Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Physicochemical and electrochemical properties of a new series of protic ionic liquids with N-chloroalkyl functionalized cations

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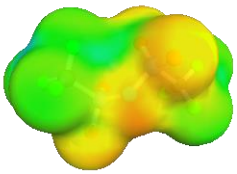
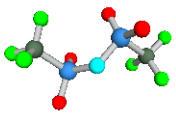
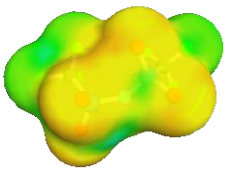
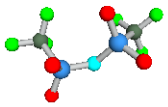
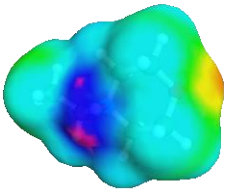
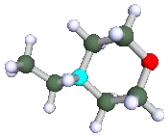
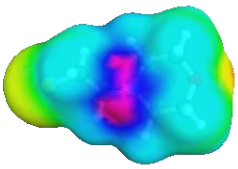
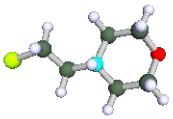
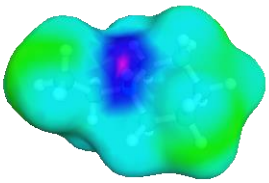
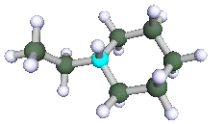
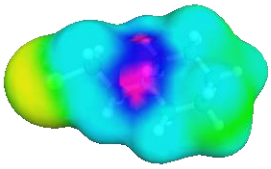
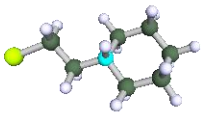
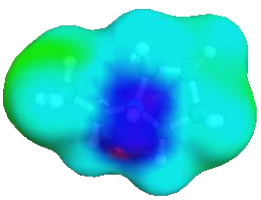
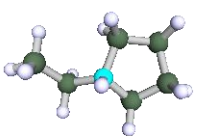
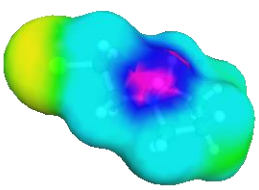
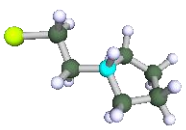
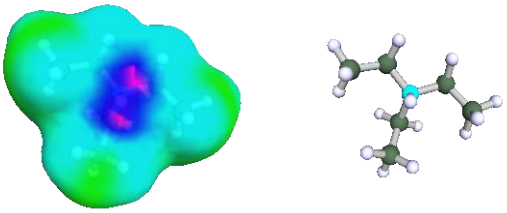
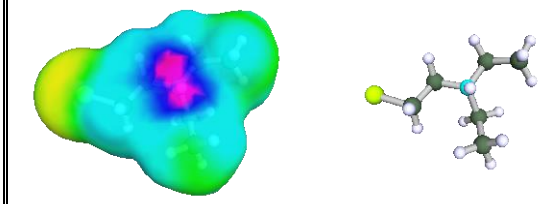
Table S1: Structure, abbreviation and Cosmo volume of the TFSI anion and the studied cations and their non-chlorinated analogues.

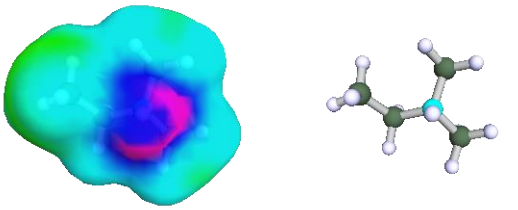
Structure and abbreviation	Cosmo Volume ($Å^3$)	Structure and abbreviation	Cosmo Volume ($Å^3$)
			
