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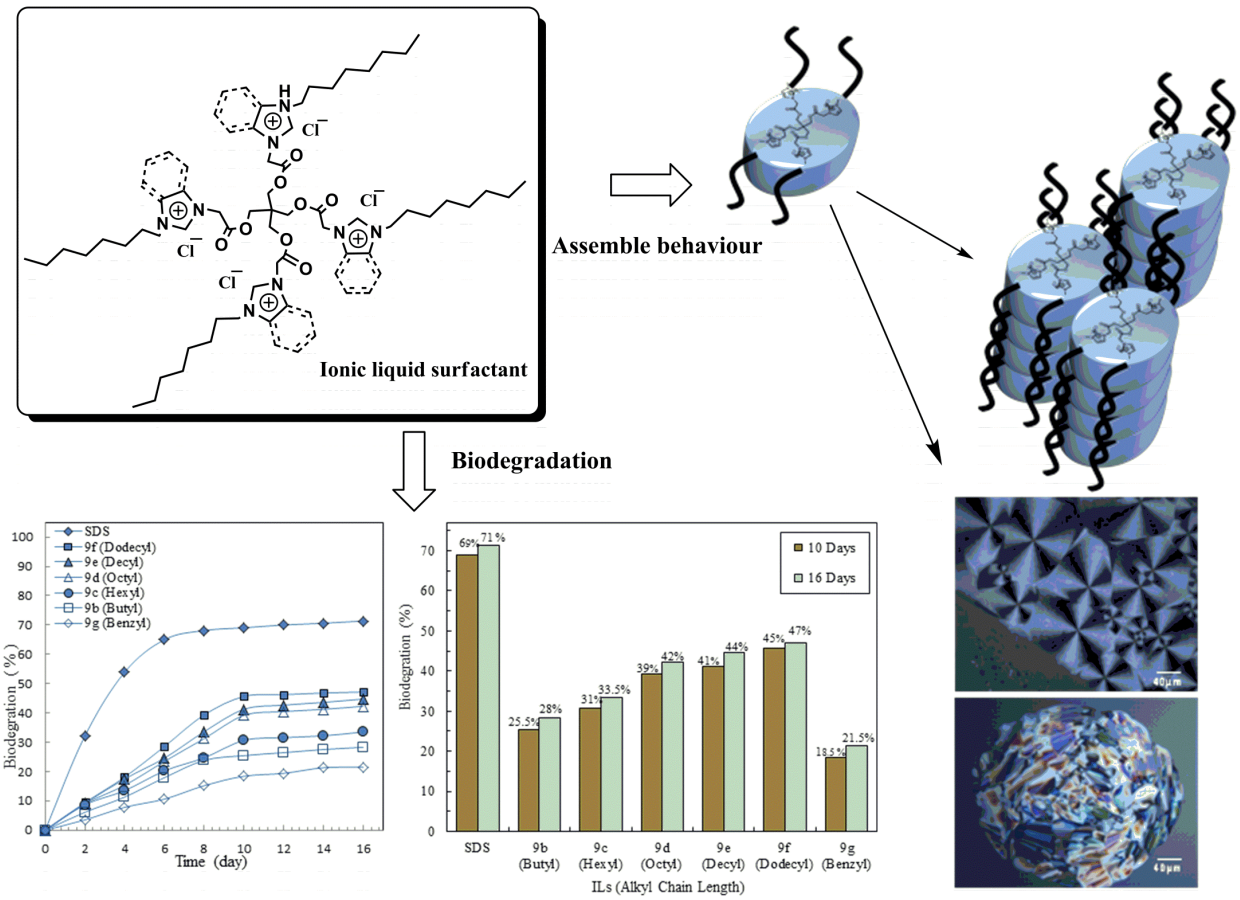

Novel tetrakis-imidazolium and benzimidazolium ILs containing tetra-ester groups with incorporated quadruple side chains were synthesized successfully as degradable surfactants of expected medical and industrial applications.

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Abstract

Novel series of tetra-cationic ionic liquids containing alkyl or phenyl side chains and ester groups within the same molecule were successfully prepared. Based on imidazolium and benzimidazolium, these ionic liquids were simply synthesized from readily available starting materials in high yield. Surfactant properties including liquid crystalline behaviour and surface properties as well as their biodegradability were investigated. Tetrakis-imidazolium ionic liquid compounds showed assembly behaviour in the pure form (*i.e.* spontaneously) and in the presence of polar or nonpolar solvents, while both imidazolium and benzimidazolium ionic liquids effectively reduced the surface tension of water in the range of 29–34 mN m^{-1}. The incorporation of tetra alkyl or phenyl side chains into imidazolium and bezimidazolium ionic liquids with tetra-ester groups, significantly improved the biodegradation. 'Closed-Bottle Test' OECD 301D and sodium *n*-dodecyl sulphate (SDS) as a reference were used for evaluation. The linear alkyl side chains (i.e. butyl, hexyl, octyl, decyl and dodecyl) in both tetrakis-imidazolium and benzimidazolium ionic liquids promote the increasing in biodegradation and phase behaviour results comparing to aromatic side-chains.

Introduction

Ionic liquids (ILs) are salts and entirely composed of ions: organic cation with delocalized charges associated with weakly coordinating anions. ILs as neoteric compounds have become increasingly classified as ''green'' solvents due to their negligible vapour pressure, non-flammability, recyclability, and potential solvation.[1-5] Generally, their chemical and physical properties can be tuned for a given application by varying both cationic and anionic components.[6,7] Currently, due to the potential and present wide applications of ILs, a comprehensive evaluation of their environmental and hazardous impacts is essential. Therefore, ILs estimation in the environment considers as an important and active core for different studies related to toxicity,[8-14] ecotoxicity,[15-18] bioaccumulation[19-21] and biodegradation.[22-25] Although the low vapour pressure and highly chemical stability of ILs may reduce air pollution compared to conventional organic solvents, many classes of ILs are water-soluble even those containing long hydrocarbon chains or with lipophilic anions. Moreover, as a result of their high stability in water, ILs may consider as persistent organic pollutants (POPs) in wastewaters. Thus, the determination of their potential environmental risk is of high priority.

Through designing linear alyklbenzenesulfonates and dialkyl quaternary compounds as biodegradable surfactants, Boethling[26] emphasized the importance of designing biodegradable chemicals to reduce pollution at the source. Due to the structural similarity among many surfactants, like quaternary ammonium compounds, as well as ILs based on imidazolium cores, the factors improving the biodegradation of surfactants could apply to ILs. Towards biodegradation improvement, the structures

design that applied to ILs based on the surfactant preparation are:[27,28] the presence of phenyl rings or linear hydrocarbon chains with ≥4 carbon atoms and the existence of esters or amides as hydrolysable groups. By achieving these factors relation to surfactant, rod-like molecules such as single-chain imidazole derivatives generated nematic (N) and bilayer smectic A (SmA) phases.[29,30] Columnar phase was generated due to the triple and quadruple-tail compounds with a tendency to form a wedge-shaped or disc-shaped molecule. Wedge-shaped molecules had an affinity to form higher-ordered molecular arrangements such as columnar (col) or cubic (cub) phases.[31,32] Generally, the higher-ordered phases were considered a good candidate for anisotropic ion conductor application.[33] Moreover, compared to single-chain mono-ionic surfactants, the surface tension of multi-ionic head groups reduced upon increasing the number of the alkyl chains (*i.e*. double- or triple- chain amphiphiles) with enhancing interfacial properties.[34,35] Further, comparatively more CH_3 groups were arranged to be on the outermost layer, which decreased surface energy.[36]

Gathergood and co-workers[37,38] used the structure design of biodegradable surfactants to improve the biodegradation of imidazolium ILs series containing incorporated alkyl side chain into functional ester or amide groups. The observed improvement was attributed to enzymatic hydrolysis susceptibility of the ester group compared to non-functional equivalent ILs: 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] and 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6]. Studies by Garcia *et al.*,[39] and Jitendra *et al.*,[40,41] of ILs series, with and without ester groups, confirmed biodegradation improvement in the presence of an ester linkage. Further, Morrissey *et al.*,[42] supported the above previous studies that revealed an ester group is the favorite over an amide when investigated the biodegradability of synthesized ILs series containing a wide range of ether and poly ether esters. All of these studies as well as Gathergood *et al.*,[43] work proved that octylsulfate counter ions had the highest biodegradation.

The biodegradability of ILs has been evaluated using a number of standard methods. The methods developed by the Organisation for Economic Co-operation and Development (OECD) as series of guidelines.[44-46] Generally, the most used methods are modified Sturm and Closed Bottle Tests (OECD 301 B and D, respectively). Based on sufficient interval measurements, different parameters such as dissolved organic carbon (DOC), carbon dioxide production and oxygen uptake can be used as criteria for ILs degradation. In current study, Closed Bottle Tests (OECD 301 D) was used to assess the biodegradability of the prepared ILs. The ILs were added to an aerobic aqueous medium inoculated with wastewater microorganisms. The depletion of dissolved molecular oxygen was measured for defined period (28 days) and presented as a percentage of the theoretical maximum. The evaluated ILs with 60% or higher biodegradation level are considered ‘‘readily biodegradable’’ which was defined as compounds rapidly and completely decomposing or reaching ultimate biodegradability in aquatic environments under aerobic conditions and stringent test.

