

Unraveling the multivalent Aluminium-ion redox mechanism in 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA)

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Supporting information

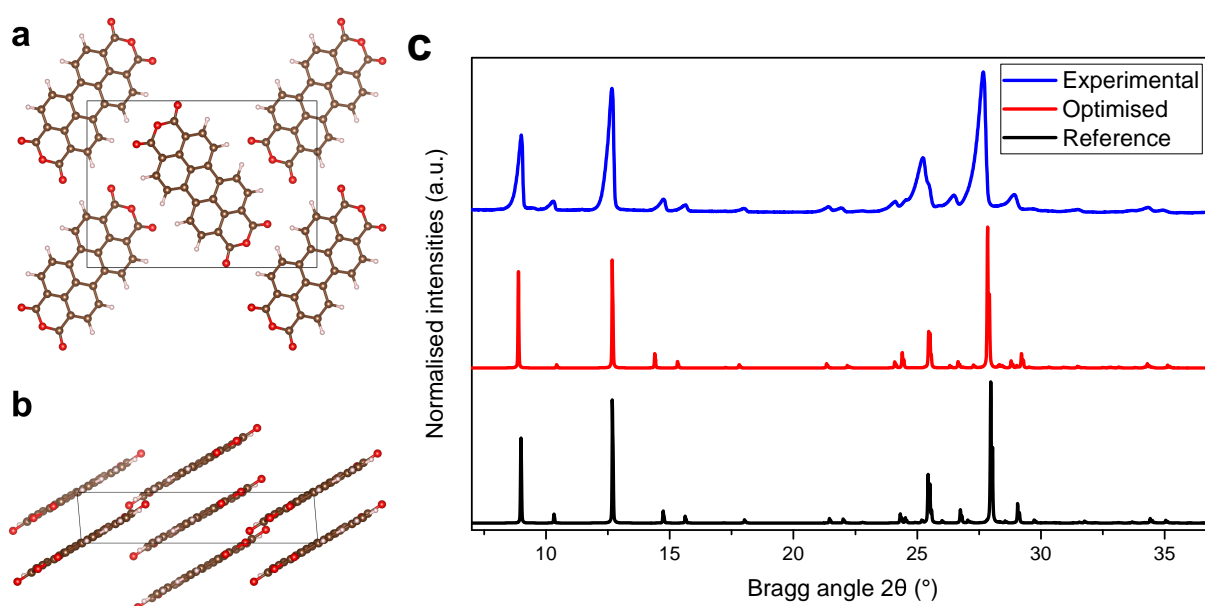


Figure S1: (a,b) Optimised geometry of the α -PTCDA unit cell, projected along the a (top) and b (bottom) crystallographic axes (colour scheme: C = brown, H = white, O = red). The individual PTCDA molecules are arranged in the typical 'herringbone' configuration and the molecular planes are all parallel, which is consistent with the known structure of the α -polymorph. (c) Comparison between the X-ray diffraction data predicted by the literature reference, [1] the relaxed structure calculated by Density Functional Theory (DFT), and the experimental powder diffraction data of the PTCDA sample used in this publication.

