Metal-organic frameworks as solid magnesium electrolytes

*Michael L. Aubrey, Rob Ameloot, Brian M. Wiers, and Jeffrey R. Long**

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General protocols

All reagents and solvents were commercially available and used without further purification. Powder X-ray diffraction data were collected using Cu Kα (λ = 1.5406 Å) radiation source on a Bruker D8 Advance diffractometer. SEM was performed at the University of California Robert D. Ogg Electron Microscope Lab on a Hitachi S-5000 SEM.

Elemental analysis. Elemental analysis of carbon, hydrogen, and nitrogen and sulfur were obtained from the Microanalytical Laboratory of the University of California, Berkeley. Because of solvent volatility the elemental analysis often fit poorly with the data provided by ^1H NMR analysis; thus, stoichiometry determined from elemental analysis was determined by fitting $Mg(TFSI)_2$ to the sulfur content, and then the content of triglyme was left as a free variable to fit carbon and hydrogen. Elemental analysis was further complicated since trace amounts of formate and dimethyl amine were observable by ^1H NMR believed to be charge balancing defect sites within Mg_2(dobdc) and Mg_2(dobpdc). In all cases the triglyme content was found to be less than what was determined from TGA or NMR as was expected.

Langmuir surface area measurements. Langmuir surface areas were measured by a volumetric method using a Micromeritics ASAP2020 instrument. A sample was transferred in an N_2-filled glovebox to a pre-weighed analysis tube, capped with a transeal, evacuated and heated to 180 ºC at 0.5 ºC per minute until pressure stabilized at 11 μbar. N_2 isotherms at 77 K were measured in liquid nitrogen using UHP-grade gas sources.

Thermogravimetric Analysis. TGA data were collected using a TA Instruments TGA Q5000. Linear temperature scans at 5 ºC/min were completed under N_2 flow from room temperature to 300 ºC. At 300 ºC the sample purge was switched to O_2 and the temperature ramp was continued to 600 ºC. The observed mass losses are given in figures S3 and S4.

Pellet preparation for ac impedance measurements. In an argon filled glove box, the powder electrolyte was dispensed into a Garolite spacer, inner diameter of 0.388 cm, 125 μm in thickness, and was sandwiched between two polypropylene sheets. The loaded spacer was pressed between two stainless steel dyes polished to a mirror finish with a hydraulic press to a load of approximately 7,500 lbs. Sample thickness was measured following ac impedance data collection with a Mitutoyo Absolute thickness gauge accurate to 2 μm.

AC impedance measurements. Sample conductivity was characterized using a thermostatted custom-built test cell with stainless steel blocking electrodes polished to a mirror finish. With a Solartron 1260 frequency response analyzer, a Solartron 1296 dielectric interface and the SMART (v3.0.1) data acquisition and analysis program, ionic conductivity was characterized by ac impedance spectroscopy. All data was collected at 100 mV AC, a frequency sweep from 1 MHz to 100 or 1Hz, and a 1s integration time sampling 25 points per decade. The bulk conductivity was determined from the right hand minima of the semicircle observed at high frequency, R_{bulk}. The low frequency tail in the complex impedance plots was attributed cell polarization.

$$\sigma_{bulk} = \frac{l}{R_{bulk}A} \qquad (1)$$

Bulk conductivity, in S cm^{-1}, was calculated from Equation 1, where σ_{bulk} is the bulk conductivity, R_{bulk} is the real component at the right hand minima, *l* the sample thickness and A the sample area in contact with the electrode. Pseudo-activation energies were determined from the Nernst-Einstein relation, Equation 2.[1]

$$\sigma_{bulk} = \frac{\sigma_0}{T} e^{\frac{-E_a}{RT}} \qquad (2)$$

In equation 2, σ_0 is a pre-exponential factor, T is the temperature, E_a the pseudo-activation energy and R the ideal gas constant. The frequency response observed in the materials reported here mirrors that previously reported for lithium electrolytes in the same system.

Preparation of Mg_2(dobdc). Mg_2(2,5-dioxidobenzene-1,4-dicarboxylate) was prepared by a method similar to that reported previously by Caskey et. al.[2] Since product formation was observed to initiate by nucleation on borosilicate glass, upon scaling it was necessary to maintain a glass surface area to volume ratio greater than or equal to that reported. To four 1-L borosilicate glass jars filled with 4-ml borosilicate glass scintillation vials, 5.858 g (29.60 mmol) of 2,5-dihydroxybenzene-1,4-dicarboxylic acid and 23.99 g (77.27 mmol) of $Mg(NO_3)_2 \cdot 9H_2O$ dissolved in 2600 mL of 15:1:1 DMF:EtOH:H_2O was added. The screw cap jars were sealed and heated to 120 ºC for 8 hours in a convection oven. Product was removed by sonication, then collected and dried via vacuum filtration. The dark orange powder was soaked in DMF at 100 ºC for 4 days replacing the solution twice a day, then washed for 5 days in MeOH by soxhlet extraction. The powder was dried and heated to 180 ºC at 10 μbar for 4 days. Langmuir surface area: 1845 m^2/g. IR: 1577 (s), 1423 (s), 1371 (m), 1211 (s), 1120 (w), 1018 (w), 912 (w), 891 (m), 829 (s), 819 (s), 634 (w), 581 (m), 487 (w). PXRD is given in Figure S1 and TGA in Figure S3. Proton NMR showed approximately 8 mol% formate and 3 mol% dimethylamine present in the material which likely act as charge balancing ions as defect sites. Low concentrations of NMR inactive nitrates may also be present and also account for the small amount of excess nitrogen found by elemental analysis.

