Supplementary Information for

Mechanochemically Micronised Na/NaCl; a Superfine Reductant

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Synthetic Details

General Considerations

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J-Young tap NMR tubes prepared in a glovebox. NMR spectra were recorded on an Agilent ProPulse spectrometer operating at 500.06 MHz (^{1}H). Solid State NMR measurements were run at the National Research Facility at the University of Warwick on a Bruker Advance Neo 1 GHz spectrometer operating at 264.63 MHz (^{23}Na) or 98.01 MHz (^{35}Cl). Powder X-ray Diffraction (PXRD) were measured on a STOE STADI P instrument fitted with Mythen detectors and a Ge (111) primary beam monochromator, using Cu-Kα1 radiation, the data was processed using WinXPOW software. Solvents were dried by passage through a commercially available solvent purification system and stored under argon in ampoules over 4 Å molecular sieves. C_6D_6 was purchased from Merck, dried over potassium before distilling and storing over molecular sieves. Anhydrous sodium chloride was purchased from Merck and dried under vacuum for 16 hours before being taken into the glovebox. All reactions were performed in a Retsch PM100 ball mill, in a 50 ml stainless-steel milling jar filled with 7 stainless-steel balls (7 mm diameter; 4.1 g each) and sealed with a Retsch Safety Clamp under argon. Sodium was washed with hexane and dried under reduced pressure before being taken into the glovebox. [(^{Dipp}BDI)MgI(OEt$_2$)] and [(^{Mes}BDI)MgI(OEt$_2$)] (^{Dipp}BDI = HC{(Me)CN-2,6-*i*-Pr$_2$C$_6$H$_3$}$_2$; ^{Mes}BDI = HC{(Me)CN-2,4,6-CH$_3$C$_6$H$_2$}$_2$) were synthesised according to literature methods.[1,2] SEM and EDX analyses were performed at the Henry Royce Institute by Dr Phani Karamched using a Zeiss Merlin instrument: operating voltages 20V - 30kV, up to 40 nA beam current. Resolution 0.8 nm at 15 kV, 1.6 nm at 1 kV. Inlens SE and energy selective backscatter detectors. Four quadrant backscattered electron detector. Fitted with Zeiss A-STEM detector. Oxford instruments Xmax 150 EDX. Fitted with a Gatan cryo stage and cryo/vacuum transfer capability and a customised Gatan Ilion II system with customised iload system.

Preparation of n% w/w Na/NaCl

Sodium chloride (18.75 g, 320.8 mmol) was introduced into a 50 ml stainless-steel milling jar containing 7 stainless-steel balls (7 mm diameter; 4.1 g each) and milled for 4 hours (500 rpm, 1-hour intervals, 10 second interval break). Finely divided sodium (0.94 g, 40.8 mmol) was introduced, and the solids were then milled for 16 hours (500 rpm, 1-hour intervals, 10 second interval break). The solid was inspected after milling and found to be a dark black free-flowing powder, attributed as Na/NaCl (5% w/w). To generate 10% w/w Na/NaCl additional sodium (0.94 g, 40.8 mmol) was added to the black powder and milled for an additional 2 hours. Two additional portions of sodium (0.94 g, 40.8 mmol) were added until 20% w/w Na/NaCl was obtained as a black powder (22.5 g).

Synthesis of [(^{Dipp}BDI)Mg]$_2$

Into a 50 ml stainless-steel milling jar, [(^{Dipp}BDI)MgI(OEt$_2$)] (4.0 g, 6.2 mmol) and Na/NaCl (715.1 mg, 6.2 mmol, 20% w/w Na) were added along with 7 stainless steel milling balls (7 mm diameter; 4.1 g each).

The milling jar was sealed, clamped, and milled for 1 hour (500 rpm, 15-minute interval, 10 second interval break). After an hour a solid aliquot was taken, suspended in C_6D_6 and the reaction progress was probed by ^{1}H NMR spectroscopy. Additional Na/NaCl (143.0 mg, 1.24 mmol, 20% w/w Na) was added to the milling jar and the reaction was milled for a further 15 minutes. The solids were transferred to a Schlenk flask, and the milling jar was extracted with toluene (50 mL). The solution was filtered through a frit packed with Celite® 545 and the Celite® was subsequently washed with toluene (150 mL). The resulting yellow solution was then pumped to dryness *in vacuo*, yielding [(^{Dipp}BDI)Mg]$_2$ as a yellow powder. Yield: 2.56 g, 93 %. The analytical data is in accordance with the literature.[3]

Synthesis of [(^{Mes}BDI)Mg]$_2$

[(^{Mes}BDI)MgI(OEt$_2$)] (1.0 g, 1.79 mmol) and Na/NaCl (308.5 mg, 2.68 mmol, 20% w/w Na) were introduced into a 50 ml stainless-steel milling jar, along with 7 stainless steel milling balls (7 mm diameter; 4.1 g each) and diethyl ether (2 cm^3). The milling jar was sealed, clamped, and milled for 45 minutes (500 rpm, 15-minute interval, 10 second interval break). The resultant dark blue slurry was extracted into a Schlenk flask with diethyl ether (50 cm^3) and the supernatant was filtered away from the grey precipitate. The grey byproduct was subsequently washed with diethyl ether (20 cm^3) and the resultant orange filtrate was concentrated under reduced pressure to afford [(^{Mes}BDI)Mg]$_2$ as a yellow powder. Yield: 0.49 g, 77 %. The spectroscopic data is consistent with previous reports.[2]

The temperature of the outside of the jar after the milling reaction is 32.5 °C.

SEM Images

SEM 5% w/w Na/NaCl made in a ballmill

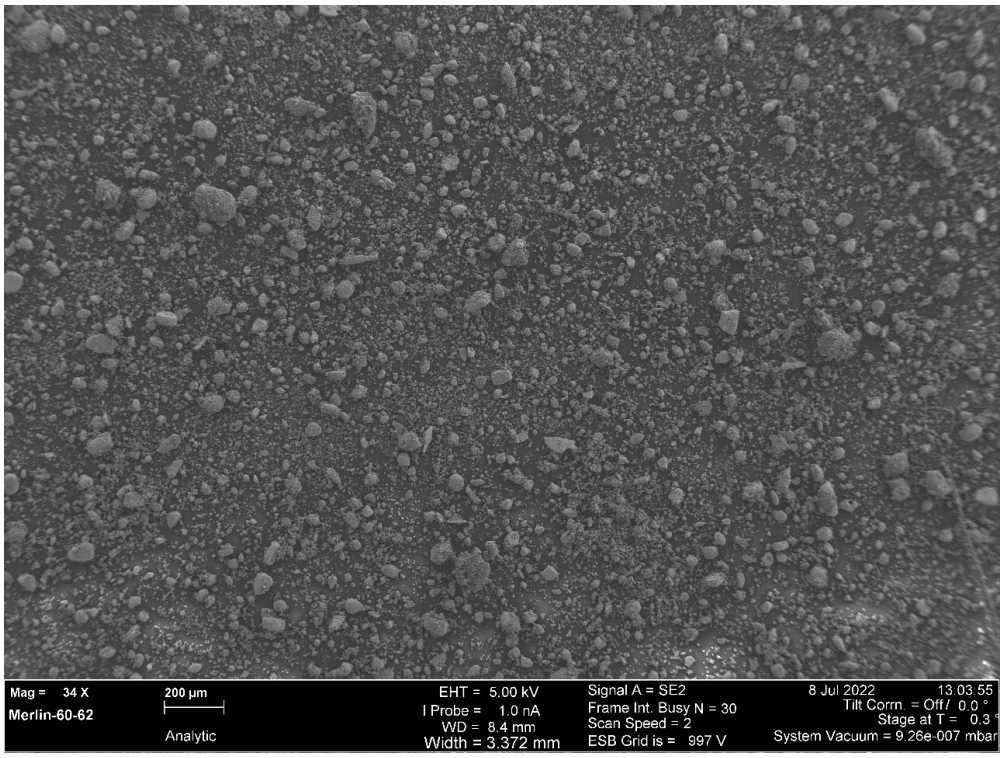

Figure S1. *SEM image of 5% w/w Na/NaCl prepared in a planetary ballmill (Retsch PM100). 34 x magnification, 200 µm scale bar*

