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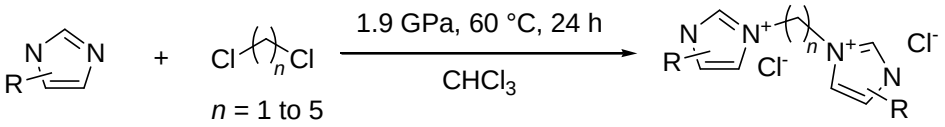

a. 1-methyl-, **b**. 1-ethyl-, **c**. 1-butyl-, **d**. 1,2-dimethyl-, **e**. 1,2,4,5-tetramethyl- and **f**. 1-methyl-2-phenylimidazole

27 - 100 % yield, 25 reactions

Tetrahedron
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Ultra-high pressure direct syntheses of bis(imidazolium-3-yl)alkane dichlorides

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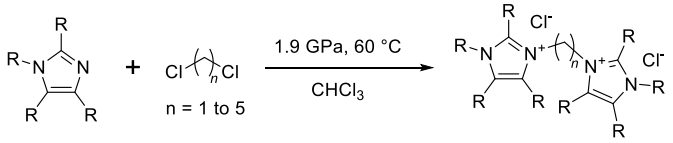
ABSTRACT

The ultra-high pressure Menshutkin reaction of *N*-substituted imidazoles and α,ω-dichloroalkanes provides access to a wide variety of bis(imidazoliumyl)alkane dichlorides in an efficient, one-pot process. Although the substitution reactions of dichloromethane at ambient pressure can be exceedingly slow, at 1.9 GPa, syntheses are usually quantitative in under 24 h. Reactions involving congested imidazole starting materials, that otherwise terminate after formation of the mono-imidazolium salt, are driven to the bis-imidazolium salt at 1.9 GPa. The rates of reaction increase with α,ω-dichloroalkane chain length, decrease with increasing bulk and imidazole *N*-substituent length, and the reactions of the more hindered imidazoles are more sensitive to the pressure-rate enhancement.

1. Introduction

As part of an on-going investigation into bis-imidazolium salts atmospherically friendly solvents and particularly ionic liquids,[1,2,3,4] we herein disclose our findings on the utility of ultra-high pressure (UHP) at 1.9 GPa for the direct synthesis of bis(imidazolium-3-yl)alkane dichlorides *via* consecutive Menshutkin reactions as illustrated in Scheme 1.



Scheme 1. The one-pot consecutive Menshutkin reaction

UHP conditions enable control over reactions in a manner dependent upon the volume changes associated with different pathways. In accord with Le Chatelier's principle, promoted reactions are those proceeding to species whose formation is accompanied by a decrease in total system volume, be that a transition state for kinetically controlled processes or a product for thermodynamically controlled processes (Fig. 1).[5,6]

The sensitivity of the kinetic response to pressure is quantified by the so-called volume of activation[7] ($\Delta V^{\ddagger}$), as defined in (1), where $\Delta V^{\ddagger}$ represents the difference in volume between starting materials and the transition state.

$$\left(\frac{\delta \ln k}{\delta P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT} \qquad (1)$$

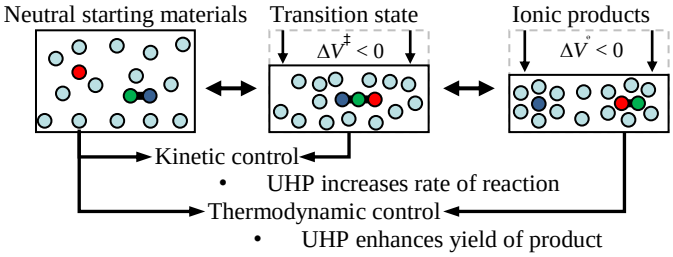


Figure 1. Depiction of volume contractions that lead to the influence of pressure on reactions in liquid media

Ionogenic reactions are particularly strongly promoted by UHP as a result of electostriction[8] reducing the volume of the solvated species due to the attractive effect that developing charges exert on the solvent.[9] The Menshutkin synthesis of imidazolium salts from imidazole and dichloroalkanes is intrinsically ionogenic, proceeding through a polar transition state to an ammonium salt product and thus lends itself well to acceleration by the application of UHP.[10,11,12]

Although, the reactivity of dichloromethane towards nucleophilic substitution is generally considered to be low the assumption of complete inactivity, in particular towards S_N2 reactions, is unwarranted. It has been previously reported that tertiary amines[13,14,15] and pyridine[16] react appreciably, albeit slowly, with dichloromethane at ambient temperature and pressure. These reactions have been discovered serendipitously,[17] for example, in basified HPLC solvents.[18]

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The preparation of methylene-bridged imidazolium salts from dichloromethane is difficult to achieve with good conversions, although it is sometimes possible to carry out reactions under forcing conditions, such as using a sealed bomb at elevated temperatures. It is more common for dichloromethane to be replaced with the appreciably more reactive dibromomethane or diiodomethane, thus necessitating a subsequent anion metathesis to obtain the chloride salt. Unfortunately, these procedures too can fail for more sterically hindered nucleophiles, such as 1-methyl-2-phenylimidazole.

Such compounds have received recent attention for their utility as high-performance anti-wear additives[19] for use under extreme conditions. For example, in space and aeronautical niches, where elevated temperature and exceedingly low pressures are routine, ionic-liquids as viscous, and practically non-volatile, substances are well-suited.[20] Some of those reported by Yao and co-workers, based on *bis*(1,2-dimethylimidazoliumyl)decane, were found to exhibit excellent tribological characteristics.[21] These same bis-imidazolium salts belong to the relatively new family of gemini surfactants,[22] with some examples being at least three-orders of magnitude more effective at reducing surface tension, and two-orders more efficient at forming micelles, than mono-imidazolium salts.[23] To investigate the properties of these compounds, we pursued a direct and universal synthesis.

2. Results and Discussion

A range of symmetrical bis(imidazoliumyl)alkane dichlorides was synthesised from the corresponding imidazoles and α,ω-dichloroalkanes (Scheme 1, Table 1). Whilst at ambient pressure dichloromethane was essentially unreactive towards any of the imidazoles, at 1.95 GPa some reactions were approaching completion within 24 h. Except for the reaction with dichloromethane, 1-methylimidazole reacted extremely rapidly with homologous α,ω-dichloroalkanes at 1.95 GPa, with most approaching completion within 3 hours. Reactions of more congested imidazoles were slower, but generally complete within 2–3 days at 1.95 GPa.

Increasing the degree of substitution of and hence steric hindrance around the imidazole nucleus resulted in decreased reaction rates with all α,ω-dichloroalkanes, as is to be expected of bimolecular reactions. For example, rates decreased in the order 1-methylimidazole > 1,2-dimethylimidazole > 1,2,4,5-tetramethylimidazole > 1-methyl-2-phenyl imidazole, with all dichloroalkanes.

In a consecutive sequence, the first step yields the chloroalkyl mono-imidazolium salt, and the second step yields the bis(imidazolium) product. Reflecting this sequence prior to reaction completion, a time dependent product distribution was obtained for all α,ω-dichloroalkanes other than dichloromethane. An example of a typical reaction progression is illustrated in Figure 2. Relative to the ambient pressure reaction, at 1.95 GPa, product distributions were shifted towards the bis-adduct. For reactions of dichloromethane however, the bis(imidazolium-3-yl)methane dichloride was the sole product observed.