Mg_2(dobdc) ⊂ [0.05Mg(4-methylphenolate)$_2$•1.5triglyme]. Cresol (1.30 g, 12.0 mmol) was dissolved in 20 mL of anhydrous triethyleneglycoldimethylether (triglyme) in a flame dried 100-mL round bottom flask under N_2 flow. To the stirring solution, 8.57 mL (6.00 mmol) of 0.7 M magnesium bis(diisopropyl)amide in THF was added dropwise. After stirring for 2 hours the THF and diisopropylamine were removed by vacuum distillation. In a nitrogen filled glovebag, the resulting solution was transferred to a dry scintillation vial containing about 100 mg (0.5 mmol) of desolvated Mg_2(dobdc), sealed and heated to 80 ºC for 7 days. The solution was decanted, replaced with with 20 mL of anhydrous triglyme and sonicated. This was repeated two additional times. The yellow-orange material was then filtered and dried by vacuum filtration affording a free flowing powder. All electrolyte materials were washed similarly. The material's composition was determined by proton NMR; that is, 15 mg of the material was dissolved in a solution of 1 mL DMSO-d_6 and 20μL of 35 wt% DCl in D_2O and all other samples NMR samples were prepared similarly, Figure S5. PXRD and TGA and room temperature ac impedance data are given in the supporting figures below. Elemental analysis: Calculated for [Mg_2(dobdc) • 0.05Mg(4-methylphenolate)$_2$ • 0.98triglyme • 0.01dimethylamine] C: 47.3%, H: 5.52%, N: 0.14%; Found C: 45.2±0.3%, H: 5.70±0.04%, N: 0.16±0.1%.

Mg_2(dobdc) ⊂ [0.07Mg(phenolate)$_2$ • 1.5triglyme]. Phenol (1.130 g, 12.00 mmol) was dissolved in 20 mL of anhydrous triglyme in a flame dried 100-mL round bottom flask under N_2 flow. To the stirring solution, 8.57 mL (6.00 mmol) of 0.7 M magnesium bis(diisopropyl)amide in THF was added dropwise. After stirring for 2 hours the THF and diisopropylamine were removed by vacuum distillation. In a nitrogen filled glovebag, the resulting solution was transferred to a dry scintillation vial containing about 100 mg (0.5 mmol) of desolvated Mg_2(dobdc), sealed and heated to 80 ºC for 7 days. The dark yellow-orange material was collected, washed with 60 mL of anhydrous triglyme and dried by vacuum filtration affording a free flowing powder. The material's composition was determined by proton NMR. PXRD and TGA and room temperature ac impedance data are also given in the supporting figures below. Elemental analysis: Calculated for [Mg_2(dobdc) • 0.07Mg(phenolate)$_2$ • 0.96triglyme • 0.01dimethylamine] C: 47.4%, H: 5.43%, N: 0.155%; Found: C: 45.2±0.3% ,H: 5.70±0.04%, N: 0.155±0.005%.

Mg_2(dobdc) ⊂ [0.06Mg(bis(trifluoromethanesulfonyl)imide)$_2$•1.4triglyme]. About 100 mg (0.5 mmol) of desolvated Mg_2(dobdc) was soaked for 7 days in 20 mL of a 0.43 M solution of Mg(bis(trifluoromethanesulfonyl)imide)$_2$, Mg(TFSI)$_2$, in triglyme at room temperature then collected, washed with 60 mL of triglyme and dried by vacuum filtration affording a dark orange free flowing powder. The TFSI content was estimated by elemental analysis and the amount of triglyme was determined by proton NMR. The NMR sample was prepared by dissolving about 15 mg of the material in a solution of 1 mL DMSO-d_6 and 20µL of 35 wt% DCl in D_2O, Figure S5. PXRD and TGA and room temperature ac impedance data are given in the supporting figures below. Elemental analysis: Calculated for [Mg_2(dobdc) • 0.06Mg(TFSI)$_2$ • 1.43triglyme •

0.01dimethylamine] C: 47.0%, H: 6.21%, N: 0.26%, S: 0.55% ; Found: C: 46.31±0.04%, H: 6.32±0.01%, N: 0.2±0.0%, S: 0.55±0.0%.

Mg_2(dobdc) ⊂ [0.39Mg(4-trifluoromethylphenolate)$_2$•6.0triglyme]. 4-trifluoromethylphenol (1.94 g, 12.0 mmol) was dissolved in 20 mL of anhydrous triglyme in a flame dried 100-mL round bottom flask under N_2 flow. To the stirring solution, 8.57 mL (6.00 mmol) of 0.7 M magnesium bis(diisopropyl)amide in THF was added dropwise. After stirring for 2 hours the THF and diisopropylamine were removed by vacuum distillation. In a nitrogen filled glovebag, the resulting solution was transferred to a dry scintillation vial containing about 100 mg (0.5 mmol) of desolvated Mg_2(dobdc), sealed and heated to 80 °C for 7 days. The dark red-orange material was collected, washed with 60 mL of anhydrous triglyme and dried by vacuum filtration affording a free flowing powder. The material's composition was determined by proton NMR. The larger amount of solvent present in this sample was attributed to absorption onto the significantly larger number of magnesium sites that may coordinate triglyme. As a control, conductivity was also measured on all samples once saturated with anhydrous triglyme and in every case only a small change in conductivity was observed. Conductivity and NMR of this sample are given in the supporting figures below.

Mg_2(dobdc) ⊂ [0.31Mg(4-trifluoromethylphenolate)$_2$•0.30Mg(TFSI)$_2$•2.4triglyme]. The material described above was soaked for 12 hours in 20 mL of a 0.43 M solution of Mg(TFSI)$_2$ in triglyme at room temperature then collected, washed with 60 mL of triglyme and dried by vacuum filtration affording a dark red-orange free flowing powder. The amount of triglyme and 4-trifluoromethylphenolate in the material was determined by proton NMR and the TFSI content was estimated from elemental analysis. PXRD and

TGA and room temperature ac impedance data are given in the supporting figures below Elemental analysis: Calculated for [Mg_2(dobdc)•0.31Mg(4-trifluoromethylphenolate)$_2$ • 0.30Mg(TFSI)$_2$ • 1.82triglyme • 0.01dimethylamine] C: 45.3%, H: 5.90%, N: 0.56%, S 1.93%; Found: C: 43.46±0.05%, H: 6.24±0.11%, N: 0.63±0.03%, S: 1.92±0.01%.

Synthesis of Mg_2(dobpdc). 4,4'-Dihydroxybiphenyl-2,2'-dicarboxylic acid (0.962 g, 3.51 mmol) and $Mg(NO_3)$•$9H_2O$ (2.249 g, 7.24 mmol) were dissolved in 19 mL MeOH and 16 mL DMF then distributed across three 20-mL screw-cap vials. The solution was heated to 120 ºC for 24 hours. The phase was confirmed by PXRD and the material was desolvated as reported previously.[3]

Mg_2(dobpdc) ⊂ [0.22Mg(TFSI)$_2$•3.3triglyme]. About 125 mg (0.4 mmol) of desolvated Mg_2(dobpdc) was soaked for 7 days in a 0.43 M solution of Mg(TFSI)$_2$ in triglyme at room temperature then collected, washed with 30 mL of triglyme and dried by vacuum filtration affording a white free flowing powder. The TFSI content was estimated by elemental analysis and the amount of triglyme by proton NMR. PXRD and TGA and room temperature ac impedance data are given in the supporting figures below. Elemental analysis: Calculated for [Mg_2(dobpdc)•0.22Mg(TFSI)$_2$•2.78triglyme] C: 51.1%, 7.56%, N: 0.26%, S: 1.19%; Found: C: 51.4±0.2%, H: 7.42±0.07%, N: 0.23±0.03%, S: 1.19±0.11%.

