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Characterisation and properties of new ionic liquids with the difluoromono[1,2-oxalato(2-)-*O*,*O*′]borate anion

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Abstract

Three ionic liquids with borate anions of low symmetry, tetraethylammonium difluoromono[1,2-oxalato(2-)-*O*,*O*′]borate, 1-ethyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-*O*,*O*′]borate, and 1-butyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-*O*,*O*′]borate were synthesised and characterised by physicochemical and electrochemical measurements including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), cyclic voltammetry (CV), viscosity and conductivity measurements.

Keywords: Ionic liquids; Difluoroborates; Low symmetry; Bidentate ligands; Synthesis; Melting point; Thermal analysis; Viscosity; Electrochemical window; Conductivity

1. Introduction

Most ionic liquids (ILs) are based on the asymmetry of their bulky organic cations such as 1,3-dialkylimidazolium, tetraalkylammonium, trialkylsulfonium or alkylpyrrolidinium with different alkyl chains in combination with various inorganic or organic anions. Useful anions include electrochemically stable representatives used in lithium and lithium ion batteries such as $[PF_6]^-$, $[BF_4]^-$, $[(CF_3SO_2)_2N]^-$, $[CF_3SO_3]^-$ [1,2].

It is well known that a reduction of symmetry entails a drop in the melting point of otherwise similar substances, e.g., ethylene carbonate melts at +36.6 °C whereas the liquid range of propylene carbonate extends to −54.4 °C [3] despite its higher molar mass. Low melting points for ILs have been mainly achieved using asymmetric cations, where a correlation of low melting point and low symmetry is also often observed.

Recently, Zhou et al. reported on borates based on monodentate ligands with alkyl-, alkenyl-, and perfluoroalkyl-trifluoroborates [4–6] and Ignat'ev et al. on tris(perfluoroalkyl) trifluorophosphate anions [7]. For ILs in general cf. two recent reviews [8,9].

We report here on the synthesis, characterisation, and properties of new ILs based on the low symmetric difluoromono [1,2-oxalato(2-)-*O*,*O*′]borate-anion ($[BF_2Ox]^-$). As these borates include a bidentate ligand they can easily be structurally modified by the use of other bidentate ligands to obtain various new ILs. Members of this IL class may be useful as electrolytes in electrochemical cells such as double layer capacitors [10] or as solvents in enantioselective organic syntheses, if an optical active bidentate ligand is introduced [11].

For the tetraethylammonium salt $[TEA][BF_2Ox]$ the lower local symmetry at boron in the borate anion leads to a low melting point of about 33 °C compared to the high melting point of 382 °C for tetraethylammonium tetrafluoroborate ($[TEA][BF_4]$) [12]. Salts based on polyatomic anions of reduced symmetry and low melting points are known to show a very high solubility in many solvents in contrast to salts based on highly symmetrical ions, a feature that is important for double layer capacitors at low temperatures [10]. Combination of the $[BF_2Ox]^-$ anion with an asymmetric cation such as 1-ethyl-3-methylimidazolium ($[EMIM]^+$) further reduces the melting point, but only weakly to 18 °C.

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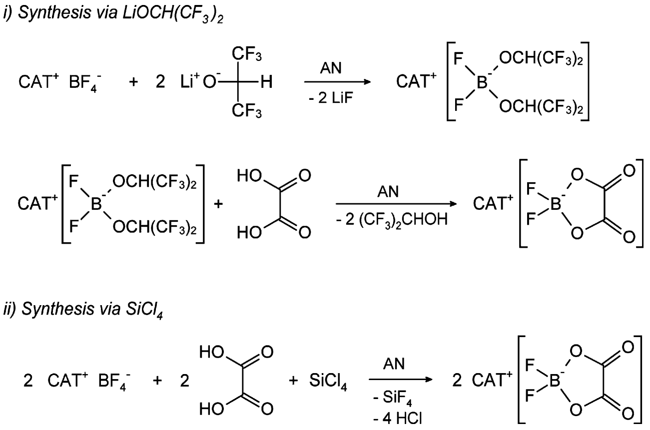

Fig. 1. Synthesis of $CAT^+[BF_2Ox]^-$: (i) cf. Ref. [13]; (ii) cf. Ref. [14].

2. Results and discussion

2.1. Synthetic aspects

Syntheses of these new ILs were carried out via established methods for adequate lithium salts disclosed in two patents [13,14]. Equations for both methods are given in Fig. 1, where CAT^+ refers to the cation ($[TEA]^+$, Li^+ or 1-butyl-3-methylimidazolium ($[BMIM]^+$)).