In general, the maximum percentages of the intermediate mono-imidazolium salt were low and especially so for reactions of the longer dichloroalkanes. The largest percentages were obtained for reactions of 1,2-dichloroethane, and decreased with increasing chain length – the maximum for this transient species decreased and occurred later in the reaction progress as the dichloroalkane chain length was extended (Fig. 3). In contrast, at ambient pressure, the reaction of 1-methyl-2-phenylimidazole with α,ω-dichloroalkanes produced significant quantities of the mono-imidazolium salt and, without application of UHP, the reaction effectively ended after the first substitution step.

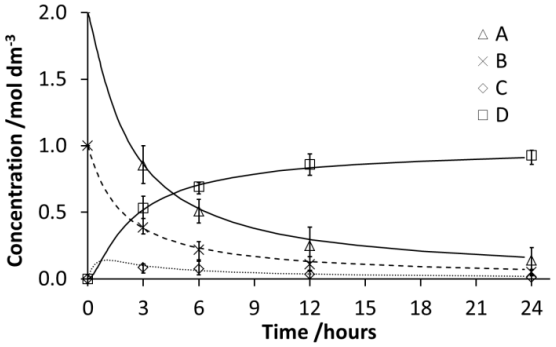

Figure 2. Progression of reaction of 1,2-dimethylimidazole and 1,3-dichloropropane at 1.95 GPa and 45 °C, where A, B, C and D are the concentrations of the imidazole, dichloropropane, the mono-imidazolium salt and the bis(imidazolium) salt, respectively.

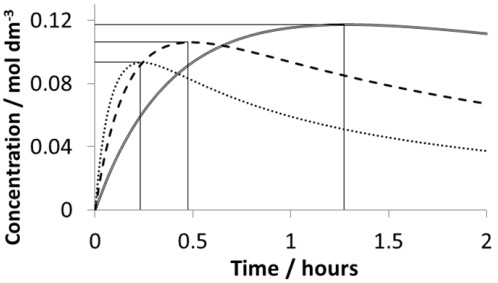

Figure 3. Variation in the early concentrations of mono-imidazolium salt for reactions of 1,2-dimethylimidazole with dichlorobutane (dotted line), dichloropropane (dashed line) and dichloroethane (solid line)

The rate constants observed for the reaction of 1,2-dimethylimidazole with several dichloroalkanes were estimated using the numerical solution to the differential equations and are listed in Table 2.

Table 2. Rate constants for the reactions of 1,2-dimethylimidazole

1,2-dimethylimidazole	k_1 / mol^{-1} dm^3 s^{-1}	k_2 / k_1
1,2-dichloroethane	$4.5 \pm 0.6\times10^{-5}$	5.9 ± 0.9
1,3-dichloropropane	$8.8 \pm 1.6\times10^{-5}$	7.1 ± 0.4
1,4-dichlorobutane	$4.2 \pm 0.4\times10^{-4}$	7.6 ± 0.7

The enhanced proclivity of the reactions to favour the bis(imidazolium) product at UHP was apparent for every reaction in this study, but was particularly obvious for the reactions of 1-methyl-2-phenylimidazole which, as stated above, yielded no bis(imidazolium) salt at ambient pressure. This effect has also been reported for the UHP-promoted consecutive Menshutkin reactions of cyclic amines, including pyrrolidines, piperidines and morpholines with dichloromethane,[24] and pyridine with α,ω-dichloroalkanes.[25] For species involved in the Menshutkin reaction, electrostriction increases as the solutes become charged and this will be enhanced upon going from the mono-imidazolium adduct to the bis-imidazolium adduct. Indeed, for reactions of tertiary amines with dihaloalkanes,[25] this has been correlated with the even greater degree of electrostriction

Table 1. Results for reactions of *N*-substituted imidazoles with various dichloroalkanes in chloroform, using conditions, A: 1.95 GPa, 60 °C; or B: 1 atm, reflux

			Isolated product yields	
Imidazole	α,ω-dichloroalkane	Conditions	of bis-imidazolium salt	of mono-imidazolium salt
1-methylimidazole	dichloromethane	A	100 % (24 h)	0 % (120 h)
		B	0 % (120 h)	0 % (120 h)
	1,2-dichloroethane	A	95 % (24 h), 70 % (3 h)	2 %
		B	77 % (24 h)	11 % (24 h)
	1,3-dichloropropane	A	93 % (3 h), >99 % (24 h)	1 % (3 h), 0 % (24 h)
		B	83 % (24 h)	7 %
	1,4-dichlorobutane	A	>99 % (3 h)	0 % (3 h)
		B	85 % (24 h)	2 % (24 h)
	1,5-dichloropentane	A	>99 % (3 h)	0 % (3 h)
		B	96 % (24 h)	5 % (24 h)
1-ethylimidazole	dichloromethane	A	76 % (24 h)	0 % (24 h)
		B	0 % (120 h)	0 % (120 h)
	1,2-dichloroethane	A	87 % (24 h)	8 % (24 h)
		B	33 % (24 h)	17 % (24 h)
	1,3-dichloropropane	A	95 % (24 h)	2 % (24 h)
		B	47 % (24 h)	11 % (24 h)
	1,4-dichlorobutane	A	>99 % (24 h)	0 % (24 h)
		B	54% (24 h)	7 % (24 h)
1-butylimidazole	dichloromethane	A	62 % (24 h)	0 % (24 h)
		B	0 % (120 h)	0 % (120 h)
	1,2-dichloroethane	A	27 % (3 h), 67 % (24 h)	4 % (24 h)
		B	20 % (24 h)	7 % (24 h)
	1,3-dichloropropane	A	51 % (3 h), 82 % (24 h)	11 % (3 h), 1 % (24 h)
		B	31 % (24 h)	10 % (24 h)
	1,4-dichlorobutane	A	70 % (3 h), 95 % (24 h)	9 % (3 h), 2 % (24 h)
		B	38 % (24 h)	8 % (24 h)
1,2-dimethylimidazole	dichloromethane	A	80 % (24 h)	0 % (24 h)
		B	0 % (120 h)	0 % (120 h)
	1,2-dichloroethane	A	33 % (3 h), 84 % (24 h)	15 % (3 h), 2 % (24 h)
		B	20 % (24 h)	8 % (24 h)
	1,3-dichloropropane	A	53 % (3 h), >99 % (24 h)	14 % (3 h), 0 % (24 h)
		B	29 % (24 h)	11 %
	1,4-dichlorobutane	A	60 % (3 h), >99 % (24 h)	9 % (3 h), 0 % (24 h)
		B	47 % (24 h)	13 %
1,2,4,5-tetramethylimidazole	dichloromethane	A	73 % (24 h)	0 % (24 h)
		B	0 % (120 h)	0 % (120 h)
	1,2-dichloroethane	A	60 % (3 h), 80 % (24 h)	17 % (3 h), 10 % (24 h)
		B	18 % (24 h)	17 %
	1,3-dichloropropane	A	93 % (24 h)	0 % (24 h)
		B	55 % (24 h)	18 %
	1,4-dichlorobutane	A	>99 % (3 h)	0 % (3 h)
		B	66 % (24 h)	8 % (3 h)
1-methyl-2-phenylimidazole	dichloromethane	A	27 % (24 h)	0 % (24 h)
		B	0 % (120 h)	0 % (120 h)

1,2-dichloroethane	A	33 % (24 h)	30 % (24 h)
	B	0 % (24 h)	0 % (24 h)
1,3-dichloropropane	A	60 % (24 h)	22 % (24 h)
	B	0 % (24 h)	0 % (24 h)
1,4-dichlorobutane	A	71 % (24 h)	16 % (24 h)
	B	0 % (120 h)	14 % (120 h)

-associated with the second transition state.