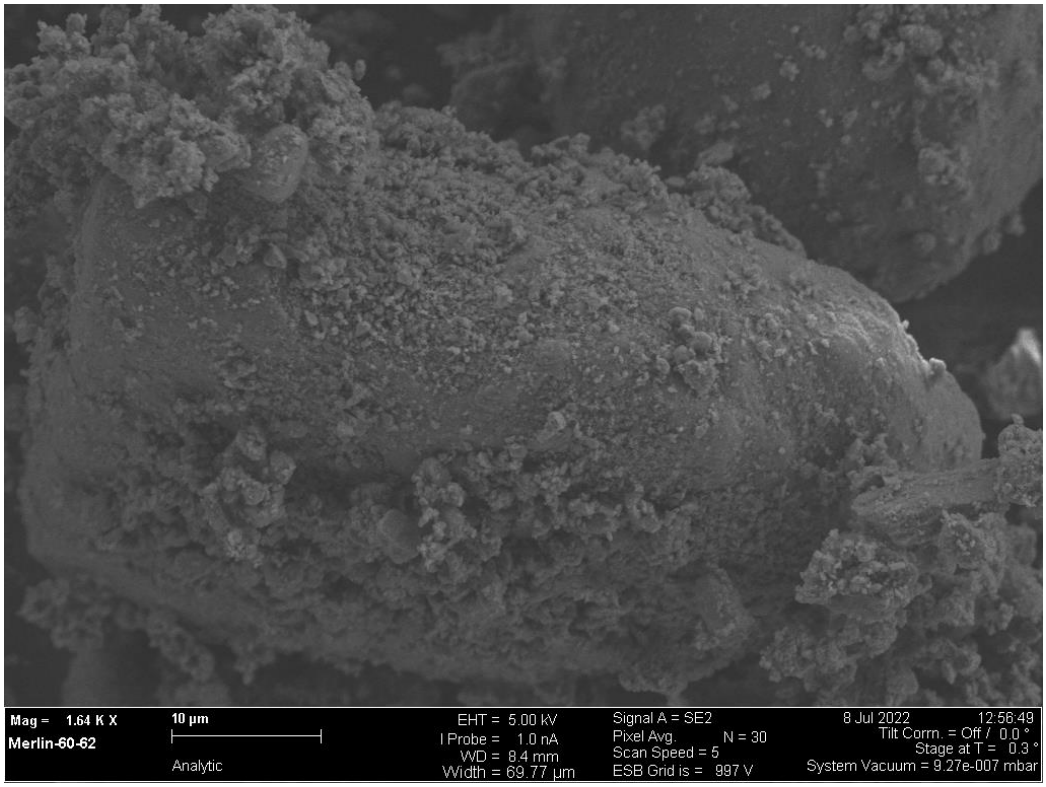

Figure S2. *SEM image of 5% w/w Na/NaCl prepared in a planetary ballmill (Retsch PM100). 1.64 K x magnification, 10 µm scale bar.*

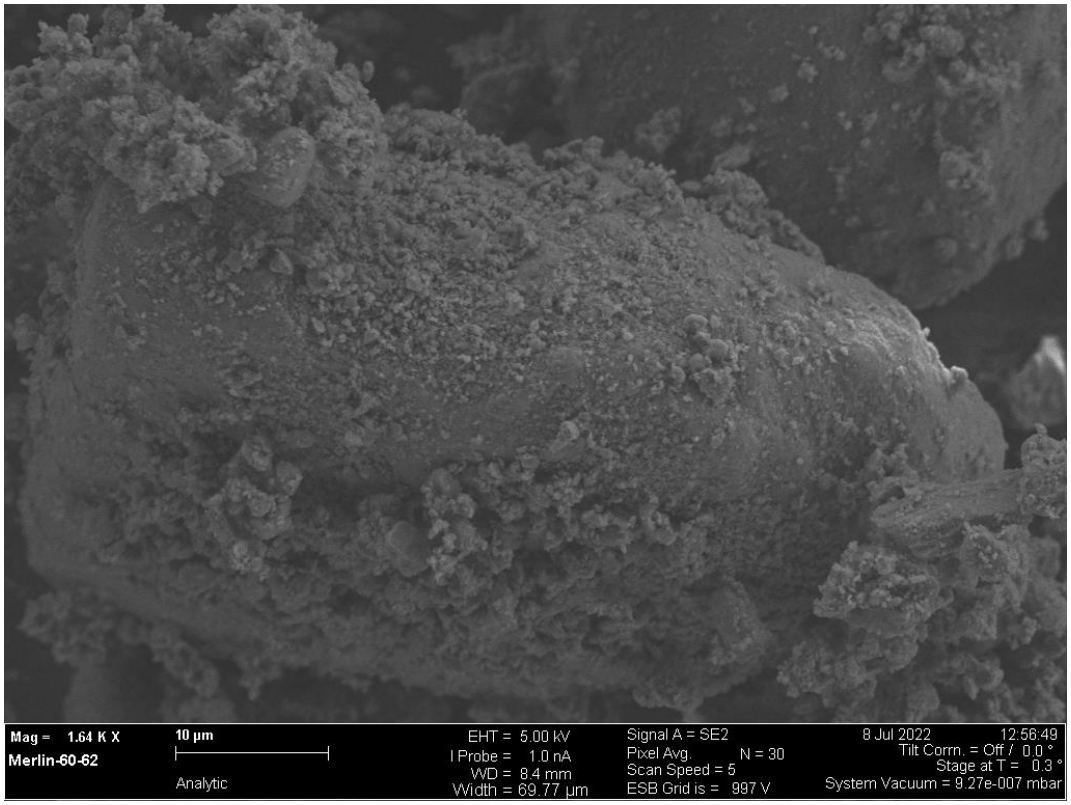

Figure S3. *SEM image of 5% w/w Na/NaCl prepared in a planetary ballmill (Retsch PM100). 1.64 K x magnification, 10 µm scale bar.*

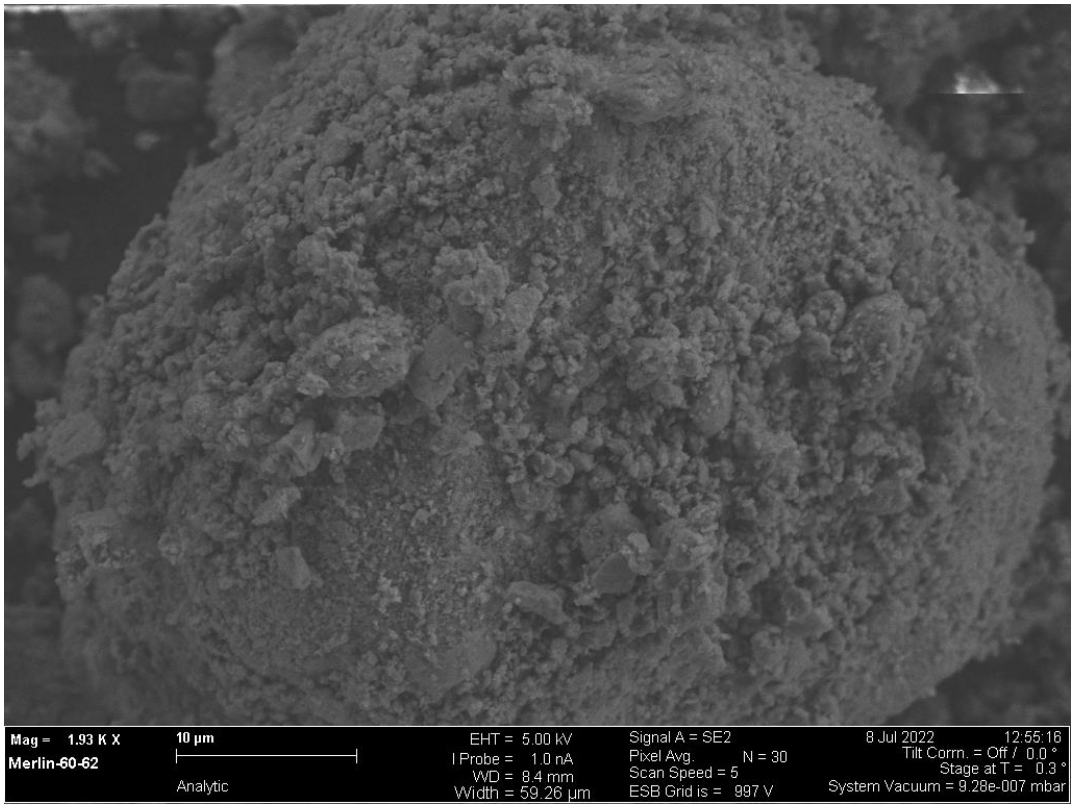

Figure S4. *SEM image of 5% w/w Na/NaCl prepared in a planetary ballmill (Retsch PM100). 1.93 K x magnification, 10 µm scale bar.*