For route (i) only low purities for the products were obtained. Compared to that, the newer one-step synthesis (ii) via $SiCl_4$ as reactant gives much better results based on NMR-monitored purity of the product. Thus, ^1H NMR measurements of $[TEA][BF_2Ox]$ made via $LiOCH(CF_3)_2$ showed some signals of impurities, whereas no signals of any impurities were recorded in ^1H and ^{13}C NMR measurements of $[TEA][BF_2Ox]$, $[EMIM][BF_2Ox]$, and $[BMIM][BF_2Ox]$ synthesised via $SiCl_4$. ^{11}B NMR and ^{19}F NMR experiments showed small additional signals attributed to traces of $[BF_4]^-$ or $[B(Ox)_2]^-$. The percentage of unconverted $[BF_4]^-$ is rather low. For example, for $[TEA][BF_2Ox]$ ^{11}B NMR measurements have shown only 0.5% of unconverted $[BF_4]^-$ obtained by the $SiCl_4$ route, whereas the percentage of unconverted $[BF_4]^-$ was much higher (13%) via $LiOCH(CF_3)_2$ route. Long term stability measurements at 60 °C over a period of one month revealed no structural changes as confirmed by NMR-spectroscopy.

To investigate whether the melting point could be further decreased by the combination of both an asymmetric cation and an asymmetric borate anion, 1-ethyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-*O*,*O′*]borate ($[EMIM][BF_2Ox]$) and 1-butyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-*O*,*O′*]borate ($[BMIM][BF_2Ox]$) were synthesised. $[EMIM][BF_2Ox]$ was prepared by a metathesis reaction of 1-ethyl-3-methylimidazolium chloride, [EMIM]Cl, with an equimolar amount of $Li[BF_2Ox]$ according to Fig. 2. $[BMIM][BF_2Ox]$ was prepared directly from $[BMIM][BF_4]$ and anhydrous oxalic acid using the $SiCl_4$-method. Details of the syntheses are given in the experimental section.

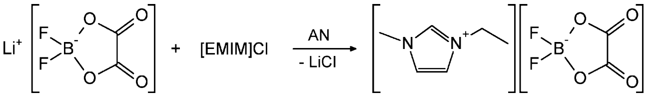

Fig. 2. Synthesis of $[EMIM][BF_2Ox]$.

2.2. Physicochemical experiments

Physicochemical properties of these salts were determined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), viscosity measurements, cyclic voltammetry (CV) experiments, and conductivity measurements. Details are given in the experimental section.

2.2.1. Thermal properties

The new ionic liquids given in Table 1 show low melting or glass transition points. For $[TEA][BF_2Ox]$ a very low melting point of 33 °C was determined. Compared to the high melting point of 382 °C for $[TEA][BF_4]$ [12], this shows that the lower symmetry of this borate anion causes a decrease of the melting point of about 350 °C. For $[EMIM][BF_2Ox]$ the melting point was 18 °C, quite similar to the melting point of 14 °C for $[EMIM][BF_4]$ [15], showing that reducing the symmetry of both the borate anion and the cation has nearly no further effect. Compared to the fluoride-free bisoxalatoborates $[TEA][B(Ox)_2]$ and $[EMIM][B(Ox)_2]$, where melting points of 118 and 56 °C are known [16], the new compounds exhibit lower melting points. $[BMIM][BF_2Ox]$ did not crystallise, but a glass transition temperature of −62 °C was observed.

TGA data (Table 1) show that the new electrolytes are thermally stable up to about 290 °C.

2.2.2. Viscosity

Viscosities obtained for the new ILs are 82 mPa s for $[TEA][BF_2Ox]$ at 40 °C, 75 mPa s for $[EMIM][BF_2Ox]$ at 25 °C, and 120 mPa s for $[BMIM][BF_2Ox]$ at 25 °C. The general effect of increasing viscosity with increasing length of the alkyl chain in 1-alkyl-3-methylimidazolium tetrafluoroborates has already been shown by Nishida et al. [15]. This is also observed for the ILs described here. Temperature dependency of viscosity η of the three ILs ($[TEA][BF_2Ox]$, $[EMIM][BF_2Ox]$, and $[BMIM][BF_2Ox]$) was found to be strongly of super-Arrhenius type [17], reflecting a high fragility. Data were fitted to the empirical Vogel–Fulcher–Tammann equation (1):

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \quad (1)$$

The expression contains three fitting parameters (η_0, B, T_0). The values for these parameters are obtained by non-linear fits of Eq. (1) to η–T datasets and are given in Table 2. The according

Table 1
TGA data of $[TEA][BF_2Ox]$, $[EMIM][BF_2Ox]$, and $[BMIM][BF_2Ox]$

Ionic liquid	T_m (°C)	T_{dec} (°C)
$[TEA][BF_2Ox]$	33	287
$[EMIM][BF_2Ox]$	18	289
$[BMIM][BF_2Ox]$	–[a]	265

[a] Glass transition temperature: −62 °C.

