Supporting Information

Probing Conformational Evolution and Associated Dynamics of $Mg(N(SO_2CF_3)_2)_2$ · Dimethoxyethane Adduct Using Solid-state ^{19}F and ^{1}H NMR

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Temperature calibration for fast magic angle spinning: It has been reported that the sample temperature within a spinning rotor can be significantly different from the probe set temperature, especially at a spinning speed > 10 kHz.[26, 27] Since the structure and dynamics of Mg(TFSI)$_2$·DME are extremely sensitive to temperature, we calibrated the sample temperature at varying spinning speed using solid lead nitrate Pb(NO$_3$)$_2$. Figure S1 shows the sample temperature calculated from Pb(NO$_3$)$_2$ chemical shift plotted as a function of rotor spinning speed when the probe temperature is set at 20 °C (A) and the sample temperature as a function of probe set temperature when the spinning speed is set at 24 kHz (B). At a spinning speed of 32 kHz, the sample temperature can reach up to 62 °C with a set temperature at 20 °C. In order to study the materials at a temperature range (-5 – 90 °C) that is relevant to the battery operation conditions, we choose a spinning speed of 24 kHz that is fast enough to remove most chemical shift anisotropy and dipolar interactions in these materials while still staying within the temperature control limits of our instrument (-30 – 80 °C).

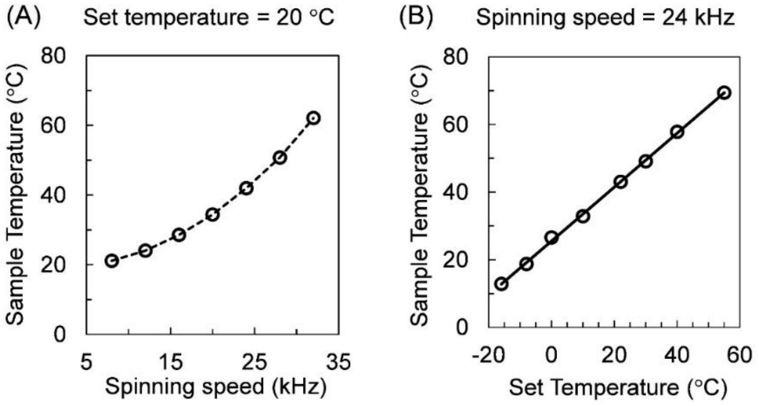

Figure S1. (A) Sample temperature calculated from Pb(NO$_3$)$_2$ chemical shift plotted as a function of rotor spinning speed when the probe temperature is set at 20 °C. (B) Sample temperature as a function of probe set temperature when the spinning speed is set at 24 kHz.

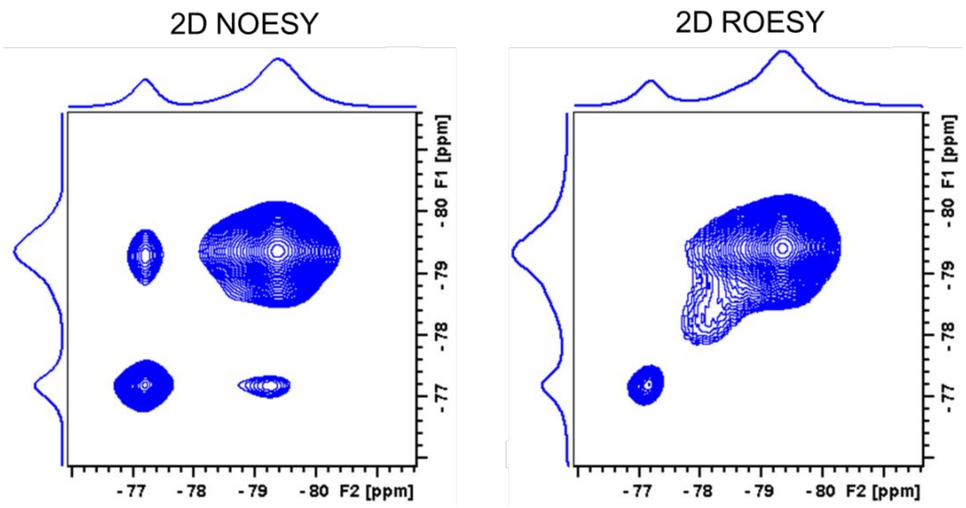

Figure S2. ^{19}F-^{19}F 2D NOESY (left panel) and ROESY (right panel) spectra of Mg(TFSI)$_2$ obtained at 8 °C with a spinning speed of 24 kHz and a mixing time of 50 ms.

