Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Lewis Acid-free Phenolate-based Magnesium Electrolyte for Rechargeable Magnesium Batteries

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Experimental Section

All synthesis and electrolyte preparation reported were carried out in argon-filled glove boxes with oxygen and water concentrations below 1 ppm level. 2, 6-di-*tert*-butylphenol, 2, 4-di-*tert*-butylphenol, 4-fluorophenol, 3-trifluoromethylphenol, pentafluorophenol were purchased from Alfar Aesar and used without further purification. 2.0 M Ethylmagnesium Chloride (EtMgCl) in THF, 2.0 M di-n-butylmagnesium (nBu_2Mg) in heptane was purchased from Sigma-Aldrich and used as received. Anhydrous THF was purchased from Alfa Aesar and was dried with 200 ºC vacuum oven dried 3 Å molecular sieves for more than 12 hours before use. Anhydrous $MgCl_2$ was purchased from Sigma-Aldrich and dried at 200 ºC in vacuum oven for more than 12 hours before use. Chevrel phase Mo_6S_8 was synthesized according to literature procedure.[1] The electrode laminates were prepared by mixing Chevrel phase (Mo_6S_8), carbon black and poly(tetrafluoroethylene) (PTFE) in an 8:1:1 ratio with water, and the resulting slurry was

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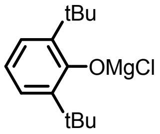
[1] M. D. Levi, E. Lancry, H. Gizbar, Z. Lu, E. Levi, Y. Gofer and D. Aurbach, *J. Electrochem. Soc.*, **2004**, *151*, A1044

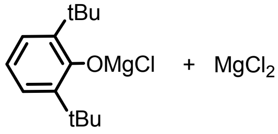
coated onto stainless steel mesh. The laminates were dried in a 75 ºC oven for two hours before they were cut to electrodes with diameter of 7/16''. The electrodes were then dried in vacuum at 100 ºC for more than 12 hours before use.

Synthesis of 0.5 M (DTBP)MgCl (DTBP = 2, 6-di-*tert*-butylphenolate) electrolyte in THF:



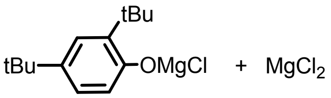
206.3 mg (1.0 mmol) 2, 6-di-*tert*-butylphenol was dissolved in 1.5 mL anhydrous THF, to which was added 0.5 mL 2.0 M EtMgCl/THF solution slowly over 10 minutes. The in *situ* generated colorless solution was stirred at room temperature for one more hour before used as electrolyte for electrochemical study.

Synthesis of 0.5 M (DTBP)MgCl-$MgCl_2$ (DTBP = 2, 6-di-*tert*-butylphenolate) electrolyte in THF:



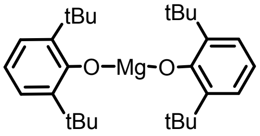
To the above 2 mL in *situ* generated 0.5 M (DTBP)MgCl solution was added 95.2 mg (1 mmol) anhydrous $MgCl_2$. The mixture was stirred at room temperature for overnight to form colorless 0.5 M (DTBP)MgCl-$MgCl_2$ solution in THF. Electrolytes of 0.5 M (DTBP)MgCl-x$MgCl_2$ (x = 0.5, 1, 2) were prepared according to the same procedure.

Synthesis of 0.5 M (2, 4-DTBP)MgCl-$MgCl_2$ (DTBP = 2, 4-di-*tert*-butylphenolate) electrolyte in THF:



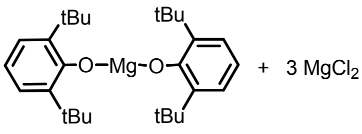
206.3 mg 2, 4-di-*tert*-butylphenol was dissolved in 1.5 mL anhydrous THF, to which was added 0.5 mL 2.0 M EtMgCl/THF slowly over 10 minutes. The in *situ* generated colorless solution was stirred at room temperature for one more hour to ensure the completion of the reaction. After one hour stirring, 95.2 mg (1 mmol) anhydrous $MgCl_2$ was added, and the mixture was stirred at room temperature for overnight to form colorless electrolyte solution.