In continuation to the synthesis of new multi-cationic ILs,[47] current study involves design and synthesis novel series of tetrakis-imidazolium and tetrakis-benzimidazolium ILs. The molecule design of ILs emphasized on increasing hydrolysable sites; multi-ester groups and incorporated alkyl or phenyl side chains with an expected higher-ordered phase (e.g. columnar phase) as targeted materials. Towards quadruple side chains of degradable IL surfactants with highly expected medical and industrial applications, the biodegradation of the synthesized halogen ILs were evaluated using the ‘Closed Bottle Test’ (OECD 301 D). The presence of ester groups with longer alkyl chains of the tetrakis-imidazolium ILs showed a more significant degradability comparing to mono and tri-cationic ILs. Further unique

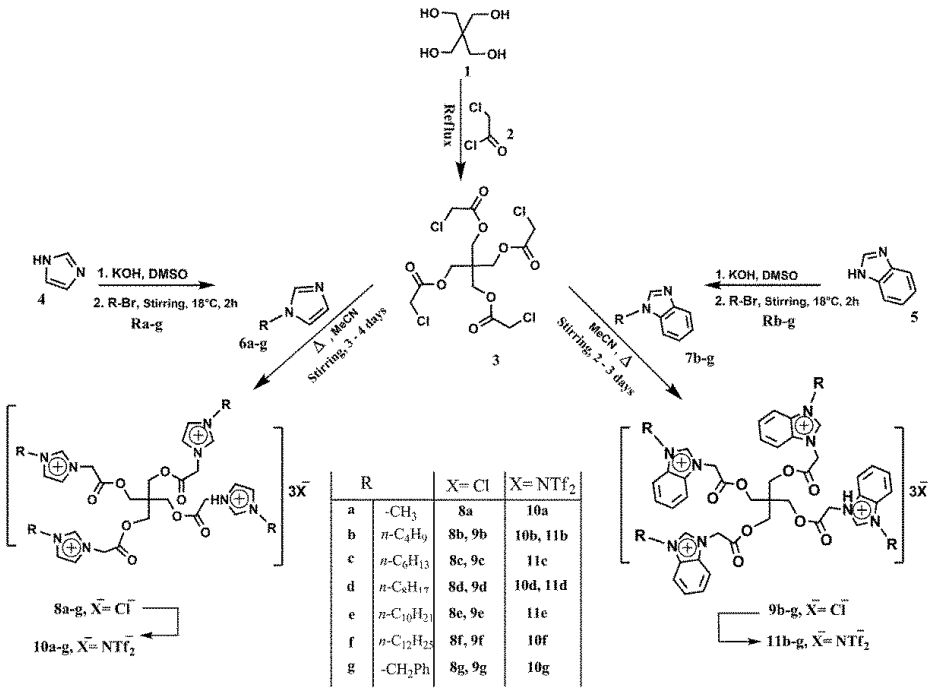
studies of their phase behaviours and surface properties were contributed. The effects of anions on phase behaviour and biodegradation are beyond the scope of this study.

Results and discussion

Synthesis

Tetrakis-imidazolium and tetrakis-benzimidazolium ILs were prepared based on a certain strategy in the previous tris-cationic study by the same authors.[47] With regard to the high purity and excellent yield of ILs, alpha position halides to carbonyl compound represented excellent starting materials. Therefore, the esterification of pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) in net chloroacetyl chloride was a perfect process to obtain active tetra-ester halides compound. The syntheses of incorporated alkyl (or phenyl) side chains IL series containing tetra ester groups depended on the production of a variety of alkyl (or phenyl) imidazoles and benzimidazoles. Alkylation of the obtained alkyl imidazoles and benzimidazoles with active tetra-ester halide in acetonitrile at 50 – 60 °C provided the quantitative yields of certain tetra-cationic IL as shown in Scheme 1. The production of alkyl (or phenyl) imidazole and benzimidazole by treating imidazole or benzimidazole solids with alkyl halides under basic conditions has been described in our previous work.[47]

A good yield of NTf_2-ILs was produced by counter-ions exchange in an aqueous solution of chloride anions and bis(trifluoromethane)sulfonimide lithium salt. Clear liquid samples of hydrophobic ILs were obtained after simple extraction with ethyl acetate and the organic layer evaporation under reduced pressure. The purity of the NTf_2-ILs was confirmed by ^{13}C and ^{9}F-NMR. All the chloride ILs prepared in the current work are viscous syrup or semi-solid to solid with melting points below 100 °C and has been set as benchmark to determine their classification as ILs[48] (as summarized in Table 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	11c
d	$n-C_8H_{17}$	8d, 9d	10d, 11d
e	$n-C_{10}H_{21}$	8e, 9e	11e
f	$n-C_{12}H_{25}$	8f, 9f	10f
g	$-CH_2Ph$	8g, 9g	10g

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

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

IL	Cations	Alkyl chains	Counter ions	Status[c]	Mol. wt	m.p (°C)	Yield (%)
8a	Im[a]	CH_3	Cl^-	Solid	770.49	52-54	98
8b	Im[a]	*n*-C_4H_9	Cl^-	Semi-solid	938.81	-	97
8c	Im[a]	*n*-C_6H_{13}	Cl^-	Syrup	1051.02	-	98
8d	Im[a]	*n*-C_8H_{17}	Cl^-	Syrup	1163.23	-	98
8e	Im[a]	*n*-$C_{10}H_{21}$	Cl^-	Syrup	1275.45	-	99
8f	Im[a]	*n*-$C_{12}H_{25}$	Cl^-	Syrup	1387.66	-	99
8g	Im[a]	-CH_2-Ph	Cl^-	Semi-solid	1074.87	-	94
9b	BIm[b]	*n*-C_4H_9	Cl^-	Solid	1139.04	48-50	99
9c	BIm[b]	*n*-C_6H_{13}	Cl^-	Solid	1251.26	54-56	98
9d	BIm[b]	*n*-C_8H_{17}	Cl^-	Syrup	1363.47	-	99
9e	BIm[b]	*n*-$C_{10}H_{21}$	Cl^-	Syrup	1475.68	-	97
9f	BIm[b]	*n*-$C_{12}H_{25}$	Cl^-	Syrup	1587.89	-	98
9g	BIm[b]	-CH_2-Ph	Cl^-	Solid	1275.10	50-52	99
10a	Im[a]	-CH_3	NTf_2^-	liquid	1329.98	-	91
10b	Im[a]	*n*-C_4H_9	NTf_2^-	liquid	1456.22	-	91
10d	Im[a]	*n*-C_8H_{17}	NTf_2^-	liquid	1540.38	-	95
10f	Im[a]	*n*-$C_{12}H_{25}$	NTf_2^-	liquid	1708.70	-	93
10g	Im[a]	-CH_2-Ph	NTf_2^-	liquid	1558.27	-	96
11b	BIm[b]	*n*-C_4H_9	NTf_2^-	liquid	1606.39	-	94
11c	BIm[b]	*n*-C_6H_{13}	NTf_2^-	liquid	1774.71	-	98
11d	BIm[b]	*n*-C_8H_{17}	NTf_2^-	liquid	1858.88	-	98
11e	BIm[b]	*n*-$C_{10}H_{21}$	NTf_2^-	liquid	2454.45	-	98

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

Liquid crystalline behaviour

Crystalline properties of compounds **8b-f** and **9b-f** were investigated thermotropically and lyotropically using optical polarizing microscope equipped with heating stage. In pure form, all compounds of tetrakis-imidazolium series exist as liquid crystals with clearing point range from 94–176 °C. In general, ILs of tetrakis-imidazolium showed clearing points higher than tetrakis-benzimidazolium for the same side chains, where attributed to the presence of benzene ring in the cationic head. The phase is identified as columnar phase based on the fan-shaped texture characteristic, where Fig. 1 showed the columnar phase of **8c** and **8f** compounds. Clearer textures were observed on cooling from isotropic, occasionally, the phase formation was very slow. Compounds with chains length ≥ C10 carbons showed smectic A (SmA) phases as illustrated in Fig. 2 for compound **8e**. Based on the chemical structures of tetrakis-imidazolium ILs, columnar phase is more favourable where the molecules had arranged as a rigid core at the centre and alkyl chains at the periphery, as illustrated in Fig. 3. Quadruple-chain crystals of tetra-coordinated silver (I) cation showed a similar columnar mesomorphism structure when incorporated with TfO^- as a counter ion. The coordination of these IL crystals based on disubstituted chelating of 2,2'-bipyridines ligands was considered as drive force for assembly beside the ionic bonds.[49]

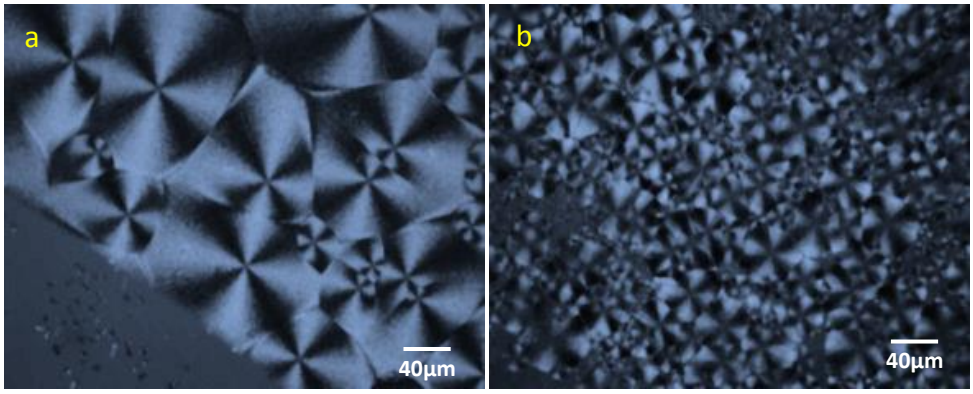


Fig. 1. Polarized optical microscopic image of columnar phase of (a) **8c** and (b) **8f** at 10× magnification.

