RSC Advances

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One-pot synthesis of symmetric imidazolium ionic liquids N,N-disubstituted with long alkyl chains

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Chemicals

Glyoxal (40 wt% in water), Oxalic acid (98%, 144-62-7), and 1-octylamine (99+%, 111-86-4) were purchased from Acros Organics (Geel, Belgium). 1-Decylamine (98%, 2016-57-1) was purchased from TCI Europe (Zwijndrecht, Belgium). 1-hexadecylamine (94%, 143-27-1) and 1-octadecylamine (≥85%, 124-30-1) were obtained from Merck (Heverlee, Belgium). 1-hexylamine (99%, 111-26-2) and nitric acid (70 wt% in water, 7697-37-2) were bought from Sigma-Aldrich (Diegem, Belgium). 1-Dodecylamine (98%, 124-22-1) and 1-tetradecylamine (98%, 2016-42-4) were purchased from Janssen-Chemica (Beerse, Belgium). Acetic acid, glacial (100%, 64-19-7), hydrochloric acid (37 wt% in water, 7647-01-0) and formaldehyde (36 wt% in water, 50-00-0) were obtained from Fisher Scientific Limited (Loughborough, UK). Petroleum ether (b.p. 40-65 °C, technical grade) and acetonitrile (≥99.8%) were obtained from VWR (Heverlee, Belgium). Petroleum ether was distilled prior to use to remove high boiling residues. All other chemicals were used as received without further purification.

Materials and instrumentation

Nuclear magnetic resonance spectra were performed on a spectrometer (Bruker Avance 400) operating at a ^{1}H frequency of 400 MHz. Fourier transform infrared spectra were recorded with a resolution of 2 cm^{-1} on a spectrometer (Bruker Vertex 70) in ATR mode (Bruker Platinum ATR module). TGA and DSC analysis were carried out on a TA Instruments TGA Q500 and a TA Instruments DSC Q2000 respectively, in aluminium sample pans with a heating/cooling rate of 10 °C min^{-1} operating under a nitrogen flow of 60 mL min^{-1}. Ionic liquids were pre-dried for 60 min at 80 °C prior to the TGA measurement. Vacuum measurement were carried out with a digital manometer (Pfeiffer TPG 201). Disposable funnel filters (Chemrus® disposable filter funnel, PP body with PE fritted disk, 18 mL, 25 mm Ø, 10 µm pore Ø) were used for the sample filtration (with exception of the fluoride samples, which melted PP plastics).

Experimental

Synthetical procedure 1: Synthesis of 1,3-di(alkyl)imidazolium acetate with alkyl-chains up to 12 carbons. In a closed vial with a septum equipped with a magnetic stirrer (800 rpm), an amine (2 eq, 20 mmol) is cooled down in a ice-bath. To the amine, it is slowly added a mixture of acetic acid (1.5 eq, 15 mmol, 0.90g) and formaldehyde (36% w/w, 1eq, 10mmol, 0.83g) premixed in a second closed vial (46.5:53.5 v/v formaldehyde:acetic acid). After the addition the sample is removed from the ice bath and stirred for 30 minutes. Then, glyoxal (40% w/w, 1 eq, 10 mmol, 1.115 mL) is added and the reaction is stirred at room temperature overnight. The crude reaction mixture is then dissolved in acetonitrile/petroleum ether and transferred to a separating funnel. The acetonitrile layer (40mL) is then washed with petroleum ether until the petroleum ether layer remains colourless (3x 40mL). The acetonitrile is then removed via a rotatory evaporator. To fully remove acetonitrile traces, the dry oil is dissolved in a small volume of methanol (10 ml) and then dried via a rotatory evaporator (3x). The dry oil is then further dried under a vigorous flow of air at 90 - 100 °C until the excess of acetic acid is fully stripped. The product was characterised via ^{1}H NMR, ^{13}C NMR, FTIR, TGA, and DSC.
Synthetical procedure 2: Synthesis of 1,3-Di(tetradecyl)imidazolium. In a vial containing a magnetic stirrer (800 rpm) closed with a septum, 1-tetradecylamine (2eq, 20 mmol, 4.27g) is added. To the amine, it is added a mixture of acetic acid (1.5eq, 15mmol, 0.90g) and formaldehyde (36% w/w, 1eq, 10mmol 0.83g) premixed in another closed vial (46.5:53.5 v/v formaldehyde : acetic acid). After the addition the sample is stirred for 30 minutes; then, glyoxal (40% w/w, 1eq, 10mmol, 1.115mL) is slowly added and the reaction is stirred at room temperature overnight. The following day the crude reaction mixture is diluted with methanol (3mL) and left to react for other 24h. The solution is then dried via rotatory evaporation. The crude reaction mixture is then dissolved in acetonitrile/petroleum ether and transferred to a separating funnel. The acetonitrile layer (40mL) is then washed with petroleum ether until the petroleum ether layer remains colourless (3x 40mL). The acetonitrile is then removed via a rotatory evaporator. To fully remove acetonitrile traces, the dry oil is dissolved in a small volume of methanol (10 ml) and then dried via a rotatory evaporator (3x). The dry oil is then further dried under a vigorous flow of air at 90 - 100 °C until the excess of acetic acid is fully stripped. The product was characterised via ^{1}H NMR, ^{13}C NMR, FTIR, TGA, and DSC.
Synthetical procedure 3: Synthesis of 1,3-Di(hexadecyl)imidazolium. In a vial containing a magnetic stirrer (800 rpm) closed with a septum, a solution of an 1-hexadecylamine (2eq, 20 mmol, 4.83g) in toluene (10mL) is cooled down in an ice bath. To the amine, it is slowly added and a mixture of acetic acid (1.5eq, 15mmol, 0.90g) and formaldehyde (36% w/w, 1eq, 10mmol 0.83g) premixed in another closed vial (46.5:53.5 v/v formaldehyde:acetic acid). After the addition the sample stirred for 30 minutes. Then, glyoxal (1eq, 10mmol, 1.115mL) is added and the reaction is stirred at room temperature overnight. The following day toluene is removed via a rotatory evaporator and then the crude is dissolved in methanol (10 mL). The solution is centrifuged, filtered and the solvent removed via a rotatory evaporator. The dry oil is then further dried under a vigorous flow of air at 90 - 100 °C until the excess of acetic acid is fully stripped. The product was characterised via ^{1}H NMR, ^{13}C NMR, FTIR, TGA, and DSC.
Synthetical procedure 4: Hydrochloric acid metathesis. The hydrochloric acid is sufficiently acidic (pKa = -8.0) to fully push the metathesis process. Unfortunately, hydrochloric acid has a low boiling point (b.p. -84.9 °C) with respect to water (b.p. 100 °C) and acetic acid (b.p. 118 °C) and therefore it cannot be isolated via acetic acid evaporation. Hence, the 1,3-di(alkyl)imidazolium chloride

were synthesized via phase separation in its pure form. The synthesised chloride ILs are soluble in water, but they can be salted out via increasing the ionicity of the aqueous layer. Acetic acid was therefore removed via metathesis with a concentrated solution of hydrochloric acid. The hydrochloric acid excess was removed via evaporation under a flow of air. The 1,3-di(alkyl)imidazolium acetate salt (1 mmol) was contacted to hydrochloric acid (36 wt% in water, 2 mL) in a sample vial, and then the biphasic system was shook (2 h). The procedure was repeated three times and then the organic layer was dried under a flow of air, heating the sample above of the material melting point to favour the complete exsiccation.

Synthetical procedure 5: Nitric acid metathesis The nitric acid is sufficiently acidic (pKa = -1.4) to fully push the metathesis process. Unfortunately, nitric acid has a low boiling point (b.p. 83 °C) with respect to water (b.p. 100 °C) and acetic acid (b.p. 118 °C) and therefore it cannot be isolated via acetic acid evaporation. Hence, the 1,3-di(alkyl)imidazolium nitrate were synthesized via phase separation in a pure form. Because the synthesised nitrate ILs are not soluble in water, the residual acetic acid and nitric acid can be removed via rinsing with water. The 1,3-di(alkyl)imidazolium acetate salt (1 mmol) was dissolved in water (10 mL, 30mL for 1,3-di(hexadecyl)imidazolium). Then, nitric acid (65 wt% in water, 2 eq. 2 mmol, 0.13 mL) was added to the solution. After the addition of nitric acid, a water-insoluble product surfaced. After 48 hours, the insoluble salt was filtered, rinsed with water and recovered with an organic solvent (DCM was used in relation to its higher stability to oxidation agents with respect of ethers. MTBE could be also used but it was potentially unstable and therefore discontinued). The organic solvent was removed via a rotary evaporator, heating the sample above of the salt melting point to favour the complete exsiccation.

Synthetical procedure 6: Oxalate evaporation metathesis. The oxalic acid is sufficiently acidic (pKa = 1.25) to push to completion the metathesis process. Additionally, oxalic acid has a high boiling point (b.p. 365 °C) and a reduced solubility. Therefore, it can be isolated via both evaporation and precipitation. The 1,3-di(alkyl)imidazolium hydroxalate were synthesized quantitatively in a pure form via acetic acid evaporation. The 1,3-di(alkyl)imidazolium acetate salt (1 mL) was dissolved with an excess of oxalic acid (1.2-2 eq). The acetic acid was dried via a rotary evaporator at high vacuum above of the melting point of the mixture (below 0.1 mbar). The excess of oxalic acid could be then removed via sublimation by heating the sample at low pressure (below 0.1 mbar).

Synthetical procedure 7: Oxalate precipitation metathesis. The imidazolium hydroxalate salt (0.5 g) was dissolved in 20mL of deionized water. To favour the salt dissolution the aqueous solution was heated up to favour the sample homogenization (50-70 °C). When the salt was fully dissolved, an excess of the desired calcium salt was added (1.5-2 eq). The reaction was stirred over 2 h at room temperature (22 °C). After that the reaction had taken place, the sample was filtered through a filter funnel (10 um) and a syringe filter (2 um) in order to fully remove any particulate present in solution. The aqueous solution was dried under a flow of air overnight. To verify the reacion completion, the product was characterised via ^{1}H NMR and ^{13}C NMR.

Analytical procedure 1: TGA calorimetry analysis. Thermo-gravimetric analysis was carried out using aluminium sample pans filled with about 10 mg of the ionic liquid in analysis. The analysis was carried out via pre-drying the sample at 80 C for 2 h and then analysis the sample with a ramped temperature analysis from 25 to 500 °C with a step of 10 C min^{-1}. Decomposition onset point was determined via the calculation of the intercept between the tangent at the 1% of weight loss with the line tangent ant the first steepest point of the decomposition curve.

Analytical procedure 2: DSC calorimetry analysis. Calorimetric analysis was carried out via scanning the sample in a pocked hermetic pan to allow water desorption during the first heating cycle. The analysis was carried out between 0 and 150 C with a scan step of 10 C min^{-1}, with a waiting time at the boundary temperatures of 5 min. If the analysis was not reproducible the analysis was repeated with a heating scan step of 10 C min^{-1}, a cooling scan step of 5 C min^{-1}, and a waiting time at the upper boundary temperature of 10 min. If not even under this condition it resulted reproducible the temperature at the upper boundary temperature was adjusted to 20 min. The scanning temperature range was eventually adjusted where needed after the first analysis.

Analytical procedure 3: Foaming properties analysis. Preliminary foaming properties analysis were carried out following an ASTM standard via a Bartsch foam test with a capped graduated cylinder (100 mL). The sample in analysis was dissolved in a concentration of 0.1% w/v of surfactant in 40 mL of deionized water. The solution was gently poured into the graduated cylinder. The cylinder was then capped and inversed 10 times with a rate of 0.5 turn s^{-1}. The volume of the foam produced was immediately measured and after 1 minute. These data were used to estimate the surfactants foamability and foam stability.

Characterisation

Top layer of the rection directed to the synthesis of 1,3-di(butyl)imidazolium acetate (i.e. 1,3,5-tributylhexahydro-1,3,5-triazine).

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.91 (3 H, t, J 7.20), 1.17 - 1.59 (4 H, m), 2.27 - 2.52 (2 H, m), 3.04 - 3.54 (2 H, m).

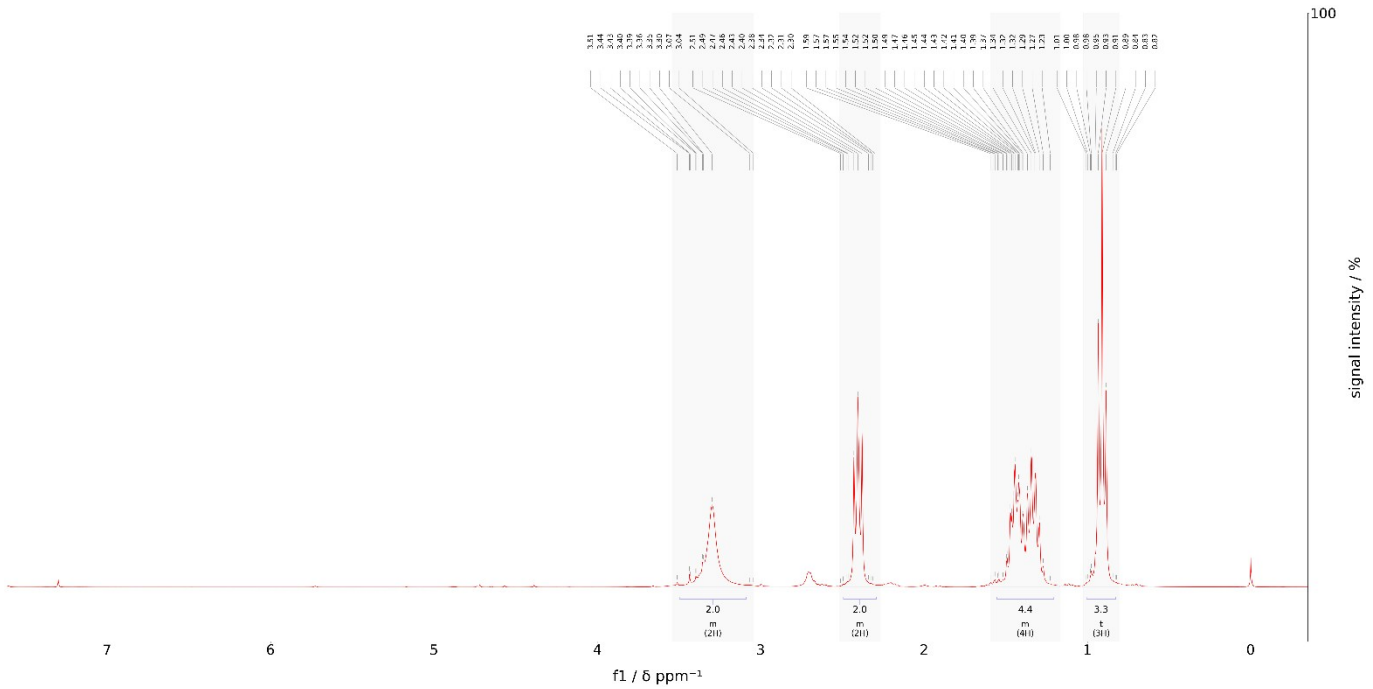

Figure S 1. ^{1}H NMR of the top layer after the addition of the formaldehyde-acetic acid mixture in the reaction for the synthesis of 1,3-di(butyl)imidazolium acetate in deuterochloroform.

1,3-Di(octyl)imidazolium acetate.

The synthesis was carried out following the general procedure with 1-octylamine (99%, 25.654g, 20.065mL, 0.2 mol), formaldehyde (36.5-38%, 8.34g, 7.65mL, 0.1mol), acetic acid (99.9%, 9.01g, 8.59mL, 0.15mol), glyoxal (40%, 14.51g, 11.15mL, 0.1mol). Isolated yield 34.94g, 92 % (≈0.5 eq of residual acetic acid). Pale to dark orange oil. Decomposition temperature: 223 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.87 (6 H, t, J 6.45), 1.29 (24 H, dt, J 19.11, 4.48), 1.88 (4 H, p, J 7.28, 7.27), 2.02 (3 H, s), 4.34 (4 H, t, J 7.40), 7.10 (2 H, d, J 1.59), 11.67 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 176.7, 139.6, 121.2, 49.9, 31.7, 30.3, 29.0, 29.0, 26.2, 23.7, 22.6, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 2955, 2924, 2856, 1701, 1580, 1466, 1379, 1251, 1165, 1045, 1000, 875, 771, 723, 650, 610, 445.

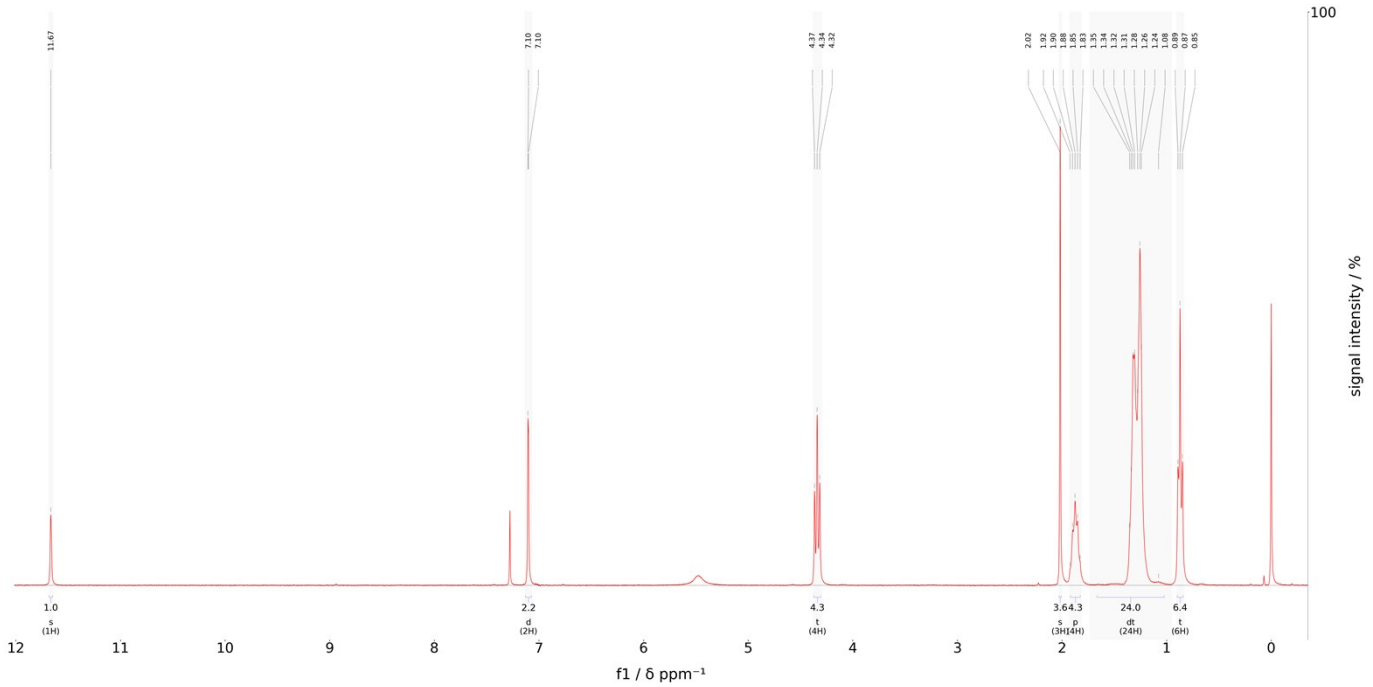

Figure S 2. ^{1}H NMR of 1,3-Di(octyl)imidazolium acetate in deuterochloroform.

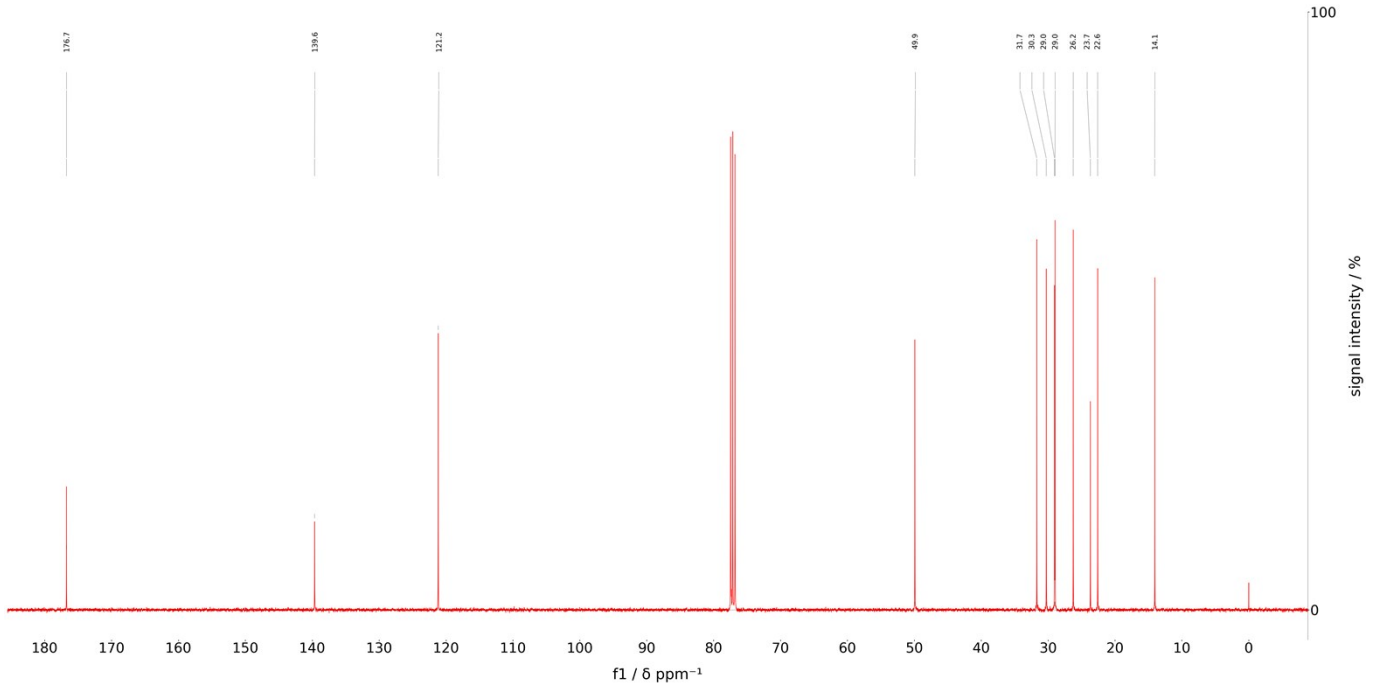

Figure S 3. ^{13}C NMR of 1,3-Di(octyl)imidazolium acetate in deuterochloroform.

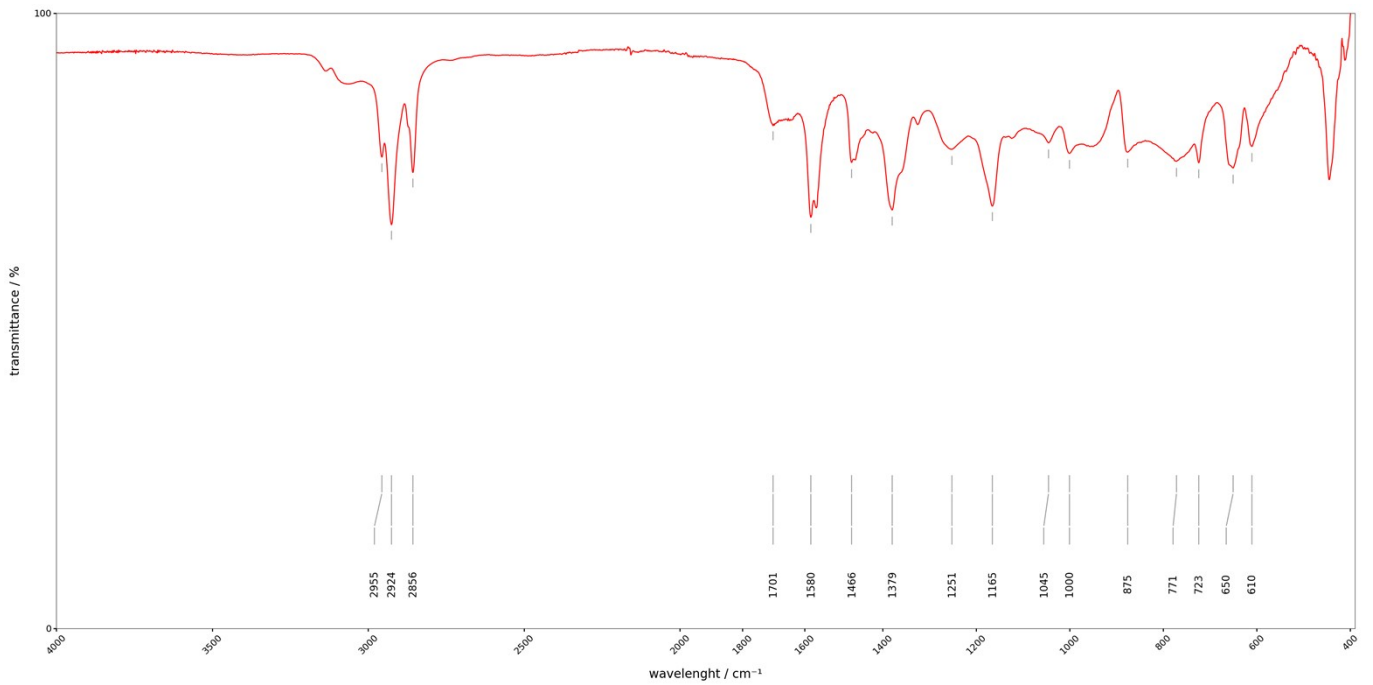

Figure S 4. FTIR of 1,3-Di(octyl)imidazolium acetate.

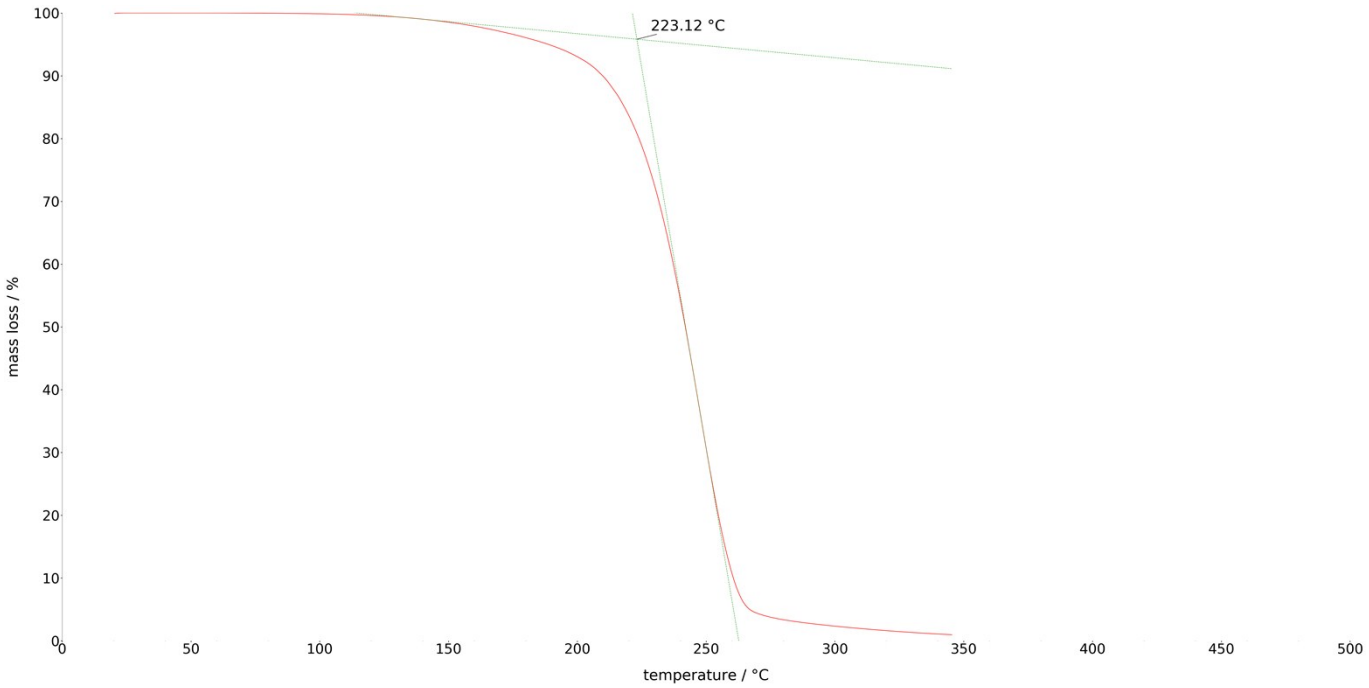

Figure S 5. TGA of 1,3-Di(octyl)imidazolium acetate in an alluminum pan.

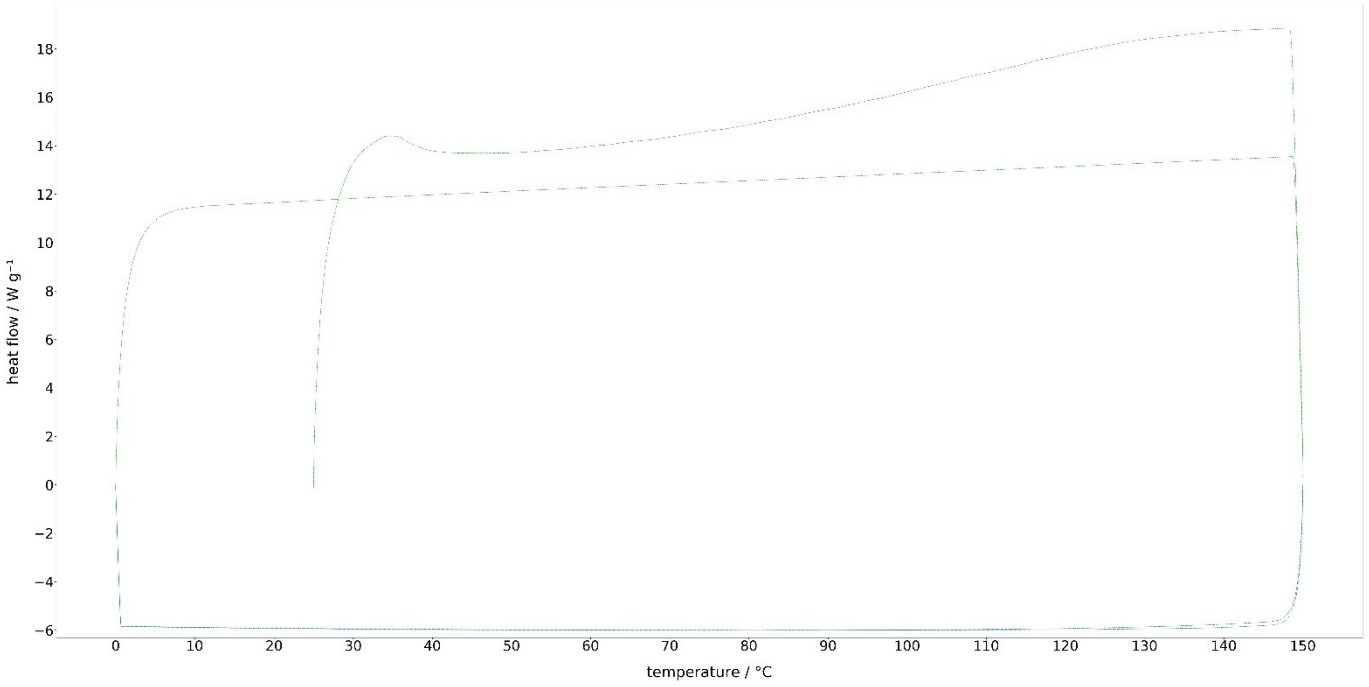

Figure S 6. DSC of 1,3-Di(octyl)imidazolium acetate.

1,3-Di(octyl)imidazolium nitrate.

The synthesis was carried out following the general procedure with 1,3-di(octyl)imidazolium acetate (0.8061 g, 2.29 mmol). Isolated yield 0.8200 g, 100 %. Orange viscous oil. Decomposition temperature: 285 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.83 - 0.91 (6 H, m), 1.23 - 1.36 (20 H, m), 1.89 (4 H, dq, J 14.98, 7.85, 7.46), 4.26 (4 H, t, J 7.41), 7.26 (2 H, d, J 1.68), 10.17 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 137.2, 122.4, 50.1, 31.7, 30.3, 29.0, 28.9, 26.2, 22.6, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3135, 3089, 3039, 2955, 2924, 2855, 1744, 1671, 1564, 1465, 1334, 1162, 1122, 1070, 1039, 951, 869, 829, 770, 723, 657, 646, 585, 557, 550, 540, 532, 515, 509, 501, 491, 484, 480, 469, 465, 460, 448, 442, 437, 431, 425, 420, 414, 403.

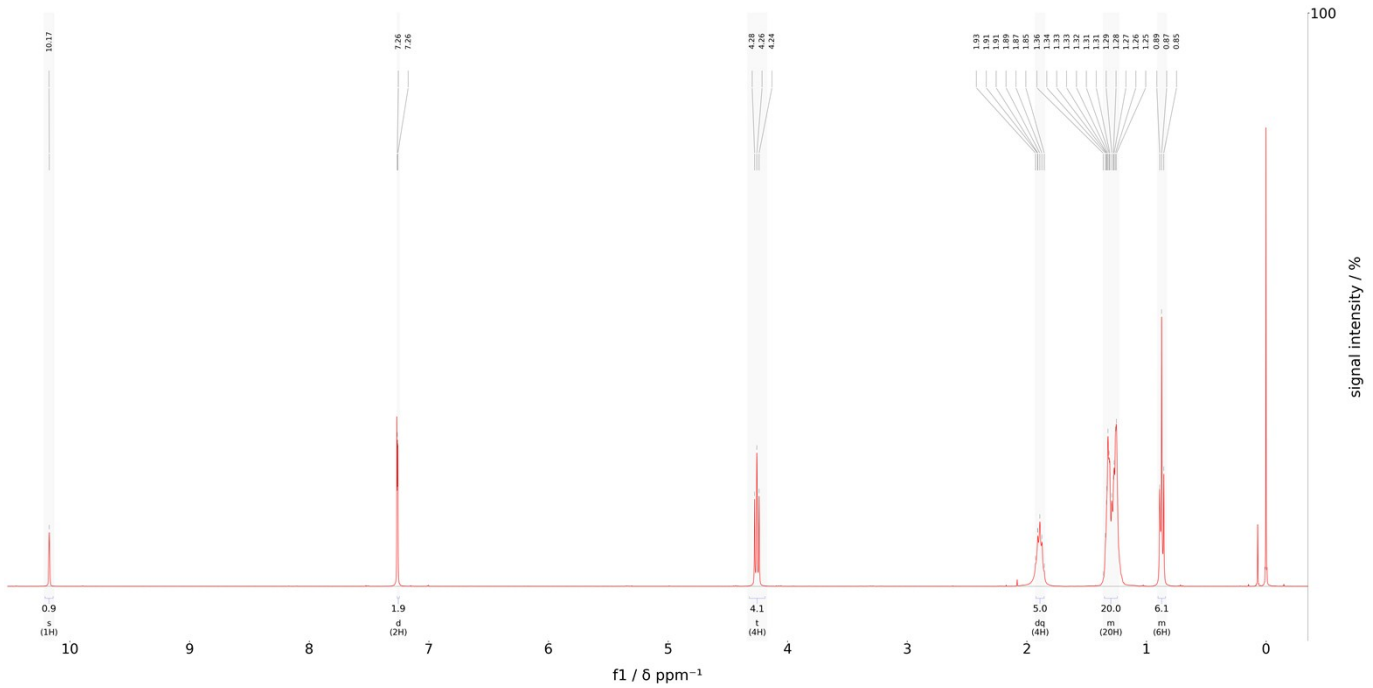

Figure S 7. ^{1}H NMR of 1,3-Di(octyl)imidazolium nitrate in deuterochloroform.

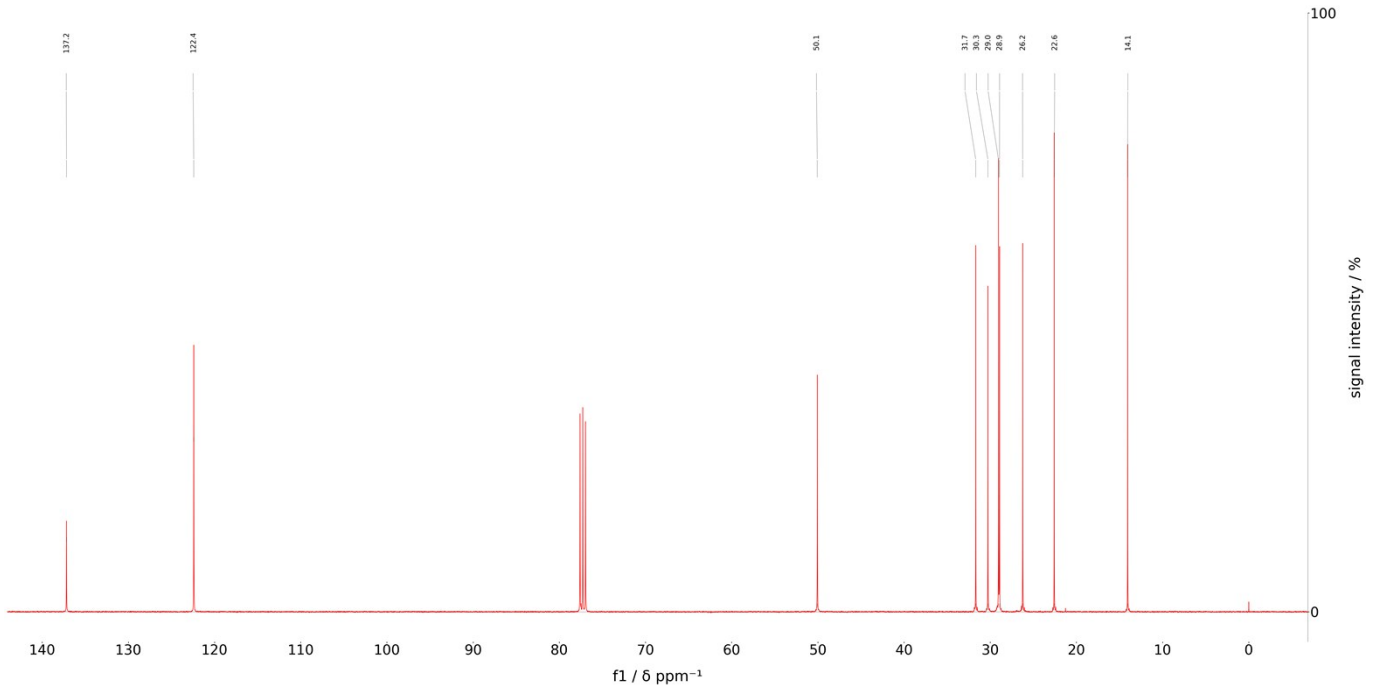

Figure S 8. ^{13}C NMR of 1,3-Di(octyl)imidazolium nitrate in deuterochloroform.

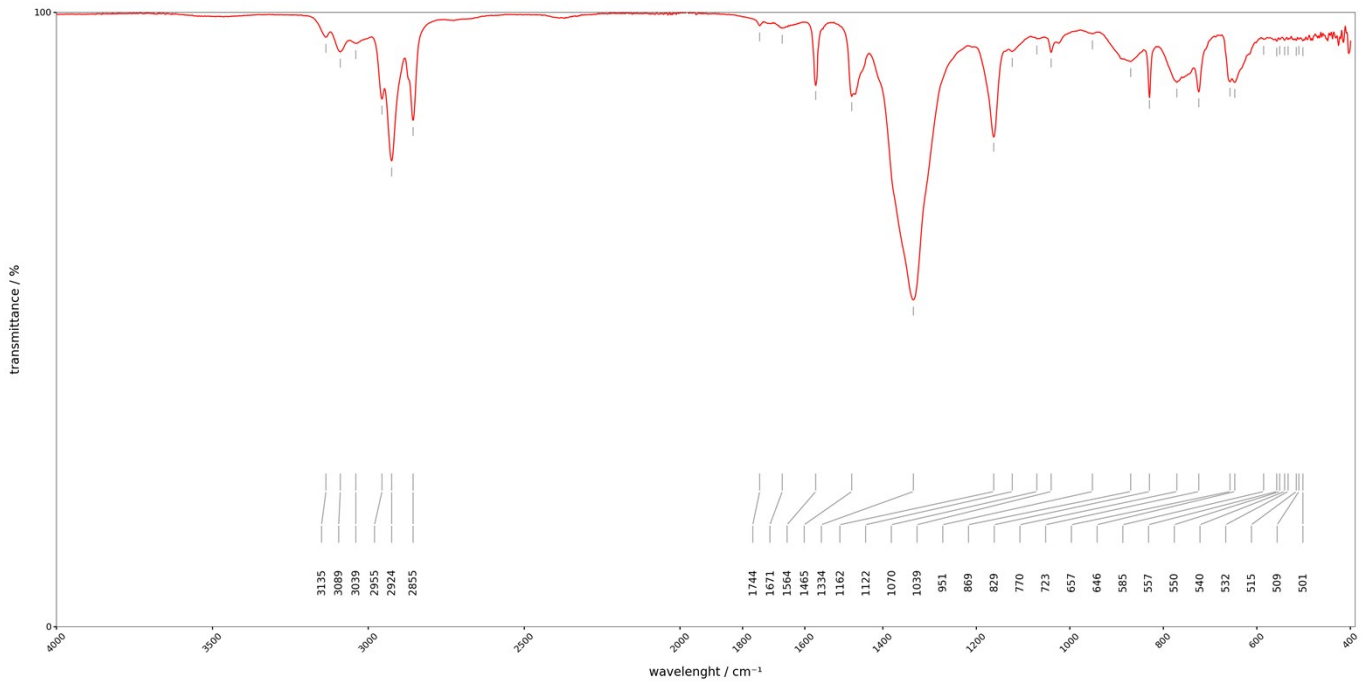

Figure S 9. FTIR of 1,3-Di(octyl)imidazolium nitrate.

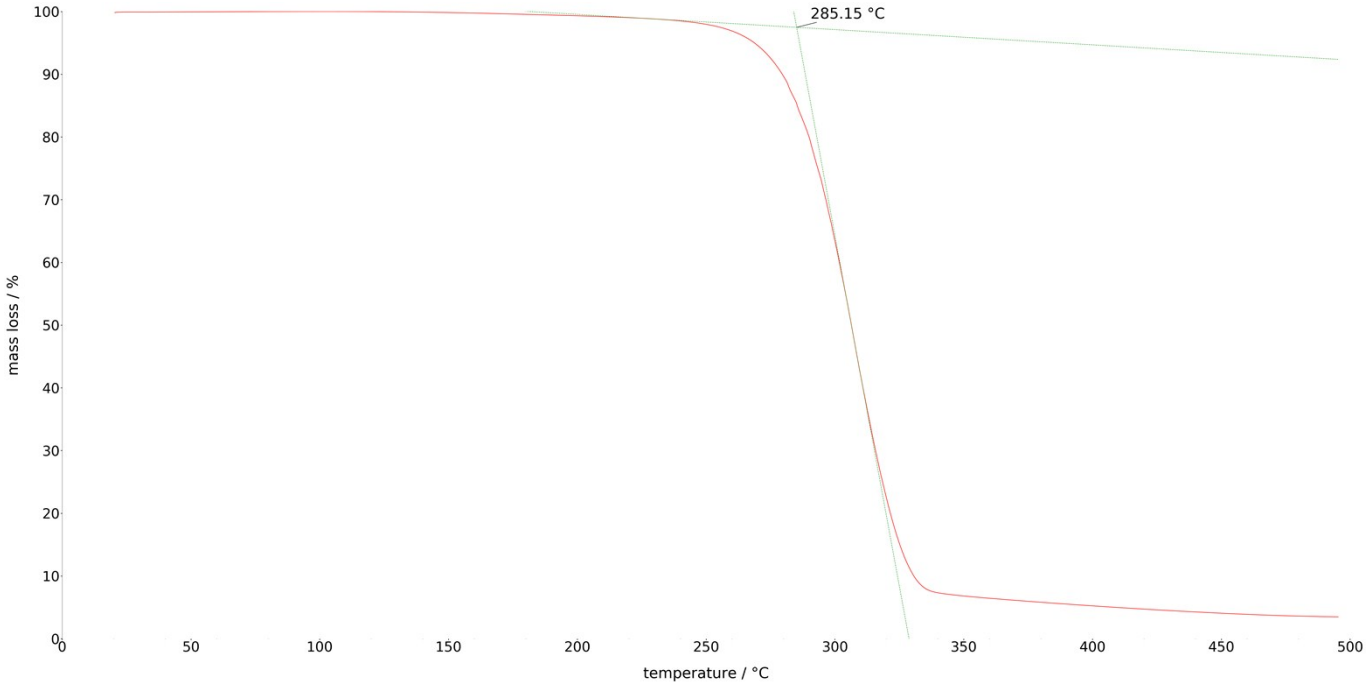

Figure S 10. TGA of 1,3-Di(octyl)imidazolium nitrate in an alluminum pan.

