Electronic Supplementary Information for:

Enhanced Oxidative Stability of non-Grignard Magnesium Electrolytes through Ligand Modification

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Index *Page*

Experimental Section

General considerations. Ethylmagnesium chloride and all phenols were purchased from Sigma Aldrich, and used as received. Tetrahydrofuran solvent was purchased from VWR, and distilled over sodium with a benzophenone-ketyl indicator. ^{27}Al NMR was performed on a Varian VNMRS-700 MHz spectrometer in THF with chemical shifts reported relative to a solution of $AlCl_3$ in D_2O with a drop of concentrated HCl. ^{1}H, ^{13}C, and ^{19}F NMR were performed on a Varian MR-400 MHz spectrometer in THF. Conductivity measurements were carried out using a YSI Model 3200 conductivity meter equipped with a 3253 conductivity cell at room temperature. Mass spectrometry was preformed on a Micromass LCT Time-of-Flight mass spectrometer with electrospray ionization. Raman spectra were collected using a Renishaw inVia Raman microscope with a Leica microscope, RenCam CCD detector, 785 nm laser, 1200 lines/mm grating, and 50 μm slit. The spectra were collected in extended scan mode (10 second scan with 100 accumulations) in the range of 2000 – 200 cm^{-1}.

Synthesis. All compounds were prepared and handled using standard Schlenk techniques under N_2 and an N_2-filled glove box (Vacuum Atmospheres). All electrolyte solutions were synthesized in the exact same manner, with details for $(FMPCM)_2$-$AlCl_3$ in THF presented here. 4-(trifluoromethyl)phenol (14 mmol, 2.27 g) was dissolved in dry THF (7 mL) with stirring in a 25 mL three neck round bottom flask equipped with a stir bar, rubber septa, glass stopper and a gas inlet adapter. Then, 2 M EtMgCl in THF (14 mmol, 7 mL) was slowly added via syringe. This solution was stirred for 8 hours, giving a suspension of 4-(trifluoromethyl)phenolatemagnesium chloride (FMPMC)/THF. A solution of $AlCl_3$ (0.5 M in 14 mL) was prepared by mixing $AlCl_3$ (0.934 g, 7 mmol) with THF (14 mL) in a 25 mL three neck round bottom flask under N_2 purge that is cooled to 0 ^{o}C in an ice bath. This solution was warmed to room temperature and then added via syringe to the phenolate solution, and stirred for 5 hours, giving a clear solution of 0.5 M $(FMPMC)_2$-$AlCl_3$/THF.

NMR solution structures.

In an effort to assign the ^{27}Al NMR spectra of the as-synthesized electrolyte, we prepared a series of solutions comprised of differing ratios between the Lewis acid ($AlCl_3$) and base (FMPMC) At high base-to-acid ratios, the main solution species should be the tetrakisphenolate $[Al(FMP)_4^{-}]$. Accordingly, the NMR spectrum of $(FMPMC)_4$-$AlCl_3$/THF shows a single sharp peak at 50 ppm (referenced to $AlCl_3$ in HCl), expected for the tetrahedral anion. As the ratio of base to acid decreases, three additional broader peaks are observed at 60, 73, and 86 ppm. These peaks are attributed to a sequential loss of ligand, $Al(FMP)_3Cl$, $Al(FMP)_2Cl_2^{-}$, and $Al(FMP)Cl_3^{-}$ respectively. These spectra also exhibited a sharp peak at 102 ppm, which was assigned as Al_2Cl_6 and used as an internal standard.[1] At high acid-to-base ratios of the electrolyte $[(FMPMC)$-$(AlCl_3)_4$/THF], the spectra show the expected $AlCl_3$ peak at 63 ppm and a second sharp peak at 91 ppm. The sharpness of the 91 ppm peak suggests that aluminium is tetrahedrally coordinated, while its upfield shift with respect to the dimer Al_2Cl_6 (102 ppm) suggests an increased number of organic ligands and so the 91 ppm shift is assigned to $Al_2(FMP)_2Cl_4$. The similarity in shift to $Al(FMP)Cl_3^{-}$ (86 ppm) further supports the assignment of a single organic ligand on each metal center, and such organochloroaluminate dimers have been previously reported.[2] A complete table of ^{27}Al NMR shifts at the differing acid base ratios and their assignments are presented in Table S1.

NMR Data

(FMPMC)$_2$–AlCl$_3$/THF – ^{1}H 7.4 – 6.9(m) ^{13}C 163.8, 163.5, 163.2, 126.8, 126.07, 126.04, 126.00, 124.1, 119.76, 119.69, 119.62 ^{19}F –62.7, –62.9.

(BPMC)$_2$–AlCl$_3$/THF – ^{1}H 7.0 – 6.6(m), 1.21, 1.20 ^{13}C 157.5, 156.1, 154.9, 141.1, 138.6, 128.6, 127.9, 125.3, 125.2, 125.1, 124.7, 119.0, 118.9, 118.8, 118.7, 33.43, 33.39, 33.29, 31.1, 31.0, 30.9.

(PMC)$_2$–AlCl$_3$/THF – ^{1}H 7.1–6.5(m) ^{13}C 160.3, 160.2, 160.1, 128.8, 128.6, 128.5, 128.3, 128.2, 120.0, 119.9, 119.8, 119.7, 119.6, 117.1, 116.8.

