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## Supplementary Material

### **1,3-Di(alkoxy)imidazolium-based Ionic Liquids: Improved Synthesis and Crystal Structures**

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## Materials

The starting material 1-hydroxyimidazole 3-oxide,[35321-46-1], is easily accessible by cyclisation of glyoxime and formaldehyde under the addition of hydroxylamine hydrochloride. It was prepared according to literature procedures.<sup>S1,S2,S3</sup> All above mentioned chemicals required for the preparation of [35321-46-1], dimethyl sulfate (99.8%), diethyl sulfate (98 %), NaHCO<sub>3</sub>, FeCl<sub>3</sub> and FeCl<sub>3</sub>•6 H<sub>2</sub>O, were purchased from Sigma Aldrich.

Lithium bis(trifluoromethylsulfonyl)amide (certified purity 99.3%) was purchased from Shanghai Sinofluoro Scientific Co., Ltd.

HCl (37%), and HNO<sub>3</sub> (65%) were purchased from Carl Roth GmbH. & Co. KG.

## Instrumentation and Analytical Data

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DPX 300 (magnetic flux density: 7.04925 Tesla). <sup>19</sup>F NMR spectra were recorded on a Bruker Avance II+ 600 MHz. IR spectra were recorded on a Perkin Elmer Spectrum GX FT-IR instrument and on a Bruker alpha FT-IR spectrometer in ATR mode.

Thermogravimetric analyses were performed on a TGA-7 (Perkin Elmer, Norwalk, Ct., USA) using approximately 2 to 10 mg samples weighed into a platinum-pan (50 µL). Dry nitrogen was used as purge gas (sample purge: 20 mL min<sup>-1</sup>, balance purge: 40 mL min<sup>-1</sup>). The weight calibration was performed with a 100-mg calibration standard. The temperature calibration was performed with magnetic calibration standards of nickel (magnetic transition temperature: 354°C) and Alumel (magnetic transition temperature: 163°C). Heating rate: 10 K min<sup>-1</sup>.

Differential scanning calorimetry measurements were performed on a Perkin-Elmer Diamond DSC system equipped with a Pyris intracooler 1P. Samples of approximately 1–3 mg were accurately weighed (0.0005 mg) using a UM3 ultramicrobalance (Mettler, Greifensee, Switzerland) into aluminium pans (25 mL) and heated at a rate of 10 K min<sup>-1</sup> starting at -20 °C. Dry nitrogen was used as the purging gas (20 mLmin<sup>-1</sup>) The temperature calibration was performed with pure benzophenone (mp 48.0 °C) and caffeine (236.2°C), and energy calibration with indium (purity 99.999%, mp 156.6°C, heat of fusion 28.45 J g<sup>-1</sup>).

Elemental analysis:

Fe was measured using ICP-OES (Horiba-Jobin Yvon ACTIVA) at the wavelength of 259.940 nm, and after disintegration with nitric acid (65%) using standard plasma and calibration conditions.