Mg_2(dobpdc) ⊂ [0.31Mg(4-trifluoromethylphenolate)$_2$•3.8triglyme]. 4-trifluoromethylphenol (1.94 g, 12.0 mmol) was dissolved in 20 mL of anhydrous triglyme in a flame dried 100-mL round bottom flask under N_2 flow. To the stirring solution, 8.57 mL (6.00 mmol) of 0.7 M magnesium bis(diisopropyl)amide in THF was added dropwise. After stirring for 2 hours the THF and diisopropylamine were removed by vacuum distillation. In a nitrogen filled glovebag, the resulting solution was transferred to a dry scintillation vial containing about 125 mg (0.4 mmol) of desolvated Mg_2(dobpdc), sealed and heated to 80 ºC for 7 days. The light red material was collected, washed with 30 mL of anhydrous triglyme and dried by vacuum filtration affording a free flowing powder. The material's composition was determined by proton NMR. PXRD and TGA and room temperature ac impedance data are given in the supporting figures below. Elemental analysis: Calculated for [Mg_2(dobpdc)•0.31Mg(4-trifluoromethylphenolate)$_2$ • 2.64 triglyme • 0.05 dimethylamine] C:52.19%, H:7.57%, N: 0.413%; Found: C: 53.42±0.14%, H: 7.38±0.52%, N: 0.445±0.03%.

Mg_2(dobpdc) ⊂ [0.21Mg(4-trifluoromethylphenolate)$_2$ • 0.46Mg(TFSI)$_2$ • 4.8triglyme]. The material described above was soaked for 12 hours in a 0.43 M solution of Mg(TFSI)$_2$ in triglyme at room temperature then collected, washed with 20 mL of triglyme and dried by vacuum filtration affording a light red free flowing powder. The amount of triglyme and 4-trifluoromethylphenolate in the material was determined by proton NMR and the TFSI content was determined by elemental analysis. PXRD and TGA and room temperature ac impedance data are given in the supporting figures below. Elemental analysis: Calculated for [Mg_2(dobpdc) • 0.21 Mg(4-trifluoromethylphenolate)$_2$ • 0.46Mg(TFSI)$_2$ • 3.07triglyme] C: 49.0%, H: 7.13%, N: 0.60%, S: 2.1%; Found: C: 49.4±0.4%, H: 7.10±0.14%, N: 0.56±0.05%, S: 2.1±0.3%.

Supporting Figures

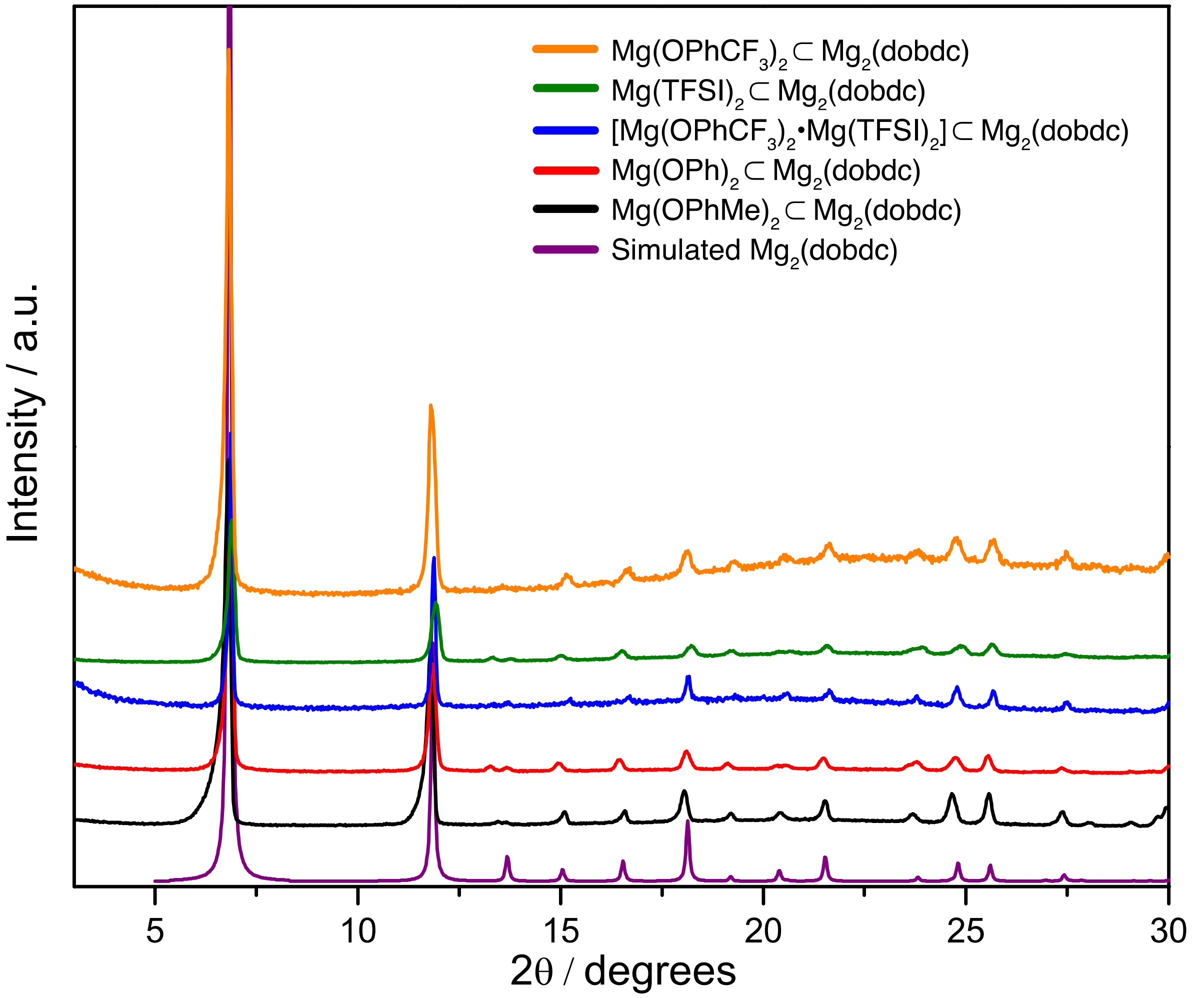

Figure S1: PXRD for materials containing Mg_2(dobdc)

