

Electronic Supplementary Information for

Solvent-Free Lithium and Sodium Containing Electrolytes Based on Pseudo-Delocalized Anions

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1. General Information

Materials

All chemicals were used as received without further purification. LiTFSI (Lithium bis(trifluoromethanesulfonyl)imide) and NaTFSI (**Sodium bis(trifluoromethylsulfonyl)imide**) were both purchased from Solvionic (99.5%) further dried at 60 °C under vacuum and stored in an Argon filled glove box with O₂ and H₂O levels below 1 ppm. Lithium hydroxide powder (98%), sodium hydroxide pellets (97%), acetonitrile (AN; anhydrous 99.8%), Di-methyl amine solution 40 wt.% in H₂O, 1,3-propane sultone and 1,4-butane sultone were all purchased from Sigma-Aldrich.

Analytical methods

The synthesized salts were fully examined by LC-MS and elemental analysis and NMR spectroscopy. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker 400 MHz spectrometer at 298 K, using the solvent residual peak as internal standard for H in D₂O. The elemental analysis was done as a service by Mikrolab Kolbe AG, Germany. The water content was measured using a *Metrohm 381 Karl-Fisher* Coulometer and found to be 0.1- 0.2 wt%. The thermal stability was studied by thermogravimetric analysis (TGA) using a Netzsch TG 209 F1 instrument with a resolution of 0.1 µg under N₂ gas atmosphere (flow of 20 mL min⁻¹) coupled to Vector 22 Bruker FTIR-spectrometer to perform evolved gas analysis. Melting points and glass transition temperatures were measured by differential scanning calorimetry (DSC, TA Instruments Q1000) for samples of *ca.* 10 mg using sealed aluminium pans.

The ionic conductivities were measured using a Novocontrol broadband dielectric spectrometer equipped with an Alpha-S high-resolution dielectric analyzer between 10⁻² to 10⁷ Hz. The powder samples were melted inside a Teflon spacer with an inner diameter of 4 mm and 1 mm thickness placed over a coin cell case. A stainless steel disk was deposited on top and pressed while hot (90 °C) to guarantee the complete filling of the Teflon spacer. The coin cell was completed with a spring and sealed inside the glove box. The ESW was tested by linear sweep voltammetry (LSV) from the open-circuit potential at 2 mV/s until a significant current density was recorded. The electrochemical measurements were performed at 100°C using a two-electrode cell with a stainless-steel disk as a working electrode and lithium foil as a counter and reference electrodes using a 70 µm thick glass-fibre veil as a separator. To avoid misinterpretation of the data due to multiple cations, this electrochemical characterization was limited to the electrolytes only containing Li⁺, and in particular, the composition of 20 mol% of LiMM3411 and 80 mol% of LiTFSI, having the lowest glass transition temperature.

2. Chemical Synthesis

- LiMM₃₃₁₁ & NaMM₃₃₁₁

Both LiMM₃₃₁₁ and NaMM₃₃₁₁ were synthesized according to our previous report for LiMM₄₄₁₁ and NaMM₄₄₁₁¹, with some minor modifications. The synthesis was carried out through three consecutive steps (Fig. S1). Compared to our previous method¹ for synthesizing of LiMM₄₄₁₁ and NaMM₄₄₁₁ (Fig. S2-b), the reaction media in the second step was changed to acetonitrile to hinder the possible reaction between water and propane sultone at elevated temperature since propane sultone is much more reactive than butane sultone. Caution should be taken when handling propane sultone, since it is a known carcinogenic compound.²

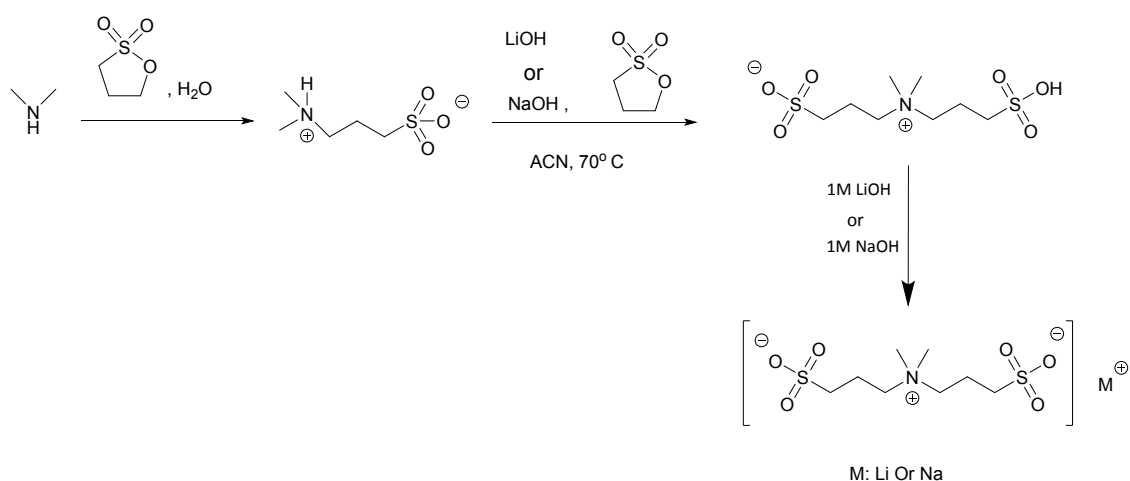


Figure S1. Synthesis route of LiMM₃₃₁₁ and NaMM₃₃₁₁.