Synthesis of $(DTBP)_2Mg$ (DTBP = 2, 6-di-*tert*-butylphenolate):



A literature procedure[2] was followed for the synthesis. 2, 6-di-*tert*-butylphenol (2.5 g, 12.1 mmol) was dissolved in 10 mL hexane, to which 3.5 mL 2.0 M nBu_2Mg/heptane was added slowly over 15 minutes. After adding all nBu_2Mg, a lot of white solid precipitated from the solution. The mixture was stirred at room temperature for one more hour to ensure the reaction completion. One hour later, white precipitation was collected via filtration. Further drying the collected white solid in vacuum afforded the analytical pure $(DTBP)_2Mg$ as the product.

Preparation of 0.25 M $(DTBP)_2Mg$-$3MgCl_2$:



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[2] Henderson, K. W.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E.; Parkinson, J. A.; Sherrington, D. C. *Dalton Trans.* **2003**, 1365

217.2 mg (0.5 mmol) and 142.8 mg (1.5 mmol) anhydrous $MgCl_2$ were combined in 2 mL anhydrous THF. The mixture was allowed to stir at room temperature overnight to generate colorless electrolyte solution. 0.25 M $(DTBP)_2Mg$-$xMgCl_2$ (x = 1, 2, 4) were prepared according to the same procedure with different amount of $MgCl_2$ for each electrolyte.

Synthesis and preparation of 0.5 M ArOMgCl-$MgCl_2$ (Ar = 4-fluorophenolate; 3-trifluoromethylphenolate; or pentafluorophenol): The same procedure as the one for the preparation of (DTBP)MgCl-$MgCl_2$ was used. To the corresponding phenol in THF was added one equivalent EtMgCl. Then one equivalent anhydrous $MgCl_2$was added to the in *situ* solution. The mixture was stirred at room temperature to form the desired ArOMgCl-$MgCl_2$ electrolytes.

Electrochemical measurement: the electrochemical characterizations in this paper were carried on a multi-channel potentiostat (Parstat MC, Princeton Applied Research, TN) in an argon-filled glove box with water and oxygen concentrations below 1 ppm.

Cyclic voltammetry (CV): the typical three-electrode setup was used with platinum disk (2 mm in diameter, CH instrument) as the working electrode, freshly polished magnesium ribbons as counter and reference electrodes. Three continuous scans were performed for each measurement at 0.1 V/s scan rate.

Conductivity: impedance spectroscopy was used to measure the electrolytes' conductivities. The conductivity cell was made with two platinum wires, one is for working electrode, and the other one is for both counter and reference electrodes. The cell was calibrated with 0.1 M aqueous KCl solution.

Diffusion coefficient: The similar procedure was used according to a literature report.[3] Chronoamperometry was used to measure the electrolytes' diffusion coefficient with the same three-electrode setup for CV measurement. The potential was set at – 0.5 V vs Mg/Mg^{2+} for 70 seconds allowing the Mg^{2+} reduction at the surface of the working platinum electrode. Then the corresponding diffusion coefficient was calculated according to the following equation. All the other parameters in the equation: Q, the total coulombic charge; n, the number of electrons needed for the reduction taking place at the working electrode surface (here n = 2 for Mg^{2+} reduction); F, Faraday constant, 96485 C mol^{-1}; A, the area of the working electrode surface, 0.0314 cm^{-2}; C_o, the bulk magnesium concentration in the electrolyte; D, the diffusion coefficient; t, time the experiment runs; Q_{dl}, the double layer capacitive charge; Q_{ads}, charge associated with absorbed species in the electrolyte. The linear fitting of Q (C) and $t^{1/2}$ ($s^{1/2}$) was made with the chronoamperpmetry experiment, and the induced slope allows the calculation of the corresponding diffusion coefficient.

$$Q = \frac{2nFAC_oD^{1/2}}{\pi^{1/2}} t^{1/2} + Q_{dl} + Q_{ads}$$

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[3] Benmayza, A.; Ramanathan, M.; Arthur, T. S.; Matsui, M.; Mizuno, F.; Guo, J.; Glans, P-A.; Parkash, J. *J. Phys. Chem. C* **2013**, *117*, 26881.