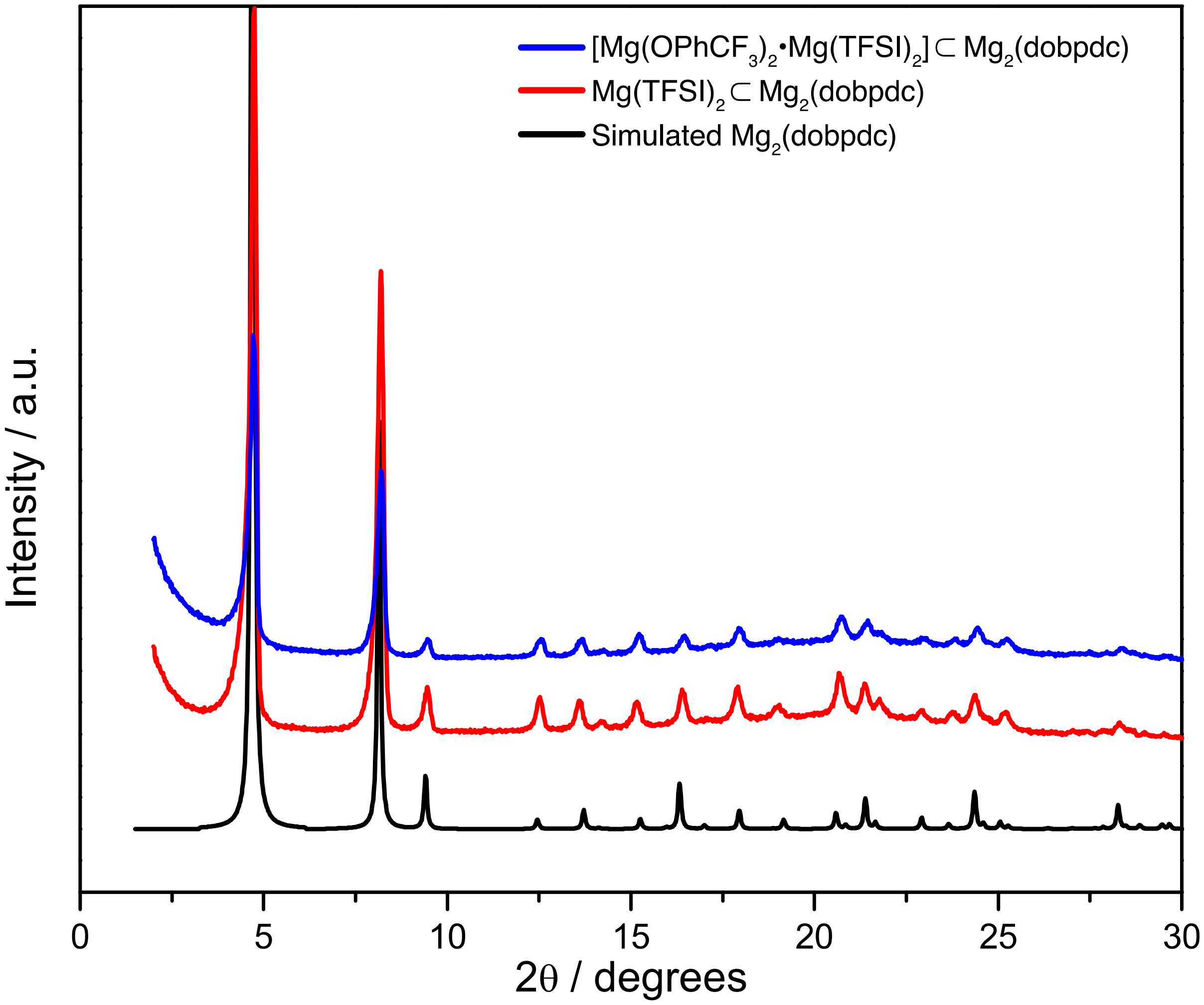

Figure S2: PXRD for materials containing Mg_2(dobpdc)