Hence, $\Delta V_2^{\neq}$ for the second substitution is more negative than $\Delta V_1^{\neq}$ for the first substitution and the effect of pressure is to increase k_2 more than k_1, promoting the second step rate to a larger degree than the first and causing a diminution of the amount of mono-imidazolium intermediate observed.

For reactions of 1,2-dichloroethane, 1,3-propane and 1,4-butane this holds true but, by this reasoning, the activation barrier should be greatest for dichloromethane; the results however do not reflect this. The second alkylation step for the reaction of dichloromethane differs to those of the homologous α,ω-dichloroalkanes in that the cationic imidazolium group is *geminal* to the leaving group. The cationic nature of the 1-chloromethylimidazolium intermediate will therefore increase the electrophilic character of the methylene carbon. This effect, in addition to that derived from the pressure-rate enhancement, appears to accelerate the second step to a point where the indeterminate monoalkylation product is not detectable. A similar situation reported for the reaction of pyridine with dichloromethane, wherein no intermediate mono-adduct was detected,[25] was also ascribed to a significantly larger second rate constant.

Whilst at UHP, all reactions proceeded at roughly comparable rates, at ambient pressure reactions of more hindered imidazoles were very slow. Thus, a greater increase in reaction rate on application of UHP is associated with increasingly hindered nucleophiles. This sensitivity to pressure can be rationalised with application of the Hammond postulate.[26] On affording the transition state, excessive crowding of the reaction centre may cause an increased elongation of the electrophile-nucleofuge bond in the transition state.[27] This will tend to increase the polarity and charge-separation, to which the activation volume is related.[28] Subsequently, an increased steric hindrance causes the transition state to occur later along the reaction coordinate,[29] more closely resembling the cationic product and being in receipt of increased stabilisation due to electrostriction.[10,11] Conversely, an early transition state is consistent with contemporary analysis of the Menshutkin reaction[30] providing leeway for the transition state position to be delayed.[31]

The reactions with dichloromethane of five imidazoles were characterised more thoroughly. Over 24 h reactions were monitored periodically and the concentration *versus* time profiles fitted using the integrated rate expression are provided in Table 3.

Table 3. Bimolecular rate constants, k_1, for reactions of *N*-substituted imidazoles with dichloromethane, at 45 °C and 1.94 GPa

N-imidazole	k_1 / mol^{-1} dm^3 s^{-1}
1-methylimidazole	$2.1\times10^{-5} \pm 3.5\times10^{-6}$
1-butylimidazole	$1.1\times10^{-5} \pm 2.0\times10^{-6}$
1,2-dimethylimidazole	$1.7\times10^{-5} \pm 9.0\times10^{-6}$
1,2,4,5-tetramethylimidazole	$1.4\times10^{-5} \pm 1.7\times10^{-6}$
1-methyl-2-phenylimidazole	$2.2\times10^{-6} \pm 4.0\times10^{-7}$

3. Conclusion

In summary, the ultrahigh pressure Menshutkin reaction provides a convenient means of synthesising bis(imidazolium) dichloride salts, in generally high yield in under 24 h. The method is particularly amenable to support the reactions of hindered imidazoles that do not proceed at acceptable rates at ambient pressure.

4. Experimental section

Ultra-high pressure reactions were performed with a Psika Pressure Systems Ltd. (UK) high-pressure hydraulic press using 5% methanol in castor oil as transmission fluid and 5mL PTFE reaction vessels.

^{1}H-NMR spectra were recorded on a Bruker AMX 400 NMR (400 MHz) spectrometer and a Bruker Avance DPX 250 (250 MHz) spectrometer. Signal positions are recorded as chemical shifts (δ) in parts per million (ppm) and referenced to the residual solvent peak as an internal standard. ^{13}C-NMR spectra were recorded on the same spectrometers at 100 MHz.

Mass spectra ($^m/_z$) were recorded under conditions of electrospray ionization (ESI) on a Thermo Scientific LTQ Orbitrap mass spectrometer.

Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT–IR Spectrometer with an attenuated total reflection (ATR) accessory featuring either a diamond or zinc selenide (ZnSe) crystal. The software used was Spectrum Express®.

4.1. General Procedure

A mixture of the imidazole (50 mmol) and the dichloroalkane (25 mmol) was diluted to 25 mL with chloroform and degassed by ultra-sonication. The stock solution was stored in the freezer between experimental runs. A 4 mL aliquot of the stock solution was introduced into a clean, dry, 5 mL PTFE UHP vessel, sealed with a double O-ring stopper and the head-space gas removed by inserting a syringe needle. The reaction was then pressurised to 1.9 GPa at 60 °C. After the requisite reaction time, the apparatus was depressurised and the vessel removed. The stopper was carefully removed (CAUTION! Potential for pressure build-up) and the contents transferred to a round-bottom flask, the UHP vessel was washed with acetonitrile and the washings combined with the bulk of the reaction mixture. The solvents were removed *in-vacuo*, and the residue dissolved in D_2O and analysed immediately by ^{1}H-NMR spectroscopy. For yields see Table 1.

4.2. Bis(1-methylimidazolium-3-yl)methane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 7.69 (2H, bs, C(4/5)-*H*), 7.51 (2H, bs, C(4/5)-*H*), 6.22 (2H, s, C*H*$_2$) and 3.88 (3H, s, NC*H*$_3$); ^{13}C-NMR (62.8 MHz D_2O): δ 138.1 (CH), 124.9 (CH), 121.7 (CH), 58.7 (CH_2) and 36.2 (CH_3). $^m/_z$ (ESI): 177.1133 (M-HCl$_2$]$^+$),

213.0787 (M-Cl]$^+$), $C_9H_{14}N_4$ requires 177.1135, found 177.1140. IR (powder) ν: 3435, 3385, 3079, 3029, 2091, 1739, 1644, 1642, 1580, 1555, 1474, 1454, 1418, 1330, 1289, 1170, 1079, 1017, 871, 772, 733, 680, 620, 573 cm^{-1}. Anal. Calcd (%) for $C_9H_{14}N_4Cl_2.H_2O$ (MW 267.16): C, 40.48; H, 6.04; N, 20.97, Found (%): C, 39.74; H, 6.07; N, 20.62.

4.3. 1,2-Bis(1-methylimidazolium-3-yl)ethane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 8.64 (2H, s, C(2)-*H*), 7.38 (2H, s, C(4/5)-*H*), 7.31 (2H, s, C(4/5)-*H*), 4.63 (4H, s, NCH_2) and 3.77 (6H, s, NCH_3); ^{13}C-NMR (62.8 MHz D_2O): δ 136.8 (CH), 124.5 (CH), 122.1 (CH), 48.7 (CH_2) and 36.0 (CH_3). $^m/_z$ (ESI): 191.1286 (M-HCl$_2$]$^+$), 227.0957 (M-Cl]$^+$), $C_{10}H_{15}N_4^{2+}$ requires 191.1296, found 191.1291. IR (powder) ν: 3381, 3059, 2929, 2856, 2100, 1738, 1641, 1573, 1561, 1455, 1379, 1342, 1164, 1114, 850, 773, 715, 638, 619 cm^{-1}. Anal. Calcd (%) for $C_{10}H_{16}N_4Cl_2.2H_2O$ (MW 299.20): C, 40.14; H, 6.74; N, 18.72, Found (%): C, 39.84; H, 7.50; N, 18.75.