The synthesis of zwitterionic di-methyl ammonio-propane sulfonate (Z311) was initiated by dropwise addition of propane sultone (6 mL, 68.4 mmol) to a solution of dimethyl amine (200 mL, 200 mL, %40 weight in water, 25 times excess) cooled to 0°C during a period of 30 min. As the consumption of starting materials was verified by NMR a removal of excess of dimethyl amine in vacuo was performed. Subsequently, neutralization of the reaction mixture was made with diluted HCl (1 M), before disposal of the dimethyl amine solution. The crude colorless product was collected and recrystallized using ethanol (96%), followed by drying in a vacuum oven at 50°C for 24 h. 10.3 g of 3-(dimethylammonio)propane-1-sulfonate (Z311), as a pure crystalline product, *i.e.* 61.6 mmol, corresponding to 90% yield, was achieved. The second step of the synthesis was performed by stirring a slurry of stoichiometric amounts of Z311 (0.953 g, 5.7 mmol), LiOH (0.1362 g, 5.7 mmol) or NaOH (0.22792 g, 5.7 mmol) with propane sultone (0.5 ml, 5.7 mmol) in 20 mL of anhydrous acetonitrile at 70 °C for 72 h (Figure S1). By vacuum filtration the crude product was isolated and then dissolved in

10 mL water, an insoluble white supernatant was filtered off and by removal of water in vacuo, a crude colorless product was obtained, which was further purified by recrystallization in methanol then dried in vacuum oven for 48 h at 40 °C, to obtain a colorless crystalline material, "3- (dimethyl (3-sulfopropyl) ammonio) propane-1-sulfonate" HMM₃₃₁₁ (1.55 g, 5.36 mmol, 94% yield). The corresponding lithium or sodium salts LiMM₃₃₁₁ (1.5 g, 5.08 mmol, 98%) and NaMM₃₃₁₁ (1.57 g, 5.14 mmol, 97%) were acquired, by neutralizing HMM₃₃₁₁ (1.5 g, 5.18 mmol) with 1 M LiOH or NaOH solution, followed by removal of water in vacuo and drying in vacuum oven at 70 °C for 72 h, respectively.

Z311: ¹H-NMR (400 MHz, D₂O) δ = 3.18 (t, 2H, NCH₂); 2.87 (t, 2H, SCH₂); 2.79 (s, 6H, 2xCH₃); 2.05 (m, 2H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 56.15 (NCH₂); 47.45 (SCH₂); 42.65 (2xCH₃); 19.81 (CH₂) ppm. Elem. Anal. Calc. (C₅H₁₃NO₃S): C, 35.9; H, 7.84; N, 8.38; S, 19.17. Found: C, 36.16; H, 7.96; N, 8.27; S, 18.78.

HMM3311: ¹H-NMR (400 MHz, D₂O) δ = 3.18 (t, 2H, NCH₂); 2.87 (t, 2H, SCH₂); 2.79 (s, 6H, 2xCH₃); 2.05 (m, 2H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 56.15 (NCH₂); 47.45 (SCH₂); 42.65 (2xCH₃); 19.81 (CH₂) ppm. Elem. Anal. Calc. (C₈H₁₉NO₆S₂ · 1.0 H₂O): C, 31.26; H, 6.89; N, 4.54; S, 20.86. Found: C, 31.15; H, 6.55; N, 4.56; S, 18.358.

LiMM3311: ¹H-NMR (400 MHz, D₂O) δ = 3.38 (t, 4H, NCH₂); 3.01 (s, 6H, 2xCH₃); 2.86 (t, 4H, SCH₂); 2.11 (m, 4H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 62.49 (NCH₂); 50.37 (SCH₂); 47.15 (2xCH₃); 18.06 (CH₂) ppm. Elem. Anal. Calc. (LiC₈H₁₈NO₆S₂ · 1.0 H₂O): C, 30.67; H, 6.43; N, 4.47; S, 20.47; Li, 2.22. Found: C, 30.33; H, 6.75; N, 4.09; S, 18.57; Li: 2.42.

NaMM3311: ¹H-NMR (400 MHz, D₂O) δ = 3.38 (t, 4H, NCH₂); 3.01 (s, 6H, 2xCH₃); 2.86 (t, 4H, SCH₂); 2.11 (m, 4H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 62.49 (NCH₂); 50.36 (SCH₂); 47.16 (2xCH₃); 18.07 (CH₂) ppm. Elem. Anal. Calc. (NaC₈H₁₈NO₆S₂): C, 30.86; H, 5.83; N, 4.5; S, 20.59; Na, 7.38. Found: C, 31.03; H, 5.74; N, 4.73; S, 20.43; Na: 7.33.

- **LiMM3411 and NaMM3411** Asymmetric lithium and sodium salts of MM3411, were prepared as shown in (Fig. S2-a). Firstly, zwitterionic di-methyl ammonio-butanefulfonate (ZDMBS) was synthesized according to the by some of us previously reported method. ¹

