly behaviour. Compounds containing 8 carbon atoms are still possible to assembly by addition of solvents either polar or nonpolar. These ILs surfactants are useful in wide temperature range with Krafft temperature lower than 10 °C and effectively reduce the water surface tension to 29 mN/m. The imidazolium ILs resulted significant increasing in phase behaviour properties and biodegradation compared to benzimidazolium ILs. Generally, ILs bearing imidazolium cations exhibit higher percentages of degradation as compared to those with benzimidazolium.

The factors that improved the biodegradation of surfactants have successfully been used to develop the biodegradation and self-assemble behaviour of the synthesized tri-cationic ILs. Further, comparing to mono-cationic ILs, these developed properties of synthesized tris-imidazolium and benzimidazolium ILs are highly enhanced by increasing the ILs hydrophobicity. Precisely, ILs incorporating the long linear alkyl (*i.e.* octyl, decyl, dodecyl) in the side chains presented on the border of the 60% pass level of readily biodegradation results with capability to self-assemble spontaneously or in the presence of a solvent.

The resistance to aerobic biodegradation is generally increased for compounds with halogens (chloride) as a counter ion.[38] Therefore, a more detailed study of counter-ion effect on biodegradation is in progress towards readily biodegradable for these tris-imidazolium and benzimidazolium ILs. Antibacterial evolution for current ILs will be reported in future work. Furthermore, determination of the physical properties of the synthesized ILs (e.g. solubility, thermal stability, cyclic voltammetry and fluorescence) will be reported in due course.

Experimental

1-Methylimidazole (99%) and 1-butylimidazol (98%) were purchased from Aldrich and distilled before usage to remove the detrimental impurities. 1-hexylimidazole, 1-octylimidazole, 1-decylimidazole, 1-dodecylimidazole, 1-benzylimidazole, 1-butylbenzimidazole, 1-hexylbenzimidazole, 1-octylbenzimidazole, 1-decylbenzimidazole, 1-dodecylbenzimidazole, and 1-benzylbenzimidazole were prepared as described below. 1-bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane and benzyl bromide were obtained from commercial sources and used without further purification. All ILs were kept in fridge (5 °C) and freezer (–18 °C) for further evaluation of their properties. General grade solvents and reagents were purchased from commercial suppliers and used without further purification. The IR spectra were obtained with a Perkin Elmer 400 Fourier Transform Infrared (FTIR) spectrometer. Both of ^{1}H and ^{13}C-NMR spectra were recorded on Jeol Lambda and ECA-DELTA as well as Bruker spectrometers at 400 MHz while ^{19}F-NMR was recorded using Bruker spectrometers 400 MHz. High-resolution mass spectra were recorded on Agilent Technologies 6530 Accurate Q-TOF LC–MS system, applying DMSO /MeOH eluents for ILs sample compounds while Agilent 5975 system for EI/MS (NUS, Singapore) for the rest compounds. Thin layer chromatography was carried out on pre-coated silica gel plates (0.25 mm, 20 × 20 cm, 60F254, E. Merck).

Procedure for Synthesis of compound **3**

This compound was prepared according to modification applied to a procedure described in literature.[58] 1,1,1-Tris(hydroxymethyl)ethane **1** (10 g, 83.3 mmol) was dissolved and refluxed with minimum amount of chloroacetyl chloride **2** until all HCl gas was liberated (pursue by wet litmus paper). The reaction mixture was evaporated in *vacuo* until the excess of acid chloride was removed. The crude product was purified by co-evaporation with toluene (4-5 times) to produce pale-yellow viscous syrup solidified after few days. Re-crystallization from dry acetonitrile gave compound **3** as colourless crystals.

General Procedure for Synthesis of **6c-g** *and* **7b-g**

These compounds were prepared according to modification applied to a procedure described in literature.[59] Potassium hydroxide (8.24 g, 147 mmol) was added to a solution of imidazole (5g) or benzimidazole (8.67g), (73.4 mmol) in DMSO (30 mL) and the mixture was stirred for 30 min at room temperature. The corresponding alkyl halide (61.2 mmol) was added portion-wise under vigorous stirring in a water bath and the stirring was continued for overnight. The mixture was quenched with water (200 mL) and extracted with diethyl ether (3 × 25 mL). The combined extracts were washed with water, dried over anhydrous magnesium sulphate and the solvent was evaporated off under reduced pressure.

Tris-((*N*-methyl-imidazoliumyl-acetayloxy)methyl)ethane chloride (8a)