(MePMC)$_2$–AlCl$_3$/THF ^{1}H 6.8–6.6 (m) ^{13}C 157.7, 157.4, 155.5, 155.3, 129.39, 129.34, 129.24, 129.19, 129.10, 129.05, 128.84, 128.79, 125.27, 119.62, 119.55, 119.50, 119.31, 119.25, 114.95, 114.92, 19.92, 19.89, 19.87.

(MPMC)$_2$–AlCl$_3$/THF ^{1}H 6.91–6.57 (m) ^{13}C 154.87, 154.39, 154.30, 154.14, 152.99, 152.79, 121.35, 121.31, 120.86, 120.75, 116.80, 115.44, 115.16, 115.13, 114.97, 114.92, 56.19, 56.19, 56.16, 56.12, 56.07.

(PFPMC)$_2$–AlCl$_3$/THF ^{13}C 141.84, 139.45, 139.05, 136.63, 135.08, 134.24, 131.84 ^{19}F –162.45, –163.4, –164.4, –165.4, –171.3, –178.6.

***X-ray Structure Determination for $C_{62}H_{82}Cl_2Mg_5O_{18}$* (CCDC # 962673)**

Colorless needles of **en5055** were grown from a tetrahydrofuran/hexane solution at 23 ºC. A crystal of dimensions 0.44 x 0.30 x 0.23 mm was mounted on a Bruker SMART APEX-I CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.081 cm from the crystal. A total of 4905 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 351974 reflections to a maximum 2θ value of 70.00° of which 29000 were independent and 23284 were greater than 2σ(I). The final cell constants (Table S3) were based on the xyz centroids of 9459 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{62}H_{82}Cl_2Mg_5O_{18}$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0423 and wR2 = 0.1067 [based on I > 2sigma(I)], R1 = 0.0575 and wR2 = 0.1178 for all data. Two THF ligands and one phenolate ligand are disordered and were refined with partial occupancy orientations constrained to sum to one. Additional details are presented in Table S3 and are given as Supporting Information in a CIF file.[3–5]

***X-ray Structure Determination for $C_{31}H_{52}F_3O_7Mg_2AlCl_6$* (CCDC # 962674)**

Colorless blocks of **en51302a** were grown from a hexane/tetrahydrofuran solution of the compound at 23 ° C. A crystal of dimensions 0.18 x 0.10 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 4336 images were collected with an oscillation width of 1.0° in ω. The exposure time was 1 sec. for the low angle images, 5 sec. for high angle. The integration of the data yielded a total of 243483 reflections to a maximum 2θ value of 136.46° of which 7714 were independent and 7043 were greater than 2σ(I). The final cell constants Table S4) were based on the xyz centroids 143984 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group Pbca with Z = 8 for the formula $C_{31}H_{52}F_3O_7Mg_2AlCl_6$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The THF ligands are extensively disordered. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0807 and wR2 = 0.2135 [based on I > 2sigma(I)], R1 = 0.0843 and wR2 = 0.2162 for all data. Additional details are presented in Table S4 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.[3,6]

Electrochemistry. Cyclic voltammograms were recorded using a CH Instruments Electrochemical Workstation 1000A with a Pt-disk working electrode and Mg-foil counter- and reference electrodes. Measurements were carried out at a scan rate of 25 mV/s, starting at OCP (ranging from 1.5 – 1.7 vs $Mg^{2+/0}$) and scaned cathodically. All electrolyte solutions were 0.5 M (based on Mg) in THF, and measurements were performed using a custom-designed sealed cell in an N_2 box to avoid concentration change during the measurements. Referencing to the $Fc^{+/0}$ couple was carrier out in a 0.5M $(FMPMC)_2$-$AlCl_3$/THF solution containing 10 mM ferrocene in THF with a Pt wire working electrode, a Mg foil auxiliary electrode, and a Mg foil reference electrode. Electrolyte stability was examined by opening a vial of the electrolyte to air, and allowing it to stir for 1 hour, followed by stirring for an additional 5 hours while lightly capped to minimize solvent evaporation. The slurry of Mo_6S_8 was made by mixing an 8:1:1 weight-ratio mixture of Mo_6S_8, super-P carbon powder, and polyvinylidine fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP). The cathode slurry was placed on a Pt current collector and dried in an oven at 120 ºC. The active material loading was approximately 2 mg/cm^2. The cathode was placed in an electrochemical cell with a Mg foil anode and 0.5M $(FMPMC)_2$–$AlCl_3$/THF electrolyte. The charge-discharge tests of the cell were carried on a Vencon UBA4 battery analyzer charger and conditioner (Toronto, Canada) with cut-off voltages of 2.0 and 0.2 V vs. $Mg^{2+/0}$.