$[TFSI]^-$ conformer 1	219.69	$[TFSI]^-$ conformer 2	222.21
			
$[C_2Morph]^+$	159.75	$[C_{2\text{-}Cl}\text{-}Morph]^+$	182.91
			
$[C_2Pip]^+$	170.25	$[C_{2\text{-}Cl}\text{-}Pip]^+$	191.74
			
$[C_2Pyrr]^+$	150.86	$[C_{2\text{-}Cl}\text{-}Pyrr]^+$	174.11



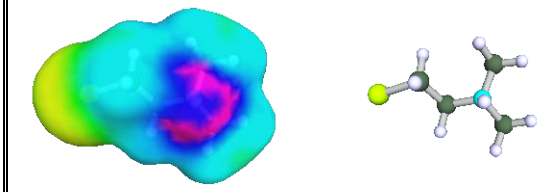
$[HN_{222}]^+$ 165.51



$[HN_{2\text{-}Cl\text{-}22}]^+$ 188.22



$[HN_{211}]^+$ 121.98



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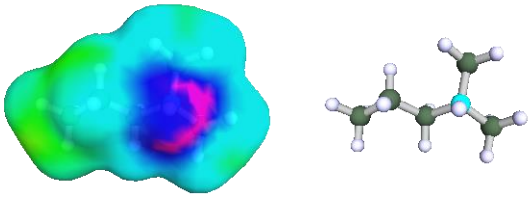