A solution of 1-methylimidazole (1.34 g, 1.3 mL, 16.3 mmol) in acetonitrile anhydrous (5mL) was added drop-wise to a stirred solution of tris-((2-chloro-acetayloxy)methyl)ethane (compound **3**) (1.9g, 5.43 mmol) in acetonitrile anhydrous (15 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred vigorously for 3 hours and refluxed at 50-55 °C for 3-4 days. The acetonitrile top layer was decanted and the IL washed with diethyl ether (3 × 10 mL), then residual solvent removed *in vacuo*. The product was dried at (40 °C, 0.01 mmHg) for 48 h to provide a viscous hygroscopic semi-solid in 97% yield (3.14 g). Molecular Formula: $C_{23}H_{33}Cl_3N_6O_6$; Mol. Wt.: 595.90; FTIR (cm^{-1}): 3072 $(C\text{-}H)_{Ar}$, 2970, 2925, 2852 $(C\text{-}H)_{Aliph}$, 1744 (C=O), 1631 (C=N), 1565, 1464 $(C{=}C)_{Ar}$, 1214, 1185 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.13 (bt~s, 3H, $C\text{-}H_{Imidazole}$, major), 9.10 (bt~s, 3H, $C\text{-}H_{Imidazole}$, minor), 7.72 (t, *J* =1.95 Hz, 3H, $C\text{-}H_{Imidazole}$, major), 7.70 (t, *J* =1.95 Hz, 3H, $C\text{-}H_{Imidazole}$, minor), 7.67 (t, *J* =1.95 Hz, 3H, $C\text{-}H_{Imidazole}$, major), 7.65 (t, *J* =1.95 Hz, 3H, $C\text{-}H_{Imidazole}$, minor), 5.33 (s, 6H, $O\text{-}CH_2$, major), 5.29 (s, 6H, $O\text{-}CH_2$, minor), 4.18 (s, 6H, $N\text{-}CH_2$), 3.99 (s, 9H, α-CH_3, major), 3.94 (s, 9H, α-CH_3, minor), 1.09 (s, 3H, CH_3, major), 0.98 (s, 3H, CH_3, minor); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.81 (C=O, minor), 167.74 (C=O, major), 139.35 ($CH_{Imidazole}$, major), 137.88 ($CH_{Imidazole}$, minor), 125.14 ($CH_{Imidazole}$, major), 124.72 ($CH_{Imidazole}$, major), 124.45 ($CH_{Imidazole}$, minor), 123.36 ($CH_{Imidazole}$, minor), 68.68 (CH_2-O, minor), 67.98 (CH_2-O, major), 50.85 (CH_2-N), 39.90 (-C-), 36.80 (α-CH_3, major), 35.10 (α-CH_3, minor), 17.11 (CH_3, major), 16.99 (CH_3, minor); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{23}H_{31}N_6O_6^{5+}$: 487.2305, found: 487.2330.

Tris-((*N*-hexyl-imidazoliumyl-acetayloxy)methyl)ethane chloride (8c)

This compound was prepared analogously to **8a** using tris-((2-chloro-acetayloxy)methyl)ethane (compound **3**) (1.9 g, 5.43 mmol) and 1-hexylimidazole (**6c**) (2.48 g, 16.3 mmol) to provide a viscous hygroscopic syrup in 98% yield (4.29 g). Molecular Formula: $C_{38}H_{63}Cl_3N_6O_6$; Mol. Wt.: 806.30; FTIR (cm^{-1}): 3058 $(C\text{-}H)_{Ar}$, 2955, 2929, 2859 $(C\text{-}H)_{Aliph}$, 1749 (C=O), 1641 (C=N), 1564, 1463 $(C{=}C)_{Ar}$, 1192, 1165 (C-O);^{1}H-NMR (400 MHz,

DMSO-d_6) δ ppm: 9.66 (bt~s, 3H, C-$H_{Imidazole}$, major), 9.60 (bt~s, 3H, C-$H_{Imidazole}$, minor), 9.53 (bt~s, 3H, C-$H_{Imidazole}$, minor), 7.95 (t, J =1.71 Hz, 3H,C-$H_{Imidazole}$, major), 7.90 (t, J =1.71 Hz, 3H,C-$H_{Imidazole}$, major), 7.84 (t, J =1.71 Hz, 3H, Hz, C-$H_{Imidazole}$, minor), 7.80 (t, J =1.71 Hz, 3H, C-$H_{Imidazole}$, minor), 5.50 (s, 6H, O-CH_2, major), 5.43 (s, 6H, O-CH_2, minor), 4.25 (t, J= 7.07 Hz, 6H,α-CH_2, major), 4.16 (t, J= 7.07 Hz, 6H, α-CH_2, minor), 4.06 (bs, 6H, N-CH_2), 1.81-1.74 (m, 6H, β-CH_2), 1.24 (bs, 18H, bulk-CH_2), 0.94 (s, 3H, CH_3), 0.84 (t, 9H, J =6.83 Hz, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 168.12 (C=O), 137.33 ($CH_{Imidazole}$, minor), 137.23 ($CH_{Imidazole}$, major), 123.94 ($CH_{Imidazole}$), 122.12 ($CH_{Imidazole}$, minor), 121.98 ($CH_{Imidazole}$, major), 63.98 (CH_2-O), 49.78 (CH_2-N, major), 49.68 (CH_2-N, minor), 49.00 (α-CH_2, minor), 48.94 (α-CH_2, major)), 40.68 (-C-), 30.52 (ω-2), 29.34 (bulk-CH_2), 25.09 (β), 21.91 (ω-1), 16.62 (CH_3, minor), 16.47 (CH_3, major), 13.84 (ω); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{38}H_{61}N_6O_6^{5+}$: 697.4653, found: 697.4648.

Tris-((*N*-dodecyl-imidazoliumyl-acetayloxy)methyl)ethane chloride (8f)

This compound was prepared analogously to **8a** using tris-((2-chloro-acetayloxy)methyl)ethane (compound **3**) (1.9 g, 5.43 mmol) and 1-dodecylimidazole (**6f**) (3.85 g, 16.3 mmol) to provide a viscous hygroscopic syrup in 99% yield (5.24 g). Molecular Formula: $C_{56}H_{99}Cl_3N_6O_6$; Mol. Wt.: 1058.78; FTIR (cm^{-1}): 3058 (C-H)$_{Ar}$, 2955, 2925, 2859 (C-H)$_{Aliph}$, 1749 (C=O), 1677 (C=N), 1564, 1466 (C=C)$_{Ar}$, 1199, 1164 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.20 (bt~s, 3H, C-$H_{Imidazole}$, major), 9.14 (bt~s, 3H, C-$H_{Imidazole}$, minor), 9.08 (bt~s, 3H, C-$H_{Imidazole}$, minor), 7.71 (dt, J =8.15, 1.81 Hz, 6H, C-$H_{Imidazole}$, major), 7.67 (dt, 6H, J =8.15, 1.81 Hz, C-$H_{Imidazole}$, minor), 5.31 (s, 6H, O-CH_2, major), 5.28 (s, 6H, O-CH_2, minor), 5.26 (s, 6H, O-CH_2, minor), 4.27 (t, J= 7.25 Hz, 6H, α-CH_2, major), 4.23 (t, J= 7.25 Hz, 6H, α-CH_2, minor), 4.18 (s, 6H, N-CH_2, major), 4.14 (s, 6H, N-CH_2, minor), 1.93-1.84 (m, 6H, β-CH_2), 1.26 (bs, 54H, bulk-CH_2), 1.07 (s, 3H, CH_3, major), 1.05 (s, 3H, CH_3, minor), 0.87 (t, 9H, J =6.80 Hz, ω-CH_3); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.87 (C=O, major), 167.78 (C=O, minor), 138.82 ($CH_{Imidazole}$), 125.38 ($CH_{Imidazole}$), 123.56 ($CH_{Imidazole}$), 68.18 (CH_2-O, major), 67.87 (CH_2-O, minor), 67.60 (CH_2-O, minor), 51.22 (CH_2-N), 50.98 (α-CH_2, major), 50.69 (α-CH_2, minor), 39.87 (-C-), 33.17 (ω-2), 31.24, 30.85(2), 30.76, 30.66, 30.57, 30.22 (bulk-CH_2), 27.36 (β), 23.83 (ω-1), 17.24 (CH_3, major), 17.18 (CH_3, minor), 14.56 (ω); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{56}H_{97}N_6O_6^{5+}$: 949.7470, found: 949.7479.