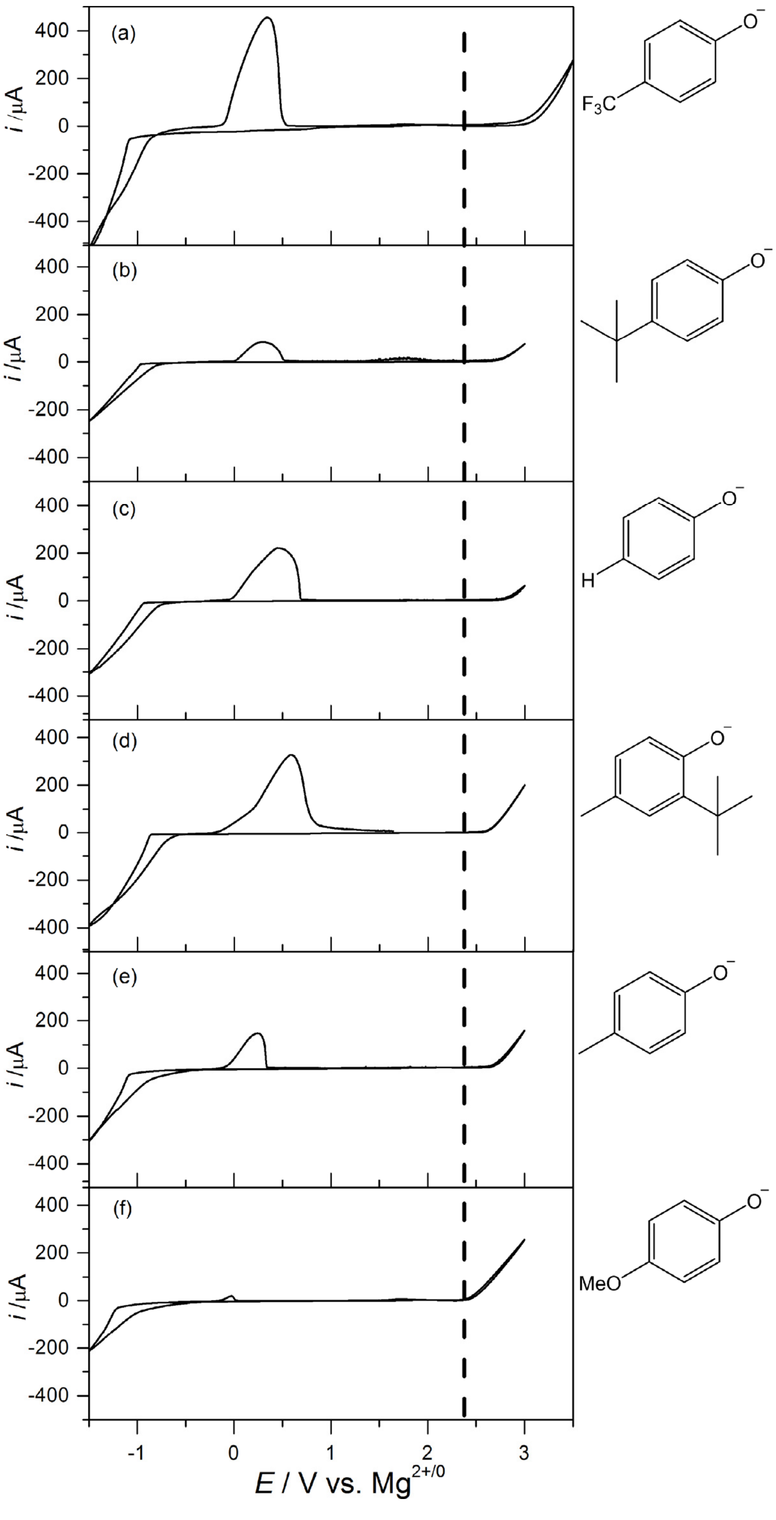


Figure S1. Cyclic voltammograms of a) $(FMPMC)_2$–$AlCl_3$/THF, b) $(BPMC)_2$–$AlCl_3$/THF, c) $(PMC)_2$–$AlCl_3$/THF, d) $(BMPMC)_2$–$AlCl_3$/THF e) $(MePMC)_2$–$AlCl_3$/THF, f) $(MPMC)_2$–$AlCl_3$/THF. The scan rate is 25 mV/s. The best previously reported electrolyte [(2–tert–butyl–4–methyl–phenolate magensium chloride)$_2$$AlCl_3$/THF, $(BMPMC)_2AlCl_3$/THF][7] was prepared and is included below for comparison. The phenolate ligands are shown for clarity.

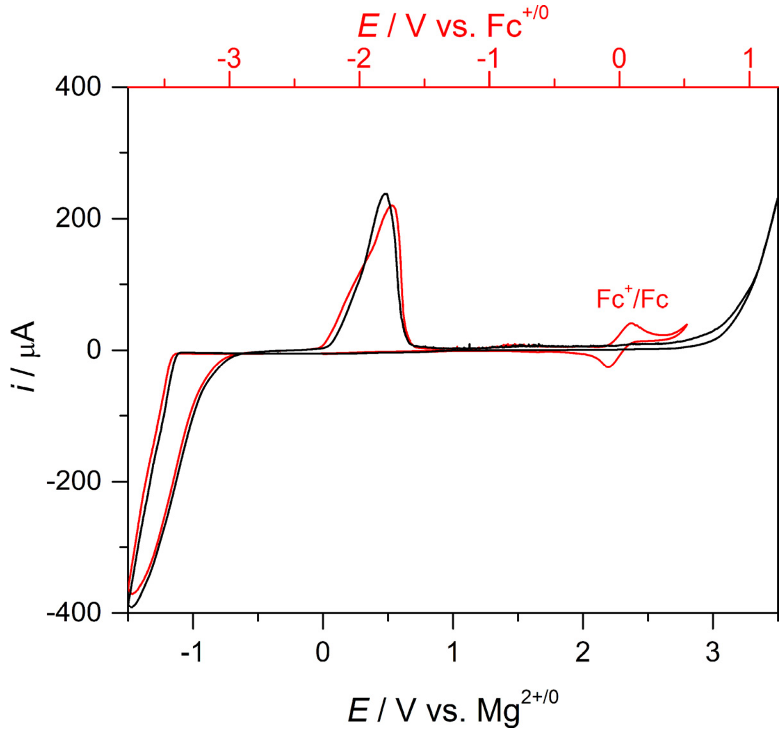


Figure S2. Cyclic voltammogram of $(FMPMC)_2$–$AlCl_3$/THF without (black) and with (red) 10 mM ferrocene. Electrochemistry was carried out with a Pt wire working electrode, a Mg foil auxiliary electrode, and a Mg foil reference electrode.