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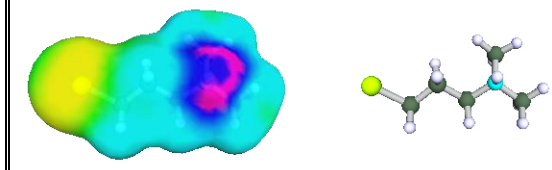
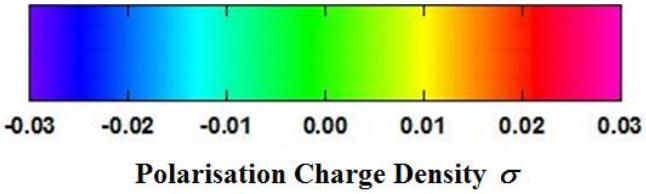
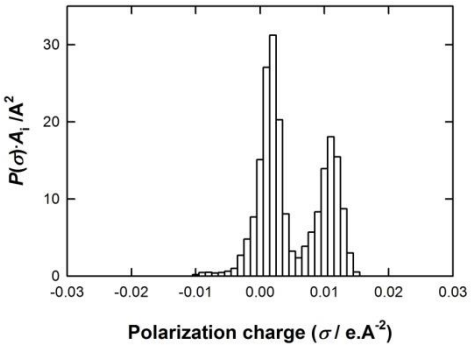
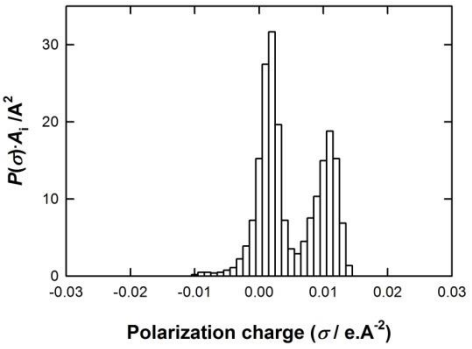
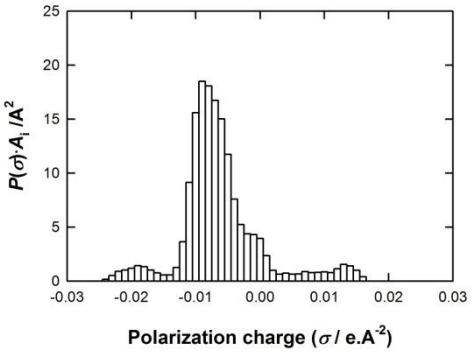
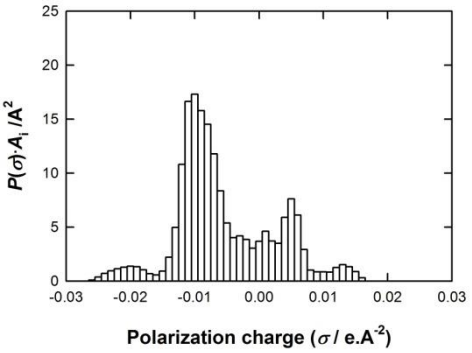
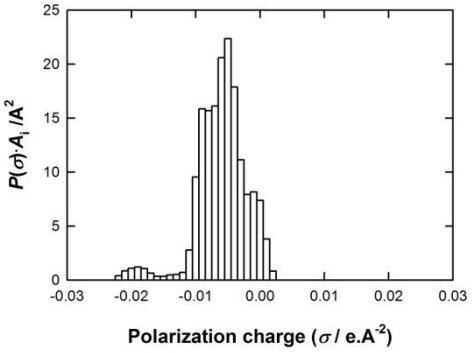
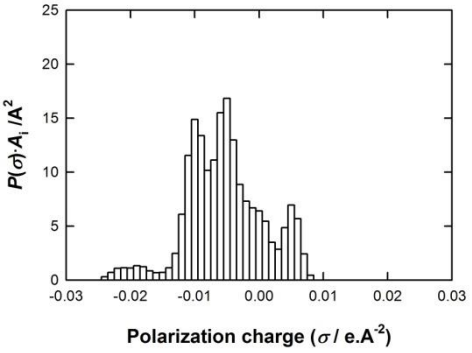
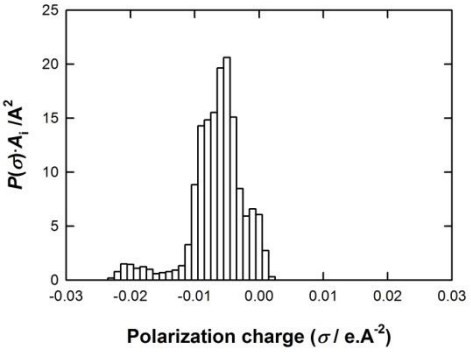
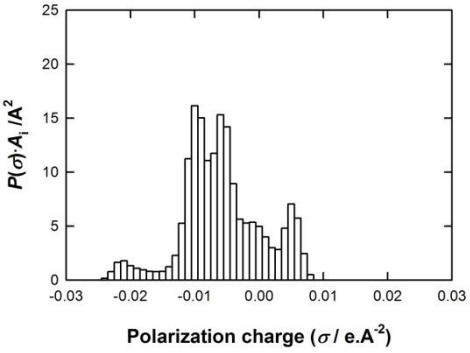
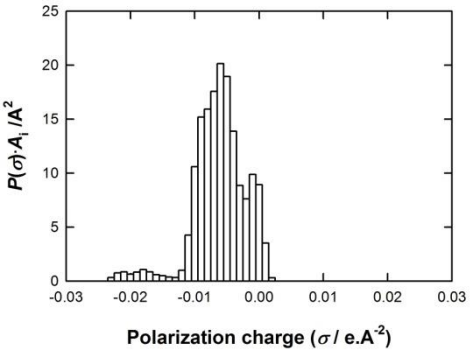
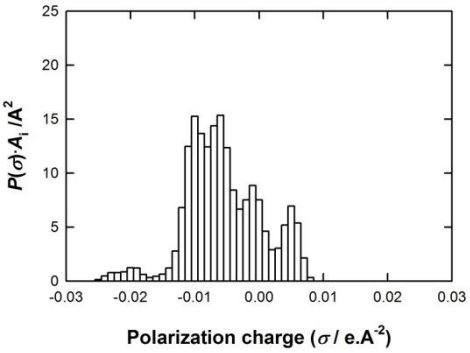
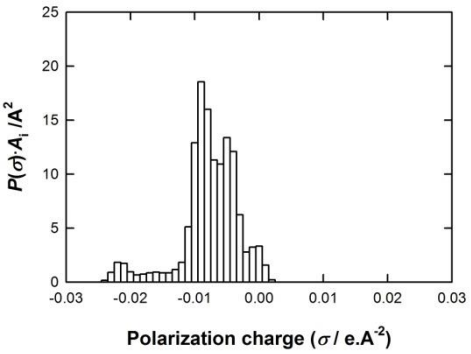
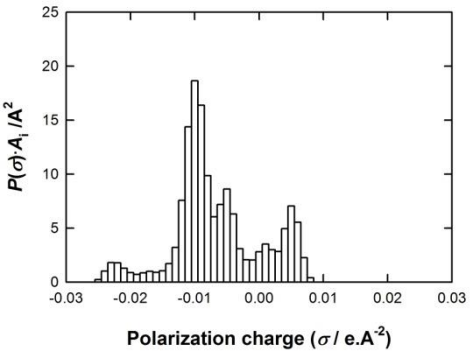