Tris-((*N*-benzyl-imidazoliumyl-acetayloxy)methyl)ethane chloride (8g)

This compound was prepared analogously to **8a** using tris-((2-chloro-acetayloxy)methyl)ethane (compound **3**) (1.9 g, 5.43 mmol) and 1-benzylimidazole (**6g**) (2.58 g, 16.3 mmol) to provide a pale yellow hygroscopic semi-solid in 91% yield (4.12 g). Molecular Formula: $C_{41}H_{45}Cl_3N_6O_6$; Mol. Wt.: 824.19; FTIR (cm^{-1}): 3063 (C-H)$_{Ar}$, 2977 (C-H)$_{Aliph}$, 1747 (C=O), 1661 (C=N), 1563, 1497 (C=C)$_{Ar}$, 1197, 1158 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 9.69 (s, 3H, C-$H_{Imidazole}$, major), 9.57 (s, 3H, C-$H_{Imidazole}$, minor), 9.44 (s, 3H, C-$H_{Imidazole}$, minor), 7.92 (t, J =1.71, 6H, C-$H_{Imidazole}$, major), 7.87 (t, J =1.71, 6H, C-$H_{Imidazole}$, minor), 7.45-7.20 (m, 15H, C-H_{Ar}), 5.56 (s, 6H, Ar-CH_2), 5.47 (s, 6H, O-CH_2, major), 5.42 (s, 6H, O-CH_2, minor), 5.36 (s, 6H, O-CH_2, minor), 4.03 (d~t, 6H, N-CH_2), 0.89 (s, 3H, CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 167.19 (C=O, minor), 166.64 (C=O, major), 137.54 ($CH_{Imidazole}$), 134.85 (-$\underline{C}_{Ar}$-CH_2-), 128.98 (2×CH_A), 128.77 (CH_{Ar}) 128.39 (2×CH_{Ar}), 124.22 ($CH_{Imidazole}$), 122.22 ($CH_{Imidazole}$, minor) 122.15 ($CH_{Imidazole}$, major), 66.48 (CH_2-O, major), 66.34 (CH_2-O, minor) 51.88 (CH_2-N), 49.68 (Ar-CH_2-), 41.10 (-C-), 16.31 (CH_3, major), 16.20 (CH_3, minor); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{41}H_{43}N_6O_6^{5+}$: 715.3244, found: 715.3274.

Tris-((*N*-butyl-benzimidazoliumyl-acetayloxy)methyl)ethane chloride (9b)

To a stirred solution of tris-((2-chloro-acetayloxy)methyl)ethane (compound **3)** (1.9g, 5.43 mmol) in acetonitrile anhydrous (15 mL), the solution of 1-butyl-benzimidazole (**7b**) (2.84 g, 16.3 mmol) in acetonitrile anhydrous (5

mL) was added drop-wise at room temperature and under nitrogen atmosphere. The reaction mixture was refluxed at 45-50 °C for 2-3 days, then at room temperature for 5 hours. The acetonitrile top layer was decanted and the IL washed with diethyl ether (3 × 10 mL), then residual solvent evaporated under reduced pressure. The product was dried at (40 °C, 0.01 mmHg) for 72 h to provide a viscous hygroscopic syrup in 97% yield (4.65 g). Molecular Formula: $C_{44}H_{57}Cl_3N_6O_6$; Mol. Wt.: 872.32; FTIR (cm^{-1}): 3025 $(C\text{-}H)_{Ar}$, 2950, 2935, 2862 $(C\text{-}H)_{Aliph}$, 1748(C=O), 1616(C=N), 1559, 1478, 1460 $(C=C)_{Ar}$, 1197, 1160 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.30 (s, 3H, $C\text{-}H_{BImidazole}$, major), 10.23 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 10.18 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 8.14-8.07 (m, 6H, CH_{Ar}), 7.71-7.61 (m, 6H, CH_{Ar}), 5.81 (s, 6H, O-CH_2, major), 5.76 (s, 6H, O-CH_2, minor), 4.58 (t, *J*=6.83, 6H, α-CH_2, major), 4.50 (t, *J*=6.83, 6H, α-CH_2, minor), 4.05 (s, 6H, N-CH_2, minor), 4.00 (s, 6H, N-CH_2, major), 1.91-1.83 (m, 6H, β-CH_2, major), 1.79-1.72 (m, 6H, β-CH_2, minor), 1.36- 1.27 (m, 6H, (ω-1)), 0.89 (t, 9H, *J* =7.32 Hz, ω-CH_3), 0.81 (s, 3H, CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 166.88 (C=O), 143.37 ($CH_{BImidazole}$, major), 142.97 ($CH_{BImidazole}$, minor), 131.43 (C_{Ar}), 129.71 (C_{Ar}), 124.80 (CH_{Ar}), 124.73 (CH_{Ar}), 115.03 (CH_{Ar}), 113.12 (CH_{Ar}), 66.22 (CH_2-O), 47.52 (CH_2-N), 45.91 (α-CH_2, major), 45.09 (α-CH_2, minor), 38.12 (-C-), 32.23 ((ω-2), minor), 31.85 ((ω-2), major), 17.98 ((ω-1), minor), 17.32 ((ω-1), major), 16.15 (CH_3), 13.80 ((ω), minor), 13.69 ((ω), major); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{44}H_{55}N_6O_6^{5+}$: 763.4183, found: 763.4223.