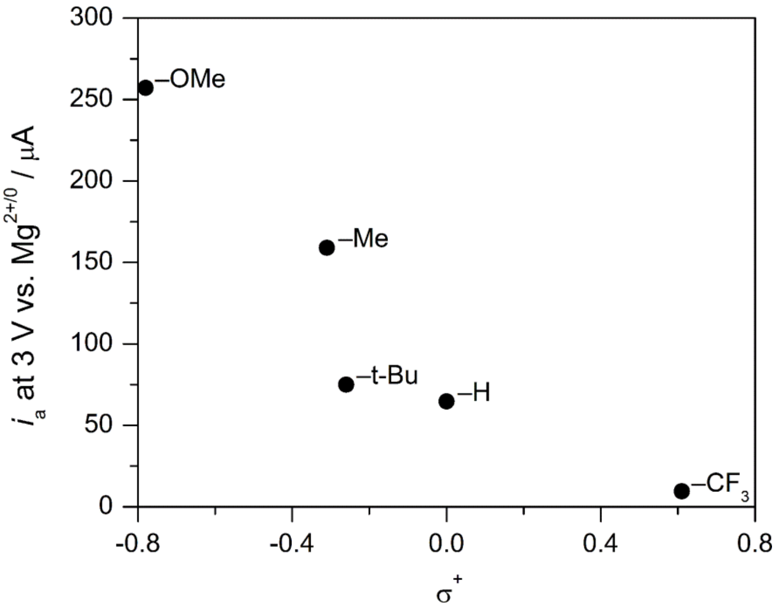


Figure S3. Hammett plot of anodic current at 3 V vs. $Mg^{2+/0}$ *vs.* σ^+ values of *p*–substituted phenols.

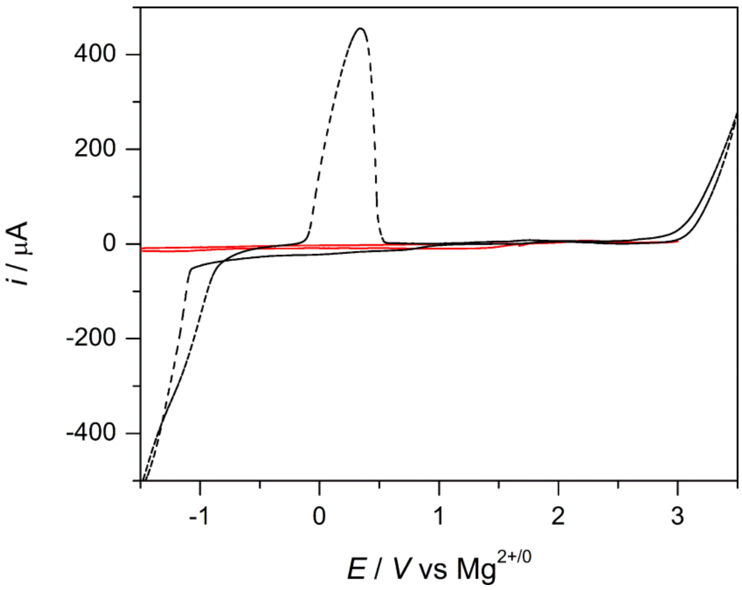


Figure S4. Cyclic voltammogram of 0.25M $AlCl_3$ in THF (—) and (FMPMC)$_2$-$AlCl_3$/THF (---).