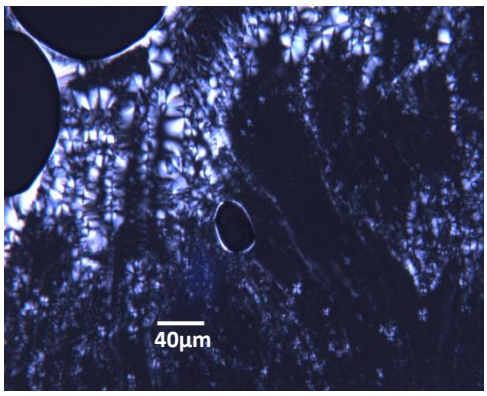


Fig. 2. Polarized optical microscopic image of smectic A texture for compound **8e** at 10× magnification.

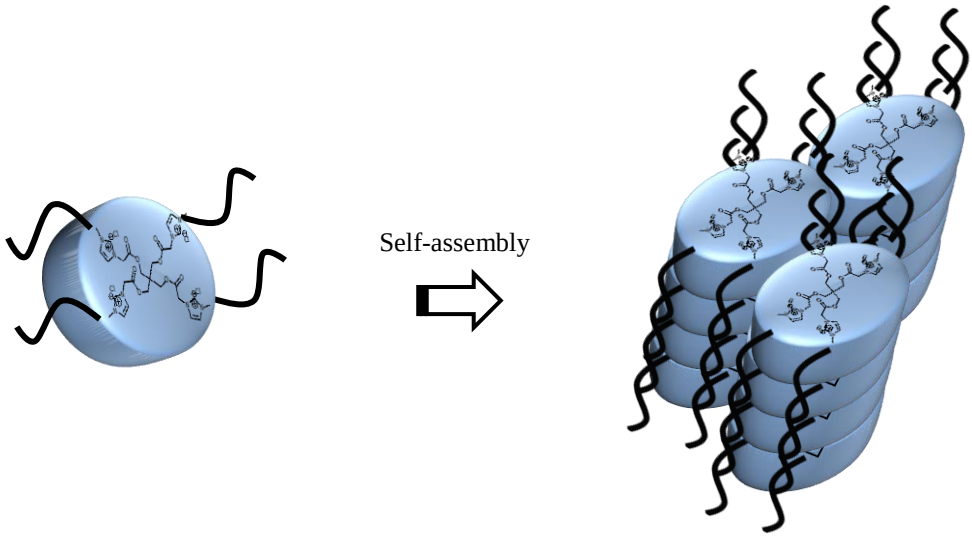


Fig. 3. Discotic shape molecular assembly in columnar.

In contact with water as polar solvent, all series of tetrakis-imidazolium ILs were very soluble, whereas at certain concentration gradients, they demonstrated a typical texture of lyotropic hexagonal phase, H_1.

With higher water content, compounds **8d** and **8e** showed an extra mesomorphism; clearly discontinuous cubic phase, I_1 due to slowly dissolving. An example for compound **8e** illustrated in Fig. 4.

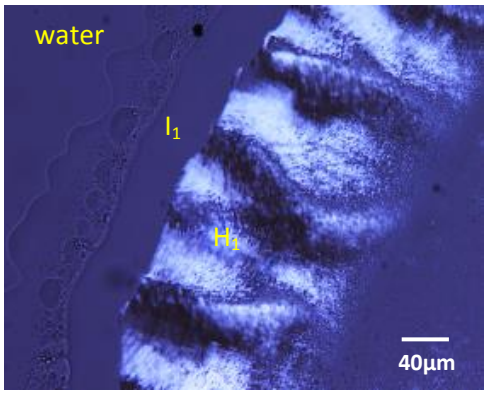


Fig. 4. Polarized optical microscopic image of **8e** contacted with water at 10× magnification.

Furthermore, for contact with non-polar solvent; 1-undecanol, the slowly dissolving of tetrakis-imidazolium ILs showed similar behaviour to polar solvent, producing an inverted hexagonal phase. Fig. 5 (a) and (b) illustrated assembly behaviour for compound **8d** after a few minutes' and 12 hours contact with 1-undecanol, respectively.

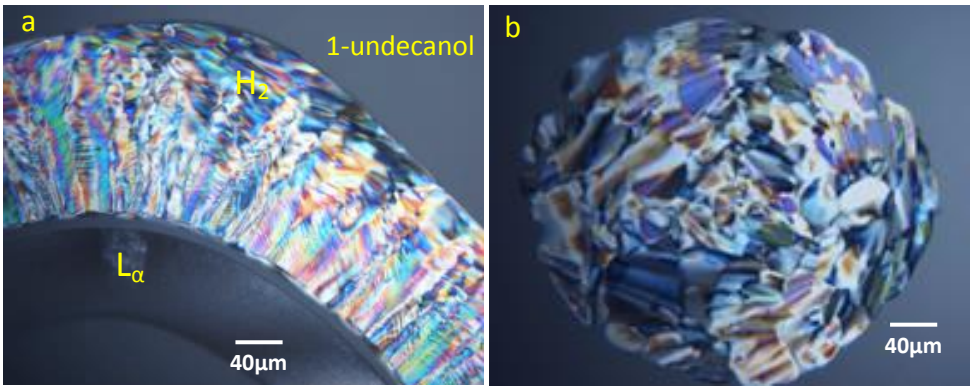


Fig. 5. Columnar phase of **8d** (a) after a few minutes' contacted with 1-undecanol, and (b) overnight at 10× magnification.

In the absence of a solvent, there was no birefringent exhibition in tetrakis-bezimidazolium series ILs where it appeared as glassy state and dark with no reflection. While in contact with water, compounds of the shorter chains length, such as **9c** were very soluble. Compound **9d** was soluble with hexagonal phase as shown in Fig. 6 (a). Longer chains such as **9e** and **9f** crystallized in water and the appearance of the crystals is shown in Fig. 6 (b) and (c), respectively.

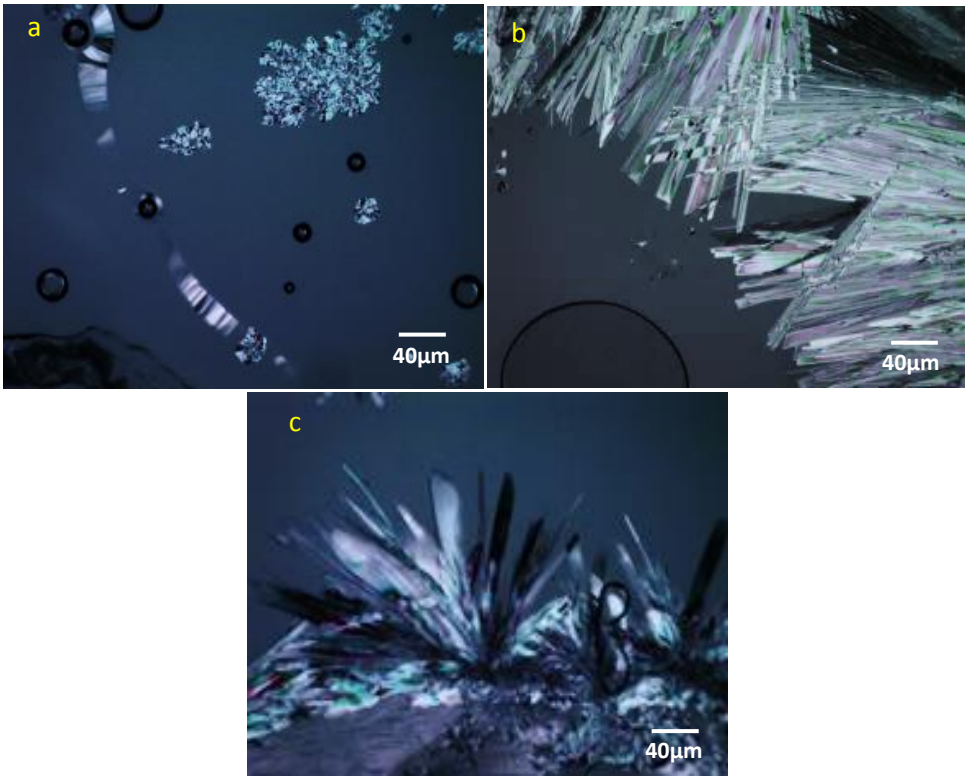


Fig. 6. Columnar phase at 10× magnification (a) **9d** showing hexagonal phase after a few minutes' contacted with water, (b) **9e** and (c) **9f** showing crystallization in water.

Lastly, all tetrakis-bezimidazolium ILs reacted similarly to the non-polar solvent which was an inverted hexagon as shown in Fig. 7 (a) and (b) for compounds **9c** and **9f**, respectively. Summarized phase behaviour results of the synthesized ILs are listed in Table 2.

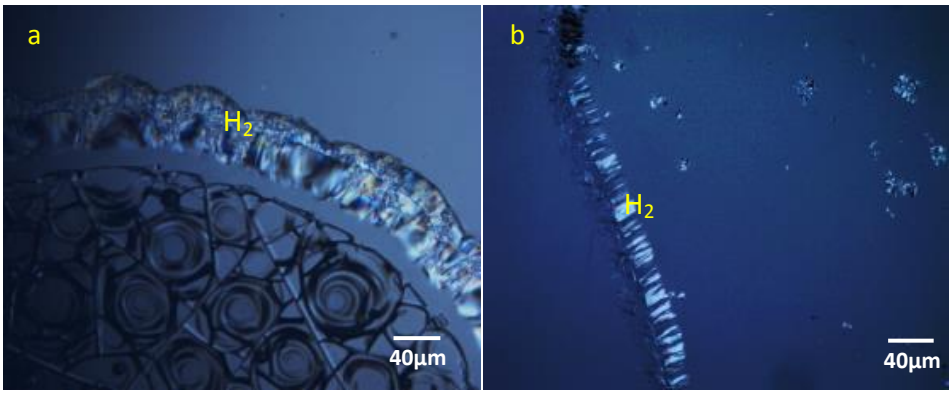


Fig. 7. Inverted hexagonal phase of (a) **9c** and (b) **9f** at 10× magnification.