Table 2
Fit parameters (Vogel–Fulcher–Tammann equation) for [TEA][BF_2Ox], [EMIM][BF_2Ox], and [BMIM][BF_2Ox]

	η_0 (Pa s)	B (K)	T_0 (K)
[TEA][BF_2Ox]	0.8017 ± 0.20	461.51 ± 54	213.441 ± 6
[EMIM][BF_2Ox]	0.1483 ± 0.02	720.56 ± 18	184.571 ± 1
[BMIM][BF_2Ox]	0.041 ± 0.01	1054.97 ± 62	167.091 ± 3

plots for [TEA][BF_2Ox], [EMIM][BF_2Ox], and [BMIM][BF_2Ox], are given in Figs. 3–5.

2.3. Electrochemical experiments

2.3.1. Electrochemical stability

Electrochemical stabilities of the three salts were determined using cyclic voltammetry (CV) at glassy carbon (GC) electrodes vs. an Ag/Ag^+/Kryptofix reference electrode according to Izutsu [18,19]. CV scans were always recorded first in anodic direction. For [TEA][BF_2Ox] in acetonitrile (AN) with [TEA][BF_4] as inert salt an electrochemical window of 4.8 V was determined. Fig. 6 shows the result for the third cycle, previous cycles are nearly identical. The CV cycles for [EMIM][BF_2Ox] and [BMIM][BF_2Ox] are similar to those of [TEA][BF_2Ox] but show small additional peaks in the anodic part that can be attributed to Cl^- impurities in these ILs caused by remaining traces of [EMIM]Cl or HCl from synthesis. The electrochemical windows of [EMIM][BF_2Ox]/[TEA][BF_4]/AN and [BMIM][BF_2Ox]/[TEA][BF_4]/AN solutions were about 4.0 and 4.1 V, respectively, at GC electrodes. Parameters and results of the CV measurements are summarised in the experimental section (Table 3).

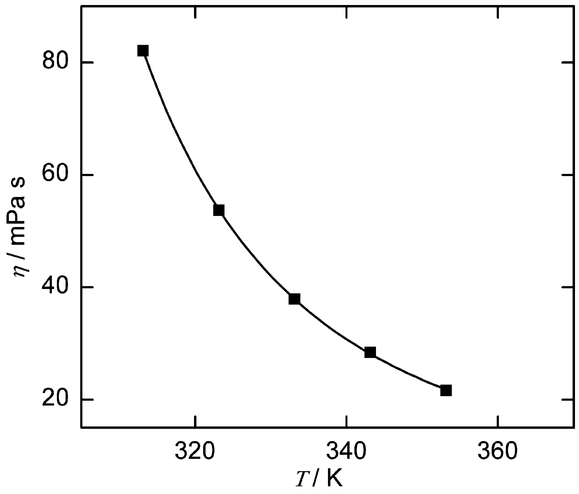

Fig. 3. Vogel–Fulcher–Tammann fit of viscosity (η) for [TEA][BF_2Ox] in the temperature (T) range of 313.15–353.15 K.

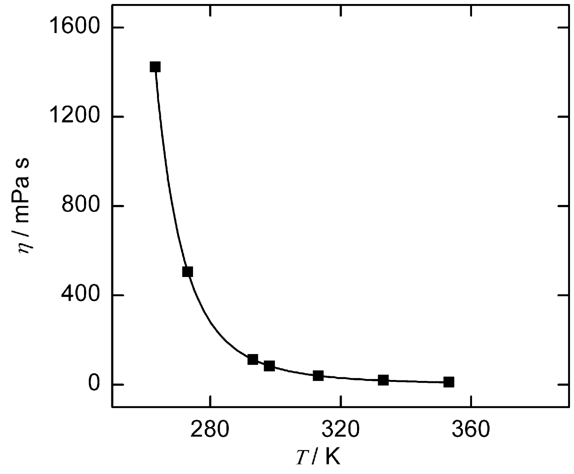

Fig. 4. Vogel–Fulcher–Tammann plot of viscosity (η) for [EMIM][BF_2Ox] in the temperature (T) range of 263.15–353.15 K.