4.4. 1,3-Bis(1-methylimidazolium-3-yl)propane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 8.67 (2H, s, C(2)-*H*), 7.39 (2H, bs, C(4/5)-*H*), 7.35 (2H, bs, C(4/5)-*H*), 4.19 (4H, t, *J* 7.3 Hz, NCH_2), 3.77 (6H, s, NCH_3) and 2.39 (2H, quin, *J* 7.2 Hz, CH_2); ^{13}C-NMR (62.8 MHz, D_2O): δ 136.7 (CH), 123.8 (CH), 122.0 (CH), 49.1 (CH_2), 35.7 (CH_3) and 29.6 (CH_2). $^m/_z$ (ESI): 205.1448 (M-HCl$_2$]$^+$), 241.1201 (M-Cl]$^+$), $C_{10}H_{15}N_4$ 205.1453, found 205.1448. IR (powder) ν: 3369, 3072, 3144, 2124, 1724, 1657, 1562, 1457, 1328, 1279, 1166, 1092, 1065, 1021, 857, 832, 763, 709, 636, 618 cm^{-1}. Anal. Calcd (%) for $C_{11}H_{18}N_4Cl_2.1.5H_2O$ (MW 304.22): C, 43.43; H, 6.96; N, 18.42 Found (%): C, 43.98; H, 7.54; N, 18.62.

4.5. 1,4-Bis(1-methylimidazolium-3-yl)butane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 8.60 (2H, s, C(2)-*H*), 7.33 (2H, s, C(4/5)-*H*), 7.31 (2H, s, C(4/5)-*H*), 4.11 (4H, t, *J* 5.2 Hz, NCH_2), 3.75 (6H, s, NCH_3), and 1.76 (4H, quin, *J* 5.2 Hz, CH_2); ^{13}C-NMR (62.8 MHz D_2O): δ 136.31 (CH), 122.6 (CH), 121.9 (CH), 48.6 (CH_2), 35.6 (CH_3) and 26.1 (CH_2). $^m/_z$ (ESI): 219.1603 (M-HCl$_2$]$^+$), 255.1358 (M-Cl]$^+$), $C_{12}H_{20}N_4$ requires 219.1609, found 219.1604. IR (powder) ν: 3376, 3247, 3145, 3061, 2868, 2958, 2107, 1643, 1577, 1562, 1454, 1429, 1388, 1364, 1334, 1291, 1238, 1169, 1156, 937, 859, 799, 695, 651, 625, 607 cm^{-1}). Anal. Calcd (%) for $C_{12}H_{20}N_4Cl_2.2H_2O$ (MW 327.25): C, 44.04; H, 7.39; N, 17.12 Found (%); C, 43.67; H, 7.46; N, 16.73.

4.6. 1,5-Bis(1-methylimidazolium-3-yl)pentane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 8.58 (2H, s, C(2)-*H*), 7.33 (2H, bs, C(4/5)-*H*), 7.30 (2H, bs, C(4/5)-*H*), 4.05 (4H, t, *J* 7.1 Hz, NCH_2), 3.75 (6H, s, *J* 2.7 Hz, NCH_3), 1.78 (4H, tt, *J* 8.0 Hz, CH_2), and 1.18 (2H, tt, *J* 6.2 Hz, CH_2); ^{13}C-NMR (62.8 D_2O): δ 135.8 (CH), 123.5 (CH), 122.1 (CH), 49.7 (CH_2), 35.6 (CH_3), 28.6 (CH_2) and 22.7 (CH_2). $^m/_z$ (ESI): 233.1753 (M-HCl$_2$]$^+$), 269.1483 (M-Cl]$^+$) $C_{11}H_{17}N_4$ requires 233.1759, found 233.1753. IR (powder) ν: 3365, 3261, 3146, 3083, 2975, 2862, 2171, 1790, 1654, 1576, 1566, 1450, 1425, 1373, 1341, 1272, 1221, 1182, 1082, 984, 898, 841, 793, 745, 651, 623 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{22}N_4Cl_2.2H_2O$ (MW 341.28): C, 45.75; H, 7.68; N, 16.42; Found (%): C, 45.16; H, 8.17; N, 16.32.

4.7. Bis(1,2-dimethylimidazolium-3-yl)methane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 7.48 (2H, bs, C(4/5)-*H*), 7.39 (2H, bs, C(4/5)-*H*), 6.47 (2H, s, NCH_2), 3.73 (6H, s, NCH_3), 2.66 (6H, s, CCH_3); ^{13}C-NMR (62.8 MHz, D_2O): δ 146.2 (C), 123.8 (CH), 120.5 (CH), 57.2 (CH_2), 35.2 (CH_3) and 9.4 (CH_3); $^m/_z$ (ESI): 103.0761 (M-Cl$_2$]$^{2+}$), $C_{11}H_{18}N_4$ requires 103.0760, found 103.0761. IR (powder) ν 3390, 3041, 3016, 2960, 1814, 1713, 1592, 1529, 1504, 1443, 1413, 1338, 1299, 1259, 1199, 1139, 1055, 1024, 994, 909, 809, 795, 761, 720, 647, 620, 607 cm^{-1}. Anal. Calcd (%) for $C_{11}H_{18}N_4Cl_2.0{,}5H_2O$: (MW 286.20): C, 46.13; H, 6.69; N, 16.50; Found (%): C, 46.02; H, 6.58; N, 19.50.

4.8. 1,2-Bis(1,2-dimethylimidazolium-3-yl)ethane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 7.32 (2H, bs, C(4/5)-*H*), 7.16 (2H, bs, C(4/5)-*H*), 4.55 (4H, s, NCH_2), 3.71 (6H, s, NCH_3), 2.43 (6H, s, CCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 145.1 (C), 123.2 (CH), 120.8 (CH), 46.9 (CH_2), 34.9 (CH_3) and 8.6 (CH_3); $^m/_z$ (ESI): 110.0840 (M-Cl$_2$]$^{2+}$) $C_{12}H_{20}N_4$ requires 110.0838, found 110.0840. IR (powder) ν: 3359, 3121, 3044, 2961, 1587, 1536, 1422, 1337, 1282, 1243, 1155, 1125, 1053, 784, 749, 728, 666, 593 cm^{-1}. Anal. Calcd (%) for $C_{12}H_{20}N_4Cl_2.3H_2O$: (MW 345.27): C, 41.74; H, 7.58; N, 16.23; Found (%): C, 41.63; H, 7.02; N, 16.00.