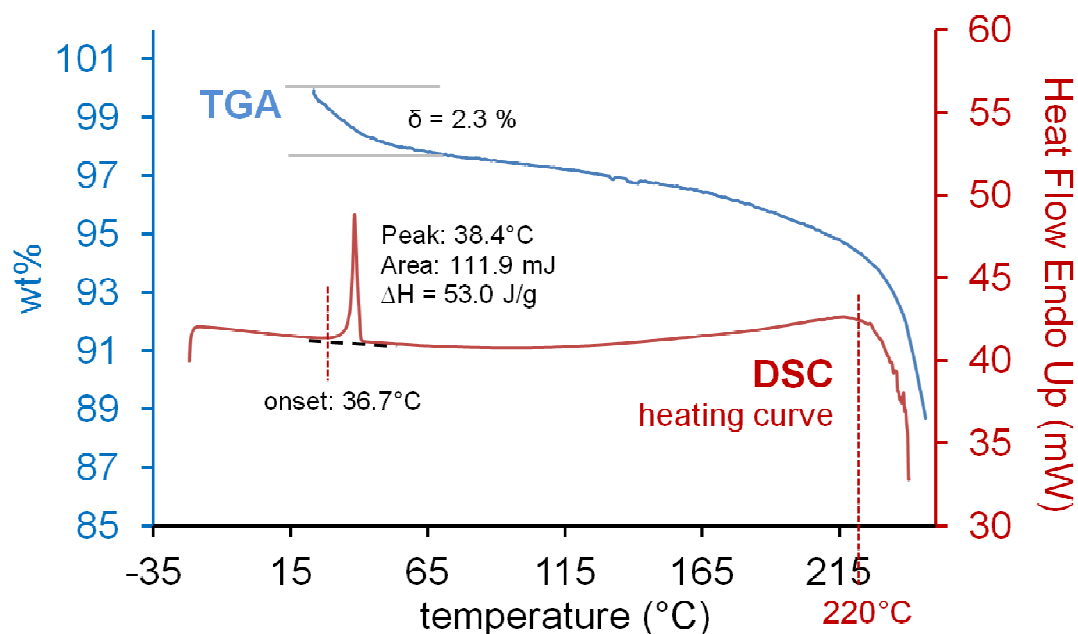
The respective contents of C, H, N, S, and Cl were determined at the Microanalytical Laboratory of the University of Vienna, Faculty of Chemistry, Währingerstr. 42, A-1090 Vienna, Austria (<http://www.univie.ac.at/Mikrolabor/>).

## Characterisation of 1,3-dialkoxyimidazolium derivatives

### 1,3-Dimethoxyimidazolium tetrachloroferrate (**1a**)

Using dimethyl sulfate (37.9 mL, 0.41 mol), 1-hydroxyimidazole 3-oxide (20.0 g, 0.20 mol), NaHCO<sub>3</sub> (16.69 g, 0.20 mol), H<sub>2</sub>O (12.5 mL), FeCl<sub>3</sub>·6 H<sub>2</sub>O (54.02 g, 0.20 mol) and HCl (37%, 16.5 mL, 0.20 mol) results in a brown magnetic phase that crystallizes after separation and solvent removal, mp 37°C, dec. ≈200°C. For a distinct separation of the magnetic phase, the reaction mixture has to be concentrated to subsequently allow adequate separation.  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 3128, 2950, 1552, 1454, 1438, 1373, 1140, 1087, 1013, 937, 839, 797, 702, 649, 615, 576. Anal. Calc. for C<sub>5</sub>H<sub>9</sub>Cl<sub>4</sub>FeN<sub>2</sub>O<sub>2</sub>: C 18.38, H 2.78, N 8.57. Found: C 18.59, H 2.68, N 8.43%. As expected, the substance shows paramagnetic response in the liquid state. The hydrochloric acidic aqueous phase from the separation step is scarcely coloured, due to a salting out effect. In contrast, a yellow-coloured, iron-containing aqueous phase is generated by adding water to the pure tetrachloroferrates as the mutual solubility is higher between these two phases. An iron content of 5.1 wt% was determined in the aqueous phase of 1:1 mixtures with **1a**.