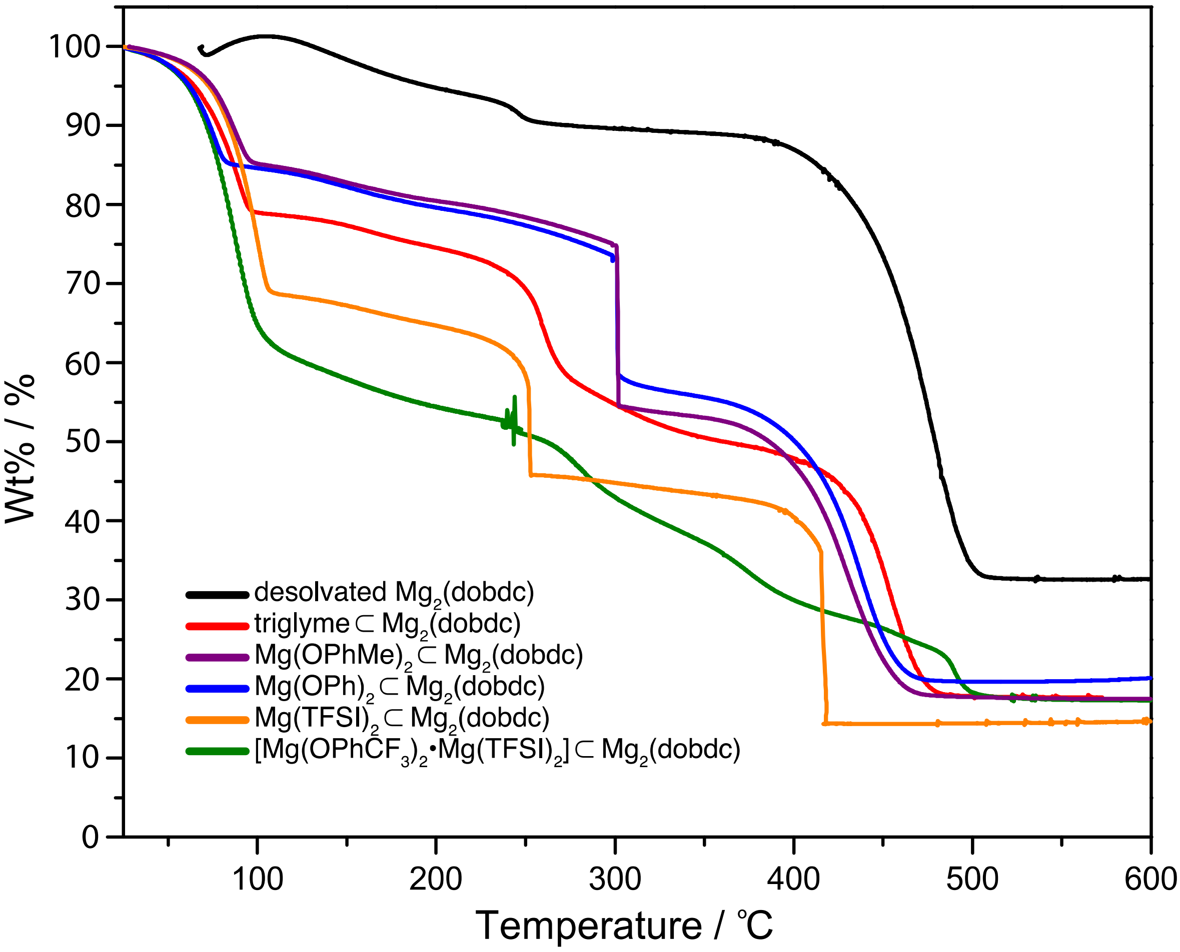

Figure S3: TGA for materials containing Mg_2(dobdc)

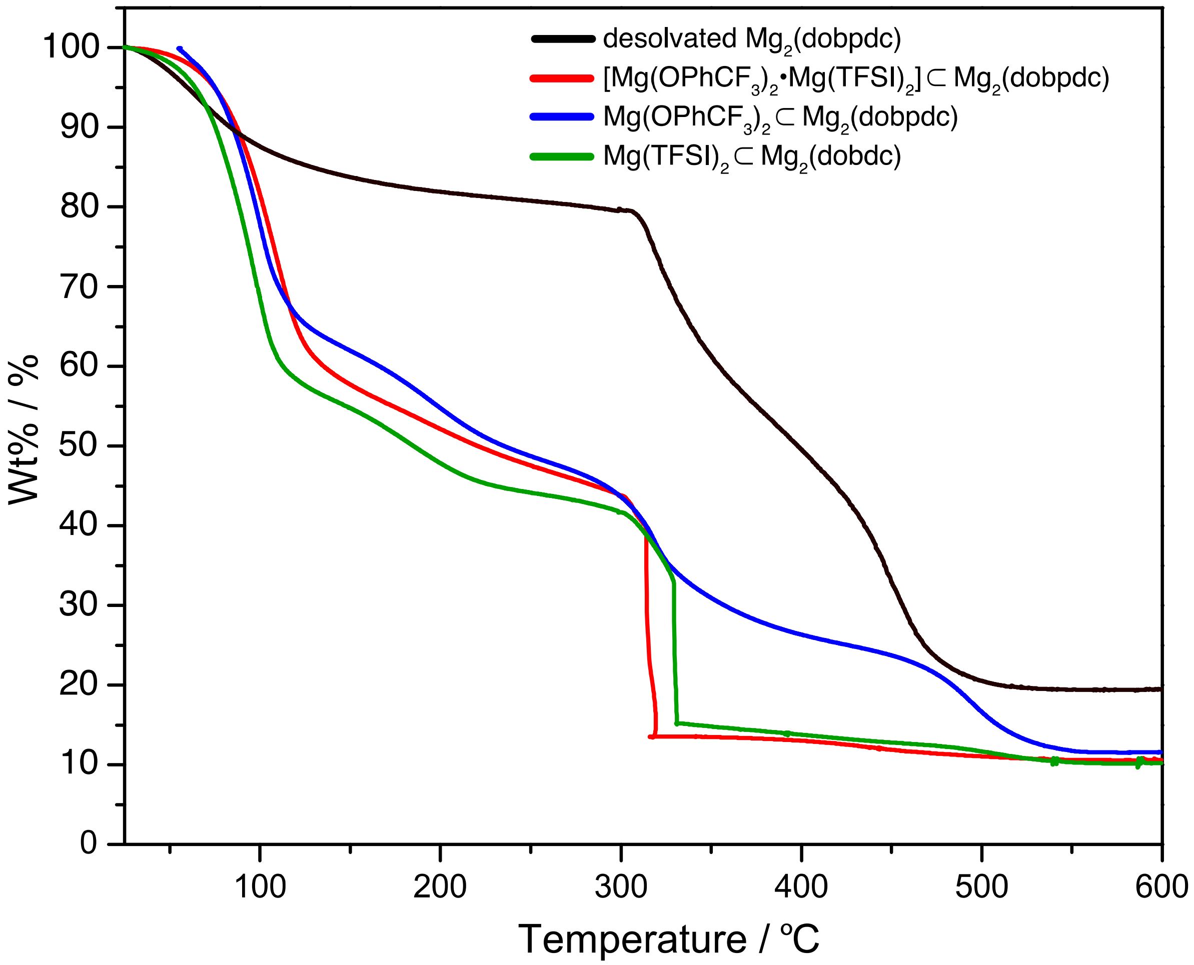

Figure S4: TGA for materials containing Mg_2(dobpdc)