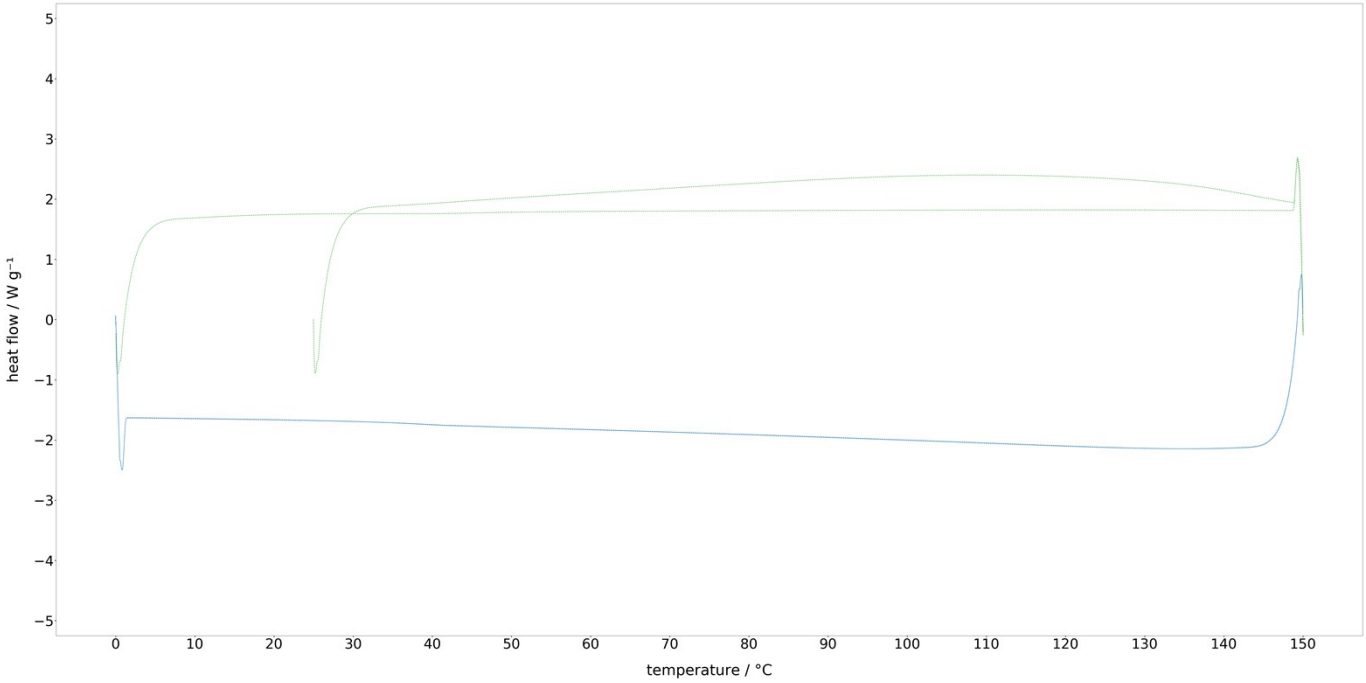

Figure S 11. DSC of 1,3-Di(octyl)imidazolium nitrate.

1,3-Di(octyl)imidazolium chloride.

The synthesis was carried out following the general procedure with 1,3-di(octyl)imidazolium acetate (0.4003g, 1.14 mmol). Isolated yield 0.3051. g, 82 %. Pale yellow colloid. Decomposition temperature: 257 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.80 - 0.94 (6 H, m), 1.19 - 1.38 (20 H, m), 1.92 (4 H, p, J 7.20, 6.99), 4.28 - 4.43 (4 H, m), 7.21 (2 H, d, J 1.64), 11.15 (1 H, d, J 1.72). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 137.5, 122.2, 50.0, 31.7, 30.4, 29.1, 29.0, 26.3, 22.6, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3379, 3132, 3060, 2956, 2923, 2872, 2854, 1637, 1562, 1407, 1377, 1332, 1307, 1246, 1162, 1122, 1023, 773, 723, 658, 607, 569, 502, 438, 410.

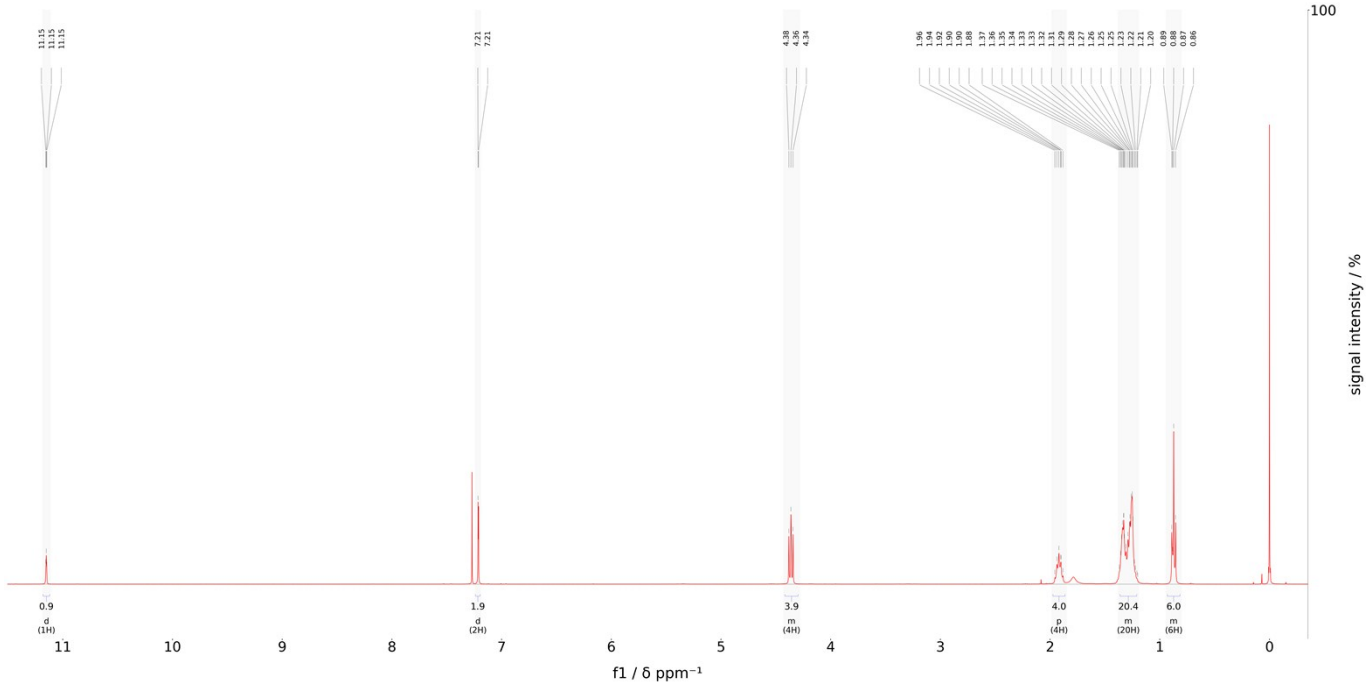

Figure S 12. ^{1}H NMR of 1,3-Di(octyl)imidazolium chloride in deuterochloroform.

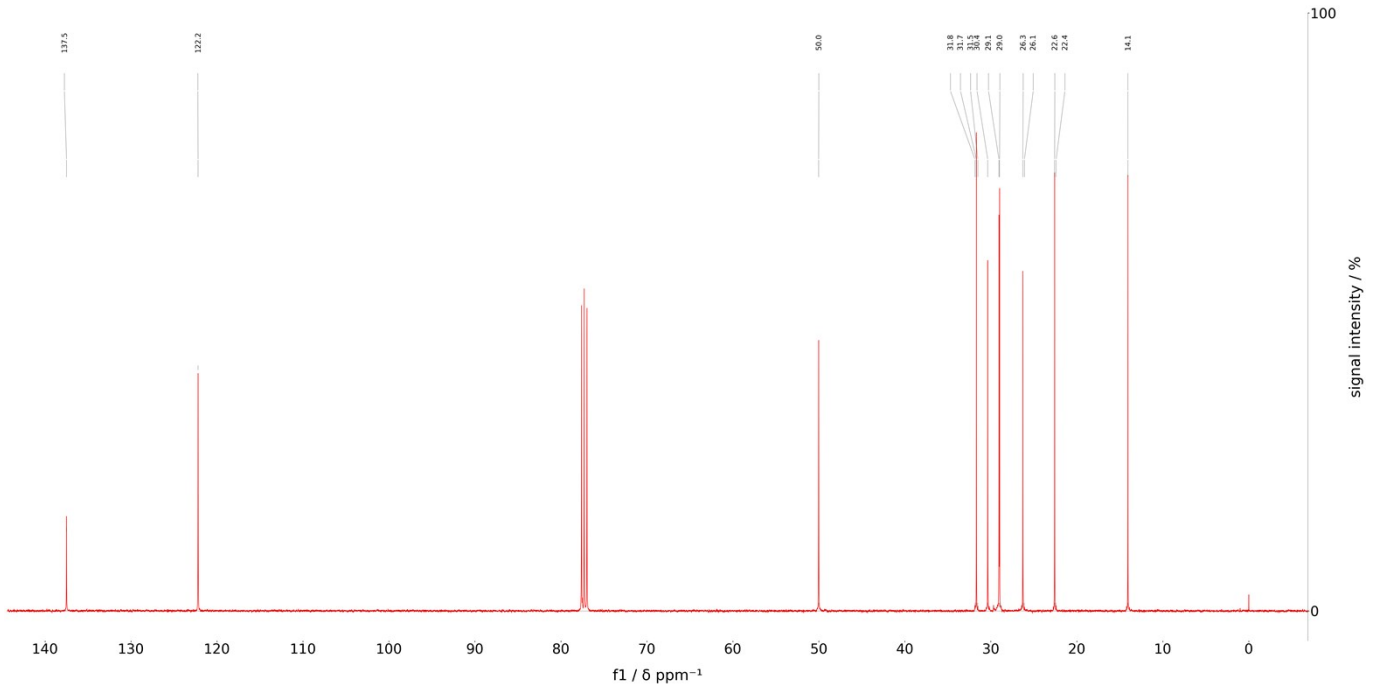

Figure S 13. ^{13}C NMR of 1,3-Di(octyl)imidazolium chloride in deuterochloroform.

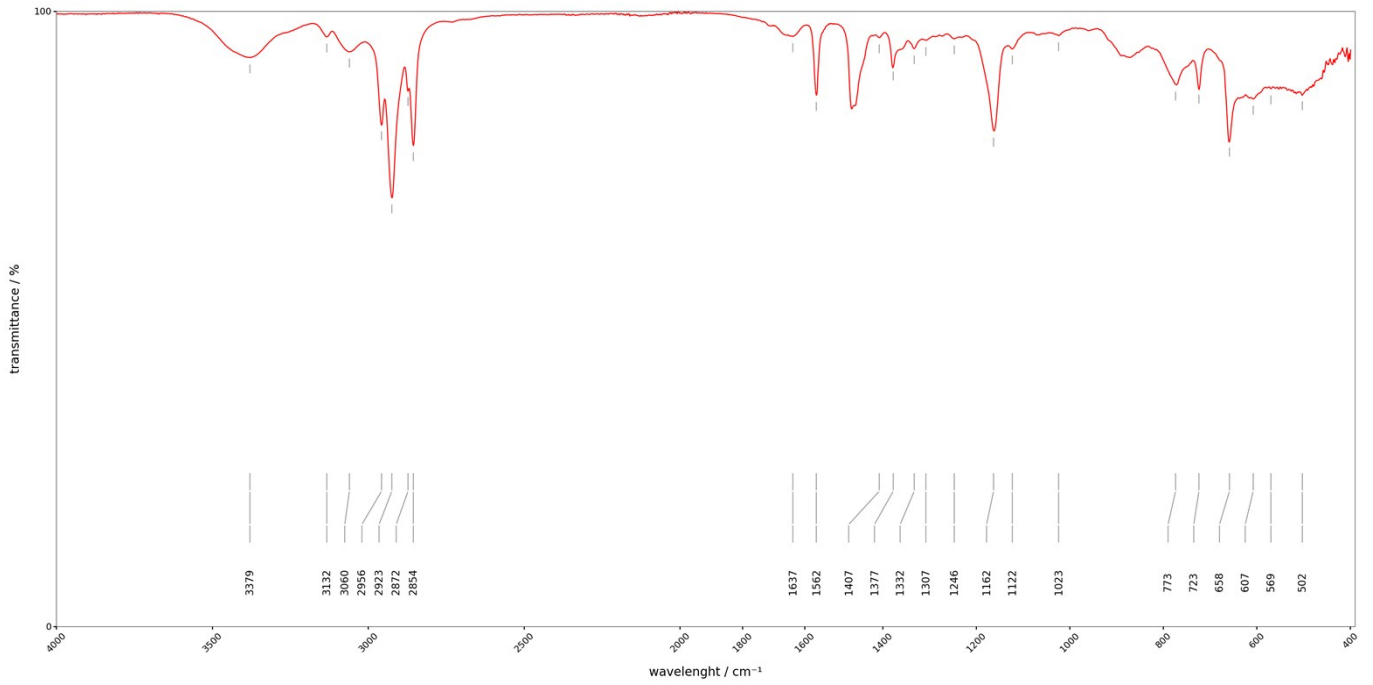

Figure S 14. FTIR of 1,3-Di(octyl)imidazolium chloride.

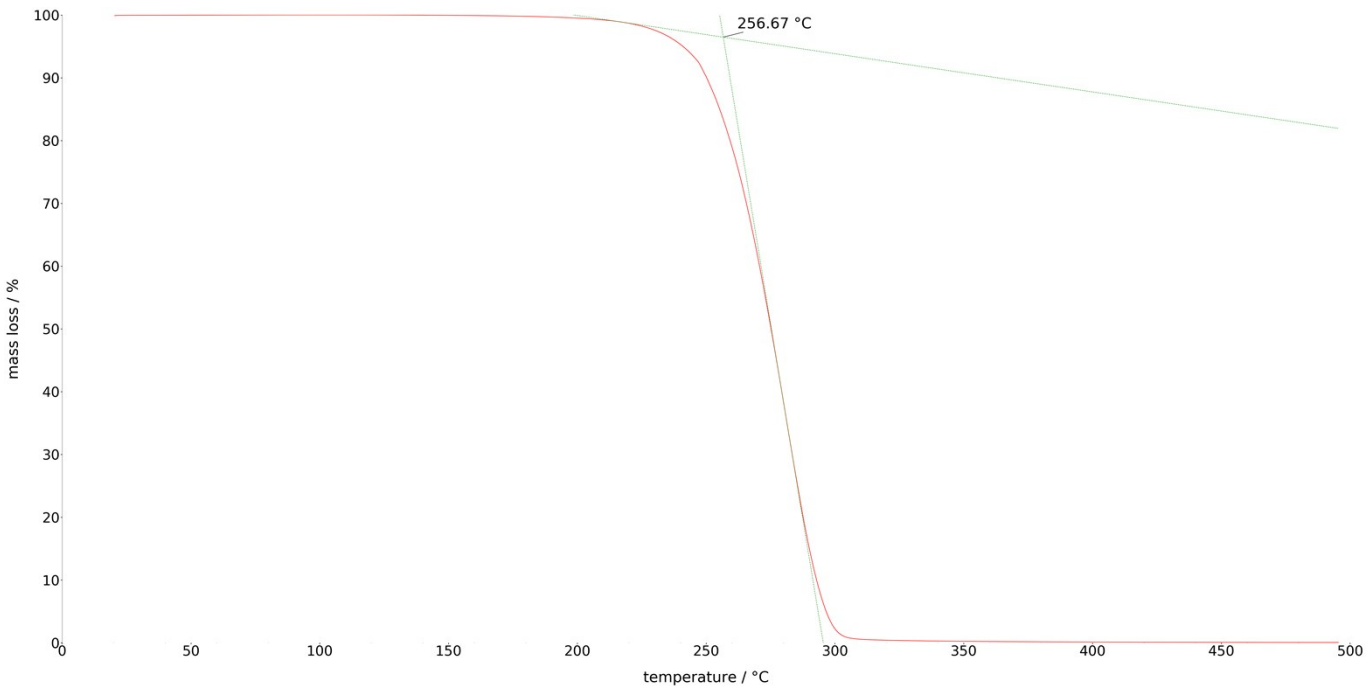

Figure S 15. TGA of 1,3-Di(octyl)imidazolium chloride in an alluminum pan.

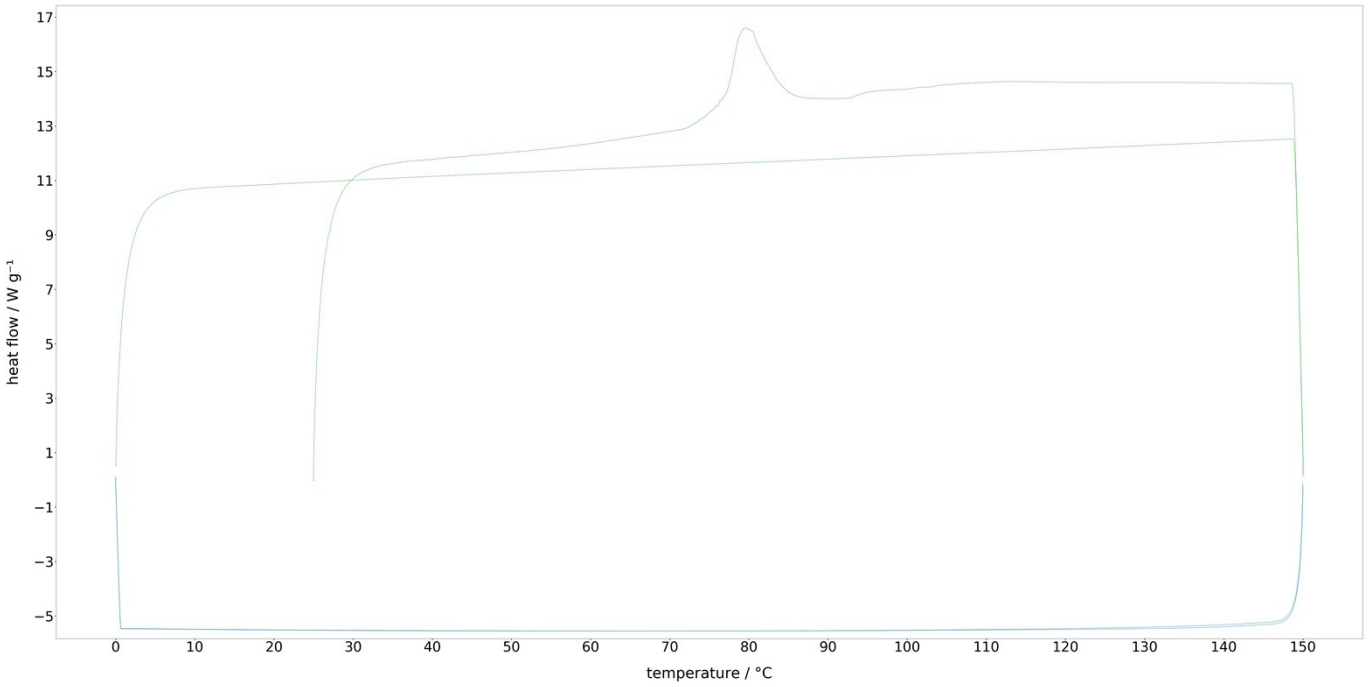

Figure S 16. DSC of 1,3-Di(octyl)imidazolium chloride.

1,3-Di(octyl)imidazolium hydroxalate.

The synthesis was carried out following the general procedure with 1,3-di(octyl)imidazolium acetate (0.8149 g, 2.31 mmol). Isolated yield 0.8925 g, 100 %. Dark amber solid. Melting point: 74 °C. Decomposition temperature: 227 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.85 (6 H, t, J 6.76), 1.26 (24 H, dd, J 14.32, 7.52), 1.82 (4 H, d, J 7.22), 4.22 (4 H, t, J 7.14), 7.33 (2 H, s), 9.17 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 161.7, 136.2, 122.2, 50.1, 31.7, 30.0, 29.0, 28.9, 26.2, 22.6, 14.0. IR (Diamond-ATR, neat, cm^{-1}): 3137, 3109, 3080, 2952, 2922, 2871, 2853, 1731, 1679, 1563, 1465, 1421, 1377, 1352, 1320, 1198, 1158, 918, 885, 838, 789, 696, 660, 597, 578, 476.

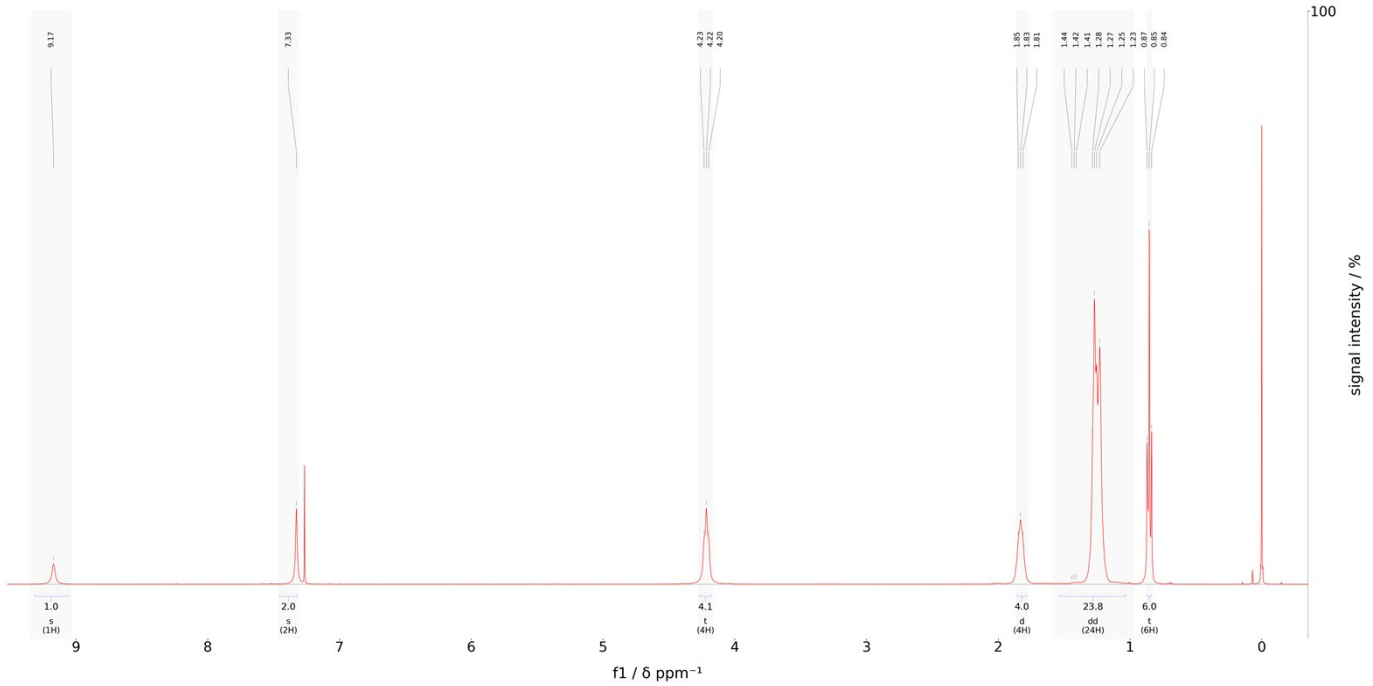

Figure S 17. ^{1}H NMR of 1,3-Di(octyl)imidazolium hydroxalate in deuterochloroform.

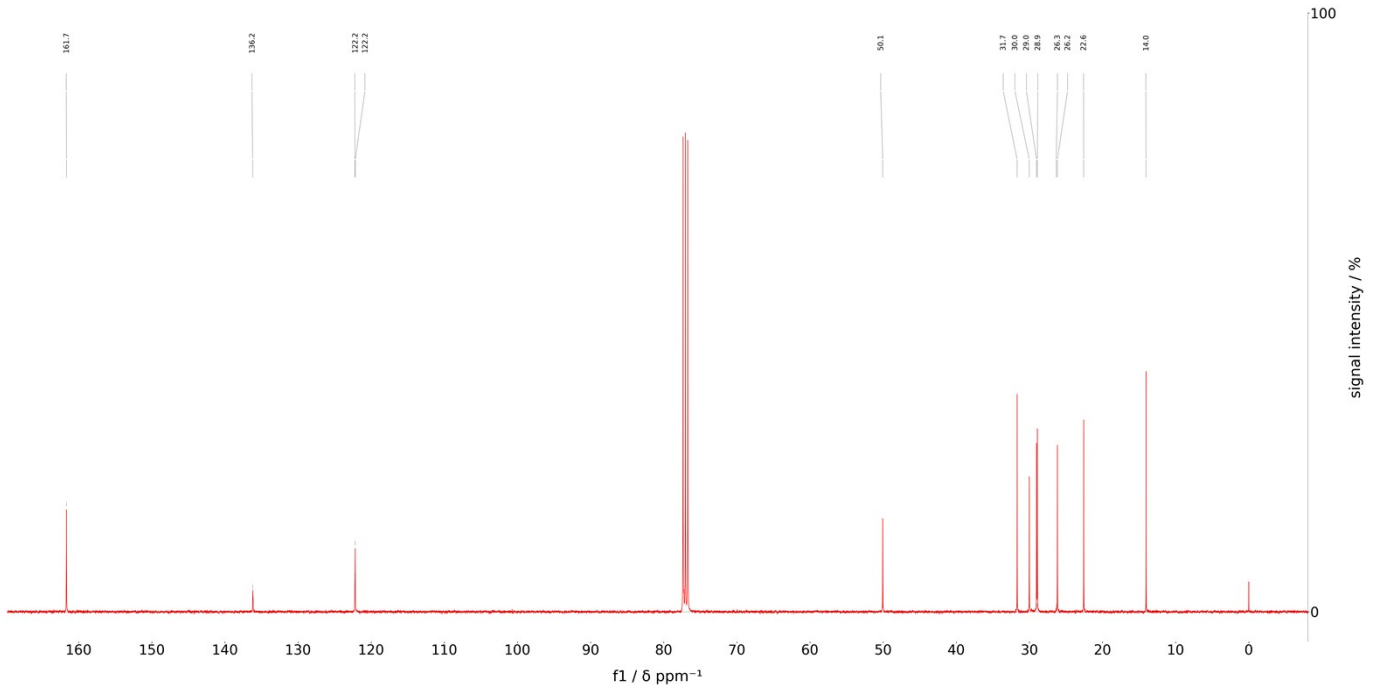

Figure S 18. ^{13}C NMR of 1,3-Di(octyl)imidazolium hydroxalate in deuterochloroform.

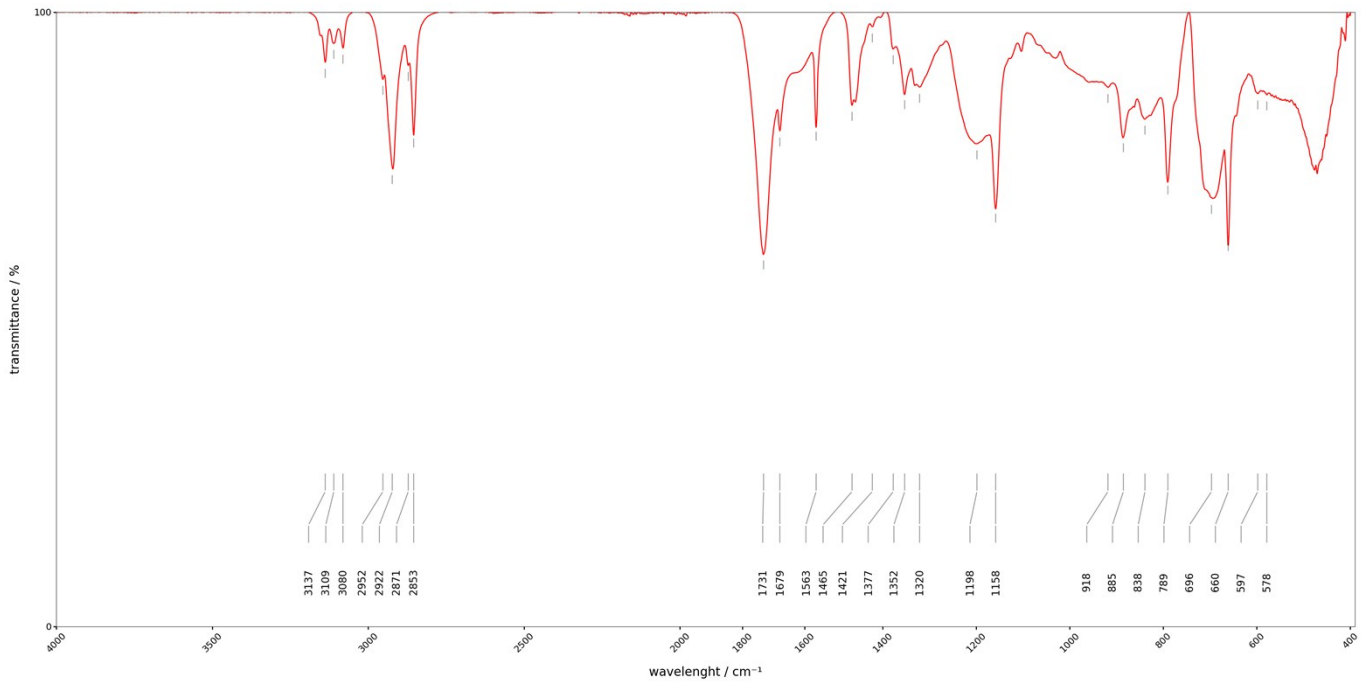

Figure S 19. FTIR of 1,3-Di(octyl)imidazolium hydroxalate.

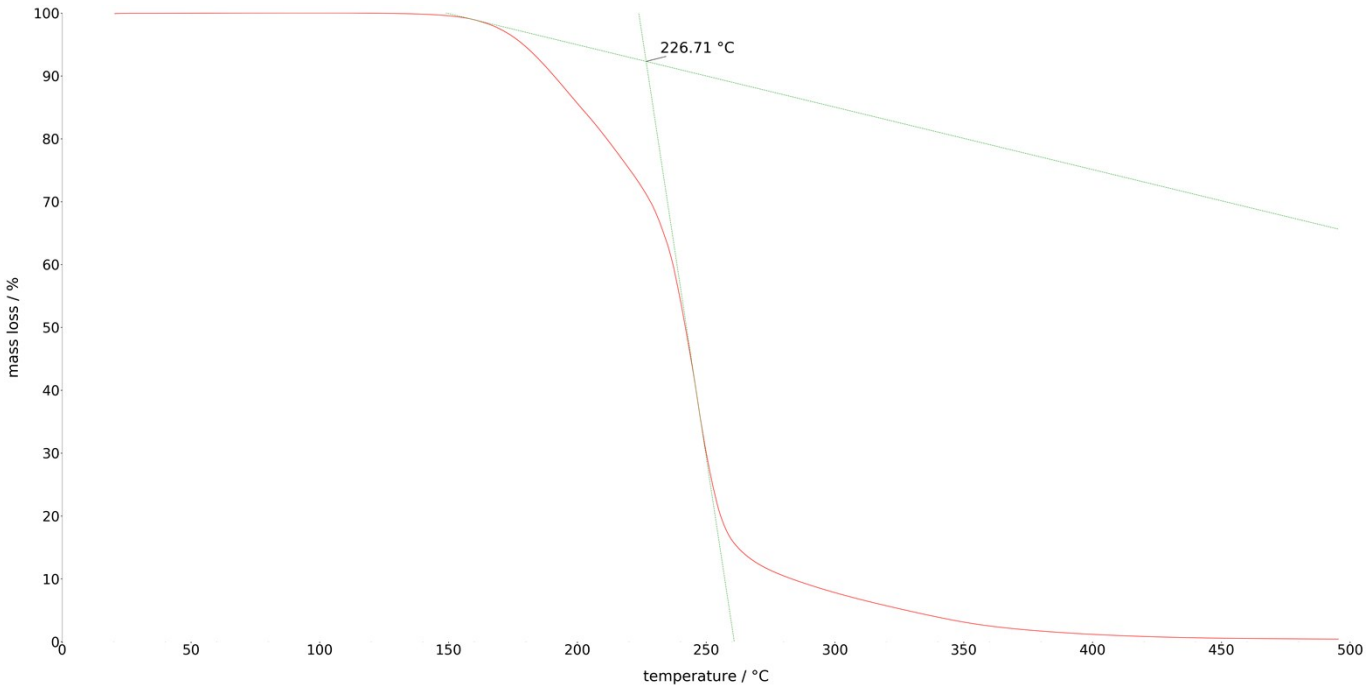

Figure S 20. TGA of 1,3-Di(octyl)imidazolium hydroxalate in an alluminum pan.

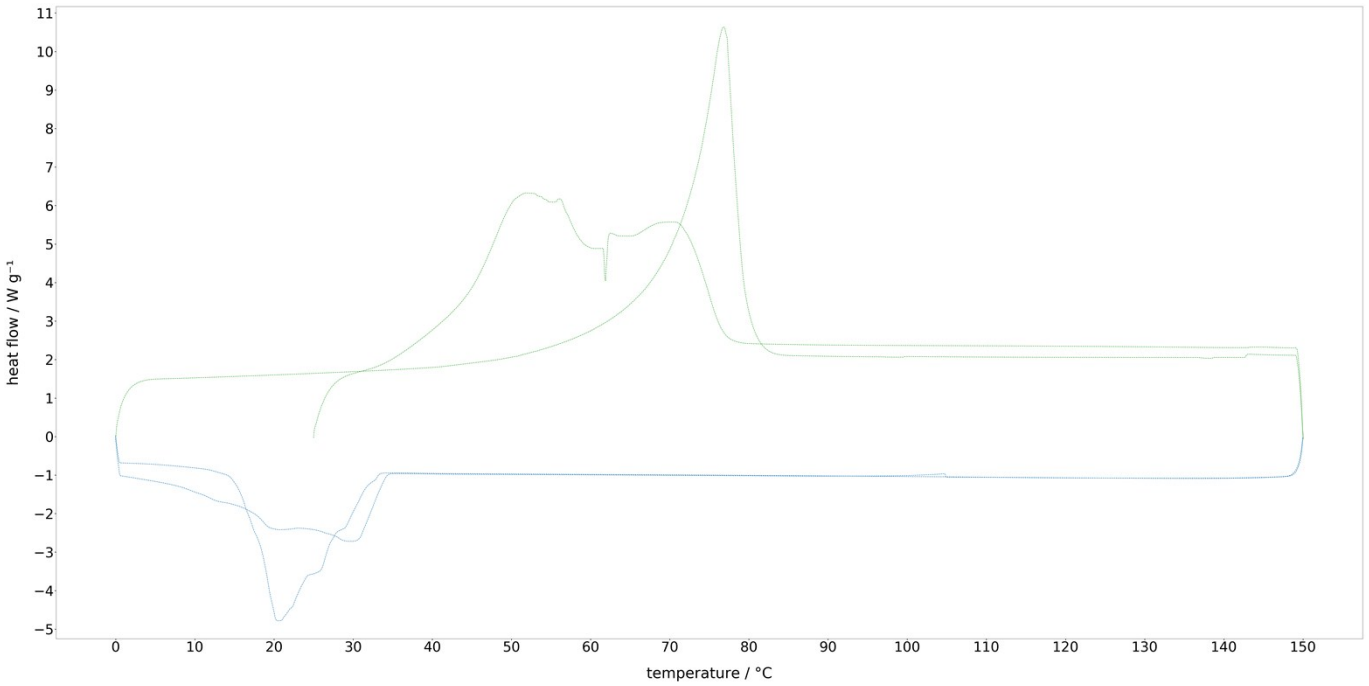

Figure S 21. DSC of 1,3-Di(octyl)imidazolium hydroxalate.

1,3-Di(decyl)imidazolium acetate.

The synthesis was carried out following the general procedure with 1-decylamine (98%, 31.32 g, 39.80 mL, 0.2 mol), formaldehyde (36.5-38%, 8.34g, 7.65mL, 0.1mol), acetic acid (99.9%, 9.01g, 8.59mL, 0.15mol), glyoxal (40%, 14.51g, 11.15mL, 0.1mol). Isolated yield 40.32g, 94 % (≈0.5 eq of residual acetic acid). Yellow to orange oil. Melting point: 49 °C. Decomposition temperature: 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.81), 1.28 (32 H, d, J 30.33), 1.87 (4 H, dd, J 9.85, 4.86), 2.02 (3 H, s), 4.35 (4 H, t, J 7.40), 7.08 (2 H, d, J 1.48), 11.94 (1 H, d, J 1.61). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 176.8, 139.7, 121.1, 49.9, 31.8, 30.3, 29.5, 29.4, 29.3, 29.0, 26.2, 23.6, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 2923, 2854, 1563, 1466, 1378, 1255, 1166, 1045, 1000, 878, 722, 651, 611, 445, 3135, 3074, 2955, 2923, 2854, 1699, 1644, 1579, 1563, 1466, 1378, 1325, 1255, 1166, 1122, 1045, 1000, 958, 878, 754, 722, 651, 611, 522, 494, 477, 471, 445, 409, 402.

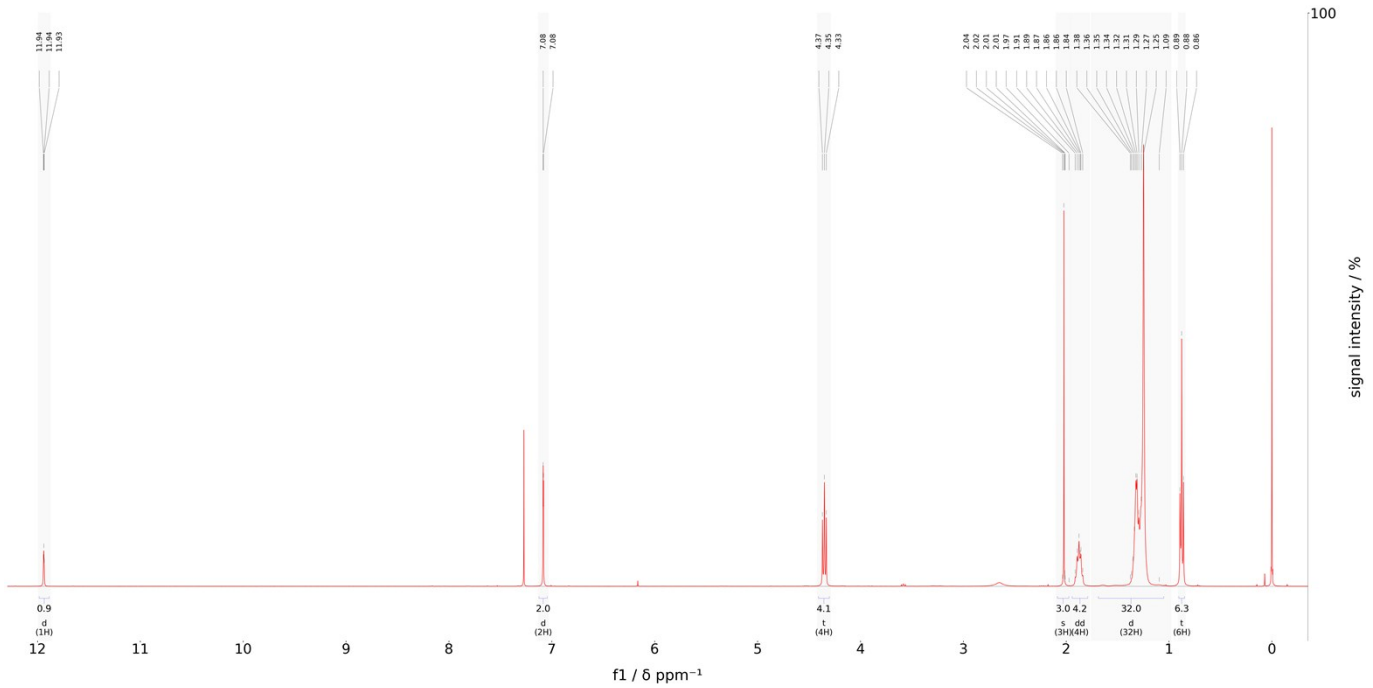

Figure S 22. ^{1}H NMR of 1,3-Di(decyl)imidazolium acetate in deuterochloroform.

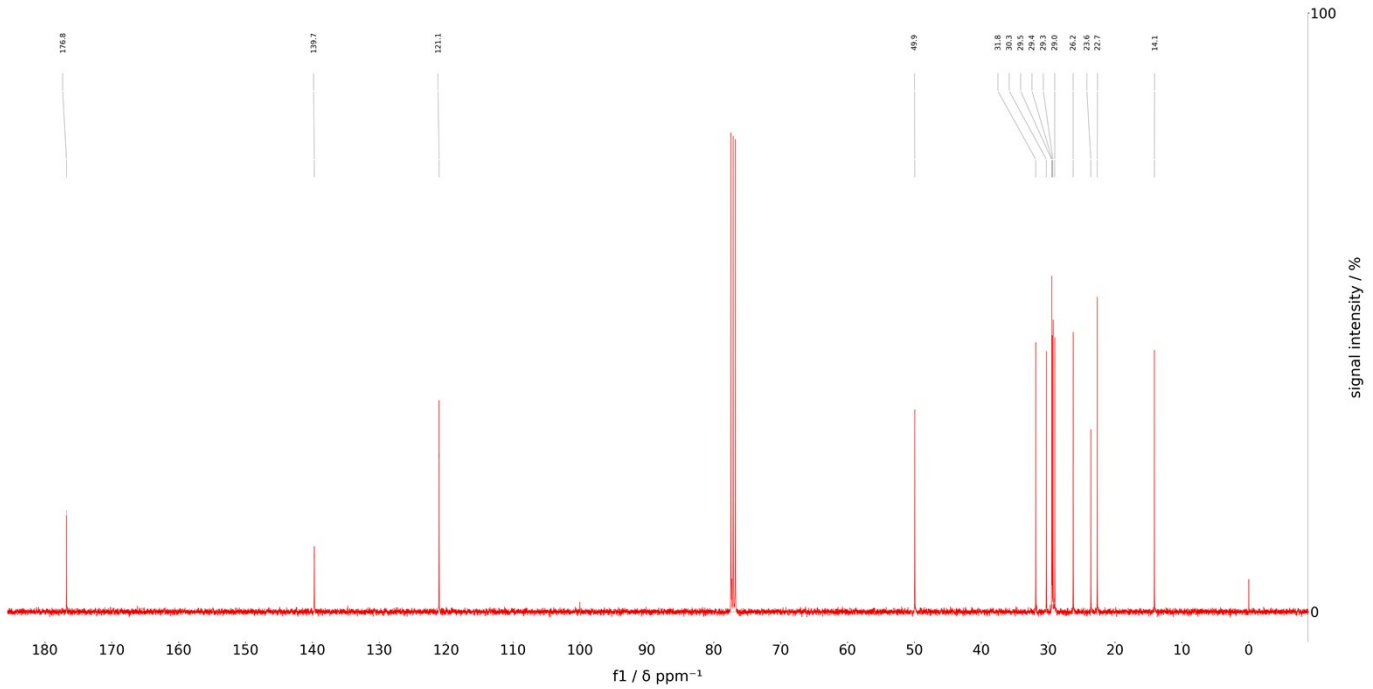

Figure S 23. ^{13}C NMR of 1,3-Di(decyl)imidazolium acetate in deuterochloroform.