The lack of ROESY cross peaks in Mg(TFSI)$_2$ suggests that TFSI anions do not experience conformational exchange under the experimental conditions, while the cross peaks shown in NOESY can be explained by spin diffusion between ^{19}F nuclei in the fluorine-rich hydrophobic layers.

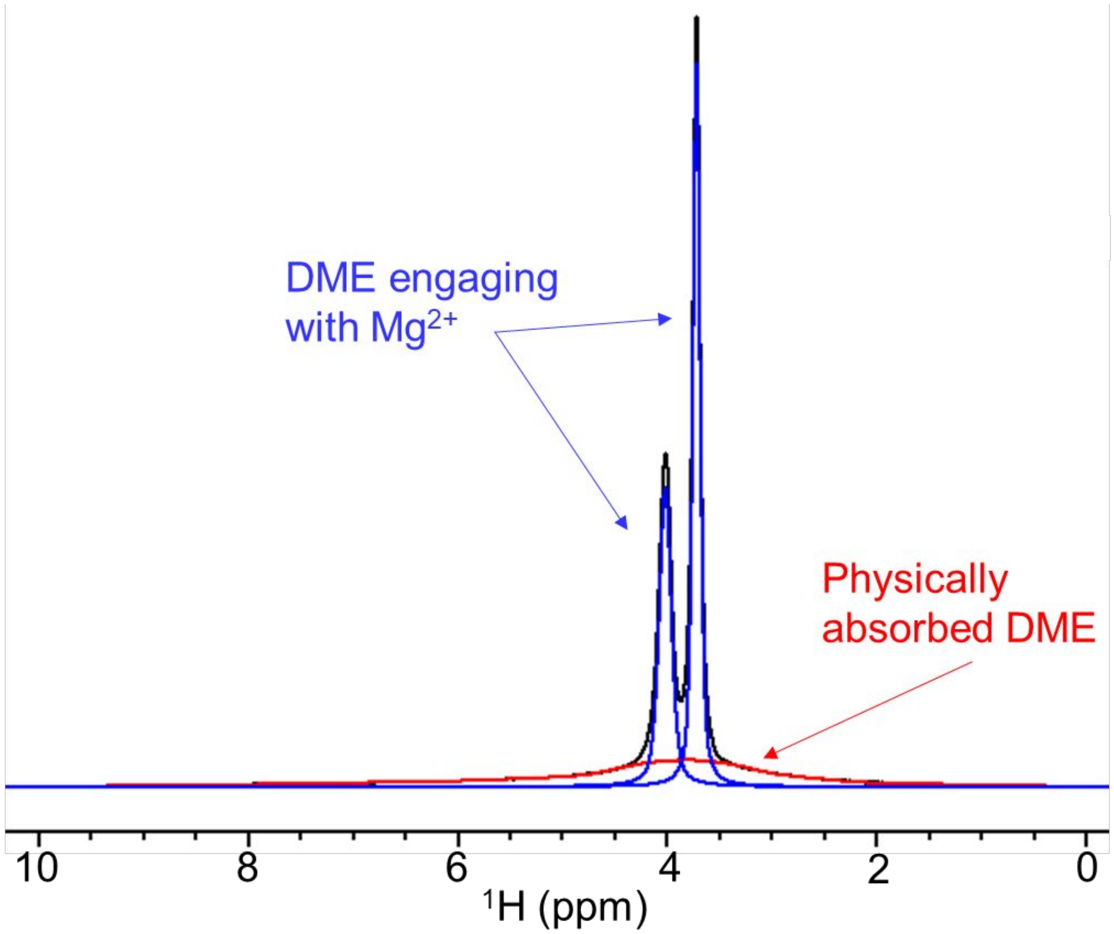

Figure S3. ^{1}H MAS NMR of $Mg(TFSI)_2{\cdot}DME$ collected at 8 °C with a spinning speed of 24 kHz. The black line is the experimental spectrum, the blue lines are the two ^{1}H resonances located at 4.20 and 3.90 ppm resulting from DME molecules engaging with Mg^{2+} in the crystalline region, and the red line is the broad peak that arises from physically absorbed DME in the disordered region.