4.9. 1,3-Bis(1,2-dimethylimidazolium-3-yl)propane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 7.30 (2H, bs, C(4/5)-*H*), 7.28 (2H, bs, C(4/5)-*H*), 4.15 (4H, t, *J* 7.5 Hz, NCH_2), 3.69 (6H, s, NCH_3), 2.51 (6H, s, CCH_3) and 2.30 (2H, quin, *J* 7.5 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 144.6 (C), 122.6 (CH), 120.4 (CH), 44.8 (CH_2), 34.6 (CH_3), 28.9 (CH_2) and 8.8 (CH_3). $^m/_z$ (ESI): 117.0918 (M-HCl$_2$]$^{2+}$), $C_{13}H_{22}N_4$ requires 117.0971, found 117.0918. IR (powder) ν: 3349, 3263, 3074, 2970, 2131, 1636, 1587, 1535, 1440, 1377, 1330, 1240, 1191, 1160, 1127, 1048, 879, 808, 766, 752, 727, 670, 658 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{22}N_4Cl_2.2H_2O$: (MW 341.28): C, 45.75; H, 7.68; N, 16.42; Found (%): C, 45.26; H, 7.66; N, 16.13.

4.10. 1,4-Bis(1,2-dimethylimidazolium-3-yl)butane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 7.23 (4H, bs, C(4/5)-*H*), 4.05 (4H, s, NCH_2), 3.56 (6H, s, NCH_3), 2.47 (6H, s, CCH_3) and 1.08 (4H, t, *J* 7.2 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 145.0 (C), 122.3 (CH), 120.5 (CH), 47.4 (CH_2), 34.5 (CH_3), 25.9 (CH_2) and 8.7 (CH_3). $^m/_z$ (ESI): 124.0997 (M-Cl$_2$]$^{2+}$), $C_{14}H_{24}N_4$ requires 124.0995, found 124.0997. IR (powder) ν: 3443, 3381, 3050, 1587, 1536, 1470, 1365, 1341, 1270, 1242, 1152, 1118, 1037, 795, 778, 730, 660, 628 cm^{-1}. Anal. Calcd (%) for $C_{14}H_{24}N_4Cl_2.1{,}5H_2O$: (MW 346.30): C, 48.56; H, 7.86; N, 16.18; Found (%): C, 48.52; H, 8.33; N, 15.65.

4.11. 1,5-Bis(1,2-dimethylimidazolium-3-yl)pentane dichloride

^{1}H-NMR (250 MHz, D_2O): δ 7.25 (4H, bs, C(4/5)-*H*), 4.02 (4H, t, *J* 7.2 Hz, NCH_2), 3.67 (6H, s, NCH_3), 2.48 (6H, s, CCH_3), 1.74 (4H, quin, *J* 7.6 Hz, CH_2) and 1.27 (2H, m, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 144.2 (C), 122.1 (CH), 120.6 (CH), 47.8 (CH_2), 34.6 (CH_3), 28.2 (CH_2), 22.4 (CH_2) and 8.8 (CH_3); $^m/_z$ (ESI): 131.1073 (M-Cl$_2$]$^{2+}$), $C_{15}H_{26}N_4$ requires 131.1073, found 131.1076. IR (powder) ν: 3387, 3036, 2945, 1586 1538, 1514, 1462, 1420, 1391, 1358, 1338, 1274, 1246, 1190, 1122, 1077, 1049, 787, 753, 739, 661 cm^{-1}. Anal. Calcd (%) for $C_{15}H_{26}N_4Cl_2.4H_2O$: (MW 405.36): C, 44.44; H, 8.45; N, 13.82; Found (%): C, 43.70; H, 7.12; N, 13.07.

4.12. Bis(1-ethylimidazolium -3-yl)methane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 9.16 (2H, s, C(2)-*H*), 7.66 (2H, bs, C(4/5)-*H*), 7.55 (2H, bs, C(4/5)-*H*), 6.59 (2H, s, NCH_2), 4.21 (4H, q, *J* 7.2 Hz, NCH_2CH$_3$), 1.43 (6H, t, *J* 7.2 Hz, CCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.2 (CH), 123.4 (CH), 122.0 (CH), 58.8 (CH_2), 45.6 (CH_2) and 14.1 (CH_3); $^m/_z$ (ESI): 205.1445 (M-HCl$_2$]$^+$), 103.0754 (M-Cl$_2$]$^{2+}$), $C_{11}H_{17}N_4$ requires 205.1448, found 205.1445. IR (powder) ν: 3362, 3245, 3040, 2983, 2116, 1642, 1579, 1560, 1544, 1512, 1448, 1396, 1350, 1324, 1228, 1166,

1109, 1080, 1034, 958, 916, 885, 805, 763, 666, 618, 607 cm^{-1}. Anal. Calcd (%) for $C_{11}H_{18}N_4Cl_2.1H_2O$: (MW 295.21): C, 44.75; H, 6.82; N, 18.98; Found (%): C, 43.85; H, 6.76; N, 18.70.

4.13. 1,2-Bis(1-ethylimidazolium-3-yl)ethane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.74 (2H, s, C(2)-*H*), 7.52 (2H, bs, C(4/5)-*H*), 7.36 (2H, bs, C(4/5)-*H*), 4.67 (4H, s, NCH_2), 4.17 (4H, q, *J* 7.4 Hz, NCH_2CH$_3$), 1.42 (6H, t, *J* 7.4 Hz, CCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.6 (CH), 123.2 (CH), 122.2 (CH), 48.8 (CH_2), 45.2 (CH_2) and 14.4 (CH_3); $^m/_z$ (ESI): 219.1601 (M-$HCl_2]^+$), 110.0844 (M-$Cl_2]^{2+}$), $C_{12}H_{19}N_4$ requires 219.1604, found 219.1601. IR (powder) ν: 3378, 3140, 3078, 3031, 2875, 2110, 1639, 1561, 1449, 1409, 1356, 1336, 1302, 1246, 1166, 1122, 962, 864, 799, 785, 652, 638, 603 cm^{-1}. Anal. Calcd (%) for $C_{12}H_{20}N_4Cl_2.2H_2O$: (MW 327.25): C, 44.04; H, 7.39; N, 17.12; Found (%): C, 44.48; H, 8.04; N, 17.33.

4.14. 1,3-Bis(1-ethylimidazolium-3-yl)propane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.73 (2H, s, C(2)-*H*), 7.44 (2H, bs, C(4/5)-*H*), 7.41 (2H, bs, C(4/5)-*H*), 4.17 (4H, t, *J* 7.4 Hz, NCH_2CH$_3$), 4.16 (4H, q, *J* 7.4 Hz, NCH_2), 1.85 (2H, quin, *J* 4.7 Hz, CH_2), 1.44 (6H, t, *J* 7.4 Hz, CH$_2$CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 134.9 (CH), 122.2 (CH), 122.1 (CH), 48.7 (CH_2), 44.9 (CH_2), 26.2 (CH_2), 14.4 (CH_3); $^m/_z$ (ESI): 233.1759 (M-$HCl_2]^+$), 117.0912 (M-$Cl_2]^{2+}$), $C_{13}H_{21}N_4$ requires 233.1761, found 233.1759. IR (powder) ν: 3378, 3134, 3048, 2980, 2946, 2866, 2161, 1564, 1460, 1357, 1258, 1156, 1095, 1050, 958, 824, 779, 741, 652, 618 cm^{-1}. Anal. Calcd (%) for $C_{13}H_{22}N_4Cl_2.0.5H_2O$: (MW 323.27): C, 49.69; H, 7.38; N, 17.83; Found (%): C, 49.32; H, 8.93; N, 17.64.

