Novel Imidazolium-based Ionic Liquids with a Crown-ether Moiety

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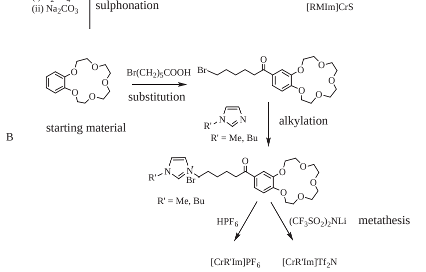
A series of novel ionic liquids comprising crown-ether functionalities in cations or anions (crowned ionic liquids) have been prepared and characterized.

Ionic liquids (ILs) as a new class of non-molecular, ionic solvents have been widely accepted as greener alternatives to classical organic solvents.[1] Nowadays, design and synthesis of functionalized ILs for being tunable to specific chemical tasks have been extensively investigated.[2] The functionalization is normally achieved by adding a functional group to the side chain of quaternary nitrogen-based cation. Introduction of a ether group on the *N*-position of the cation has resulted in a variety of publications,[3–14] among which the report on using crown ether as a functional group is still rare.[15] To our knowledge, no crown ether-involving anionic ILs have been reported. Crown ethers' macrocyclic cavity, chelate ring, macrocycle rigidity, and number and type of donor atoms can be tuned to provide a high degree of metal ion selectivity, so they are arguably the most versatile type of ion-specific extractants.[16] Incorporating these excellent properties into ILs may significantly improve the coordination of ILs with metal ions, and may therefore provide both ILs and crown ethers some promising features for the use in extraction, molecule recognition, chemical sensing, and phase-transfer catalysis or transition metal catalysis.

Here, we report the synthesis, characterization, and properties of a new series of crowned ILs. The synthetic strategies and the abbreviated names of these novel ionic liquids are summarized in Scheme 1 and Table 1.

In strategy A, monobenzo-15-crown-5 was used as starting material to prepare the anions, shown in Scheme 1. Some representative products, [RMIm]CrS (R = butyl, hexyl, octyl, benzyl), obtained from anion metathesis of imidazolium halides with sodium (monobenzo-15-crown-5)-4′-sulphonate, have been illustrated in 1–4 in Table 1. This procedure was the most widely used method to prepare ILs.[17] These ILs are named using general symbols to represent the imidazolium frameworks and using CrS to represent the crown ether anion. In principle, such a strategy makes a very big family of ILs possible by selecting different types of benzo-crown ethers as starting materials. As a typical example of preparation, monobenzo-15-crown-5 was sulfonated, then neutralized by Na_2CO_3, in accordance with the published protocol.[18] The formation of [BMIm]CrS was a simple metathesis reaction by putting certain mol of sodium salt and $[C_4mim]Cl$ into dried acetonitrile for 24 h. After the mixture was filtered, the acetonitrile was evaporated from filtrate under vacuum. The residue was further purified by silica gel column chromatography.[19] All these products (1 to 4) are viscous liquids at room temperature. The tendency of the viscosity follow the order [BMIm]CrS < [HMIm]CrS < [OMIm]CrS < $[PhCH_2MIm]$-CrS.



Scheme 1. Synthetic strategy of the novel ionic liquids comprising crown-ether functionalities.

It is reasonable to assume that [RMIm]CrS being hydrophilic are mostly due to the sulphonate anions. However the hydrophilicity may limit the applications. Introduction of hydrophobic anions is a proper way to obtain ILs without above limitation. A synthetic strategy based on appending the crown-ether group to the cations of imidazolium salts has been therefore proposed, as shown in Scheme 1. Some representative examples have been summarised in Table 1 (5 to 8). We are using the same symbol (Cr) to represent the crown-ether frameworks, and using the chemical formulas to represent anions, for example, sample 5 is marked as $[CrBIm]PF_6$. The typical example was carried out as follows. The formation of [CrBIm]Br, the precursor of ILs, was a simple substitution reaction by putting certain mol of monobenzo-15-crown-5 and $Br(CH_2)_5COOH$ into poly(phosphoric acid) (PPA), stirring at 70 °C for 4 h, then extracting with $CHCl_3$ and further evaporating in vacuum.[20] Subsequent alkylation with 1-butylimidazole was carried out at 80 °C for 24 h. Without further purification, the obtained bromide salt was treated by adding excess amount of HPF_6, or $LiTf_2N$ in water. The resulting ILs were purified by recrystallization with diethyl ether, then dried in vacuo.[19] All these products (5 to 8) are also viscous liquids at room temperature. The tendency of the viscosity follow the order $[CrBIm]Tf_2N$ < $[CrMIm]Tf_2N$ < $[CrBIm]PF_6$ < $[CrMIm]PF_6$.