SEM 5% w/w Na/NaCl made in a Schlenk Flask

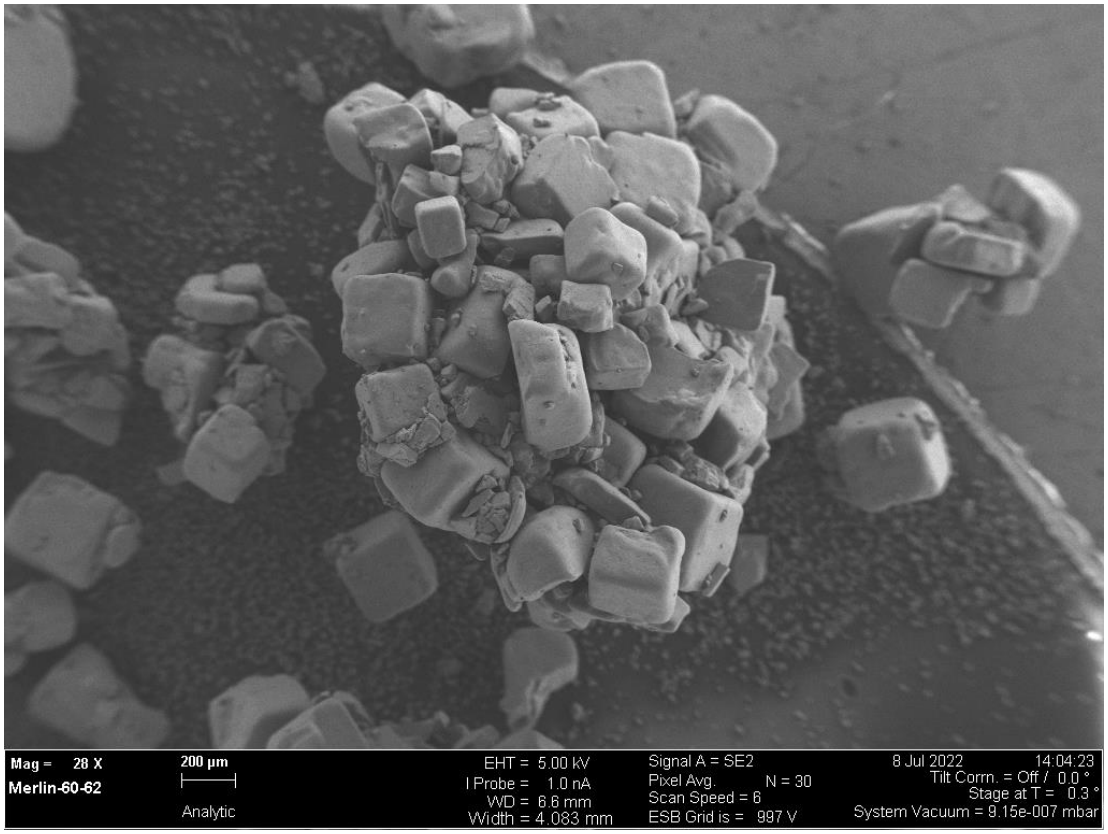

Figure S5. *SEM image of 5% w/w Na/NaCl prepared in a Schlenk flask. 28 x magnification, 200 µm scale bar.*

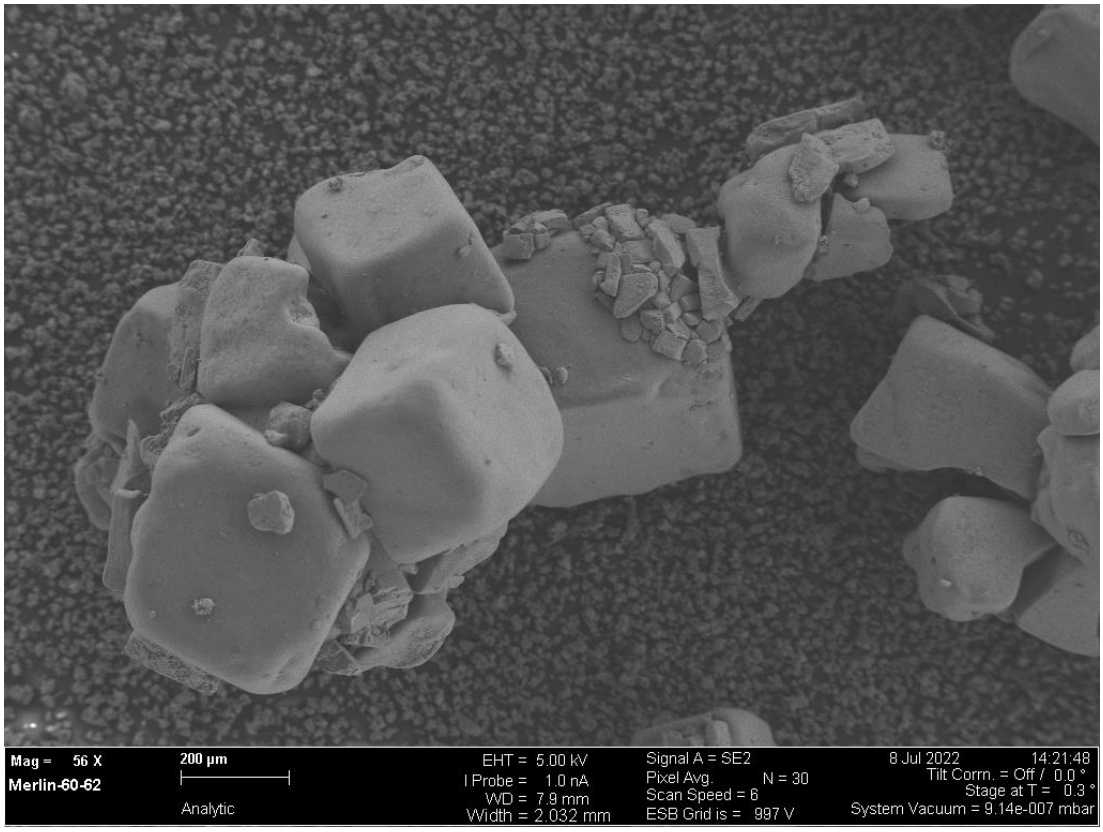

Figure S6. *SEM image of 5% w/w Na/NaCl prepared in a Schlenk flask. 56 x magnification, 200 µm scale bar.*

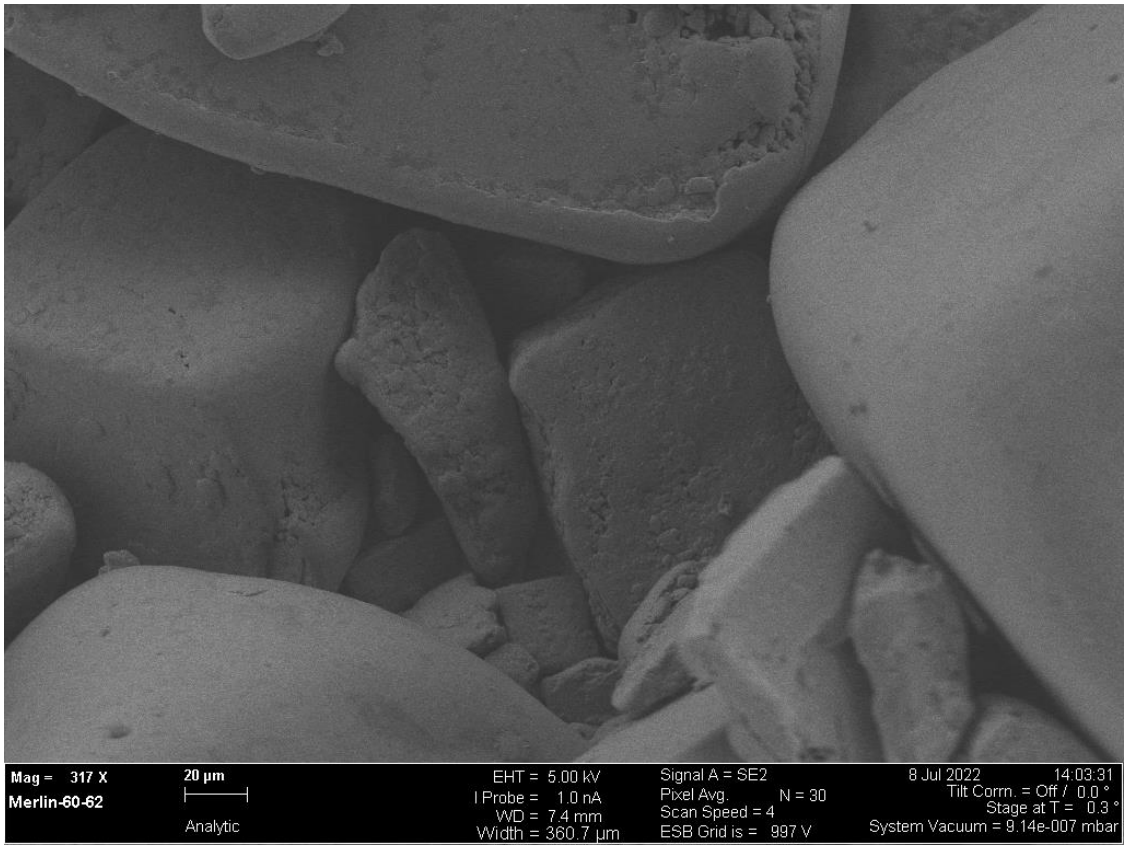

Figure S7*. SEM image of 5% w/w Na/NaCl prepared in a Schlenk flask. 317 x magnification, 20 µm scale bar.*