4.15. 1,4-Bis(1-ethylimidazolium-3-yl)butane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.72 (2H, s, C(2)-*H*), 7.43 (2H, bs, C(4/5)-*H*), 7.39 (2H, bs, C(4/5)-*H*), 4.16 (4H, dd, *J* 4.8 Hz, NCH_2CH$_3$), 4.18 (4H, t, *J* 7.6 Hz, NCH_2CH$_2$), 1.82 (4H, q, *J* 4.8 Hz CH$_2$CH_2), 1.44 (6H, t, *J* 7.2 Hz, CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.2 (CH), 122.5 (CH), 122.2 (CH), 46.4 (CH_2), 44.9 (CH_2), 29.6 (CH_2) and 14.4 (CH_3); $^m/_z$ (ESI): 247.1915 (M-$HCl_2]^+$), 124.0989 (M-$Cl_2]^{2+}$), $C_{14}H_{23}N_4$ requires 247.1917, found 247.1915. IR (powder) ν: 3379, 3134, 3075, 2976, 2923, 2828, 1823, 1630, 1556, 1450, 1376, 1304, 1220, 1156, 1055, 1033, 1018, 958, 916, 796, 784, 649 cm^{-1}. Anal. Calcd (%) for $C_{14}H_{24}N_4Cl_2.H_2O$: (MW 337.29): C, 49.85; H, 7.77; N, 16.61; Found (%): C, 50.42; H, 8.16; N, 16.55.

4.16. 1,5-Bis(1-ethylimidazolium-3-yl)pentane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.70 (2H, s, C(2)-*H*), 7.43 (2H, bs, C(4/5)-*H*), 7.39 (2H, bs, C(4/5)-*H*), 4.14 (4H, t, *J* 7.2 Hz, NCH_2CH$_2$), 4.11 (4H, q, *J* 7.5 Hz, NCH_2CH$_3$), 1.84 (4H, quin, *J* 7.6 Hz, CH_2), 1.39 (6H, t, *J* 7.5 Hz, CH$_2$CH_3), 1.22 (2H, quin, *J* 7.5 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 134.8 (CH), 122.2 (CH), 122.0 (CH), 49.1 (CH_2), 44.8 (CH_2), 28.7 (CH_2), 22.2 (CH_2), 14.4 (CH_3); $^m/_z$ (ESI): 261.2071 (M-$HCl_2]^+$), 131.1067 (M-$Cl_2]^{2+}$), $C_{15}H_{25}N_4$ requires 261.2074, found 261.2071. IR (powder) ν: 3442, 3383, 3086, 3045, 2977, 2200, 2122, 1790, 1681, 1621, 1577, 1562, 1451, 1385, 1344, 1320, 1268, 1231, 1193, 1164, 1033, 876, 789, 692, 650, 627, 584 cm^{-1}.

4.17. Bis(1-butylimidazolium-3-yl)methane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 7.71 (2H, bs, C(4/5)-*H*), 7.59 (2H, bs, C(4/5)-*H*), 6.63 (2H, s, NCH_2), 4.20 (4H, quin, *J* 7.6 Hz, NCH_2CH$_2$), 1.78 (6H, quin, *J* 7.6 Hz**,** CH$_2$CH_2), 1.23 (6H, quin, *J* 7.6 Hz, CH$_2$CH_2) and 0.82 (6H, t, *J* 7.6 Hz, CH$_2$CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 136.4 (CH), 123.8 (CH), 122.0 (CH), 58.8 (CH_2), 50.1 (CH_2), 31.0 (CH_2), 18.8 (CH_2) and 12.9 (CH_3); $^m/_z$ (ESI): 261.2072 (M-$HCl_2]^+$), 131.1068 (M-$Cl_2]^{2+}$), $C_{15}H_{25}N_4$ requires 261.2074, found 261.2072. IR (powder) ν: 3406, 3051, 2960, 2873, 1794, 1681, 1580, 1560, 1462, 1380, 1320, 1166, 1114, 906, 802, 768, 717, 665, 612 cm^{-1}.

4.18. 1,2-Bis(1-butylimidazolium-3-yl)ethane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.79 (2H, s, C(2)-*H*), 7.56 (2H, bs, C(4/5)-*H*), 7.46 (2H, bs, C(4/5)-*H)*, 4.74 (4H, t, *J* 7.2 Hz, NCH_2), 4.16 (4H, t, *J* 7.5 Hz, NCH_2), 1.78 (4H, quin, *J* 7.5 Hz, CH$_2$CH_2), 1.19 (4H, q, *J* 7.2 Hz, CH$_2$CH_2), 0.87 (6H, t, *J* 7.2 Hz, CH$_2$CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.6 (CH), 123.5 (CH), 122.2 (CH), 49.6 (CH_2), 48.7 (CH_2), 31.1 (CH_2), 18.7 (CH_2) and 12.5 (CH_3); $^m/_z$ (ESI): 275.2230 (M-$HCl_2]^+$), 138.1145 (M-$Cl_2]^{2+}$), $C_{16}H_{27}N_4$ requires 275.2230, found 275.2228. IR (powder) ν: 3377, 3066, 2959, 2873, 2112, 1642, 1560, 1461, 1367, 1336, 1162, 1112, 1023, 946, 857, 753, 637 cm^{-1}.

4.19. 1,3-Bis(1-butylimidazolium-3-yl)propane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.75 (2H, s, C(2)-*H*), 7.41 (4H, bs, C(4/5)-*H*), 4.22 (4H, t, *J* 7.2 Hz, NCH_2), 4.09 (4H, t, *J* 7.2 Hz, NCH_2), 2.42 (4H, quin, *J* 7.2 Hz, CH$_2$CH_2CH$_2$), 1.74 (4H, quin, *J* 7.5 Hz, CH$_2$CH_2), 1.22 (4H, quin, *J* 7.5 Hz, CH_2CH$_3$), 0.81 (6H, t, *J* 7.2 Hz, CH$_2$CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.4 (CH), 122.8 (CH), 122.3 (CH), 49.6 (CH_2), 46.5 (CH_2), 31.2 (CH_2), 29.7 (CH_2), 18.8 (CH_2) and 12.7 (CH_3); $^m/_z$ (ESI): 289.2385 (M-$HCl_2]^+$), 145.1225 (M-$Cl_2]^{2+}$), $C_{17}H_{29}N_4$ requires 289.2387, found 289.2385. IR (powder) ν: 3381, 3133, 1057, 2959, 2872, 2112, 1704, 1641, 1562, 1459, 1370, 1335, 1160, 1114, 1021, 949, 872, 753, 635 cm^{-1}.

4.20. 1,4-Bis(1-butylimidazolium-3-yl)butane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.77 (2H, s, C(2)-*H*), 7.46 (4H, bs, C(4/5)-*H*), 4.20 (4H, t, *J* 6.4 Hz, NCH_2), 4.15 (4H, t, *J* 7.2 Hz, NCH_2), 1.84 (4H, quin *J* 6.4 Hz, CH_2), 1.76 (4H, t, *J* 7.5 Hz, CH$_2$CH_2), 1.25 (4H, quin, *J* 7.5 Hz, CH_2CH$_3$), 0.85 (6H, t, *J* 7.2 Hz, CH$_2$CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.2 (CH), 122.6 (CH), 122.1 (CH), 49.5 (CH_2), 48.7 (CH_2), 31.2 (CH_2), 26.3 (CH_2), 18.8 (CH_2) and 12.7 (CH_3); $^m/_z$ (ESI): 303.2542 (M-$HCl_2]^+$), 152.1305 (M-$Cl_2]^{2+}$), $C_{18}H_{31}N_4$ requires 303.2543, found 303.2542. IR (powder) ν: 3383, 3133, 3064, 2959, 2872, 2106, 1632, 1562, 1462, 1373, 1334, 1160, 1114, 1024, 949, 871, 754, 634 cm^{-1}.