Table 2: Phase behaviours of synthesized tetrakis-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]	-	-	-
8c	6	ND[a]	Columnar	L_1	L_2, H_2, V_2
8d	8	ND[a]	Columnar	L_1, I_1, H_1	L_2, H_2
8e	10	176	Columnar	L_1, I_1, H_1	L_2, H_2
8f	12	172	Columnar	L_1, H_1	L_2
9b	4	107	-	-	-
9c	6	159	Glassy state	L_1, H_1	H_2, V_2
9d	8	120	Glassy state	H_1	H_2
9e	10	94	Glassy state	Crystallize	H_2
9f	12	117	Glassy state	Crystallize	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

All IL surfactants exhibited Krafft points below 10 °C, where based on their Krafft temperature, the air-water interface was preferred at room temperature. The behaviour of surfactants was investigated by systematic surface tension measurements over a wide range of concentrations at 25 °C. Data regarding the micellar assembly for the surfactants are tabulated in Table 3.

Table 3: CMC values and surface tension properties of ILs/water systems

IL	Carbon atoms in side-chain	CMC (mM)	γ_{cmc} (mN/m)	T_K (°C)
8b	4	-	-	-
8c	6	39.17	29	<10
8d	8	6.28	31	<10
8e	10	1.03	29	<10
8f	12	0.14	34	<10
8g	Benzyl	-	-	-
9b	4	-	-	-
9c	6	33.07	34	<10
9d	8	5.83	29	<10
9e	10	0.63	31	<10
9f	12	0.07	32	<10
9g	Benzyl	-	-	-

The surface tension above the CMC values was found to be in the range of 29– 34 mNm^{-1}, a similar trend to mono-imidazolium ILs containing ester groups was indicated in literature.[50] Compounds **9e** and **9f** crystallized in a high concentration of 10 mM which was above their CMC values.

Comparing tetrakis-imidazolium and tetrakis-benzimidazolium IL surfactants revealed a decrease in CMC upon the introduction of benzimidazole, as seen in the values for **9c**, **9d**, **9e** and **9f**. This reduction of the CMC could be attributed to the presence of an aromatic ring that considerably increased the surfactant hydrophobicity, whereas the CMC at surface tension itself was not much affected.

The current CMC values of tetra-IL surfactants were considerably lower than the corresponding tris-IL surfactants values as reported in a previous work by the same authors.[47] Precisely, the introduction of one additional hydrocarbon alkyl-chain to the amphiphilic antipodes affected the CMC values, while the minimum surface tension (γ_{min}) had a less effect. These interface behaviour results were found to be in line with literature.[34,36]

Biodegradation results

The biodegradation results of synthesized ILs, **8b-g** and **9b-g**, are presented in Fig. 8 and Fig. 9, respectively. Generally, ILs bearing imidazolium cations exhibited higher degradation percentage compared to those with benzimidazolium, besides, the existence of long linear alkyl side chain improved the biodegradation. For example, compound **8f** with a dodecyl side chain had a degradation percentage of 56%, while **9f** revealed a reduction in IL degradation to 47% due to the cationic part changing to benzimidazolium with the same side chain. This lower degradation in benzimidazolium ILs was attributed to the existence of aromatic rings fusion in benzimidazolium that improved the molecular stability against microbial degradation.[51]

In fact, the presence of ester group in ILs enhanced the biodegradation by providing a hydrolytic site for enzymatic attack.[22,52-54] Therefore, tetra-ester groups of the current ILs enhanced the degradation to produce the corresponding primary alcohol that metabolized *via* fatty acid β-oxidation.[38,55] Compared to the 34% degradation of imidazolium ILs as indicated in literature with mono-ester groups,[38] tetrakis-imidazolium and benzimidazolium ILs in the current study demonstrated significant biodegradation enhancement.

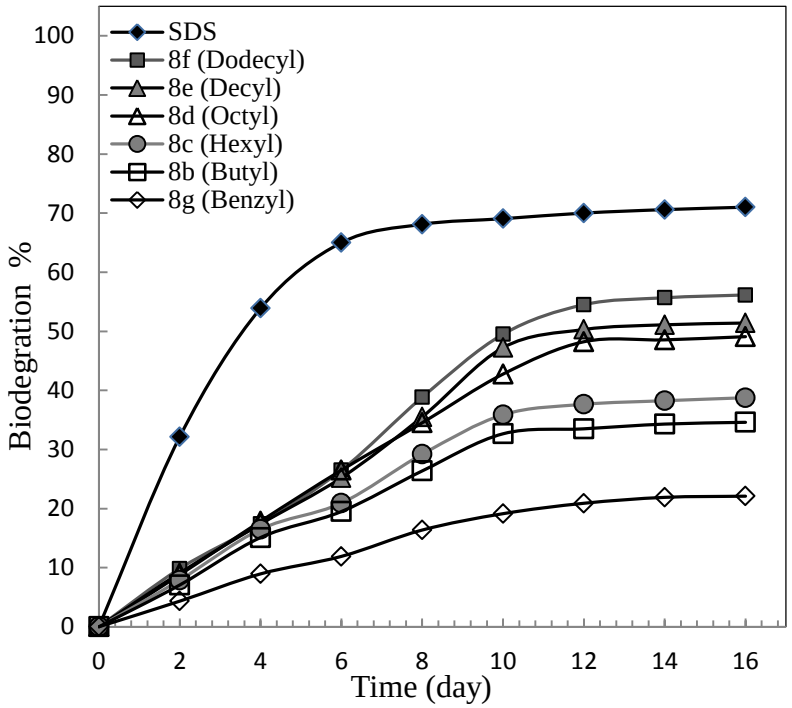


Fig 8. Biodegradation curves of tetrakis-imidazolium ILs series using closed-bottle test.

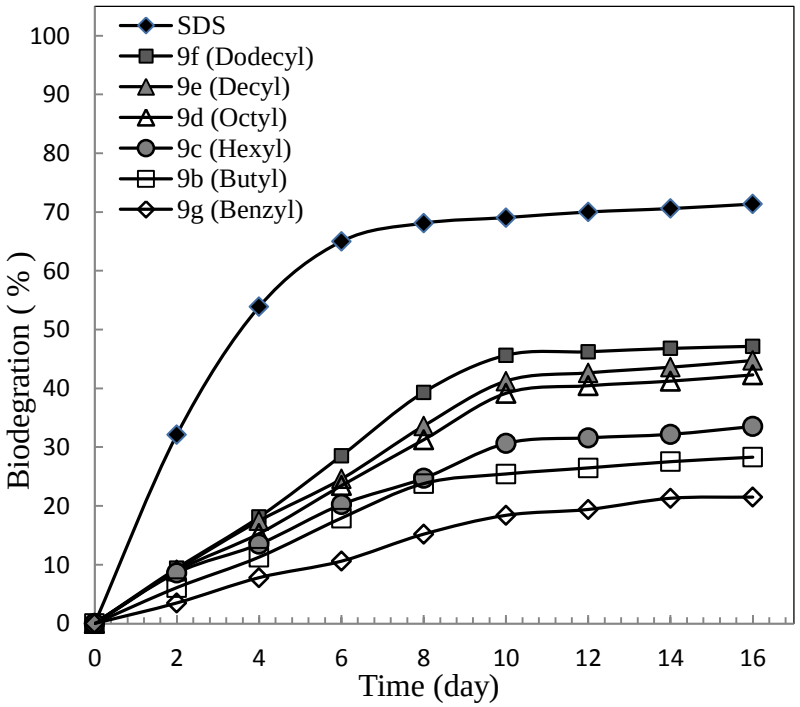


Fig 9. Biodegradation curves of tetrakis-benzimidazolium ILs series using closed-bottle test.

The influence of side chains on IL degradation was evaluated as shown in Table 4. Compound **8f** was observed to have a higher percentage of degradation, at 56%, attributed to the presence of a dodecyl side

chain.[53] In contrast, a lower percentage degradation, from 22 to 21.5%, was observed in ILs carrying aryl side chains in compounds **8g** and **9g**, respectively, as shown in Fig. 10 and Fig. 11. The results obtained from biodegradation evaluation studies are summarized in Table 4.

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

IL	Carbon atoms in side-chain	Biodegradation (%)	
		10 day	*16 day*
8b	4	33	35
8c	6	36	39
8d	8	44	49
8e	10	47	51.5
8f	12	49.5	53
8g	Benzyl	19	22
9b	4	25.5	28
9c	6	31	33.5
9d	8	39	42
9e	10	41	44
9f	12	45	47
9g	Benzyl	18	21.5

The longer alkyl side chains in the ILs provided a non-obstructed site for microbial digestion, and indicated a distinction in the degradation.[22] Moreover, a linear alkyl side chain of mono-cationic ILs with length ≥4 carbons atoms was documented[23,38-40,53,56] as an important factor in designing biodegradable compounds owing to their ability to provide potential sites for oxygenases attack.

Furthermore, two potential effects of the longer alkyl side chain could improve IL degradation[22] by either i) eliminating any structural hindrance between the cationic ring and potential binding site, thereby allowing the IL backbone to become more easily accessible to bacteria enzymatic digestion, or ii) the hydrophobicity of the ILs due to the longer alkyl side chain could influence its toxicity. Increasing the toxicity of the ILs could kill most of the microbes in the sludge, and allow capable metabolizing species to grow faster and proliferate.