$[HN_{3\text{-}Cl\text{-}11}]^+$ 166.96



a, $[TFSI]^-$ conformer 1	b, $[TFSI]^-$ conformer 2
	
c, $[C_2Morph]^+$	d, $[C_{2\text{-}Cl}\text{-}Morph]^+$
	
e, $[C_2Pip]^+$	f, $[C_{2\text{-}Cl}\text{-}Pip]^+$
	

g, $[C_2Pyrr]^+$	h, $[C_{2\text{-}Cl}\text{-}Pyrr]^+$
	
i, $[HN_{222}]^+$	j, $[HN_{2\text{-}Cl\text{-}22}]^+$
	
k, $[HN_{211}]^+$	l, $[HN_{2\text{-}Cl\text{-}11}]^+$
	

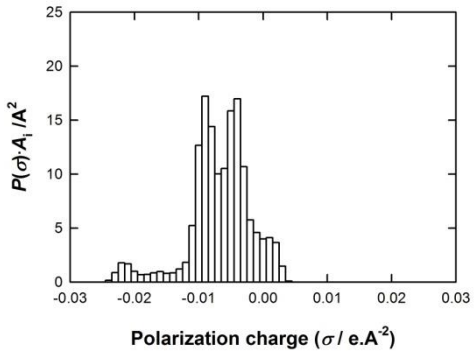
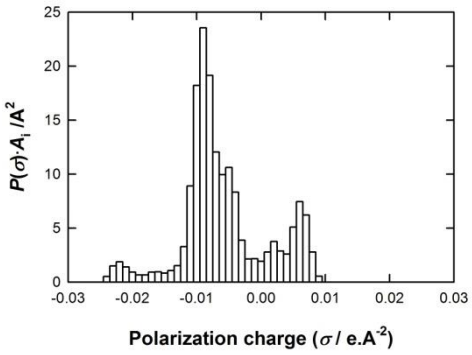
m, $[HN_{311}]^+$	n, $[HN_{3\text{-}Cl\text{-}11}]^+$
	

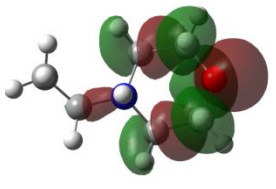
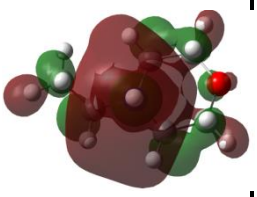
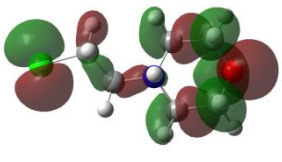
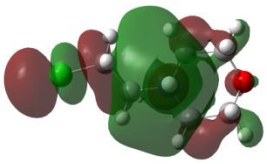
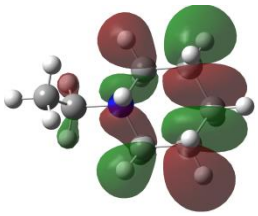
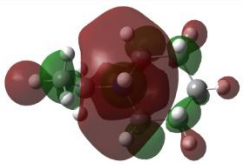
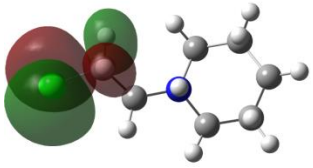
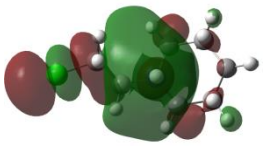
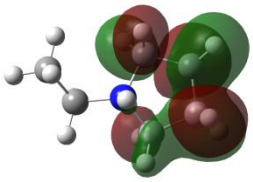
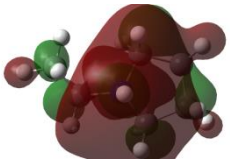
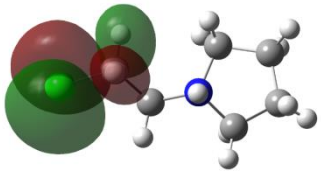
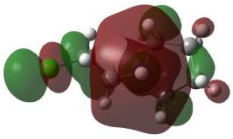
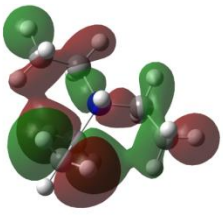
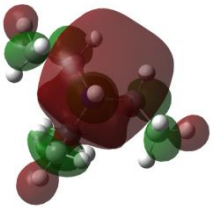
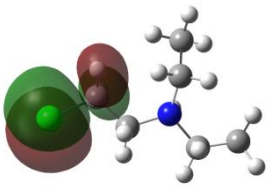
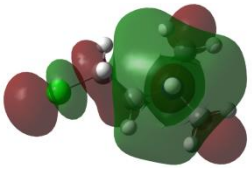
Figure S1. Sigma profiles of the TFSI anion and of the studied cations and their non-chlorinated analogues.