EDX Images

EDX 5% w/w Na/NaCl made in a ballmill

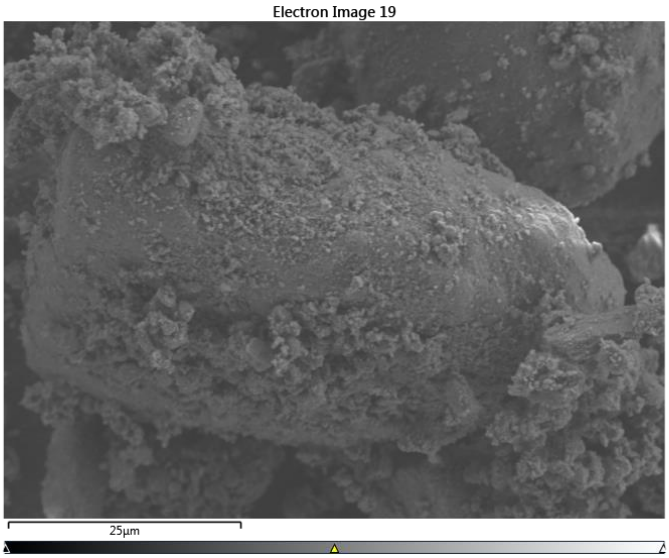

Figure S8. *SEM/EDX image of 5% w/w Na/NaCl prepared in a Ball Mill, 25 µm scale bar.*

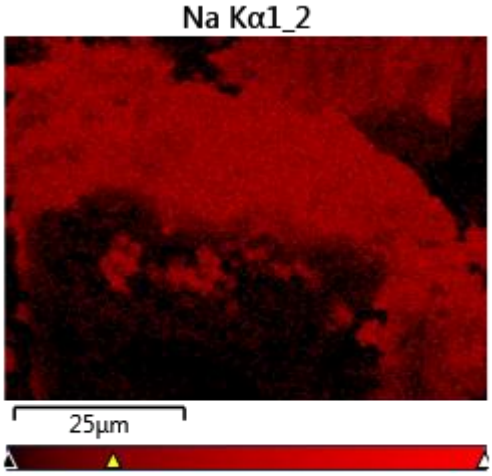

Figure S9. *EDX mapping of Na on the sample illustrated in* ***Figure 8****.*

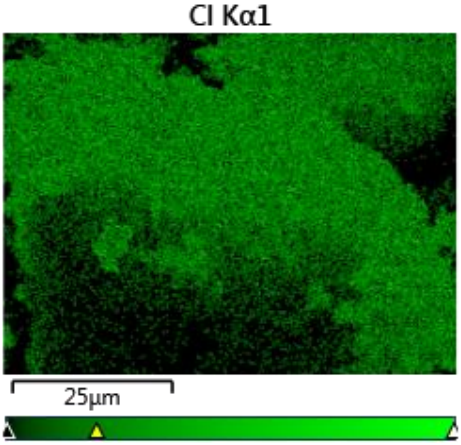

Figure 10. *EDX mapping of Cl on the sample illustrated in* ***Figure 8****.*

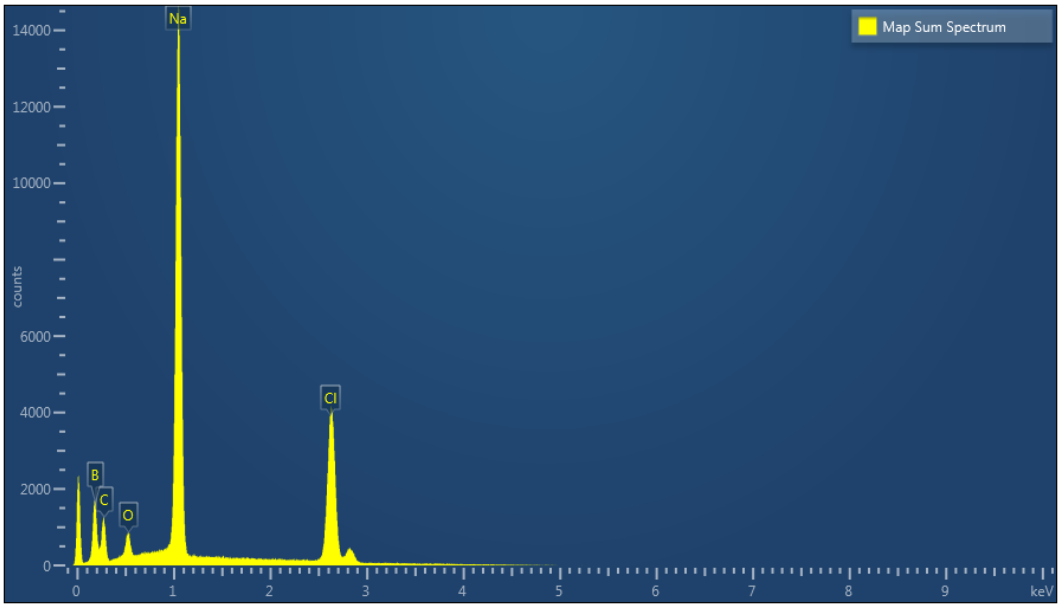

Figure S11*.EDX spectrum corresponding to* ***Figure 8****, showing elemental composition of material.*

EDX 5% w/w Na/NaCl made in a Schlenk Flask

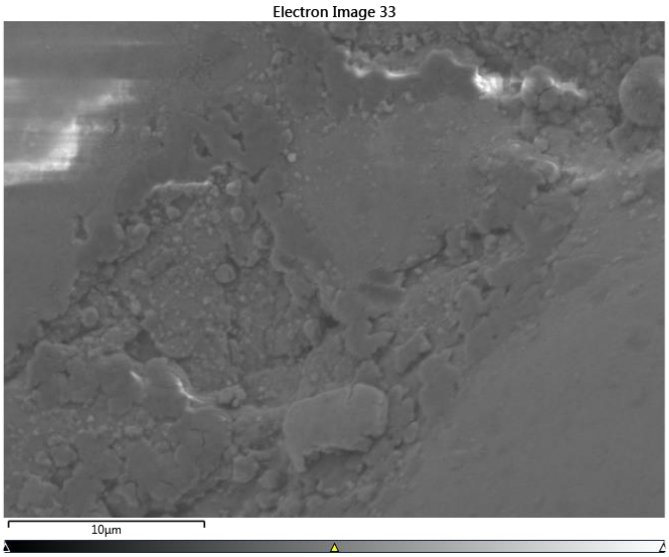

Figure 12. *SEM/EDX image of 5% w/w Na/NaCl prepared in a Schlenk flask, 10 µm scale bar.*