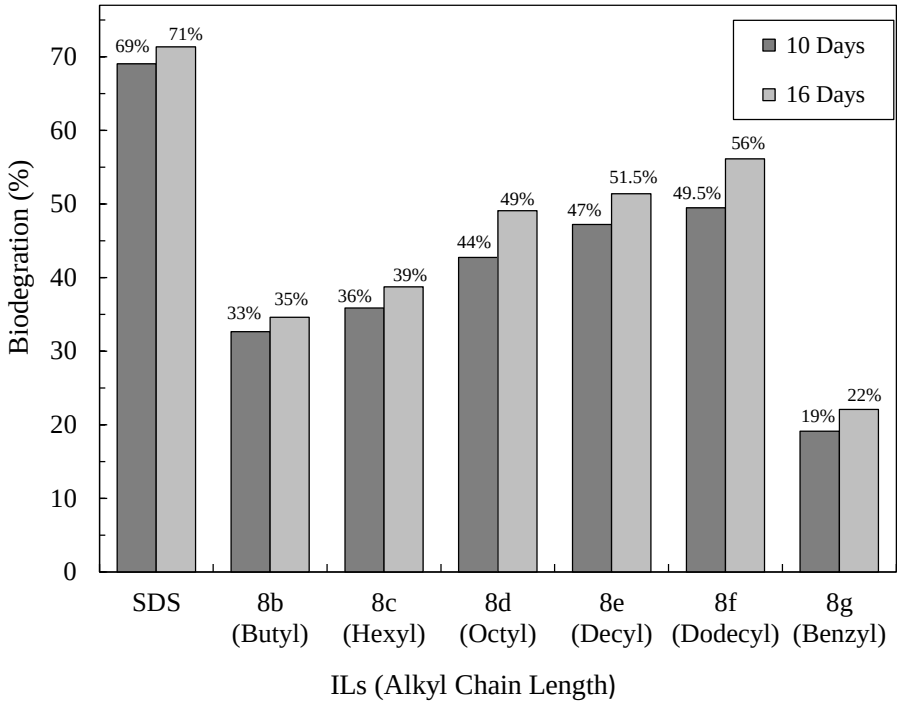


Fig 10. Biodegradation of tetrakis-imidazolium ILs series as a function of aliphatic or aromatic side chain on 10 and 16 days.

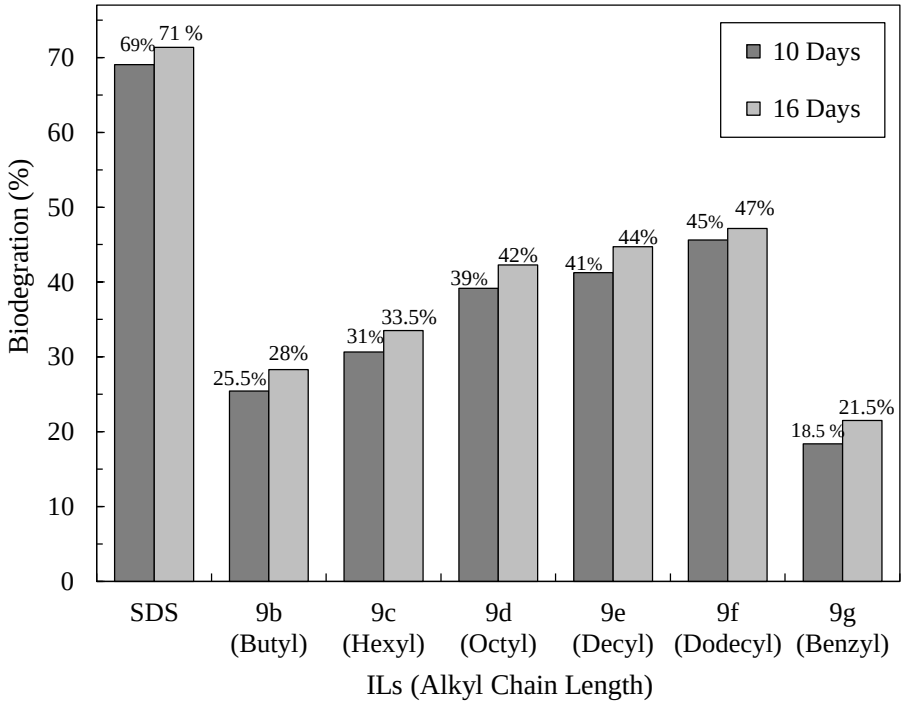


Fig 11. Biodegradation of tetrakis-benzimidazolium ILs series as a function of aliphatic or aromatic side chain on 10 and 16 days.

In the current study, each biodegradation test considered as completed after 16 days duration out of 28 days due to obtaining plateau for the last three measurements of the degradation curve,[45,51] where after this period, the results revealed negligible changes in consumption of biological oxygen demand (BOD) for all tested ILs, as shown in Fig. 8 and Fig. 9. Moreover, in comparison to tris-cationic ILs[47] and with reference to the standard SDS samples, the tetra-cationic ILs achieved complete degradation with minor differences in biodegradation values in the 10 to 16 days' readings, as illustrated Fig. 10 and Fig. 11. Finally, the tested tetrakis-imidazolium and tetrakis-benzimidazolium ILs exhibited a significant level of biodegradation. Where, the data indicated compounds; **8d**, **8e**, **8f** and **9f** were on the border of the 60% readily biodegradation pass level[22,37] at 49.5%, 51.5%, 56% and 47%, respectively after 16 days' evaluation.

Conclusions

Two series of tetrakis-imidazolium and benzimidazolium ILs with incorporated alkyl or phenyl side chains containing tetra-ester groups and chloride as anions, were synthesized successfully. Metathesis of these anions to NTf_2 at room temperature was tuned from viscous syrup, semi-solid or solid forms to clear liquids in excellent yield and purity. Both series of chloride anions were able to form a columnar/hexagonal phase. Unlike benzimidazolium, the imidazolium series readily existed as a columnar liquid crystal with the ability to be formed in polar or non-polar solvents at certain concentration. Tetrakis-imidazolium ILs displayed significant increase in phase behaviour properties and biodegradation compared to benzimidazolium ILs and effectively reduced the water surface tension to a range of 29– 34 mN m^{-1}. Comparing to tris-cationic ILs that reported in a previous study by current authors,[47] the biodegradation and assembly behaviour for synthesized tetrakis-imidazolium and benzimidazolium ILs were highly enhanced by increasing the ILs hydrophobicity. Precisely, hexyl to dodecyl in the hydrocarbon chains for both imidazolium and bezimidazolium ILs presented phase behaviours in contact with solvents whether polar or non-polar in addition to further textures for tetrakis-imidazolium ILs appeared in pure form.

In the synthesized tetra-cationic ILs, the presence of ester groups as an enzymatic hydrolysis sites with long linear alkyl chains or phenyl rings that improved the biodegradation of surfactants were successfully applied to ionic liquids. In addition, octyl, decyl, and dodecyl as side chains presented very close values to the pass level (60%) of the readily biodegradation Closed Bottle Test results. Nonetheless, owing to potential beneficial effects of biodegradable octylsulfate ($C_8H_{17}OSO_3$) as anion,[23,43] readily degradable of the current tetrakis-imidazolium and tetrakis-benzimidazolium ILs (60-70% degradation within the test period[22]) could be achieved in future study. As a matter of fact, since the fluorine compounds effectively reduce water surface tension,[57] a more detailed study of the current tetra-cationic incorporated with NTf_2 as counter-ions is in progress to explore more effective surfactant ILs.

Experimental

1-Methylimidazole and 1-butylimidazol were purchased from Aldrich and distilled before use to remove impurities detrimental to all ILs prepared. The syntheses of alkyl imidazole and benzimidazole; 1-Hexylimidazole, 1-octylimidazole, 1-decylimidazole, 1-dodecylimidazole, 1-benzylimidazol, 1-butylbenzimidazole, 1-hexylbenzimidazole, 1-octylbenzimidazole, 1-decylbenzimidazole, 1-dodecylbenzimidazole, and 1-benzylbenzimidazole were described and reported in a previous work.[47] All ILs were kept in a 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. Melting points were determined on an optical polarizing microscope with hot stage and were uncorrected. The IR spectra were obtained with a Perkin Elmer 400 Fourier Transform Infrared (FTIR) spectrometer. The ^{1}H and ^{13}C-NMR spectra were recorded on Jeol Lambda and ECA- DELTA as well as Bruker spectrometers at 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 of the 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 on a procedure described in literature.[58] Pentaerythritol (2,2-Bis(hydroxymethyl)-1,3-propanediol) **1** (10 g, 73.4 mmol) was dissolved and refluxed with a minimum amount of chloroacetyl chloride **2** for 3–5 hours or 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 a white solid. Re-crystallization from dry acetonitrile gave compound **3** as white flakes.