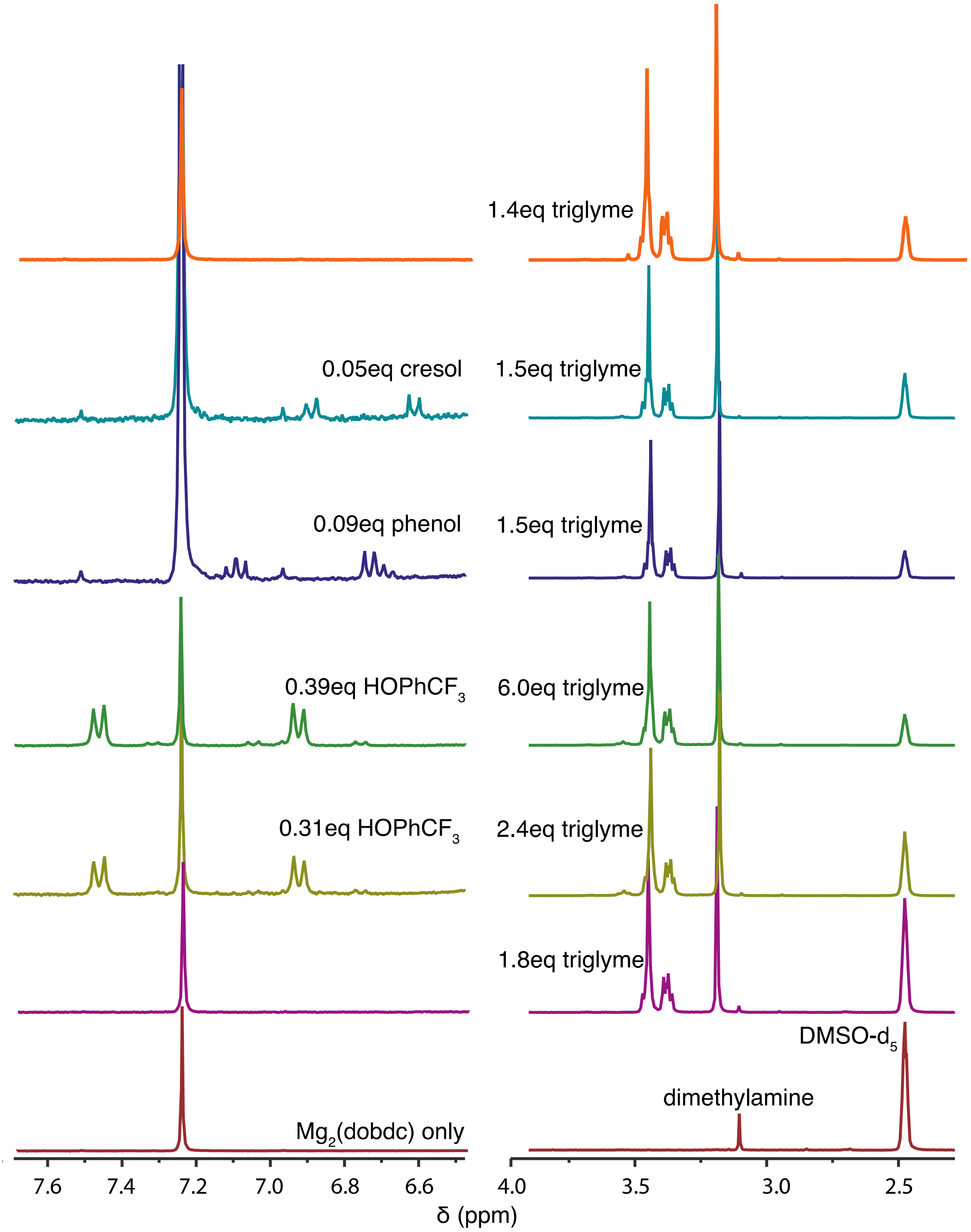

Figure S5: Selected regions of ^{1}H NMR (300 MHz) for materials containing Mg_2(dobdc). From the top: Mg_2(dobdc)•Mg(TFSI)$_2$•triglyme, Mg_2(dobdc)•Mg(OPhMe)$_2$•triglyme, Mg_2(dobdc)•Mg(OPh)$_2$•triglyme, Mg_2(dobdc)•Mg(OPhCF$_3$)$_2$•triglyme, Mg_2(dobdc)•Mg(OPhCF$_3$)$_2$•Mg(TFSI)$_2$•triglyme, Mg_2(dobdc)•triglyme, and desolvated Mg_2(dobdc)

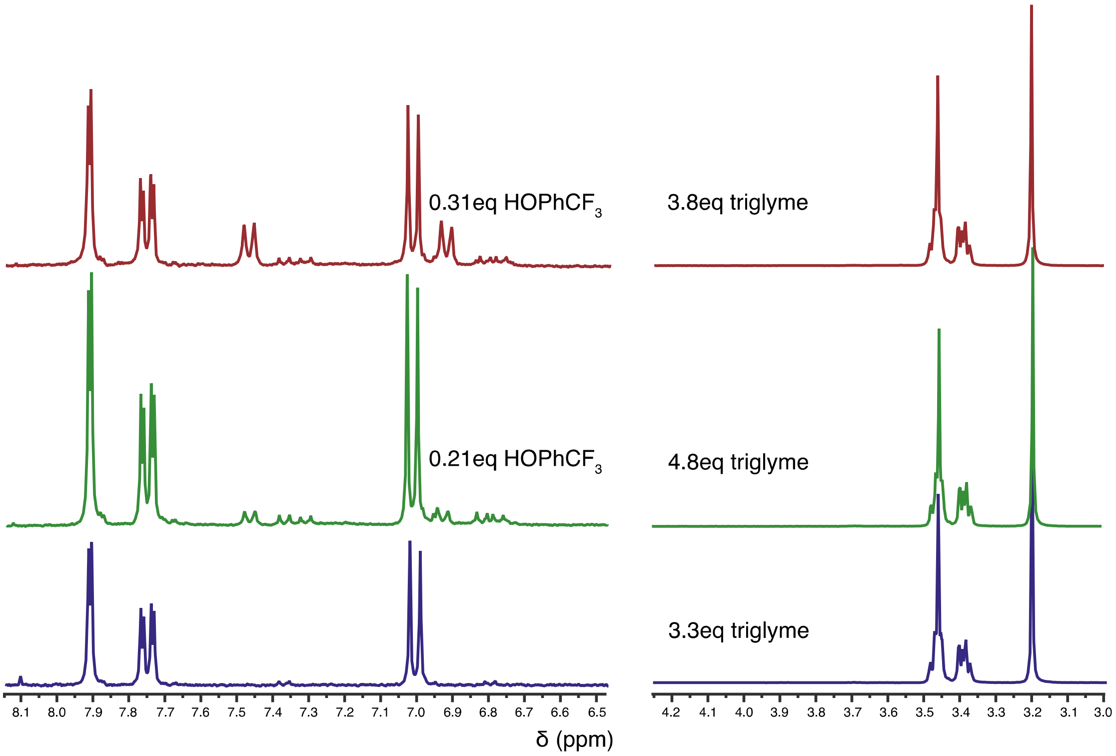

Figure S6: Selected regions of ^{1}H NMR (300 MHz) for materials containing Mg_2(dobpdc). From the top: $Mg(OPhCF_3)_2$•triglyme, $Mg(TFSI)_2$•triglyme, and $Mg(OPhCF_3)_2$•$Mg(TFSI)_2$•triglyme