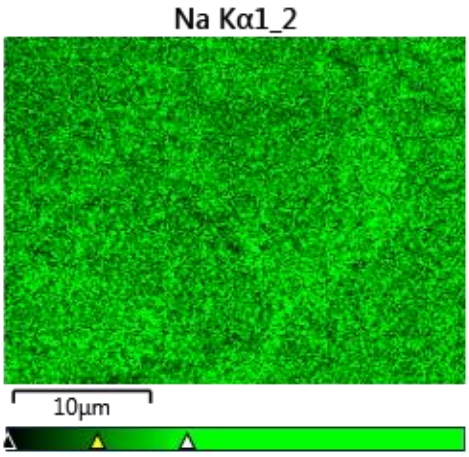

Figure S13. *EDX mapping of Na on the sample illustrated in* ***Figure 12****.*

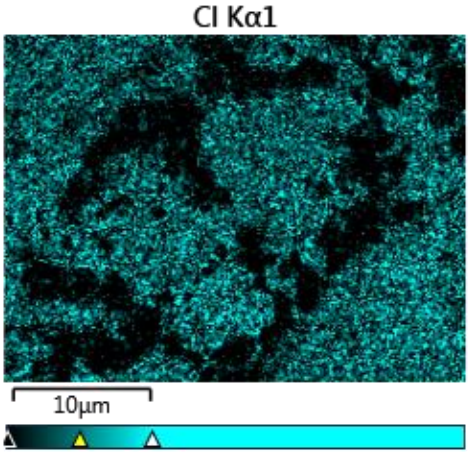

Figure S14*. EDX mapping of Na on the sample illustrated in* ***Figure 12****.*

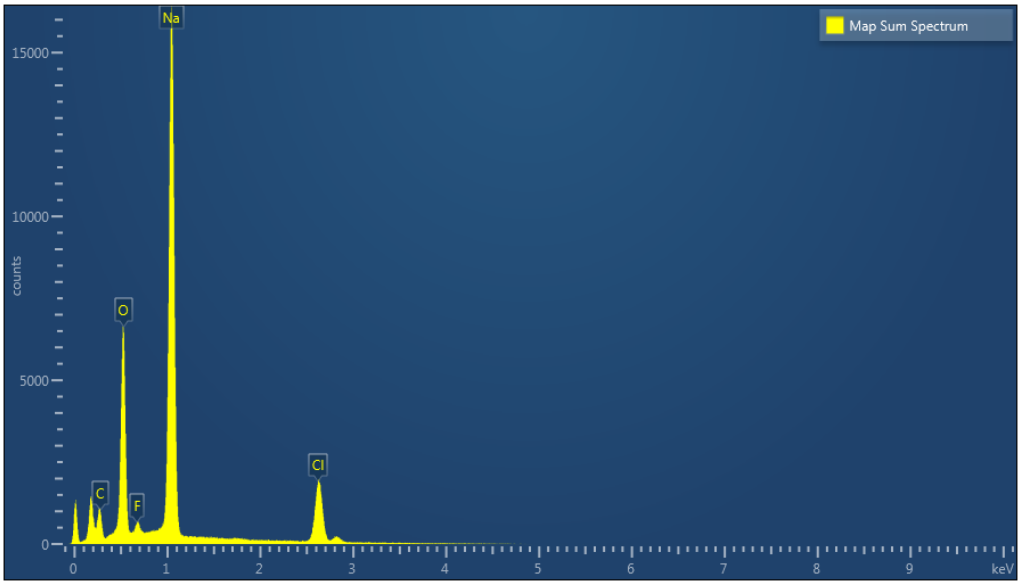

Figure S15. *EDX spectrum corresponding to* ***Figure 12****, showing elemental composition of material.*

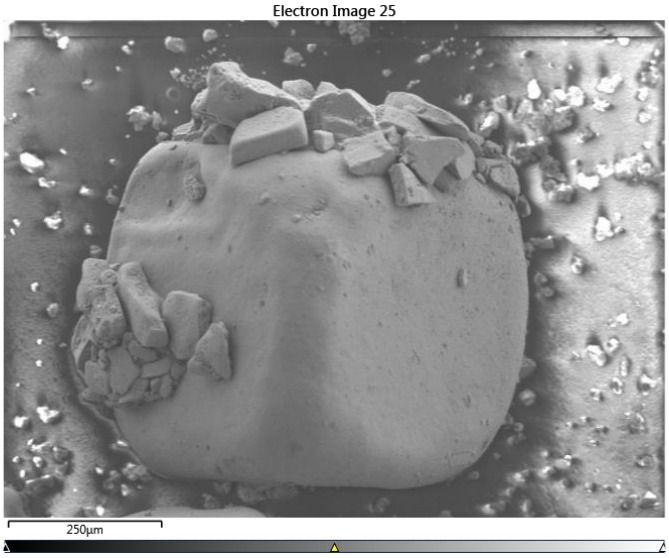

Figure S16. *SEM/EDX image of 5% w/w Na/NaCl prepared in a Schlenk flask, 250 µm scale bar.*

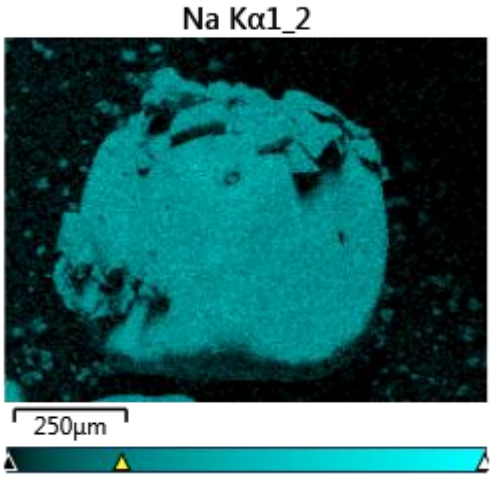

Figure S17. *EDX mapping of Na on the sample illustrated in* ***Figure 16.***

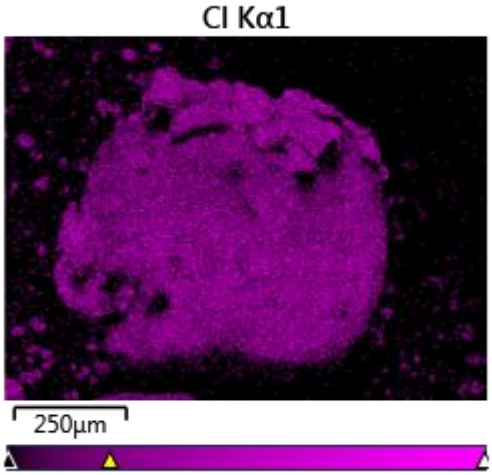

Figure S18. *EDX mapping of Na on the sample illustrated in* ***Figure 16.***

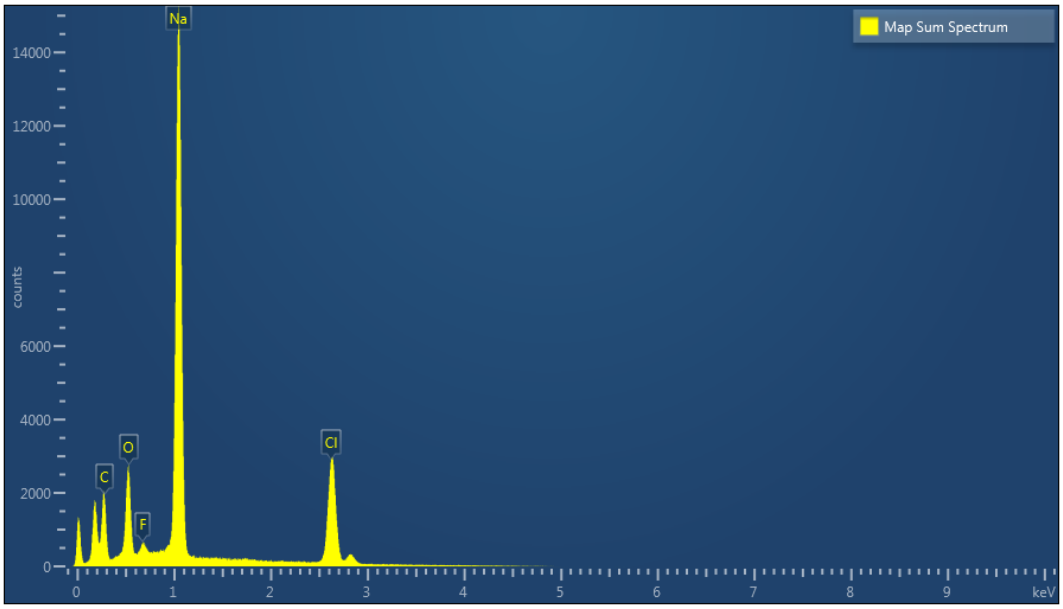

Figure S19. *EDX spectrum corresponding to* ***Figure 16****, showing elemental composition of material.*