Tetrakis-((*N*-methyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8a)

A solution of 1-methylimidazole (1.41 g, 1.37 mL, 17.2 mmol) in acetonitrile anhydrous (5mL) was added drop-wise to a stirred solution of tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9g, 4.30 mmol) in acetonitrile anhydrous (15 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred vigorously for 3 h 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 give a white hygroscopic solid (m.p 52–54°C) in 98% yield (3.25 g). Molecular Formula: $C_{29}H_{40}Cl_4N_8O_8$; mol. wt.: 770.49; FTIR (cm^{-1}): 3068 $(C\text{-}H)_{Ar}$, 2977, 2930 $(C\text{-}H)_{Aliph}$, 1744 (C=O), 1603 (C=N), 1575, 1511 $(C=C)_{Ar}$, 1215, 1162 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 7.66 (s, 4H, $C\text{-}H_{Imidazole}$, minor), 7.62 (s, 4H, $C\text{-}H_{Imidazole}$, major), 7.15 (bt~s, 4H,$C\text{-}H_{Imidazole}$, minor), 7.11 (bt~s, 4H, $C\text{-}H_{Imidazole}$, $C\text{-}H_{Imidazole}$, major), 6.94 (bt~s, 4H, $C\text{-}H_{Imidazole}$, minor), 6.90 (bt~s, 4H, $C\text{-}H_{Imidazole}$, major), 3.77 (s, 16H, $O\text{-}CH_2$, $N\text{-}CH_2$, minor), 3.73 (s, 16H, $O\text{-}CH_2$, $N\text{-}CH_2$, major), 3.67 (s, 12H, $N\text{-}CH_3$, minor), 3.63 (s, 12H, $N\text{-}CH_3$, major); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 168.09 (C=O, minor), 166.67 (C=O, major), 137.87 ($CH_{Imidazole}$, major), 137.66 ($CH_{Imidazole}$, minor), 123.74 ($CH_{Imidazole}$), 123.28 ($CH_{Imidazole}$, major), 123.19 ($CH_{Imidazole}$, minor), 63.86 (CH_2-O, minor), 63.28 (CH_2-O, major), 49.71 (CH_2-N, minor), 49.51 (CH_2-N, major), 41.60 (-C-), 35.97 (CH_3-N, major), 35.89 (CH_3-N, minor); HRMS: m/z, $[M^{+4}–3H]-4Cl^{-}$ calcd. for $C_{29}H_{37}N_8O_8^{7+}$: 625.2734, found: 625.2767.

Tetrakis-((*N*-hexyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8c)

This compound was prepared analogously to **8a** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-hexylimidazole (**6c**) (2.62 g, 17.2 mmol) to give a viscous hygroscopic syrup in 98% yield (4.43 g). Molecular Formula: $C_{49}H_{80}Cl_4N_8O_8$; mol. wt.: 1051.02; FTIR (cm^{-1}): 3060 $(C\text{-}H)_{Ar}$, 2956, 2929, 2859 $(C\text{-}H)_{Aliph}$, 1751 (C=O), 1641 (C=N), 1564, 1463 $(C=C)_{Ar}$, 1195, 1165 (C-O);^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 9.68 (bt~s, 4H, $C\text{-}H_{Imidazole}$, major), 9.56 (bt~s, 4H, $C\text{-}H_{Imidazole}$, minor), 9.42 (bt~s, 4H, $C\text{-}H_{Imidazole}$, minor), 7.97 (t, J =1.95 Hz, 4H, $C\text{-}H_{Imidazole}$, major), 7.90

(t, *J* =1.95 Hz, 4H,C-$H_{Imidazole}$, minor), 7.88 (t, *J* =1.95 Hz, 4H, Hz, C-$H_{Imidazole}$, major), 7.82 (t, *J* =1.95 Hz, 4H, C-$H_{Imidazole}$, minor), 5.53 (s, 8H, O-CH_2, major), 5.47 (s, 8H, O-CH_2, minor), 5.40 (s, 8H, O-CH_2, minor), 4.25 (t, *J*= 7.32 Hz, 8H, α-CH_2), 4.19 (s, 8H, N-CH_2, major), 4.16 (s, 8H, N-CH_2, minor), 4.14 (bs, 8H, N-CH_2, minor), 1.82–1.75 (m, 8H, β-CH_2), 1.25 (bs, 24H, bulk-CH_2), 0.85 (t, 12H, *J* =6.83 Hz, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 168.13 (C=O, major), 166.72 (C=O, minor), 137.36 ($CH_{Imidazole}$, minor), 137.25 ($CH_{Imidazole}$, major), 123.95 ($CH_{Imidazole}$), 122.09 ($CH_{Imidazole}$, minor), 121.98 ($CH_{Imidazole}$, major), 64.87 (CH_2-O, major), 64.32 (CH_2-O, minor), 49.80 (CH_2-N), 49.01 (α-CH_2, minor), 48.94 (α-CH_2, major), 48.85 (α-CH_2, minor), 41.60 (-C-), 30.55 (ω-2), 29.38 (bulk-CH_2), 25.16 (β-CH_2, minor), 25.11 (β-CH_2, major), 21.94 (ω-1), 13.88 (ω); HRMS: m/z, $[M^{+4}–3H]-4Cl^-$ calcd. for $C_{49}H_{77}N_8O_8^{7+}$: 905.5864, found: 905.5960.

Tetrakis-((*N*-dodecyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8f)

This compound was prepared analogously to **8a** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-dodecylimidazole (**6f**) (4.06 g, 17.2 mmol) to give a viscous hygroscopic syrup in 99% yield (5.90 g). Molecular Formula: $C_{73}H_{128}Cl_4N_8O_8$; mol. wt.: 1387.66; FTIR (cm^{-1}): 3128, 3062 (C-H)$_{Ar}$, 2957, 2924, 2855 (C-H)$_{Aliph}$, 1752 (C=O), 1625 (C=N), 1564, 1462 (C=C)$_{Ar}$, 1202, 1164 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.29 (bt~s, 4H, C-$H_{Imidazole}$, major), 9.24 (bt~s, 4H, C-$H_{Imidazole}$, minor), 9.19 (bt~s, 4H, C-$H_{Imidazole}$, minor), 7.76 (t, *J* =1.95 Hz, 4H, C-$H_{Imidazole}$, major), 7.74 (t, 4H, *J* =1.95 Hz, C-$H_{Imidazole}$, major), 7.71 (t, 4H, *J* =1.95 Hz, C-$H_{Imidazole}$, minor), 7.66 (t, 4H, *J* =1.95 Hz, C-$H_{Imidazole}$, minor), 5.38 (s, 8H, O-CH_2, major), 5.36 (s, 8H, O-CH_2, minor), 5.34 (s, 8H, O-CH_2, minor), 4.35 (s, 8H, N-CH_2), 4.29 (t, *J*= 7.32 Hz, 8H, α-CH_2), 1.95–1.89 (m, 8H, β-CH_2), 1.29 (bs, 72H, bulk-CH_2), 0.89 (t, 12H, *J* =7.07 Hz, ω-CH_3); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 168.92 (C=O, minor), 167.79 (C=O, major), 138.87 ($CH_{Imidazole}$), 125.44 ($CH_{Imidazole}$), 123.58 ($CH_{Imidazole}$, major), 123.43 ($CH_{Imidazole}$, minor), 65.21 (CH_2-O, minor), 64.67 (CH_2-O, major), 51.27 (CH_2-N), 51.09 (α-CH_2, major), 50.93 (α-CH_2, minor), 43.70 (-C-), 33.19 (ω-2), 31.28, 30.88(2), 30.81, 30.70, 30.59, 30.26 (bulk-CH_2), 27.42 (β-CH_2, major), 27.32 (β-CH_2, minor), 23.86 (ω-1), 14.61 (ω); HRMS: m/z, $[M^{+4}–3H]-4Cl^-$ calcd. for $C_{73}H_{125}N_8O_8^{7+}$: 1241.9620, found: 1241.9693.

Tetrakis-((*N*-benzyl-imidazoliumyl-acetayloxy)methyl)methane chloride (8g)

This compound was prepared analogously to **8a** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-benzylimidazole (**6g**) (2.72 g, 17.2 mmol) to give a pale-yellow hygroscopic semi-solid in 94% yield (4.34 g). Molecular Formula: $C_{53}H_{56}Cl_4N_8O_8$; mol. wt.: 1074.87; FTIR (cm^{-1}): 3132, 3032 (C-H)$_{Ar}$, 2930 (C-H)$_{Aliph}$, 1732 (C=O), 1612 (C=N), 1562, 1488 (C=C)$_{Ar}$, 1185, 1132 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.36 (s, 4H, C-$H_{Imidazole}$, major), 9.30 (s, 4H, C-$H_{Imidazole}$, minor), 9.25 (s, 4H, C-$H_{Imidazole}$, minor), 7.75 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, major), 7.73 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, minor), 7.72 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, minor), 7.69 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, minor), 7.68 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, minor), 7.68 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, minor), 7.67 (t, *J* =1.81 Hz, 4H, C-$H_{Imidazole}$, major), 7.46–7.20 (m, 20H, C-H_{Ar}), 5.48 (bs, 8H, Ar-CH_2-N), 5.37 (s, 8H, O-CH_2, major), 5.34 (s, 8H, O-CH_2, minor), 5.32 (s, 8H, O-CH_2, minor), 4.30 (d~t, 8H, N-CH_2, major), 4.27 (d~t, 8H, N-CH_2, minor); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 168.95 (C=O, minor), 167.74 (C=O, major), 166.82 (C=O, minor), 138.96 ($CH_{Imidazole}$), 135.26 (-C_{Ar}-CH_2-), 130.60 (2 × CH_A), 130.54 (CH_{Ar}) 129.90 (2 × CH_{Ar}), 125.70 ($CH_{Imidazole}$), 123.61 ($CH_{Imidazole}$, minor) 123.57 ($CH_{Imidazole}$,

major), 64.51 (CH_2-O, major), 64. 27 (CH_2-O, minor), 64.04 (CH_2-O, minor), 54.40 (CH_2-N), 51.19 (Ar-CH_2-), 43.80 (-C-); HRMS: m/z, $[M^{+4}–3H]–4Cl^–$ calcd. for $C_{53}H_{53}N_8O_8^{7+}$: 929.3986, found: 929.4052.