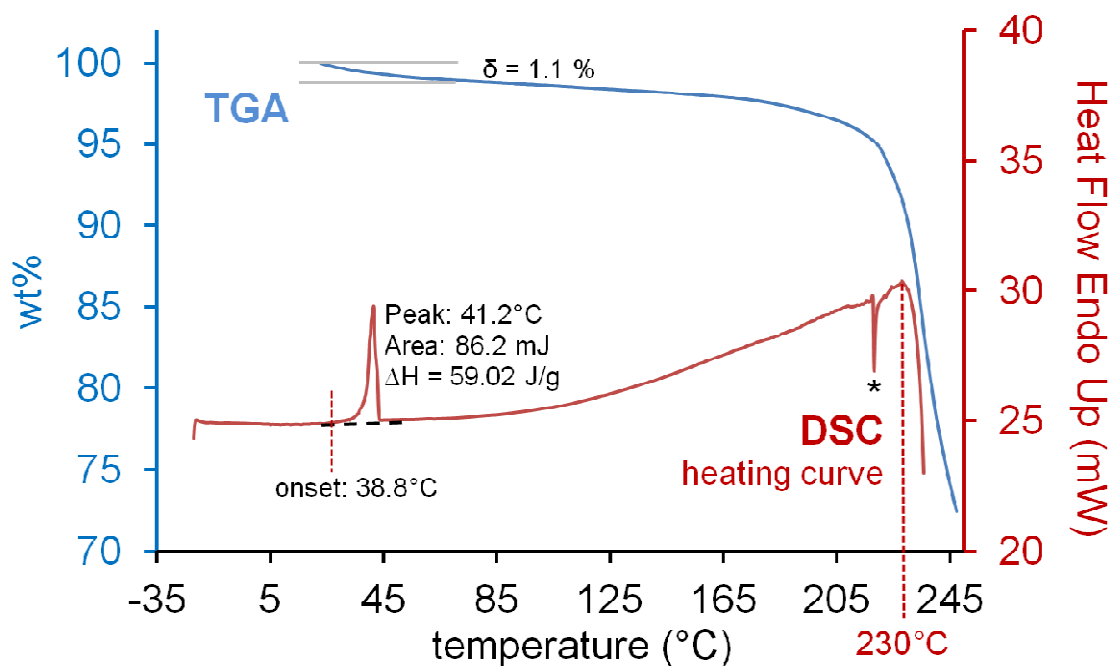
Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC): The DSC curve shows a single melting endotherm at 36.7 °C (extrapolated onset-temperature). The decomposition of the substance is indicated by the change of the baseline at around 220 °C (exothermic), which correlates well with a strong mass loss in the TGA signal. A mass loss of about 2% in the initial part of the TGA curve (20 to about 60°C) indicates the presence of some volatiles in the sample.



### 1,3-Diethoxyimidazolium tetrachloroferrate (**1b**)

Using diethyl sulfate (52.7 mL, 0.40 mol), 1-hydroxyimidazole 3-oxide (20.0 g, 0.20 mol), NaHCO<sub>3</sub> (16.79 g, 0.20 mol), H<sub>2</sub>O (30 mL), FeCl<sub>3</sub>·6 H<sub>2</sub>O (54.02 g, 0.20 mol) and HCl (37%, 16.5 mL, 0.20 mol) results in a brown magnetic subcooled melt after separation and solvent removal. The magnetic phase segregates immediately from the reaction mixture and can be separated effectually. The subcooled melt was forced to crystallize by freezing in liquid nitrogen. After rewarming, the substance remained solid at room temperature providing seed crystals for a further crystallization, which contained single crystals suitable for x-ray measurements, mp 39°C, dec. ≈200°C.  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 3135, 2989, 1552, 1474, 1444, 1397, 1192, 116, 1085, 998, 919, 857, 800, 711, 612, 591. Anal. Calc. for C<sub>7</sub>H<sub>13</sub>Cl<sub>4</sub>FeN<sub>2</sub>O<sub>2</sub>: C 23.69, H 3.69, N 7.89. Found: C 24.96, H 3.59, N 7.33%. As expected, the substance shows paramagnetic response in the liquid state. The hydrochloric acidic aqueous phase from the separation step is scarcely coloured, due to a salting out effect. In contrast, a yellow-coloured, iron-containing aqueous phase is generated by adding water to the pure tetrachloroferrates as the mutual solubility is higher between these two phases. An iron content of 1.7 wt% was determined in the aqueous phase of 1:1 mixtures with **1b**.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC): A single melting endotherm is recorded 38.8 (extrapolated onset-temperature) and the decomposition (exothermic) starts at about 230 °C, which is accompanied by a strong mass loss (TGA signal). A weak mass change of about 1% is recorded at the very beginning of the TGA curve due to the presence of some volatiles in the sample.