Tris-((*N*-decyl-benzimidazoliumyl-acetayloxy)methyl)ethane chloride (9e)

This compound was prepared analogously to **9b** using tris-((2-chloro-acetayloxy)methyl)ethane (compound **3**) (1.9 g, 5.43 mmol) and 1- decyl-benzimidazole (**7e**) (4.21 g, 16.3 mmol) to provide a viscous hygroscopic syrup in 99% yield (6.00g). Molecular Formula: $C_{62}H_{93}Cl_3N_6O_6$; Mol. Wt.: 1124.80; FTIR (cm^{-1}): 3134 $(C\text{-}H)_{Ar}$, 2958, 2923, 2854 $(C\text{-}H)_{Aliph}$, 1749 (C=O), 1619 (C=N), 1562 1485, 1463 $(C=C)_{Ar}$, 1199 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.36 (s, 3H, $C\text{-}H_{BImidazole}$, major), 10.22 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 10.12 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 8.14-8.09 (m, 6H, CH_{Ar}), 7.71-7.61 (m, 6H, CH_{Ar}, major), 7.30-7.20 (m, 6H, CH_{Ar}, minor), 5.84 (s, 6H, O-CH_2, major), 5.78 (s, 6H, O-CH_2, minor), 5.73 (s, 6H, O-CH_2, minor), 4.56 (t, *J*=7.25, 6H, α-CH_2, major), 4.51 (t, *J*=7.25, 6H, α-CH_2, minor), 4.04 (s, 6H, N-CH_2, minor), 3.99 (s, 6H, N-CH_2, major), 3.97 (s, 6H, N-CH_2, minor), 1.92- 1.85 (m, 6H, β-CH_2), 1.20 (bs, 42H, bulk-CH_2), 0.86 (s, 3H, CH_3), 0.82 (t, 9H, *J*=6.80, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 167.17 (C=O, minor), 166.44 (C=O, major), 143.37 ($CH_{BImidazole}$, major), 142.28 ($CH_{BImidazole}$, minor), 131.51 (C_{Ar}), 130.63 (C_{Ar}), 126.77 (CH_{Ar}), 126.69 (CH_{Ar}), 114.09 (CH_{Ar}, major), 113.99 (CH_{Ar}, minor), 113.77 (CH_{Ar}), 66.30 (CH_2-O, major), 66.17 (CH_2-O, minor), 47.53 (CH_2-N), 46.82 (α-CH_2, major), 46.66 (α-CH_2, minor), 38.17 (-C-), 31.29 ((ω-2), major), 30.71 ((ω-2), minor), 28.91, 28.87, 28.68, 28.57, 28.64 (bulk-CH_2), 25.71 (β), 22.10 (ω-1), 16.18 (CH_3, major), 16.11 (CH_3, minor), 13.95 (ω); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{62}H_{91}N_6O_6^{5+}$: 1015.7000, found: 1015.7055.

Tris-((*N*-dodecyl-benzimidazoliumyl-acetayloxy)methyl)ethane chloride (9f)

This compound was prepared analogously to **9b** using tris-((2-chloro-acetayloxy)methyl)ethane (compound **3**) (1.9 g, 5.43 mmol) and 1-dodecyl-benzimidazole (**7f**) (4.67 g, 16.3 mmol) to provide a viscous hygroscopic syrup in 99% yield (6.50g). Molecular Formula: $C_{68}H_{105}Cl_3N_6O_6$; Mol. Wt.: 1208.96; FTIR (cm^{-1}): 3132 $(C\text{-}H)_{Ar}$, 2955, 2925, 2855 $(C\text{-}H)_{Aliph}$, 1749 (C=O), 1619 (C=N), 1562, 1486, 1455 $(C=C)_{Ar}$, 1198 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.77 (s, 3H, $C\text{-}H_{BImidazole}$, major), 9.73 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 9.67 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 8.02-7.89 (m, 6H, CH_{Ar}), 7.73-7.57 (m, 6H, CH_{Ar}, major), 7.42-7.33 (m, 6H, CH_{Ar}, minor), 5.63 (s, 6H, O-CH_2, major), 5.60 (s, 6H, O-CH_2, minor), 5.58 (s, 6H, O-CH_2, minor), 4.54 (t, J=7.25, 6H, α-CH_2, major), 4.34 (t, J=7.25, 6H, α-CH_2, minor), 4.20 (s, 6H, N-CH_2, minor), 4.17 (s, 6H, N-CH_2, major), 4.05 (s, 6H, N-CH_2), 2.04- 1.96 (m, 6H, β-CH_2), 1.25 (bs, 54H, bulk-CH_2), 1.00 (s, 3H, CH_3), 0.86 (t, J=7.25, 9H, ω-CH_3); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.54 (C=O, minor), 166.26 (C=O, major), 142.72 ($CH_{BImidazole}$, major),

142.46 ($CH_{BImidazole}$, minor), 131.90 (C_{Ar}), 131.09 (C_{Ar}), 127.19 (CH_{Ar}), 127.09 (CH_{Ar}), 113.47 (CH_{Ar}), 113.35 (CH_{Ar}), 66.59 (CH_2-O, minor), 66.48 (CH_2-O, major), 66.07 (CH_2-O, minor), 45.41 (CH_2-N), 40.33 (α-CH_2), 38.75 (-C-), 31.75 (ω-2), 29.44 (2), 29.35, 29.25, 29.15, 28.90, 28.87 (bulk-CH_2), 26.34 ((β), minor), 26.18 ((β), major), 22.42 (ω-1), 15.72 (CH_3), 13.17 (ω); HRMS: m/z, $[M^{+3}–2H]-3Cl^-$ calcd. for $C_{68}H_{103}N_6O_6^{5+}$: 1099.7939, found: 1099.7964.