Tetrakis-((*N*-butyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride (9b)

To a stirred solution of tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3)** (1.9g, 4.30 mmol) in acetonitrile anhydrous (15 mL), the solution of 1-butyl-benzimidazole (**7b**) (3.00 g, 17.2 mmol) in acetonitrile anhydrous (5 mL) was added drop-wise at room temperature and under a nitrogen atmosphere. The reaction mixture was refluxed at 45–50 °C for 2–3 days, then at room temperature for 5 h. The acetonitrile top layer was decanted and the IL washed with diethyl ether (3 × 10 mL), then the residual solvent was evaporated under reduced pressure. The product was dried at (40 °C, 0.01 mmHg) for 72 h to give a white hygroscopic solid (m.p 48–50 °C) in 99% yield (4.85 g). Molecular Formula: $C_{57}H_{72}Cl_4N_8O_8$; mol. wt.: 1139.04; FTIR (cm^{-1}): 3133 (C-H)$_{Ar}$, 2950, 2935, 2859 (C-H)$_{Aliph}$, 1752 (C=O), 1620 (C=N), 1562, 1475, 1462 (C=C)$_{Ar}$, 1202, 1188 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.48 (s, 4H, C-H$_{BImidazole}$, major), 10.39 (s, 4H, C-H$_{BImidazole}$, minor), 10.27 (s, 4H, C-H$_{BImidazole}$ minor), 8.16 (dd, *J*=8.29 Hz, 8H, CH_{Ar}), 7.63 (dt, *J*=7.81 Hz, 8H, CH_{Ar}), 5.91 (s, 8H, O-CH_2, major), 5.86 (s, 8H, O-CH_2, minor), 5.80 (s, 8H, O-CH_2, minor), 4.58 (t, *J*=7.32 Hz, 8H, α-CH_2, major), 4.52 (t, *J*=7.32 Hz, 8H, α-CH_2, minor), 4.24 (s, 8H, N-CH_2, minor), 4.16 (s, 8H, N-CH_2, major), 4.10 (s, 8H, N-CH_2, minor), 1.91–1.83 (m, 8H, β-CH_2), 1.36–1.27 (m, 8H, (ω-1)), 0.88 (t, 12H, *J* =7.32 Hz, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 167.05 (C=O, minor), 166.41 (C=O, major), 166.35 (C=O, minor), 143.39 ($CH_{BImidazole}$), 131.51 (C_{Ar}), 130.61 (C_{Ar}), 126.69 (CH_{Ar}), 126.66 (CH_{Ar}), 114.19 (CH_{Ar}), 113.74 (CH_{Ar}), 62.97 (CH_2-O), 47.64 (CH_2-N), 46.58 (α-CH_2, major), 46.40 ((α-CH_2), minor), 41.83 (-C-), 30.69 ((ω-2), minor), 30.48 ((ω-2), major), 19.00 (ω-1), 13.33 (ω); HRMS: m/z, $[M^{+4}–3H]–4Cl^–$ calcd. for $C_{57}H_{69}N_8O_8^{7+}$: 993.5238, found: 993.5272.

Tetrakis-((*N*-hexyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride (9c)

This compound was prepared analogously to **9b** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-hexyl-benzimidazole (**7c**) (3.48 g, 17.2 mmol) to give a white hygroscopic solid (m.p 54–56°C) in 98% yield (5.27 g). Molecular Formula: $C_{65}H_{88}Cl_4N_8O_8$; mol. wt.: 1251.26; FTIR (cm^{-1}): 3137 (C-H)$_{Ar}$, 2955, 2930, 2859 (C-H)$_{Aliph}$, 1752 (C=O), 1619(C=N), 1563, 1486, 1464 (C=C)$_{Ar}$, 1204, 1188 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.46 (s, 4H, C-H$_{BImidazole}$, major), 10.34 (s, 4H, C-H$_{BImidazole}$, minor), 8.15 (dd, *J*=8.29 Hz, 8H, CH_{Ar}), 7.64 (dt, *J*=7.81 Hz, 8H, CH_{Ar}), 5.90 (s, 8H, O-CH_2, major), 5.84 (s, 8H, O-CH_2, minor), 4.58 (t, *J*=7.32 Hz, 8H, α-CH_2), 4.22 (s, 8H, N-CH_2, minor), 4.19 (s, 8H, N-CH_2, major), 4.13 (s, 8H, N-CH_2, minor), 1.93–1.86 (m, 8H, β-CH_2), 1.26 (bs, 24H, bulk-CH_2), 0.83 (t, *J*=6.83 Hz, 12H, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 167.11 (C=O, minor), 166.48 (C=O, major), 143.99 ($CH_{BImidazole}$, minor),143.38 ($CH_{BImidazole}$, major), 131.52 (C_{Ar}), 130.63 (C_{Ar}), 126.71 (2 × CH_{Ar}), 114.22 (CH_{Ar}), 113.78 (CH_{Ar}), 63.00 (CH_2-O), 47.66 (CH_2-N), 46.82 (α-CH_2), 41.86 (-C-), 30.73 ((ω-2), minor), 30.61 ((ω-2), major), 28.53 (bulk-CH_2), 25.38 (β-CH_2), 21.93 (ω-1), 13.86 (ω); HRMS: m/z, $[M^{+4}–3H]–4Cl^–$ calcd. for $C_{65}H_{85}N_8O_8^{7+}$: 1105.6490, found: 1105.6538.

Tetrakis-((*N*-octyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride (9d)

This compound was prepared analogously to **9b** using tetrakis-((2-chloro-acetayloxy)methyl)methane (compound **3**) (1.9 g, 4.30 mmol) and 1-octyl-benzimidazole (**7d**) (3.96 g, 17.2 mmol) to give a viscous

hygroscopic syrup in 99% yield (5.80g). Molecular Formula: $C_{73}H_{104}Cl_4N_8O_8$; mol. wt.: 1363.47; FTIR (cm^{-1}): 3135 $(C\text{-}H)_{Ar}$, 2924, 2925, 2854 $(C\text{-}H)_{Aliph}$, 1751 (C=O), 1614 (C=N), 1562, 1486 1464 $(C{=}C)_{Ar}$, 1199 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.49 (s, 4H, $C\text{-}H_{BImidazole}$, major), 10.37 (s, 4H, $C\text{-}H_{BImidazole}$, minor), 8.16 (dd, *J*=8.05 Hz, 8H, CH_{Ar}), 7.63 (dt, *J*=7.81 Hz, 8H, CH_{Ar}), 5.91 (s, 8H, $O\text{-}CH_2$, major), 5.85 (s, 8H, $O\text{-}CH_2$, minor), 4.57 (t, *J*=7.32 Hz, 8H, α-CH_2), 4.23 (s, 8H, $N\text{-}CH_2$, minor), 4.17 (s, 8H, $N\text{-}CH_2$, major), 4.12 (s, 8H, $N\text{-}CH_2$, minor), 1.92–1.85 (m, 8H, β-CH_2), 1.21 (bs, 40H, bulk-CH_2), 0.83 (t, 12H, *J*=6.34 Hz, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 167.84 (C=O, major), 166.51 (C=O, minor), 143.25 ($CH_{BImidazole}$), 131.57 (C_{Ar}), 130.63 (C_{Ar}), 126.79 (CH_{Ar}), 126.64 (CH_{Ar}, minor), 126.57 (CH_{Ar}, major), 114.04 (CH_{Ar}, minor), 113.88 (CH_{Ar}, major), 113.73 (CH_{Ar}), 65.07 (CH_2-O, major), 64.33 (CH_2-O, minor), 47.56 (CH_2-N), 46.77 (α-CH_2), 41.49 (-C-), 31.10 (ω-2), 28.53, 28.44, 28.33 (bulk-CH_2), 25.63 (β-CH_2), 22.00 (ω-1), 13.90 (ω); HRMS: m/z, $[M^{+4}–3H]–4Cl^-$ calcd. for $C_{73}H_{101}N_8O_8^{7+}$: 1217.7742, found: 1217.7662.

Tetrakis-((*N*-methyl-imidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)amide (10a)

A flask was charged with tetrakis-((*N*-methyl-imidazoliumyl-acetayloxy)methyl)methane chloride **(8a)** (0.77 g, 1.0 mmol) and de-ionized water (10 mL). Lithium bis-(trifluoromethanesulphonyl)imide $LiNTf_2$ (1.29 g, 4.5 mmol) in de-ionized 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 give a clear viscous hygroscopic liquid at room temperature in 91% yield (1.60 g). Molecular Formula: $C_{37}H_{40}F_{24}N_{12}O_{24}S_8$; mol. wt.: 1749.26; FTIR (cm^{-1}): 3082 $(C\text{-}H)_{Ar}$, 2976, 2922, 2856 $(C\text{-}H)_{Aliph}$, 1754 (C=O), 1652 (C=N), 1548, 1460 $(C{=}C)_{Ar}$, 1358, 1222 (C-F), 1365, 1157 (O=S=O), 1220, 1182 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 8.90 (s, 4H, $C\text{-}H_{Imidazole}$, minor), 8.88 (s, 4H, $C\text{-}H_{Imidazole}$, minor), 8.86 (s, 4H, $C\text{-}H_{Imidazole}$, minor), 8.84 (s, 4H, $C\text{-}H_{Imidazole}$, major), 7.61 (t, 8H, *J*=1.81 Hz, $C\text{-}H_{Imidazole}$, major), 7.58 (t, 8H, *J*=1.81 Hz, Hz, $C\text{-}H_{Imidazole}$, minor), 7.56 (t, 8H, *J*=1.81 Hz, $C\text{-}H_{Imidazole}$, minor), 5.19 (s, 8H, $O\text{-}CH_2$, major), 5.18 (s, 8H, $O\text{-}CH_2$, minor), 5.17 (s, 8H, $O\text{-}CH_2$, minor), 4.33 (s, 8H, $N\text{-}CH_2$, major), 4.28 (s, 8H, $N\text{-}CH_2$, minor), 4.25 (s, 8H, $N\text{-}CH_2$, minor), 3.96 (s, 12H, $N\text{-}CH_3$); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.72 (C=O, minor), 167.58 (C=O, major), 139.30 ($CH_{Imidazole}$), 126.12, 122.90, 119.69, 116.47 (q, *J*=320 Hz, CF_3), 125.18 ($CH_{Imidazole}$), 124.98 ($CH_{Imidazole}$, major), 124.94 ($CH_{Imidazole}$, minor), 65.07 (CH_2-O, minor), 64.29 (CH_2-O, major), 50.85 (CH_2-N), 44.27 (-C-), 36.89 (CH_3-N). ^{19}F (336, MHz) δ ppm: –80.06; HRMS: m/z, $[M^{+4}]–4NTF_2^-$ calcd. for $C_{29}H_{37}N_8O_8^{7+}$: 625.2734, found: 625.2771; m/z, $[NTF_2]^-$ calcd. for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9177.