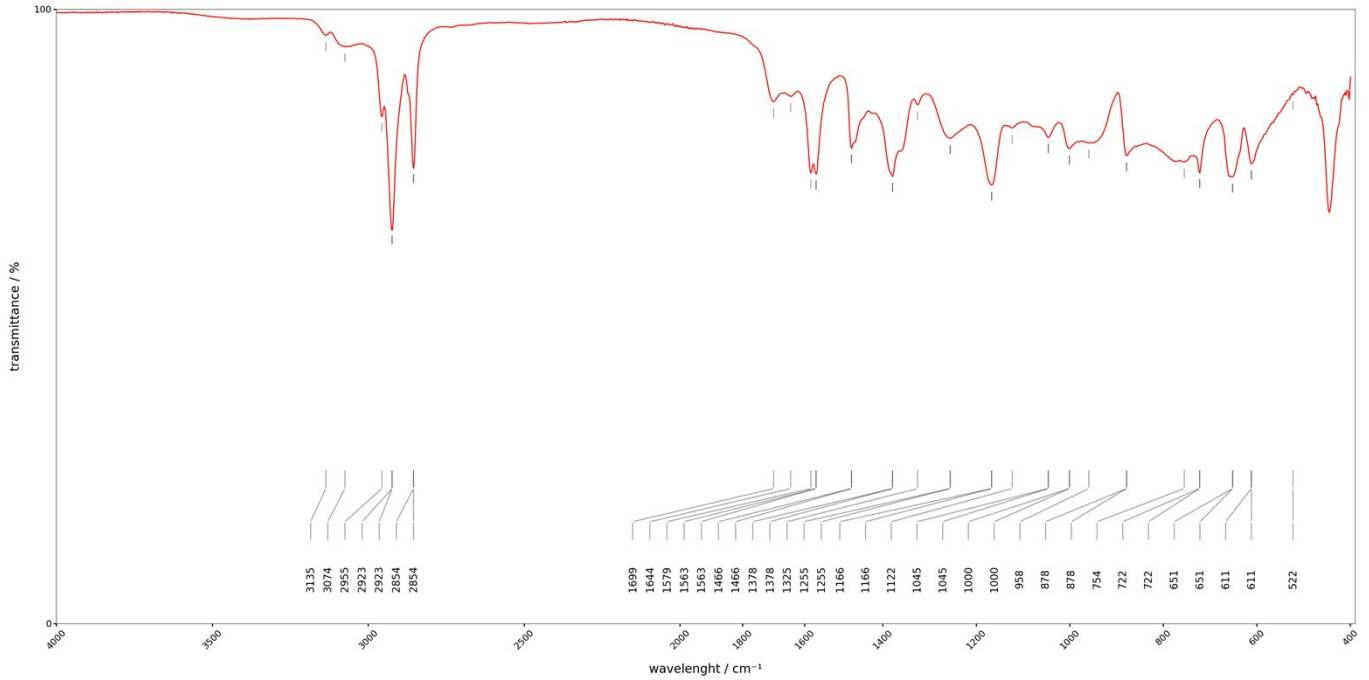

Figure S 24. FTIR of 1,3-Di(decyl)imidazolium acetate.

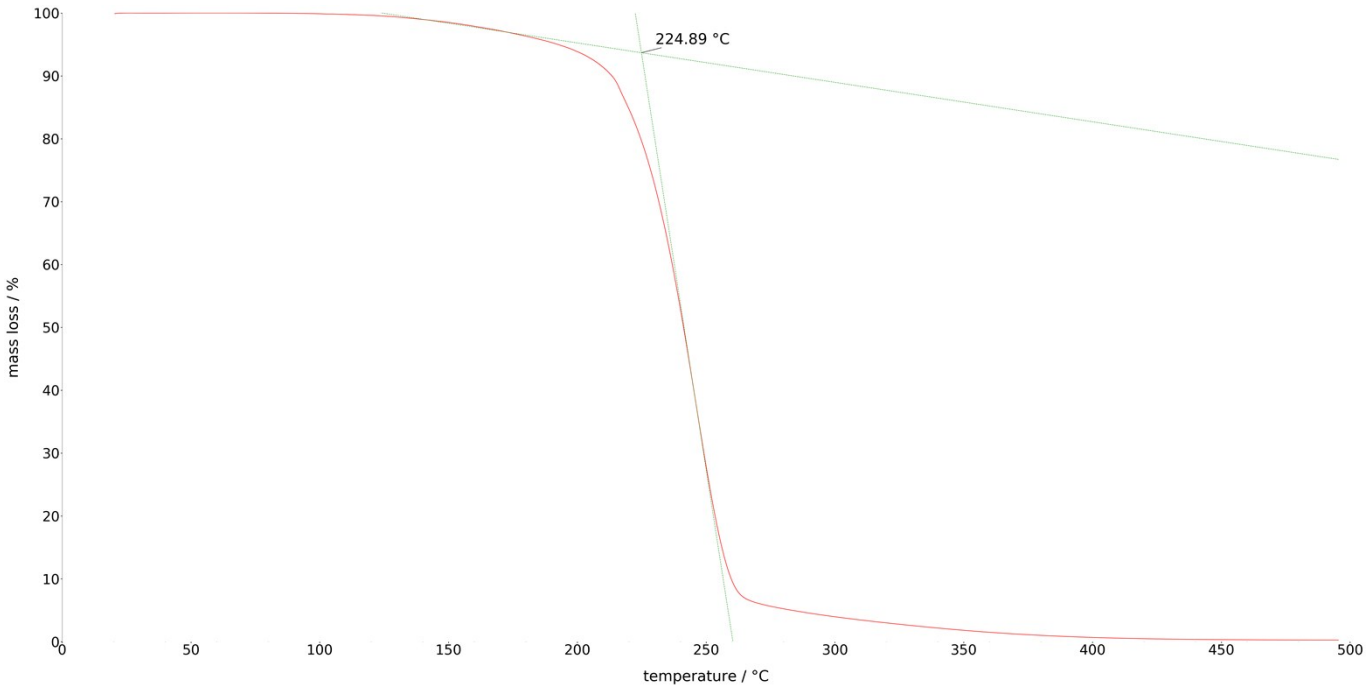

Figure S 25. TGA of 1,3-Di(decyl)imidazolium acetate in an alluminum pan.

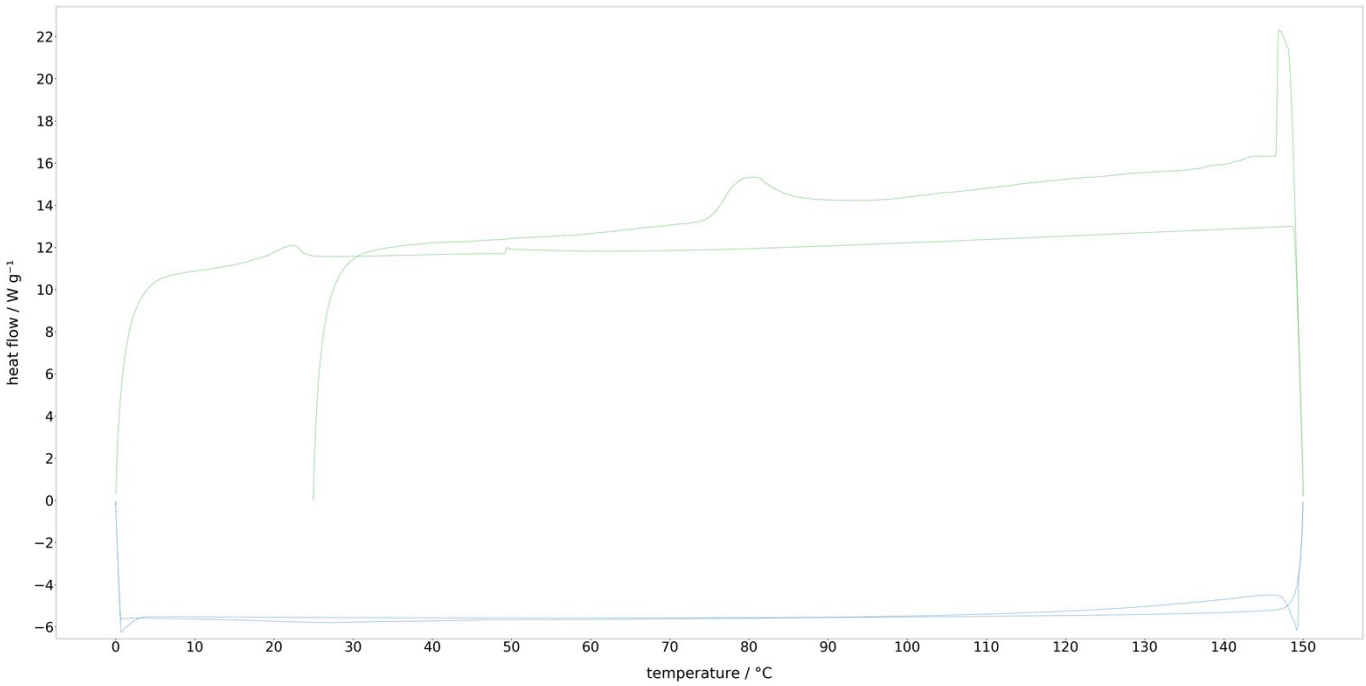

Figure S 26. DSC of 1,3-Di(decyl)imidazolium acetate.

1,3-Di(decyl)imidazolium nitrate.

The synthesis was carried out following the general procedure with 1,3-di(decyl)imidazolium acetate (0.8202 g, 2.01 mmol). Isolated yield 0.8359 g, 101 %. Amber solid. Melting point: 27 °C. Decomposition temperature: 296 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.87 (6 H, t, J 6.78), 1.28 (29 H, d, J 26.69), 1.89 (4 H, p, J 7.68, 7.47), 4.25 (4 H, t, J 7.39), 7.40 (2 H, d, J 1.68), 10.00 (1 H, d, J 1.72). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 137.2, 122.4, 50.1, 31.9, 30.3, 29.5, 29.4, 29.3, 29.0, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3136, 3089, 3040, 2955, 2922, 2853, 1744, 1654, 1564, 1466, 1335, 1162, 1077, 1039, 873, 829, 754, 722, 658, 646, 562, 537, 515, 504, 499, 489, 482, 473, 467, 459, 451, 444, 428, 418, 405.

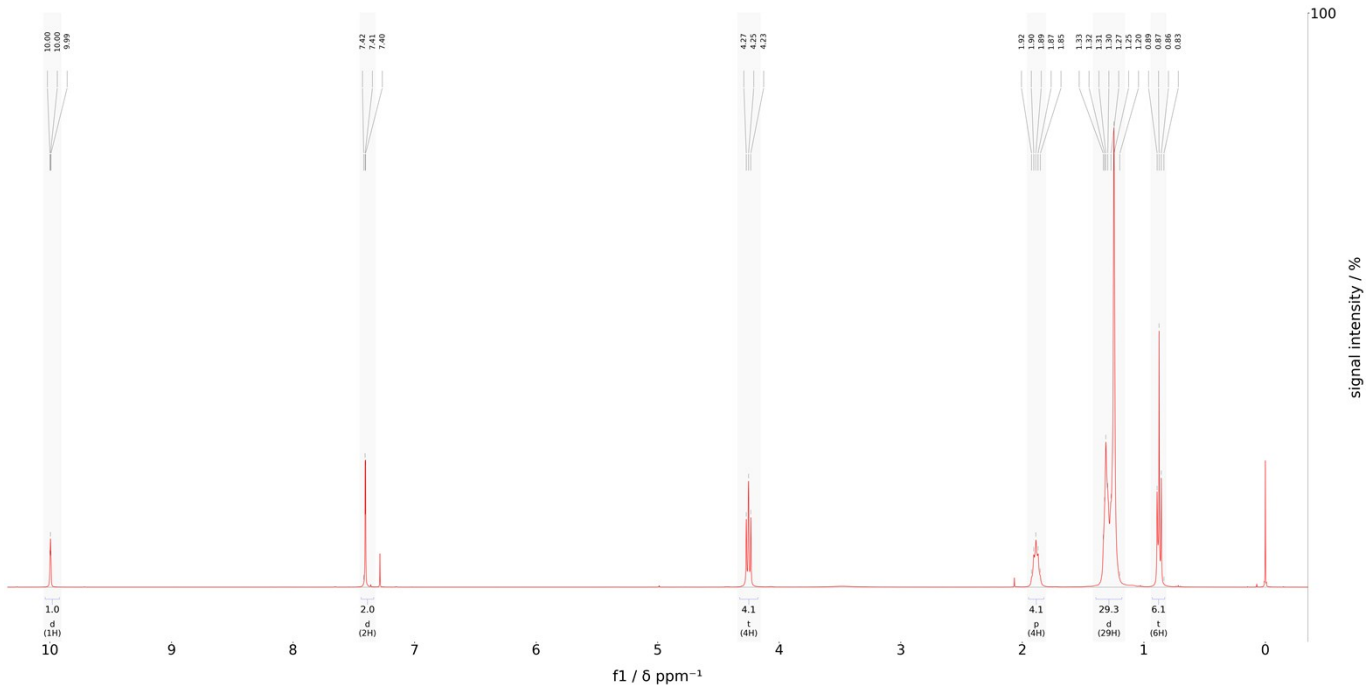

Figure S 27. ^{1}H NMR of 1,3-Di(decyl)imidazolium nitrate in deuterochloroform.

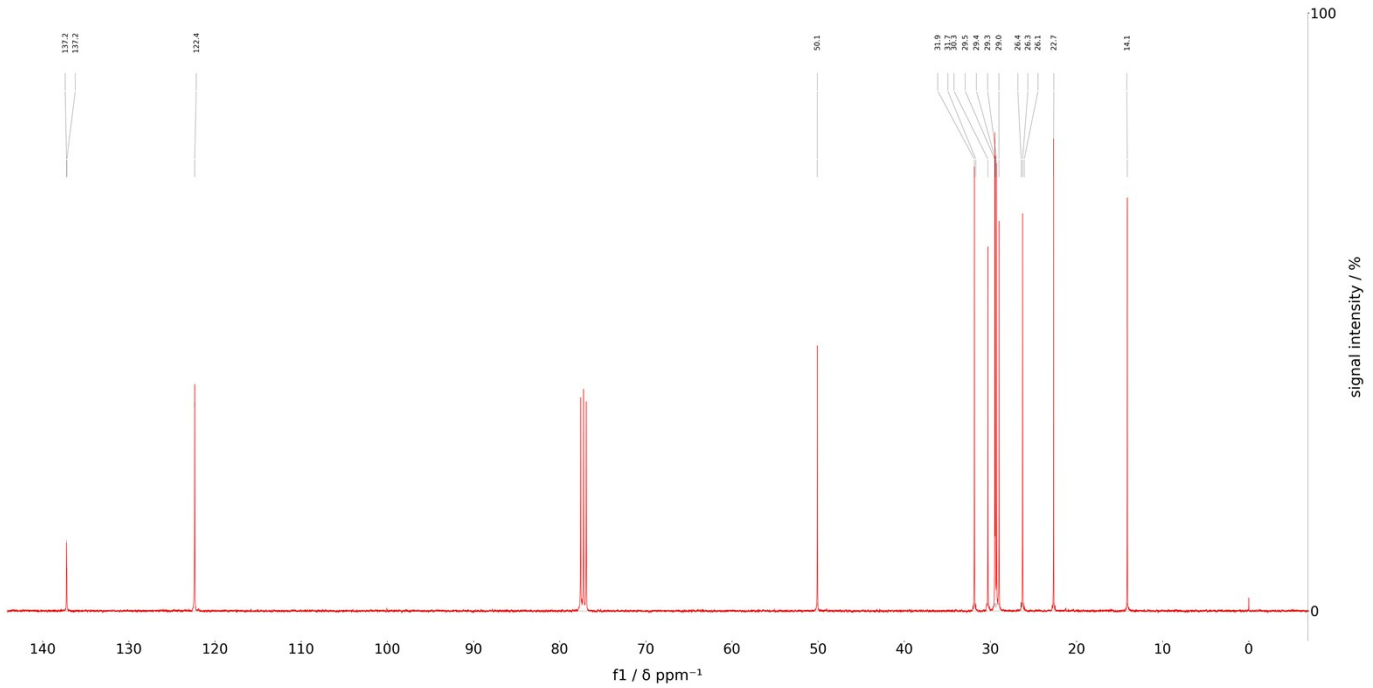

Figure S 28. ^{13}C NMR of 1,3-Di(decyl)imidazolium nitrate in deuterochloroform.

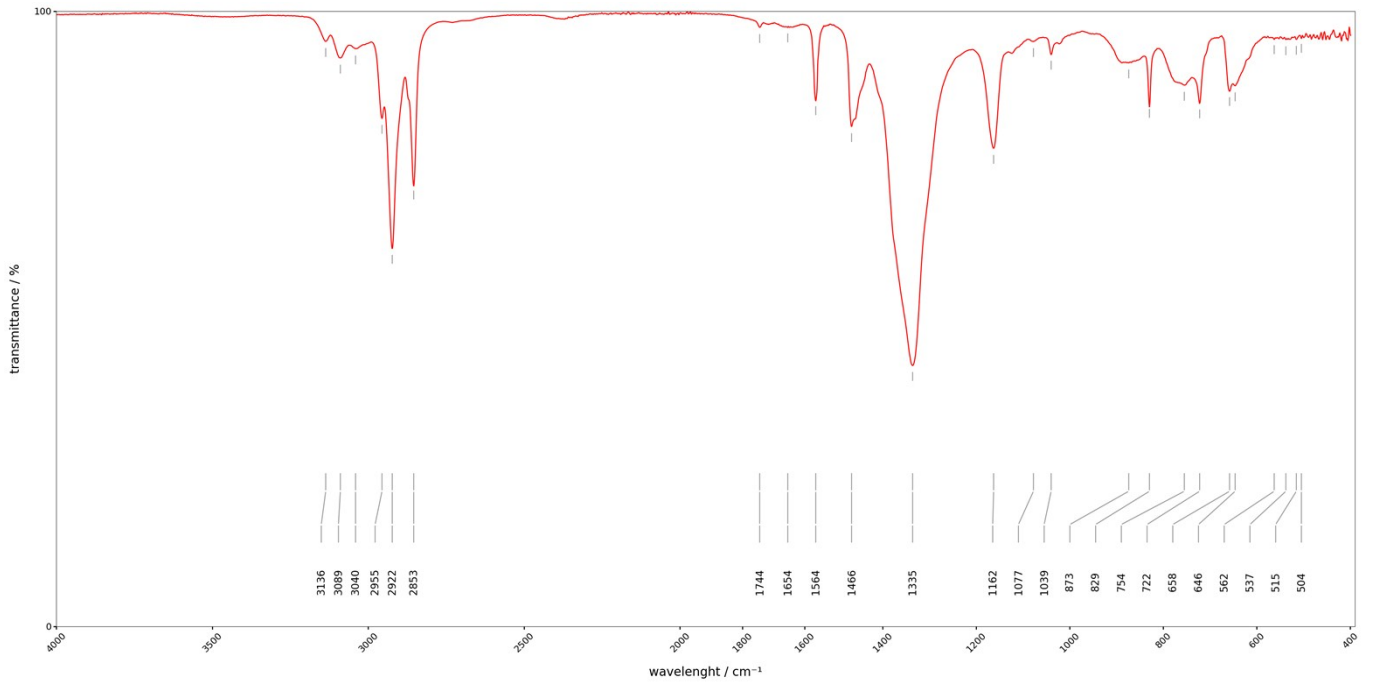

Figure S 29. FTIR of 1,3-Di(decyl)imidazolium nitrate.

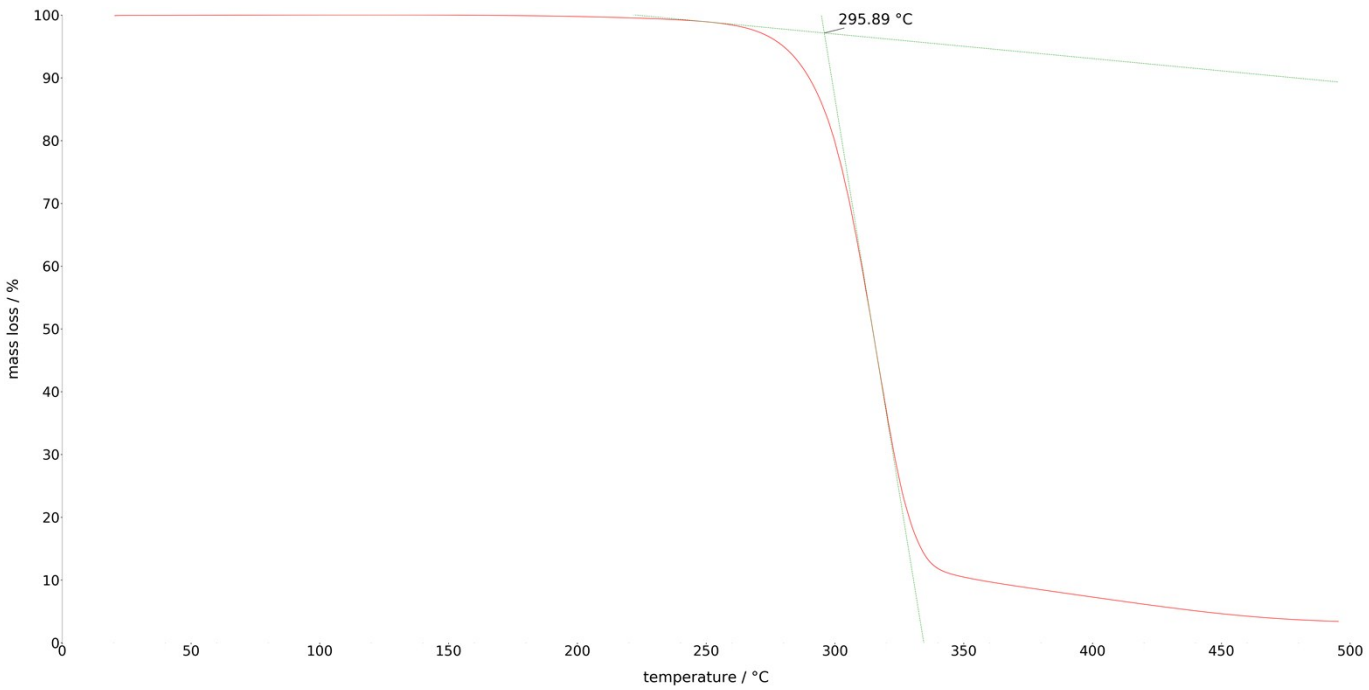

Figure S 30. TGA of 1,3-Di(decyl)imidazolium nitrate in an alluminum pan.

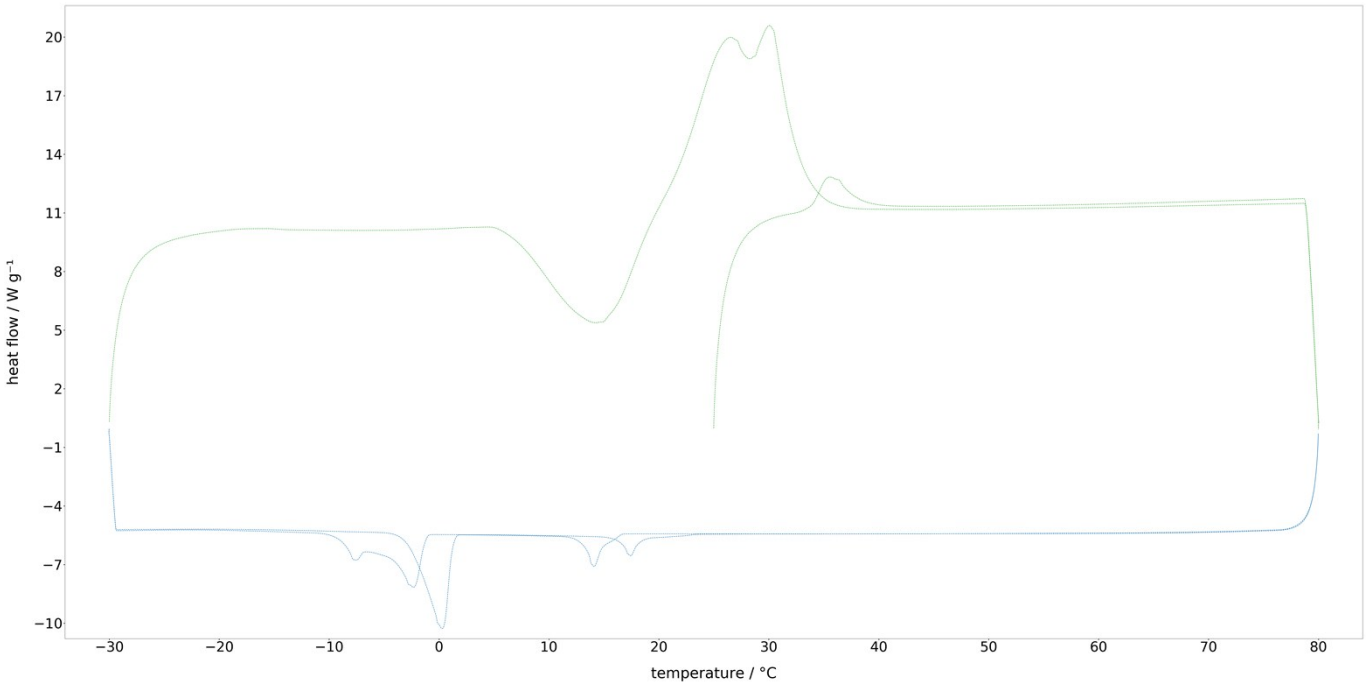

Figure S 31. DSC of 1,3-Di(decyl)imidazolium nitrate.

1,3-Di(decyl)imidazolium chloride.

The synthesis was carried out following the general procedure with 1,3-di(decyl)imidazolium acetate (0.8135 g, 1.99 mmol). Isolated yield 0.7132 g, 93 %. Viscous red deliquescent solid. Melting point: 57 °C. Decomposition temperature: 256 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.72), 1.29 (32 H, d, J 34.20), 1.92 (4 H, p, J 7.21, 7.16), 4.36 (4 H, t, J 7.43), 7.30 (2 H, s), 10.90 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 137.8, 121.9, 50.1, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 2956, 2922, 2872, 2853, 1647, 1562, 1466, 1406, 1376, 1333, 1307, 1165, 1123, 1078, 1021, 888, 775, 721, 658, 544, 472, 429.

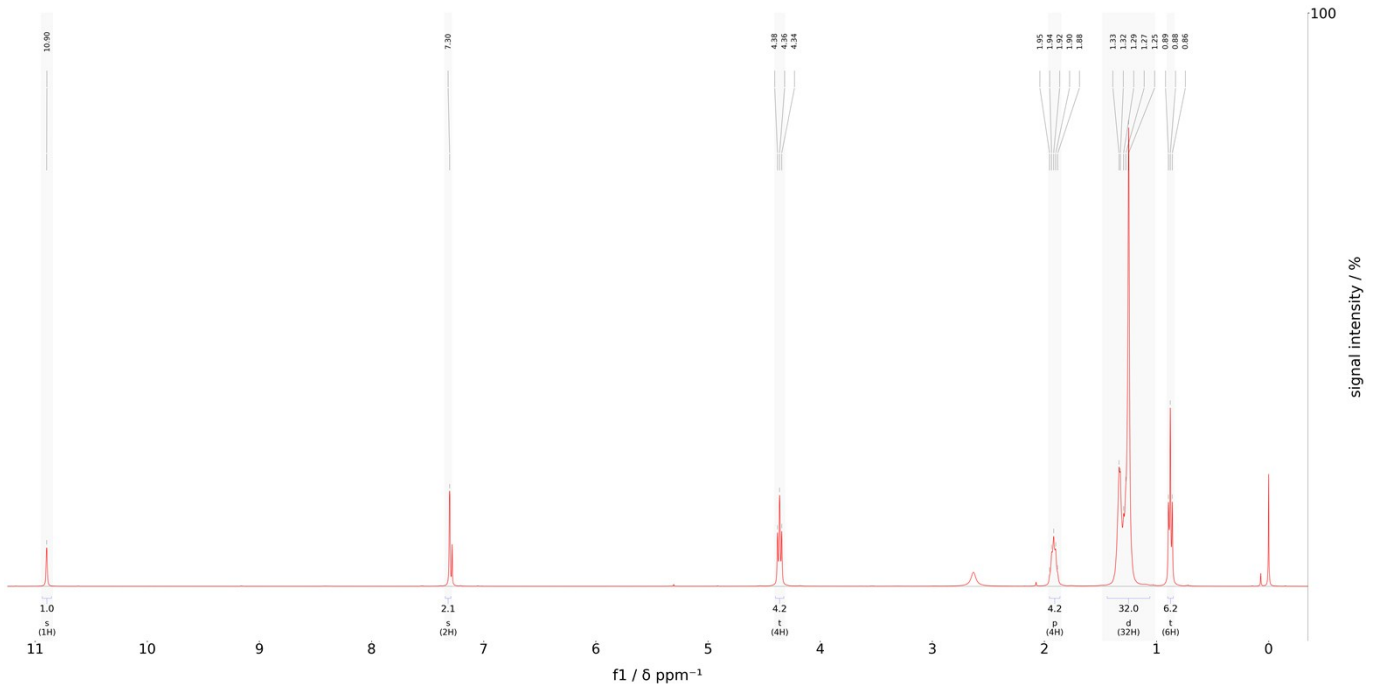

Figure S 32. ^{1}H NMR of 1,3-Di(decyl)imidazolium chloride in deuterochloroform.

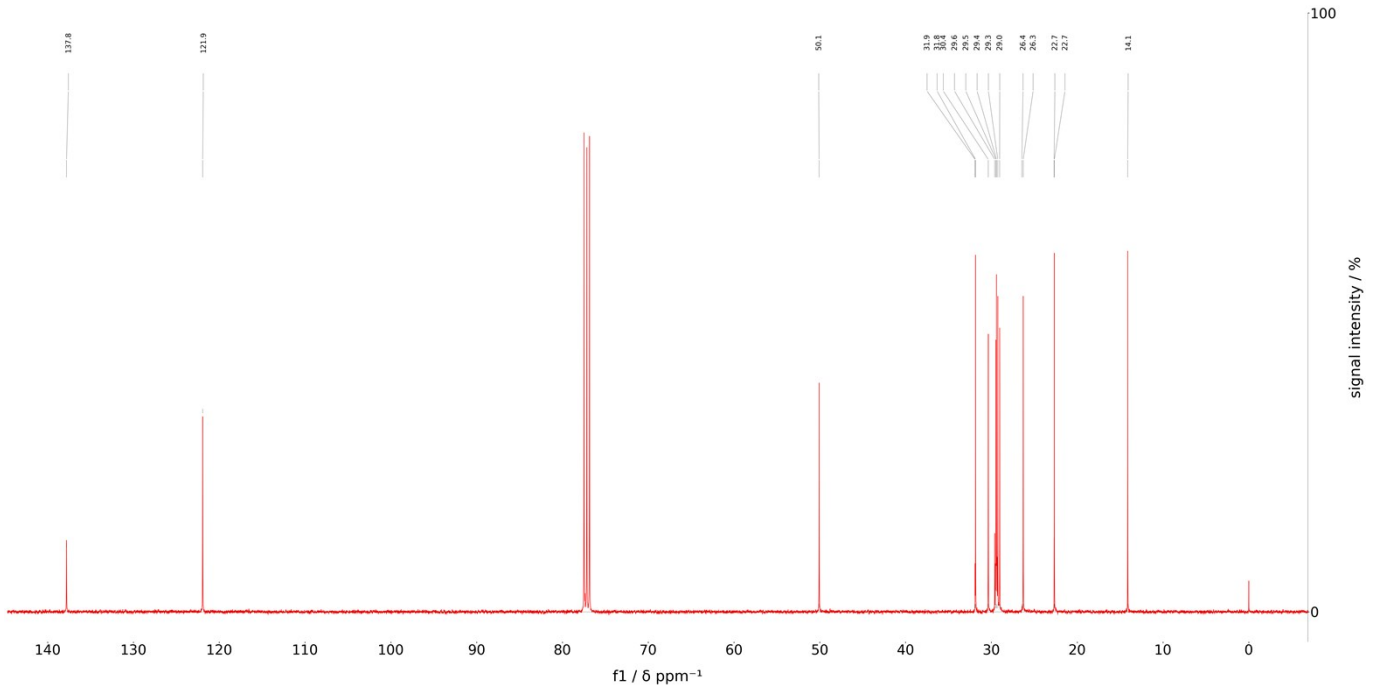

Figure S 33. ^{13}C NMR of 1,3-Di(decyl)imidazolium chloride in deuterochloroform.

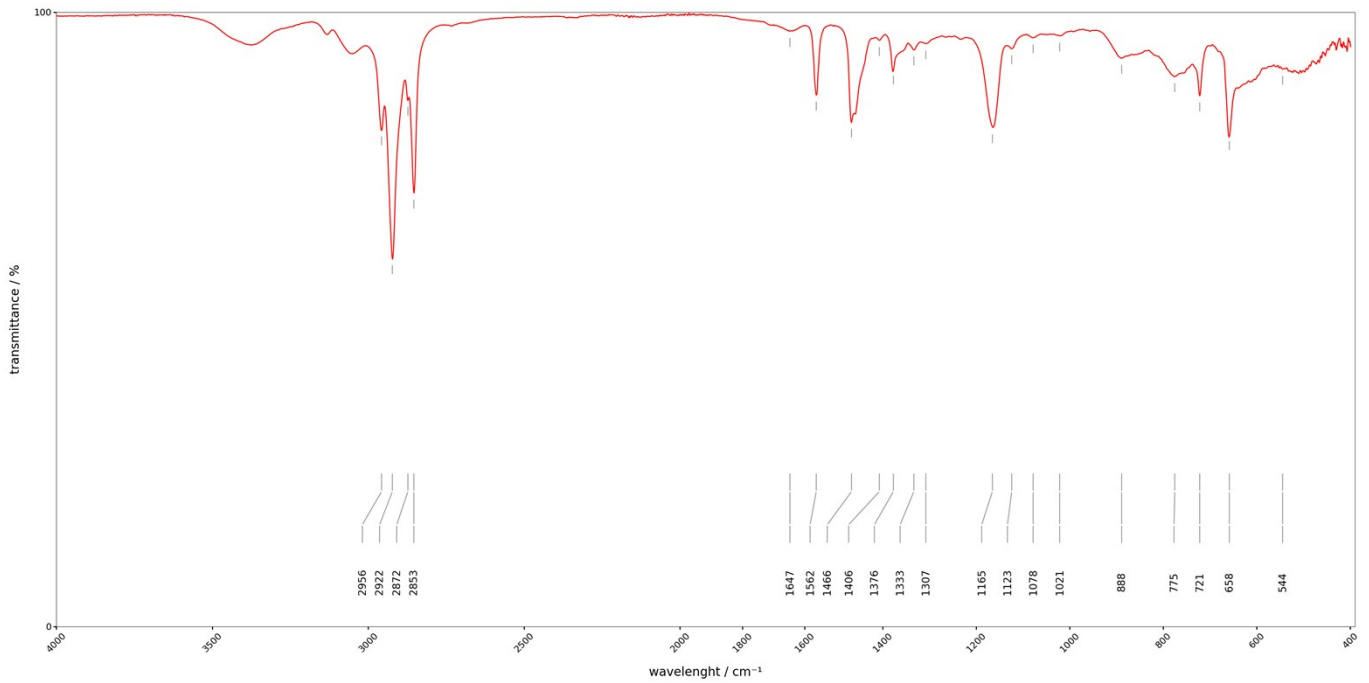

Figure S 34. FTIR of 1,3-Di(decyl)imidazolium chloride.

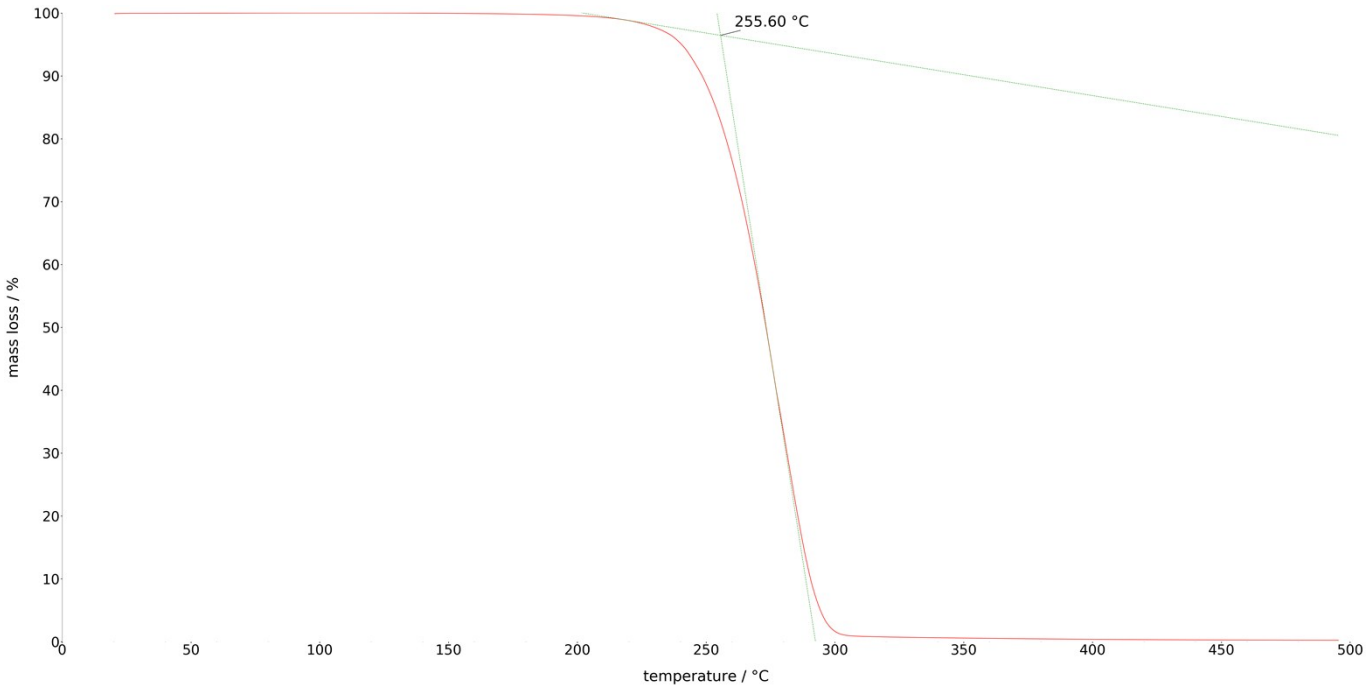

Figure S 35. TGA of 1,3-Di(decyl)imidazolium chloride in an alluminum pan.

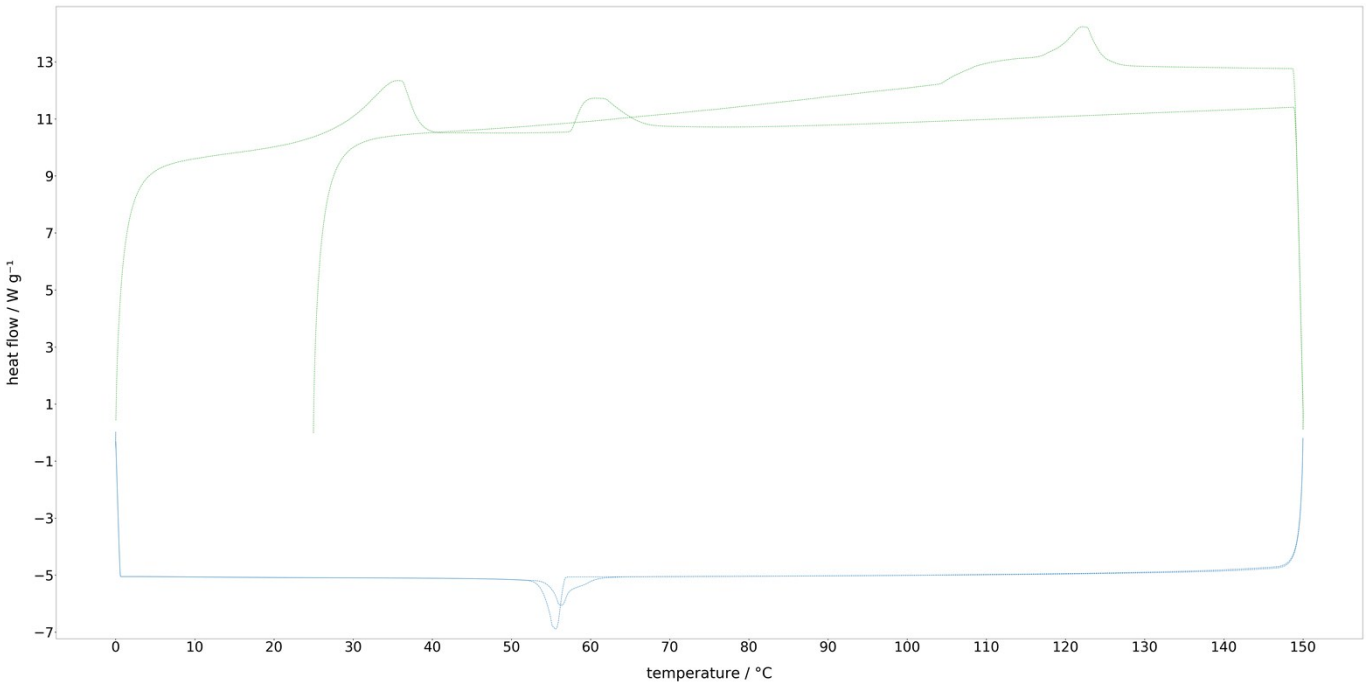

Figure S 36. DSC of 1,3-Di(decyl)imidazolium chloride.

1,3-Di(decyl)imidazolium hydroxalate.

The synthesis was carried out following the general procedure with 1-decylamine (98%, 31.32 g, 39.80 mL, 0.2 mol), formaldehyde (36.5-38%, 8.34g, 7.65mL, 0.1mol), acetic acid (99.9%, 9.01g, 8.59mL, 0.15mol), glyoxal (40%, 14.51g, 11.15mL, 0.1mol). Isolated yield 40.32g, 94 % (≈0.5 eq of residual acetic acid). Dark red solid. Melting point: 70 °C. Decomposition temperature: 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.87 (6 H, t, J 6.81), 1.28 (32 H, d, J 26.20), 1.86 (4 H, t, J 7.19), 4.34 (4 H, t, J 7.35), 7.14 (2 H, s), 11.12 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 164.3, 138.3, 122.0, 49.9, 31.8, 30.3, 29.5, 29.4, 29.3, 29.0, 26.2, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3376, 3130, 3067, 2956, 2922, 2872, 2853, 1563, 1529, 1466, 1406, 1376, 1334, 1295, 1215, 1165, 1125, 1042, 721, 659, 533, 502, 434.