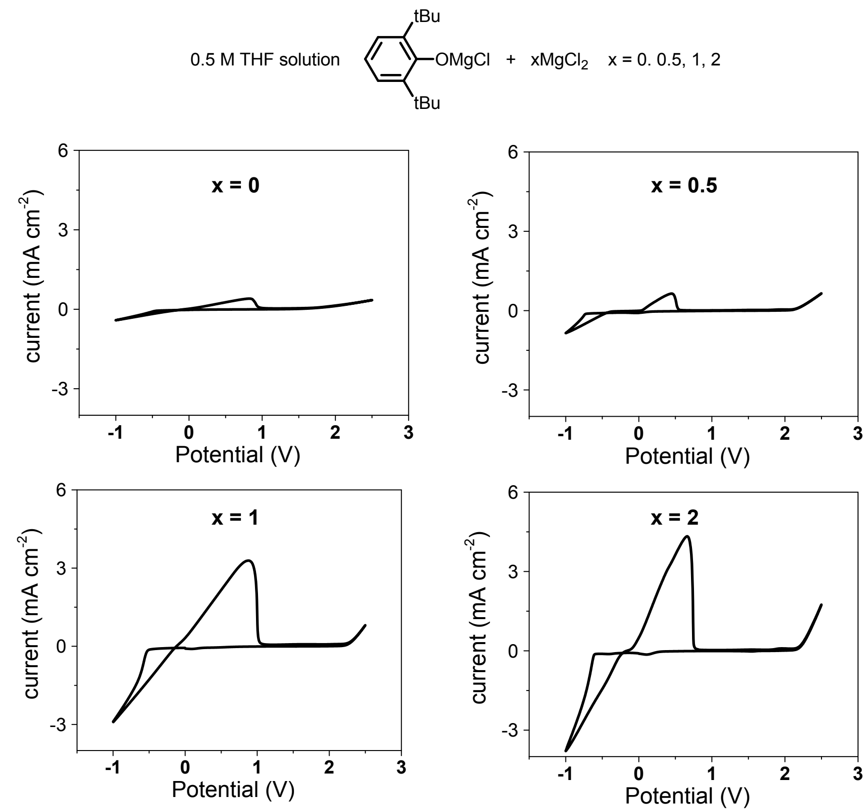


Figure S1. Cyclic voltammograms for different (DTBP)MgCl/$MgCl_2$ ratio

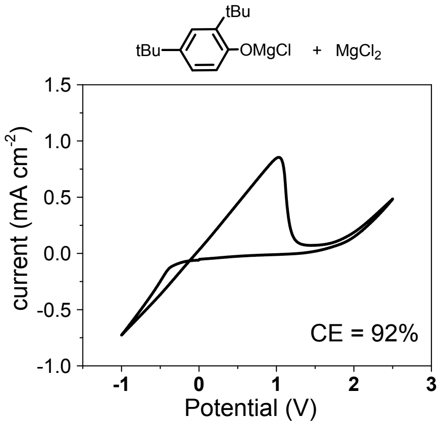


Figure S2. Cyclic voltammogram for 0.5 M (2, 4-DTBP)MgCl-$MgCl_2$ in THF

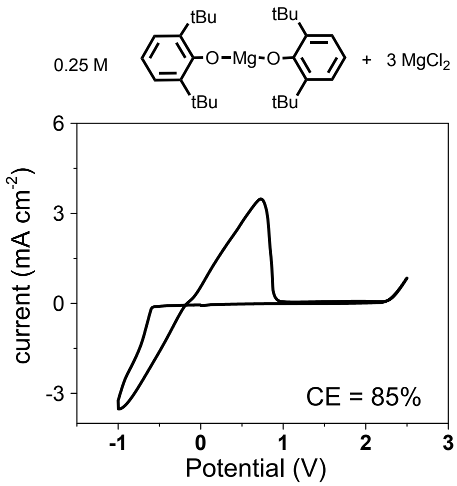


Figure S3. Cyclic voltammogram for 0.25 M $(DTBP)_2Mg\text{-}3MgCl_2$ in THF