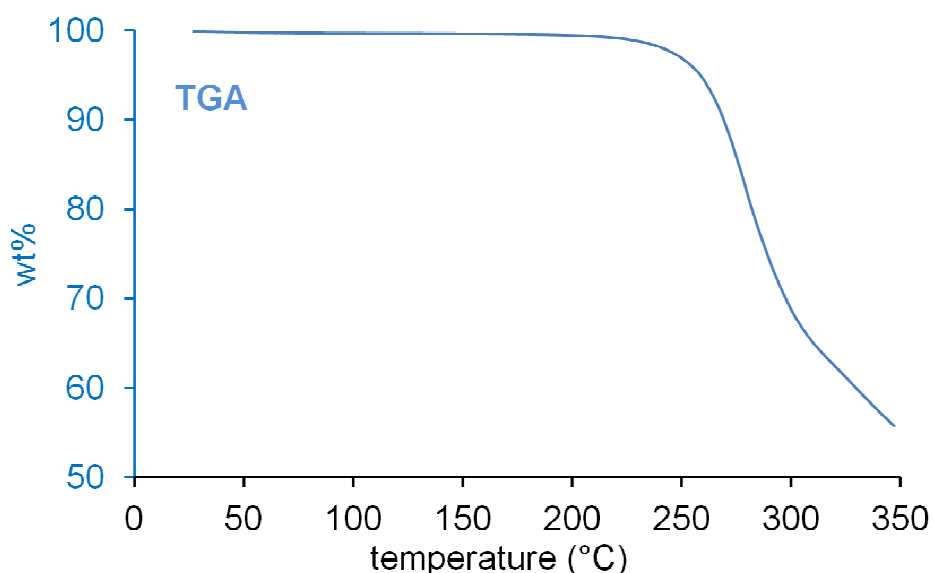
\*rupture of the capsule

*1,3-Dimethoxyimidazolium bis(trifluoromethylsulfonyl)amide (3a)* [951021-03-7]

Pathway A (**3a,A**)

Using dimethyl sulfate (56.9 mL, 0.60 mol), 1-hydroxyimidazole 3-oxide (30.0 g, 0.30 mol), NaHCO<sub>3</sub> (25.2 g, 0.30 mol), H<sub>2</sub>O (20 mL), FeCl<sub>3</sub>·6 H<sub>2</sub>O (81.02 g, 0.30 mol), HCl (37%, 24.6 mL, 0.30 mol) and LiNTf<sub>2</sub> (103.3 g, 0.36 mol) results in a yellow liquid (90.2 g, 73.5%).  $[\alpha]_D^{20}$  1.425. No solidification until -25°C, dec. ≈220°C.  $v_{\max}$  (neat)/cm<sup>-1</sup> 3140, 1559, 1458, 1348, 1179, 1133, 1053, 1014, 944, 790, 764, 741, 706, 654, 612.  $\delta_H$  (*d*<sub>6</sub>-DMSO, 300 MHz) 4.26 (s, 6H, OCH<sub>3</sub>), 8.20 (s, 2H), 10.27 (s, 1H).  $\delta_C$  (*d*<sub>6</sub>-DMSO, 75 MHz) 69.6, 117.2, 119.7 (q, *J*<sub>C-F</sub> 322), 129.6.  $\delta_F$  (*d*<sub>6</sub>-DMSO, 600 MHz) 78.8 (s, 6F). Anal. Calc. for C<sub>7</sub>H<sub>9</sub>F<sub>6</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C 20.54, H 2.22, N 10.27, S 15.63. Found: C 20.44, H 2.115, N 10.00, S 15.97%. Fe 1.8 ppm ± 0.4 ppm.