Tris-((*N*-methyl-imidazoliumyl-acetayloxy)methyl)ethane bis(trifluoromethylsulfonyl)amide (10a)

A flask was charged with tris-((*N*-methyl-imidazoliumyl-acetayloxy)methyl)ethane chloride **8a** (0.6 g, 1.0 mmol) and deionized water (10 mL). Lithium bis-(trifluoromethanesulphonyl)imide $LiNTf_2$ (1.0 g, 3.5 mmol) in deionized water (3 mL) was added in one portion and the suspension was stirred vigorously for 7 h at room temperature. The mixture was extracted with Ethyl acetate (3×5mL) after stirring for 1h each time. The combined organic layers were evaporated on the rotary evaporator and under high vacuum for 8 h to remove the solvent and produce a clear viscous hygroscopic liquid at room temperature in 81% yield (1.08 g). Molecular Formula: $C_{29}H_{33}F_{18}N_9O_{18}S_6$; Mol. Wt.: 1329.98; FTIR (cm^{-1}): 3070 (C-H)$_{Ar}$, 2970, 2932, 2857 (C-H)$_{Aliph}$, 1750 (C=O), 1642 (C=N), 1555, 1468 (C=C)$_{Ar}$, 1359, 1220 (C-F), 1362, 1150 (O=S=O), 1220, 1184(C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 8.70 (s, 3H, C-$H_{Imidazole}$, minor), 8.68 (s, 3H, C-$H_{Imidazole}$, minor), 8.66 (s, 3H, C-$H_{Imidazole}$, major), 7.39 (dt, 6H, J =10.79, 1.76, Hz, C-$H_{Imidazole}$), 4.98 (s, 6H, O-CH_2, major), 4.97 (s, 6H, O-CH_2, minor), 4.94 (s, 6H, O-CH_2, minor), 3.98 (s, 6H, N-CH_2, major), 3.95 (s, 6H, N-CH_2, minor), 3.93 (s, 6H, N-CH_2, minor), 3.75 (s, 9H, α-CH_3), 0.87 (s, 3H, CH_3); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.90 (C=O, minor), 167.75 (C=O, major), 139.32 ($CH_{Imidazole}$), 126.07, 122.89, 119.71, 116.52 (q, J=320, CF_3), 125.22 ($CH_{Imidazole}$), 124.91 ($CH_{Imidazole}$), 68.76 (CH_2-O, minor), 68.00 (CH_2-O, major), 50.82 (CH_2-N), 40.19 (-C-), 36.85 (α-CH_3), 17.03 (CH_3). ^{19}F (336, MHz) δ ppm: –80.12; HRMS: m/z, $[M^{+3}–2H]-3NTF_2^-$ calcd. for $C_{23}H_{31}N_6O_6^{5+}$: 487.2305, found: 487.2285; m/z, $[NTF_2]^-$calcd. for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9169.

Tris-((*N*-benzyl-imidazoliumyl-acetayloxy)methyl)ethane bis(trifluoromethylsulfonyl)amide (10g)

This compound was prepared analogously to **10a** using tris-((*N*-benzyl-imidazoliumyl-acetayloxy)methyl)ethane chloride **8g** (0.82 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)imide $LiNTf_2$ (1.0 g, 3.5 mmol) to provide a clear viscous hygroscopic liquid at room temperature in 91% yield (1.41 g). Molecular Formula: $C_{47}H_{45}F_{18}N_9O_{18}S_6$; Mol. Wt.: 1558.27; FTIR (cm^{-1}): 3070 (C-H)$_{Ar}$, 2990 (C-H)$_{Aliph}$, 1750 (C=O), 1661 (C=N), 1555, 1487 (C=C)$_{Ar}$, 1340, 1210 (C-F), 1372, 1154 (O=S=O), 1207, 1169 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.05 (s, 3H, C-$H_{Imidazole}$, minor), 9.03 (s, 3H, C-$H_{Imidazole}$, minor), 9.01 (s, 3H, C-$H_{Imidazole}$, major), 7.67 (bt~s, 6H, C-$H_{Imidazole}$, minor), 7.63 (bt~s, 6H, C-H_{Imi}, major), 7.59 (bt~s, 6H, C-$H_{Imidazole}$, minor), 7.43-7.21 (m, 15H, C-H_{Ar}), 5.45 (s, 6H, Ar-CH_2, minor), 5.43 (s, 6H, Ar-CH_2, major), 5.19 (s, 6H, O-CH_2), 4.18 (s, 6H, N-CH_2, minor), 4.15 (s, 6H, N-CH_2, major), 4.13 (s, 6H, N-CH_2, minor), 1.05 (s, 3H, CH_3, minor), 1.03 (s, 3H, CH_3, minor), 1.01 (s, 3H, CH_3, major); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.74 (C=O, major), 167.69 (C=O, minor), 138.88 ($CH_{Imidazole}$, minor), 138.79 ($CH_{Imidazole}$, major), 135.05 (-$\underline{C}_{Ar}$-CH_2-), 130.66 (2×CH_A), 129.88 (2×CH_A), 126.09, 122.91, 119.73, 116.55 (q, J=319, CF_3), 125.65 ($CH_{Imidazole}$), 123.71 ($CH_{Imidazole}$), 68.15 (CH_2-O, minor), 68.01 (CH_2-O, major), 67.43 (CH_2-O, minor), 54.49 (CH_2-N), 50.97 (Ar-CH_2-), 40.14 (-C-), 17.07 (CH_3, minor), 17.00 (CH_3, major). ^{19}F (336, MHz) δ ppm: –79.97; HRMS: m/z, $[M^{+3}–2H]-3NTF_2^-$ calcd. for $C_{41}H_{43}N_6O_6^{5+}$: 715.3244, found: 715.3281; m/z, $[NTF_2]^-$calcd. for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9164.