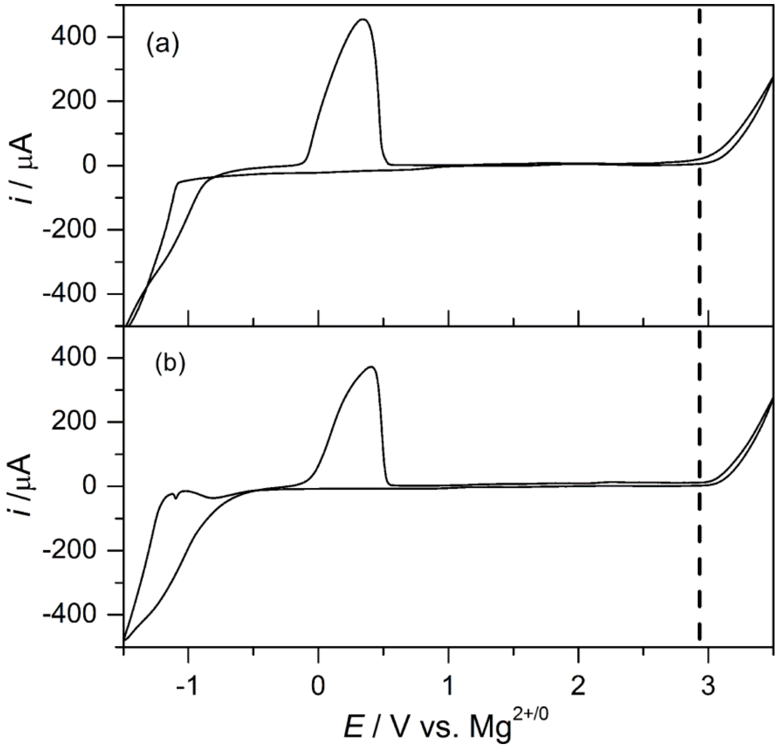


Figure S5. Cyclic voltammograms of Pt electrodes in 0.5 M a) (FMPMC)$_2$-$AlCl_3$/THF and b) (PFPMC)$_2$-$AlCl_3$/THF solutions. The scan rate is 25 mV/s and the dashed line is added as a guide to the eye.

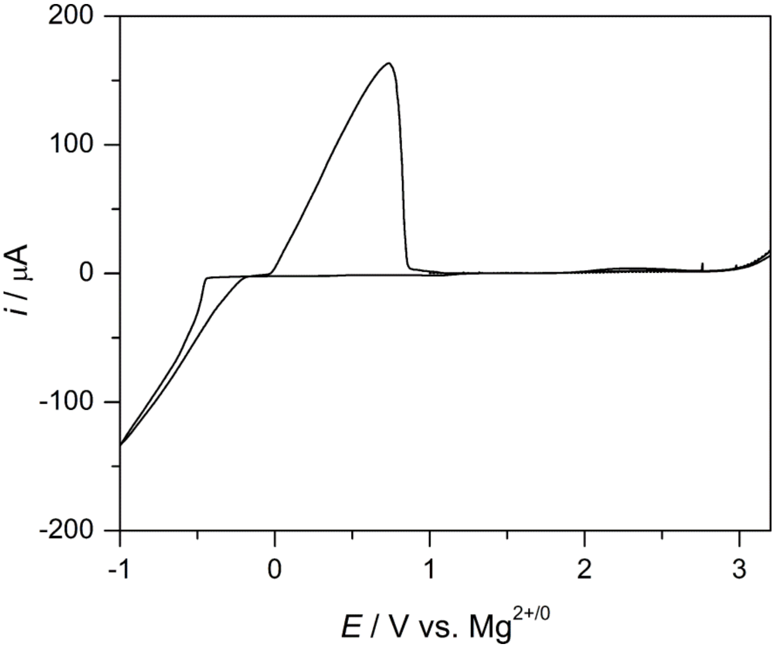


Figure S6. Steady-state cyclic voltammogram of $(FMPMC)_2$–$AlCl_3$/THF performed at a scan rate of 1 mV/s.

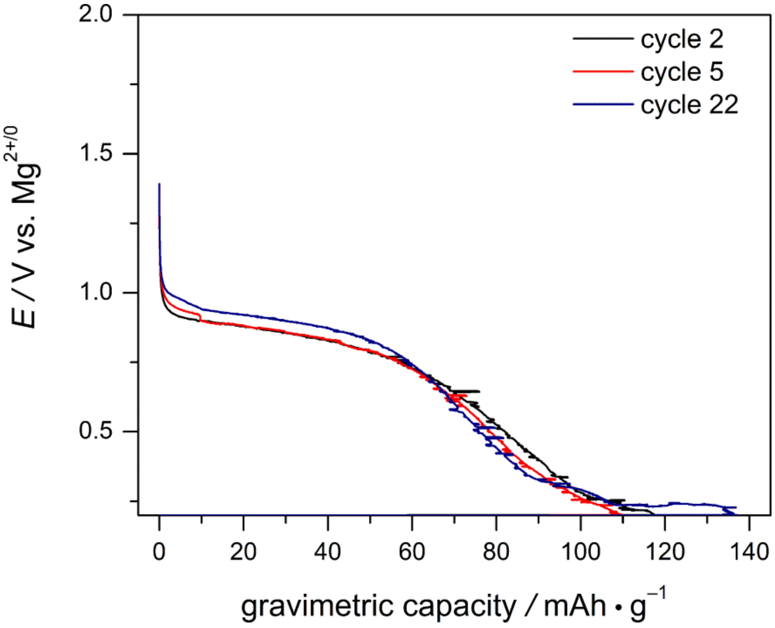


Figure S7. Discharge curves of Mo_6S_8 *vs.* Mg-foil in $(FMPMC)_4$-$AlCl_3$/THF electrolyte.

Table S1. ^{27}Al NMR assignments and shifts for $(FMPMC)_x$–$AlCl_3$/THF at various Lewis acid–to–base ratios.