DSC measurement was carried out in the temperature range from -100 to 100 °C at a heating rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$. The results are summarized in Table 1. The novel ionic liquids display only glass transition between 0 to -35 °C. For the ionic liquids containing CrS^- anion, T_g increases from -34 to -26 to -11 °C, with increasing the length of the alkyl substituent in the cation. On the other hand, for the ionic liquids containing crowned cations, T_g varys in the order, $[CrMIm]PF_6$ > $[CrBIm]PF_6$ > $[CrMIm]Tf_2N$ > $[CrBIm]Tf_2N$, indicating that the Tf_2N^- anion lowers the glass transition temperature of new ILs.

The thermal stability of the ILs was investigated with a heat-

Table 1. Properties of novel ionic liquids comprising crown-ether-functionalities

No.	IL	MW	R/R′	Anion	T_g/°C	T_{dec}/°C	Water content^a/ppm
1	[BMIm]CrS	487	R = butyl	CrS$^-$	−34	267	4800
2	[HMIm]CrS	515	R = hexyl	CrS$^-$	−26	247	3142
3	[OMIm]CrS	543	R = octyl	CrS$^-$	−11	248	2631
4	[PhCH$_2$MIm]CrS	521	R = benzyl	CrS$^-$	−19	250	2500
5	[CrMIm]PF$_6$	593	R′ = methyl	PF$_6$$^-$	0	358	1562
6	[CrBIm]PF$_6$	635	R′ = butyl	PF$_6$$^-$	−11	364	1200
7	[CrMIm]Tf$_2$N	728	R′ = methyl	Tf$_2$N$^-$	−17	327	637
8	[CrBIm]Tf$_2$N	770	R′ = butyl	Tf$_2$N$^-$	−22	328	333

R/R′, represents alkyl group. [BMIm], 1-*n*-butyl-3-methylimidazolium; [HMIm], 1-*n*-hexyl-3-methylimidazolium; [OMIm], 1-*n*-octyl-3-methylimidazolium [PhCH$_2$MIm], 1-benzyl-3-methylimidazolium; CrS, (monobenzo-15-crown-5)-4′-sulphonate; Cr, (monobenzo-15-crown-5)-4′-(1-oxohexyl) ^{a}The water content was determined using a Karl Fischer titrator and anhydrous methanol as the solvent. Duplicate measurements were performed on each sample with results agreeing to within 5%.

ing rate of 10 °C min^{-1} from 25 to 500 °C in the nitrogen flow. It can be seen from Table 1 that the thermal decomposition temperatures (T_{dec}) of the ILs containing crowned cations are generally 80–100 °C higher than those of the ILs having crowned anions. The observed T_{dec}'s are in the order, [CrMIm]PF$_6$ > [CrMIm]Tf$_2$N and [CrBIm]PF$_6$ > [CrBIm]Tf$_2$N, indicating that the ILs using PF$_6$$^-$ as anion is thermally stable than those using Tf$_2$N$^-$ as anion. One proposed decomposition mechanism involves proton abstraction to produce volatile acids from the anion and carbene derivatives of the imidazolium cation.[21,22]

NMR, SIMS-MS, and IR were used to verify the structure and composition of the ILs. It is known for the solutions that a correlation may exist between the chemical shift of the imidazolium ring protons (especially that on C2) and the hydrogen-bonding capacity of the anion.[17] Generally, more strong H-bonding species may lead to higher δ values. The ILs containing crowned anions show H-C2 shifts at 8.53–8.56, which are lower than those containing Cl$^-$ anion ([BMIm]Cl: δ 10.70, [HMIm]Cl: δ 10.54, [OMIm]Cl: δ 10.38, [PhCH$_2$MIm]Cl: δ 10.42). This phenomenon is strongly indicative of a weak capacity of the CrS$^-$ anion to be engaged in hydrogen bonds in solution with the imidazolium cations. A negative ion ($C_{14}H_{19}O_8S^-$, $m/z = 347.0806$) was found for [BMIm]CrS by secondary ion mass spectrometry (SIMS), verifying the structure and composition of novel anion. For the ILs containing crowned cations, H-C2 shift is in the order, [CrMIm]PF$_6$ (δ 8.93) < [CrMIm]Tf$_2$N (δ 9.02) and [CrBIm]PF$_6$ (δ 8.74) < [CrBIm]Tf$_2$N (δ 9.03), indicating a weaker hydrogen-bonding capacity of PF$_6$$^-$ anion than that of Tf$_2$N$^-$ anion. Since a positive ion ($C_{27}H_{41}N_2O_6^+$, $m/z = 489.2951$) was found for [CrBIm]Tf$_2$N by secondary ion mass spectrometry (SIMS), the crown ether group was believed to connect with the quaternary nitrogen.