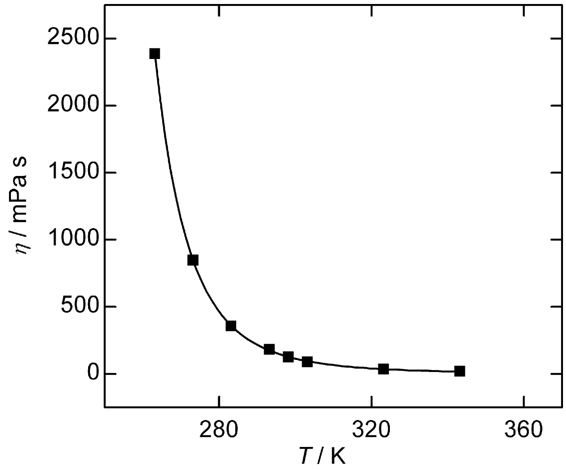

Fig. 5. Vogel–Fulcher–Tammann plot of viscosity (η) for [BMIM][BF_2Ox] in the temperature (T) range of 263.15–343.15 K.

2.3.2. Conductivity

The conductivity of a pure ionic liquid mainly depends on its viscosity, ion sizes of anions and cations, and the ion–ion interaction [20]. Similar to the influence on the viscosity of the ionic liquid, the length of the alkyl group in the 1-alkyl-3-methylimidazolium cation also influences the conductivity. The ionic liquids showed specific conductivities decreasing with increasing alkyl chain length. Conductivity measurements resulted in specific conductivities (κ) of 5.4 mS cm^{-1} for

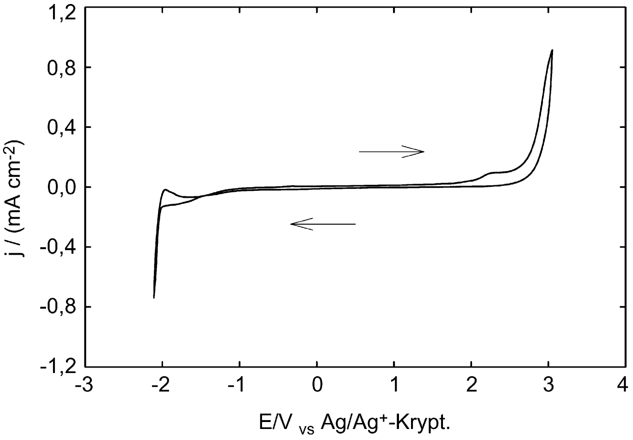

Fig. 6. CV of [TEA][BF_2Ox], third cycle. Scan rate: 5 mV s^{-1}, open-circuit potential: 0.06 V.

Table 3
Parameters of CV measurements

	[TEA][BF_2Ox]	[EMIM][BF_2Ox]	[BMIM][BF_2Ox]
Working electrode	Glassy carbon	Glassy carbon	Glassy carbon
Counter electrode	Platinum plate	Platinum plate	Platinum plate
Reference electrode	Ag/Ag^+/Kryptofix	Ag/Ag^+/Kryptofix	Ag/Ag^+/Kryptofix
Starting potential (V)	0.06	0.18	0.36
Cathodic/anodic limit (V)	−2.1/2.7	−1.5/2.5	−1.6/2.5
Electrochemical window (V)	4.8	4.0	4.1
Scan-rate (mV s^{-1})	5	5	5
Cycles	3	3	3
Electrolyte concentration	0.1 M in 1.0 M [TEA][BF_4]/AN	0.1 M in 1.0 M [TEA][BF_4]/AN	0.1 M in 1.0 M [TEA][BF_4]/AN
Temperature (°C)	20	20	20

[EMIM][BF_2Ox] and 2.5 mS cm^{-1} for [BMIM][BF_2Ox] at 25 °C. Compared to specific conductivities of [EMIM][BF_4] (14 mS cm^{-1}) and [BMIM][BF_4] (3.5 mS cm^{-1}) [15], the values for [EMIM][BF_2Ox] and [BMIM][BF_2Ox] are lower due to the larger anion size of $[BF_2Ox]^-$ with its oxalate moiety.

To conclude, three ionic liquids, [TEA][BF_2Ox] as well as the so far unknown [EMIM][BF_2Ox] and [BMIM][BF_2Ox] were synthesised. Their properties were investigated, including thermal stability, viscosity, voltage window, and conductivity. The substances may be useful as electrolytes for double layer capacitors at low temperature applications.

Furthermore compounds with similar structures appear to be easily accessible by variation of the chelating moiety in the anion opening up the way to an interesting new class of ionic liquids with many structural and thus many application possibilities.