NMR Spectra

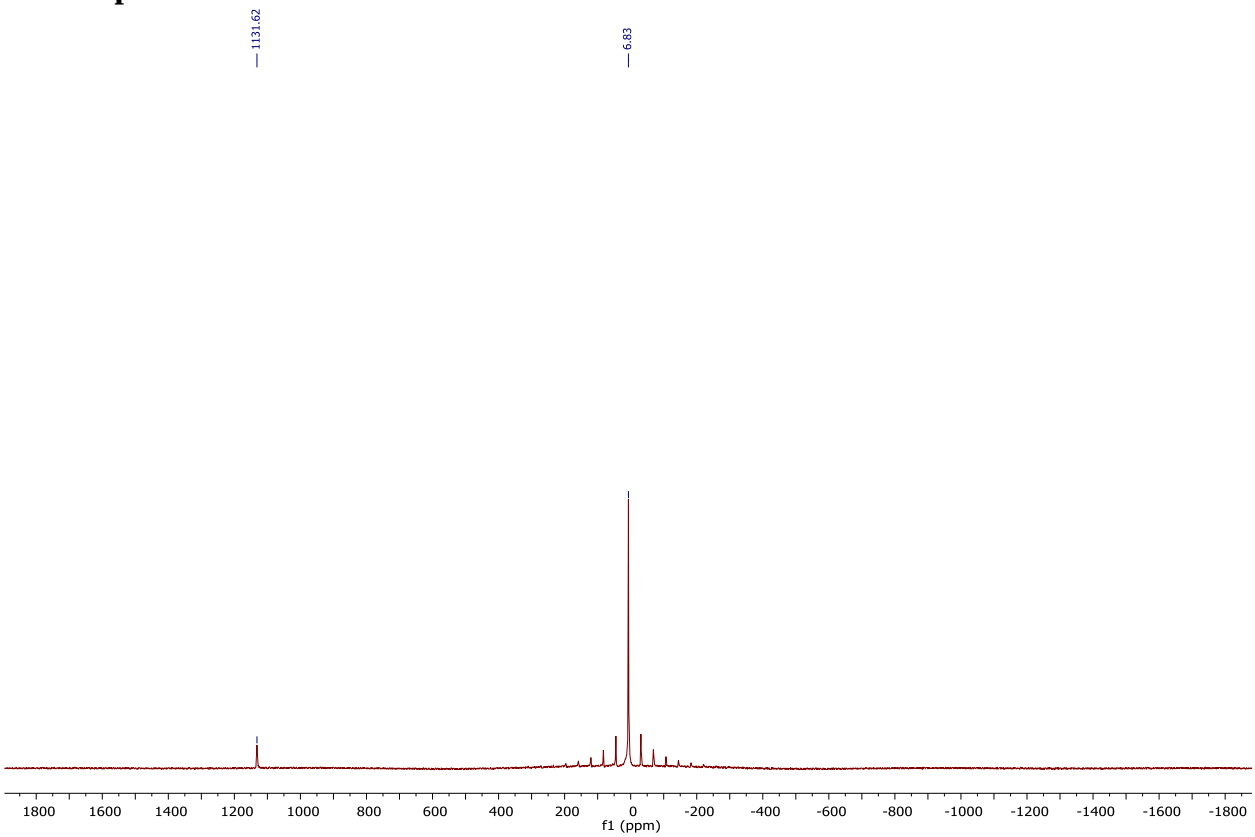

Figure S20*.* *^{23}Na SS-NMR spectrum (264.63 MHz, 294.6 K, 10 KHz MAS) for 5% w/w Na/NaCl.*

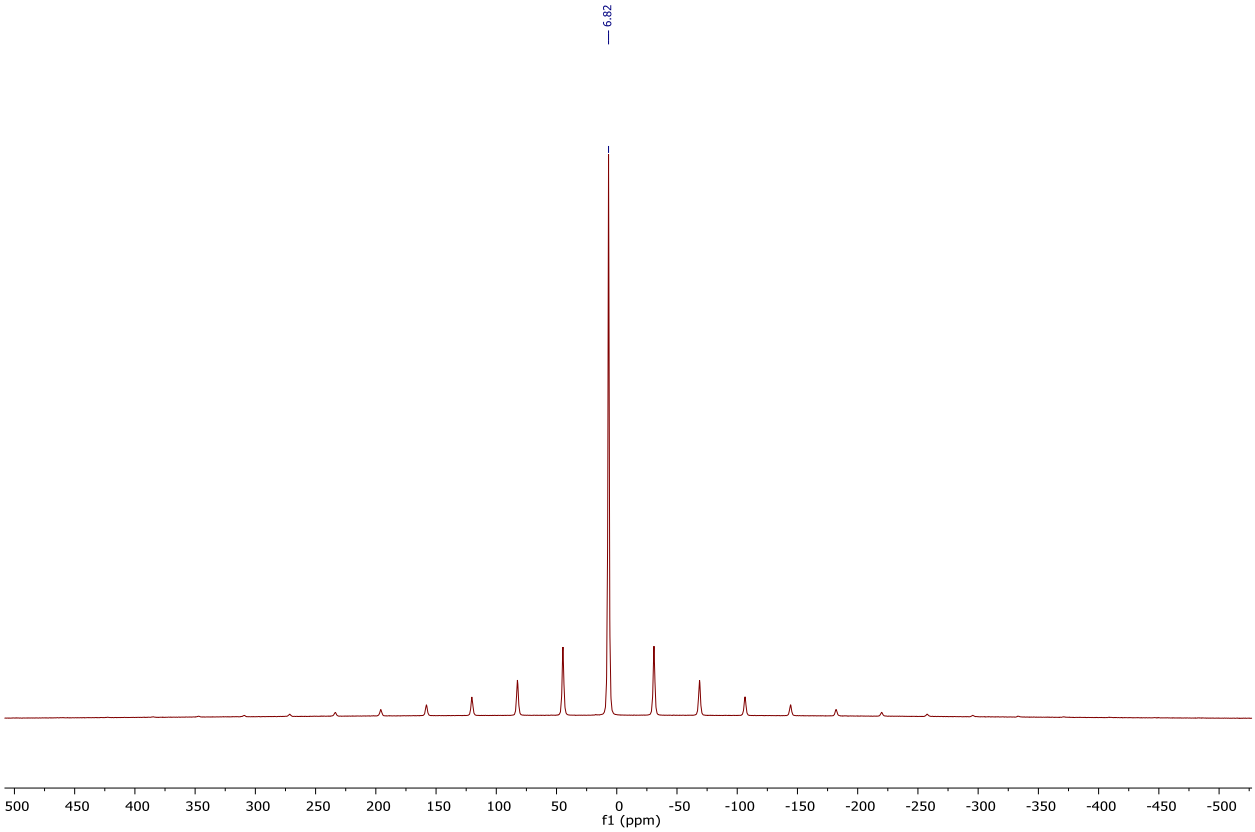

Figure S21. *^{23}Na SS-NMR spectrum (264.63 MHz, 294.6 K, 10 KHz MAS)) for 5% w/w Na/NaCl, displaying the expanded NaCl region.*

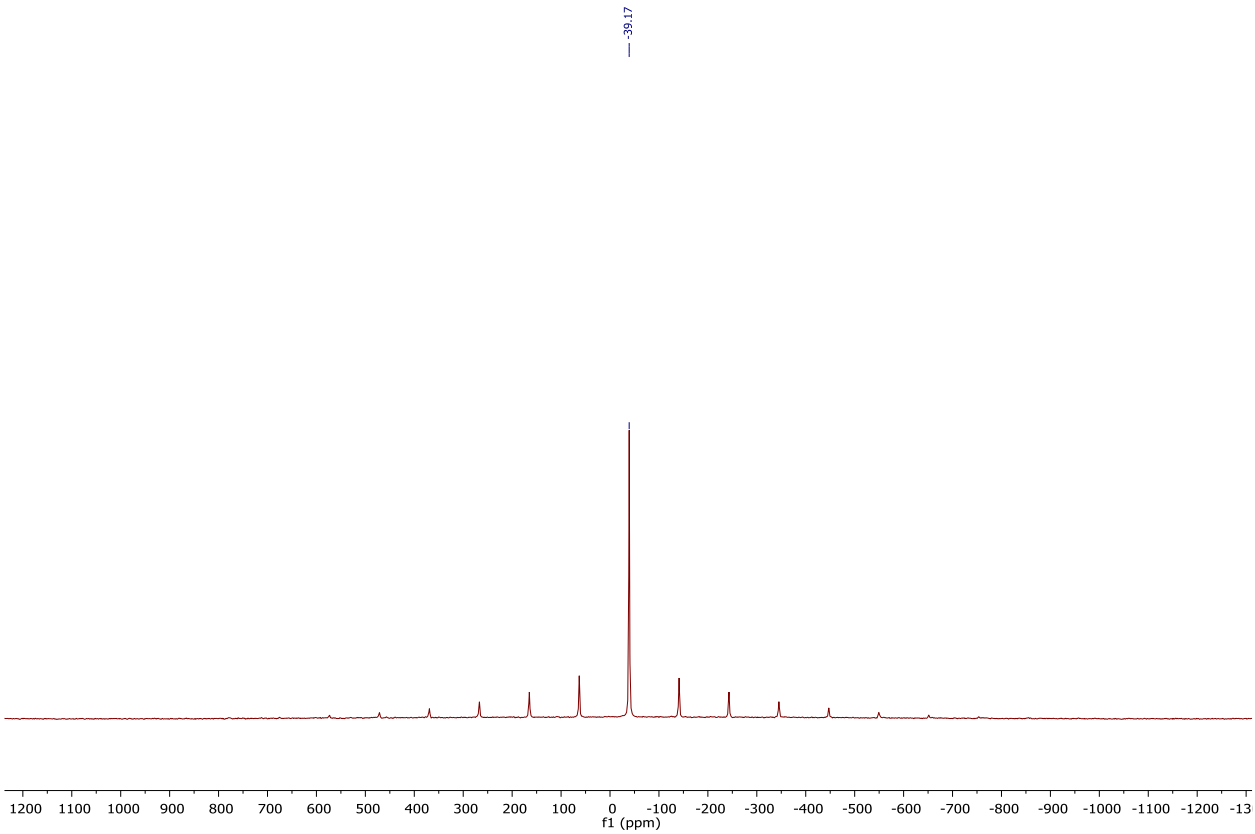

Figure S22. *^{35}Cl SS-NMR spectrum (98.01 MHz, 294.6 K, 10 KHz MAS) for 5% w/w Na/NaCl.*