Overall, a new family of crowned ILs has been prepared and characterized. We hope that the ILs functionalized by the size-selective nature of the crown ether may display potential utility in catalytic application as well as in separation and electrochemical sensing. The investigation on their coordination properties is being carried out.

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19 [BMIm]CrS ^{1}H NMR (300 MHz, D$_2$O, δ/ppm): 8.56 (s, 1H), 7.32 (s, 1H), 7.29–6.93 (m, 3H), 7.27 (s, 1H), 4.09 (m, 4H), 4.04 (t, 2H, $J = 7.2$ Hz), 3.80 (m, 4H), 3.73 (s, 3H), 3.63–3.58 (m, 8H), 1.69 (m, 2H), 1.16 (m, 2H), 0.77 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR (D$_2$O, δ/ppm): 148.78, 146.14, 136.29, 134.19, 121.98, 120.73, 117.88, 111.04, 108.81, 68.39, 67.94, 67.15, 66.66, 66.47, 47.80, 36.41, 29.81, 17.30, 11.20. IR (KBr, ν/cm^{-1}): 3147, 3079, 2961, 2934, 2872, 1593, 1573, 1509, 1459, 1414, 1364, 1346, 1338, 1263, 1169, 1129, 1112, 1035, 952, 939, 862, 693, 625, 611. SIMS-MS (MeOH matrix): *m/z* CrS$^-$: 347.0806. [CrBIm]Tf$_2$N ^{1}H NMR (CDCl$_3$, δ/ppm): 9.03 (s, 1H), 7.59 (d, 1H, $J = 8.1$ Hz), 7.47 (s, 1H), 7.35 (s, 1H), 7.29 (s, 1H), 6.87 (d, 1H, $J = 8.4$ Hz), 4.47–4.21 (m, 8H), 3.92 (m, 4H), 3.77 (m, 8H), 2.96 (t, 2H, $J = 6.9$ Hz), 1.95–1.76 (m, 6H), 1.43–1.33 (m, 4H), 0.96 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl$_3$, δ/ppm): 198.58, 153.11, 148.42, 135.31, 130.15, 123.09, 122.46, 122.32, 121.88, 117.61, 112.51, 111.79, 70.60, 69.86, 69.73, 68.97, 68.77, 68.63, 68.22, 49.78, 49.71, 37.33, 31.83, 29.78, 25.43, 23.17, 19.23, 13.13. IR (KBr, ν/cm^{-1}): 3150, 3115, 3084, 2959, 2939, 2875, 1676, 1597, 1566, 1516, 1460, 1432, 1354, 1334, 1272, 1192, 1132, 1057, 940, 853, 616. SIMS-MS (MeOH matrix): *m/z* [CrBIm]$^+$: 489.2951. [CrBIm]PF$_6$ ^{1}H NMR (CDCl$_3$, δ/ppm): 8.74 (s, 1H), 7.60 (d, 1H, $J = 8.7$ Hz), 7.48 (s, 1H), 7.32 (s, 1H), 7.28 (s, 1H), 6.88 (d, 1H, $J = 8.1$ Hz), 4.19 (s, 8H), 3.93 (s, 4H), 3.76 (s, 8H), 2.96 (t, 2H, $J = 6.6$ Hz), 1.89–1.75 (m, 6H), 1.39–1.32 (m, 4H), 0.95 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl$_3$, δ/ppm): 198.75, 153.23, 148.54, 135.12, 130.06, 123.06, 122.41, 122.27, 112.45, 111.78, 70.81, 70.07, 69.93, 69.16, 68.95, 68.76, 68.36, 49.75, 37.34, 31.72, 29.61, 25.43, 23.18, 19.26, 13.24. IR (KBr, ν/cm^{-1}): 3161, 3115, 3076, 2957, 2938, 2874, 1675, 1596, 1566, 1515, 1457, 1430, 1363, 1272, 1167, 1131, 1055, 941, 843, 642.

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