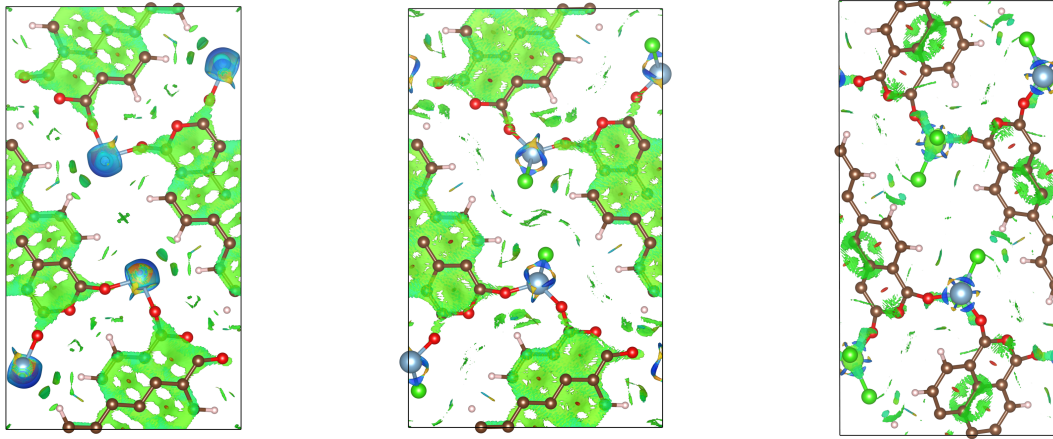


Figure S2: Visualisation of non-covalent interactions of PTCDA intercalated with Al^{3+} (left), AlCl_2^+ (center), AlCl_2^+ (right), using the method developed by Contreras-García *et al.*[2] The green regions overlapping the aromatic regions of the PTCDA molecules represent π - π -stacking interactions in the lattice. It can be seen that the AlCl_2^+ -intercalated structure presents the strongest interactions, as indicated by the fuller regions. On the other hand, the intermolecular interactions are greatly reduced in the case of AlCl_2^+ intercalation. Isosurfaces value: 0.3.

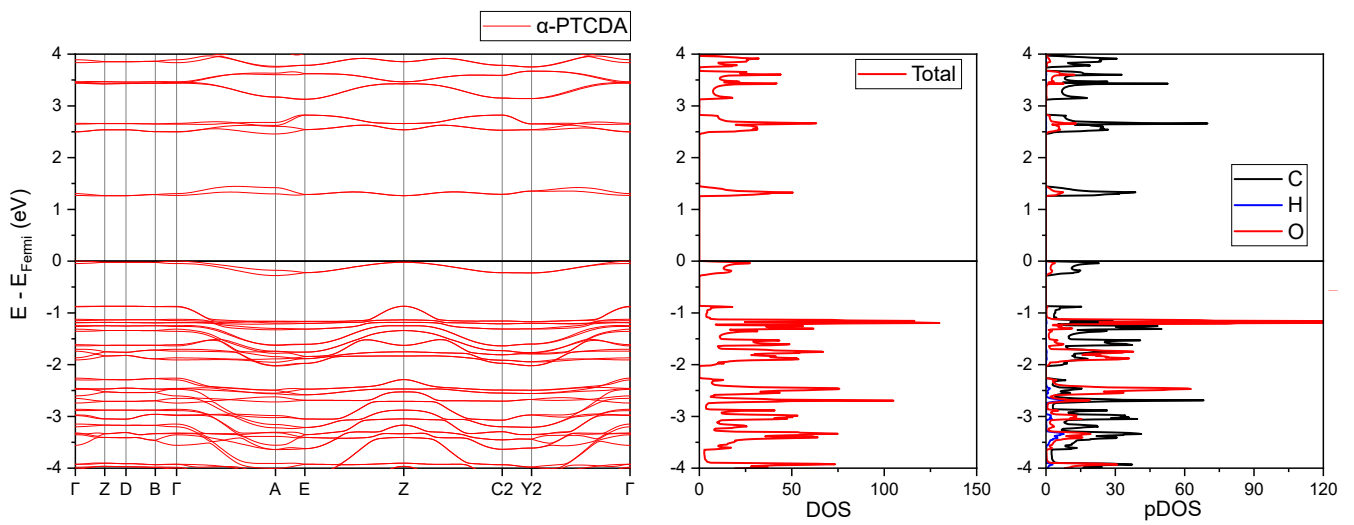


Figure S3: Band diagram, density of states (DOS) and projected density of states (pDOS) for the calculated structure of α -PTCDA.