4.21. 1,5-Bis(1-butylimidazolium-3-yl)pentane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 8.70 (2H, s, C(2)-*H*), 7.39 (4H, bs, C(4/5)-*H*), 4.13-4.06 (8H, m, *J* 6.8, 7.2 Hz, NCH_2), 1.85-1.69 (8H, m, *J* 6.8, 7.2 Hz, CH_2), 1.18 (6H, m, *J* 6.8, 7.6 Hz, CH_2CH$_3$ and NCH$_2$CH$_2$CH_2CH$_2$), 0.80 (6H, t, *J* 7.6 Hz, CH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 135.1 (CH), 122.4 (CH), 122.2 (CH), 49.3 (CH_2), 31.2 (CH_2), 28.6 (CH_2), 24.96 (CH_2) 22.12 (CH_2) 18.7 (CH_2) and 12.6 (CH_3); $^m/_z$ (ESI): 317.2700 (M-$HCl_2]^+$), 159.1383 (M-$Cl_2]^{2+}$), $C_{19}H_{33}N_4$ requires 317.2700, found 317.2700. IR (powder) ν: 3375, 3133, 3069, 2958, 2930, 2871, 2112, 1765, 1715, 1637, 1562, 1461, 1376, 1330, 1160, 1114, 1058, 1035, 990, 869, 753, 638 cm^{-1}.

4.22. Bis(1-methyl-2-phenylimidazolium-3-yl)methane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 7.69 (4H, m, C*H*), 7.53 (4H, m, NC*H*), 7.37 (2H, m, C*H*), 7.25 (4H, d, *J* 7.6 Hz, C*H*), 6.41 (2H, s,

NCH_2N), 3.58 (6H, s, NCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 133.6 (CH), 130.1 (CH), 129.7 (CH), 124.2 (CH), 121.7 (CH), 118.8 (CH), 58.1 (CH_2) and 35.8 (CH_2); $^{m}/_{z}$ (ESI): 165.0914 (M-Cl_2]$^{2+}$), $C_{21}H_{22}N_4$ requires 165.0917, found 165.0914. IR (powder) ν: 3445, 3396, 3044, 1583, 1501, 1435, 1238, 1169, 1095, 1032, 937, 782, 713, 692 cm^{-1}. Anal. Calcd (%) for $C_{21}H_{22}N_4Cl_2.2H_2O$: (MW 437.37): C, 57.67; H, 5.99; N, 12.81; Found (%): C, 57.04; H, 5.88; N, 12.56.

4.23. 1,2-Bis(1-methyl-2-phenylimidazolium-3-yl)ethane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 7.92 (4H, m, C*H*), 7.82 (4H, s, NC*H*), 7.69 (2H, m, C*H*), 7.30 (4H, d, *J* 4 Hz, C*H*), 4.38 (4H, s, NCH_2), 3.56 (6H, s, NCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 145.0 (CH), 133.2 (CH), 130.1 (CH), 129.6 (CH), 124.3 (CH), 121.4 (CH), 119.4 (CH), 47.75 (CH_2) and 35.6 (CH_3); $^{m}/_{z}$ (ESI): 172.0994 (M-Cl_2]$^{2+}$), $C_{22}H_{24}N_4$ requires 172.0995, found 172.0994. IR (powder) ν: 3393, 3055, 2103, 1633, 1605, 1582, 1507, 1474, 1439, 1327, 1251, 1218, 1171, 1097, 1026, 938, 776, 708, 602 cm^{-1}. Anal. Calcd (%) for $C_{22}H_{24}N_4Cl_2.4H_2O$: (MW 487.43): C, 54.21; H, 6.62; N, 11.49; Found (%): C, 54.28; H, 6.43; N, 11.36.

4.24. 1,3-Bis(1-methyl-2-phenylimidazolium-3-yl)propane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 7.71 (4H, m, C*H*), 7.60 (4H, m, NC*H*), 7.43 (2H, s, C*H*), 7.36 (4H, m, C*H*), 3.86 (4H, t, *J* 7.2 Hz, NCH_2), 3.56 (6H, s, NCH_3) and 2.03 (2H, quin, *J* 7.2 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 132.8 (CH), 129.9 (CH), 129.8 (CH), 123.5 (CH), 121.2 (CH), 120.5 (CH), 45.0 (CH), 35.2 (CH_2) and 29.8 (CH_3); $^{m}/_{z}$ (ESI): 179.1075 (M-Cl_2]$^{2+}$), $C_{23}H_{26}N_4$ requires 179.1145, found 179.1075. IR (powder) ν: 3481, 3402, 3344, 3234, 3071, 1633, 1580, 1510, 1451, 1330, 1247, 1156, 1085, 945, 786, 787, 715 cm^{-1}. Anal. Calcd (%) for $C_{23}H_{26}N_4Cl_2.2H_2O$: (MW 465.42): C, 59.36; H, 6.50; N, 12.04; Found (%): C, 59.18; H, 6.40; N, 11.88.

4.25. 1,4-Bis(1-methyl-2-phenylimidazolium-3-yl)butane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 7.68 (4H, m, C*H*), 7.56 (4H, m, NC*H*), 7.43 (2H, d, *J* 2.0 Hz, C*H*), 7.38 (4H, d, *J* 6.8 Hz, C*H*), 3.80 (4H, t, *J* 6.8 Hz, NCH_2), 3.56 (6H, s, NCH_3) and 1.40 (4H, quin, *J* 6.8 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 144.6 (CH), 132.7 (CH), 129.9 (CH), 129.7 (CH), 123.2 (CH), 121.4 (CH), 120.8 (CH), 47.4 (CH_2), 35.2 (CH_2) and 25.4 (CH_3); $^{m}/_{z}$ (ESI): 186.11150 (M-Cl_2]$^{2+}$), $C_{24}H_{28}N_4$ requires 186.1152, found 186.1150. IR (powder) ν: 3467, 3403, 3047, 3020, 1704, 1619, 1580, 1516, 1480, 1468, 1449, 1392, 1319, 1258, 1241, 1159, 1113, 1094, 1050, 1004, 953, 813, 784, 719, 707, 618, 555 cm^{-1}. Anal. Calcd (%) for $C_{24}H_{28}N_4Cl_2.2H_2O$: (MW 479.45): C, 60.12; H, 6.73; N, 11.68; Found (%): C, 59.76; H, 6.70; N, 11.40.