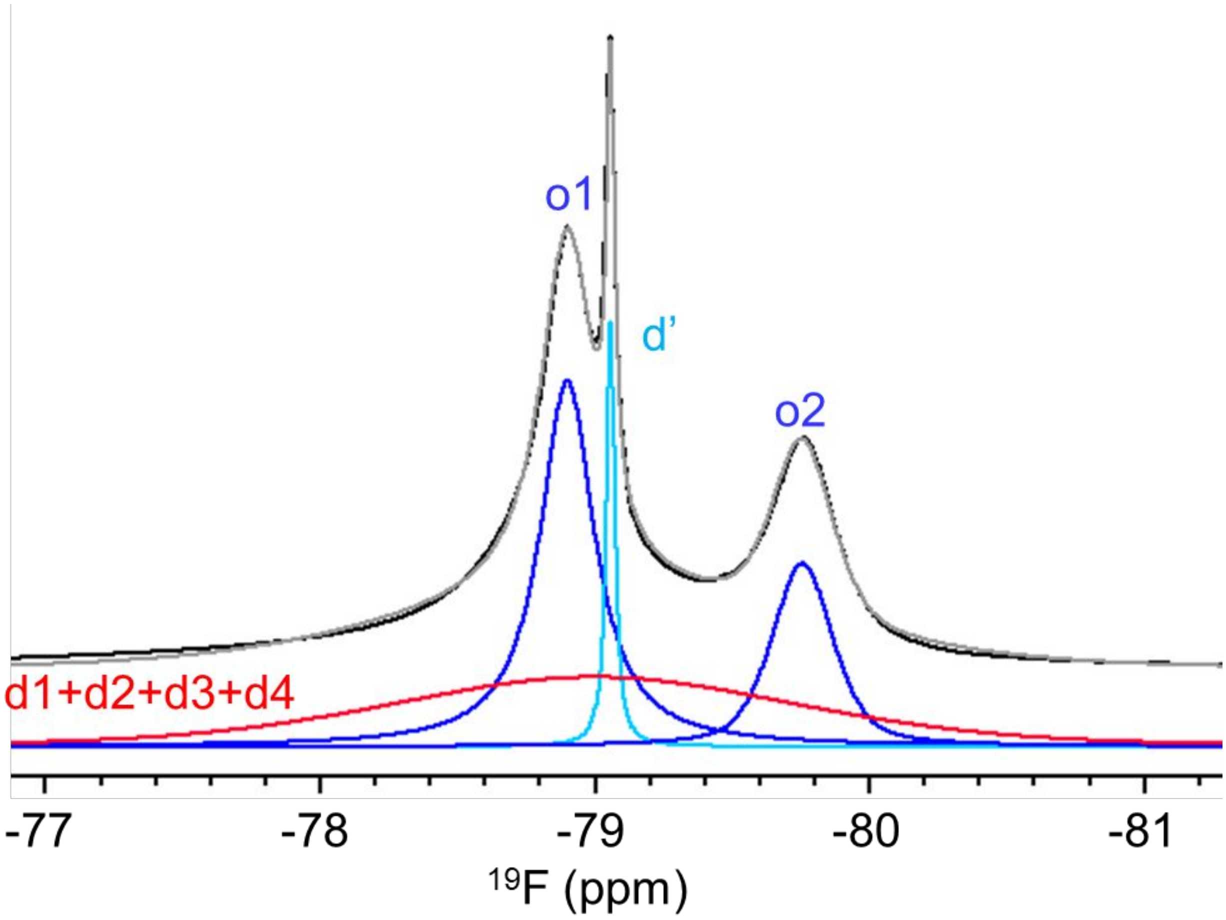

Figure S4. ^{19}F MAS spectrum of Mg(TFSI)$_2$·DME collected at 67 °C with a spinning speed of 24 kHz. Black line is the experimental spectrum, grey line is the sum of all deconvolution peaks. Red broad peak is from TFSI in disordered regions with fast exchange between d1, d2, d3, and d4 sites, two blue lines O1 and O2 are from TFSI in the crystalline region, and d' is the very fast tumbling TFSI in the disordered region.