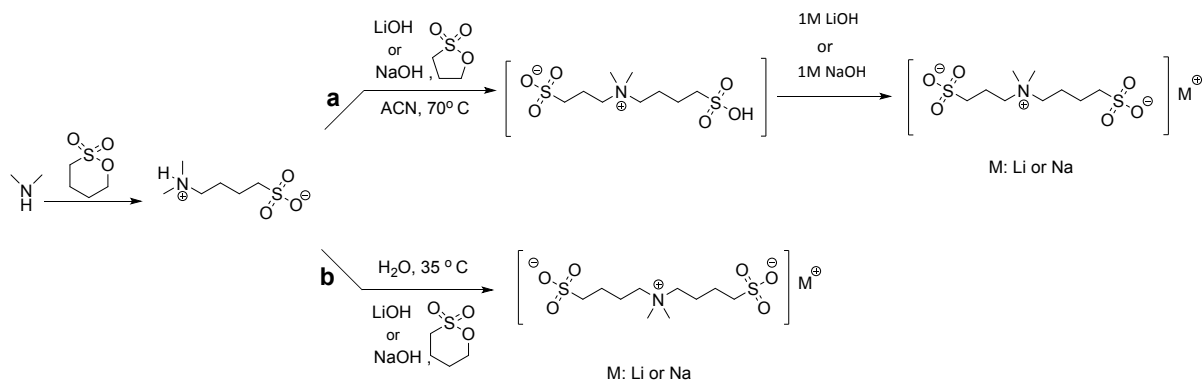


Figure S2. Synthesis route of (a) Li & NaMM₃₄₁₁, (b) Li & NaMM₄₄₁₁

1,4-butane sultone (3ml, 29.5mmol) was added dropwise to the aqueous solution of di-methyl amine (40 wt%, 100 mL, 30 times molar excess) during 10 min while stirring. The reaction mixture stirred at room temperature for 24 h. After removing excess of di-methyl amine solution in vacuo, a colorless crystalline crude product as zwitterionic di-methyl ammonio-butane sulfonate (ZDMBS) was collected. Recrystallizing of the crude product from ethanol (96%) and thereafter drying in a vacuum oven at 50 °C for 24 h, resulted the desired compound to a 94% yield, 5 g, i.e. 27.5 mmol. In second step, stoichiometric amounts of ZDMBS (2 g, 11 mmol), propane sultone (1 ml, 11 mmol) and LiOH (0.264 g, 11 mmol) or NaOH (0.441 g, 11 mmol) were added to 50 mL of anhydrous acetonitrile at 70 °C for 72 h. After collecting of the crude product by vacuum filtration, it was dissolved in 10 mL water. Filtration was applied to get rid of the insoluble white supernatant. Removal of water in vacuo and recrystallization in methanol resulted in the desired product. After drying in vacuum oven for 48 h at 40 °C, a colorless crystalline material was obtained, “3-(dimethyl (4-sulfobutyl) ammonio) propane-1-sulfonate” HMM₃₄₁₁ (3.2 g, 10.5 mmol, 96% yield). A final step, neutralization of HMM₃₄₁₁ (1.6 g, 5.27 mmol) with 1 M LiOH or NaOH solution was followed by removal of water in vacuo and drying in vacuum oven at 70 °C for 72 h. The corresponding lithium or sodium salts LiMM₃₄₁₁ (1.61 g, 5.2 mmol, 99%) and NaMM₃₃₁₁ (1.68 g, 5.16 mmol, 98%), were obtained.

HMM3411: ¹H-NMR (400 MHz, D₂O) δ = 3.31 (t, 2H, NCH₂); 3.22 (t, 2H, NCH₂); 2.96 (s, 6H, 2xCH₃); 2.82 (t, 4H, SCH₂); 2.06 (m, 2H, -CH₂-); 1.75 (m, 2H, -CH₂-); 1.65 (m, 2H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 63.54 (NCH₂); 62.25 (NCH₂); 50.4 (SCH₂) 49.91 (SCH₂); 47.17 (2xCH₃); 20.99 (CH₂); 20.77 (CH₂); 18.04 (CH₂) ppm.

LiMM3411: ¹H-NMR (400 MHz, D₂O) δ = 3.33 (t, 2H, NCH₂); 3.24 (t, 2H, NCH₂); 2.96 (s, 6H, 2xCH₃); 2.84 (t, 4H, SCH₂); 2.08 (m, 2H, -CH₂-); 1.80 (m, 2H, -CH₂-); 1.67 (m, 2H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 63.55 (NCH₂); 62.27 (NCH₂); 50.35 (SCH₂) 49.89 (SCH₂); 47.15 (2xCH₃); 20.97 (CH₂); 20.75 (CH₂); 18.03 (CH₂) ppm. Elem. Anal.: Calc. (LiC₉H₂₀NO₆S₂ · 0.5H₂O): C, 33.96; H, 6.75; N, 4.4; S, 20.15; Li, 2.18. Found: C, 33.98; H, 6.95; N, 4.00; S, 19.6; Li: 1.90.

NaMM3411: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.33 (t, 2H, NCH_2); 3.24 (t, 2H, NCH_2); 2.96 (s, 6H, $2\times\text{CH}_3$); 2.84 (t, 4H, SCH_2); 2.08 (m, 2H, $-\text{CH}_2-$); 1.80 (m, 2H, $-\text{CH}_2-$); 1.67 (m, 2H, $-\text{CH}_2-$) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 63.55 (NCH_2); 62.24 (NCH_2); 50.39 (SCH_2); 49.89 (SCH_2); 47.15 ($2\times\text{CH}_3$); 20.96 (CH_2); 20.75 (CH_2); 18.03 (CH_2) ppm. Elem. Anal.: Calc. ($\text{NaC}_9\text{H}_{20}\text{NO}_6\text{S}_2 \cdot 0.5 \text{H}_2\text{O}$): C, 32.33; H, 6.33; N, 4.19; S, 19.18. Found: C, 32.7; H, 6.61; N, 4.36; S, 18.75.