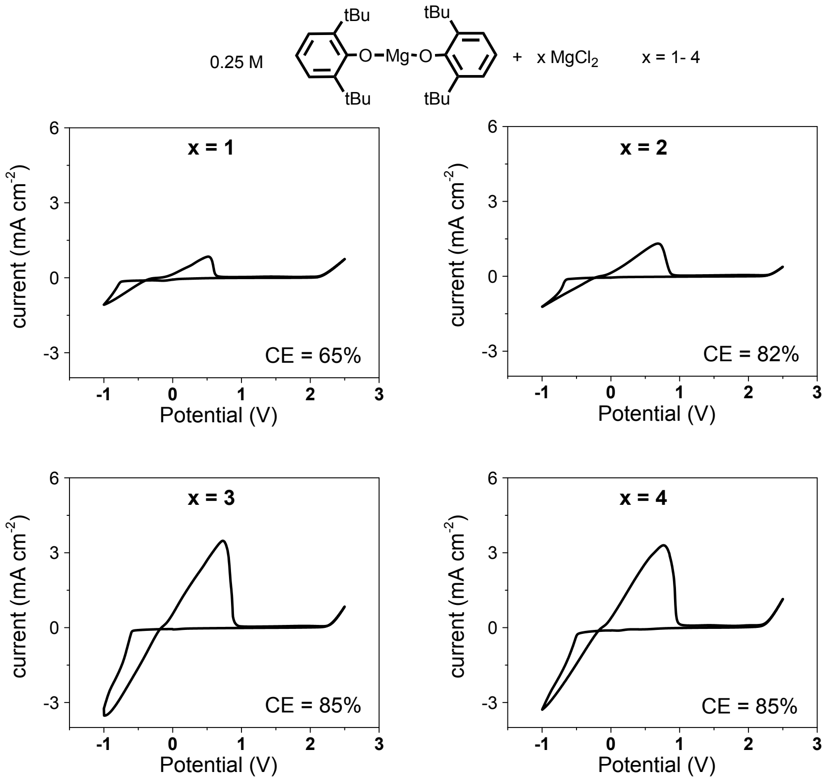


Figure S4. Cyclic voltammograms for different $(DTBP)_2Mg/MgCl_2$ ratio

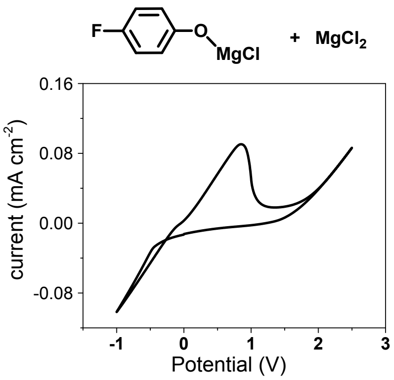


Figure S5. Cyclic voltammogram for 0.5 M ArOMgCl-$MgCl_2$ (Ar = 4-fluorophenolate) in THF

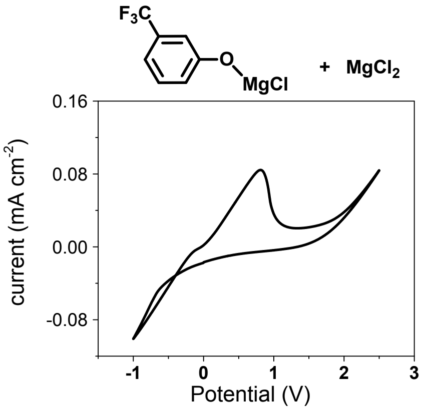


Figure S6. Cyclic voltammogram for 0.5 M ArOMgCl-$MgCl_2$ (Ar = 3-trifluoromethylphenolate) in THF