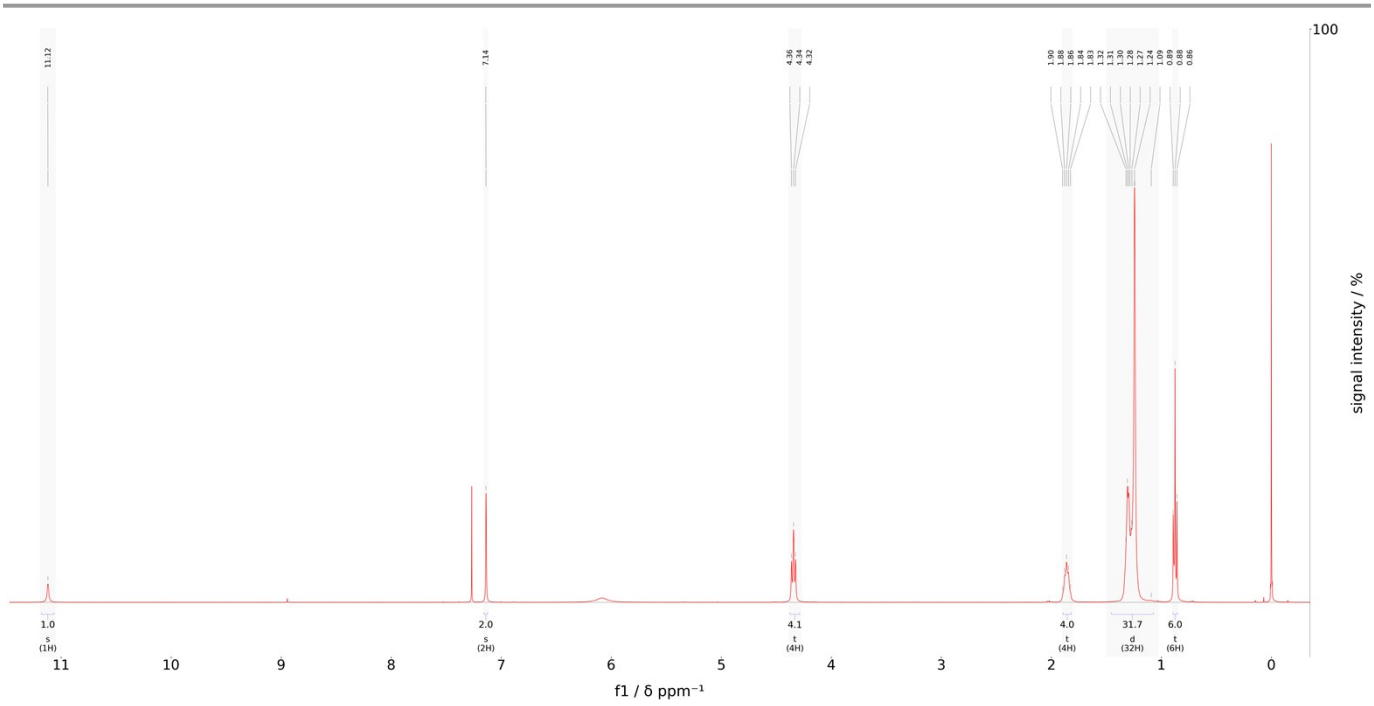

Figure S 37. ^{1}H NMR of 1,3-Di(decyl)imidazolium hydroxalate in deuterochloroform.

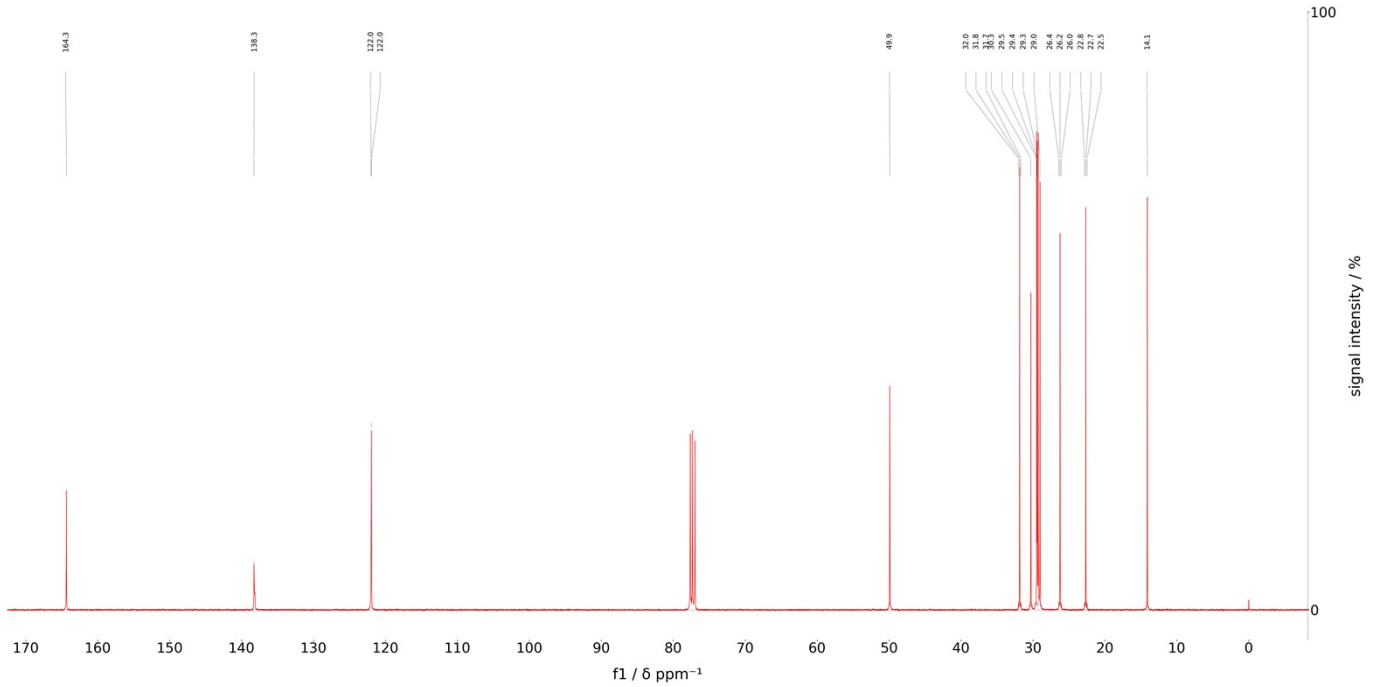

Figure S 38. ^{13}C NMR of 1,3-Di(decyl)imidazolium hydroxalate in deuterochloroform.

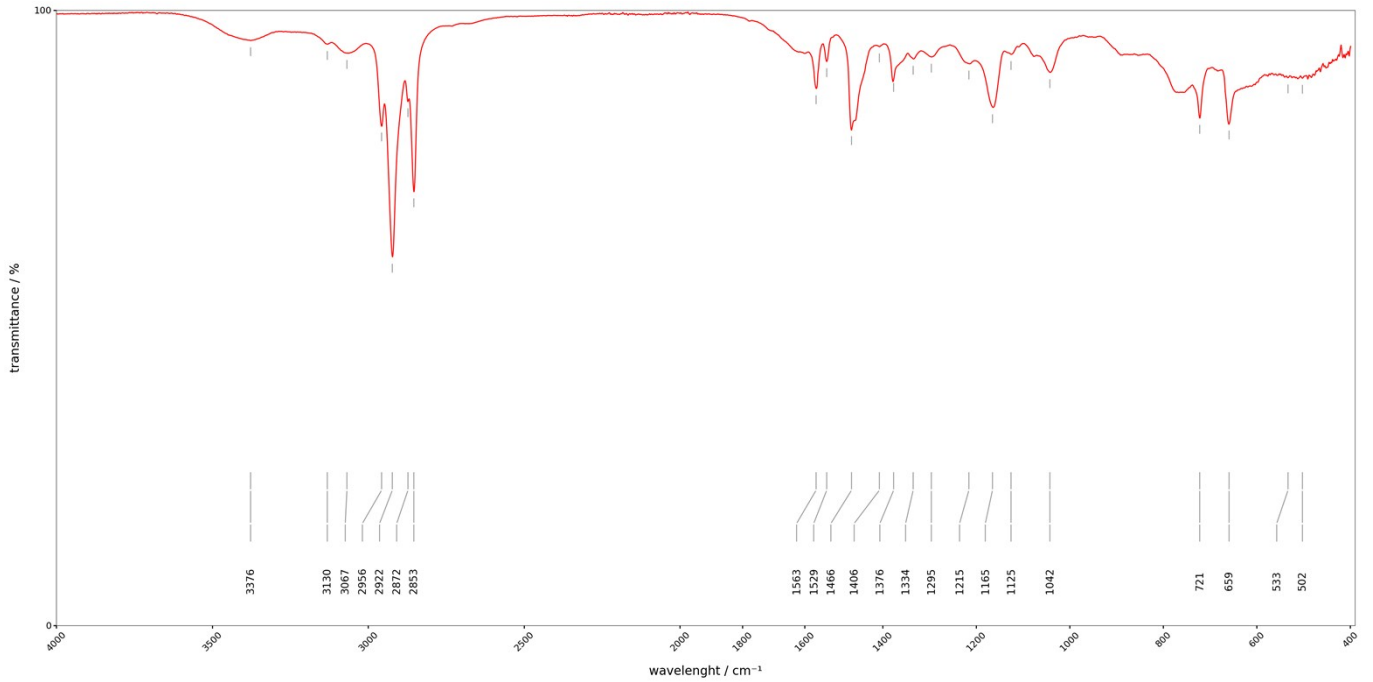

Figure S 39. FTIR of 1,3-Di(decyl)imidazolium hydroxalate.

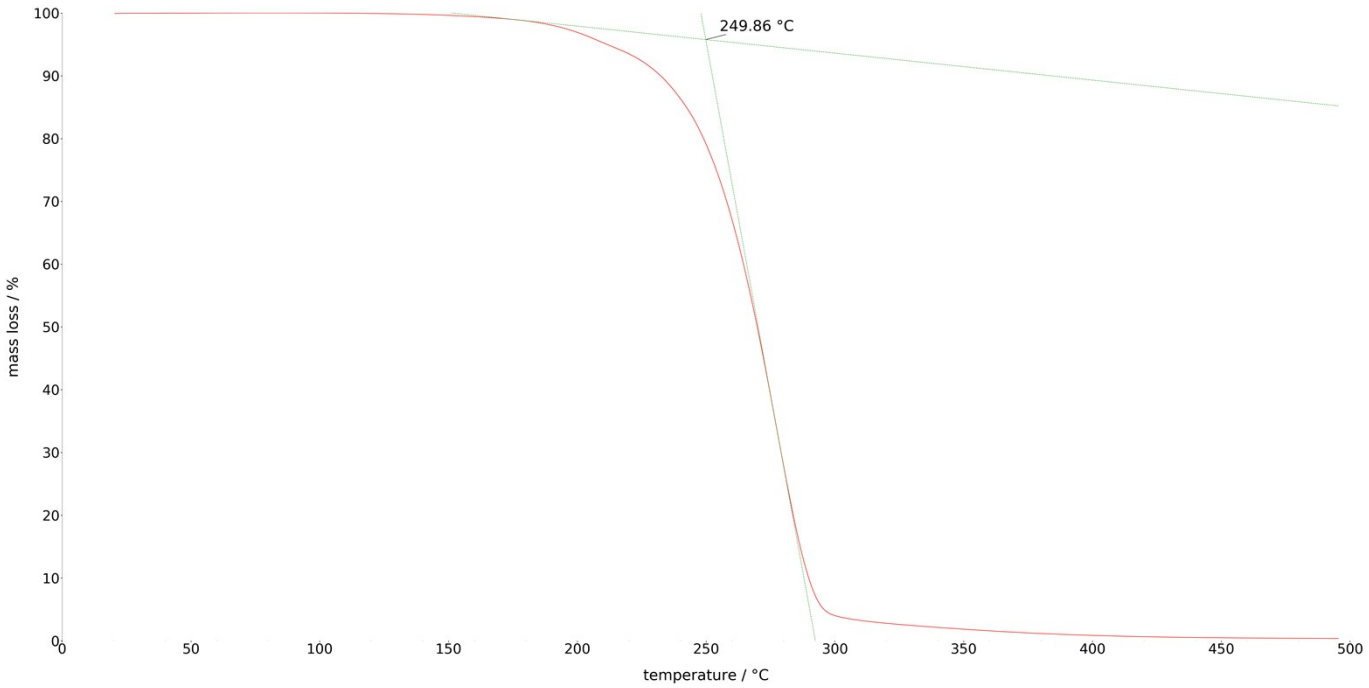

Figure S 40. TGA of 1,3-Di(decyl)imidazolium hydroxalate in an alluminum pan.

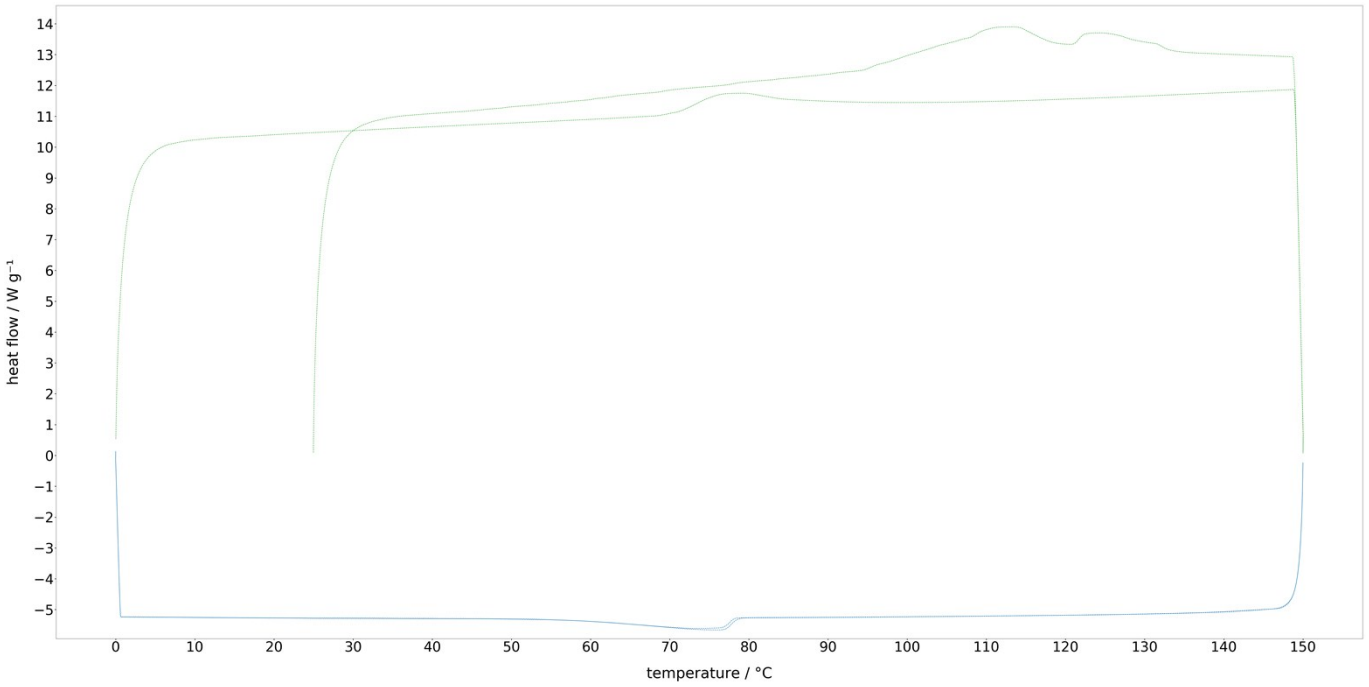

Figure S 41. DSC of 1,3-Di(decyl)imidazolium hydroxalate.

1,3-Di(dodecyl)imidazolium acetate.

The synthesis was carried out following the general procedure with 1-Dodecylamine (98%, 37.571 g, 47.75 mL, 0.2 mol), formaldehyde (36.5-38.0 wt% in water-methanol, 8.34 g, 7.65 mL, 0.1 mol), acetic acid (99.9%, 9.01 g, 8.59 mL, 0.15 mol), glyoxal (40 %, 14.51 g, 11.15 mL, 0.1 mol). Isolated yield 44.292 g, 85 % (≈0.5 eq of residual acetic acid). Orange to beige solid. Melting point: 31 °C. Decomposition temperature: 227 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.81), 1.18 - 1.39 (40 H, m), 1.87 (4 H, p, J 7.59, 7.57), 4.34 (4 H, t, J 7.40), 7.10 (2 H, d, J 1.30), 2.02 (3 H, s), 11.78 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 176.7, 139.6, 121.0, 50.0, 31.9, 30.2, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 23.4, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}):

3159, 3106, 2952, 2914, 2870, 2849, 1708, 1572, 1560, 1470, 1459, 1449, 1374, 1313, 1301, 1291, 1230, 1171, 1128, 1113, 1038, 1007, 942, 839, 762, 741, 730, 718, 661, 632, 607, 505, 438, 429, 416, 410.

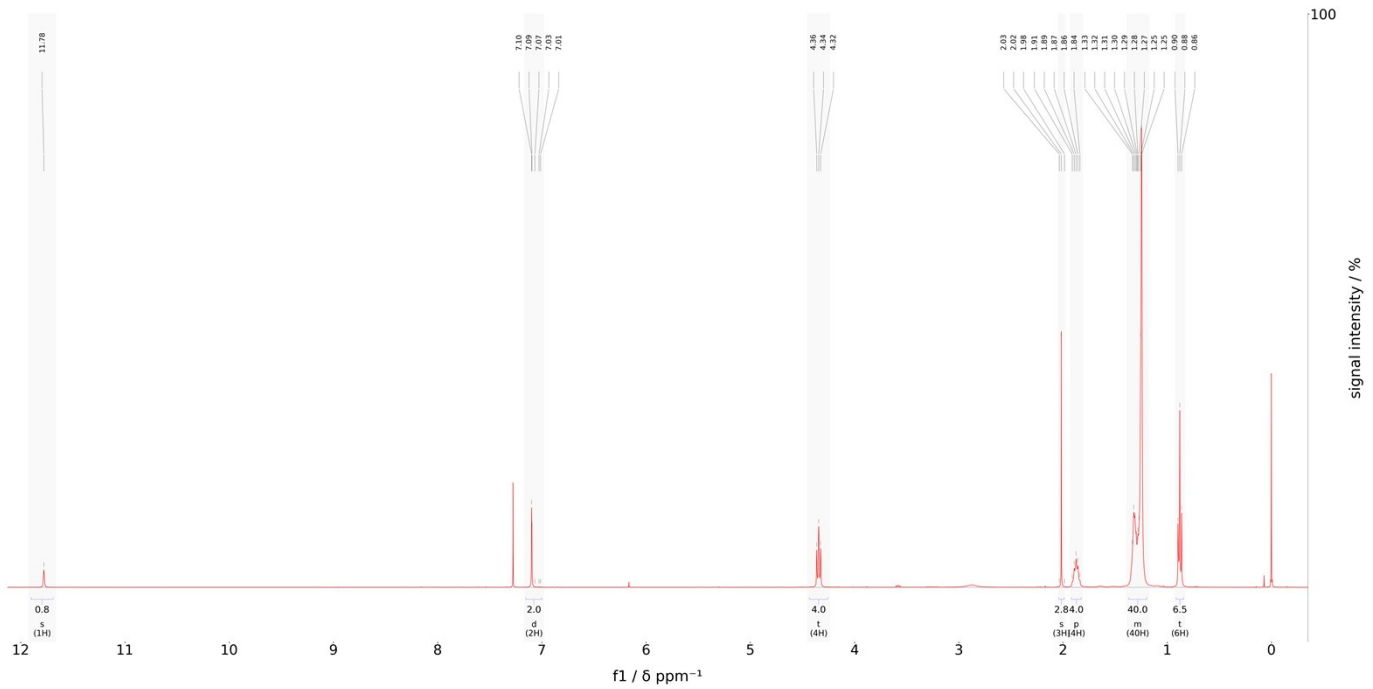

Figure S 42. ^{1}H NMR of 1,3-Di(dodecyl)imidazolium acetate in deuterochloroform.

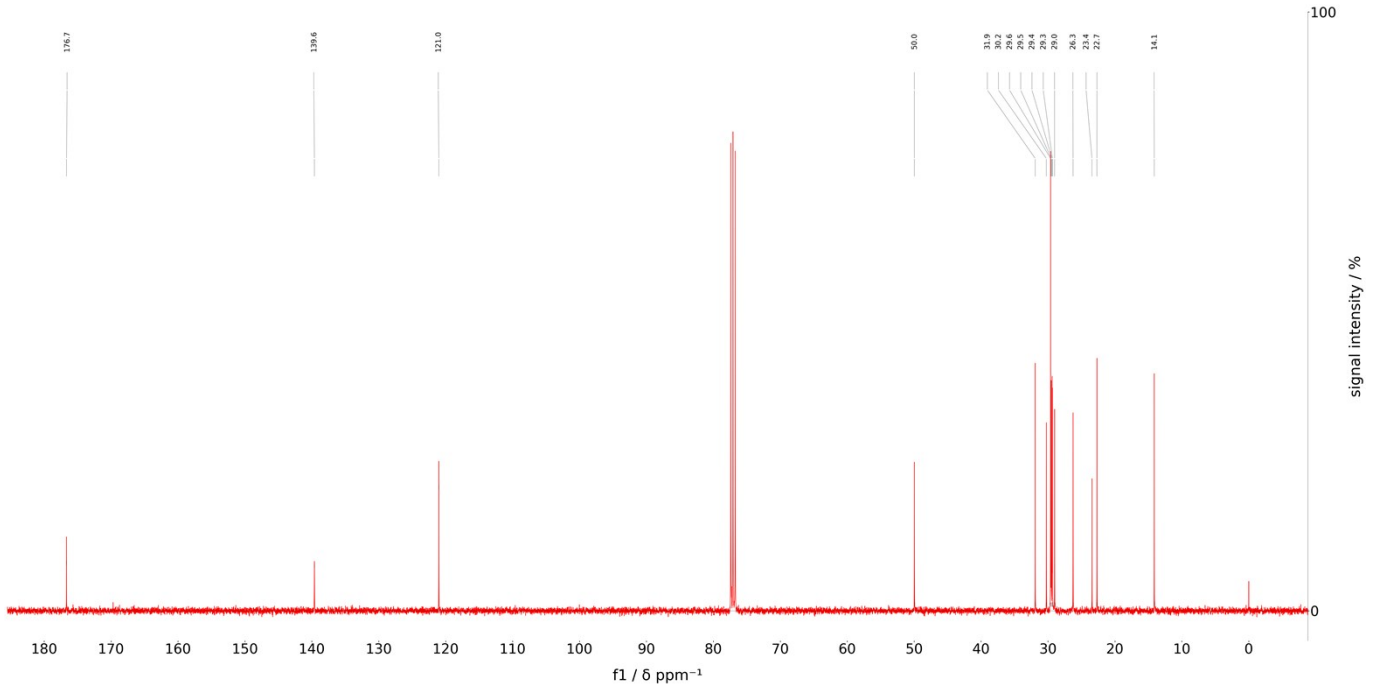

Figure S 43. ^{13}C NMR of 1,3-Di(dodecyl)imidazolium acetate in deuterochloroform.

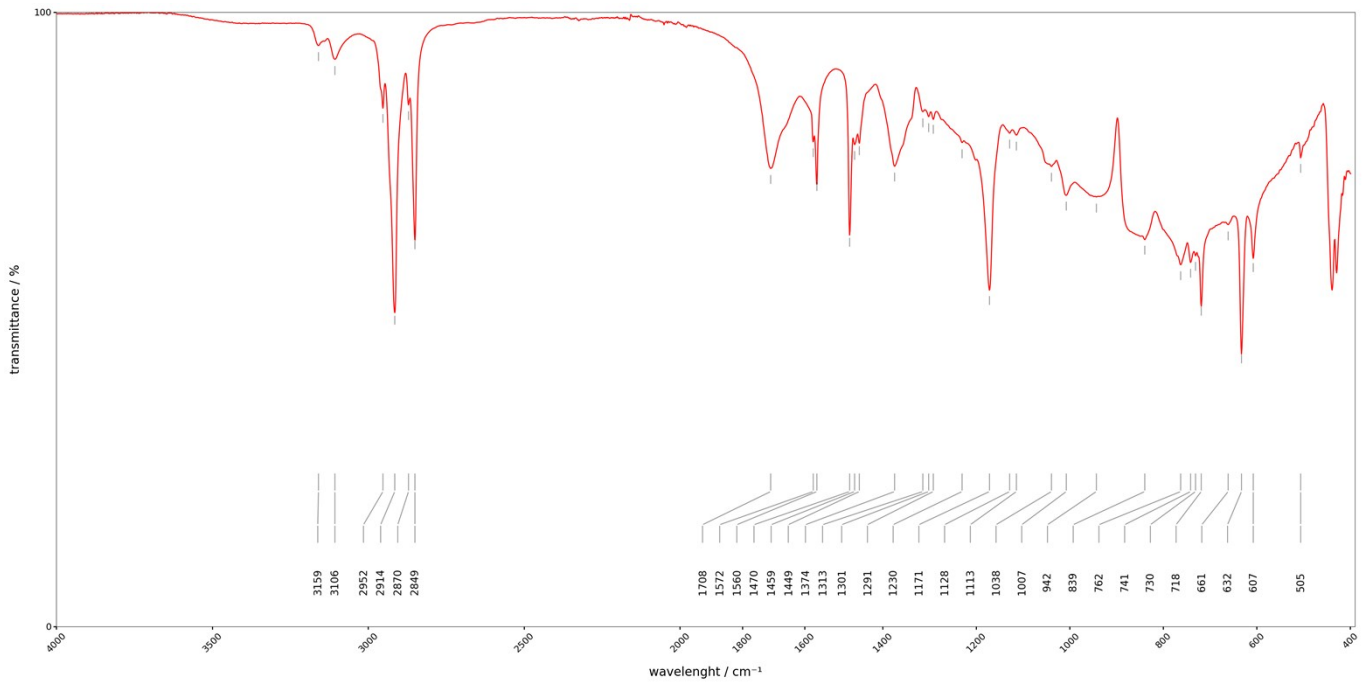

Figure S 44. FTIR of 1,3-Di(dodecyl)imidazolium acetate.

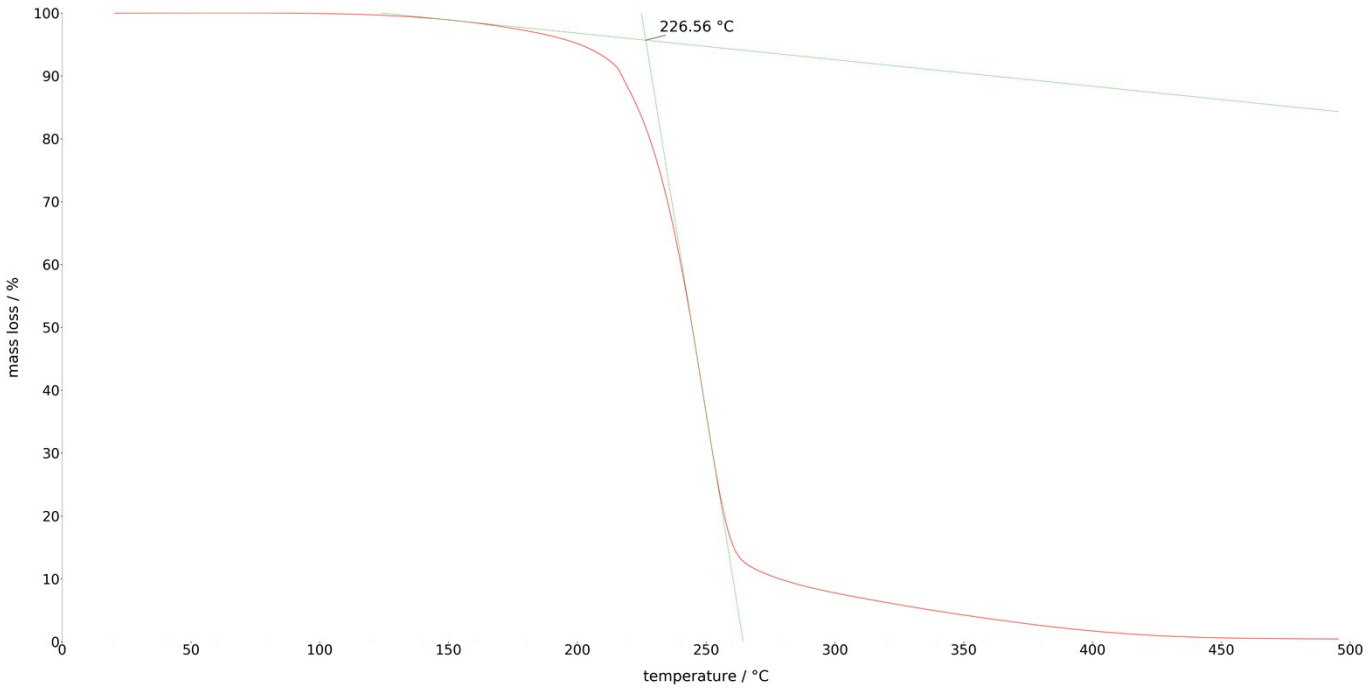

Figure S 45. TGA of 1,3-Di(dodecyl)imidazolium acetate in an alluminum pan.

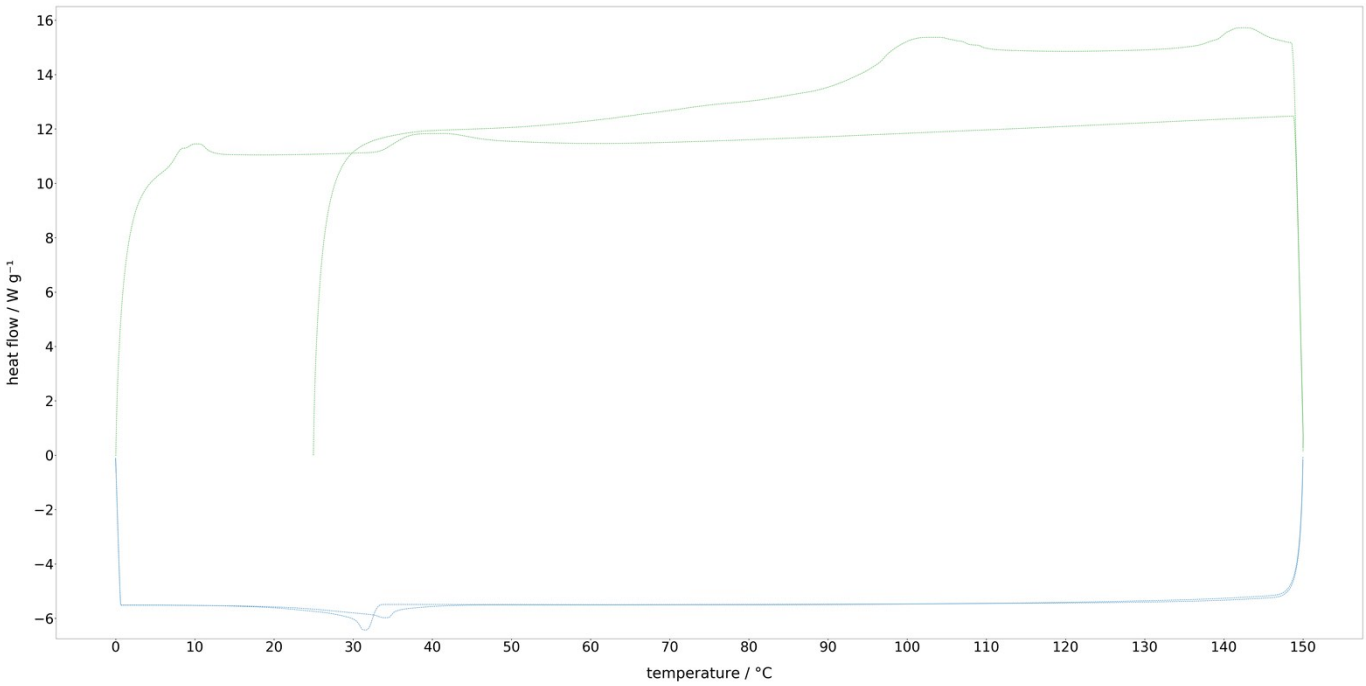

Figure S 46. DSC of 1,3-Di(dodecyl)imidazolium acetate.

1,3-Di(dodecyl)imidazolium nitrate.

The synthesis was carried out following the general procedure with 1,3-di(dodecyl)imidazolium acetate (0.8018 g, 1.0 mL, 1.73 mmol). Isolated yield 0.7819 g, 97 %. Dark red solid. Melting point: 98 °C. Decomposition temperature: 288 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 7.24 (2 H, d, J 1.60), 0.88 (7 H, t, J 6.80), 1.18 - 1.36 (46 H, m), 1.89 (4 H, p, J 8.09, 7.85), 4.25 (4 H, t, J 7.41), 10.15 (1 H, d, J 1.71). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 138.4, 121.5, 50.3, 31.9, 30.2, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3419, 3136, 3094, 2954, 2918, 2850, 2019, 2009, 1967, 1949, 1634, 1563, 1466, 1340, 1221, 1159, 1125, 1087, 1040, 993, 947, 856, 828, 775, 720, 658, 603, 571, 518, 491, 485, 477, 469, 455, 446, 430, 426, 419, 411, 404.

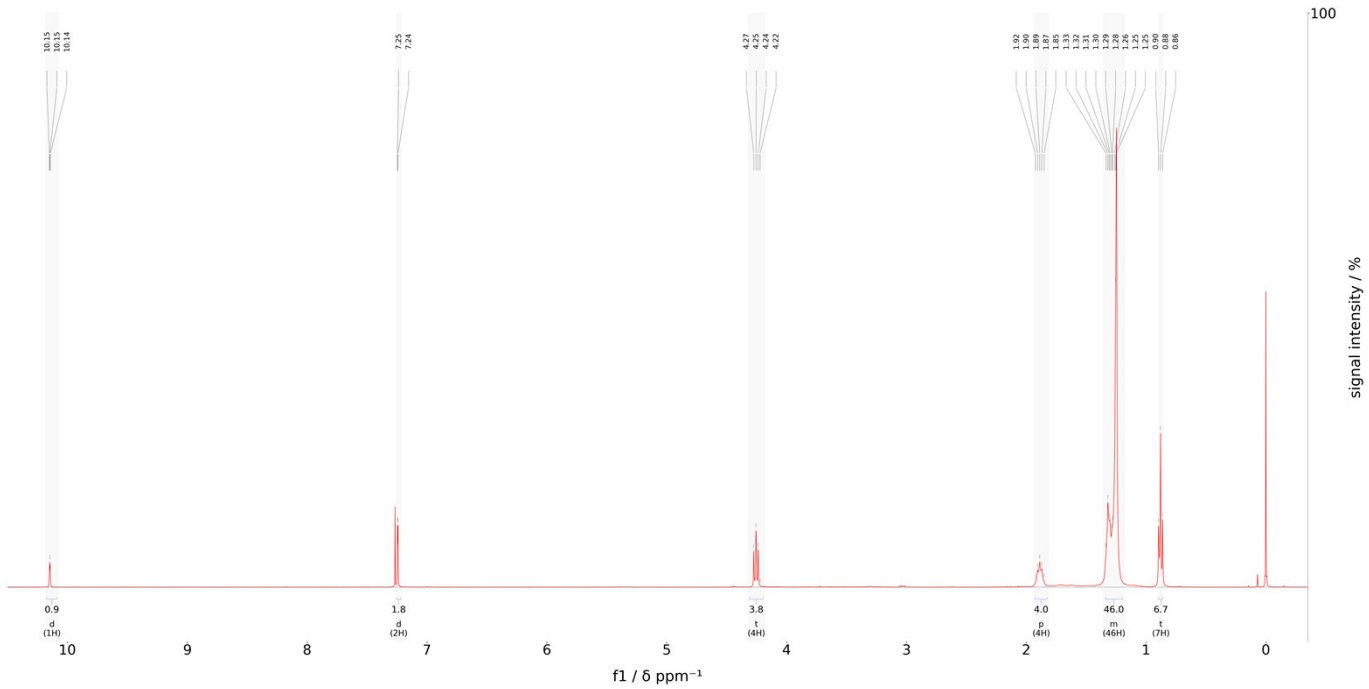

Figure S 47. ^{1}H NMR of 1,3-Di(dodecyl)imidazolium nitrate in deuterochloroform.

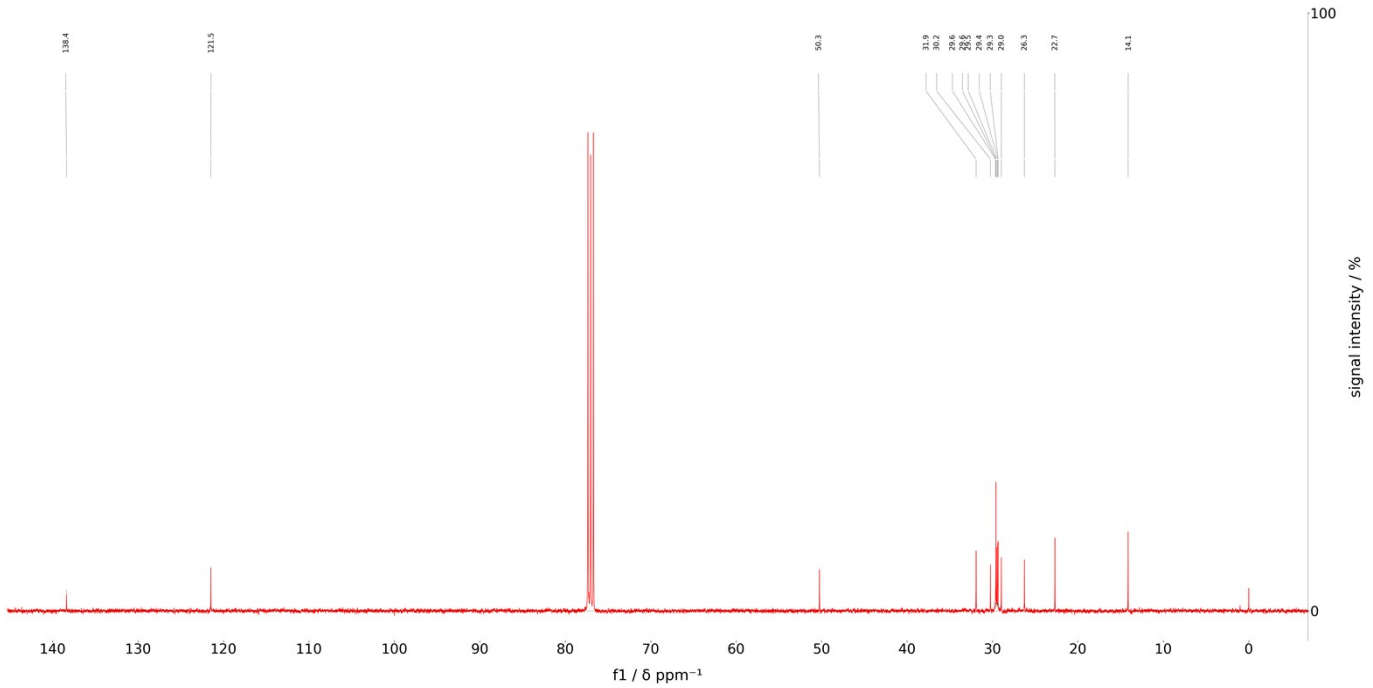

Figure S 48. ^{13}C NMR of 1,3-Di(dodecyl)imidazolium nitrate in deuterochloroform.

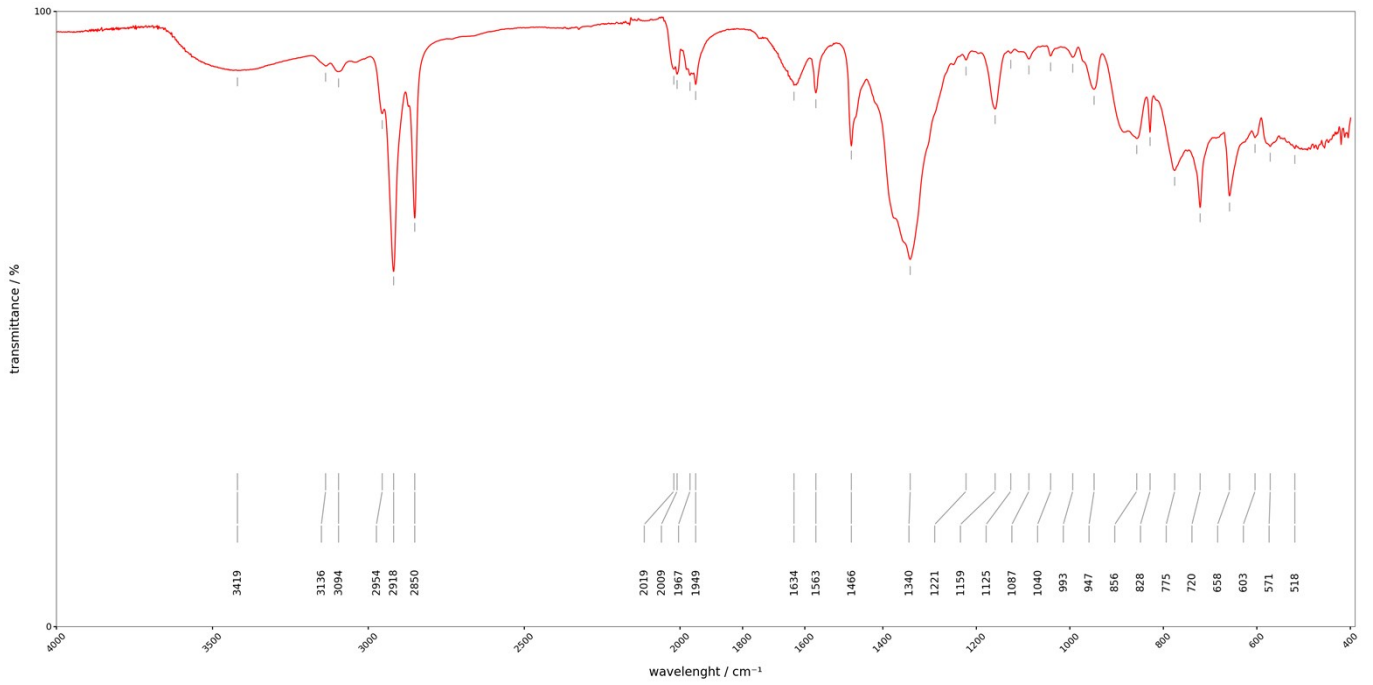

Figure S 49. FTIR of 1,3-Di(dodecyl)imidazolium nitrate.