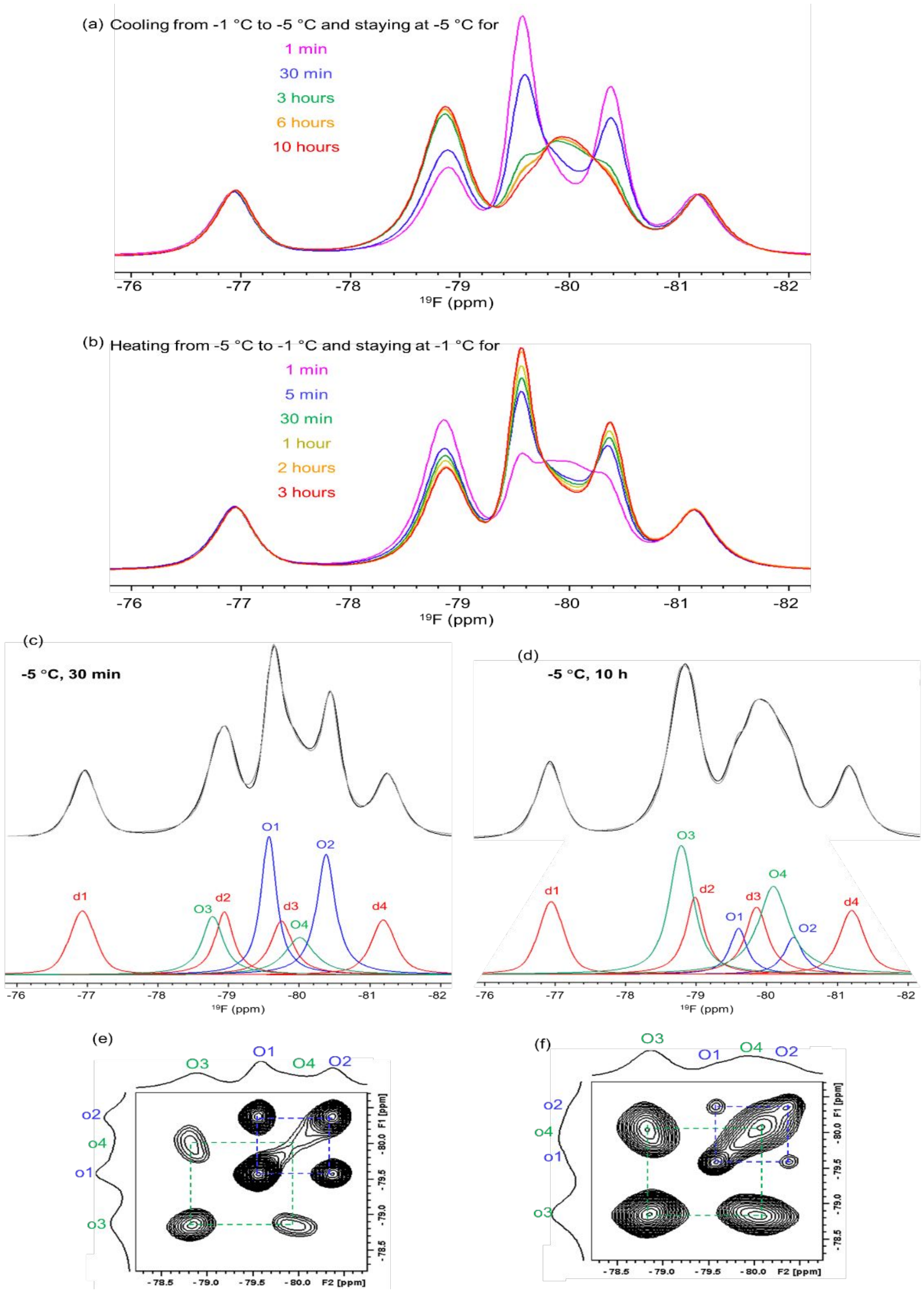

Figure S5. ^{19}F MAS spectra of Mg(TFSI)$_2$·DME when cooling from -1 °C to -5 °C then held at -5 °C until equilibrium (a), and heating from -5 °C to -1 °C and held at -1 °C until equilibrium (b). Deconvolution of the spectra (c) and (d) show clearly that the resonances at the disordered region do not change with time, but at the crystal region O3 and O4 resonances increase at the cost of O1 and O2 resonances. The grey line is the sum of devolution peaks, compared to the experimental spectrum (black). The peak positions for the deconvolution were obtained from 2D NOESY spectra collected at -5 °C after the temperature stabilizing for 1 hour (e) and 10 hours (f).