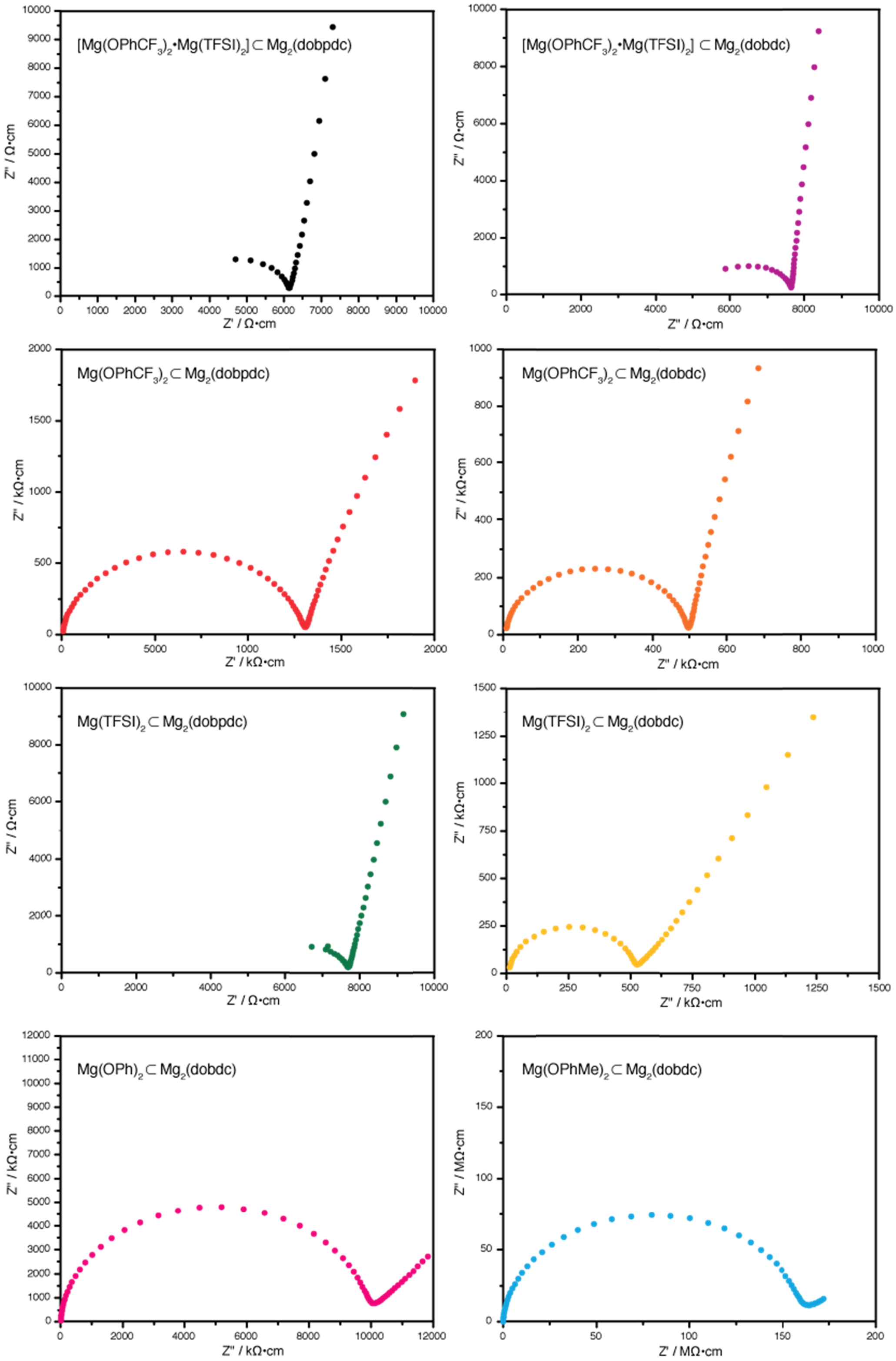

Figure S7: Room temperature Nyquist plots for the materials given in Table 1.