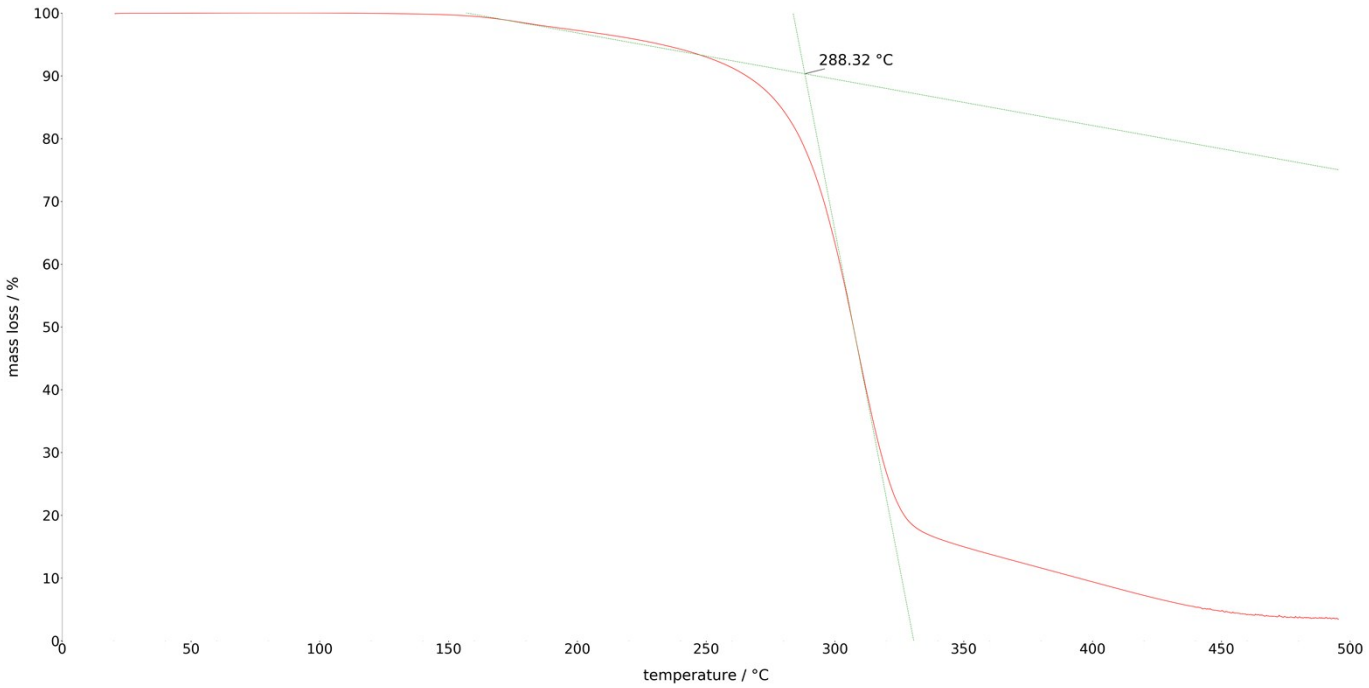

Figure S 50. TGA of 1,3-Di(dodecyl)imidazolium nitrate in an alluminum pan.

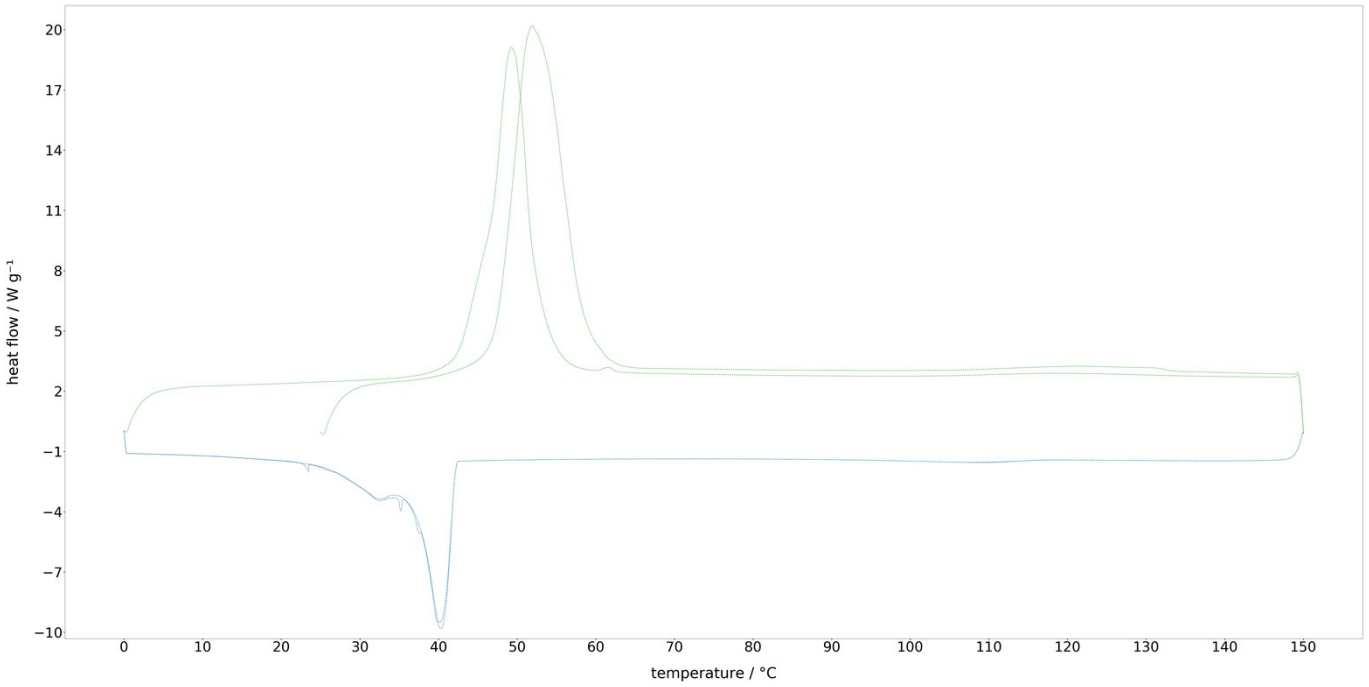

Figure S 51. DSC of 1,3-Di(dodecyl)imidazolium nitrate.

1,3-Di(dodecyl)imidazolium chloride.

The synthesis was carried out following the general procedure with 1,3-di(dodecyl)imidazolium acetate (0.8015 g, 1.0 mL, 1.73 mmol). Isolated yield 0.7194 g, 95 %. Dark red solid. Melting point: 42 °C. Decomposition temperature: 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.78), 1.20 - 1.37 (36 H, m), 1.91 (4 H, q, J 7.39, 7.37), 4.36 (4 H, t, J 7.46), 7.17 (2 H, d, J 1.46), 11.18 (1 H, d, J 1.98). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 137.4, 122.3, 50.0, 31.9, 30.4, 29.6, 29.5, 29.4, 29.3, 29.1, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3390, 3132, 3062, 2953, 2918, 2850, 1643, 1562, 1464, 1404, 1376, 1364, 1305, 1287, 1272, 1246, 1164, 1126, 1108, 1087, 960, 854, 807, 778, 748, 721, 661, 638, 602, 415.

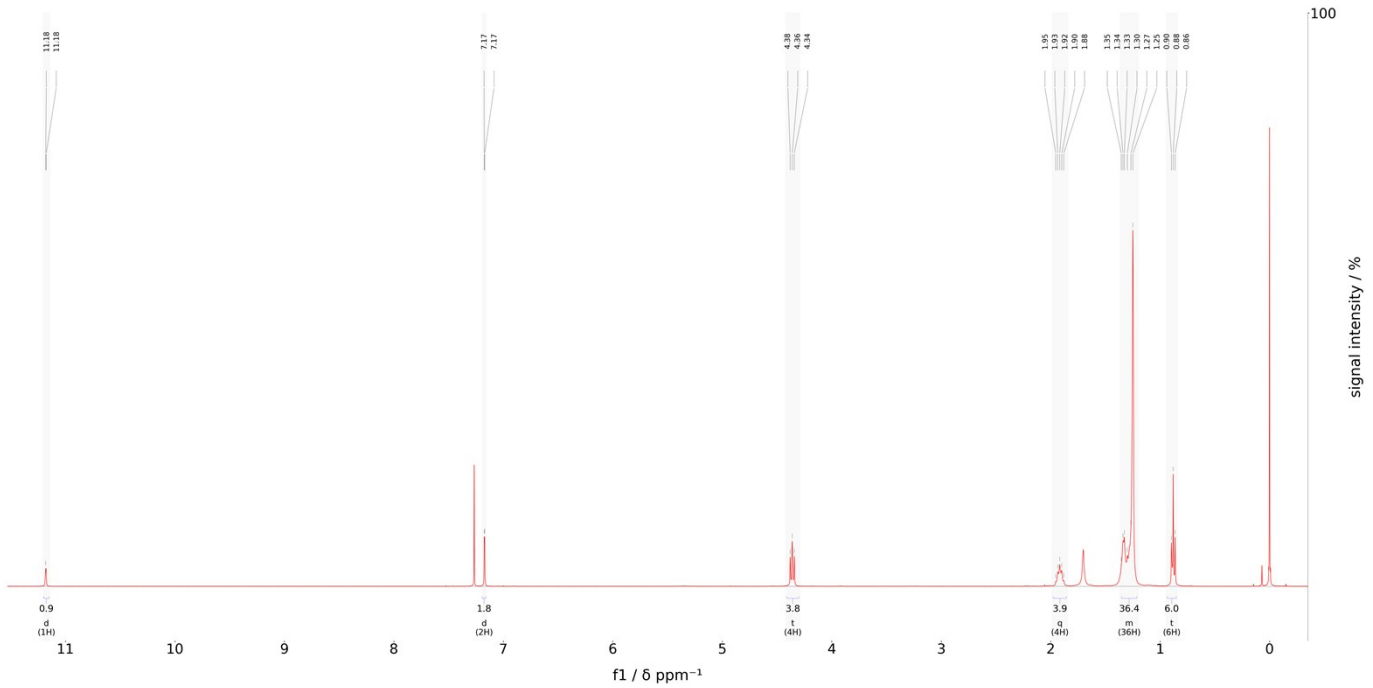

Figure S 52. ^{1}H NMR of 1,3-Di(dodecyl)imidazolium chloride in deuterochloroform.

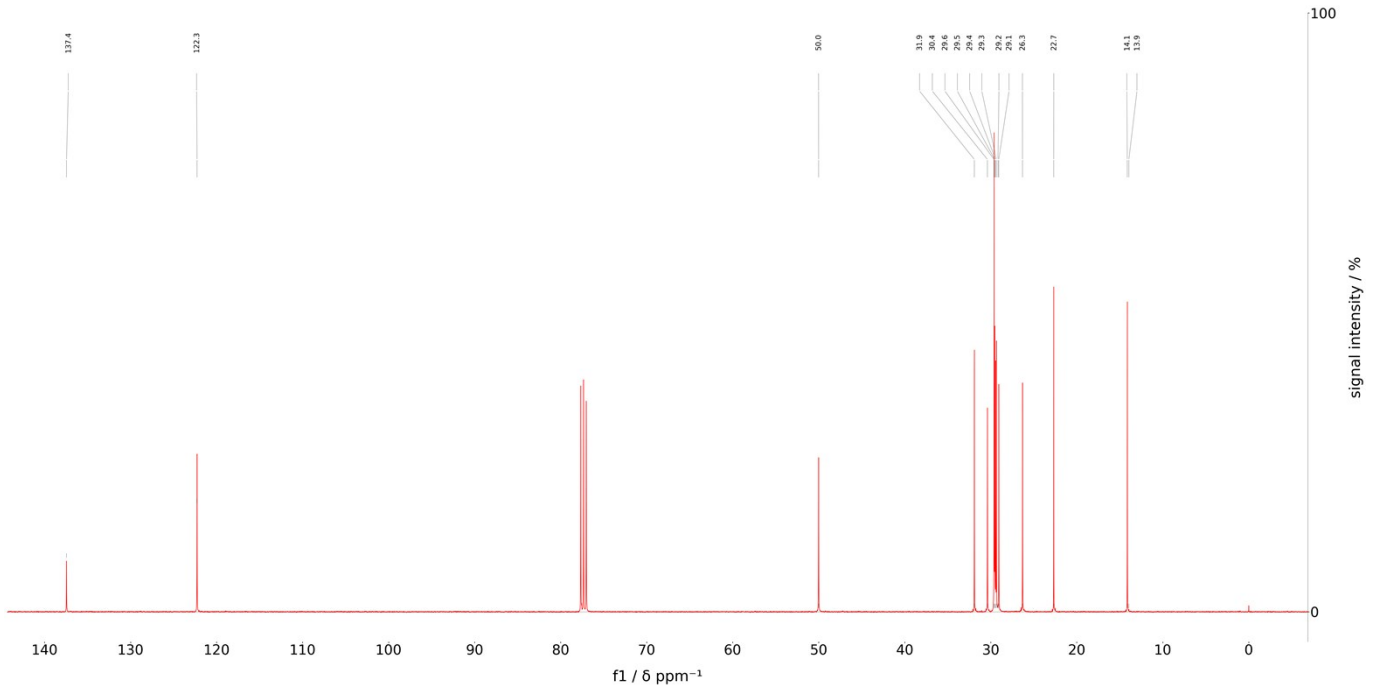

Figure S 53. ^{13}C NMR of 1,3-Di(dodecyl)imidazolium chloride in deuterochloroform.

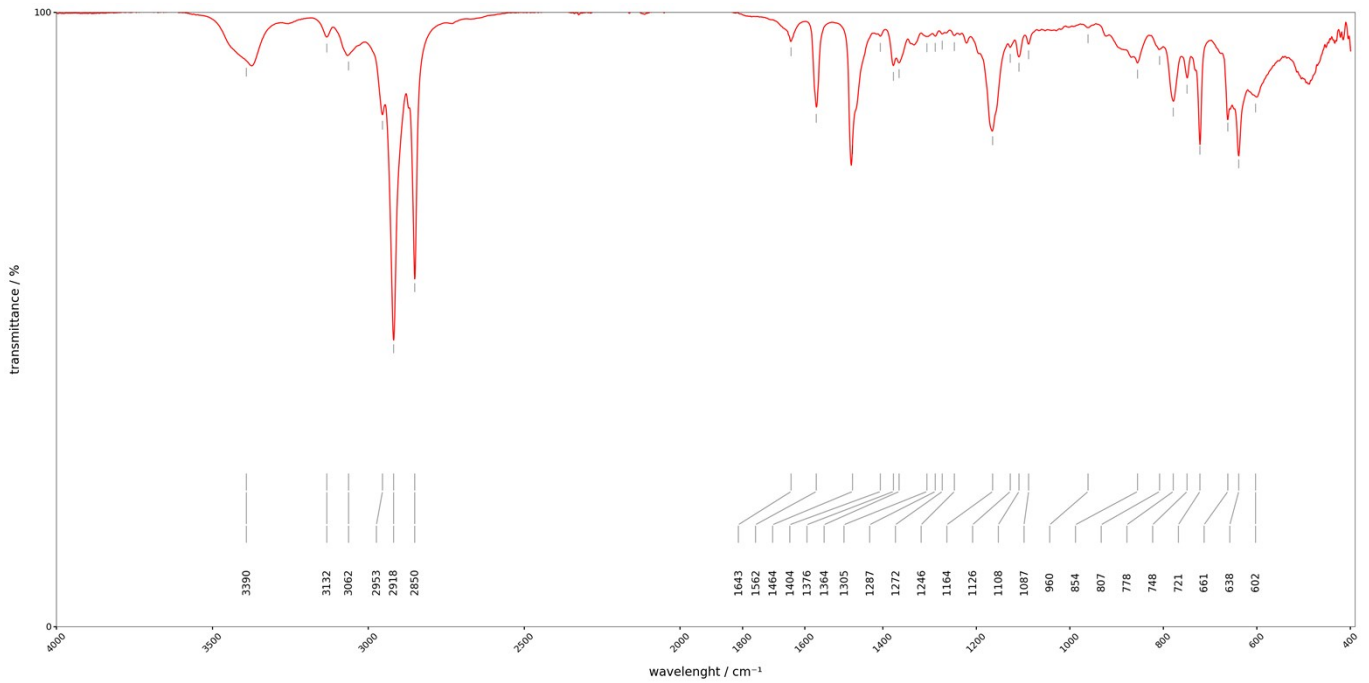

Figure S 54. FTIR of 1,3-Di(dodecyl)imidazolium chloride.

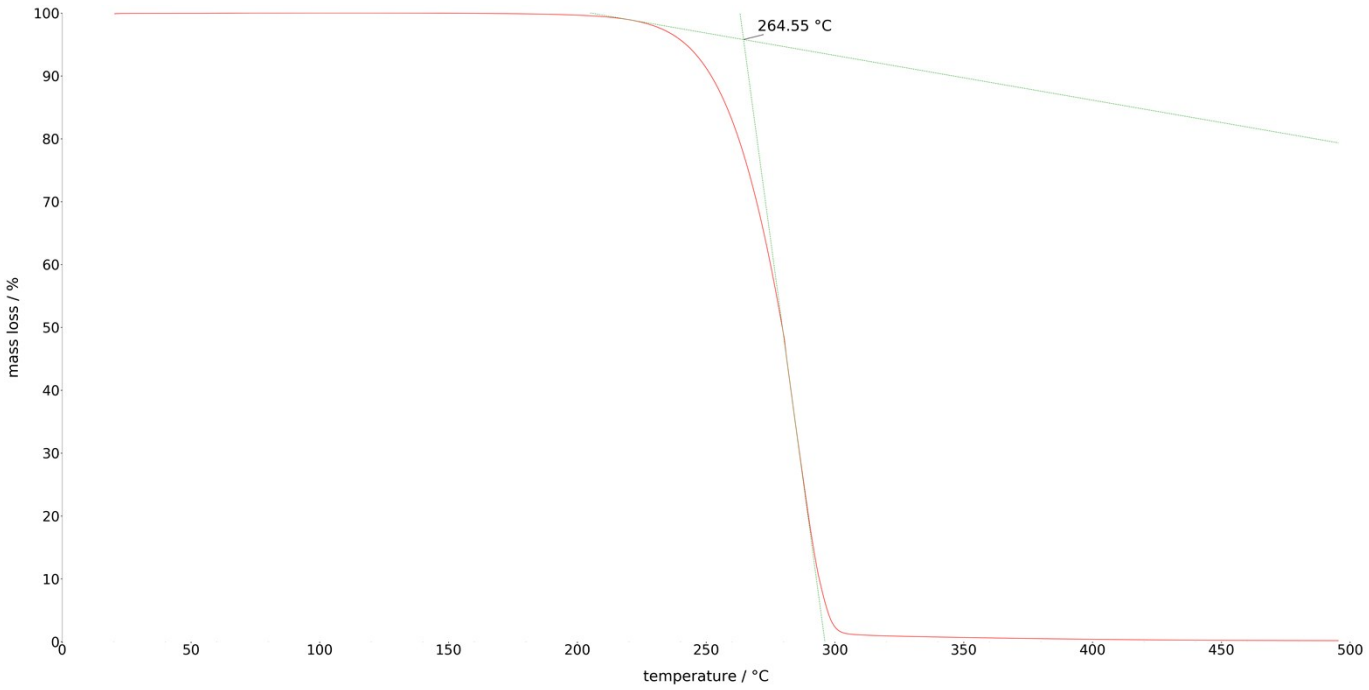

Figure S 55. TGA of 1,3-Di(dodecyl)imidazolium chloride in an alluminum pan.

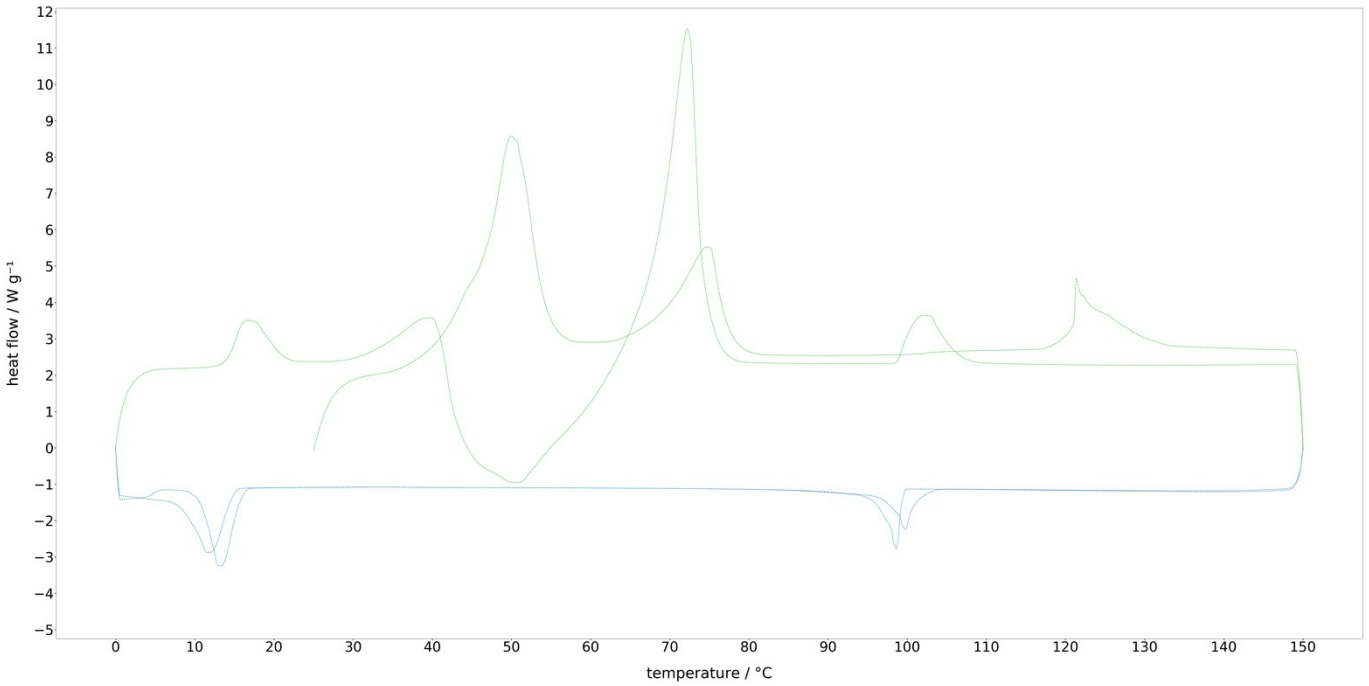

Figure S 56. DSC of 1,3-Di(dodecyl)imidazolium chloride.

1,3-Di(dodecyl)imidazolium hydroxalate.

The synthesis was carried out following the general procedure with 1,3-di(dodecyl)imidazolium acetate (0.8008 g, 1.0 mL, 1.73 mmol). Isolated yield 0.3752 g, 44 %. Pale yellow solid. Melting point: 125 °C. Decomposition temperature: 229 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.81), 1.28 (39 H, d, J 25.55), 1.86 (4 H, p, J 7.64, 7.21), 4.30 (4 H, t, J 7.35), 7.16 (2 H, d, J 1.12), 10.66 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 163.4, 138.7, 121.5, 50.1, 31.9, 30.3, 29.6, 29.5, 29.4, 29.3, 29.0, 26.2, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3139, 3100, 3083, 2954, 2917, 2871, 2850, 1594, 1563, 1462, 1405, 1370, 1328, 1286, 1256, 1218, 1159, 1086, 963, 925, 841, 813, 789, 711, 656, 637, 601, 543, 458.

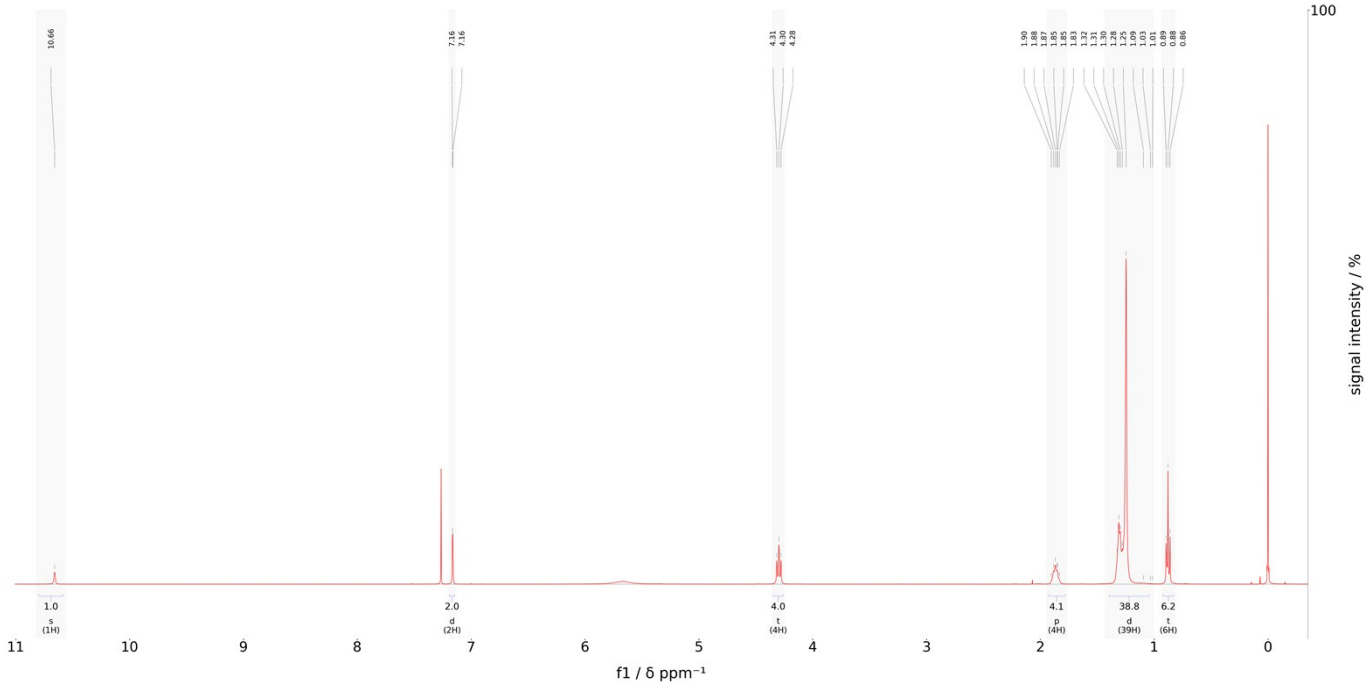

Figure S 57. ^{1}H NMR of 1,3-Di(dodecyl)imidazolium hydroxalate in deuterochloroform.

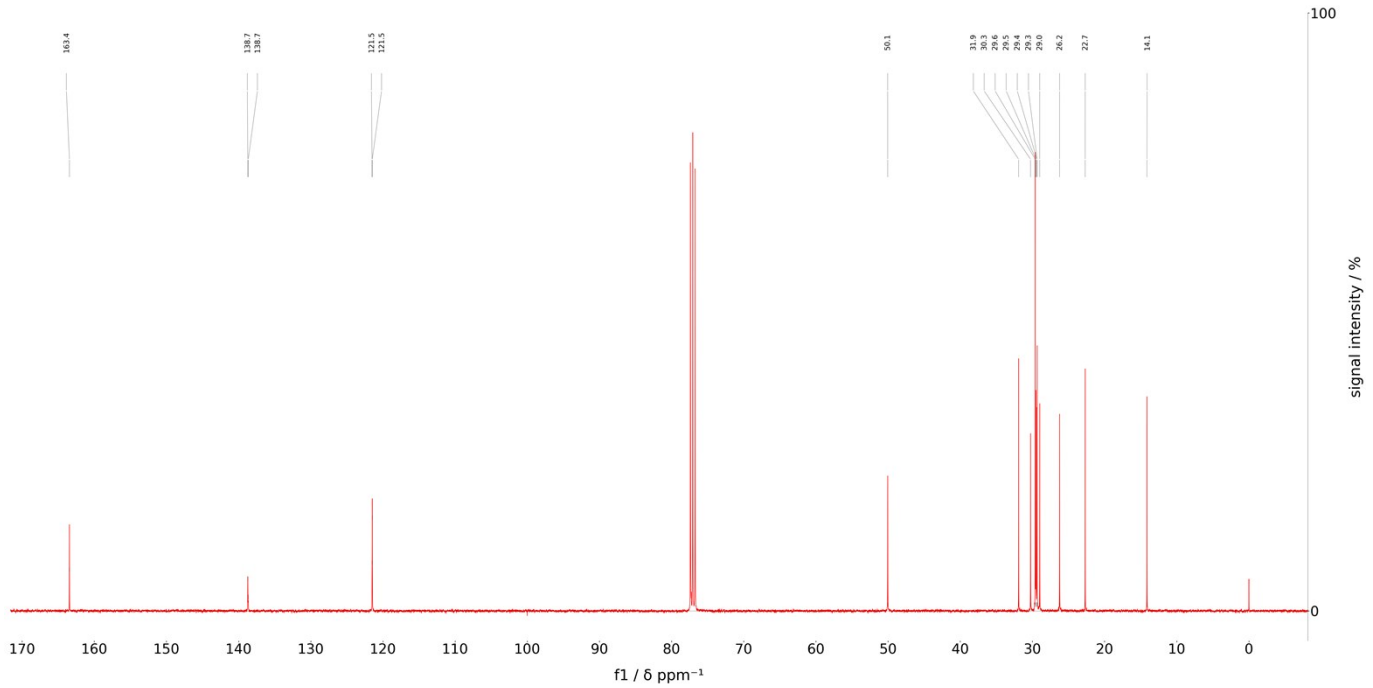

Figure S 58. ^{13}C NMR of 1,3-Di(dodecyl)imidazolium hydroxalate in deuterochloroform.

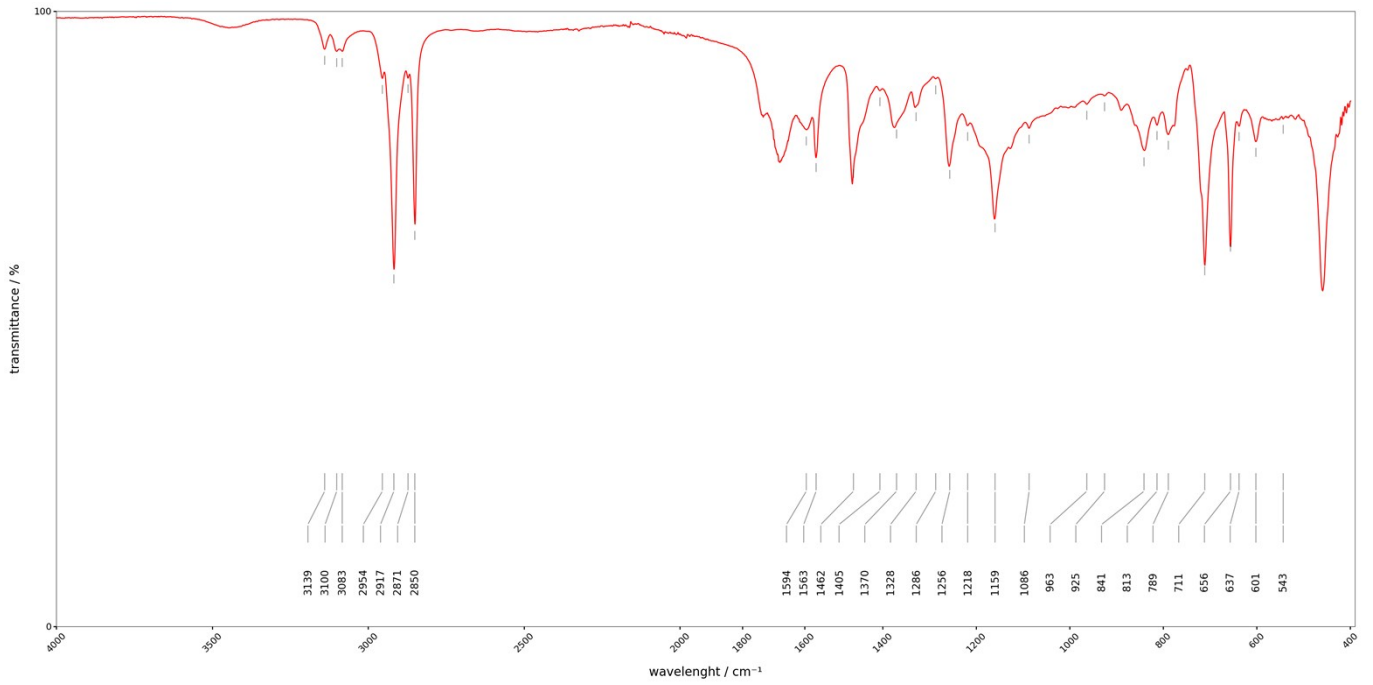

Figure S 59. FTIR of 1,3-Di(dodecyl)imidazolium hydroxalate.

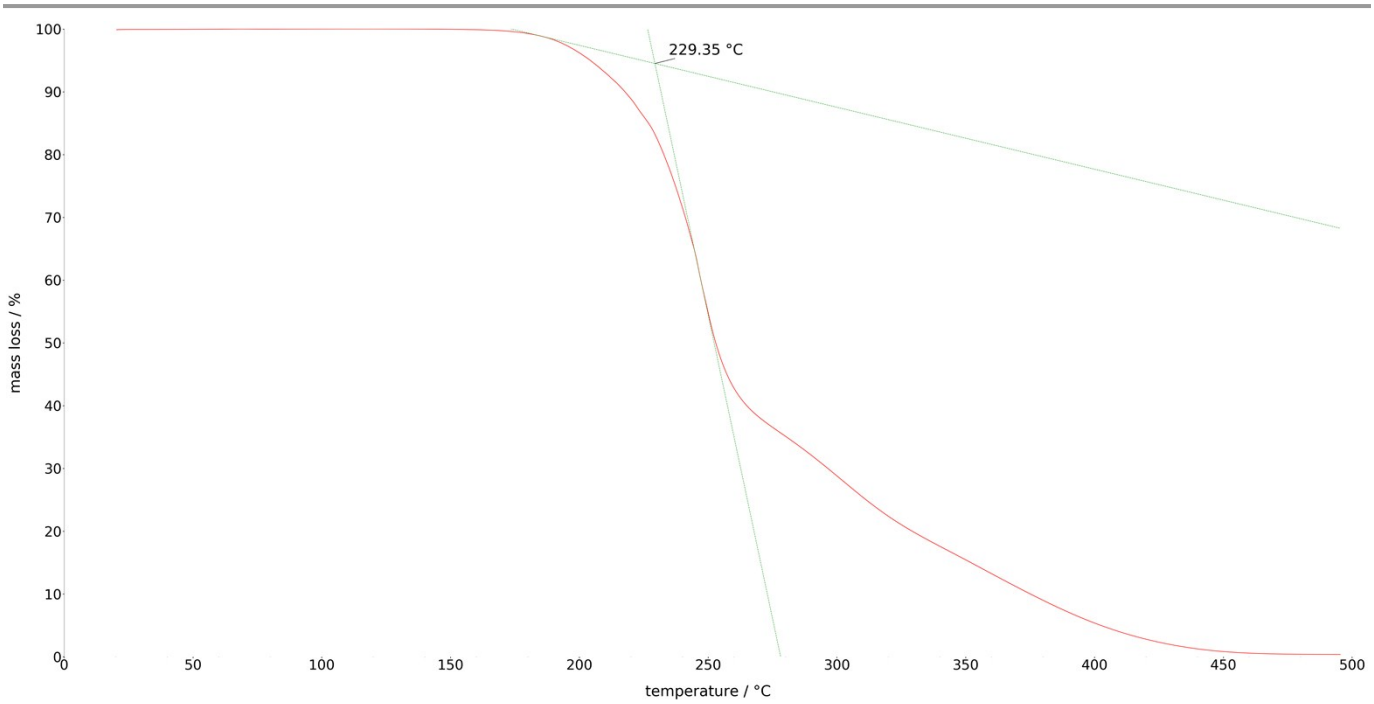

Figure S 60. TGA of 1,3-Di(dodecyl)imidazolium hydroxalate in an alluminum pan.

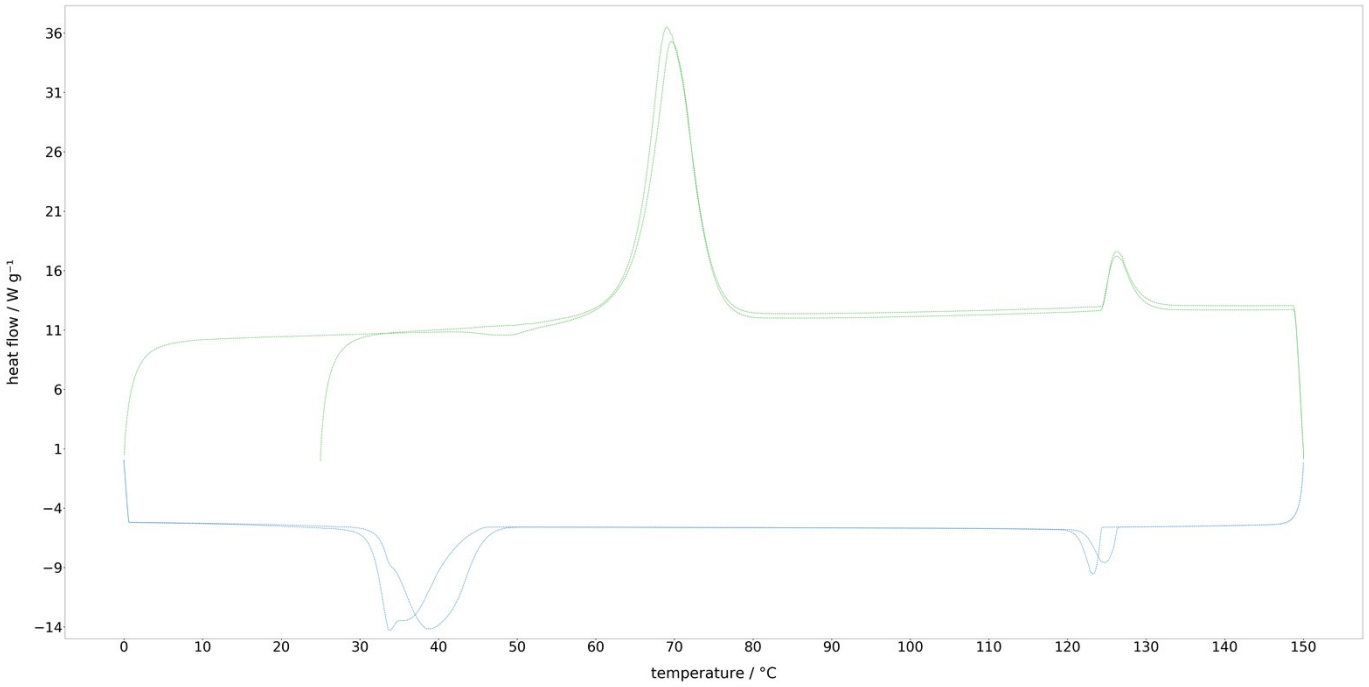

Figure S 61. DSC of 1,3-Di(dodecyl)imidazolium hydroxalate.

1,3-Di(tetradecyl)imidazolium acetate.

The synthesis was carried out following the general procedure with 1-Tetradecylamine (98.5 %, 4.2688 g, 4.775 mL, 0.02 mol), formaldehyde (36.5-38.0 %, 0.834 g, 0.765 mL, 0.01 mol), acetic acid (99.9 %, 0.901 g, 0.859 mL, 0.015 mol), glyoxal (40 %, 1.451 g, 1.115 mL, 0.01 mol). Isolated yield 4.451 g, 86 % (≈0.5 eq of residual acetic acid). Yellow solid. Melting point: 43 °C. Decomposition temperature: 229 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.74), 0.97 - 1.70 (48 H, m), 1.87 (4 H, p, J 7.50, 7.42), 2.01 (3 H, s), 4.33 (4 H, t, J 7.39), 7.11 (2 H, d, J 1.44), 11.35 - 11.58 (1 H, m). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 176.2, 139.1, 121.1, 50.0, 31.9, 30.2, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.0, 26.2, 22.8, 22.7, 14.1. IR (Diamond-ATR, neat,

cm^{-1}): 3160, 3105, 2952, 2913, 2870, 2849, 1708, 1573, 1562, 1470, 1453, 1376, 1312, 1300, 1170, 1128, 1114, 1050, 1007, 943, 874, 771, 762, 742, 718, 660, 632, 607, 515, 505, 471, 459, 440, 417, 412, 403.

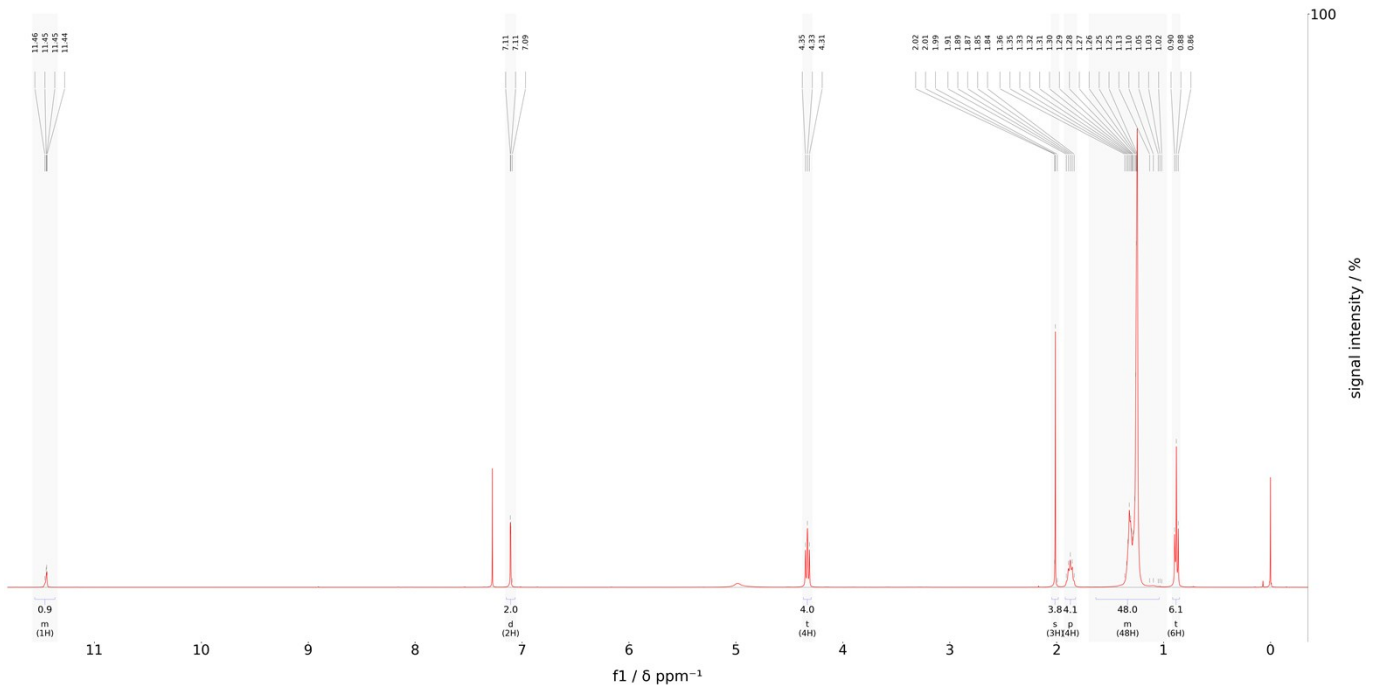

Figure S 62. ^{1}H NMR of 1,3-Di(tetradecyl)imidazolium acetate in deuterochloroform.