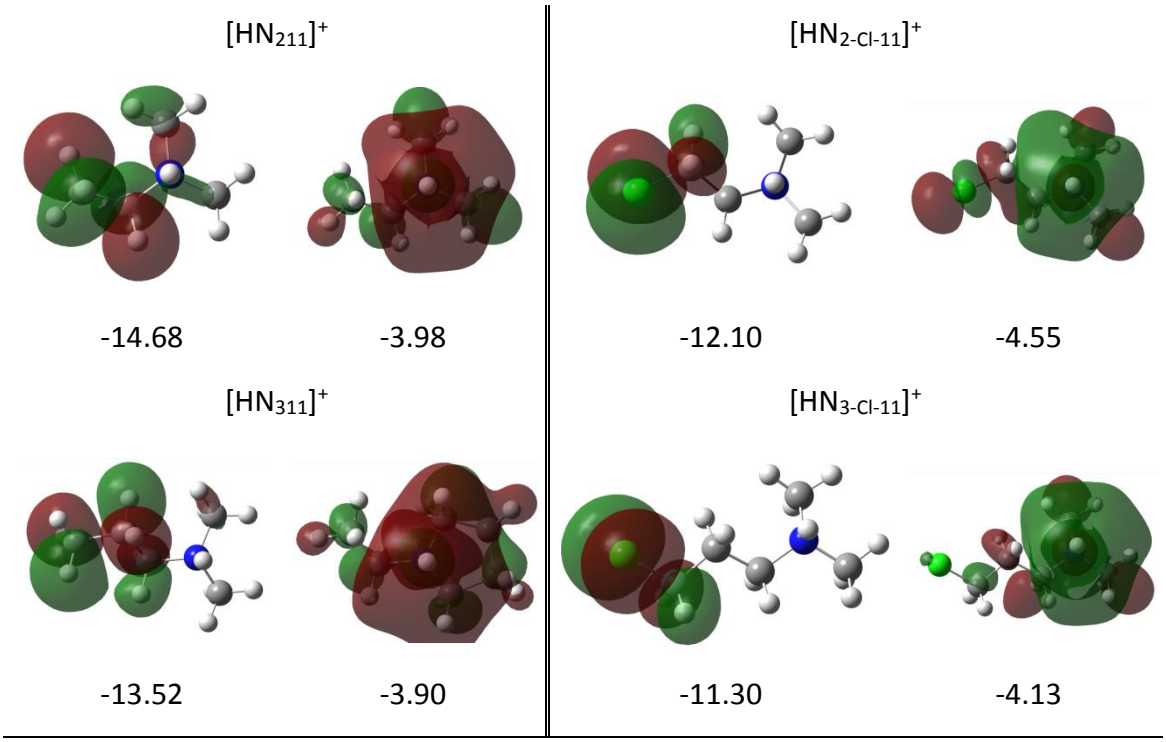
Table S2. Thermal decomposition parameters of the N-chloroalkyl functionalized PILs.