3. ^1H and ^{13}C NMR Spectra of Synthesized salts

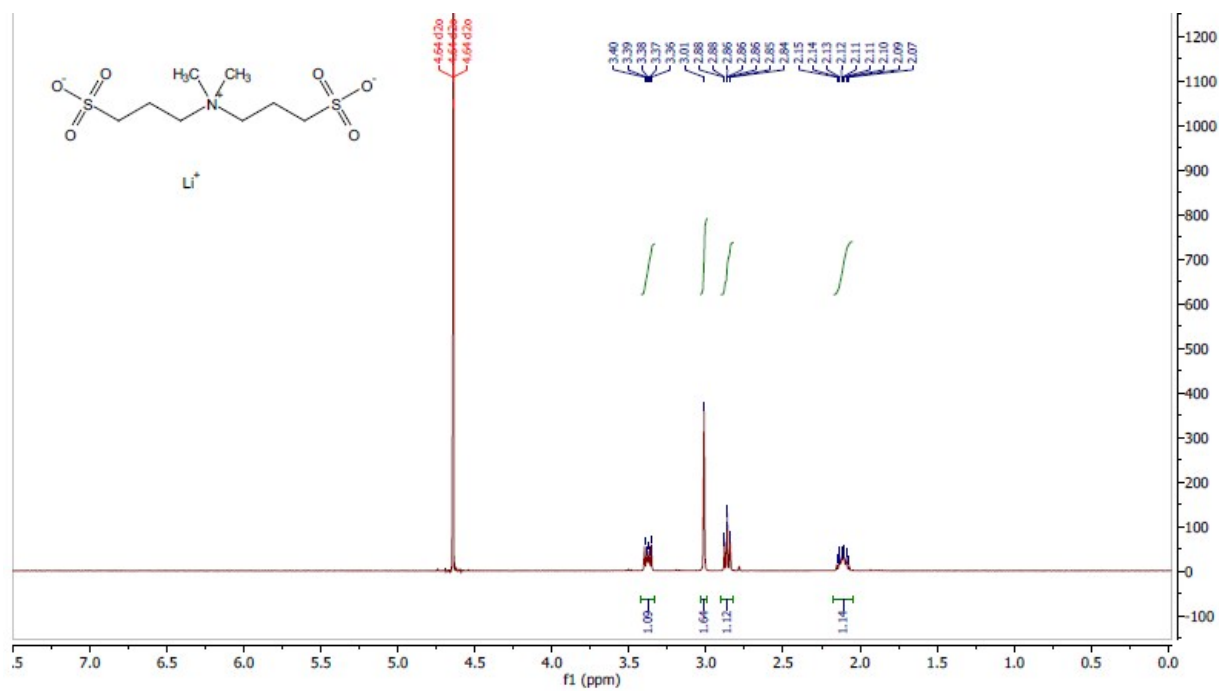


Figure S3. ^1H NMR of LiMM3311

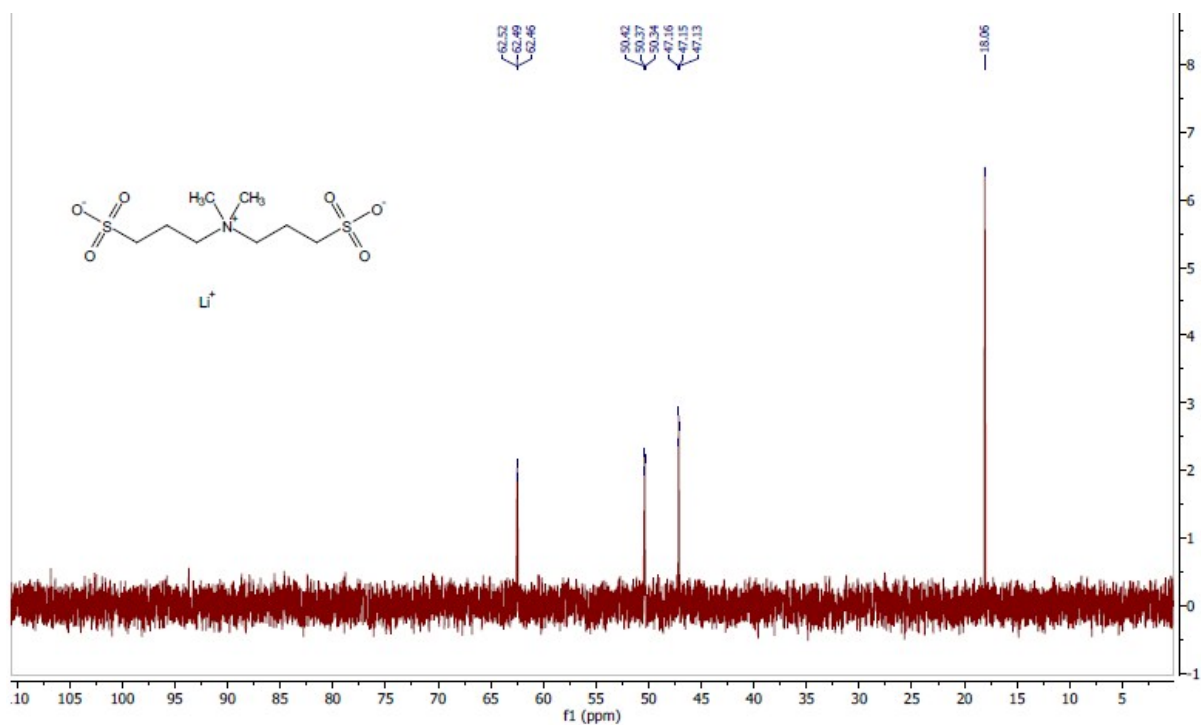


Figure S4. ^{13}C NMR of LiMM3311

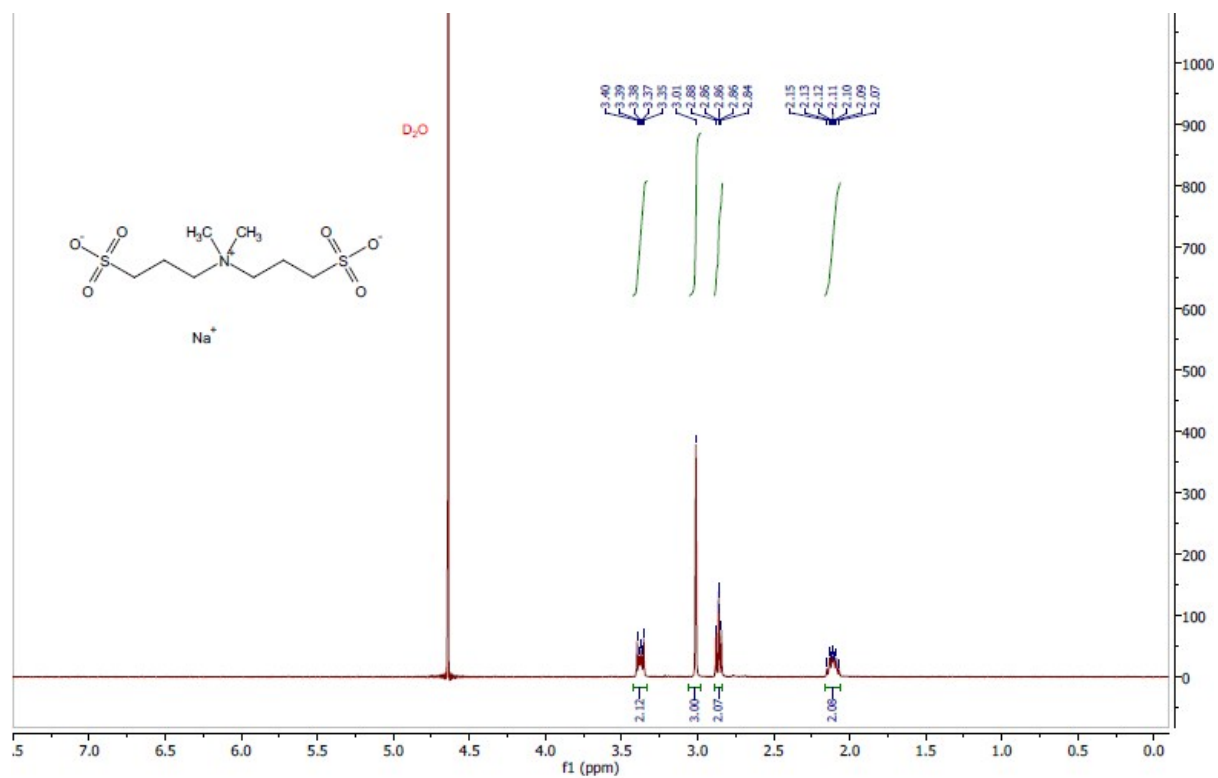


Figure S5. 1H NMR of NaMM3311

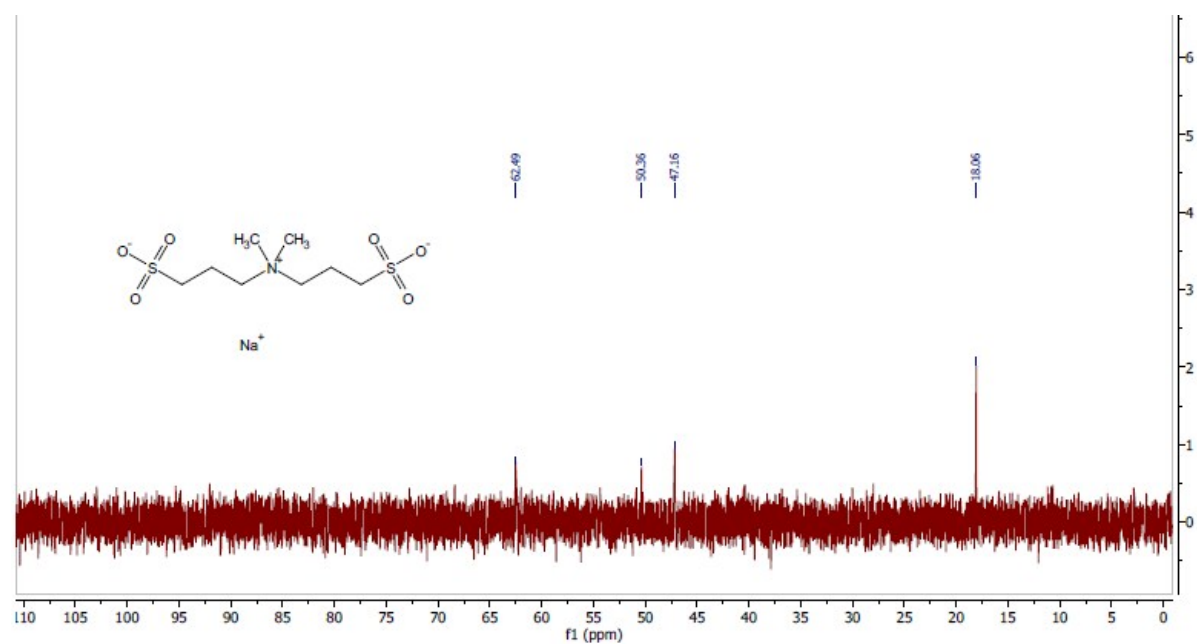


Figure S6. ^{13}C NMR of NaMM3311

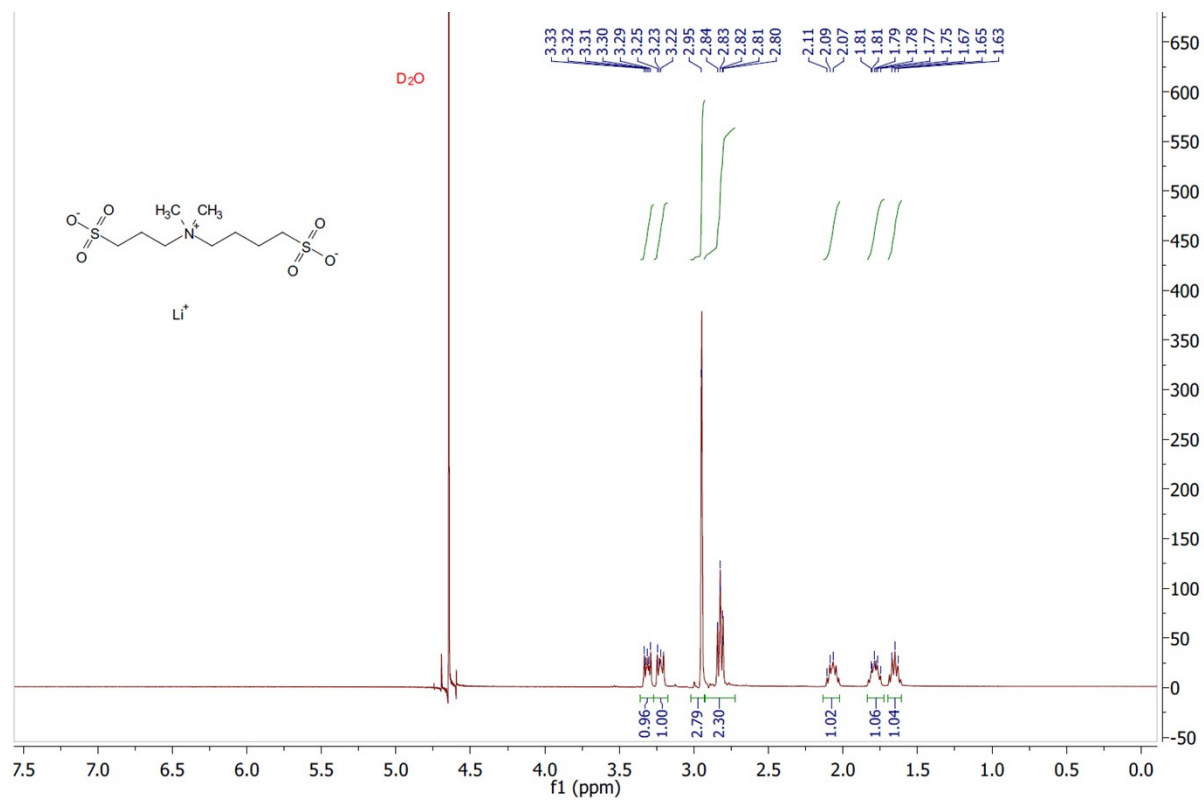


Figure S7. ¹H NMR of LiMM3411

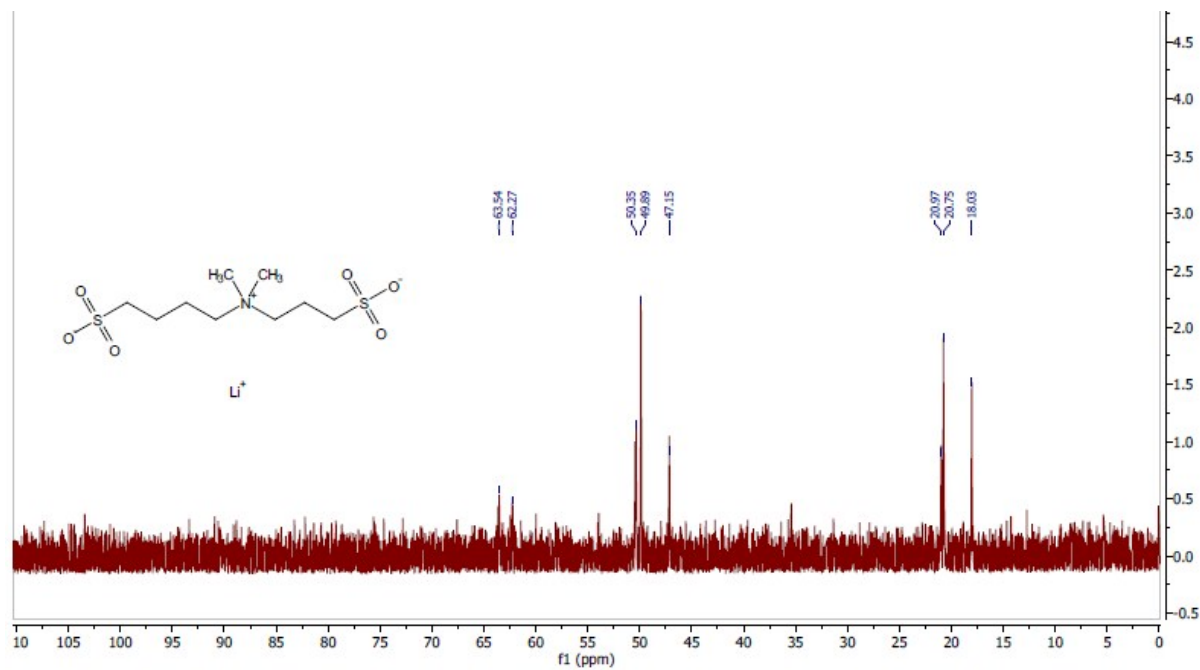


Figure S8. ¹³C NMR of LiMM3411

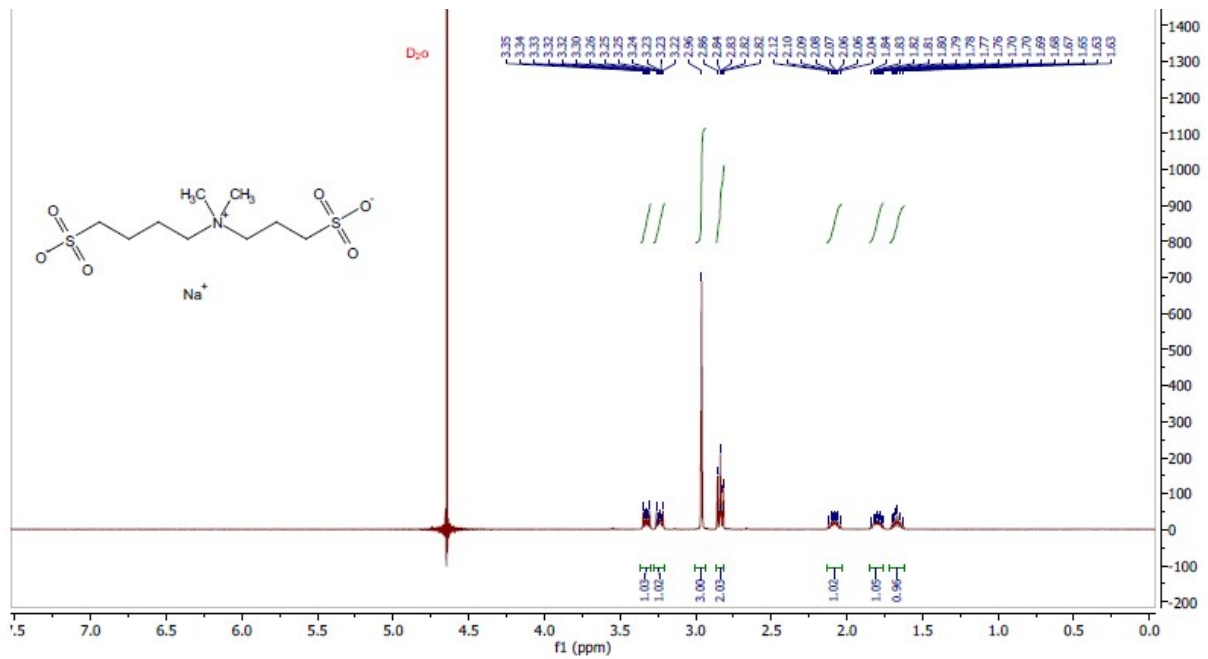