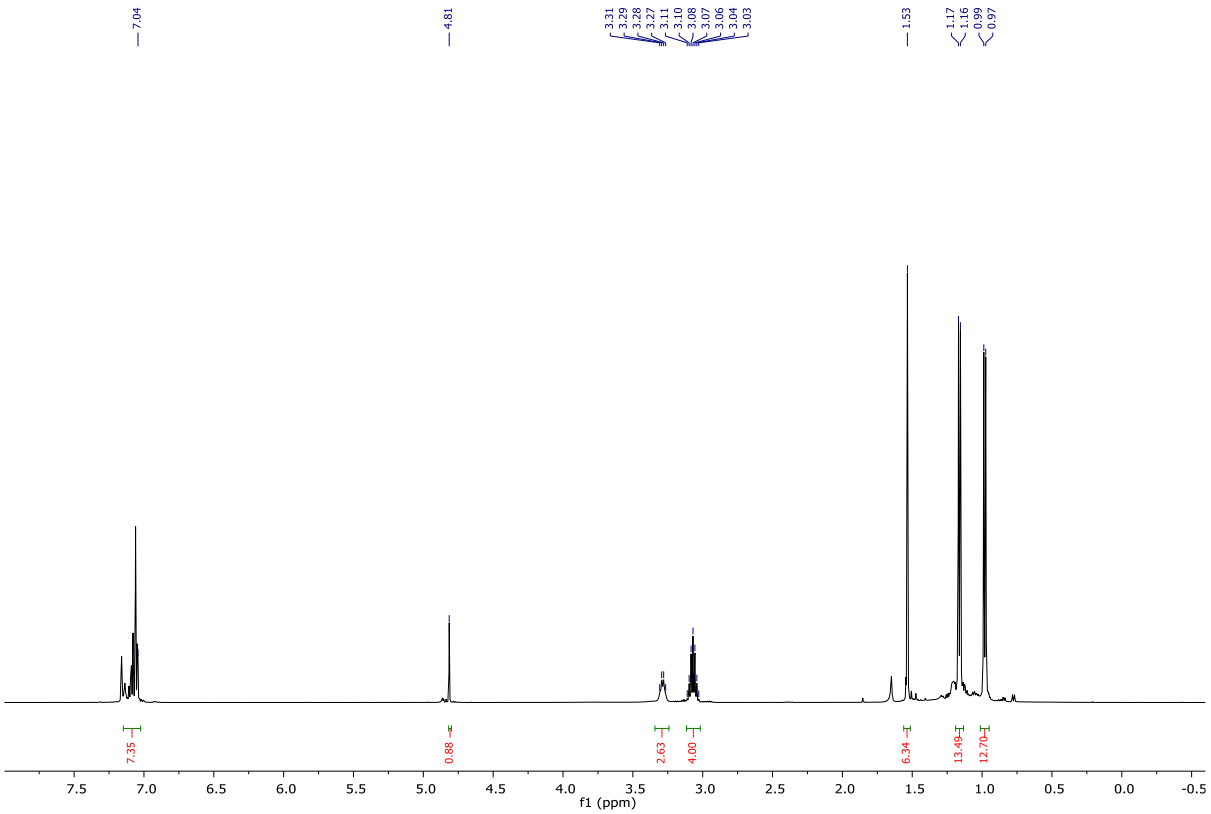

Figure S23. *^{1}H NMR Spectrum (C_6D_6, 298 K, 500.06 MHz) after milling [(^{Dipp}BDI)MgI(OEt_2)] for 1 hour with 20% w/w Na/NaCl.*

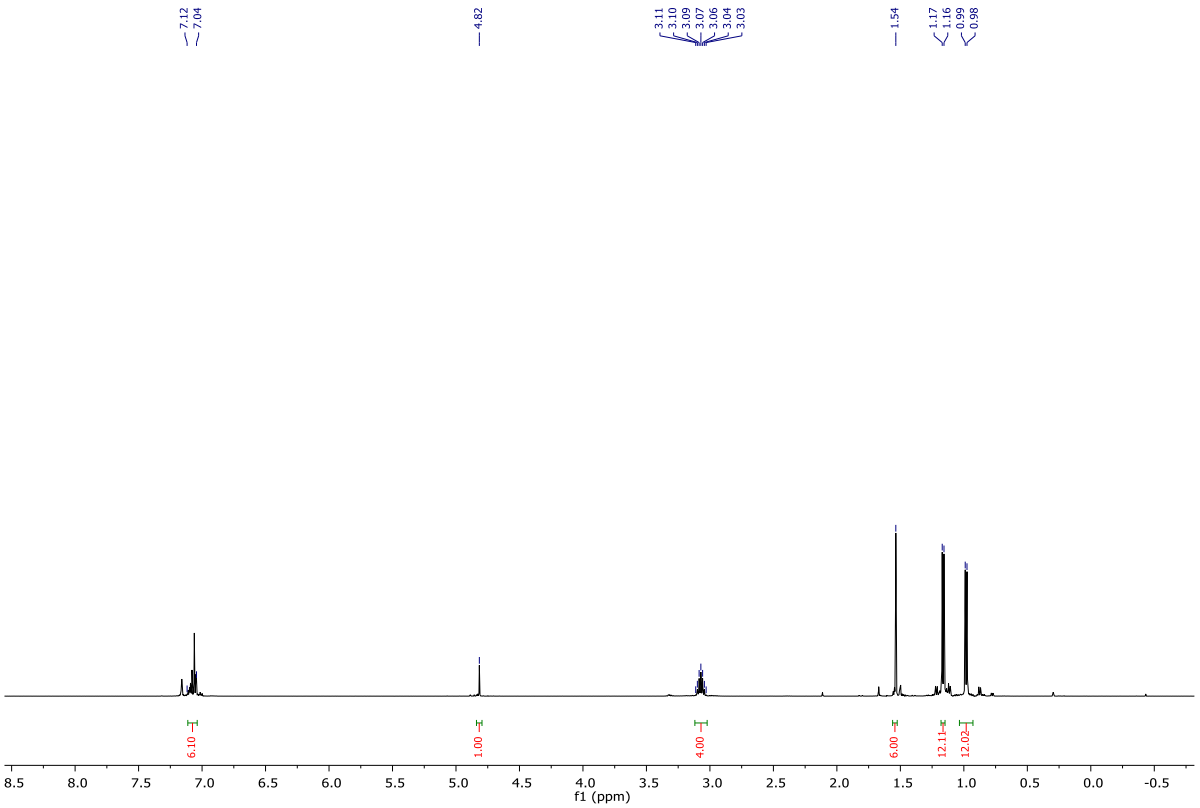

Figure S24. *^{1}H NMR Spectrum (C_6D_6, 298 K, 500.06 MHz) for [(^{Dipp}BDI)Mg]$_2$.*