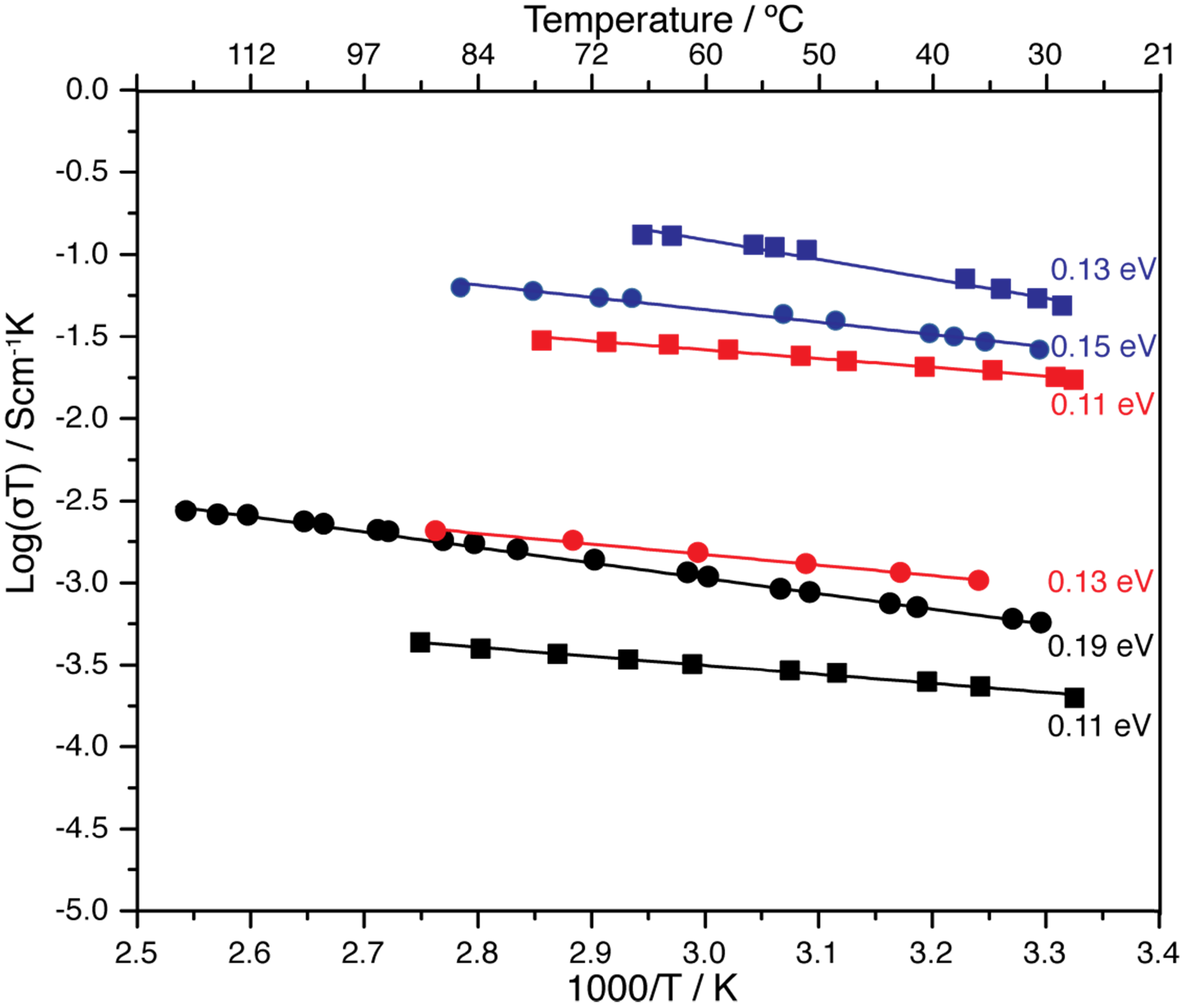

Figure S8: Temperature dependence on conductivity linearized using equation 2, pseudo-activation energies were determined from the slope. The host material Mg_2(dobdc) is depicted as circles and Mg_2(dobpdc) as squares. The guest species $Mg(OPhCF_3)_2$ is shown in black, $Mg(TFSI)_2$ in red, and the materials containing both magnesium salts as guests are given in blue.

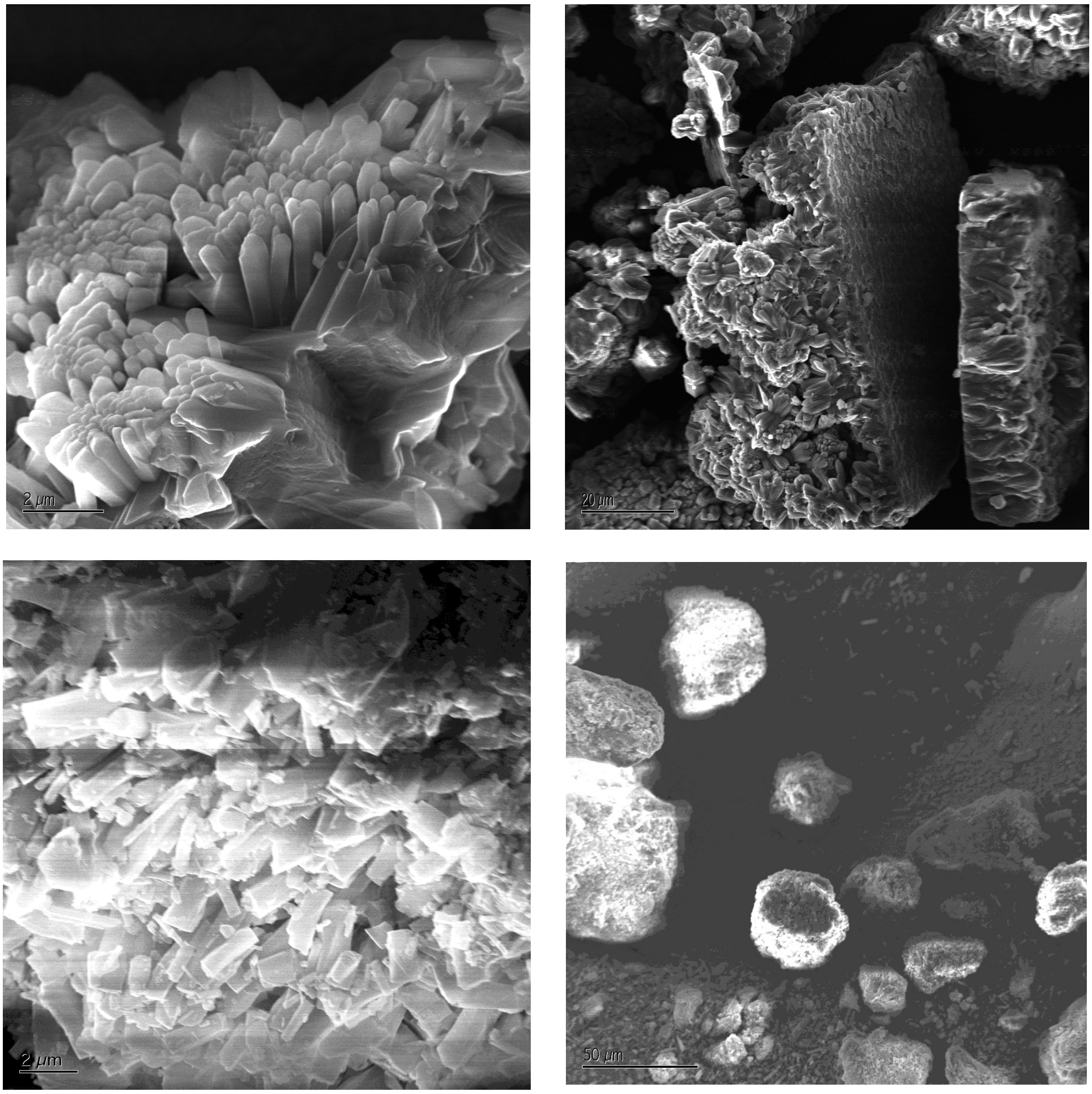

Figure S9: SEM images describing morphology of Mg_2(dobdc) (top two images) and Mg_2(dobpdc) (bottom two images). Scale bars read 2µm (top left) 20µm (top right), 2µm bottom left, and 50 µm (bottom right)

References

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