Tetrakis-((*N*-octyl-imidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)amide (10d)

This compound was prepared analogously to **10a** using tetrakis-((*N*-octyl-imidazoliumyl-acetayloxy) methyl)methane chloride **8d** (1.16 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide $LiNTf_2$ (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 95% yield (2.03 g). Molecular Formula: $C_{65}H_{96}F_{24}N_{12}O_{24}S_8$; mol. wt.: 2142.00; FTIR (cm^{-1}): 3065 $(C\text{-}H)_{Ar}$, 2955, 2932, 2857 $(C\text{-}H)_{Aliph}$, 1751 (C=O), 1657 (C=N), 1560, 1467 $(C{=}C)_{Ar}$, 1353, 1220 (C-F), 1360, 1148 (O=S=O), 1199, 1177 (C-O); ^{1}H-NMR (400 MHz, CD_3OD) δ ppm: 9.06 (bt~s, 4H, $C\text{-}H_{Imidazole}$, minor),

9.02 (bt~s, 4H, C-$H_{Imidazole}$, minor), 8.99 (bt~s, 4H, C-$H_{Imidazole}$, major), 7.78 (t, *J*=1.81 Hz, 4H, C-$H_{Imidazole}$, major), 7.71 (t, 4H, *J*=1.81 Hz, C-$H_{Imidazole}$, minor), 7.66 (t, *J*=1.81 Hz, 4H, C-$H_{Imidazole}$, major), 7.62 (t, 4H, *J*=1.81 Hz, C-$H_{Imidazole}$, minor), 5.39 (s, 8H, O-CH_2, major), 5.28 (s, 8H, O-CH_2, minor), 4.30 (t, *J*= 7.25 Hz, 8H, α-CH_2), 4.25 (s, 8H, N-CH_2), 1.93–1.86 (m, 8H, β-CH_2), 1.30 (bs, 40H, bulk-CH_2), 0.90 (t, *J* =6.68 Hz, 12H, ω-CH_3); ^{13}C-NMR (100 MHz, CD_3OD) δ ppm: 167.83 (C=O, minor), 167.71 (C=O, major), 138.67 ($CH_{Imidazole}$), 125.37, 122.14, 118.91, 115.69 (q, *J*=321 Hz, CF_3), 125.42 ($CH_{Imidazole}$), 123.64 ($CH_{Imidazole}$), 66.17 (CH_2-O, minor), 65.67 (CH_2-O, major), 52.35 (CH_2-N), 51.08 (α-CH_2), 42.52 (-C-), 33.09 (ω-2), 31.20, 30.42, 30.12 (bulk-CH_2), 27.33 (β), 23.82 (ω-1), 14.58 (ω). ^{19}F (336, MHz) δ ppm: –80.03; HRMS: m/z, $[M^{+4}–3H]–4NTF_2^-$ calcd. for $C_{57}H_{93}N_8O_8^{7+}$ 1017.7116 found: 1017.7171; m/z, $[NTF_2]^-$ calcd. for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9196.

Tetrakis-((N-butyl-benzimidazoliumyl-acetayloxy)methyl)methane bis(trifluoromethylsulfonyl)amide (11b)

This compound was prepared analogously to **10a** using tetrakis-((*N*-butyl-benzimidazoliumyl-acetayloxy)methyl)methane chloride **9b** (1.14 g, 1.0 mmole) and Lithium bis-(trifluoromethanesulphonyl)-imide $LiNTf_2$ (1.29 g, 4.5 mmol) to give a clear viscous hygroscopic liquid at room temperature in 94% yield (2.00 g). Molecular Formula: $C_{65}H_{72}F_{24}N_{12}O_{24}S_8$; mol. wt.: 2117.81; FTIR (cm^{-1}): 3135 (C-H)$_{Ar}$, 2953, 2928, 2857 (C-H)$_{Aliph}$, 1750 (C=O), 1625 (C=N), 1566, 1470 (C=C)$_{Ar}$, 1361, 1222 (C-F), 1361, 1162 (O=S=O), 1202 (C-O); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 10.53 (s, 4H, C-$H_{BImidazole}$, major), 10.46 (s, 4H, C-$H_{BImidazole}$, minor), 9.37 (s, 4H, C-$H_{BImidazole}$, minor), 8.12–8.03 (m, 8H, C-$H_{BImidazole}$), 7.58–7.41 (m, 8H, C-H_{Ar}), 5.95 (s, 8H, O-CH_2, major), 5.88 (s, 8H, O-CH_2, minor), 4.56 (t, *J*=7.32 Hz, 6H, α-CH_2, major), 4.51 (t, *J*=7.32 Hz, 8H, α-CH_2, minor), 4.23 (s, 8H, N-CH_2), 1.92–1.87 (m, 8H, β-CH_2), 1.33–1.26 (m, 8H, (ω-1)-CH_2), 0.88 (t, *J*=7.32 Hz, 12H, ω-CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6) δ ppm: 167.22 (C=O, minor), 167.60 (C=O, major), 143.21 ($CH_{BImidazole}$), 132.30 (C_{Ar}), 131.60 (C_{Ar}), 126.87 (CH_{Ar}), 126.62 (CH_{Ar}), 124.24, 121.03, 117.82, 114.61 (q, *J*=321 Hz, CF_3), 114.73 (CH_{Ar}), 113.85 (CH_{Ar}), 64.09 (CH_2-O, minor), 63.82 (CH_2-O, major), 46.68 (CH_2-N), 46.42 (α-CH_2), 40.72 (-C-), 31.23 (ω-2), 20.06 (ω-1), 13.45 (ω). ^{19}F (336, MHz) δ ppm: –80.00; HRMS: m/z, $[M^{+4}–3H]–4NTF_2^-$ calcd. for $C_{57}H_{69}N_8O_8^{7+}$: 993.5238, found: 993.5241; m/z, $[NTF_2]^-$ calcd. for $C_2F_6NO_4S_2^-$: 279.9173, found: 279.9177.

Liquid crystal behaviour

The liquid crystalline properties of compounds **8b-f** and **9b-f** were investigated thermotropically and lyotropically by an optical polarising microscopy. A contact penetration technique[59] was applied in lyotropic investigation with two different types of solvent, one of which is polar (water) and the other non-polar (1-undecanol). It was carried out at room temperature (around 25 ºC). The images were recorded at 10× magnification.

Air-water interface tension

The critical micelle concentration was determined based on surface tension measurement through applying DuNouy ring method. The surface tensions were measured using a KSV Sigma 702 tensiometer at 25 ± 0.5ºC in five replications for each measurement with a standard deviation of less than 0.1 mN m^{-1}. From surface tension plot against logarithmic concentration, the critical micelle concentration (CMC) was

obtained from the intersection of two regression lines, where one of them is concentration dependent. Solutions were prepared using deionised water with surface tension of 71.96 ± 0.09 mN m^{-1}.

Krafft point (T_K)

The Krafft temperature, (T_k), was determined by applying slow heating of 1 % (w/v) aqueous solution of ILs surfactant in a water bath. The solution samples were heated on an IKA hot plate stirrer equipped with temperature controller IKA ETS-D4 at 5 ºC. min^{-1} over the range of 10 ºC to 50 ºC. The temperature of the clear solution formed was observed while using optical monitoring for transparency changes.[60]

Closed Bottle Test

'Closed-Bottle Test' (OECD 301D)[45] was used to evaluate the biodegradability of tetrakis-imidazolium and benzimidazolium ILs (i.e. **8b-g** and **9b-g**). The test method was based on biochemical oxygen demand (BOD) due to IL microbial degradation.[51] 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. CyberScan dissolve oxygen meter $DO300$ (Eutech Instruments; The Netherlands) was used for DO measurements.

Capped Scotch bottles containing 100 ml solution of 100 mg/L concentration IL or reference sample in distilled water, were used to prepare test samples that inoculated with 1 mL of microbial effluent collected from a wastewater treatment plant. Three groups of samples were prepared as the following: inoculum and IL samples in Group 1, Group 2 contained only the inoculum (test blank), while the inoculum and SDS reference sample were in Group 3. The bottles of solutions were incubated in the dark at 25 ±1°C for 28 days under continuous shaking (200 rpm). The DO values were recorded after every 48 hours where each group sample was replicated 3 times. Since the majority of biodegradation changes were only noticed within the first 16 days period of time, 10 and 16 day results were considered.

Equation 1 was considered to calculate the BOD values based on observed DO [61] as follows:

$$BOD = \frac{DO_o - DO_t}{\varphi} \qquad (1)$$

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 the theoretical DO volume that obtained from the reference sample.

Further, the percentage biodegradability was calculated according to the expression in the following equation:[51]

$$\%\, Biodegradation = \frac{BOD}{ThOD\,(\frac{mg\ O_2}{mg\ \ sample\ weight})} \times 100 \qquad (2)$$

where $ThOD$ represents the theoretical oxygen demand which is defined as the amount of oxygen consumed by the microorganisms in the sample corrected for the uptake of O_2 by the blank inoculums[51].

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