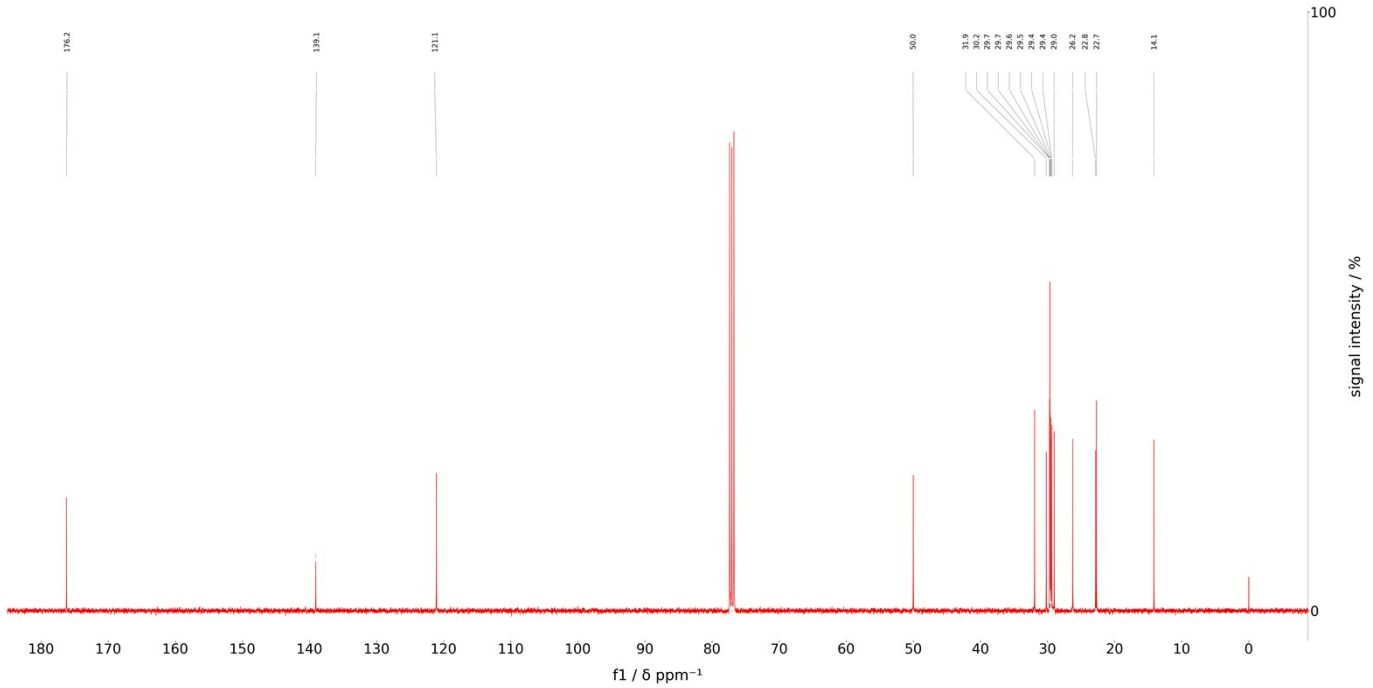

Figure S 63. ^{13}C NMR of 1,3-Di(tetradecyl)imidazolium acetate in deuterochloroform.

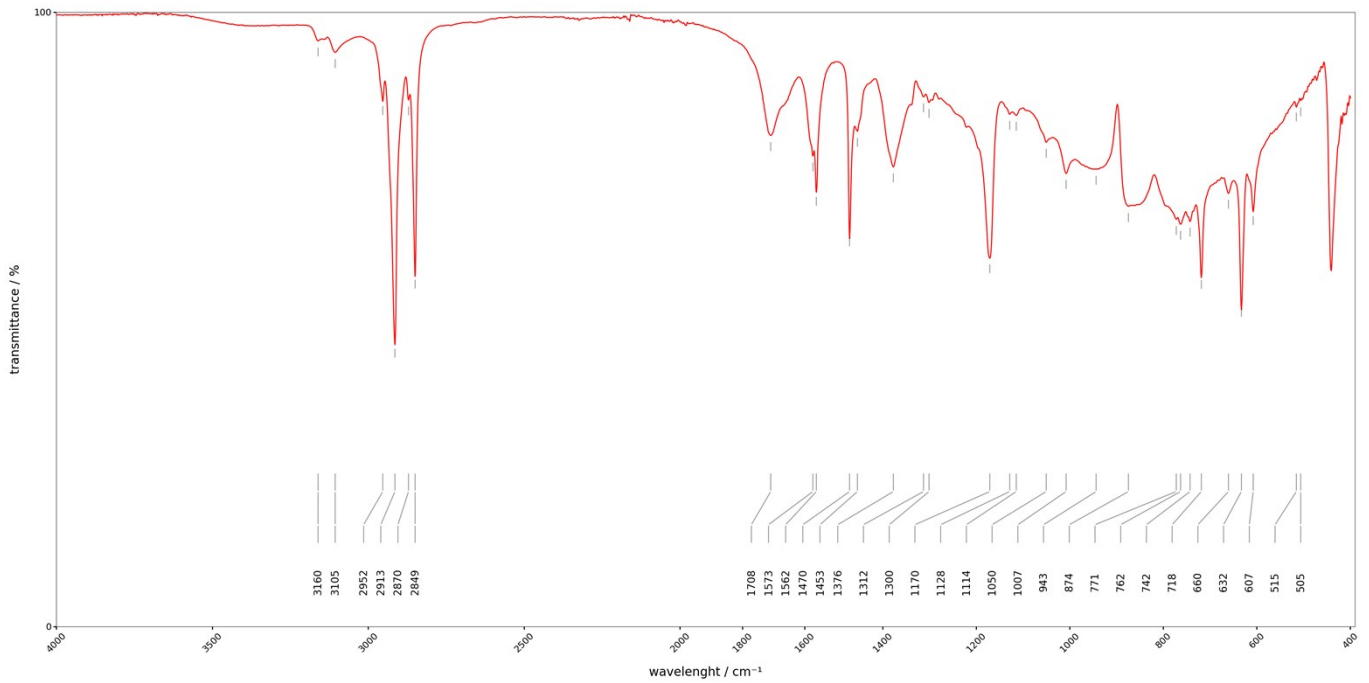

Figure S 63. FTIR of 1,3-Di(tetradecyl)imidazolium acetate.

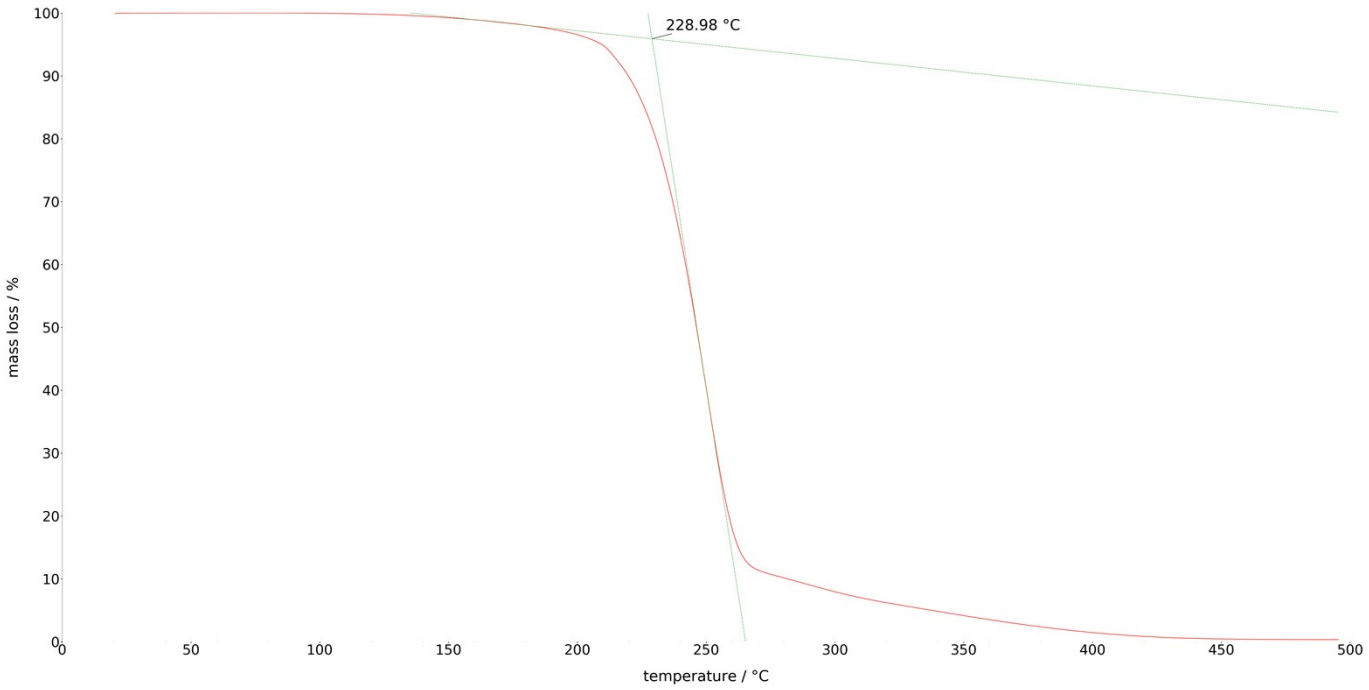

Figure S 65. TGA of 1,3-Di(tetradecyl)imidazolium acetate in an alluminum pan.

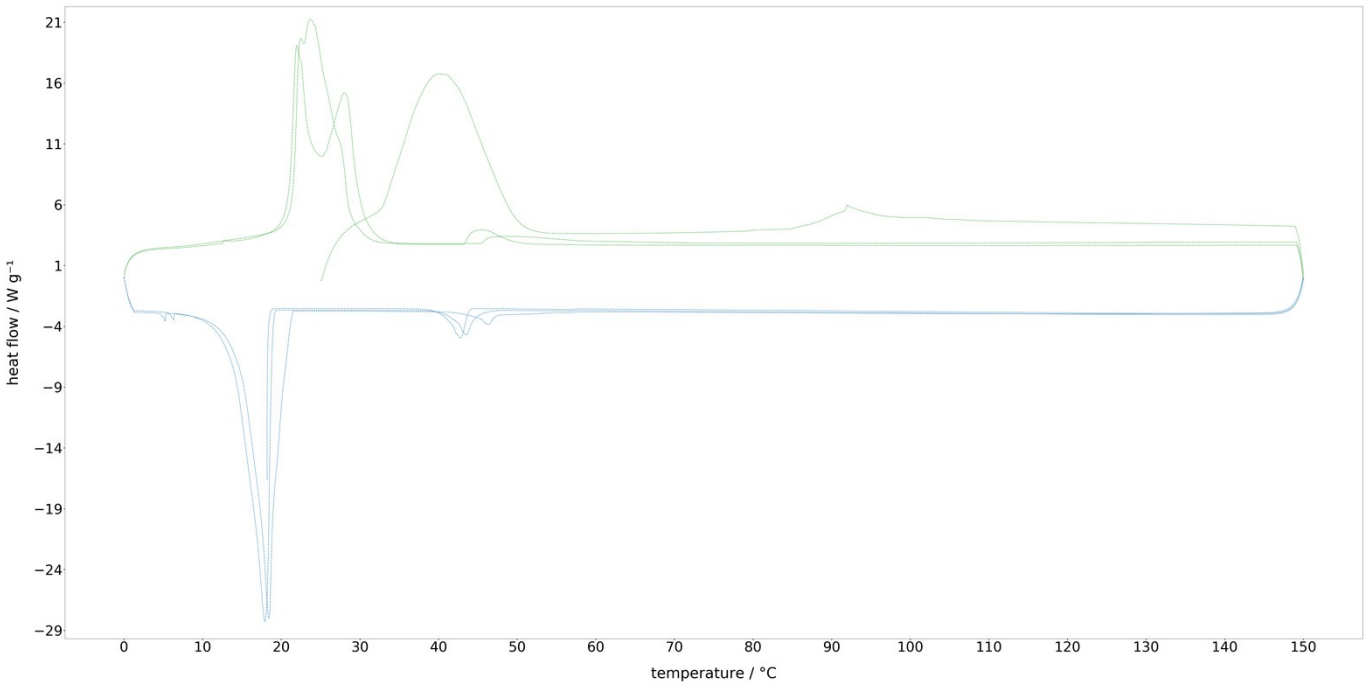

Figure S 66. DSC of 1,3-Di(tetradecyl)imidazolium acetate.

1,3-Di(tetradecyl)imidazolium nitrate.

The synthesis was carried out following the general procedure with 1,3-di(Tetradecyl)imidazolium acetate (0.3979 g, 1.0 mL, 0.77 mmol). Isolated yield 0.3938 g, 98 %. Yellow solid. Melting point: 111 °C. Decomposition temperature: 285 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.77), 0.96 - 1.53 (48 H, m), 1.88 (4 H, q, J 7.13, 6.90), 4.25 (4 H, t, J 7.39), 7.33 (2 H, d, J 1.57), 10.11 (1 H, d, J 1.71). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 138.1, 121.8, 50.2, 31.9, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.0, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3461, 3135, 3092, 3038, 2953, 2916, 2849, 1745, 1651, 1563, 1466, 1339, 1214, 1162, 1128, 1094, 1059, 1041, 1019, 972, 941, 889, 848, 828, 806, 777, 753, 720, 693, 686, 678, 659, 621, 605, 586, 579, 572, 564, 556, 549, 541, 530, 522, 515, 507, 500, 492, 484, 478, 470, 456, 444, 439, 428, 422, 416, 411, 404.

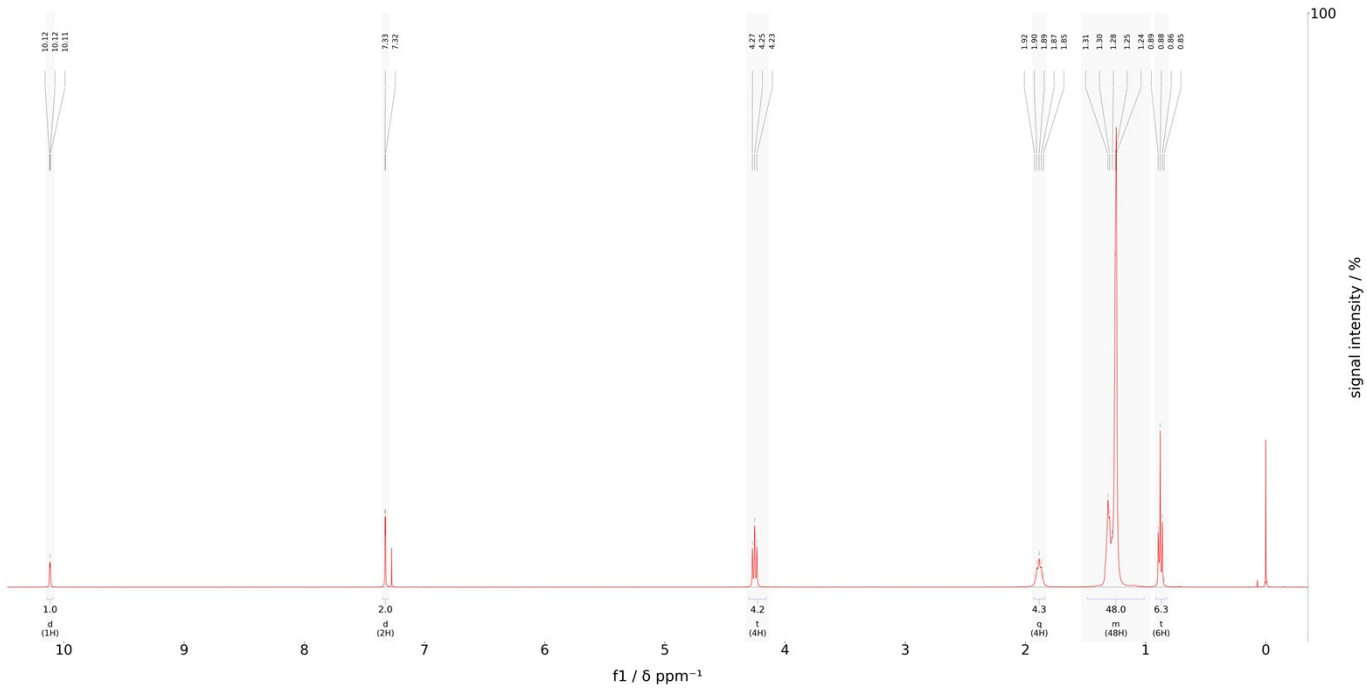

Figure S 67. ^{1}H NMR of 1,3-Di(tetradecyl)imidazolium nitrate in deuterochloroform.

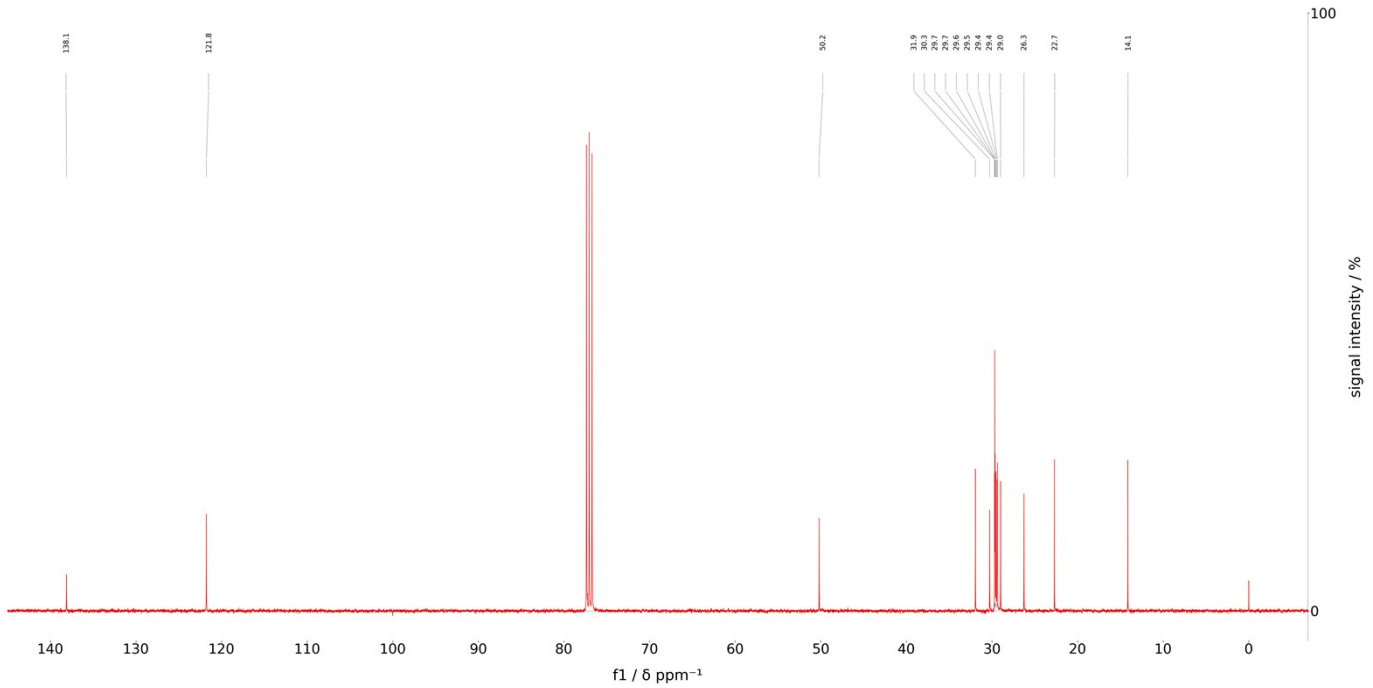

Figure S 68. ^{13}C NMR of 1,3-Di(tetradecyl)imidazolium nitrate in deuterochloroform.

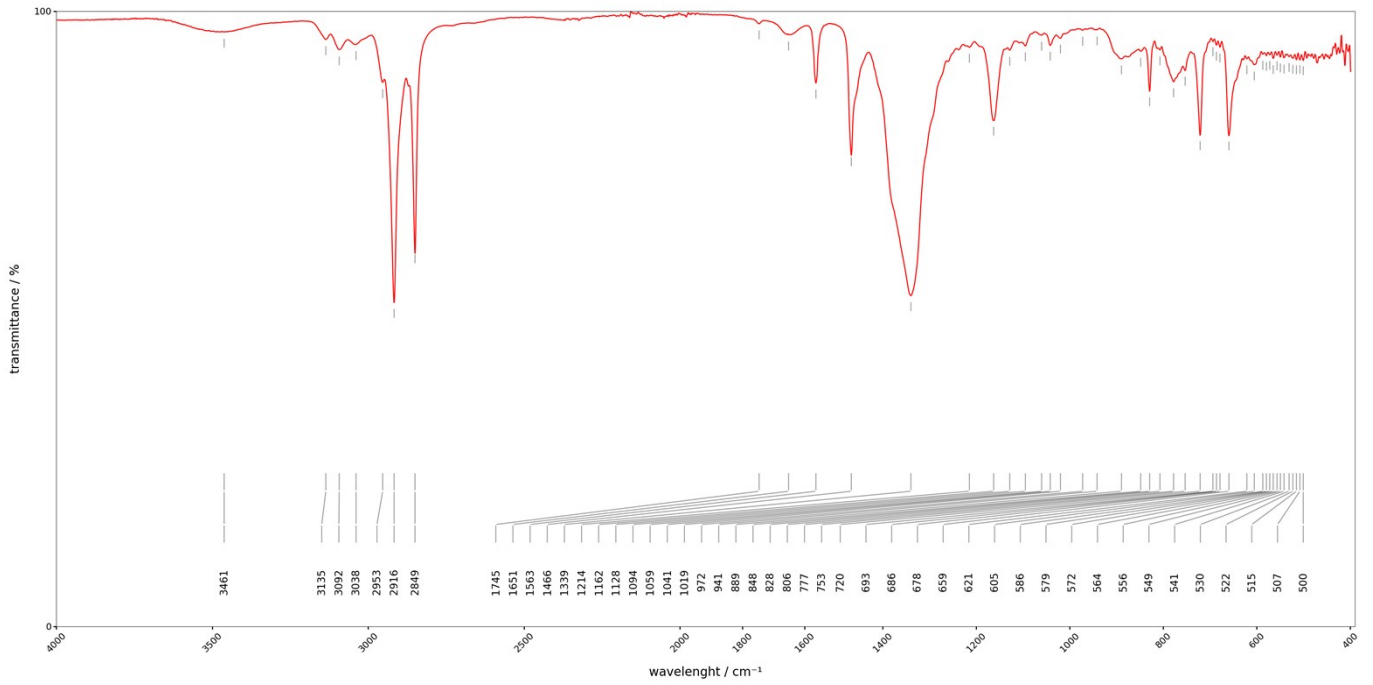

Figure S 69. FTIR of 1,3-Di(tetradecyl)imidazolium nitrate.

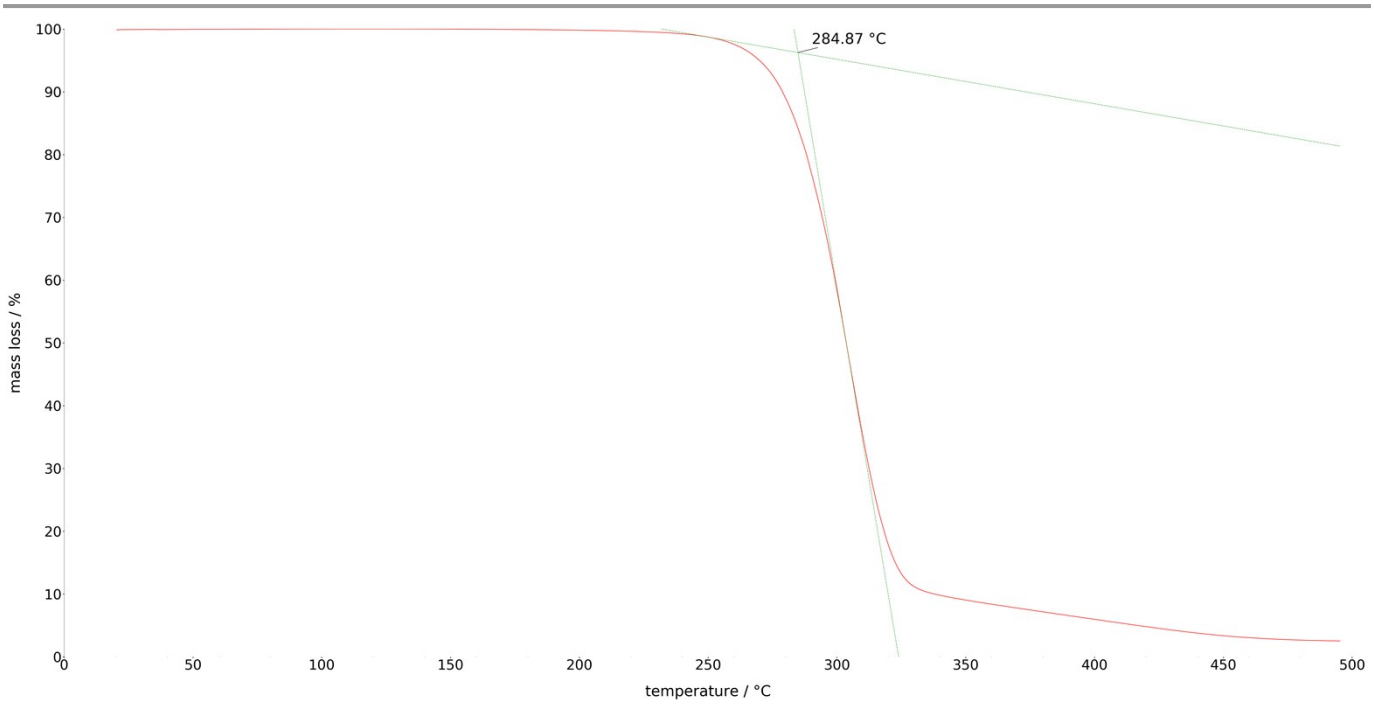

Figure S 70. TGA of 1,3-Di(tetradecyl)imidazolium nitrate in an alluminum pan.

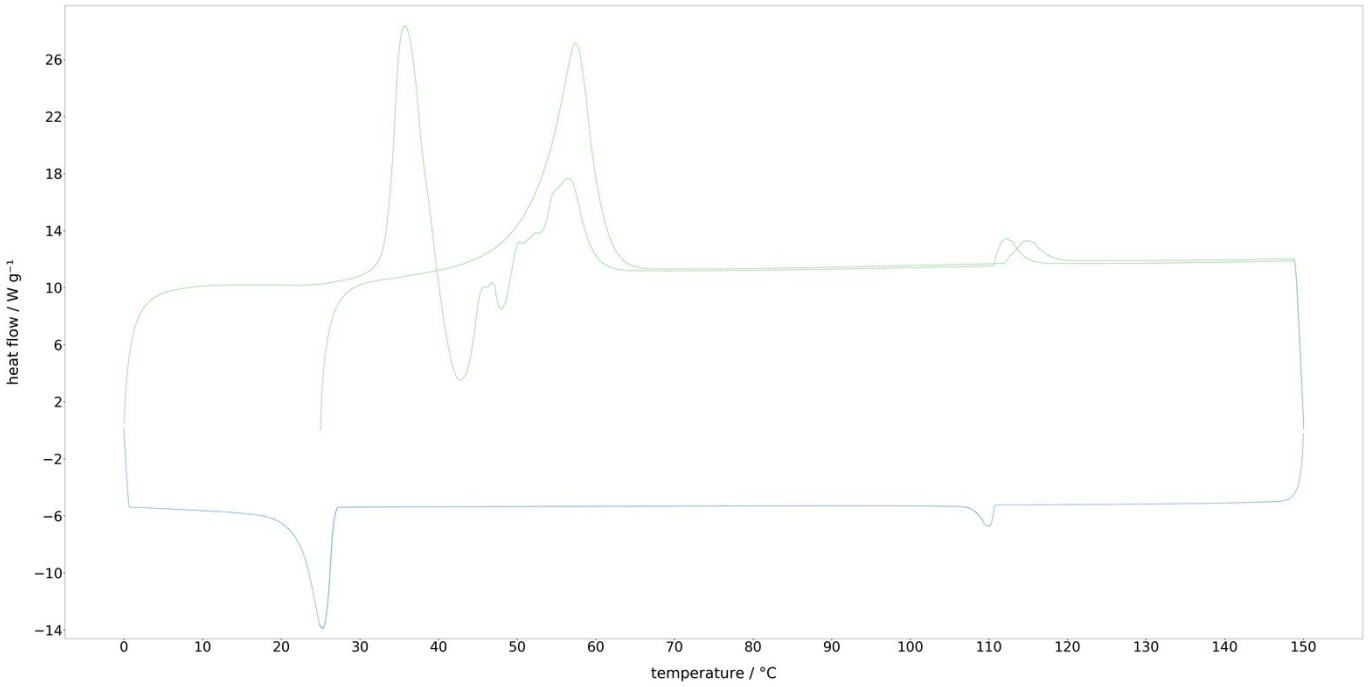

Figure S 71. DSC of 1,3-Di(tetradecyl)imidazolium nitrate.

1,3-Di(tetradecyl)imidazolium chloride.

The synthesis was carried out following the general procedure with 1,3-di(Tetradecyl)imidazolium acetate (0.4012 g, 1.0 mL, 0.77 mmol). Isolated yield 0.564 g, 91 %. Yellow to orange solid. Melting point: 43 °C. Decomposition temperature: 260 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 7.26 (2 H, d, J 1.46), 0.88 (6 H, t, J 6.74), 1.29 (48 H, dd, J 31.53, 4.41), 1.92 (4 H, t, J 7.39), 4.36 (4 H, t, J 7.43), 11.06 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 138.0, 121.8, 50.1, 31.9, 30.4, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.0, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3447, 3371, 3256, 3133, 3038, 2954, 2918, 2871, 2850, 1643, 1564, 1464, 1403, 1376, 1365, 1338, 1307, 1258, 1235, 1213, 1191, 1137, 1109, 1094, 1063, 1034, 869, 849, 813, 775, 750, 721, 662, 637, 495, 446, 440, 428, 414.

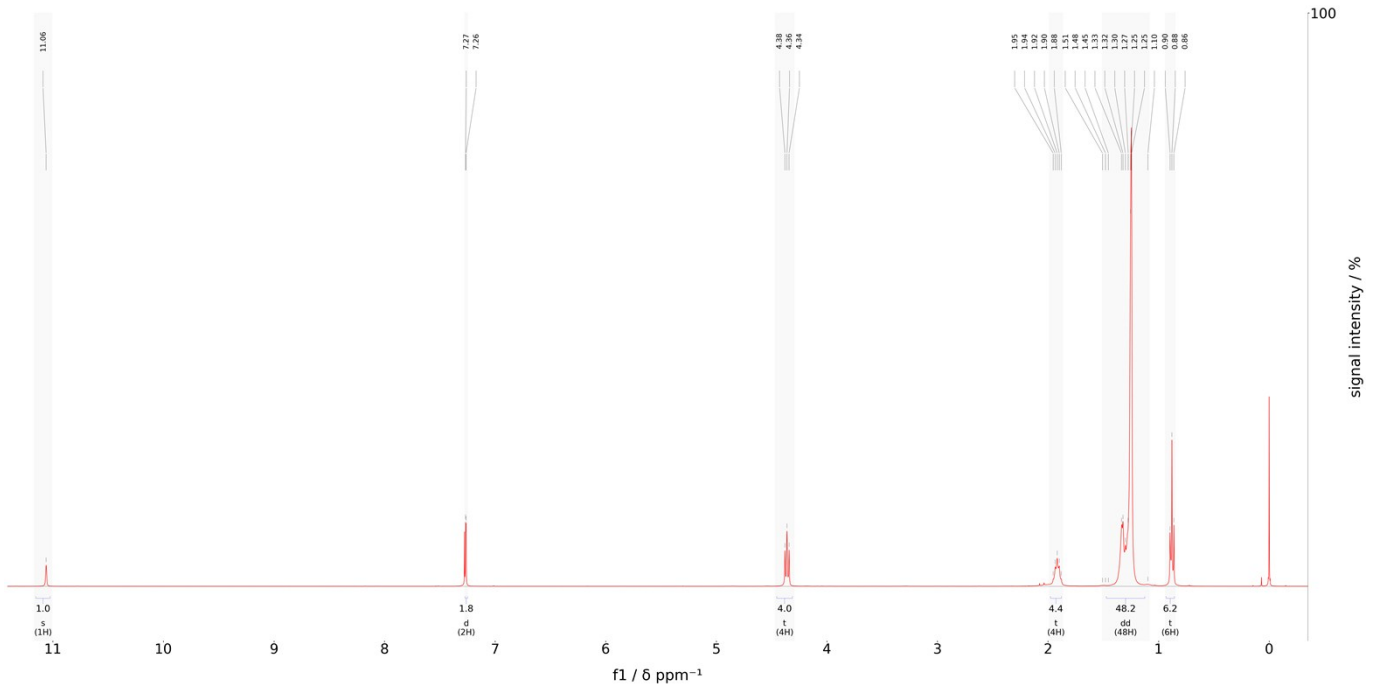

Figure S 72. ^{1}H NMR of 1,3-Di(tetradecyl)imidazolium chloride in deuterochloroform.

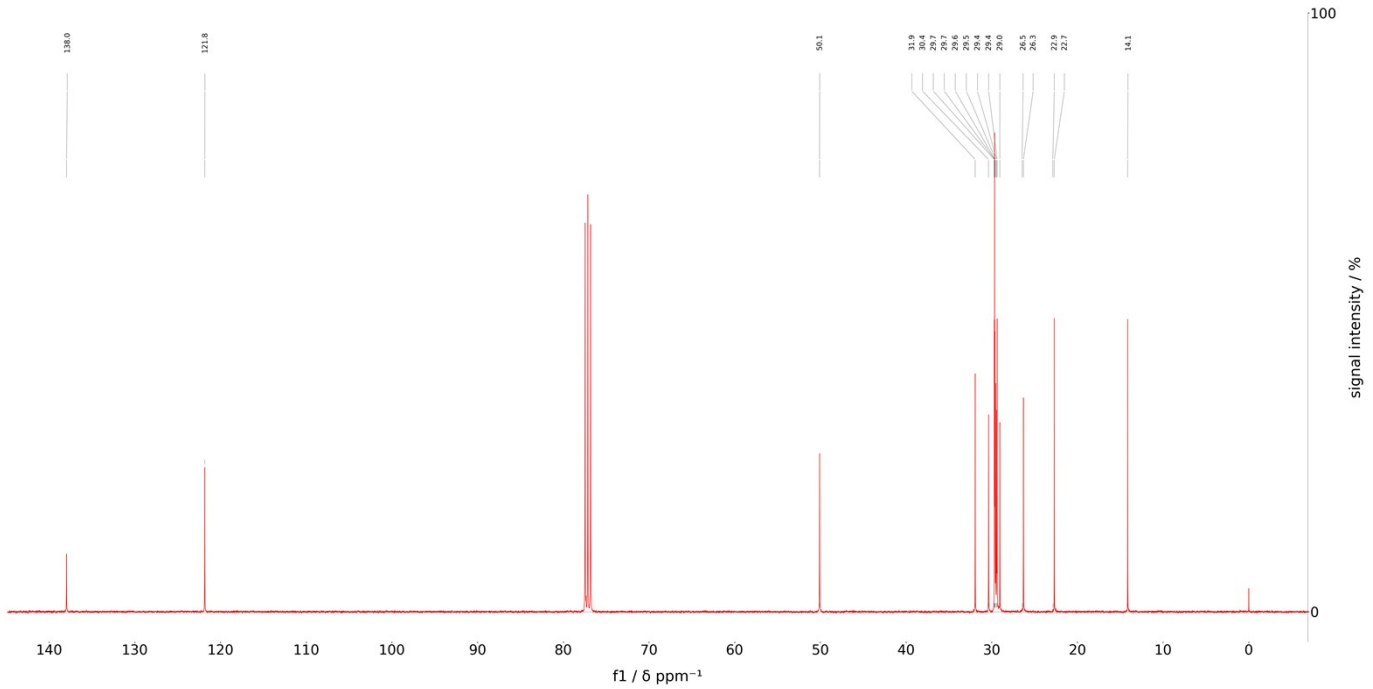

Figure S 73. ^{13}C NMR of 1,3-Di(tetradecyl)imidazolium chloride in deuterochloroform.

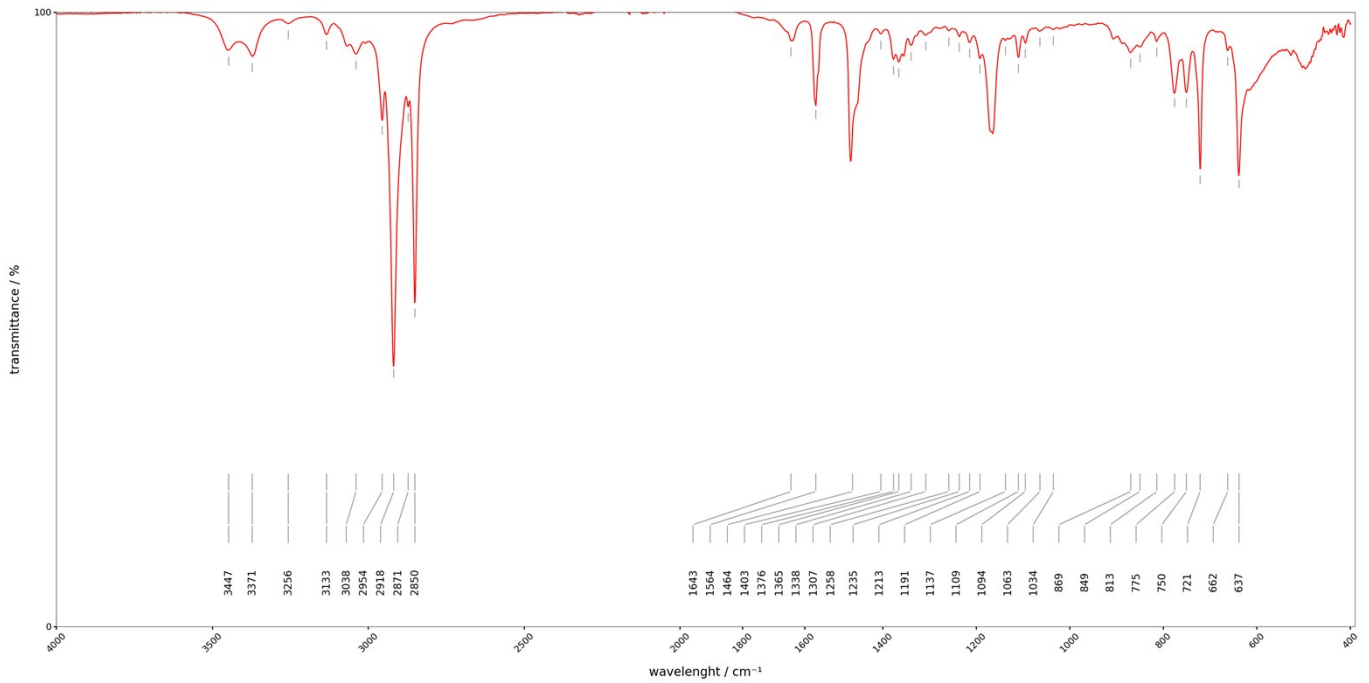

Figure S 74. FTIR of 1,3-Di(tetradecyl)imidazolium chloride.

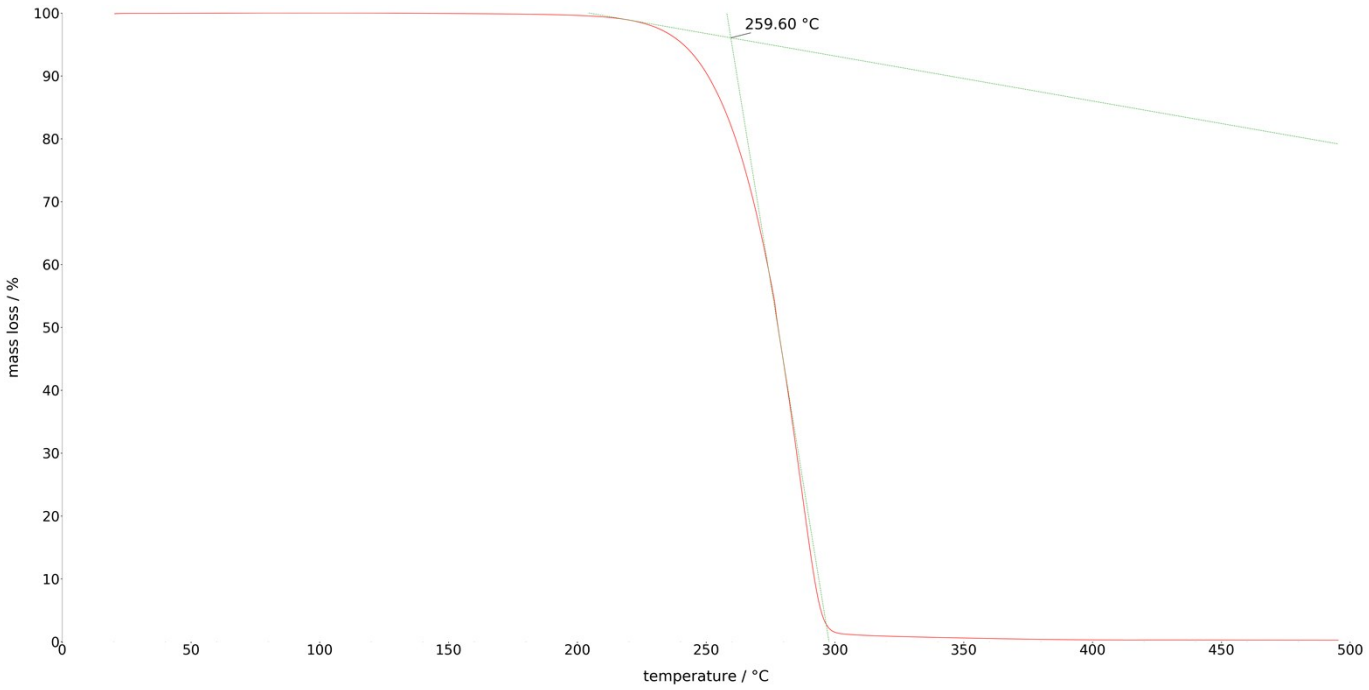

Figure S 75. TGA of 1,3-Di(tetradecyl)imidazolium chloride in an alluminum pan.

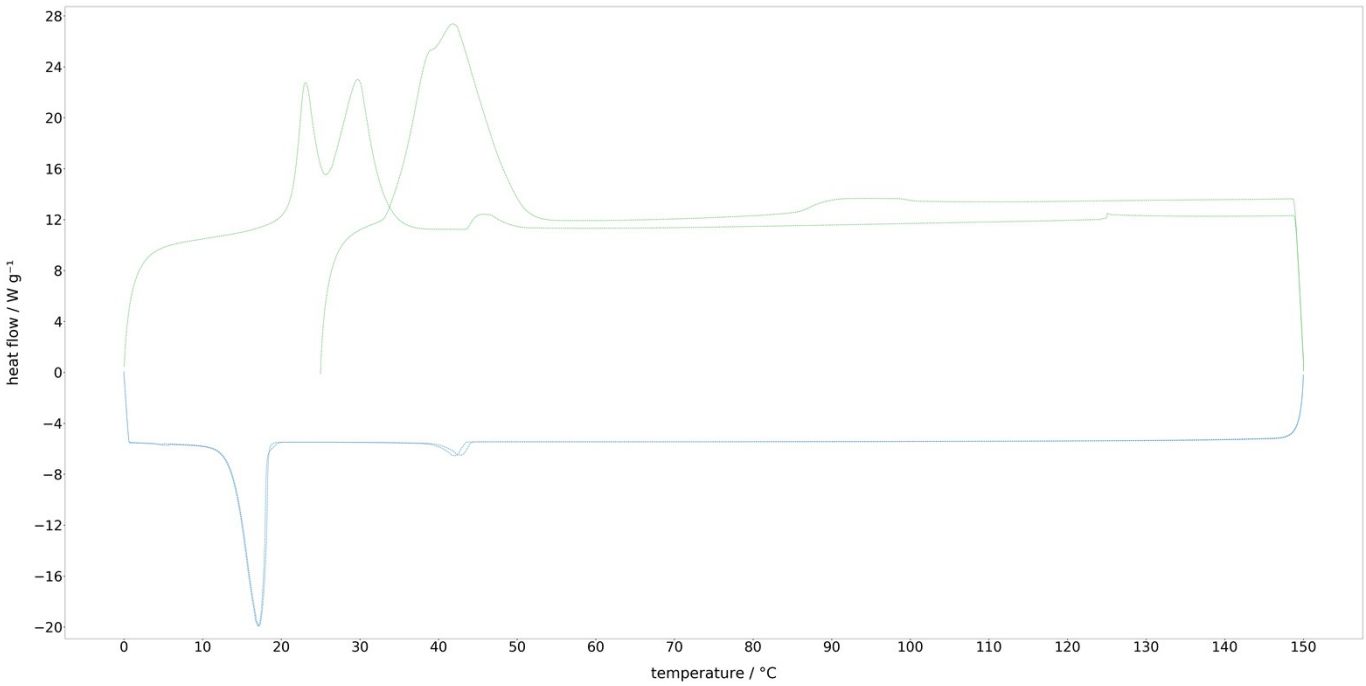

Figure S 76. DSC of 1,3-Di(tetradecyl)imidazolium chloride.