Tris-((*N*-octyl-benzimidazoliumyl-acetayloxy)methyl)ethane bis(trifluoromethylsulfonyl)amide (11d)

This compound was prepared analogously to **10a** using tris-((*N*-octyl-benzimidazoliumyl-acetayloxy)methyl) ethane chloride **9d** (1.04 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)imide $LiNTf_2$ (1.0 g, 3.5 mmol) to provide a clear viscous hygroscopic liquid at room temperature in 90% yield (1.60 g). Molecular Formula: $C_{62}H_{81}F_{18}N_9O_{18}S_6$; Mol. Wt.: 1774.71; FTIR (cm^{-1}): 3120 $(C\text{-}H)_{Ar}$, 2945, 2920, 2850 $(C\text{-}H)_{Aliph}$, 1742 (C=O), 1618 (C=N), 1566, 1483 1460 $(C{=}C)_{Ar}$, 1360, 1220 (C-F), 1350, 1172 (O=S=O), 1192(C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.03 (s, 3H, $C\text{-}H_{BImidazole}$, major), 9.97 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 9.91 (s, 3H, $C\text{-}H_{BImidazole}$, minor), 8.13-8.05 (m, 6H, CH_{Ar}), 7.54-7.45 (m, 6H, CH_{Ar}, minor), 7.12-7.03 (m, 6H, CH_{Ar}, major), 5.83 (s, 6H, $O\text{-}CH_2$, major), 5.79 (s, 6H, $O\text{-}CH_2$, minor), 4.37 (t, *J*=7.07, 6H, $\alpha\text{-}CH_2$, major), 4.29 (t, *J*=7.07, 6H, $\alpha\text{-}CH_2$, minor), 4.02 (s, 6H, $N\text{-}CH_2$, minor), 3.97 (s, 6H, $N\text{-}CH_2$, major), 1.92-1.86 (m, 6H, $\beta\text{-}CH_2$), 1.22 (bs, 30H, bulk-CH_2), 0.85 (s, 3H, CH_3), 0.80 (t, 9H, *J*=6.80, $\omega\text{-}CH_3$); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 168.10 (C=O, major), 166.72 (C=O, minor), 143.28 ($CH_{BImidazole}$), 131.72 (C_{Ar}), 130.76 (C_{Ar}), 126.94 (CH_{Ar}), 126.71 (CH_{Ar}), 124.46, 121.23, 118.00, 114.76 (q, *J*=322, CF_3), 113.96 (CH_{Ar}), 113.78 (CH_{Ar}), 62.78 (CH_2-O, minor), 62.13 (CH_2-O, major), 47.62 (CH_2-N), 46.95 ($\alpha\text{-}CH_2$), 38.43 (-C-), 31.24 (ω-2), 28.58 (2), 28.47 (bulk-CH_2), 25.77 (β), 22.15 (ω-1), 21.07 (CH_3, major), 20.78 (CH_3, minor), 14.10 ((ω), minor), 13.94 ((ω), major). ^{19}F (336, MHz) δ ppm: –80.02; HRMS: m/z, $[M^{+3}–2H]–3NTF_2^-$ calcd. for $C_{56}H_{79}N_6O_6^{5+}$: 931.6061, found: 931.6028; m/z, $[NTF_2]^-$calcd. for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9201.

Liquid crystal behaviour

Liquid crystalline properties of compounds **8b-f** and **9b-f** were investigated thermotropically and lyotropically. Optical polarising microscopy (Olympus BH-2 OPM equipped with Mettler FF82 hot stage and Mettler FP80 Central Processor), was used to identify the optical textures and the transition temperatures. A contact penetration technique[60] was applied in lyotropic investigation. It was carried out at room temperature with water and 1-undecanol as polar and nonpolar solvents, respectively. The images were recorded at 50× magnification.

Air-water interface tension

The surface tensions were measured using KSV Sigma 702 tensiometer at 25 ± 0.5 ºC. The measurements were based DuNouy ring method in five replications with a standard deviation of less than 0.1 mN m^{-1}. The critical micelle concentration, cmc, was obtained from surface tension against logarithmic concentration plot through the intersection of two regression lines, where one of them is concentration dependent. Solutions were prepared using deionized water which was also filtered through 0.25 μm pore membrane producing 71.96 ± 0.09 mN m^{-1}, 0.9996±0.0002 g mL^{-1} and 1.0 ±0.1 μS cm^{-1} values for surface tension, density and conductivity, respectively.

Krafft point (T_K)

The determination of Krafft temperature, (T_k), applied slow heating of 1 % (w/v) aqueous solution of ILs surfactant in water bath. It was heated on an IKA hot plate stirrer equipped with temperature controller IKA ETS-D4 at 5 ºC. min^{-1} over the range 10 ºC to 50 ºC. The changes of transparency was optically monitored to observe the temperature of clear solution formed.[61]

Closed Bottle Test

The biodegradability of synthesized ILs (*i.e.* **8b-g** and **9b-g**) was evaluated using Closed-Bottle test (OECD 301D) standard protocols.[55] The analysis was based on biochemical oxygen demand (BOD) due to IL microbial

degradation as reported.[38] The BOD values were derived from the quantified respirometric dissolved oxygen (DO) in a culture containing either IL or sodium *n*-dodecyl sulphate; SDS as a reference sample. The DO was measured using CyberScan dissolve oxygen meter $DO300$ (Eutech Instruments; The Netherlands).