Solution	Peak Shift (ppm)	Assignment
4:1 FMPMC–$AlCl_3$/THF	51	$(FMP)_4Al$
2:1 FMPMC–$AlCl_3$/THF	51	$(FMP)_4Al$
	62	$(FMP)_3AlCl^{(-)}$/$(FMP)_3Al$
	74	$(FMP)_2AlCl_2^{(-)}$/$(FMP)_2AlCl$
	88	$(FMP)AlCl_3^{(-)}$/$(FMP)AlCl_2$
	102	Al_2Cl_6
3:2 FMPMC–$AlCl_3$/THF	51	$(FMP)_4Al$
	62	$(FMP)_3AlCl^{(-)}$/$(FMP)_3Al$
	74	$(FMP)_2AlCl_2^{(-)}$/$(FMP)_2AlCl$
	87	$(FMP)AlCl_3^{(-)}$/$(FMP)AlCl_2$
	91	$(FMP)_2Al_2Cl_4$
	102	Al_2Cl_6
1:4 FMPMC–$AlCl_3$/THF	63	$AlCl_3$
	91	$(FMP)_2Al_2Cl_4$
	102	Al_2Cl_6
$AlCl_3$/THF	62	$AlCl_3$
	102	Al_2Cl_6

Table S2. ^{27}Al NMR assignments for 0.5 M electrolyte solutions.

Solution	Peak Shift (ppm)	Assignment
$(FMPMC)_2$–$AlCl_3$/THF	51	$(FMP)_4Al$
	62	$(FMP)_3AlCl^{(-)}/(FMP)_3Al$
	74	$(FMP)_2AlCl_2^{(-)}/(FMP)_2AlCl$
	88	$(FMP)AlCl_3^{(-)}/(FMP)AlCl_2$
	102	Al_2Cl_6
$(PMC)_2$–$AlCl_2$/THF	60	$(P)_3AlCl^{(-)}/(P)_3Al$
	73	$(P)_2AlCl_2^{(-)}/(P)_2AlCl$
	86	$(P)AlCl_3^{(-)}/(P)Al_2$
	102	Al_2Cl_6
$(MPMC)_2$–$AlCl_3$/THF	71	$(MP)_2AlCl_2^{(-)}/(MP)_2AlCl$
	87	$(MP)AlCl_3^{(-)}/(MP)AlCl_2$
	102	Al_2Cl_6
$(BPMC)_2$–$AlCl_3$/THF	72	$(BP)_2AlCl_2^{(-)}/(BP)_2AlCl$
	86	$(BP)AlCl_3^{(-)}/(BP)AlCl_2$
	102	Al_2Cl_6
$(MePMC)_2$–$AlCl_3$/THF	71	$(MeP)_2AlCl_2^{(-)}/(MeP)_2AlCl$
	87	$(MeP)AlCl^{(-)}/(MeP)AlCl_2$
	102	Al_2Cl_6
$(PFPMC)_2$–$AlCl_3$/THF	45	$(PFP)_4Al$
	60	$(PFP)_3AlCl^{(-)}/(PFP)_3Al$
	74	$(PFP)_2AlCl_2^{(-)}/(PFP)_2AlCl$
	88	$(PFP)AlCl_3^{(-)}/(PFP)AlCl_2$
	102	Al_2Cl_6

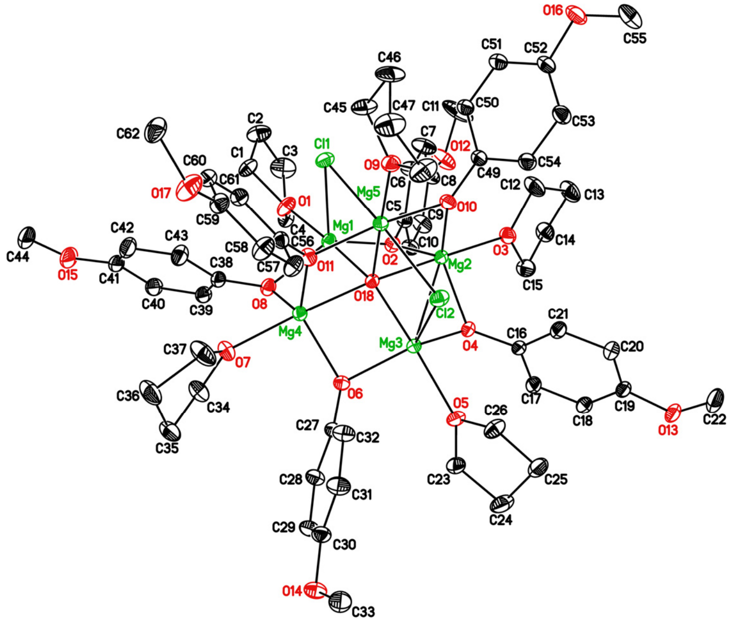


Figure S8. X-ray crystal structure of $Mg_5Cl_2C_{62}H_{82}O_{18}$ crystallized from the $(MPMC)_2$-$AlCl_3$/THF electrolyte solution.

Table S3. Crystal data and structure refinement for en5055 (CCDC # 962673)

Identification code	en5055
Empirical formula	$C_{62}H_{82}Cl_2Mg_5O_{18}$
Formula weight	1307.73
Temperature	85(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 14.4018(5) Å
	b = 24.2154(8) Å β = 104.534(1)°
	c = 19.5295(7) Å
Volume	6592.6(4) $Å^3$
Z, ρ_{calc}	4, 1.318 g/cm^3
Absorption coefficient	0.214 mm^{-1}
F(000)	2768
Crystal size	0.44 × 0.30 × 0.23 mm
θ range for data collection	1.37 – 35.00°
Limiting indicies	$-23 \leq h \leq 23$
	$-38 \leq k \leq 38$
	$-31 \leq l \leq 31$
Reflections collected/unique	351974 / 29000 [R(int) = 0.0626]
Completeness to θ = 35.00°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9524 and 0.9116
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	29000 / 165 / 878
$G.o.F.$ on F^2	1.006
Final R incides [$I > 2\sigma(I)$]	$R1$ = 0.0423; $wR2$ = 0.1067
R indices (all data)	$R1$ = 0.0575, $wR2$ = 0.1178
Largest diff. peak and hole	1.238 and –0.275 eA^{-3}