3. Experimental

All procedures related to electrolyte preparation, electrochemical measurement, and cell fabrication were carried out in a nitrogen-filled glove box (O_2 and $H_2O < 10$ ppm) (Mecaplex). The synthesis of the new salts was also carried out under inert gas atmosphere. The following materials were used as received: lithium tetrafluoroborate ($LiBF_4$), (Stella Chemifa, battery grade); tetraethylammonium tetrafluoroborate ([TEA][BF_4]), (Merck, selectipur); silicon tetrachloride ($SiCl_4$), (Aldrich, 99.998%); anhydrous oxalic acid, (Fluka, puriss. p.a.); ethyl chloride, (Fluka, purum); butyl chloride, (Merck, for synthesis); sodium tetrafluoroborate ($NaBF_4$), (Aldrich, 98%); acetonitrile (AN) (Baker, HPLC grade); lithium hydride (LiH) (Fluka, for synthesis); *n*-hexane (Merck, p.a.); 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Merck, for synthesis); glassy carbon working electrode (Methrom, Filderstadt); platinum plate counter electrode; non-aqueous Ag/Ag^+ reference electrode, (BAS, Riverside UK), with Kryptofix®22, (Merck, for synthesis), as a cryptand for the reference electrode. Dichloromethane (Acros Organics, p.a.) was distilled prior to usage. 1-Methylimidazole (Merck, for synthesis) was distilled from KOH (Merck, p.a.). [EMIM]Cl, [BMIM]Cl, and [BMIM][BF_4] were synthesised in our lab (see below).

NMR spectra were obtained on a Bruker Avance 300 spectrometer (^{1}H at 300.1 MHz, $^{13}C\{^1H\}$ at 75.5 MHz, and ^{19}F at 282.4 MHz) and on a Bruker Avance 400 spectrometer (^{1}H at 400.1 MHz and ^{11}B at 128.4 MHz) using acetonitrile-D_3 as solvent. Chemical shifts (δ) are reported with respect to internal TMS (^{1}H, ^{13}C), CCl_3F (^{19}F), and $Et_2O\cdot BF_3$ (^{11}B), respectively. As we were not able to do elemental analyses due to the hygroscopic nature of the compounds, the purities stated here are derived from ^{11}B NMR measurements. ^{1}H NMR spectra showed no significant signals of any impurities, while the ^{13}C-satellites (representing an internal standard of 0.55% for each signal with respect to the main signal) were readily detected. From this observation it is concluded that the cations are inert during the syntheses and therefore it suffices to monitor the reactions taking place at the borate-anions by ^{11}B NMR. The sensitivity of the spectrometer to trace impurities was checked with various [TEA][BF_4]-solutions containing known amounts of [TEA][$B(Ox)_2$], showing that signals of impurities down to 0.05 mol% with respect to the main signal can be detected by the performed ^{11}B NMR measurements. For the major impurity in the new ILs, residual $[BF_4]^-$, the signal to noise ratio determined according to [21] is given too.

3.1. Synthesis and characterisation of salts

3.1.1. Synthesis of lithium 1,1,1,3,3,3-hexafluoro-2-propanolate (LiHFIP)

3.88 g LiH were suspended in 200 ml *n*-hexane at 0 °C. Then 120.0 g HFIP were added drop-wise to the LiH suspension over 4 h. During the addition of HFIP, an intense generation of gas and formation of a flocculent precipitate was observed. After stirring the reaction batch over night, the *n*-hexane was evaporated and the product was dried under vacuum at 70 °C. The raw product was sublimated twice at 70 °C under vacuum. Yield: 68.15 g (80.3%). NMR data are according to expectations, showing no impurities.

3.1.2. Synthesis of tetraethylammonium difluoromono[1,2-oxalato(2-)-O,O′]borate ([TEA][BF_2Ox]) via $LiOCH(CF_3)_2$ (Fig. 1(i))

4.88 g of [TEA][BF_4] were dissolved in AN at room temperature. After slow addition of 7.82 g LiHFIP, the solution was stirred at 60 °C for 3 h. During this time, lithium fluoride (LiF) precipitated. LiF was removed from the liquid by filtration. 2.03 g of anhydrous oxalic acid were added to the obtained filtrate and the reaction was conducted at 60 °C for 1 h with stirring. Finally, AN was evaporated at 60 °C under vacuum, yielding 4.45 g (72.4%) product.