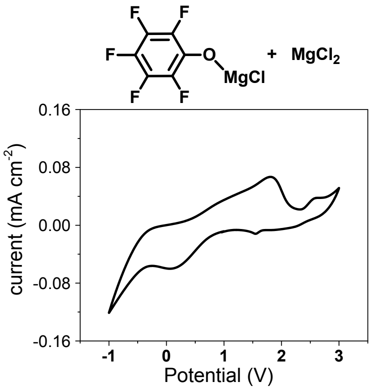


Figure S7. Cyclic voltammogram for 0.5 M ArOMgCl-$MgCl_2$ (Ar = 3-trifluorophenolate) in THF

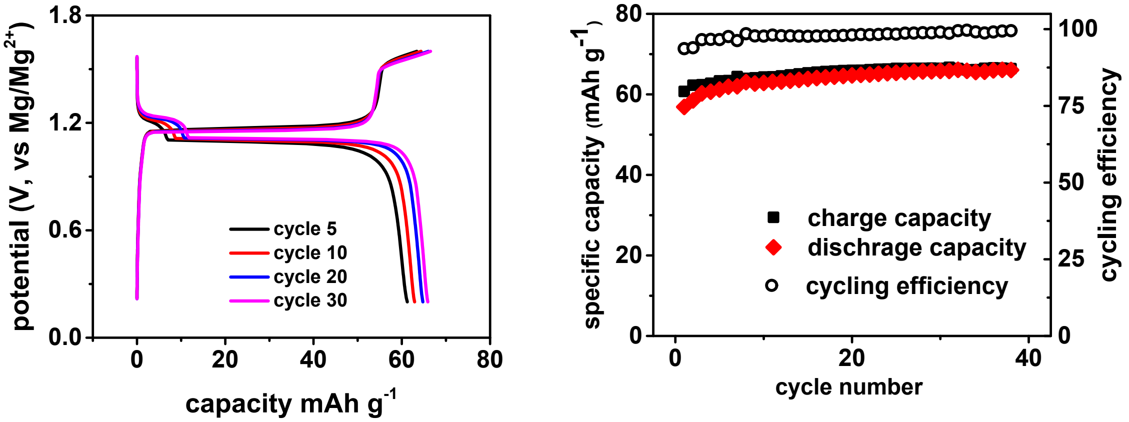


Figure S8. Coin cell performance using 0.5 M (DTBP)MgCl-$MgCl_2$ as the electrolyte, Chevrel phase Mo_6S_8 as the cathode and freshly polished magnesium disc as the anode: (a) charge-discharge profiles for cycle 5th (black), 10th (red), 20th (blue) and 30th (purple) at a current rate of 0.05 C (6.4 mA g^{-1}) at 25 ℃; (b) charge-discharge capacity performance and cycling efficiency.