All samples were prepared in capped Scotch bottles, each containing 100 ml of sample solution at 100 mg/L concentration of IL or reference sample in distilled water. Each sample bottle was inoculated with 1 mL of microbial effluent collected from a wastewater treatment plant. Samples were prepared in three different groups of 3 replicates per each sample. Group 1 contained both inoculum and the IL samples, Group 2 contained only the inoculum (test blank) and Group 3 contained the inoculum and the reference sample (SDS). The solutions were incubated in the dark at 25 ±1°C for 28 days under continuous shaking (200 rpm), and the DO values were recorded after every 48 hours. Since the majority of biodegradation changes are only noticed within the first 16 days period of time, 10 and 16 days results were considered.

The BOD values were calculated based on observed DO using Equation 3 as reported in literature,[62]

$$BOD = \frac{DO_o - DO_t}{\varphi} \quad (3)$$

where DO_o is initial dissolved oxygen and DO_t is the dissolved oxygen at time t. While φ is fractional oxygen volume defined as the ratio of the experimental DO volume to theoretical DO volume that obtained from reference sample.

Further, the percentage biodegradation was calculated according to Equation 4 as following:[38]

$$\%\, Biodegradation = \frac{BOD}{ThOD\,(\frac{mg\ O_2}{mg\ \ sample\ weight})} \times 100 \quad (4)$$

where $ThOD$ represent the theoretical oxygen demand; the amount of oxygen consumed by the microorganisms in sample corrected for the uptake of O_2 by the blank inoculums.[38]

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References

1. K. R. Seddon, *Nat. Mater.*, 2003, **2**, 363-365.
2. J. S. Wilkes, *Green Chem.*, 2002, **4**, 73-80.
3. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis, 2 Volume Set*, Wiley, 2007.
4. J. H. Davis, James, *Chem. Lett.*, 2004, **33**, 1072-1077.
5. P. Wasserscheid, R. v. Hal and A. Bosmann, *Green Chem.*, 2002, **4**, 400-404.
6. D. W. Rooney and K. R. Seddon, in *Handbook of Solvents*, ed. G. Wypych, ChemTec Publishing, Toronto, Ontario 2001, pp. 1459-1484.
7. R. Sheldon, *Chem. Commun.*, 2001, 2399-2407.
8. R. A. Sheldon, *Green Chem.*, 2005, **7**, 267-278.
9. C. M. Gordon, *Appl. Catal. A: General*, 2001/12/20/, **222**, 101-117.
10. M. K. Munshi, P. S. Biradar, S. M. Gade, V. H. Rane and A. A. Kelkar, *RSC Adv.*, 2014, **4**, 17124-17128.

11. H. Li, Q. Zhang, X. Liu, F. Chang, D. Hu, Y. Zhang, W. Xue and S. Yang, *RSC Adv.*, 2013, **3**, 3648-3654.
12. T. Welton, *Chem. Rev.*, 1999, **99**, 2071-2084.
13. K. V. Axenov and S. Laschat, *Materials*, 2011, **4**, 206-259.
14. W. Chi, H. Jeon, S. Kim, D. Kim and J. Kim, *Macromol. Res.*, 2013, **21**, 315-320.
15. D. Zhao, Y. Liao and Z. Zhang, *CLEAN–Soil, Air, Water*, 2007, **35**, 42-48.
16. A. G. Santos, B. D. Ribeiro, D. S. Alviano and M. A. Z. Coelho, *RSC Adv.*, 2014, **4**, 37157-37163.
17. H. Hajfarajollah, B. Mokhtarani, A. sharifi, M. Mirzaei and A. Afaghi, *RSC Adv.*, 2014, **4**, 13153-13160.
18. M. Petkovic, J. L. Ferguson, H. Q. N. Gunaratne, R. Ferreira, M. C. Leitao, K. R. Seddon, L. P. N. Rebelo and C. S. Pereira, *Green Chem.*, 2010, **12**, 643-649.
19. S. Stolte, M. Matzke, J. Arning, A. Boschen, W.-R. Pitner, U. Welz-Biermann, B. Jastorff and J. Ranke, *Green Chem.*, 2007, **9**, 1170-1179.
20. R. P. Swatloski, J. D. Holbrey, S. B. Memon, G. A. Caldwell, K. A. Caldwell and R. D. Rogers, *Chem. Commun.*, 2004, 668-669.
21. A. Garcia-Lorenzo, E. Tojo, J. Tojo, M. Teijeira, F. J. Rodriguez-Berrocal, M. P. Gonzalez and V. S. Martinez-Zorzano, *Green Chem.*, 2008, **10**, 508-516.
22. J. Pernak, K. Sobaszkiewicz and I. Mirska, *Green Chem.*, 2003, **5**, 52-56.
23. S. Morrissey, B. Pegot, D. Coleman, M. T. Garcia, D. Ferguson, B. Quilty and N. Gathergood, *Green Chem.*, 2009, **11**, 475-483.
24. A. S. Wells and V. T. Coombe, *Org. Process Res. Dev.*, 2006, **10**, 794-798.
25. J. Ranke, K. Mölter, F. Stock, U. Bottin-Weber, J. Poczobutt, J. Hoffmann, B. Ondruschka, J. Filser and B. Jastorff, *Ecotoxicol. Environ. Saf.*, 2004, **58**, 396-404.
26. B. Jastorff, R. Stormann, J. Ranke, K. Molter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nuchter, B. Ondruschka and J. Filser, *Green Chem.*, 2003, **5**, 136-142.
27. K. M. Docherty and J. C. F. Kulpa, *Green Chem.*, 2005, **7**, 185-189.
28. K. J. Kulacki and G. A. Lamberti, *Green Chem.*, 2008, **10**, 104-110.
29. A. Latala, M. Nedzi and P. Stepnowski, *Green Chem.*, 2010, **12**, 60-64.
30. M. Matzke, S. Stolte, K. Thiele, T. Juffernholz, J. Arning, J. Ranke, U. Welz-Biermann and B. Jastorff, *Green Chem.*, 2007, **9**, 1198-1207.
31. B. Jastorff, K. Molter, P. Behrend, U. Bottin-Weber, J. Filser, A. Heimers, B. Ondruschka, J. Ranke, M. Schaefer, H. Schroder, A. Stark, P. Stepnowski, F. Stock, R. Stormann, S. Stolte, U. Welz-Biermann, S. Ziegert and J. Thoming, *Green Chem.*, 2005, **7**, 362-372.
32. R. S. Boethling, in *Designing Safer Chemicals*, American Chemical Society, 1996, vol. 640, ch. 8, pp. 156-171.
33. R. S. Boethling, in *Cationic Surfactants, Surfactant Science Series* eds. J. Cross and E. J. Singer, Marcel Dekker, New York, 1994, vol. 53, pp. 95-135.
34. P. H. Howard, R. S. Boethling, W. Stiteler, W. Meylan and J. Beauman, *Science of The Total Environment*, 1991, **109–110**, 635-641.
35. N. Gathergood and P. J. Scammells, *Australian J. Chem.*, 2002, **55**, 557-560.
36. N. Gathergood, M. T. Garcia and P. J. Scammells, *Green Chem.*, 2004, **6**, 166-175.
37. N. Gathergood, P. J. Scammells and M. T. Garcia, *Green Chem.*, 2006, **8**, 156-160.
38. D. Coleman and N. Gathergood, *Chem. Soc. Rev.*, 2010, **39**, 600-637.
39. S. Wadud, R. Onodera and M. M. Or-Rashid, *Appl Microbiol Biotechnol*, 2001, **55**, 219-225.
40. X. Cheng, X. Bai, S. Jing, H. Ebert, M. Prehm and C. Tschierske, *Chemistry – A Eur. J.*, 2010, **16**, 4588-4601.
41. N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123-150.
42. F. Sander, S. Tussetschläger, S. Sauer, M. Kaller, K. V. Axenov and S. Laschat, *Liq. Cryst.*, 2011, **39**, 303-312.
43. T. Ichikawa, M. Yoshio, A. Hamasaki, S. Taguchi, F. Liu, X.-b. Zeng, G. Ungar, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2012, **134**, 2634-2643.
44. S. T. Handy, *Chem. Eur. J.*, 2003, **9**, 2938-2944.