3.1.2.1. Analysis. ^{1}H NMR (300.1 MHz, CD_3CN, TMS): δ 3.17 (8H, quartet, $J = 7.3$, $4CH_2–CH_3$), 2.8 (s, unidentified impurity), 2.2 (s, unidentified impurity), 1.2 (12H, tt, $J = 7.27$, $^{3}J_{HN} = 1.9$, $4CH_2–CH_3$).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_3CN, TMS): δ 161.0 (s, CO), 53.1 (t, $^{1}J_{CN} = 2.9$, $N–CH_2–CH_3$), 7.7 (s, CH_3).

^{11}B NMR (128.4 MHz, CD_3CN, $Et_2O{\cdot}BF_3$): δ 8.1 (s, $B(Ox)_2$, traces), 3.6 (t, $^{1}J_{BF} = 2.7$, BF_2, 87%), −0.6 (s, BF_4, 13%).

3.1.3. Syntheses of 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl)

[EMIM]Cl was synthesised according to a slightly modified literature method [22,23] from 1-methylimidazole and ethyl chloride. [BMIM]Cl was synthesised from 1-methylimidazole and butyl chloride accordingly. The raw products were recrystallised from AN three times and finally dried 5 days at high vacuum (about 1×10^{-6} mbar) yielding colourless crystals (79 and 84%, respectively). NMR data are according to expectations, showing no impurities.

3.1.4. Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$])

[BMIM][BF_4] was synthesised according to Ref. [24] from [BMIM]Cl and $NaBF_4$. A solution of 610.3 g (5.56 mol) $NaBF_4$ in 0.7 l H_2O (Millipore) was added to a stirred solution of 962.2 g (5.51 mol) [BMIM]Cl in 1.3 l H_2O. The resulting biphasic system was separated and both layers were individually extracted with dichloromethane (three times, 250 ml each). The combined dichloromethane solutions were washed with water (four times, 50 ml) and then dried with $MgSO_4$ over night. After filtration and removing the dichloromethane at reduced pressure, the product was dried for 5 days at about 1×10^{-6} mbar. A colourless liquid was obtained (1007 g, 81%). NMR data are in accordance with data published in [24], showing no impurities.

3.1.5. Synthesis of tetraethylammonium difluoromono[1,2-oxalato(2-)-O,O′]borate ([TEA][BF$_2$Ox]) via SiCl$_4$ (Fig. 1(ii))

[TEA][BF_4] (30.25 g, 0.139 mol) and anhydrous oxalic acid (12.55 g, 0.139 mol) were dissolved in 300 ml AN in a 500 ml flask. $SiCl_4$ (8.0 ml, 0.070 mol) was added drop-wise to the stirred solution over 6 h at room temperature. With the beginning of the addition of $SiCl_4$, a gas was generated. After the addition of $SiCl_4$, the reaction mixture was stirred over night. The termination of the reaction was judged by confirming that gas generation stopped completely. The next day AN was evaporated at 40–50 °C under vacuum for 20 h giving colourless crystals at room temperature (33.93 g, 91.4%).

3.1.5.1. Analysis. ^{1}H NMR (300.1 MHz, CD_3CN, TMS): δ 3.16 (4H, quartet, $J = 7.3$, $2CH_2–CH_3$), 1.20 (6H, tt, $J = 7.3$, $^{3}J_{HN} = 1.9$, $2CH_2–CH_3$).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_3CN, TMS): δ 159.6 (s, CO), 51.7 (t, $^{1}J_{CN} = 3.3$, $N–CH_2–CH_3$), 6.3 (s, CH_3).

^{11}B NMR (128.4 MHz, CD_3CN, $Et_2O{\cdot}BF_3$): δ 3.6 (t, $^{1}J_{BF} = 2.7$, BF_2, 99.5%), −0.6 (s, BF_4, 0.5%). The signal to noise ratio for the $[BF_4]^-$ signal was 207.

^{19}F NMR (282.4 MHz, CD_3CN, CCl_3F): δ −150.1 (4F, s, $^{10}BF_4$), −150.2 (4F, s, $^{11}BF_4$, 4%), −152.3 (2F, s, $^{10}BF_2$), −152.3 (2F, m, $^{11}BF_2$, 96%).

[TEA][BF_2Ox] was already mentioned in a patent [25] but apart from a melting point in the range 20–30 °C no details were given.

3.1.6. Synthesis of 1-butyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-O,O′]borate ([BMIM][BF$_2$Ox] via SiCl$_4$ (Fig. 1(ii))

The synthesis was conducted according to [TEA][BF_2Ox], (3.1.5.), using [BMIM][BF_4] (23.63 g, 0.104 mol), $SiCl_4$ (6.0 ml, 0.052 mol), and anhydrous oxalic acid (9.41 g, 0.105 mol) giving a colourless ionic liquid (26.12 g, 90.1%).