Thermogravimetric analysis (TGA): Below about 250 °C no change in sample mass is recorded indicating the absence of any volatiles. Above this temperature a clear mass loss is observed due to the thermal decomposition of the compound.



Pathway B (**3a,B**)

Using dimethyl sulfate (37.9 mL, 0.41 mol), 1-hydroxyimidazole 3-oxide (20.0 g, 0.20 mol), NaHCO<sub>3</sub> (16.8 g, 0.20 mol), H<sub>2</sub>O (12.5 mL), HCl (37%, 16.5 mL, 0.20 mol) and LiNTf<sub>2</sub> (57.4 g, 0.20 mol) results in a yellow liquid (81.9 g, 73.8%).  $[\alpha]_D^{20}$  1.425. No solidification until -25°C.  $v_{\max}$  (neat)/cm<sup>-1</sup> 3137, 1556, 1456, 1346, 1328, 1176, 1132, 1051, 1013, 943, 789, 740, 706, 653, 611, 569, 509.  $\delta_H$  (*d*<sub>6</sub>-DMSO, 300 MHz) 4.26 (s, 6H, OCH<sub>3</sub>), 8.24 (s, 2H), 10.30 (s, 1H).  $\delta_C$  (*d*<sub>6</sub>-DMSO, 75 MHz) 69.5, 117.1, 119.6 (q, *J*<sub>C-F</sub> 320), 129.6. Anal. Calc. for C<sub>7</sub>H<sub>9</sub>F<sub>6</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C 20.54, H 2.22, N 10.27, S 15.63. Found: C 20.35, H 2.36, N 10.27, S 14.68%. Cl 0.1 mg Cl/g IL.

*1,3-Diethoxyimidazolium bis(trifluoromethylsulfonyl)amide (3b)* [1017254-66-8]

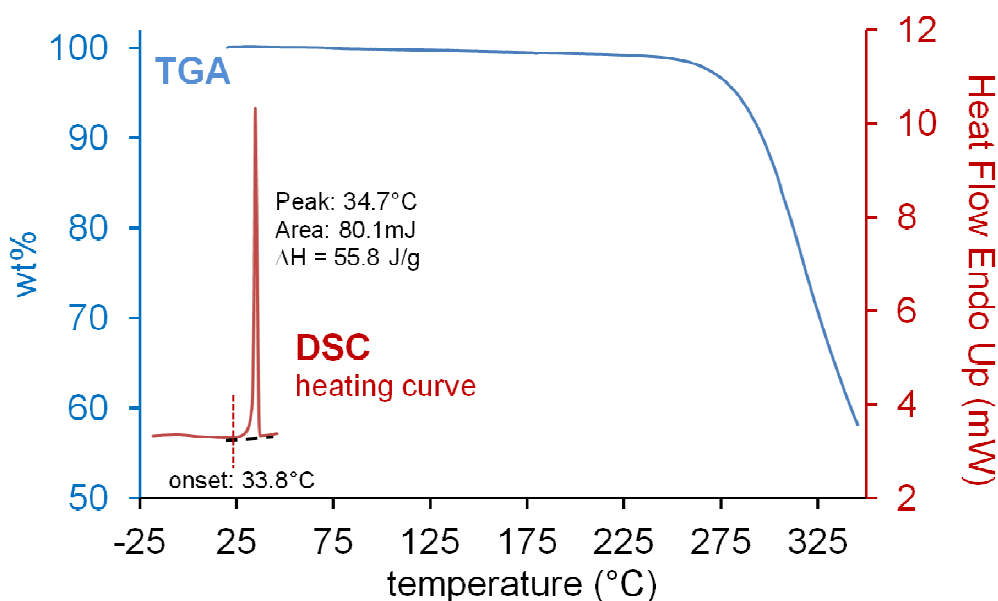
Pathway A (**3b,A**)

