## **Supporting Information**

## Molecular-Level Environments of Intercalated Chloroaluminate Anions in Rechargeable Aluminum-Graphite Batteries Revealed by Solid-State NMR Spectroscopy

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**Figure S1.** Scanning electron microscopy (SEM) images with energy dispersive X-ray spectroscopy (EDS) elemental mapping for graphite electrodes rinsed with (a) anhydrous methanol (CH<sub>3</sub>OH) and (b) carbon tetrachloride (CCl<sub>4</sub>), which were harvested from Al-graphite cells galvanostatically charged to 2.45 V at 60 mA/g. The results show that anhydrous methanol was more effective in washing away the excess AlCl<sub>3</sub>:[EMImCl] (molar ratio 1.5:1) ionic liquid electrolyte from the surfaces of the harvested electrodes. Data was collected using a Helios NanoLab 660 SEM with an Oxford EDX detector.



**Figure S2.** Solid-state <sup>27</sup>Al single-pulse MAS NMR spectra acquired on a fully intercalated graphite electrode, illustrating the effects of MAS on residual electrolyte. The electrode was harvested from an Al-graphite cell galvanostatically charged to 2.45 V at 60 mA/g and subsequently rinsed with anhydrous methanol. A static spectrum was initially acquired (blue), as well as one after 1 minute of MAS at 10 kHz (red). Electrolyte trapped within the electrode pores is gradually expelled due to centrifugal forces from sample rotation. The <sup>27</sup>Al signal at approximately 103 ppm, associated with AlCl<sub>4</sub><sup>-</sup> anions in the residual electrolyte, increased in intensity with increasing MAS time and then equilibrated. All solid-state <sup>27</sup>Al MAS NMR measurements reported in Figure 2 (main text) were acquired after spinning for 6 hours (green), when equilibration was achieved.



**Figure S3.** Nucleus-independent chemical shift (NICS) for a coronene bilayer (diameter = 7.3 Å) as a function of (a) interlayer spacing and (b) lateral displacement of the probe ("ghost") atom from the central position with fixed interlayer spacing of 9.2 Å. *Inset:* DFT-optimized structure of the coronene bilayer and illustration of the lateral displacement of the probe atom (purple). Dashed lines are shown to guide the eye.



**Figure S4.** Solid-state <sup>27</sup>Al single-pulse MAS NMR spectrum of metallic aluminum powder (2 µm diameter particles), acquired at 20 kHz MAS and 14.1 T, reveals a Knight-shifted signal at 1639 ppm associated with aluminum metal. The <sup>27</sup>Al shift was referenced to 1M aqueous Al(NO3)<sub>3</sub>. To enable sample rotation in the magnetic field, the aluminum powder was diluted with KBr powder using a mass ratio of 1:9.

at the aluminum nucleus for the [AlCl4]-coronene bilayer system with varying interlayer spacings.			
	Principle Components of Electric Field Gradient (EFG) Tensor (V)		
Interlayer spacing of [ AlCl4 <sup>-</sup> ]-coronene bilayer (Å)	V <sub>xx</sub> (atomic units)	V <sub>yy</sub> (atomic units)	V <sub>zz</sub> (atomic units)
6.5	0.1827	0.3012	-0.4839
7	0.1596	0.2177	-0.3773
7.5	0.1075	0.1327	-0.2402
8	0.0698	0.0764	-0.1462
8.5	0.0325	0.0425	-0.0750
9	0.0107	0.0191	-0.0298
9.2	0.0041	0.0147	-0.0188
9.5	0.000088	0.0001	-0.00019
10	0.000008	0.000008	-0.000015
10.5	0.000176	0.000181	-0.000357

**Table S1.** DFT-calculations of the principle components of the traceless electric field gradient (EFG) tensor at the aluminum nucleus for the [AlCl<sub>4</sub><sup>-</sup>]-coronene bilayer system with varying interlayer spacings.

## <u>References</u>

1 A. C. Forse, J. M. Griffin, V. Presser, Y. Gogotsi and C. P. Grey, J. Phys. Chem. C, **2014**, 118, 7508–7514.