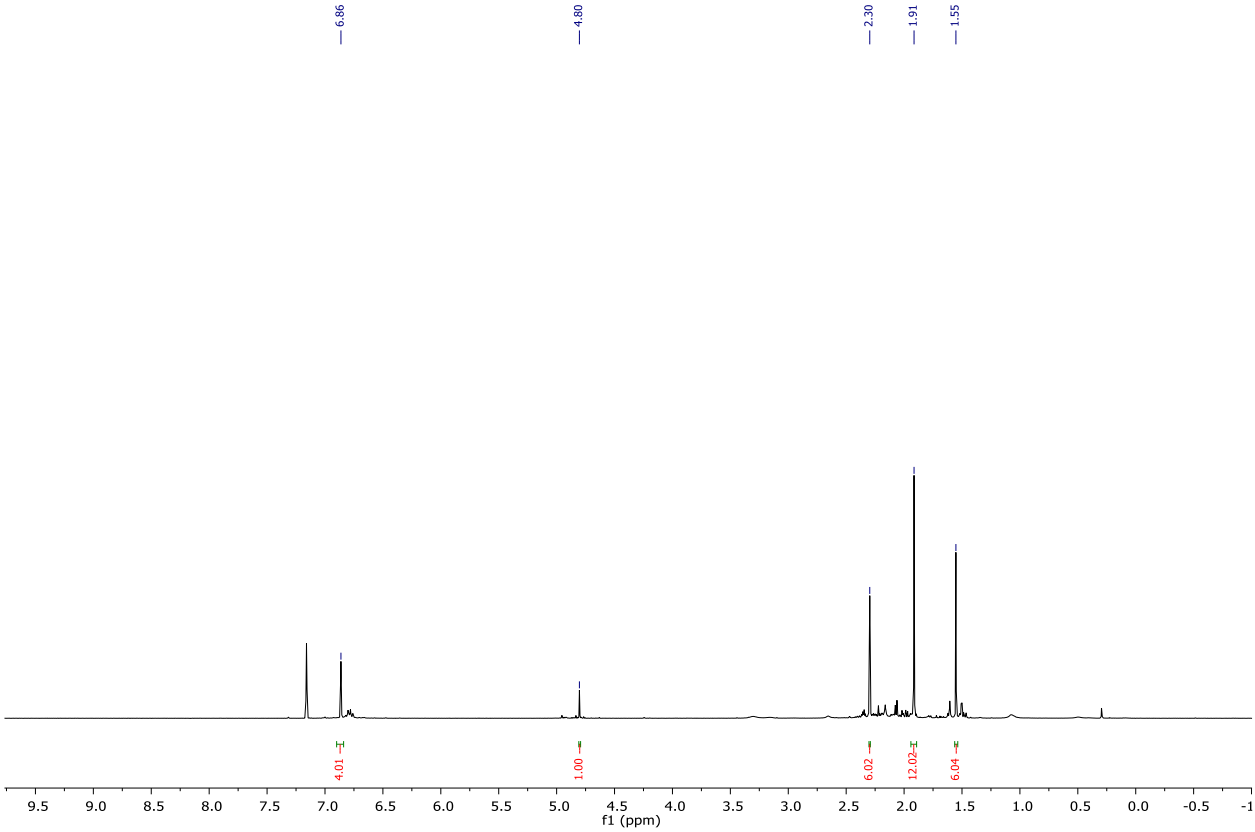

Figure S25. *^{1}H NMR Spectrum (C_6D_6, 298 K, 500.06 MHz) for [(^{Mes}BDI)Mg]$_2$.*

Powder X-ray Diffraction

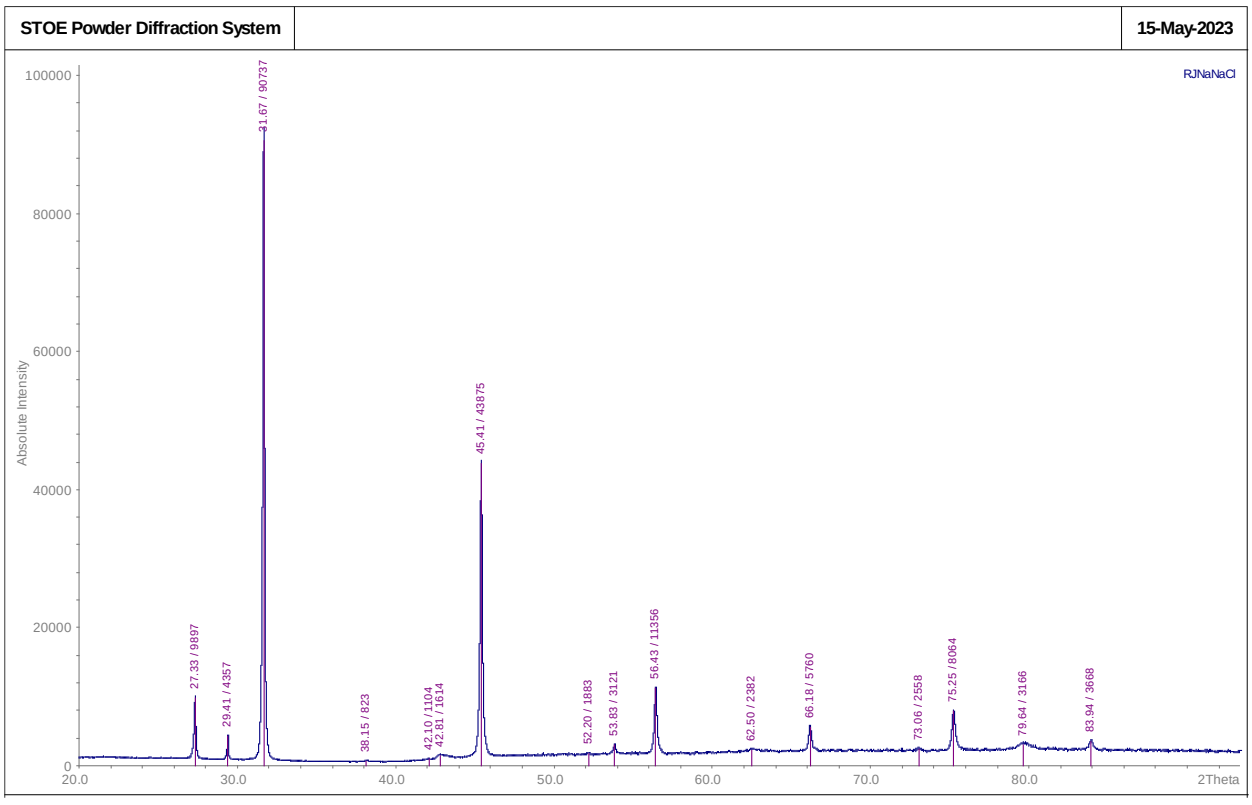

Figure S26. *Powder X-ray Diffraction Pattern for 5% w/w Na/NaCl.*

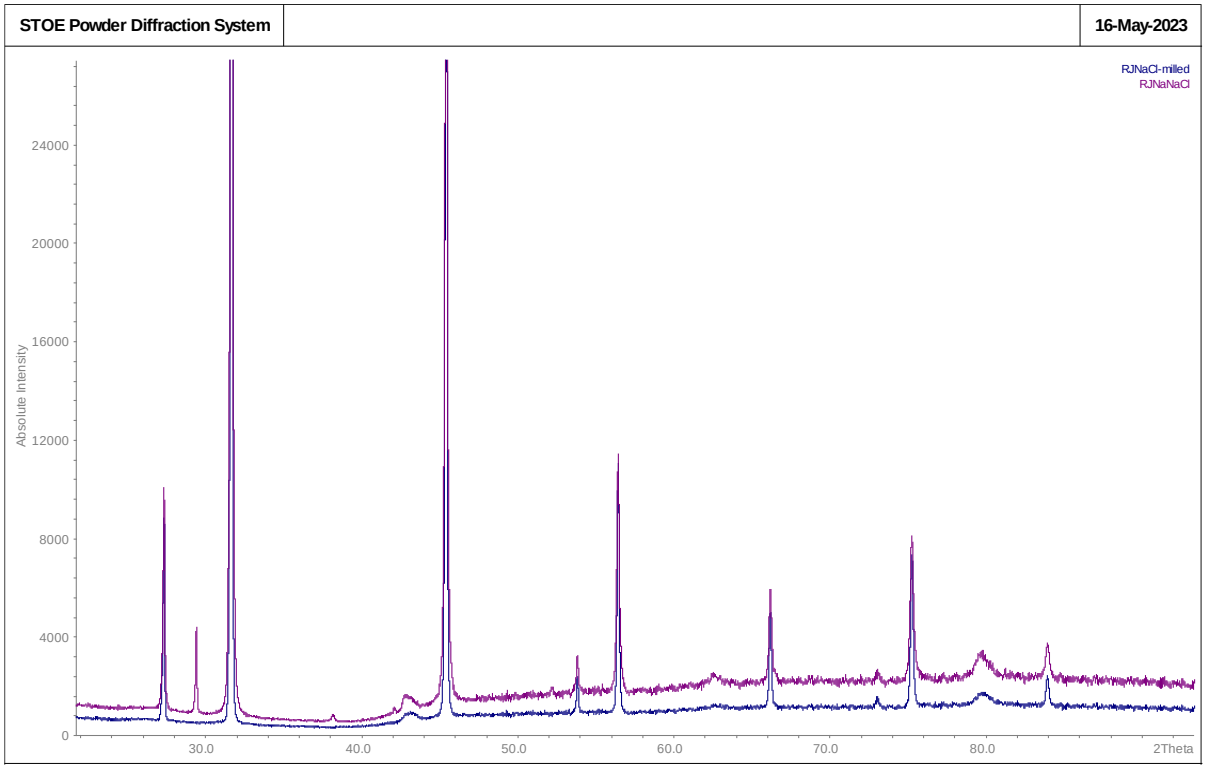

Figure S27. *Powder X-ray Diffraction Pattern for 5% w/w Na/NaCl overlayed on top of the pattern for NaCl.*

References

1. J. Prust, K. Most, I. Müller, E. Alexopoulos, A. Stasch, I. Usón and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2032-2037.
2. S. J. Bonyhady, C. Jones, S. Nembanna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938-955.
3. S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754-1757.