1,3-Di(tetradecyl)imidazolium hydroxalate.

The synthesis was carried out following the general procedure with 1,3-di(Tetradecyl)imidazolium acetate (0.6894 g, 1.69 mmol). Isolated yield 0.6537 g, 88 %. Yellow solid. Melting point: 130 °C. Decomposition temperature: 229 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.75), 1.27 (48 H, dd, J 20.76, 4.48), 1.86 (4 H, t, J 6.98), 4.29 (4 H, t, J 7.28), 7.18 (2 H, s), 10.53 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 163.6, 138.5, 121.7, 50.0, 31.9, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.0, 26.2, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3139, 3103, 3082, 2954, 2917, 2872, 2849, 1679, 1595, 1563, 1464, 1375, 1328, 1256, 1160, 1094, 1003, 970, 890, 838, 811, 711, 656, 637, 601, 459.

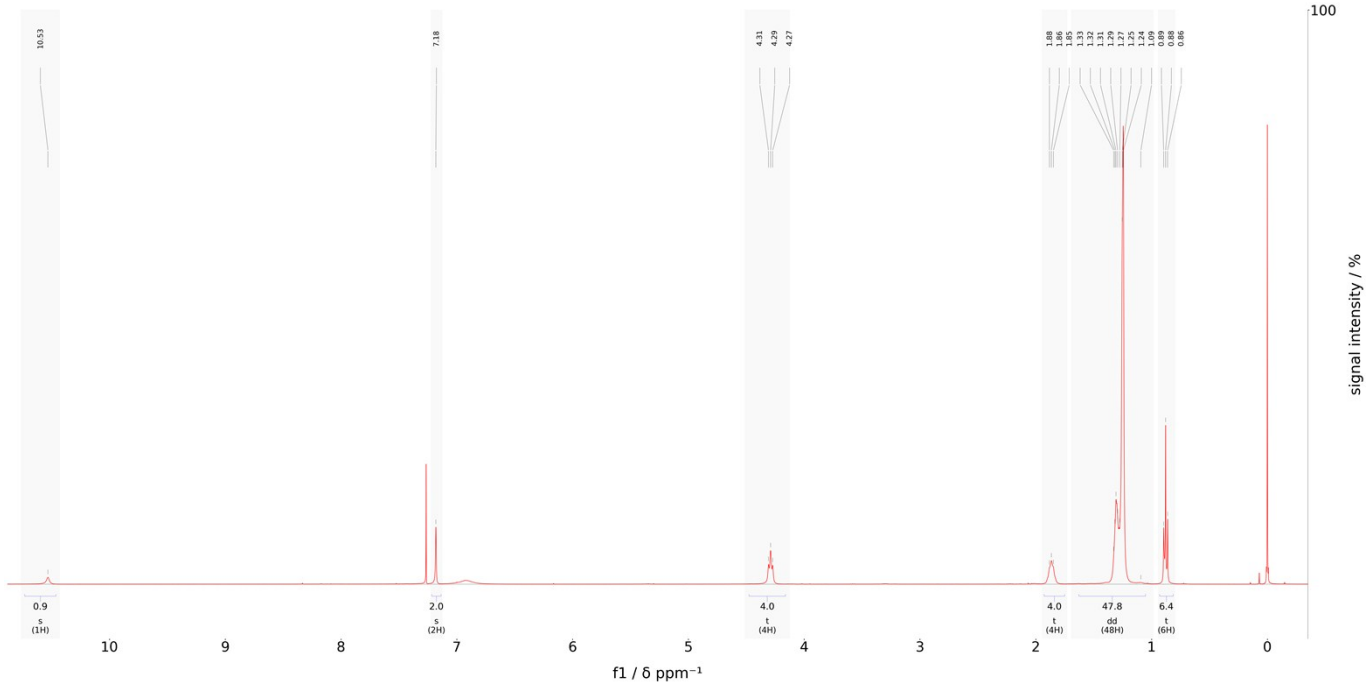

Figure S 77. ^{1}H NMR of 1,3-Di(tetradecyl)imidazolium hydroxalate in deuterochloroform.

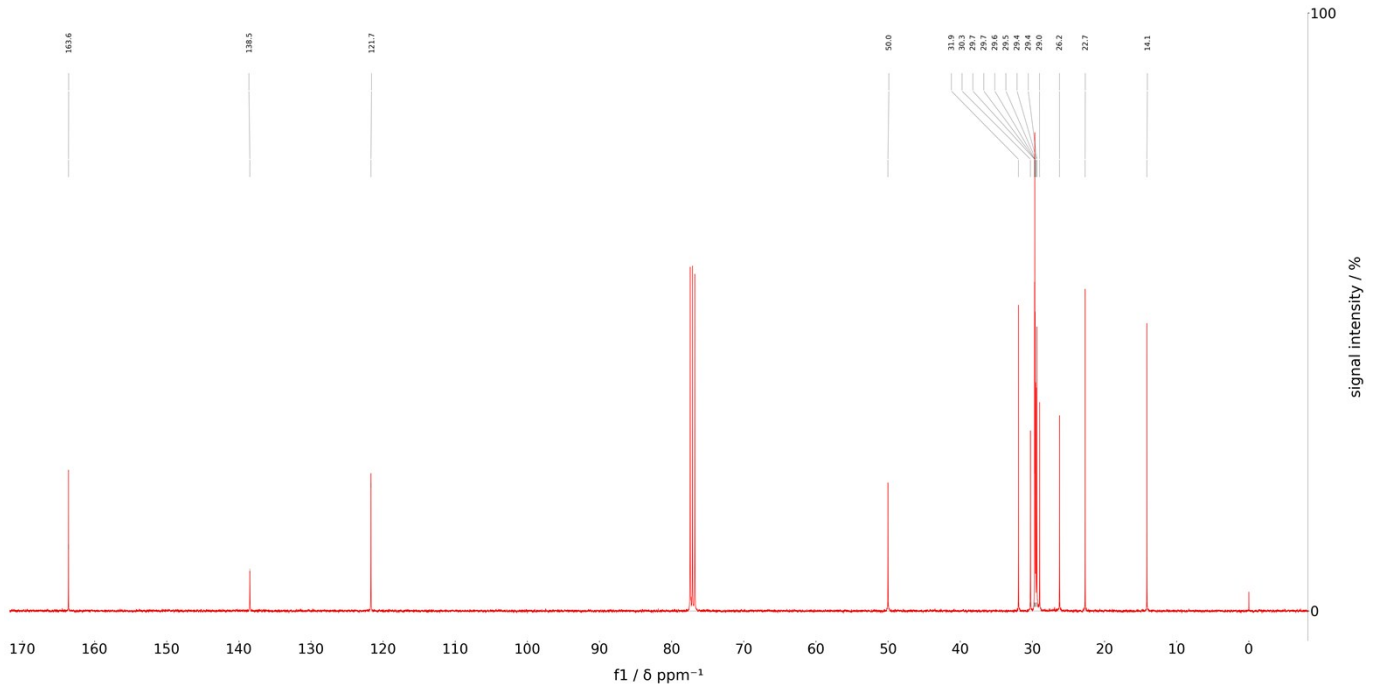

Figure S 78. ^{13}C NMR of 1,3-Di(tetradecyl)imidazolium hydroxalate in deuterochloroform.

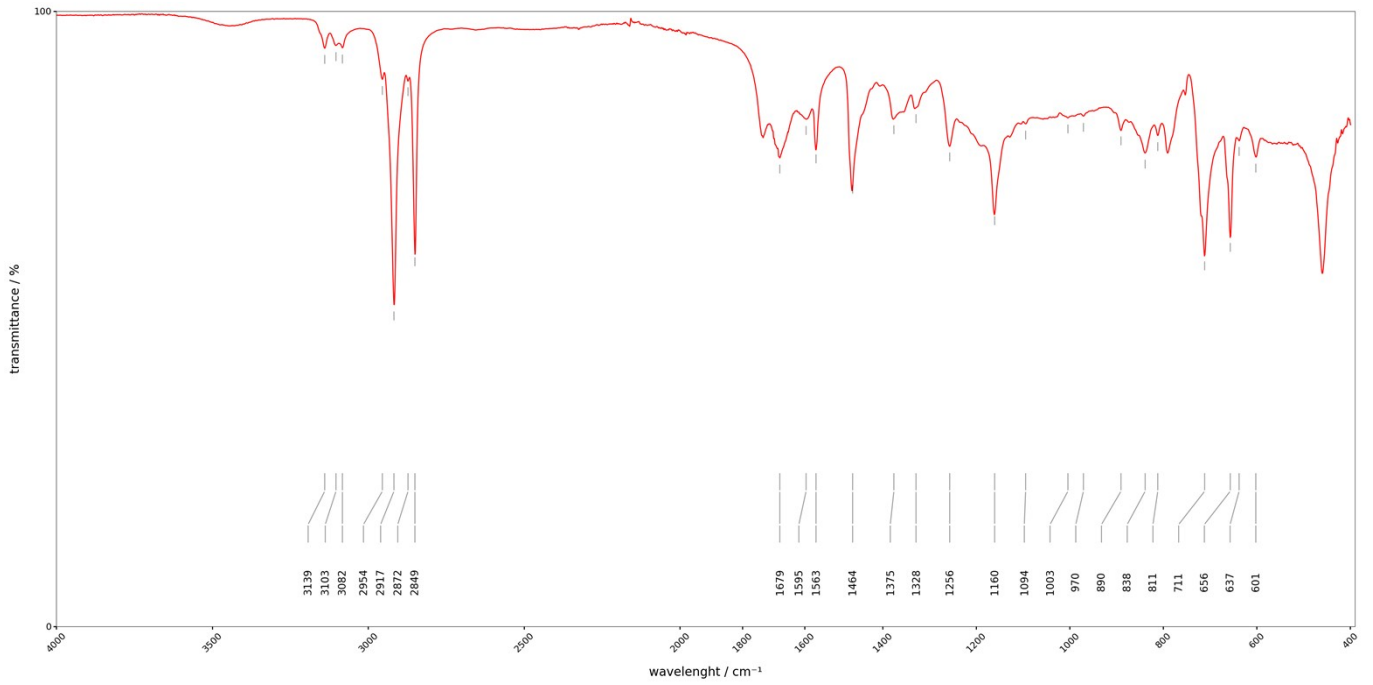

Figure S 79. FTIR of 1,3-Di(tetradecyl)imidazolium hydroxalate.

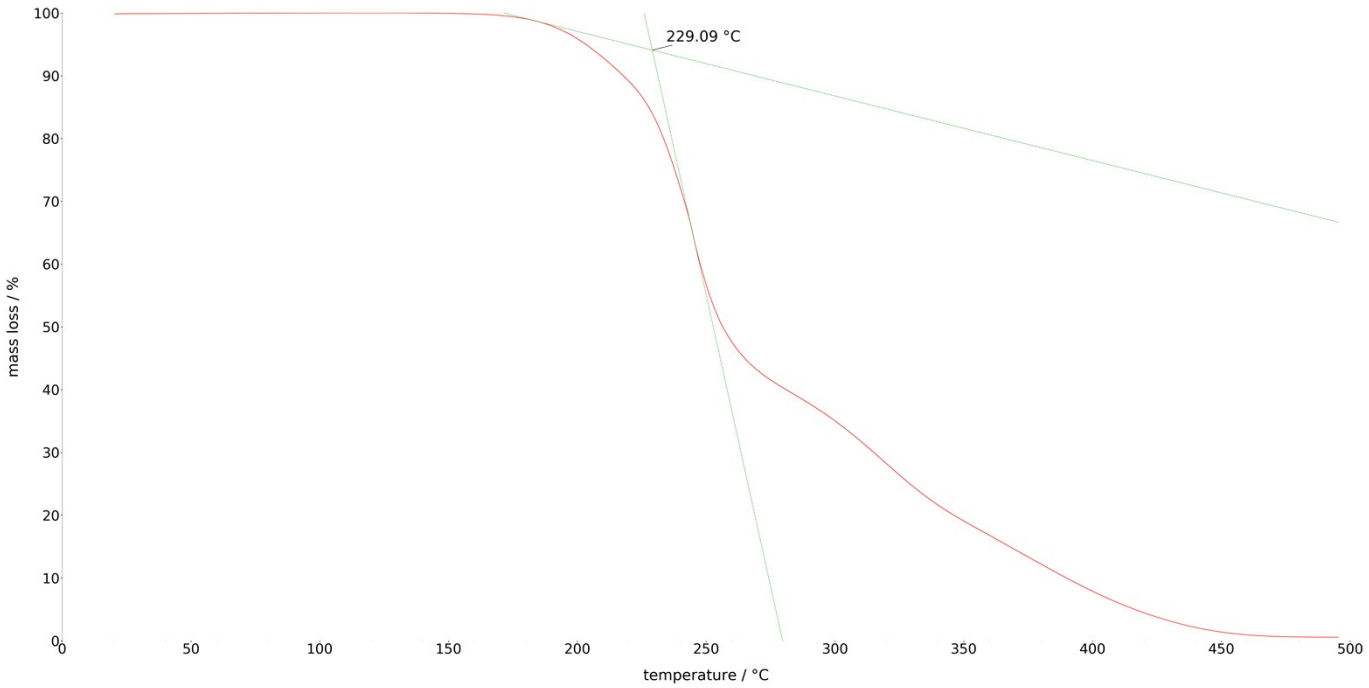

Figure S 80. TGA of 1,3-Di(tetradecyl)imidazolium hydroxalate in an alluminum pan.

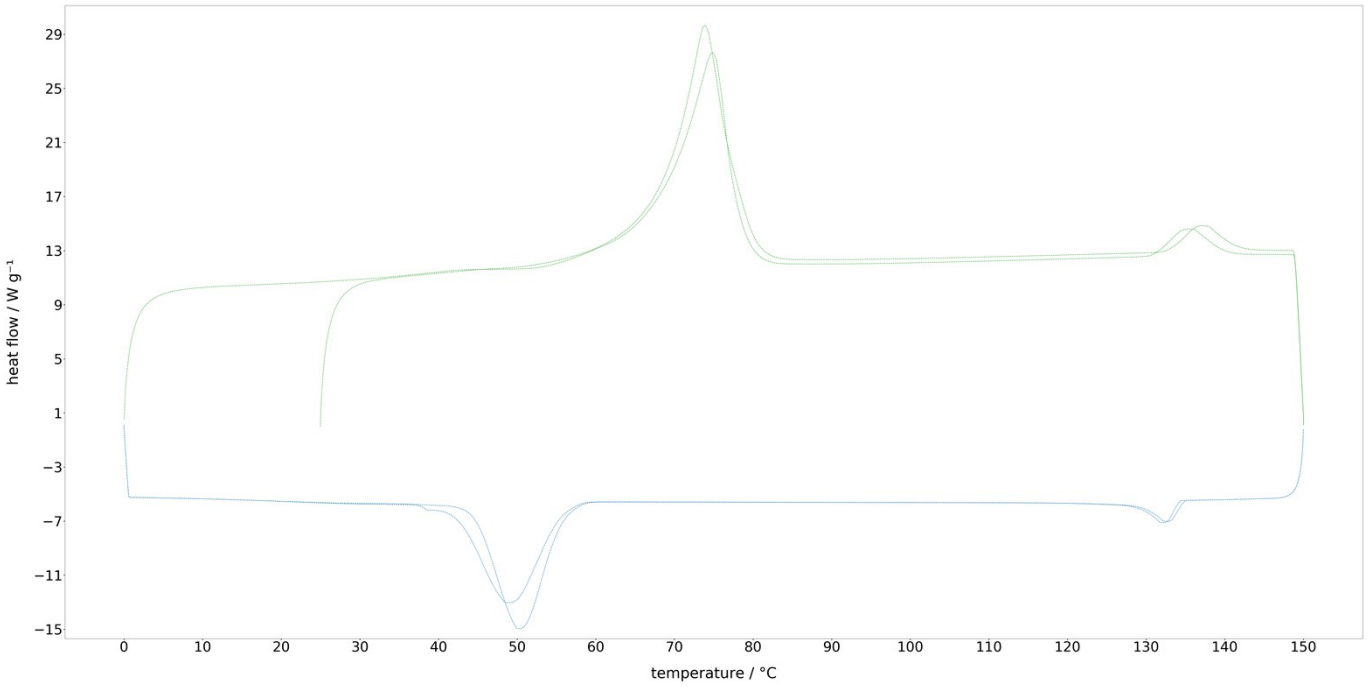

Figure S 81. DSC of 1,3-Di(tetradecyl)imidazolium hydroxalate.

1,3-Di(hexadecyl)imidazolium acetate.

The synthesis was carried out following the general procedure with 1-Hexadecylamine (94.0%, 28.67 g, 0.012 mol), formaldehyde (36.5-38.0 %, 4.92 g, 4.43 mL, 0.059mol), acetic acid (99.9 %, 5.32 g, 5.07 mL, 0.0885 mol), glyoxal (40 wt% in water, 8.56 g, 6.58 mL, 0.059 mol). Isolated yield 25.29 g, 66 % (≈0.5 eq of residual acetic acid). Amber to dark brown solid. Melting point: 50 °C. Decomposition temperature: 228 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.64), 1.17 - 1.37 (56 H, m), 1.87 (4 H, t, J 7.36), 2.02 (5 H, s), 4.32 (4 H, t, J 7.41), 7.09 (2 H, s), 11.02 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 176.7, 139.8, 121.0, 49.9, 31.9, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.0, 26.3, 23.5, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3157, 3103,

2953, 2913, 2870, 2849, 1705, 1561, 1470, 1456, 1376, 1294, 1172, 1099, 1043, 1007, 962, 878, 767, 739, 717, 672, 661, 633, 607, 507, 484, 468, 442, 414, 403.

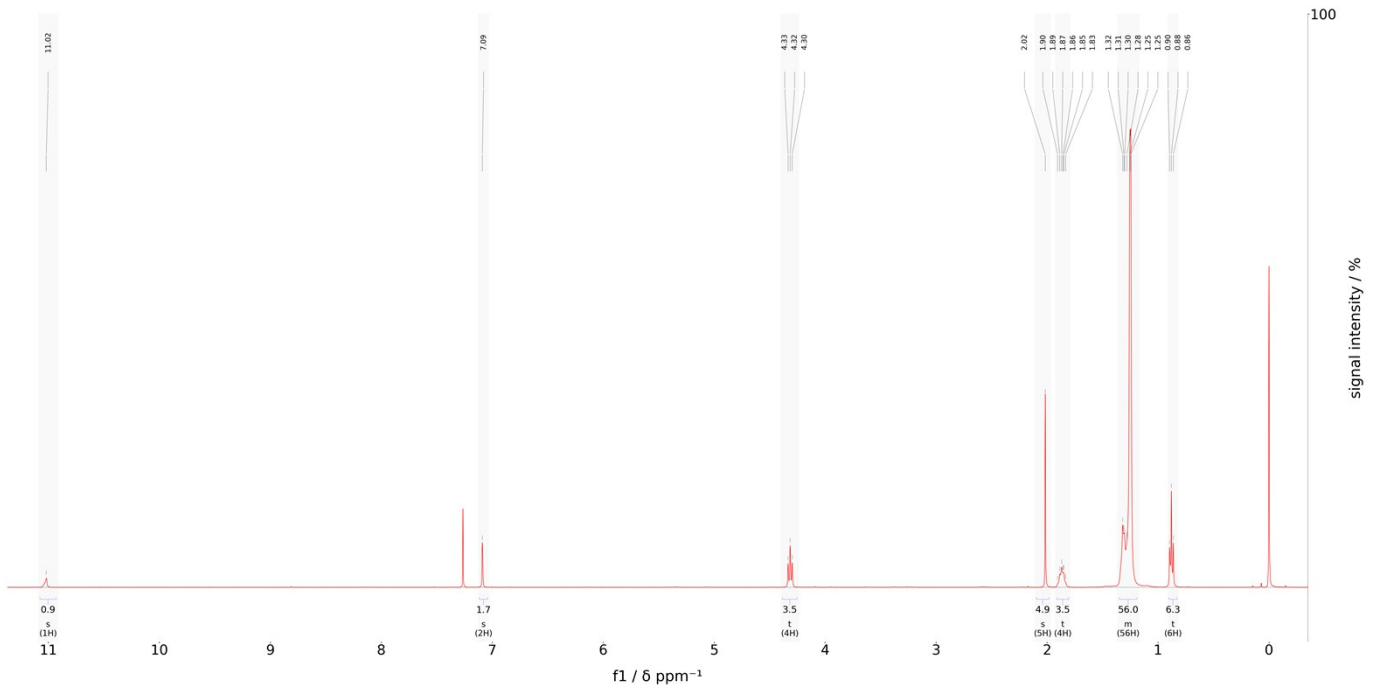

Figure S 82. ^{1}H NMR of 1,3-Di(hexadecyl)imidazolium acetate in deuterochloroform.

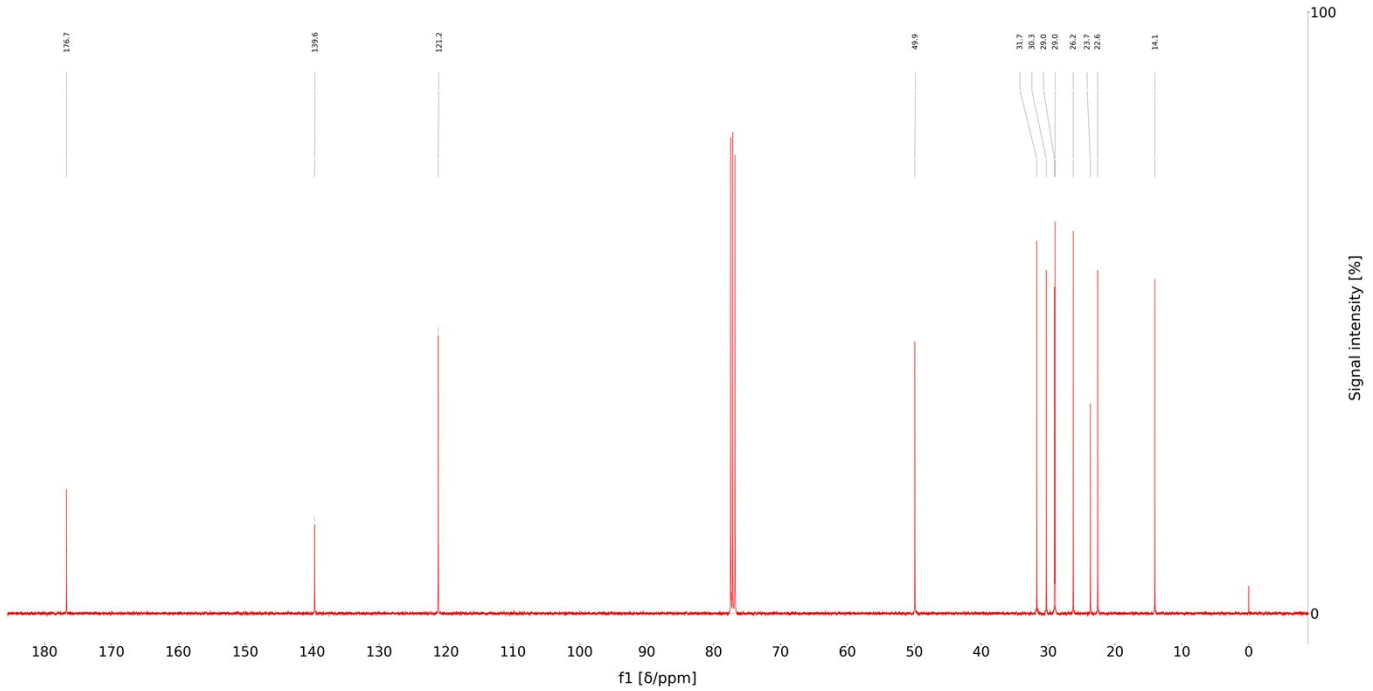

Figure S 83. ^{13}C NMR of 1,3-Di(hexadecyl)imidazolium acetate in deuterochloroform.

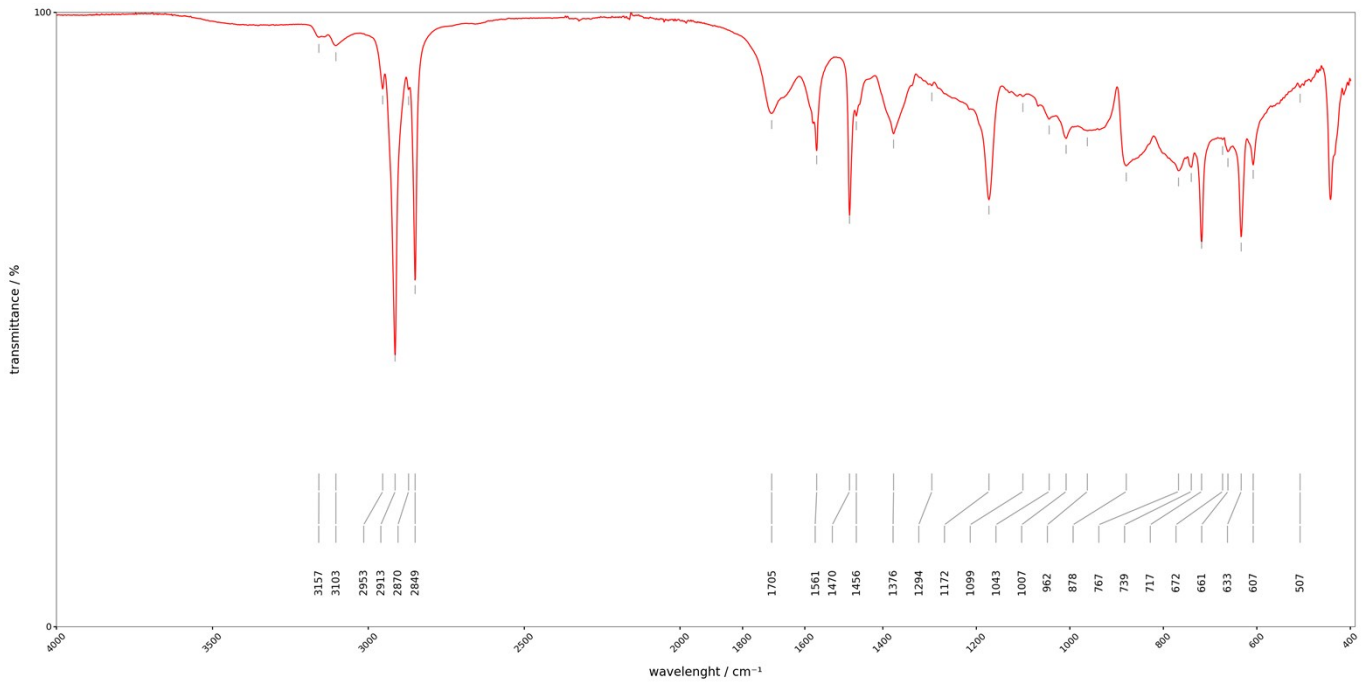

Figure S 84. FTIR of 1,3-Di(hexadecyl)imidazolium acetate.

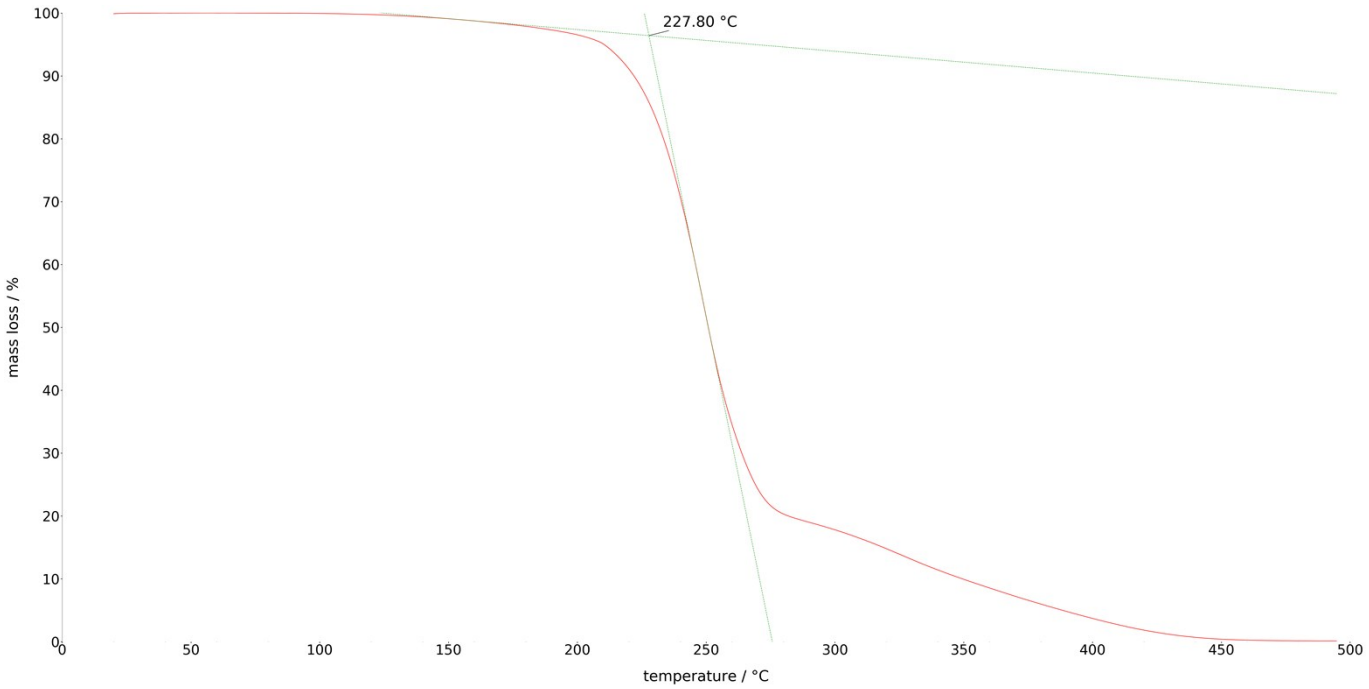

Figure S 85. TGA of 1,3-Di(hexadecyl)imidazolium acetate in an alluminum pan.

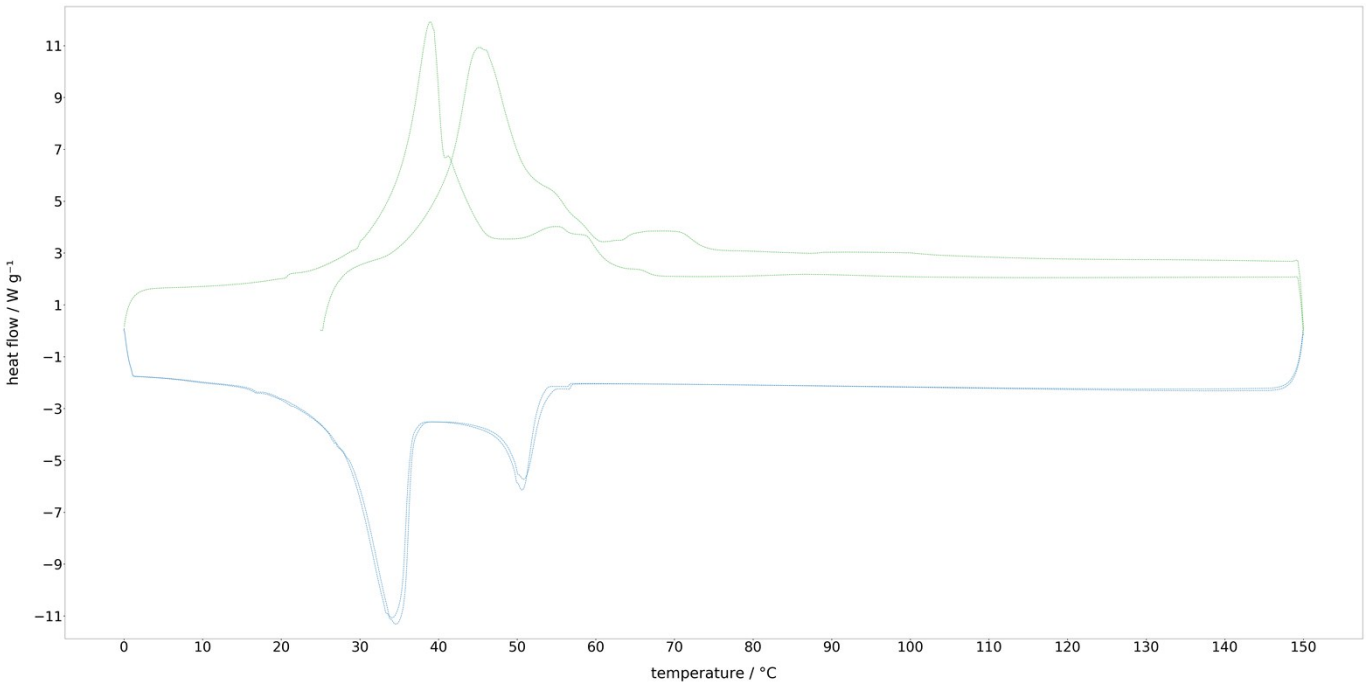

Figure S 86. DSC of 1,3-Di(hexadecyl)imidazolium acetate.

1,3-Di(hexadecyl)imidazolium nitrate.

The synthesis was carried out following the general procedure with 1,3-di(hexadecyl)imidazolium acetate (0.7951 g, 1.0 mL, 1.38 mmol). Isolated yield 0.7915 g, 99 %. Amber to dark brown solid. Melting point: 127 °C. Decomposition temperature: 290 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 7.25 (2 H, d, J 1.58), 4.25 (4 H, t, J 7.40), 0.88 (6 H, t, J 6.77), 1.19 - 1.35 (56 H, m), 1.89 (4 H, p, J 7.75, 7.74), 10.21 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 137.6, 122.1, 50.1, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.0, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3460, 3135, 3091, 3044, 2953, 2916, 2849, 1745, 1656, 1563, 1466, 1338, 1214, 1162, 1100, 1067, 1040, 889, 829, 779, 740, 720, 659, 610, 573, 548, 533, 520, 515, 509, 500, 492, 486, 481, 476, 469, 464, 459, 453, 443, 439, 428, 413, 408.

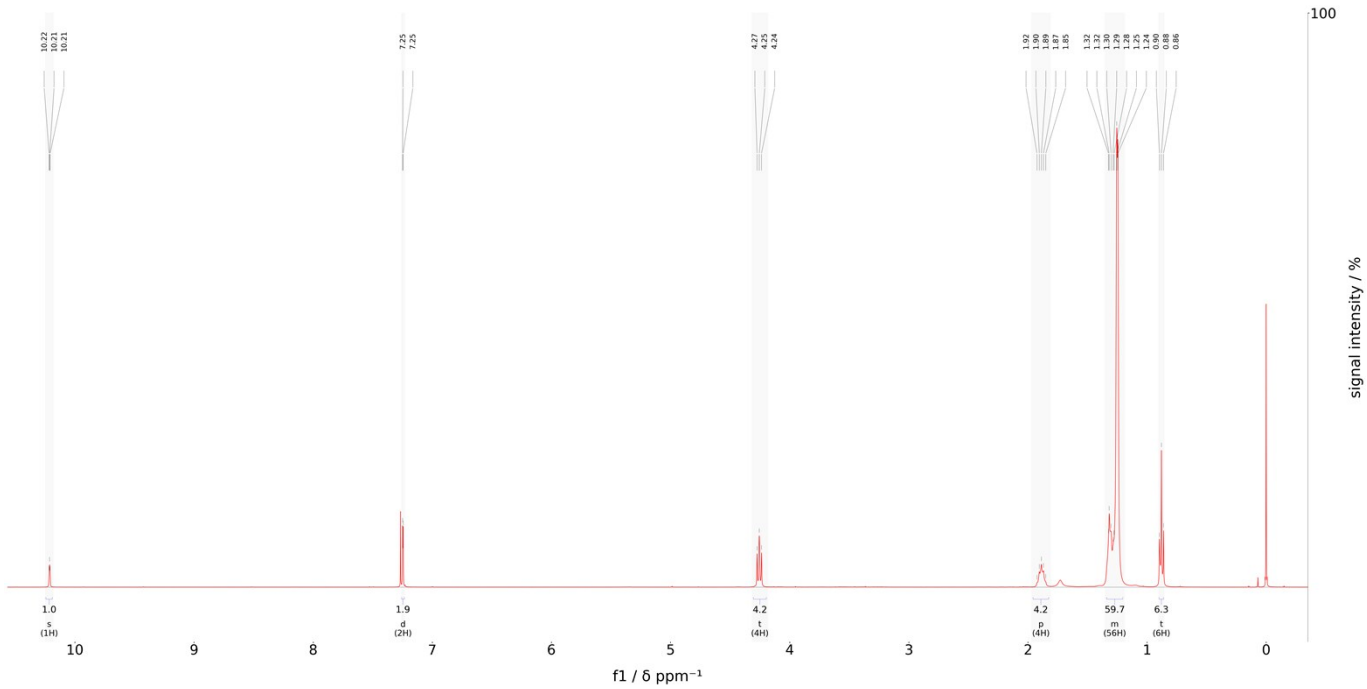

Figure S 87. ^{1}H NMR of 1,3-Di(hexadecyl)imidazolium nitrate in deuterochloroform.

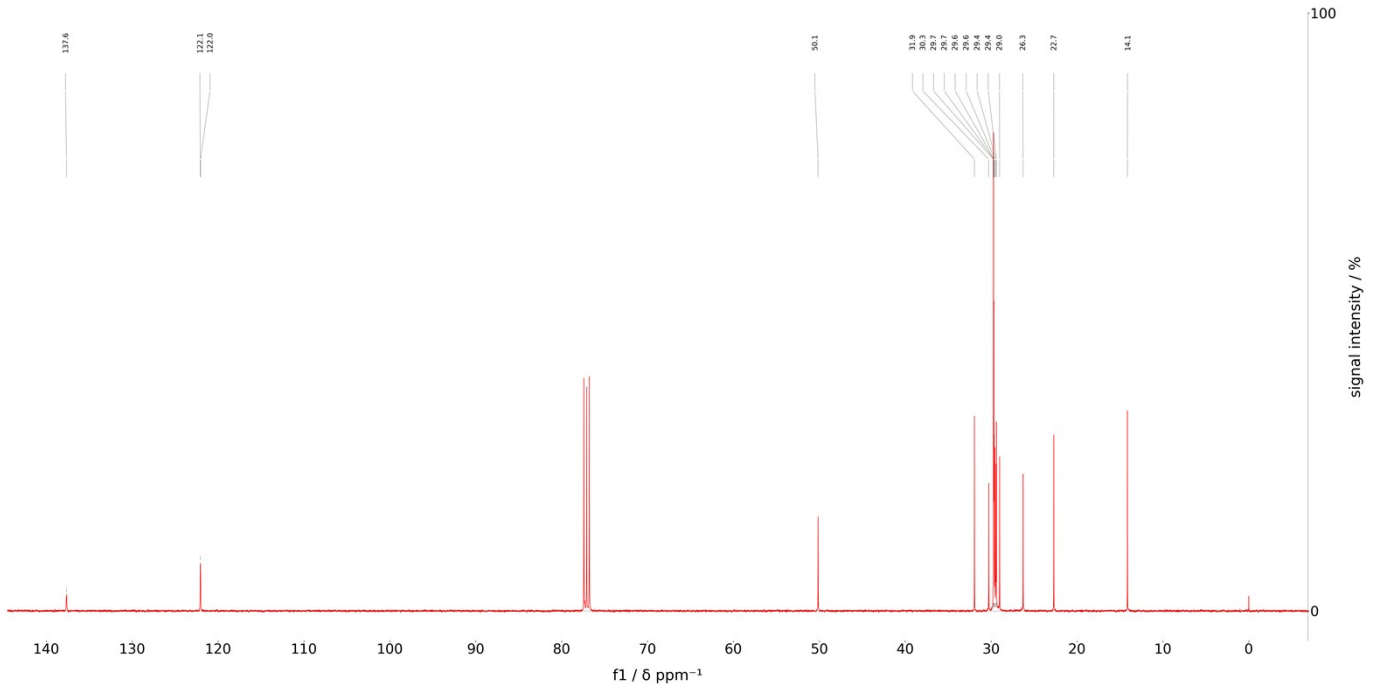

Figure S 88. ^{13}C NMR of 1,3-Di(hexadecyl)imidazolium nitrate in deuterochloroform.

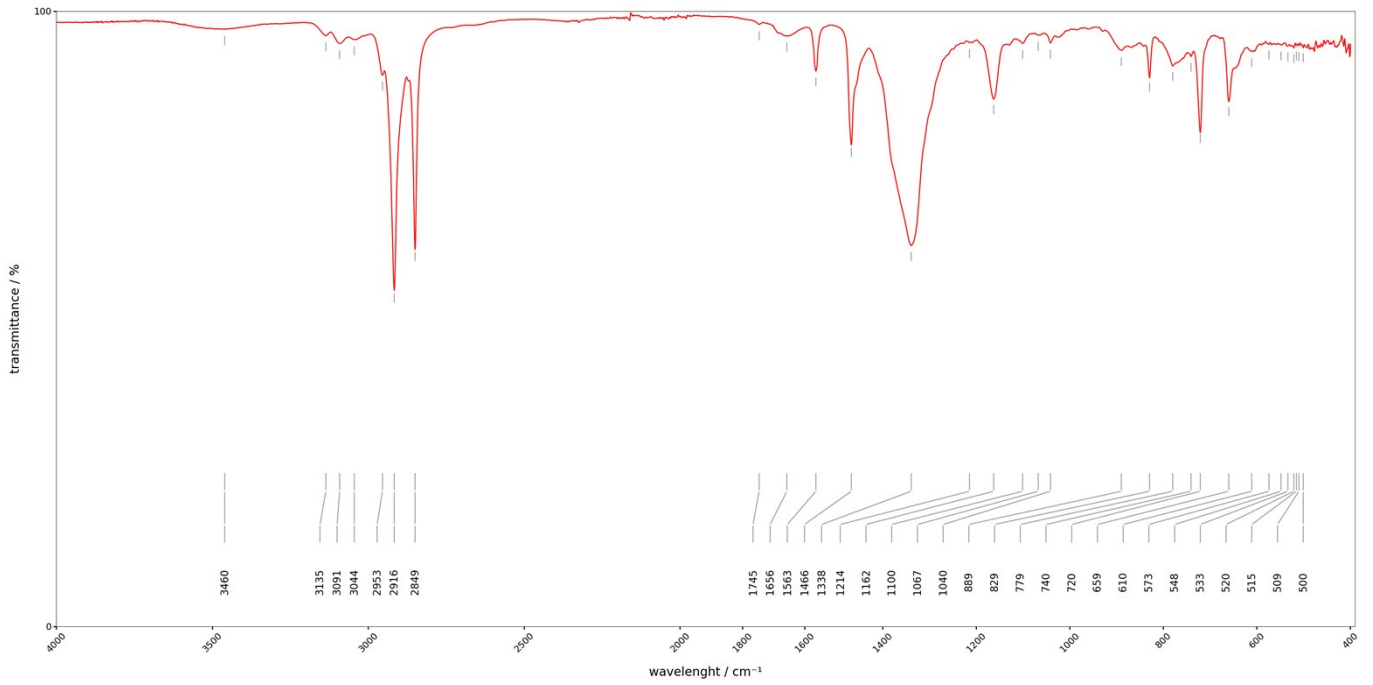

Figure S 89. FTIR of 1,3-Di(hexadecyl)imidazolium nitrate.