Using diethyl sulfate (158.0 mL, 1.20 mol), 1-hydroxyimidazole 3-oxide (60.0 g, 0.60 mol), NaHCO<sub>3</sub> (50.4 g, 0.60 mol), H<sub>2</sub>O (55 mL), FeCl<sub>3</sub> anhydrous (97.3 g, 0.60 mol), HCl (37%, 49.2 mL, 0.60 mol) and LiNTf<sub>2</sub> (206.6 g, 0.72 mol) results in light brown crystals (181.3 g, 69.1%), mp 31.7°C.  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3119, 1557, 1480, 1397, 1351, 1335, 1185, 1137, 1053, 1007, 867, 826, 764, 742, 725, 633, 607.  $\delta_{\text{H}}$  (*d*<sub>6</sub>-DMSO, 300 MHz) 1.33 (t, *J* 7.0, 6H, CH<sub>2</sub>CH<sub>3</sub>), 4.51 (q, *J* 7.1, 4H, CH<sub>2</sub>CH<sub>3</sub>), 8.25 (s, 1H), 8.26 (s, 1H), 10.27 (s, 1H).  $\delta_{\text{C}}$  (*d*<sub>6</sub>-DMSO, 75 MHz) 12.7, 78.3, 117.8, 119.5 (q, *J*<sub>C-F</sub> 322), 130.3. Anal. Calc. for C<sub>9</sub>H<sub>13</sub>F<sub>6</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C 24.72, H 3.00, N 9.61, S 14.63. Found: C 24.83, H 3.02, N 9.50, S 14.95%. Cl 0.04 mg Cl/g IL

Pathway B (**3b,B**)

Using diethyl sulfate (52.7 mL, 0.41 mol), 1-hydroxyimidazole 3-oxide (20.0 g, 0.20 mol), NaHCO<sub>3</sub> (16.8 g, 0.20 mol), H<sub>2</sub>O (12.5 mL), HCl (37%, 16.5 mL, 0.20 mol) and LiNTf<sub>2</sub> (60.29 g, 0.21 mol) results in light brown crystals (71.3 g, 81.5%). mp 34°C, dec. ≈ 230°C.  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3117, 1556, 1479, 1397, 1350, 1335, 1182, 1136, 1051, 1006, 866, 825, 790, 764, 741, 724, 606, 568, 512.  $\delta_{\text{H}}$  (*d*<sub>6</sub>-DMSO, 300 MHz) 1.33 (t, *J* 7.0, 6H, CH<sub>2</sub>CH<sub>3</sub>), 4.51 (q, *J* 7.0, 4H, CH<sub>2</sub>CH<sub>3</sub>), 8.26 (s, 1H), 8.27 (s, 1H), 10.27 (s, 1H).  $\delta_{\text{C}}$  (*d*<sub>6</sub>-DMSO, 75 MHz) 12.8, 78.3, 117.8, 119.5 (q, *J*<sub>C-F</sub> 322), 130.3. Anal. Calc. for C<sub>9</sub>H<sub>13</sub>F<sub>6</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C 24.72, H 3.00, N 9.61, S 14.63. Found: C 24.72, H 3.38, N 14.48, S 14.48%. Cl 2.3 mg Cl/g IL.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC): The melting endotherm is recorded at 33.8 °C (extrapolated onset temperature) and the TGA experiment indicates that the sample is thermally stable below 250 °C. Above this temperature strong decomposition takes place associated with a distinct mass loss.



References

- <sup>S1</sup> K. Hayes, *J. Heterocycl. Chem.* **1974**, *11*, 615.  
<sup>S2</sup> G. Laus, J. Stadlwieser, W. Kloetzer, *Synthesis* **1989**, *10*, 773.  
<sup>S3</sup> I. Suzuki, I. Erdelmeier, J.-C. Yadan, I. Pelisson, *WO 2008006824 A1*.