Figure S9. ¹H NMR of NaMM3411

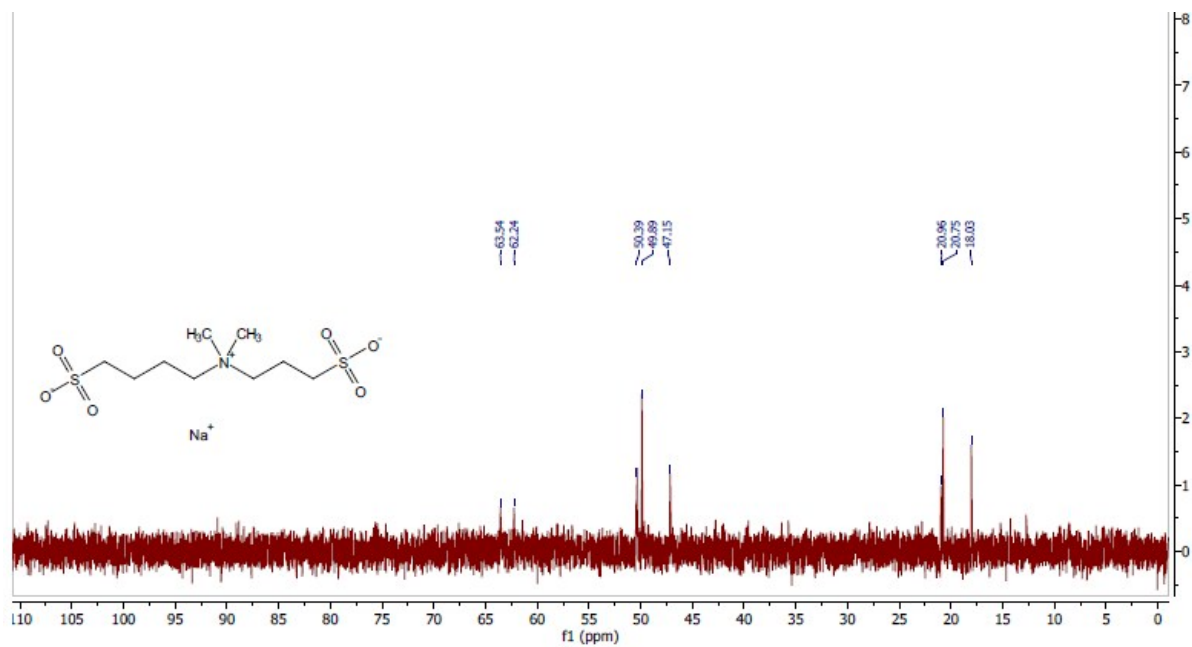


Figure S10. ¹³C NMR of NaMM3411

4. Additional Tables and Figures

Table S1. Molar fractions of the different salts in the mixtures.

MM3311				MM3411			
LiTFSI	NaTFSI	LiMM3311	NaMM3311	LiTFSI	NaTFSI	LiMM3411	NaMM3411
0.9	0	0.1	0	0.9	0	0.1	0
0.8	0	0.2	0	0.8	0	0.2	0
0.7	0	0.3	0	0.7	0	0.3	0
0.6	0	0.4	0	0.6	0	0.4	0
0.5	0	0.5	0	0.5	0	0.5	0
0.9	0	0	0.1	0.9	0	0	0.1
0.8	0	0	0.2	0.8	0	0	0.2
0.7	0	0	0.3	0.7	0	0	0.3
0.6	0	0	0.4	0.6	0	0	0.4