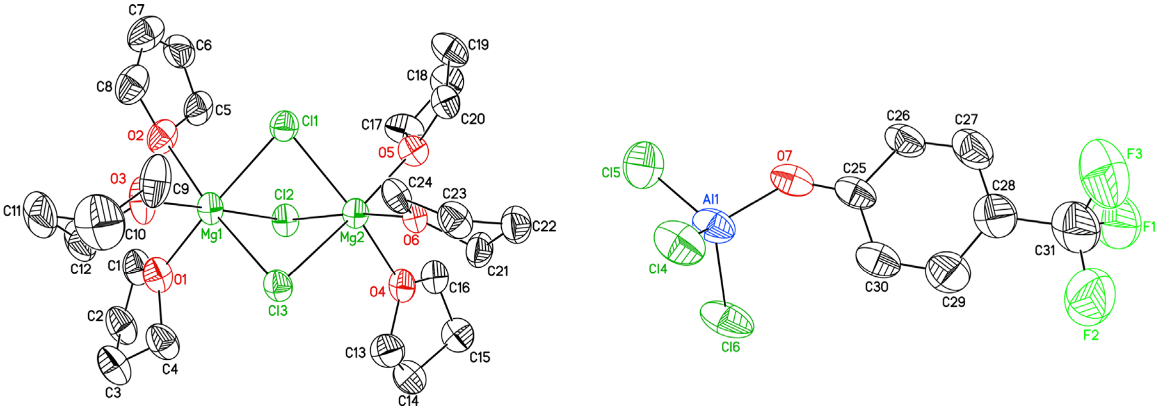
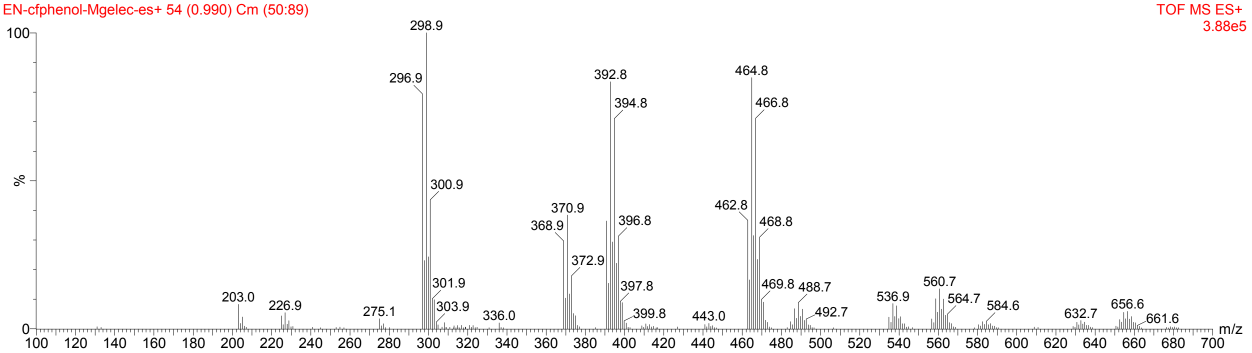


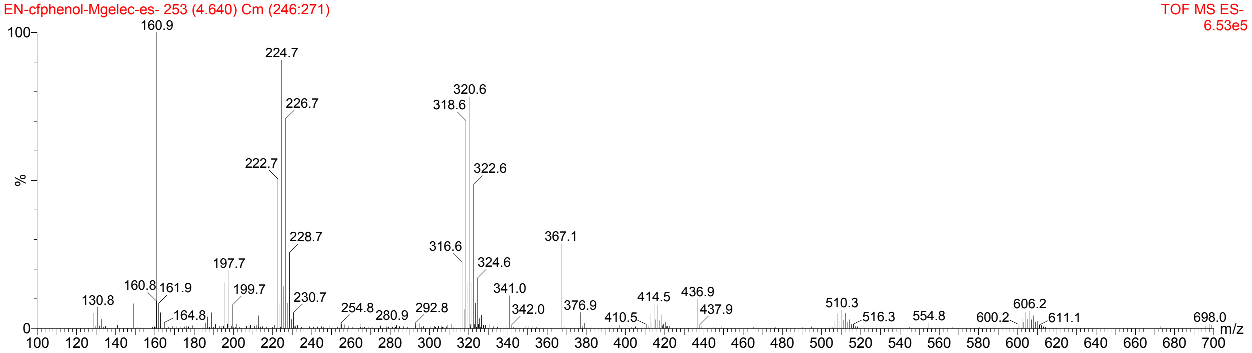
Figure S9. X-ray crystal structures of the molecular ions $[Mg_2Cl_3(THF)_6]^+$ and $[(FMP)AlCl_3]^-$ crystallized from the $(FMPMC)_2$-$AlCl_3$/THF electrolyte solution.