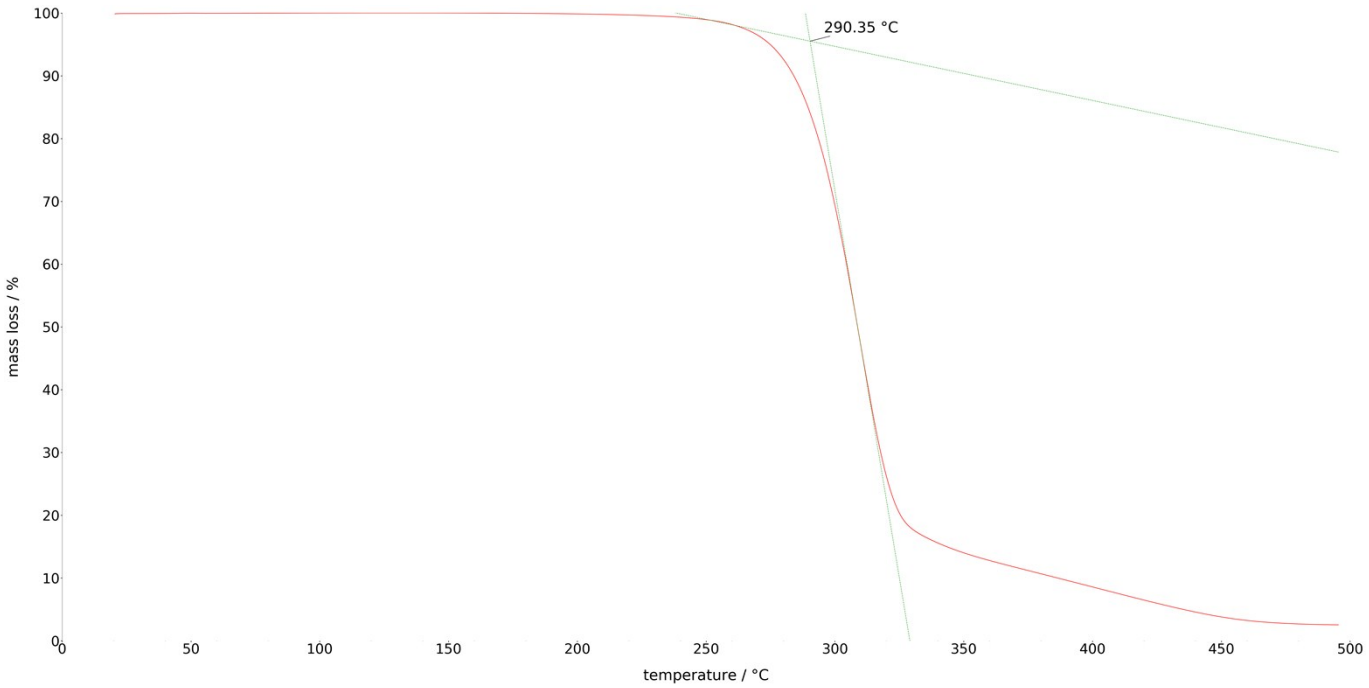

Figure S 90. TGA of 1,3-Di(hexadecyl)imidazolium nitrate in an alluminum pan.

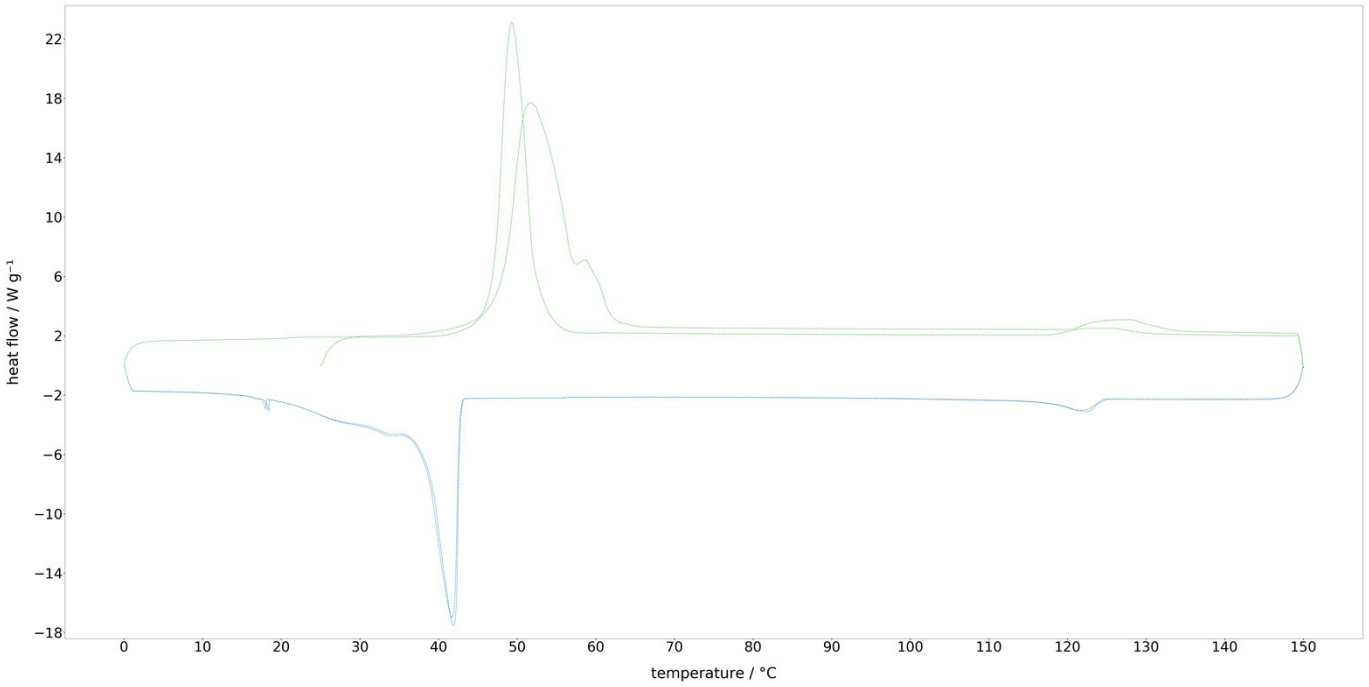

Figure S 91. DSC of 1,3-Di(hexadecyl)imidazolium nitrate.

1,3-Di(hexadecyl)imidazolium chloride.

The synthesis was carried out following the general procedure with 1,3-di(hexadecyl)imidazolium acetate (0.7951 g, 1.0 mL, 1.38 mmol). Isolated yield 0.6950 g, 91 %. Amber to dark brown solid. Melting point: 128 °C. Melting temperature: 38 °C. Decomposition temperature: 260 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 1.91 (4 H, p, J 7.16, 7.01), 0.87 (6 H, d, J 7.07), 1.23 - 1.33 (56 H, m), 4.36 (4 H, t, J 7.41), 7.37 (2 H, s), 10.72 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 138.0, 121.7, 50.2, 31.9, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.1, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 3394, 2954, 2917, 2849, 1671, 1562, 1466, 1407, 1375, 1331, 1248, 1163, 1128, 1100, 887, 862, 842, 779, 739, 721, 658, 575, 523, 500, 493, 484, 461, 453, 445, 430, 418.

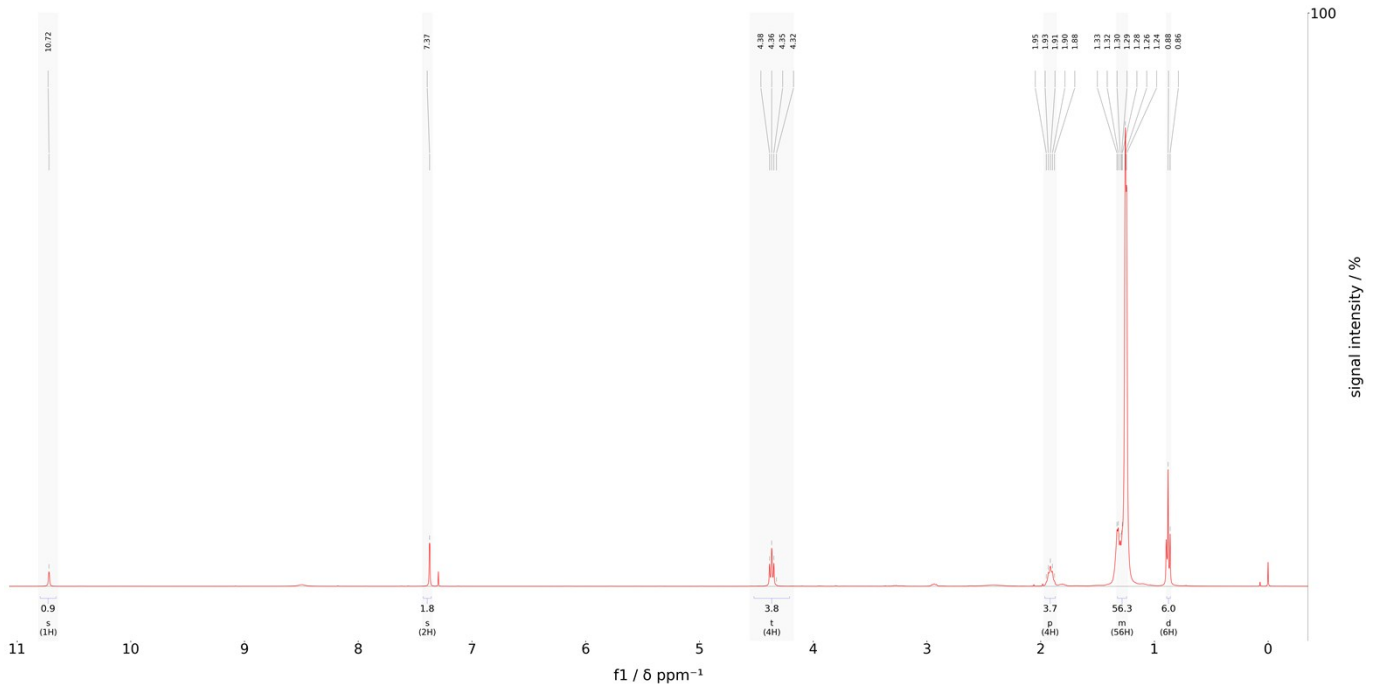

Figure S 92. ^{1}H NMR of 1,3-Di(hexadecyl)imidazolium chloride in deuterochloroform.

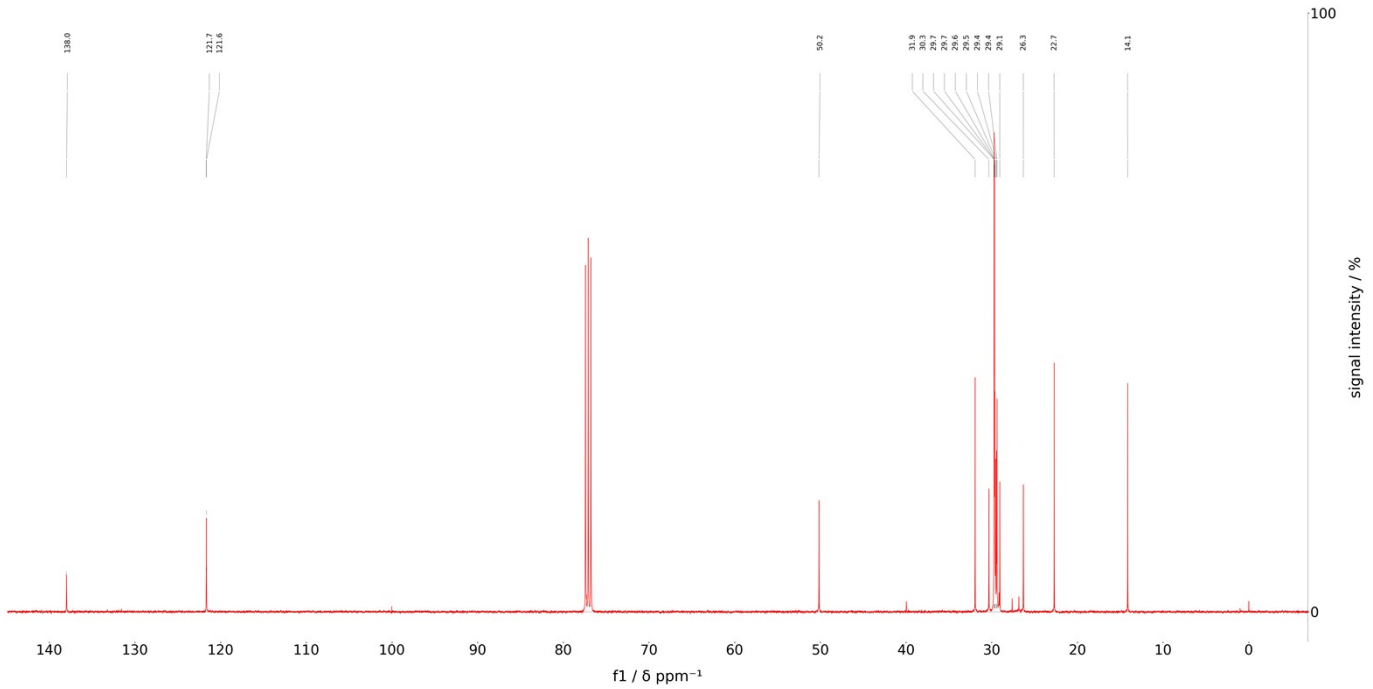

Figure S 93. ^{13}C NMR of 1,3-Di(hexadecyl)imidazolium chloride in deuterochloroform.

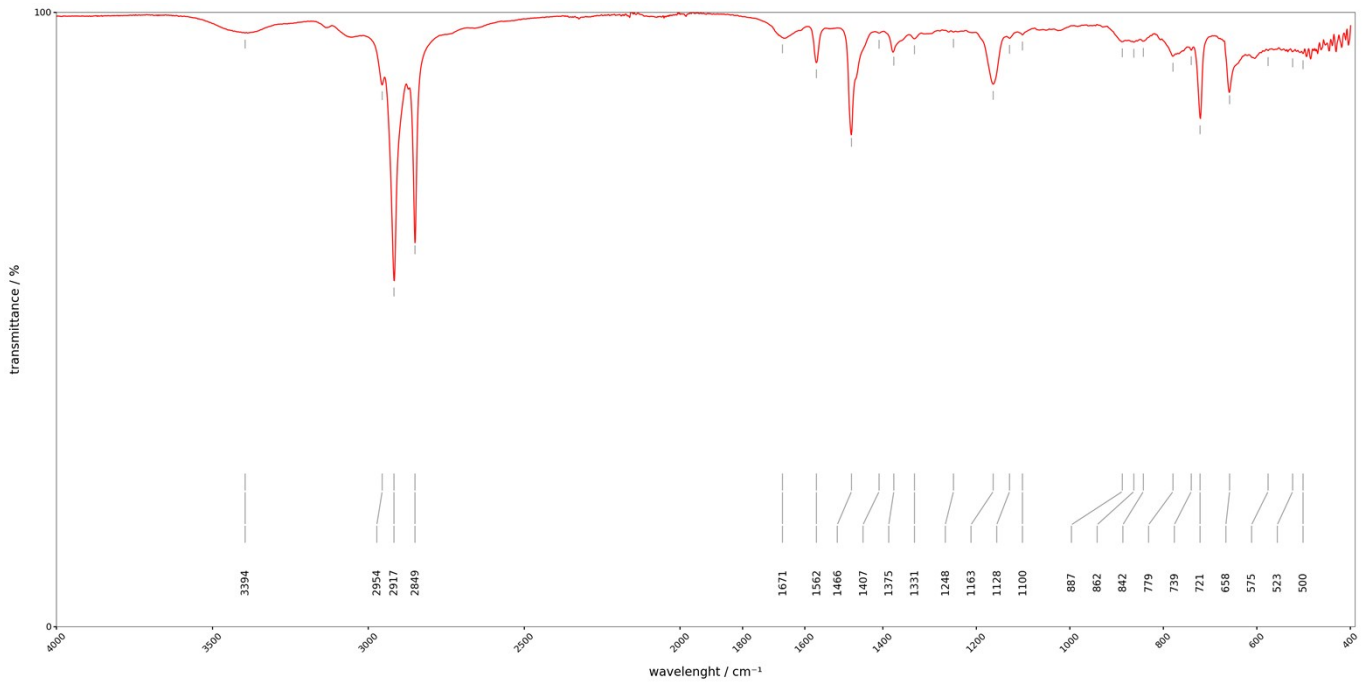

Figure S 94. FTIR of 1,3-Di(hexadecyl)imidazolium chloride.

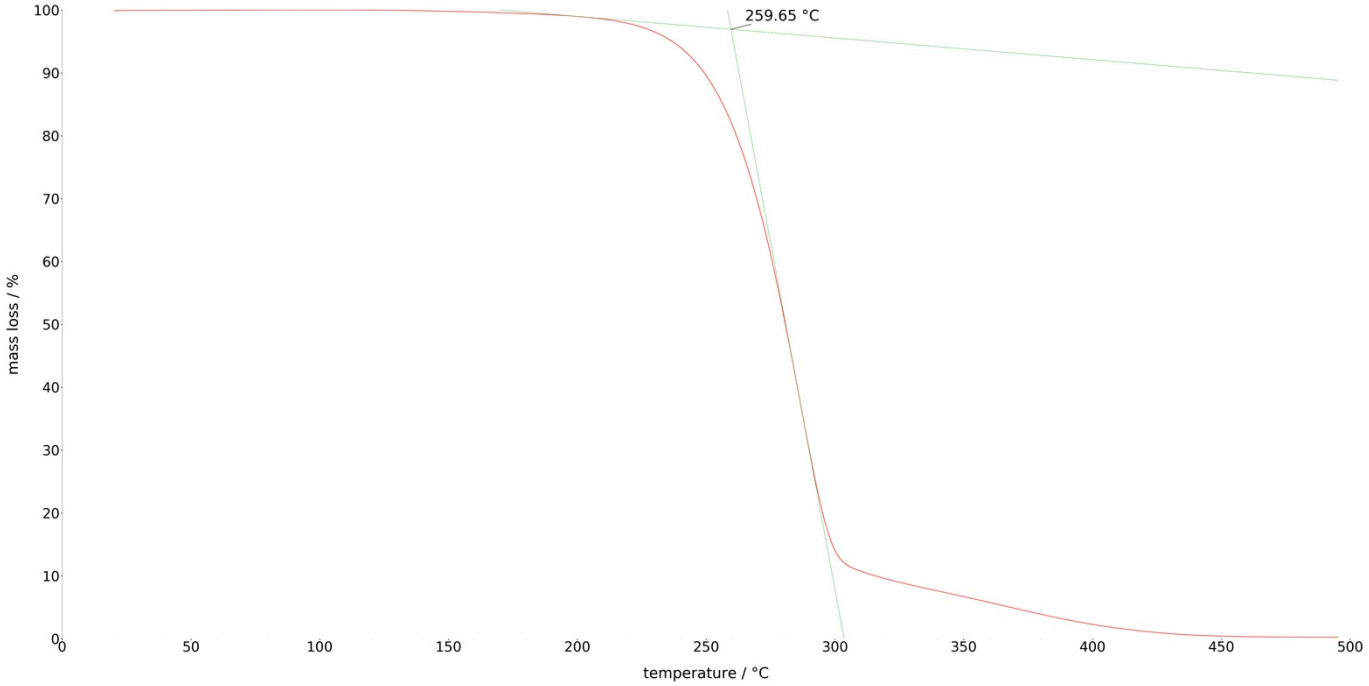

Figure S 95. TGA of 1,3-Di(hexadecyl)imidazolium chloride in an alluminum pan.

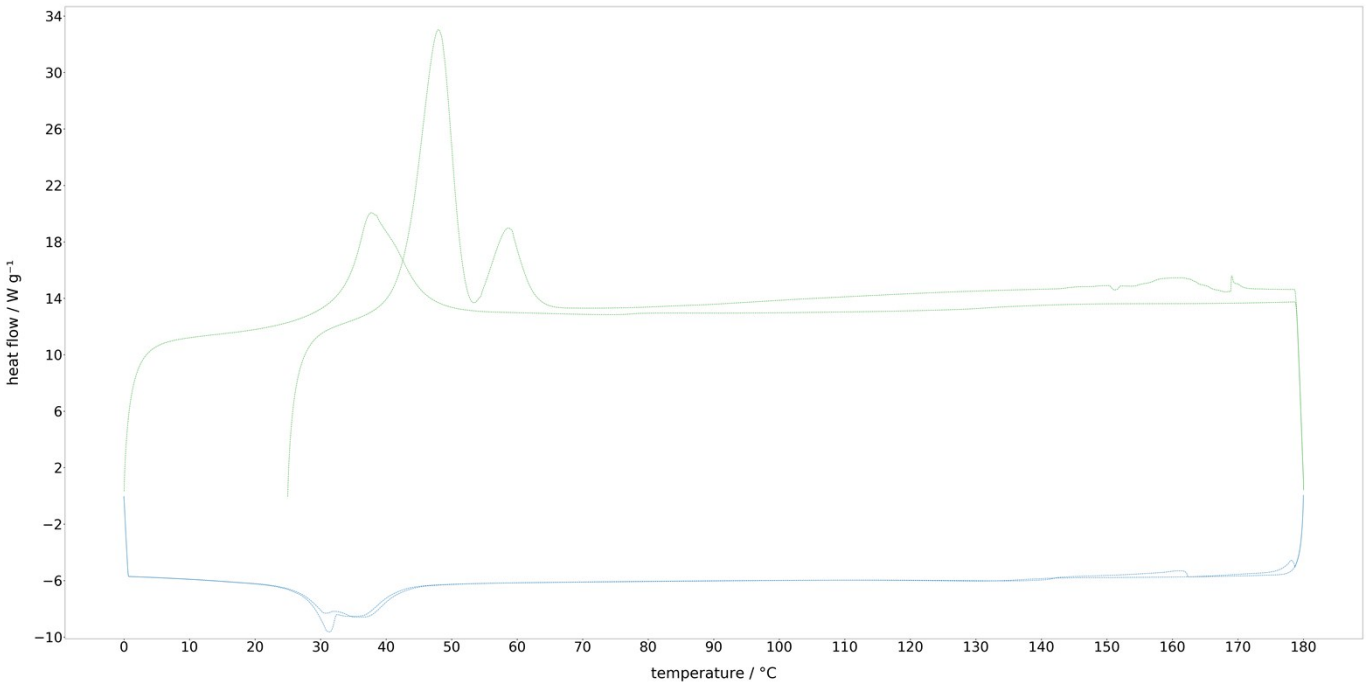

Figure S 96. DSC of 1,3-Di(hexadecyl)imidazolium chloride.

1,3-Di(hexadecyl)imidazolium hydroxalate.

The synthesis was carried out following the general procedure with 1,3-di(hexadecyl)imidazolium acetate (0.7943 g, 1.0 mL, 1.38 mmol). Isolated yield 0.4425 g, 53 %. Amber to dark brown solid. Melting point: 109 °C. Decomposition temperature: 229 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, δ/ppm): 0.88 (6 H, t, J 6.77), 1.23 - 1.34 (56 H, m), 1.84 (4 H, q, J 7.10, 7.00), 4.37 (4 H, t, J 7.39), 7.11 (2 H, s), 11.29 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, δ/ppm): 168.0, 140.8, 120.9, 49.8, 31.9, 30.4, 29.7, 29.7, 29.6, 29.4, 29.4, 29.1, 29.7, 26.3, 22.7, 14.1. IR (Diamond-ATR, neat, cm^{-1}): 2955, 2917, 2872, 2849, 1554, 1466, 1375, 1334, 1295, 1162, 1128, 1064, 1020, 888, 839, 780, 742, 720, 661, 604, 455, 446, 429, 416.

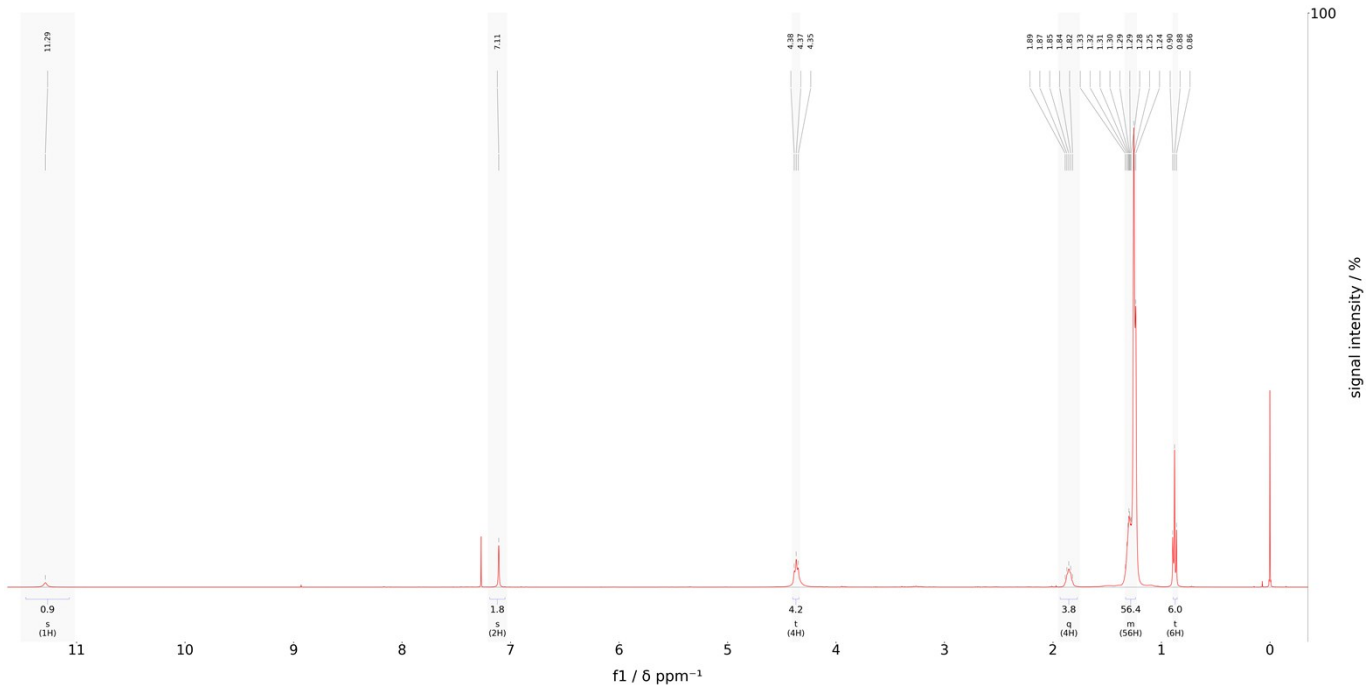

Figure S 97. ^{1}H NMR of 1,3-Di(hexadecyl)imidazolium hydroxalate in deuterochloroform.

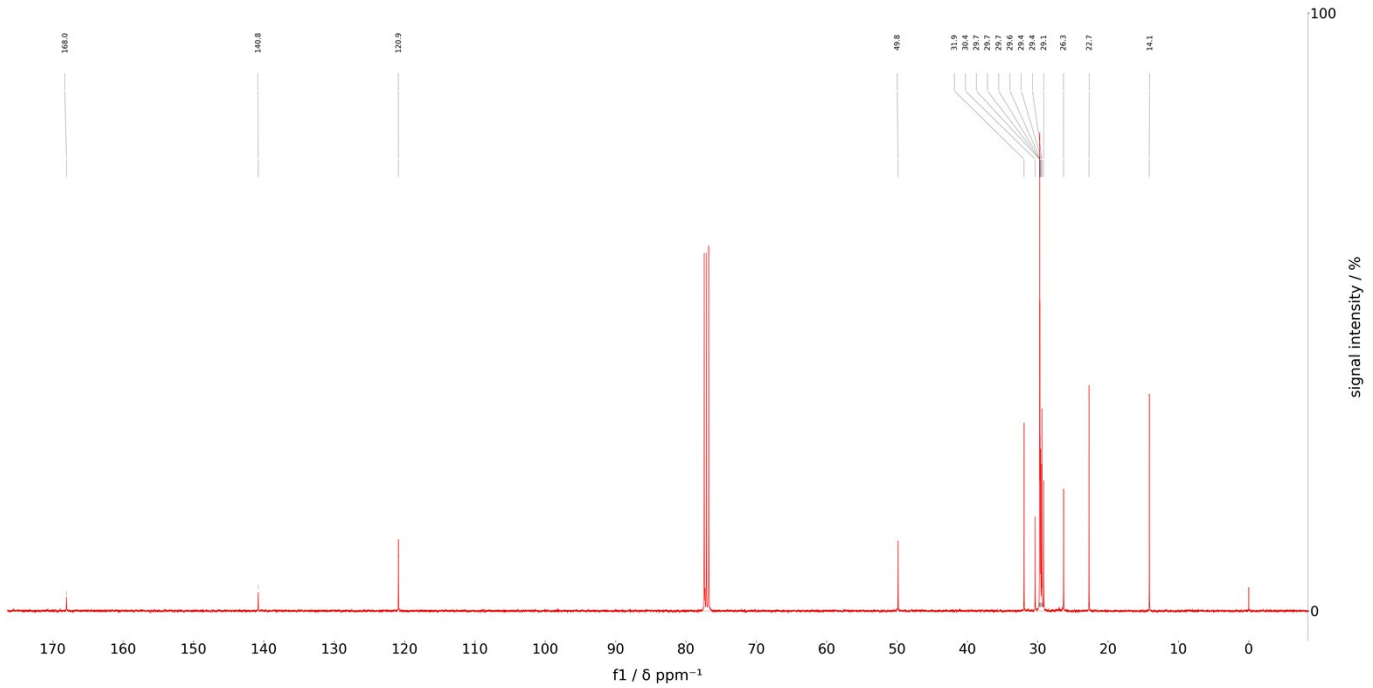

Figure S 98. ^{13}C NMR of 1,3-Di(hexadecyl)imidazolium hydroxalate in deuterochloroform.

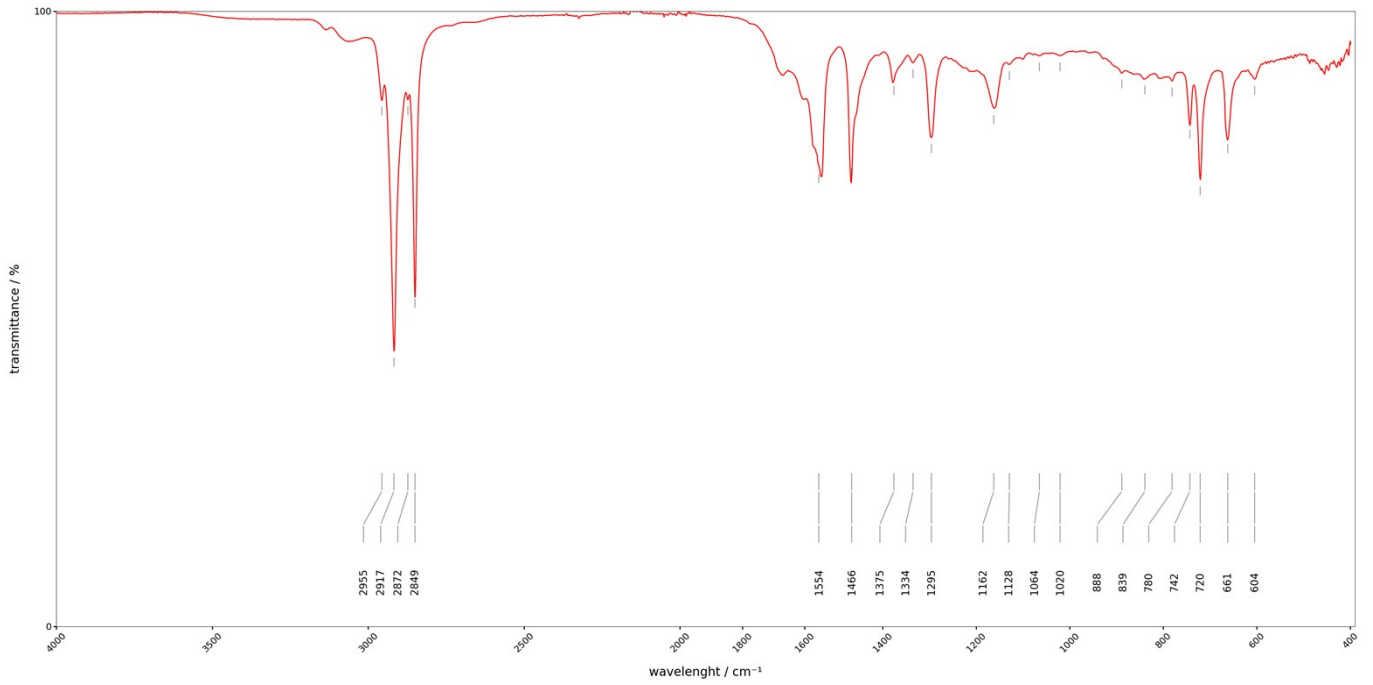

Figure S 99. FTIR of 1,3-Di(hexadecyl)imidazolium hydroxalate.

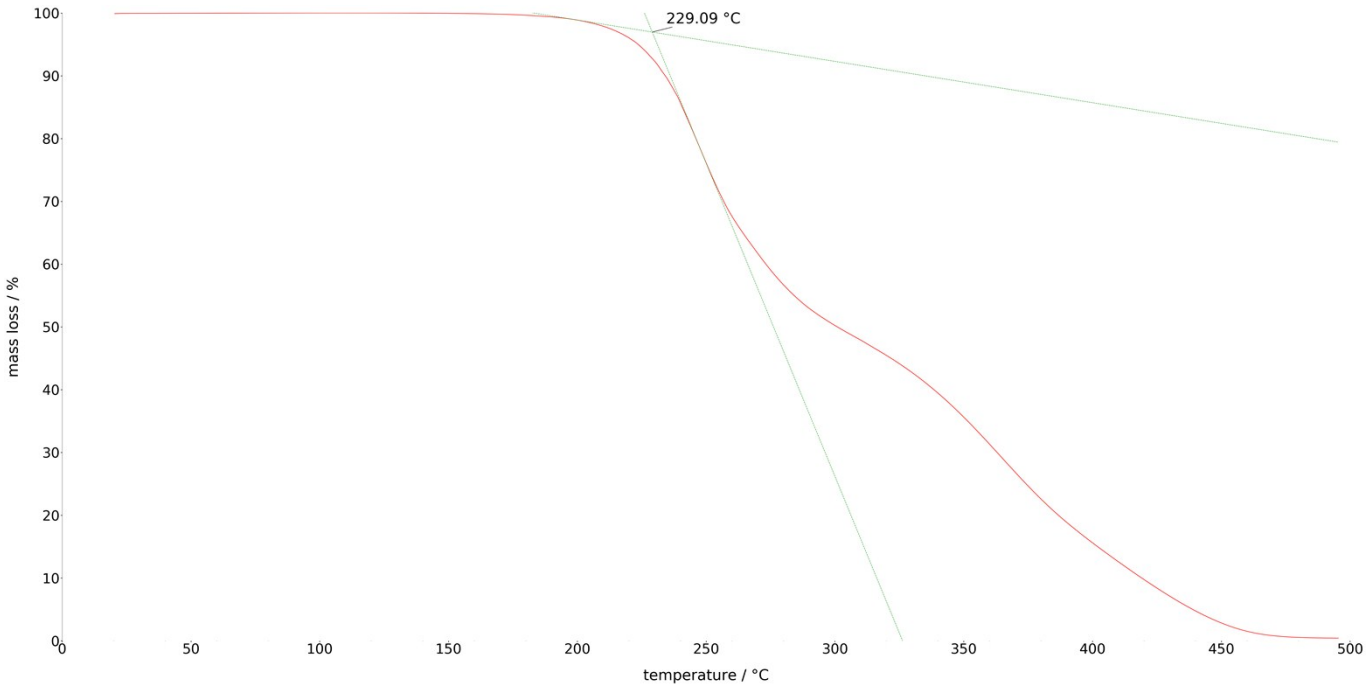

Figure S 100. TGA of 1,3-Di(hexadecyl)imidazolium hydroxalate in an alluminum pan.

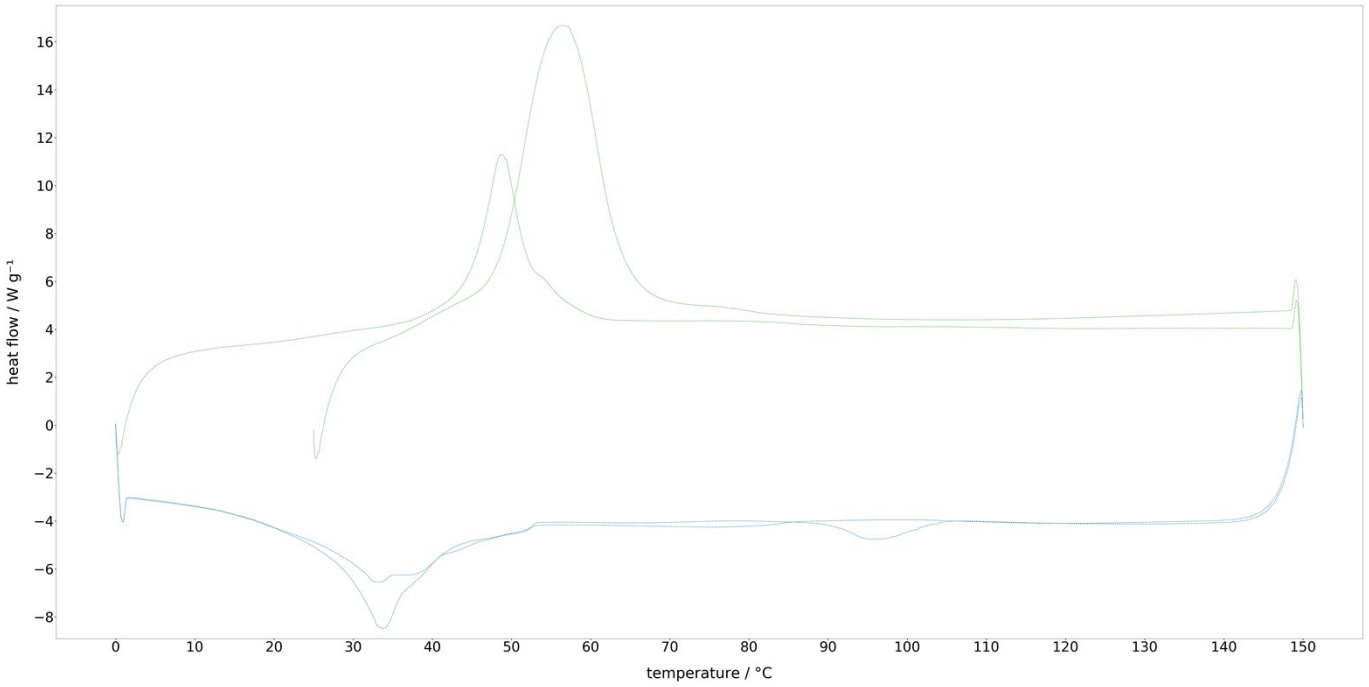

Figure S 101. DSC of 1,3-Di(hexadecyl)imidazolium hydroxalate.

Table S 1. Table reporting the calorimetry result for the phase transitions recorded during the 3rd cycle of the calorimetric experiment.

		Heating curve / [°C (J mol^{-1})]				Cooling curve / [°C (J mol^{-1})]	
Cation	Anion	1st transition	2nd transition	3rd transition	4th transition	1st transition	2nd transition
[C_8C_8IM]	[Ac]	-	-	-	-	-	-
[C_8C_8IM]	[NO_3]	-	-	-	-	-	-
[C_8C_8IM]	[Cl]	-	-	-	-	-	-
[C_8C_8IM]	[Ox]	73.68 (0.206)		-	-	25.62 (-0.146)	-
[$C_{10}C_{10}$IM]	[Ac]	17.98 (0.007)	49.14 (0.002)	-	-	-	-
[$C_{10}C_{10}$IM]	[NO_3]	12.37 (-0.047)	27.11 (0.103)	-	-	1.92 (-0.038)	14.01 (-0.009)
[$C_{10}C_{10}$IM]	[Cl]	30.75 (0.043)	56.94 (0.015)	-	-	-	56.38 (-0.015)
[$C_{10}C_{10}$IM]	[Ox]	69.85 (0.011)	-	-	-	78.26 (-0.015)	-
[$C_{12}C_{12}$IM]	[Ac]	6.58 (0.027)	30.84 (0.008)	-	-	-	30.56 (-0.013)
[$C_{12}C_{12}$IM]	[NO_3]	14.77 (0.032)	41.38 (-0.083)	68.67 (0.025)	97.71 (0.017)	13.56 (-0.025)	99.12 (-0.017)
[$C_{12}C_{12}$IM]	[Cl]	42.11 (0.136)	-	-	-	45.28 (-0.149)	-
[$C_{12}C_{12}$IM]	[Ox]	65.21 (0.199)	125.38 (0.02)	-	-	34.05 (-0.146)	130.23 (-0.02)
[$C_{14}C_{14}$IM]	[Ac]	18.23 (0.118)	43.3 (0.006)	-	-	20.88 (-0.132)	43.84 (-0.006)
[$C_{14}C_{14}$IM]	[NO_3]	33.32 (0.115)	42.75 (-0.031)	48.97 (0.067)	110.64 (0.008)	26.63 (-0.084)	110.71 (-0.008)
[$C_{14}C_{14}$IM]	[Cl]	20.97 (0.031)	25.37 (0.075)	42.87 (0.006)	-	18.06 (-0.112)	43.34 (-0.007)
[$C_{14}C_{14}$IM]	[Ox]	68.19 (0.151)	130.47 (0.013)	-	-	54.52 (-0.127)	134.74 (-0.017)
[$C_{16}C_{16}$IM]	[Ac]	33.56 (0.09)	50.07 (0.012)	-	-	46.06 (-0.08)	52.62 (-0.018)
[$C_{16}C_{16}$IM]	[NO_3]	42.62 (0.119)	125.17 (0.008)	-	-	46.75 (-0.124)	118.26 (-0.005)
[$C_{16}C_{16}$IM]	[Cl]	31.78 (0.078)	127.56 (0.003)	-	-	43.7 (-0.089)	140.83 (-0.005)
[$C_{16}C_{16}$IM]	[Ox]	44.18 (0.043)	68.55 (0.002)	109.2 (0.003)	-	54.1 (-0.046)	106.65 (-0.008)

To increase data reproducibility, the data reported are derived from the third cycle of the thermo-calorimetric analysis. The first analysis cycle had markedly different transitions for virtually all the compounds, generally attributed to the stabilization of material by the inclusion of water molecules in the structure. The thermos-calorimetric graph of each ionic liquid is available within the electronic supporting information.

References

1 P. S. Piispanen, M. Persson, P. Claesson and T. Norin, *J. Surfactants Deterg.*, 2004, **7**, 161–167.