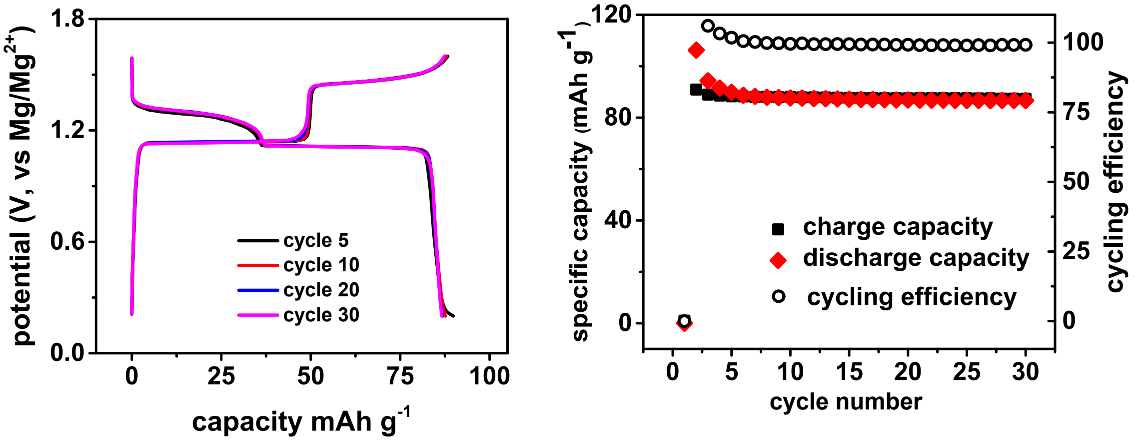


Figure S9. Coin cell performance using 0.25 M $(DTBP)_2Mg\text{-}3MgCl_2$ as the electrolyte, Chevrel phase Mo_6S_8 as the cathode and freshly polished magnesium disc as the anode: (a) charge-discharge profiles for cycle 5th (black), 10th (red), 20th (blue) and 50th (purple) at a current rate of 0.05 C (6.4 mA g^{-1}) at 55 ℃; (b) charge-discharge capacity performance and cycling efficiency.

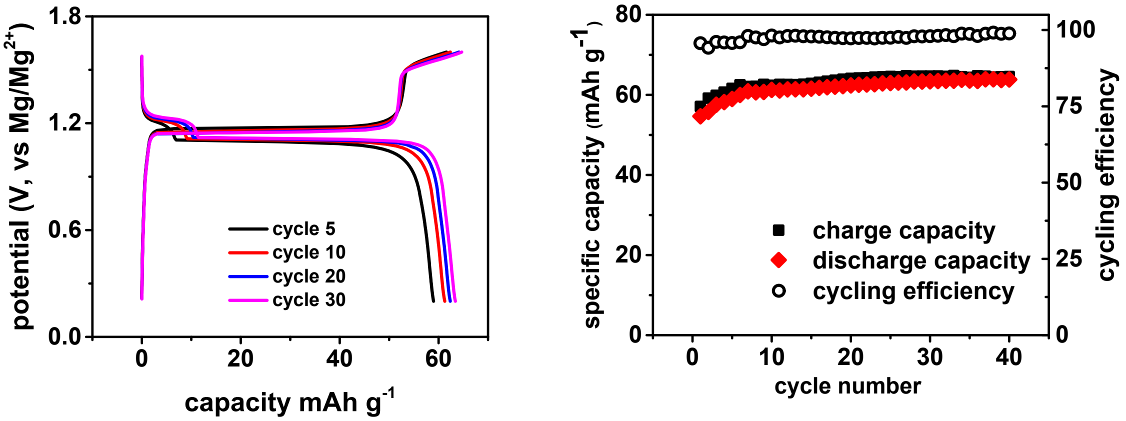
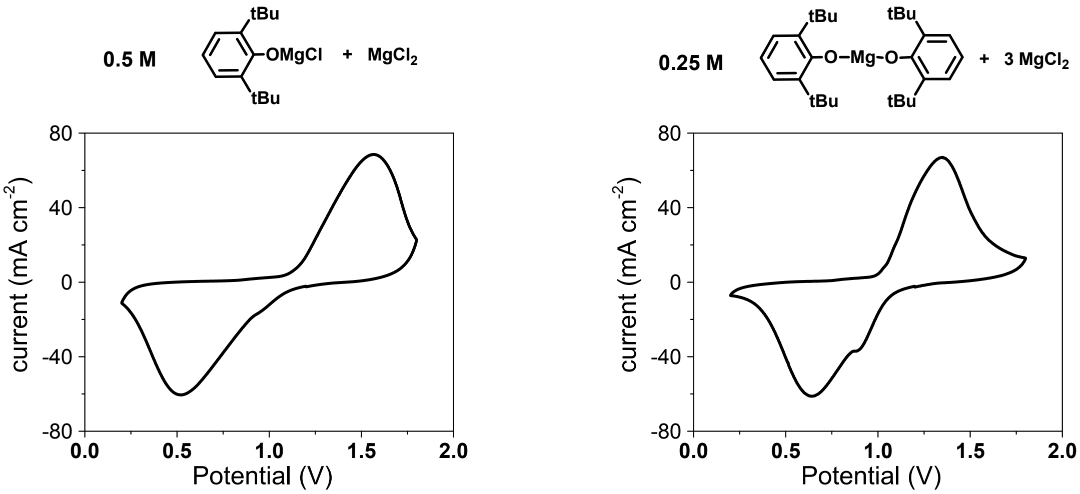