45. G.-h. Tao, L. He, N. Sun and Y. Kou, *Chem. Commun.*, 2005, 3562-3564.
46. J. Neumann, S. Steudte, C.-W. Cho, J. Thoming and S. Stolte, *Green Chem.*, 2014, **16**, 2174-2184.
47. S. Stolte, S. Abdulkarim, J. Arning, A.-K. Blomeyer-Nienstedt, U. Bottin-Weber, M. Matzke, J. Ranke, B. Jastorff and J. Thoming, *Green Chem.*, 2008, **10**, 214-224.
48. S. Steudte, S. Bemowsky, M. Mahrova, U. Bottin-Weber, E. Tojo-Suarez, P. Stepnowski and S. Stolte, *RSC Adv.*, 2014, **4**, 5198-5205.
49. J. W. Goodby, G. W. Gray, D. Demus, J. Goodby, G. W. Gray, H. W. Spiess and V. Vill, in *Handbook of Liquid Crystals*, Wiley-VCH Verlag GmbH, 2008, pp. 17-23.
50. E. J. R. Sudholter, J. B. F. N. Engberts and W. H. De Jeu, *J. Phys. Chem.*, 1982, **86**, 1908-1913.
51. G. S. Attard, S. Fuller, O. Howell and G. J. T. Tiddy, *Langmuir*, 2000, **16**, 8712-8718.
52. B. J. Boyd, C. J. Drummond, I. Krodkiewska and F. Grieser, *Langmuir*, 2000, **16**, 7359–7367.
53. K. M. Docherty, J. K. Dixon and C. F. Kulpa Jr, *Biodegradation*, 2007, **18**, 481-493.
54. M. J. Scott and M. N. Jones, *Biochimica et Biophysica Acta (BBA) - Biomembranes*, 2000, **1508**, 235-251.
55. *OECD guideline for testing of chemicals*, adopted by the council July 1992—ready biodegradability.
56. M. T. Garcia, N. Gathergood and P. J. Scammells, *Green Chem.*, 2005, **7**, 9-14.
57. S. P. M. Ventura, M. Gurbisz, M. Ghavre, F. M. M. Ferreira, F. Gonçalves, I. Beadham, B. Quilty, J. A. P. Coutinho and N. Gathergood, *ACS Sustainable Chem. Eng.*, 2013, **1**, 393-402.
58. J. Ropponen, K. Nattinen, M. Lahtinen and K. Rissanen, *CrystEngComm*, 2004, **6**, 559-566.
59. O. V. Starikova, G. V. Dolgushin, L. I. Larina, P. E. Ushakov, T. N. Komarova and V. A. Lopyrev, *Russian J. Org. Chem.*, 2003, **39**, 1467-1470.
60. K. Rendall, G. J. T. Tiddy and M. A. Trevethan, *J. Chem. Soc., Faraday Trans.1: Physical Chemistry in Condensed Phases*, 1983, **79**, 637-649.
61. A. Piasecki and D. Piłakowska-Pietras, *J Surfact Deterg*, 2007, **10**, 125-130.
62. V. Massardier-Nageotte, C. Pestre, T. Cruard-Pradet and R. Bayard, *Polym. Degrad. Stability*, 2006, **91**, 620-627.