When cooling the material down from 82 °C to 38 °C and finally 8 °C for approximately 3 hours at each temperature until no change in ^{19}F and ^{1}H NMR is observed, compared with the previous spectra at 38 °C and 8 °C, it is clear that the heating process at 82 °C is not completely reversible, a few percent of DME in the second coordination shell and fast tumbling TFSI in the disordered region do not return to their original state. Also, both d` and $CH_2$`/CH_3` peaks decreased its intensity simultaneously as the decrease in temperature which suggests that the thermally activated fast molecular motion of TFSI in the disordered region and DME molecules became slower at the lower temperature.

We only calculated the exchange rate constants of the disordered region (site d1, d2, d3 and d4 of Figure 2 and 3) from -5 °C to 16 °C because the two other resonances (site O1 and O2) from the crystalline region begin to dominate the spectra at higher temperatures (Figure 4a) due to the broadening of the disordered sites, and the exchange between the disordered region and the crystalline region also begin to happen so the exchange rate constants calculated either from 2D EXSY or from line-shape analysis are not reliable at higher temperatures.

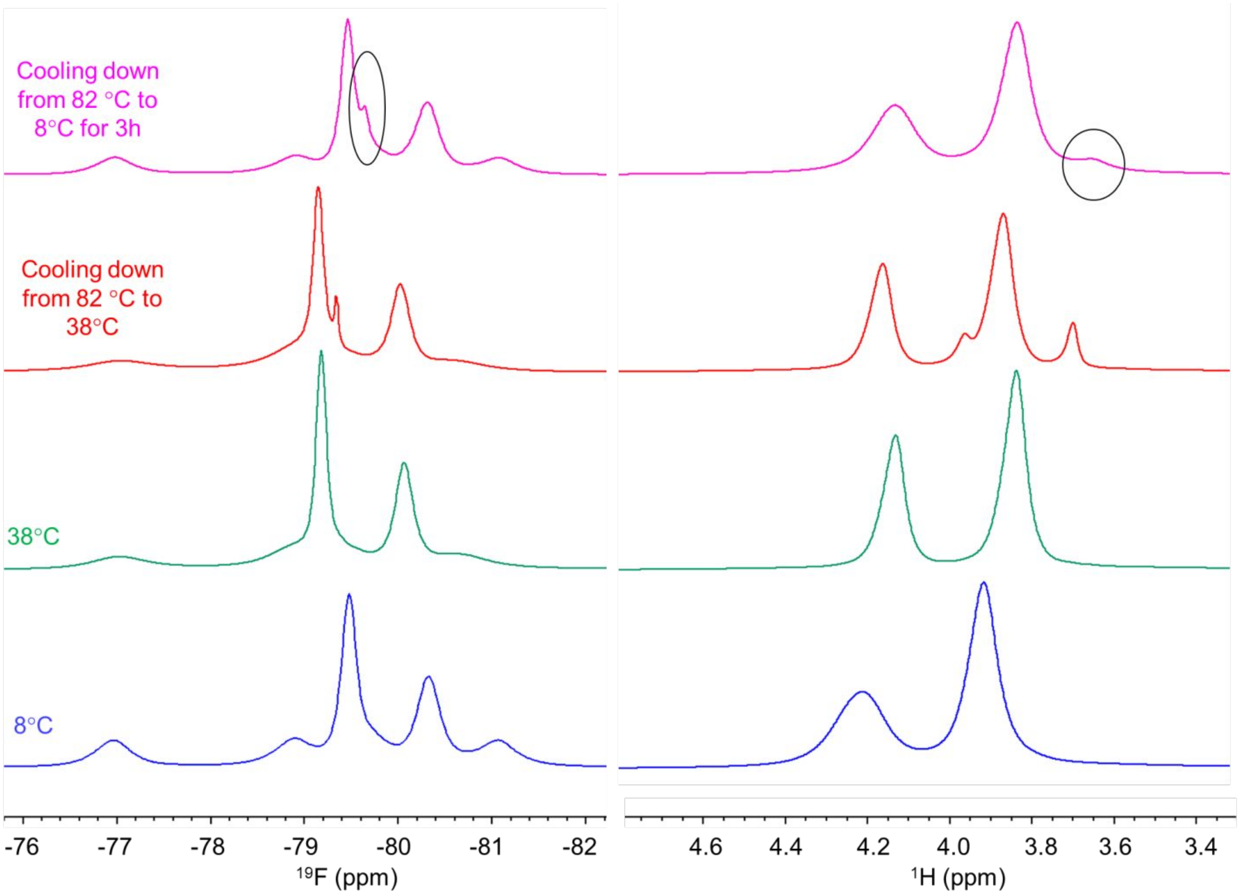

Figure S6. ^{19}F and ^{1}H MAS spectrum of Mg(TFSI)$_2$·DME at 8 °C (blue) and 38 °C (green) and cooling down from 82 °C back to 38 °C (red) and 8 °C (pink), with a spinning speed of 24 kHz.

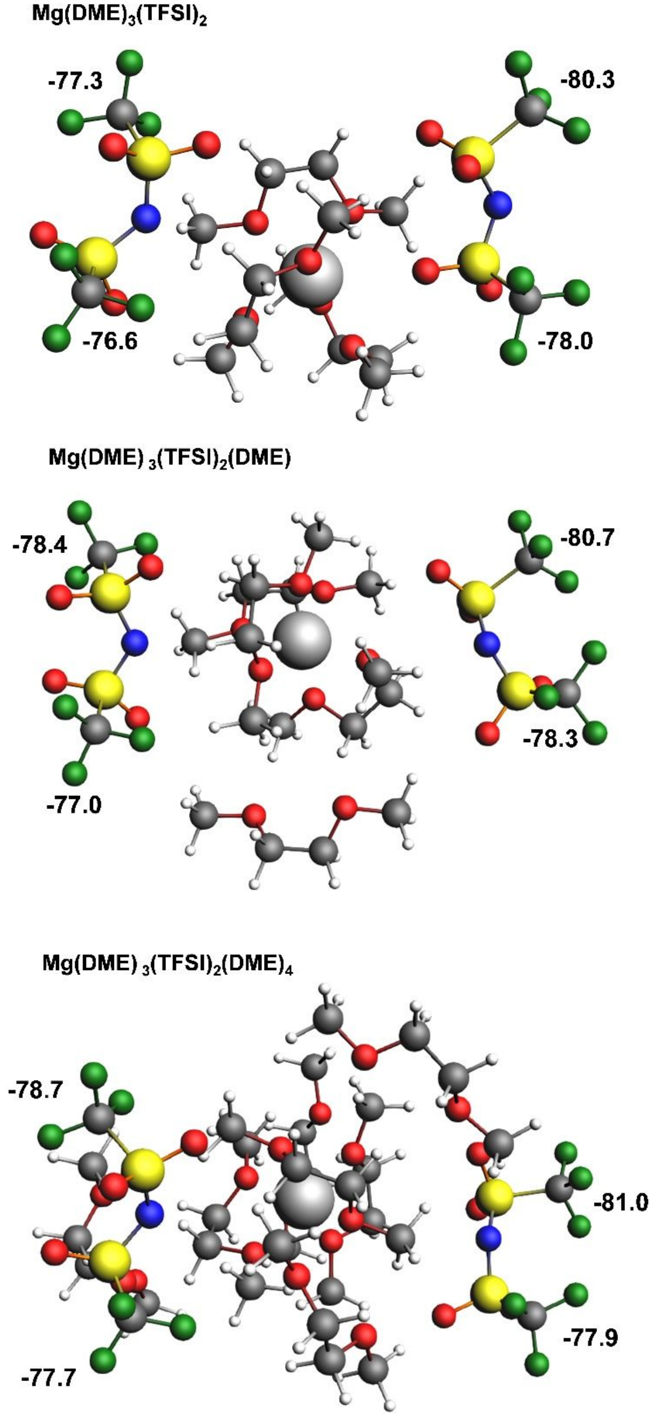

Figure S7. Chemical shift values of $Mg(TFSI)_2{\cdot}DME$ clusters calculated using TZ2PJ basis in ADF.