PILs	$T_{5\%onset}$ (°C)	Observed mass loss (%)	Calculated mass loss[(a)] (%)
$[C_{2\text{-}Cl}Morph][TFSI]$	280	16	15
$[C_{2\text{-}Cl}Pip][TFSI]$	314	10	15
$[C_{2\text{-}Cl}Pyrr][TFSI]$	315	12	15
$[HN_{2\text{-}Cl\text{-}22}][TFSI]$	306	16	15
$[HN_{2\text{-}Cl\text{-}11}][TFSI]$	305	17	16
$[HN_{3\text{-}Cl\text{-}11}][TFSI]$	337	14	16

[(a)] Calculated mass loss corresponding to the elimination of chloroethene ($M_{chloroethane}$=62.5 g·mol^{-1} divided by M_w of the tested PILs).

Table S3: Energy of HOMO and LUMO orbitals and their isosurface projection for N-chloroalkyl functionalized cations and their alkyl functionalized analogues.

HOMO Orbital Energy (eV)	LUMO Orbital Energy (eV)	HOMO Orbital Energy (eV)	LUMO Orbital Energy (eV)
$[C_2Morph]^+$		$[C_{2\text{-}Cl}\text{-}Morph]^+$	
			
-11.79	-3.63	-11.92	-4.32
$[C_2Pip]^+$		$[C_{2\text{-}Cl}\text{-}Pip]^+$	
			
-13.35	-3.24	-11.88	-4.07
$[C_2Pyrr]^+$		$[C_{2\text{-}Cl}\text{-}Pyrr]^+$	
			
-13.76	-3.70	-11.93	-4.21
$[HN_{222}]^+$		$[HN_{2\text{-}Cl\text{-}22}]^+$	
			
-14.27	-3.27	-11.93	-3.96



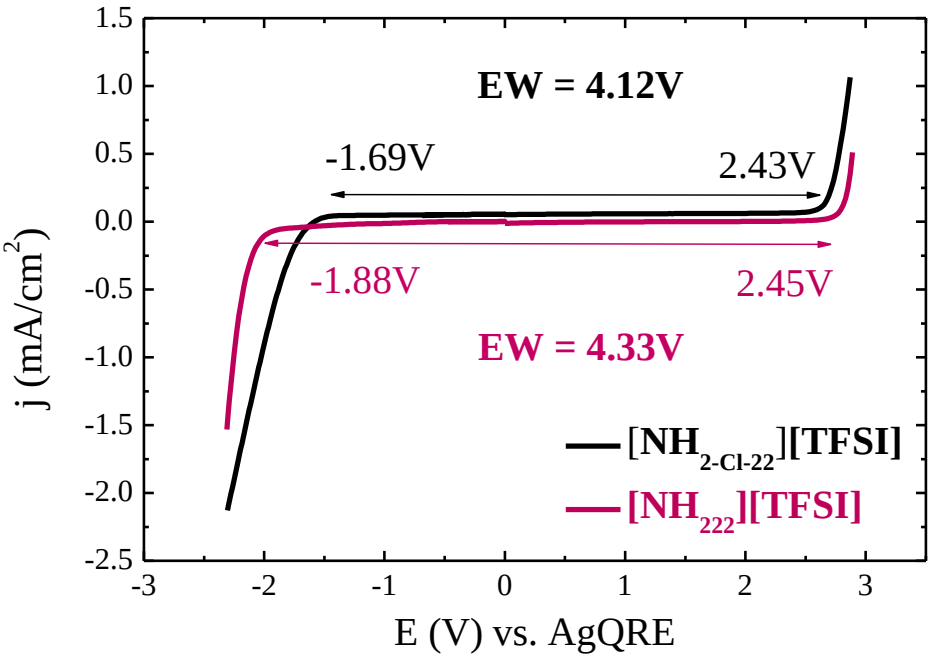


Figure S2. Comparison of electrochemical stability on glassy carbon electrode for $[HN_{2\text{-}Cl\text{-}22}][TFSI]$ and $[HN_{222}][TFSI]$ PILs ($v = 10\ mV{\cdot}s^{-1}$).