4.26. 1,5-Bis(1-methyl-2-phenylimidazolium-3-yl)pentane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 7.66 (4H, m, C*H*), 7.60 (4H, m, NC*H*), 7.44 (2H, m, C*H*), 7.39 (4H, m, C*H*), 3.82 (4H, t, *J* 7.2 Hz, NCH_2), 3.57 (6H, s, NCH_3) 1.43 (4H, quin, *J* 7.2 Hz, CH_2) 0.90 (2H, quin, *J* 7.2 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 144.6 (C), 132.6 (CH), 130.1 (CH), 129.6 (CH), 123.1 (CH), 121.4 (CH), 121.0 (C), 47.9 (CH_2), 35.2 (CH_3), 28.2 (CH_2) and 21.7 (CH_2); $^{m}/_{z}$ (ESI): 193.1230 (M-Cl_2]$^{2+}$), $C_{25}H_{30}N_4Cl_2.4H_2O$ requires 193.1230, found 193.1230. IR (powder) ν: 3503, 3405, 3366, 3118, 3068, 1603, 1580, 1511, 1470, 1444, 1411, 1363, 1328, 1245, 942, 785, 777, 705, 699, 619, 603 cm^{-1}. Anal. Calcd (%) for $C_{25}H_{31}N_4Cl_2.4H_2O$: (MW 529.50): C, 56.71; H, 7.23; N, 10.58; Found (%): C, 57.02; H, 6.92; N, 10.48.

4.27. Bis(1,2,4,5-tetramethylimidazolium-3-yl)methane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 6.36 (2H, s, NCH_2), 3.60 (6H, s, NCH_3), 2.57 (6H, s, CCH_3), 2.14 (6H, s, CCH_3) and 1.98 (6H, s, CCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 144.0 (CH_2), 128.2 (CH_2), 125.3 (CH_2), 54.7 (CH_2), 32.0 (CH_3), 10.0 (CH_3), 7.9 (CH_3) and 7.6 (CH_3); $^{m}/_{z}$ (ESI): 261.2075 (M-HCl_2]$^{+}$), 131.1071 (M-Cl_2]$^{2+}$), $C_{15}H_{25}N_4$ requires 261.2074, found 261.2075. IR (powder) ν: 3446, 3370, 2985, 2121, 1652, 1623, 1542, 1507, 1443, 1396, 1364, 1329, 1239, 1205, 1140, 1077, 1037, 865, 846, 822, 711, 590, 567 cm^{-1}. Anal. Calcd (%) for $C_{15}H_{26}N_4Cl_2.3H_2O$: (MW 387.35): C, 46.51; H, 8.33; N, 14.46; Found (%): C, 45.34; H, 8.38; N, 14.02.

4.28. 1,2-Bis(1,2,4,5-tetramethylimidazolium-3-yl)ethane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 4.40 (4H, s, NCH_2), 3.55 (6H, s, NCH_3), 2.31 (6H, s, CCH_3), 2.13 (6H, s, CCH_3), 1.99 (6H, s, CCH_3). ^{13}C-NMR (62.8 MHz, D_2O): δ 142.7 (C), 127.3 (C), 125.2 (C), 43.8 (CH_2), 31.7 (CH_3), 9.0 (CH_3), 7.6 (CH_3) and 7.2 (CH_3); $^{m}/_{z}$ (ESI): 275.2232 (M-HCl_2]$^{+}$), 138.1149 (M-Cl_2]$^{2+}$), $C_{16}H_{27}N_4$ requires 275.2230, found 275.2232. IR (powder) ν: 3427, 3385, 2975, 2117, 1644, 1617, 1541, 1525, 1481, 1442, 1379, 1357, 1339, 1272, 1230, 1182, 1135, 1077, 1047, 851, 835, 768, 667, 613, 564 cm^{-1}. Anal. Calcd (%) for $C_{16}H_{28}N_4Cl_2.2.5H_2O$: (MW 392.37): C, 48.98; H, 8.47; N, 14.28; Found (%): C, 48.56; H, 8.44; N, 14.17.

4.29. 1,3-Bis(1,2,4,5-tetramethylimidazolium-3-yl)propane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 4.09 (4H, t, *J* 7.1 Hz, NCH_2), 3.53 (6H, s, NCH_3), 2.53 (6H, s, CCH_3), 2.47 (6H, s, CCH_3), 2.11 (6H, s, CCH_3) and 1.08 (2H, quin, *J* 7.1 Hz CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 142.1 (C), 126.4 (C), 124.6 (C), 41.6 (CH_3), 31.2 (CH_2), 28.7 (CH_2), 9.3 (CH_3), 7.6 (CH_3) and 7.5 (CH_3); $^{m}/_{z}$ (ESI): 289.2388 (M-HCl_2]$^{+}$), 145.1227 (M-Cl_2]$^{2+}$), $C_{17}H_{29}N_4$ requires 289.2387, found 289.2388. IR (powder) ν: 3370, 3284, 2983, 2923, 2110, 1643, 1528, 1430, 1376, 1351, 1227, 1206, 1177, 1064, 1037, 853, 824, 767, 644, 577, 561 cm^{-1}. Anal. Calcd (%) for $C_{17}H_{30}N_4Cl_2.4H_2O$: (MW 433.42): C, 47.11; H, 8.84; N, 12.93; Found (%): C, 46.74; H, 8.96; N, 12.68.

4.30. 1,4-Bis(1,2,4,5-tetramethylimidazolium-3-yl)butane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 3.97 (4H, t, *J* 5.0, NCH_2), 3.50 (6H, s, NCH_3), 2.45 (6H, s, CCH_3), 2.13 (6H, s, CCH_3), 2.13 (6H, s, CCH_3) and 1.66 (4H, quin, *J* 5.0 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 142.0 (C), 126.5 (C), 124.6 (C), 44.2 (CH_2), 31.2 (CH_3), 25.9 (CH_2), 9.3 (CH_3), 7.54 (CH_3), 7.53 (CH_3); $^{m}/_{z}$ (ESI): 303.2546 (M-HCl_2]$^{+}$), 152.1307 (M-Cl_2]$^{2+}$), $C_{18}H_{31}N_4$ requires 303.2543, found 303.2546. IR (powder) ν: 3386, 3340, 2986, 2875, 2100, 1649, 1609, 1533, 1448, 1416, 1373, 1224, 1167, 1078, 1042, 838, 759, 692 cm^{-1}. Anal. Calcd (%) for $C_{18}H_{32}N_4Cl_2.4H_2O$: (MW 447.44): C, 48.32; H, 9.01; N, 12.52; Found (%): C, 47.40; H, 8.48; N, 12.58.

4.31. 1,5-Bis(1,2,4,5-tetramethylimidazolium-3-yl)pentane dichloride

^{1}H-NMR (400 MHz, D_2O): δ 3.93 (4H, t, *J* 7.6 Hz, NCH_2), 3.46 (6H, s, NCH_3), 2.48 (6H, s, CCH_3), 2.48 (6H, s, CCH_3), 2.10 (6H, s, CCH_3), 1.73 (4H, quin, *J* 7.6 Hz, CH_2) and 1.26 (2H, q, *J* 7.6 Hz, CH_2). ^{13}C-NMR (62.8 MHz, D_2O): δ 141.9 (C), 125.8 (C),

124.7 (C), 45.1 (CH_2), 31.1 (CH_3), 28.5 (CH_2), 22.9 (CH_2), 9.2 (CH_3) and 7.54 (CH_3), 6.7 (CH_3); $^{m}/_{z}$ (ESI): 159.1384 (M-Cl_2]$^{2+}$), $C_{19}H_{34}N_4$ requires 159.1386, found 159.1384. IR (powder) ν: 3368, 2927, 2865, 2116, 1703, 1645, 1531, 1433, 1373, 1227, 1132, 1076, 1046, 863, 839, 739, 599 cm^{-1}.

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