3.1.6.1. Analysis. ^{1}H NMR (300.1 MHz, CD_3CN, TMS): δ 8.59 (1H, s, C(2)H), 7.43 (1H, t, $J = 1.8$, C(4)H), 7.39 (1H, t, $J = 1.8$, C(5)H), 4.15 (2H, t, $J = 7.3$, CH_2), 3.86 (3H, s, CH_3), 1.80 (2H, quintet, $J = 7.5$, CH_2), 1.29 (2H, sextet, $J = 7.5$, CH_2), 0.88 (3H, t, $J = 7.3$, CH_3).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_3CN, TMS): δ 159.8 (s, CO), 135.8 (s, CH), 123.3 (s, CH), 121.9 (s, CH), 48.9 (s, CH_2), 35.5 (s, CH_3), 31.2 (s, CH_2), 18.6 (s, CH_2), 12.4 (s, CH_3).

^{11}B NMR (128.4 MHz, CD_3CN, $Et_2O{\cdot}BF_3$): δ 3.6 (t, $^{1}J_{BF} = 2.4$, BF_2, 96%), −0.4 (s (br), BF_4, 4%). The signal to noise ratio for the $[BF_4]^-$ signal was 20.

^{19}F NMR (282.4 MHz, CD_3CN, CCl_3F): δ −152.3 (2F, s, $^{10}BF_2$), −152.4 (2F, quartet, $^{1}J_{FB} = 2.4$, $^{11}BF_2$, 100%).

3.1.7. Synthesis of lithium difluoromono[1,2-oxalato(2-)-O,O′]borate (Li[BF$_2$Ox]) via SiCl$_4$ (Fig. 1(ii))

The synthesis was conducted according to [TEA][BF_2Ox] (Section 3.1.5), using $LiBF_4$ (13.06 g, 0.139 mol), $SiCl_4$ (8.0 ml, 0.070 mol), and anhydrous oxalic acid (12.55 g, 0.139 mol) giving colourless crystals (17.25 g, 86.3%).

3.1.7.1. Analysis. $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_3CN, TMS): δ 160.3 (*s*, CO).

^{11}B NMR (128.4 MHz, CD_3CN, $Et_2O{\cdot}BF_3$): δ 3.6 (*s*, BF_2, 98%), −0.8 (*quintet*, $^{1}J_{BF} = 4.1$, BF_4, 2%). The signal to noise ratio for the $[BF_4]^-$ signal was 190.

^{19}F NMR (282.4 MHz, CD_3CN, CCl_3F): δ −153.0 (2F, s, $^{10}BF_2$), −153.0 (2F, s, $^{11}BF_2$, 96%), −153.6 (4F, s, $^{10}BF_4$), −153.6 (4F, quartet, $^{1}J_{FB} = 4.1$, $^{11}BF_4$, 4%).

3.1.8. Synthesis of 1-ethyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-O,O′]borate ([EMIM][BF$_2$Ox]) (Fig. 2)

In a typical experiment, an equimolar mixture of Li[BF_2Ox] and [EMIM]Cl in AN was stirred at room temperature for 15 h.

The resulting suspension was filtered through a PTFE membrane filter (0.2 μm) to remove LiCl. The collected solution was evaporated at 60 °C under vacuum for 15 h yielding a colourless ionic liquid. To depress LiCl contamination in the raw product, the obtained liquid was redissolved in CH_2Cl_2, refluxed for a few hours, and then stored in a freezer over night. The resulting suspension was filtered through a PTFE filter (0.2 μm). After evaporation, the product was dried at 90 °C under vacuum for 15 h to obtain [EMIM][BF_2Ox], a colourless liquid at room temperature (85.4%).

3.1.8.1. Analysis. ^{1}H NMR (300.1 MHz, CD_3CN, TMS): δ 8.60 (1H, s, C(2)H), 7.42 (1H, t, $J = 1.8$, C(4)H), 7.37 (1H, t, $J = 1.7$, C(5)H), 4.18 (2H, q, $J = 7.3$, CH_2), 3.84 (3H, s, CH_3), 1.44 (3H, t, $J = 7.3$, CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN, TMS): δ 159.7 (s, CO), 135.5 (s, CH), 123.3 (s, CH), 121.9 (s, CH), 44.5 (s, CH_2), 35.4 (s, CH_3), 14.2 (s, CH_3).

^{11}B NMR (128.4 MHz, CD_3CN, $Et_2O\cdot BF_3$): δ 3.6 (*t*, $^1J_{BF} = 2.4$, BF_2, 96%), −0.5 (s (s), BF_4, 4%). The signal to noise ratio for the $[BF_4]^-$ signal was about 3000.