Table S4. Crystal data and structure refinement for en51302a (CCDC # 962674)

Identification code	en51302a
Empirical formula	$C_{31}H_{52}AlCl_6Mg_2O_7$
Formula weight	882.03
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, *Pbca*
Unit cell dimensions	a = 19.9228(4) Å b = 15.0009(3) Å c = 28.215(2)
Volume	8432.4(6) $Å^3$
Z, ρ_{calc}	8, 1.390 g/cm^3
Absorption coefficient	4.679 mm^{-1}
F(000)	3680
Crystal size	0.18 × 0.10 × 0.10 mm
θ range for data collection	3.13 – 68.23°
Limiting indicies	$-23 \leq h \leq 24$ $-18 \leq k \leq 18$ $-33 \leq l \leq 33$
Reflections collected/unique	243483 / 7714 [R(int) = 0.1127]
Completeness to θ = 68.23°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6519 and 0.4863
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7714 / 776 / 728
G.o.F. on F^2	1.072
Final R incides [$I > 2\sigma(I)$]	$R1$ = 0.0807; $wR2$ = 0.2135
R indices (all data)	$R1$ = 0.0843, $wR2$ = 0.2162
Extinction coefficient	0.00066(4)
Largest diff. peak and hole	0.711 and –0.726 eA^{-3}



$Mg_2Cl_3(THF)^+$ (226.9), $Mg_2Cl_3(THF)_3^+$ (298.6), $Mg_2Cl_3(THF)_3^+$ (370.9), $Mg_3Cl_5(THF)_2^+$ (392.8), $Mg_3Cl_5(THF)_3^+$ (464.8), $Mg_3Cl_5(THF)_4^+$ (536.9), $Mg_3Cl_5(THF)_6^+$ (584.6)



$AlCl_3^-$ (130.8), FMP^- (160.9), $Al_2Cl_3^-$ (197.7), $Al(FMP)Cl^-$ (224.7), $Al_2Cl_3(FMP)^-$ (320.6), $Al(FMP)_2Cl_2^-$ (414.5), $Al(FMP)_3^-$ (510.3), $Al(FMP)_4^-$ (698.0)

Figure S10. Electrospray ionization mass spectra of $(FMPMC)_2–AlCl_3$/THF electrolyte in positive-ion mode (top) and negative-ion mode (bottom)

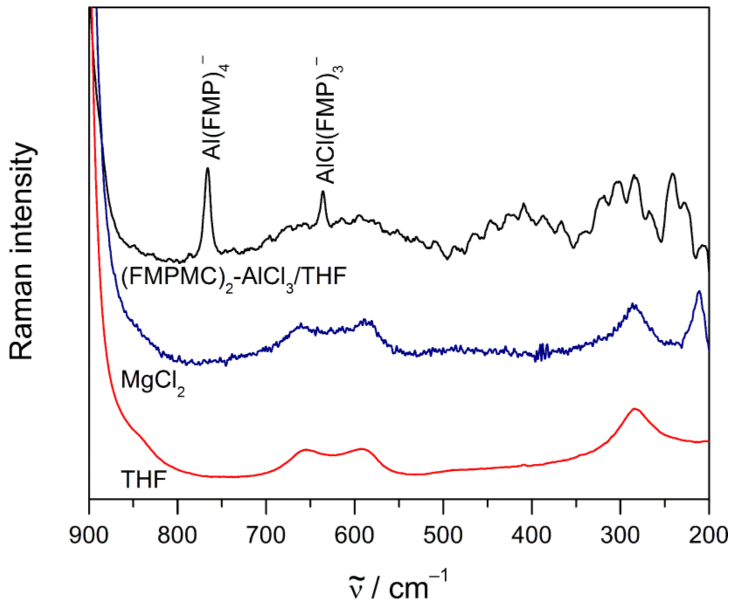


Figure S11. Raman spectra of (FMPMC)$_2$-AlCl$_3$/THF electrolyte.[8–11]

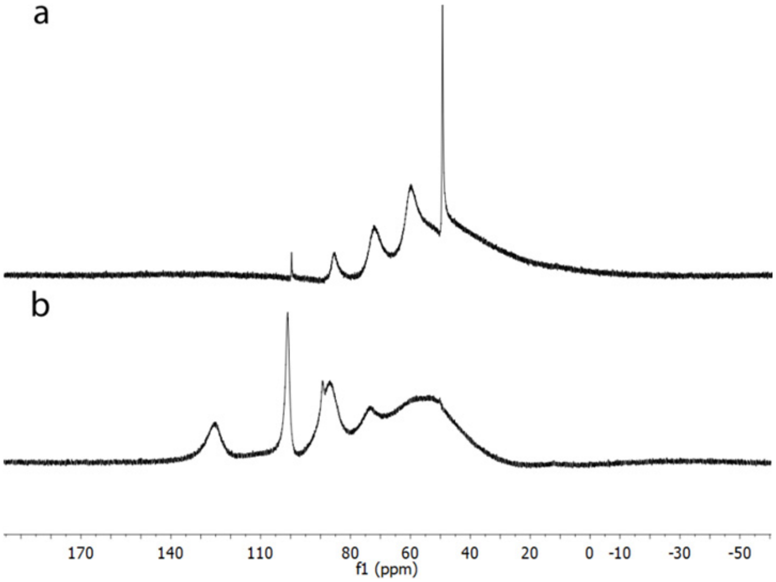


Figure S12. ^{27}Al NMR spectra of (FMPMC)$_2$–AlCl$_3$/THF a) before and b) after electrolysis at 3.5 V *vs*. Mg$^{2+/0}$ for 90 minutes.

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