0.5	0	0	0.5	0.5	0	0	0.5
0	0.9	0.1	0	0	0.9	0.1	0
0	0.8	0.2	0	0	0.8	0.2	0
0	0.7	0.3	0	0	0.7	0.3	0
0	0.6	0.4	0	0	0.6	0.4	0
0	0.5	0.5	0	0	0.5	0.5	0
0	0.9	0	0.1	0	0.9	0	0.1
0	0.8	0	0.2	0	0.8	0	0.2
0	0.7	0	0.3	0	0.7	0	0.3
0	0.6	0	0.4	0	0.6	0	0.4
0	0.5	0	0.5	0	0.5	0	0.5
0.8	0.1	0	0.1	0.5	0.3	0	0.2
0.7	0.2	0	0.1				
0.5	0.3	0	0.2				
0.3	0.3	0	0.4				

Table S1. Molar fractions of the different salts in the mixtures (cont.).

MM4411			
LiTFSI	NaTFSI	LiMM3311	NaMM3311
0.9	0	0.1	0
0.8	0	0.2	0
0.7	0	0.3	0
0.6	0	0.4	0
0.5	0	0.5	0
0.9	0	0	0.1
0.8	0	0	0.2
0.7	0	0	0.3
0.6	0	0	0.4
0.5	0	0	0.5
0	0.9	0.1	0
0	0.8	0.2	0
0	0.7	0.3	0
0	0.6	0.4	0
0	0.5	0.5	0
0	0.9	0	0.1
0	0.8	0	0.2
0	0.7	0	0.3
0	0.6	0	0.4
0	0.5	0	0.5

Figure S11. Imaginary part of dielectric modulus as a function of frequency for $\text{Li}_{0.8}\text{Na}_{0.2}(\text{TFSI})_{0.8}(\text{MM3411})_{0.2}$ at different temperature.

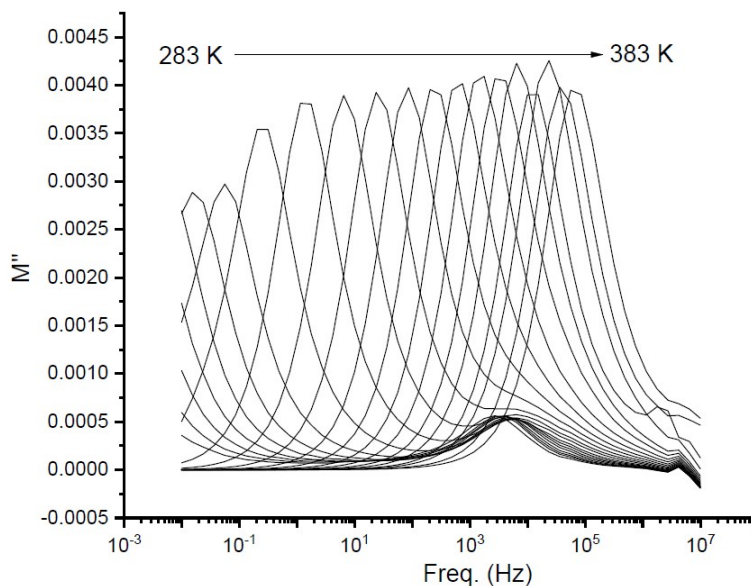


Table S2. Conductivity data extracted from Figure S11, for $\text{Li}_{0.8}\text{Na}_{0.2}(\text{TFSI})_{0.8}(\text{MM3411})_{0.2}$.