^{19}F NMR (282.4 MHz, CD_3CN, CCl_3F): δ −149.7 (4F, s, $^{10}BF_4$), −149.8 (4F, s, $^{11}BF_4$, 9%), −152.1 (2F, s, $^{10}BF_2$), −152.2 (2F, m, $^1J_{FB} = 2.2$, $^{11}BF_2$, 91%).

3.2. Physicochemical experiments

3.2.1. TGA measurements

Thermogravimetric measurements were conducted on a Netzsch TG 209 with the samples placed in an open Al_2O_3 pan and heated from room temperature up to 720 K at a heating rate of 10 K min^{-1} under argon atmosphere. The temperature of decomposition (T_{dec}) was assigned to the TG-onset temperature, which is the intersection of the baseline below their decomposition temperature with the tangent to the mass loss vs. temperature plots in the TGA experiment.

3.2.2. DSC measurements

Differential scanning calorimetry (DSC) of [TEA][BF_2Ox] and [BMIM][BF_2Ox] was carried out on a Netzsch DSC 205 Phoenix under argon atmosphere at samples hermetically sealed in Al pans and cooled to −60 and −150 °C, respectively, and then reheated at a cooling and heating rate of 10 K min^{-1}. The melting points (T_m) were determined from the DSC thermograms during the programmed reheating steps.

Differential scanning calorimetry of [EMIM][BF_2Ox] was carried out on a Mettler DSC 30 under nitrogen atmosphere at samples hermetically sealed in Al pans. As the samples did not crystallise during the maximum possible cooling time of the DSC, they were cooled to −30 °C over night under inert atmosphere in a freezer and then inserted into the DSC precooled at −20 °C. After cooling to −50 °C at 2 K min^{-1}, the samples were reheated with a heating rate of 2 K min^{-1}. The melting point (T_m) was determined from the DSC thermograms during the programmed reheating steps.

3.2.3. Viscosity measurements

The viscosity measurements were carried out using an Anton Paar MCR 100 Rheometer under argon atmosphere at controlled temperature.

3.3. Electrochemical experiments

3.3.1. Electrolyte preparation for CV measurements

An appropriate amount of [TEA][BF_2Ox], [EMIM][BF_2Ox], or [BMIM][BF_2Ox] was dissolved in a 1.0 mol kg^{-1} solution of the inert salt [TEA][BF_4] (Merck, selectipur) in AN (Merck, selectipur), resulting in a clear solution with a concentration of 0.1 mol l^{-1} for the investigated ILs. The water content of AN (35 ppm) was determined by Karl Fischer titration (Mettler DL18). As reference electrode, a nonaqueous Ag/Ag$^+$–Kryptofix electrode was used according to Izutsu, but slightly modified by us [18,19,26]. A solution consisting of 0.205 mol l^{-1} $AgNO_3$ and 0.410 mol l^{-1} Kryptofix 22 was prepared in AN. 25 μl of this Ag$^+$/Kryptofix solution and 1 ml of the electrolyte solution were mixed and filled into the glass vessel (BAS, Riverside UK) of the reference electrode. The reference solution is separated from the electrolyte solution in the measurement cell by a vycor cap (BAS). Finally, a blank Ag-wire (BAS) was immersed into the solution of the reference electrode.

3.3.2. Electrochemical stability

The electrochemical stability was measured using cyclic voltammetry. All measurements were carried out in a specially designed cell with a three-electrode arrangement. The working electrode was a carefully polished glassy carbon disc electrode (surface area: 0.0707 cm^2), the counter electrode was a platinum plate. The reference electrode was made as described above. CV measurements were performed with an Autolab PGSTAT30 controlled by GPES Software from Eco Chemie B.V., Utrecht, The Netherlands. Parameters of CV measurements are summarised in Table 3.

3.3.3. Electrolytic conductivity

Conductivity of [EMIM][BF_2Ox] and [BMIM][BF_2Ox] were measured at 25 °C and at frequencies of 3.5, 5.0, 6.5, and 8.0 kHz with a symmetrical Wheatstone bridge with a Wagner earth, a frequency generator, and a decade resistor from Tettex (Zurich). [EMIM][BF_2Ox] and [BMIM][BF_2Ox] were filled in specially designed, gas tight conductivity cells in the glove box. The measurement cells containing ~3 ml of the ionic liquid were thermostatted to ±3 mK [27–29]. Temperature was checked with a F-250 MkII thermometer from Automatic Systems Laboratories (Milton Keynes, UK).

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