Figure S10. Coin cell performance using 0.25 M $(DTBP)_2Mg\text{-}3MgCl_2$ as the electrolyte, Chevrel phase Mo_6S_8 as the cathode and freshly polished magnesium disc as the anode: (a) charge-discharge profiles for cycle 5th (black), 10th (red), 20th (blue) and 50th (purple) at a current rate of 0.05 C (6.4 mA g^{-1}) at 25 ℃; (b) charge-discharge capacity performance and cycling efficiency.



(a) (b)

Figure S11. Three-electrode (Mo_6S_8 as cathode, magnesium ribbons as reference and counter) cyclic voltammograms for (a) 0.5 M (DTBP)MgCl-$MgCl_2$/THF; (b) 0.25 M $(DTBP)_2Mg$-3$MgCl_2$/THF.

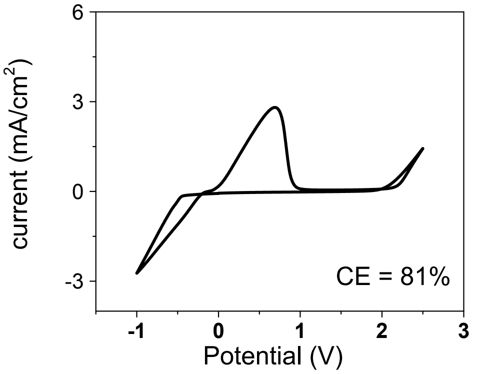


Figure S12. Cyclic voltammograms for 0.5 M (DTBP)MgCl-$MgCl_2$ in THF using stainless steel (ss) as working, Mg discs as counter and reference electrodes

Crystallographic Measurement. Single crystals suitable for X-ray diffraction were obtained via slow hexane diffusion into (DTBP)MgCl-$MgCl_2$ THF solution, or slow hexane diffusion into $(DTBP)_2Mg$-$3MgCl_2$ THF solution. The crystallographic measurement was performed at 298(2) K using a Bruker APEX-II CCD area detector diffractometer (Mo-K radiation, λ = 0.71073 Å). In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the nonhydrogen atoms. Semi-empirical absorption corrections were applied.[4] Subsequent refinement on F2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non–hydrogen atoms.[5] Further details are available from the CIF files (CCDC 1048119).

Table S1. Crystallographic Data and Refinement Parameters for $[Mg_2Cl_3(THF)_6][(DTBP)_3Mg]$.

Chemical formula	$C_{66}H_{111}Cl_3O_9Mg_3$
Molecular weight	1372.04
T(K)	138
λ (Å)	0.71073
a (Å)	14.3956(4)
b (Å)	15.2219(4)
c (Å)	18.5435(5)
α (°)	88.650(2)
β (°)	74.452(1)
γ (°)	85.5435(5)
V (Å^3)	3900.96(18)
Space group	P-1
Z	2
D_{cal} (g/cm^3)	1.168
U (cm^{-1})	1.96
R1, wR2 (I > 2σ(I))	0.0795, 0.2700

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[4] Sheldrick, G. M. SADABS-2008/1, Absorption Correction Program; Bruker AXS, Madison, WI

[5] Sheldrick, G. M. SHELXTL-2008/4, Structure Determination Software Suite; Bruker AXS, Madison, WI