Temperature (K)	Frequency at M'' Maximum (Hz)	Ionic Conductivity (S cm ⁻¹)	Temperature (K)	Frequency at M'' Maximum (Hz)	Ionic Conductivity (S cm ⁻¹)
288.15	Out of range	--	338.15	84.51	5.8053E-9
293.15	Out of range	--	343.15	253.18	1.7216E-8
298.15	Out of range	--	348.15	749.11	4.3568E-8
303.15	Out of range	--	353.15	1776.6	1.0105E-7
308.15	0.01527	8.4094E-13	358.15	3474.6	2.2425E-7
313.15	0.05579	2.7741E-12	363.15	6488.6	4.4593E-7
318.15	0.25824	1.6392E-11	368.15	12690	8.618E-7
323.15	1.4088	9.8889E-11	373.15	23698	1.4192E-6
328.15	6.304	4.7135E-10	378.15	36495	2.7707E-6
333.15	24.637	1.8147E-9	383.15	71376	4.6102E-6

Table S3. Vogel temperatures (T_0) from the VFT equation (Eq. 1) fits.

MM3311	T_0 (K)	MM4411	T_0 (K)	MM3411	T_0 (K)
		$\text{Li}(\text{TFSI})_{0.8}(\text{MM4411})_{0.2}$	263.2	$\text{Li}(\text{TFSI})_{0.8}(\text{MM3411})_{0.2}$	254.7
$\text{Li}(\text{TFSI})_{0.7}(\text{MM3311})_{0.3}$	264.0	$\text{Li}(\text{TFSI})_{0.7}(\text{MM4411})_{0.3}$	271.6	$\text{Li}(\text{TFSI})_{0.7}(\text{MM3411})_{0.3}$	261.7
				$\text{Li}_{0.8}\text{Na}_{0.2}(\text{TFSI})_{0.8}(\text{MM3411})_{0.2}$	252.0
$\text{Li}_{0.7}\text{Na}_{0.3}(\text{TFSI})_{0.7}(\text{MM3311})_{0.3}$	272.1	$\text{Li}_{0.7}\text{Na}_{0.3}(\text{TFSI})_{0.7}(\text{MM4411})_{0.3}$	267.8	$\text{Li}_{0.7}\text{Na}_{0.3}(\text{TFSI})_{0.7}(\text{MM3411})_{0.3}$	263.6
				$\text{Na}(\text{TFSI})_{0.6}(\text{MM3411})_{0.4}$	245.4

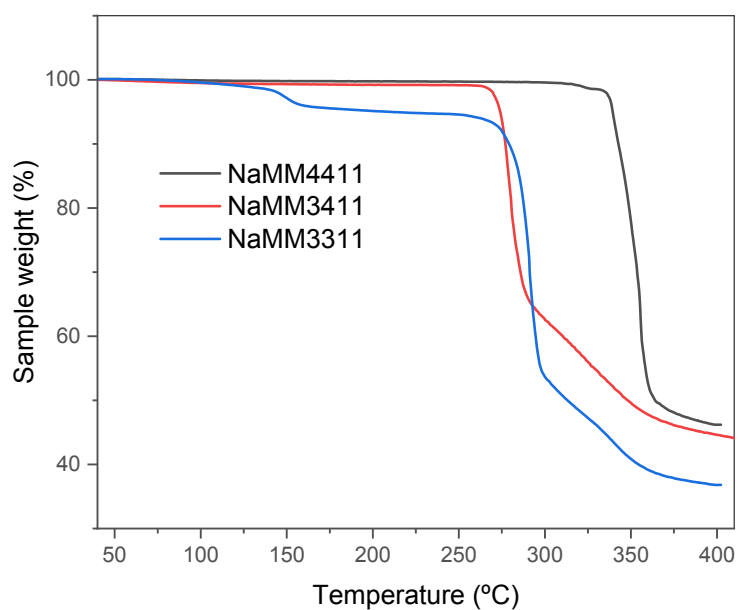


Figure S12. TGA traces of pure NaMM salts

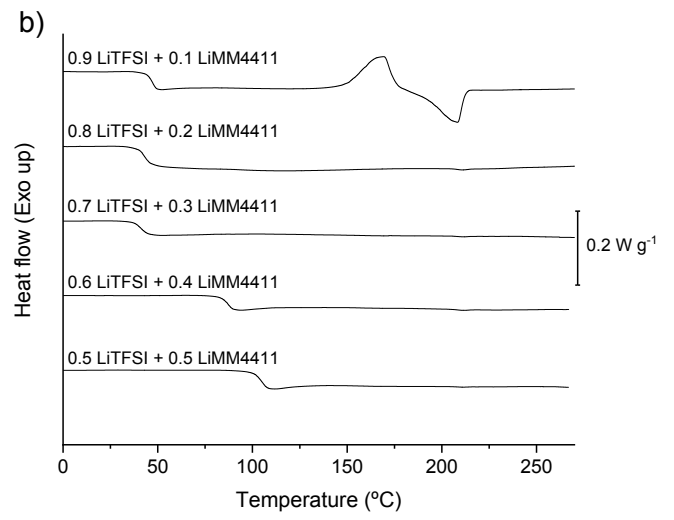
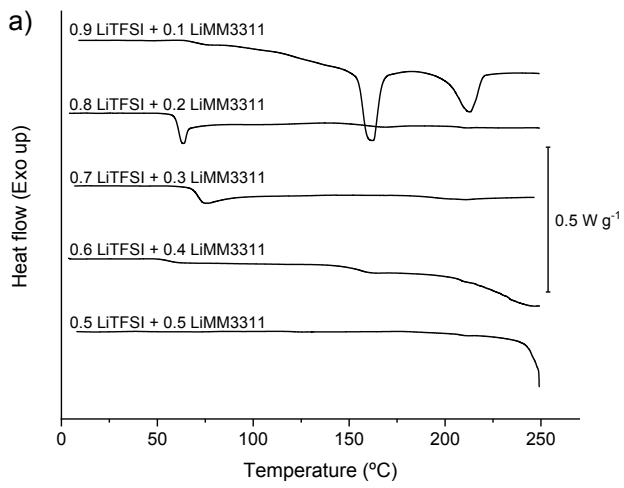


Figure S13. DSC traces of LiTFSI with a) LiMM3311 and b) LiMM4411 with compositions in molar fractions.

5. References

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