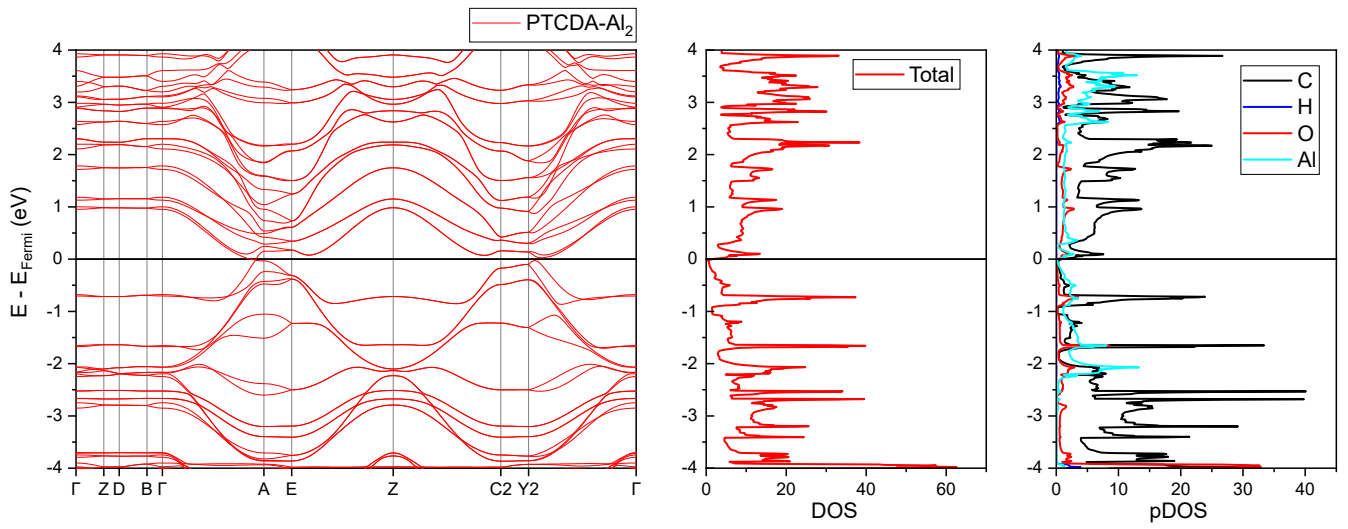


Figure S4: Band diagram, density of states (DOS) and projected density of states (pDOS) for the calculated structure of PTCDA- Al_2 .

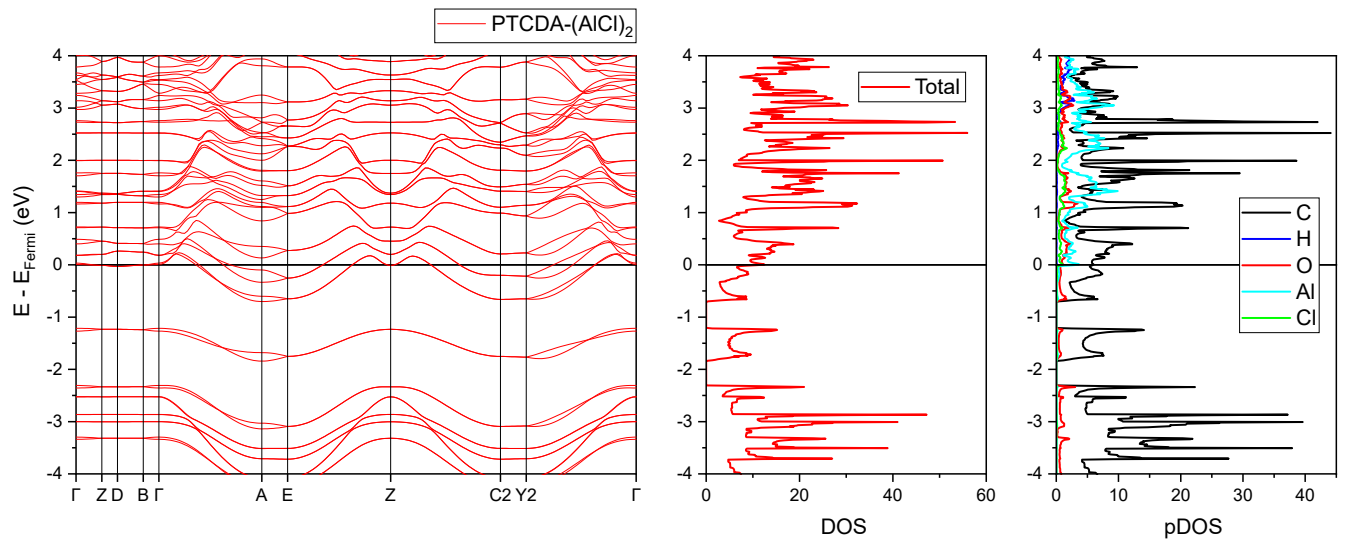


Figure S5: Band diagram, density of states (DOS) and projected density of states (pDOS) for the calculated structure of PTCDA- $(\text{AlCl})_2$.

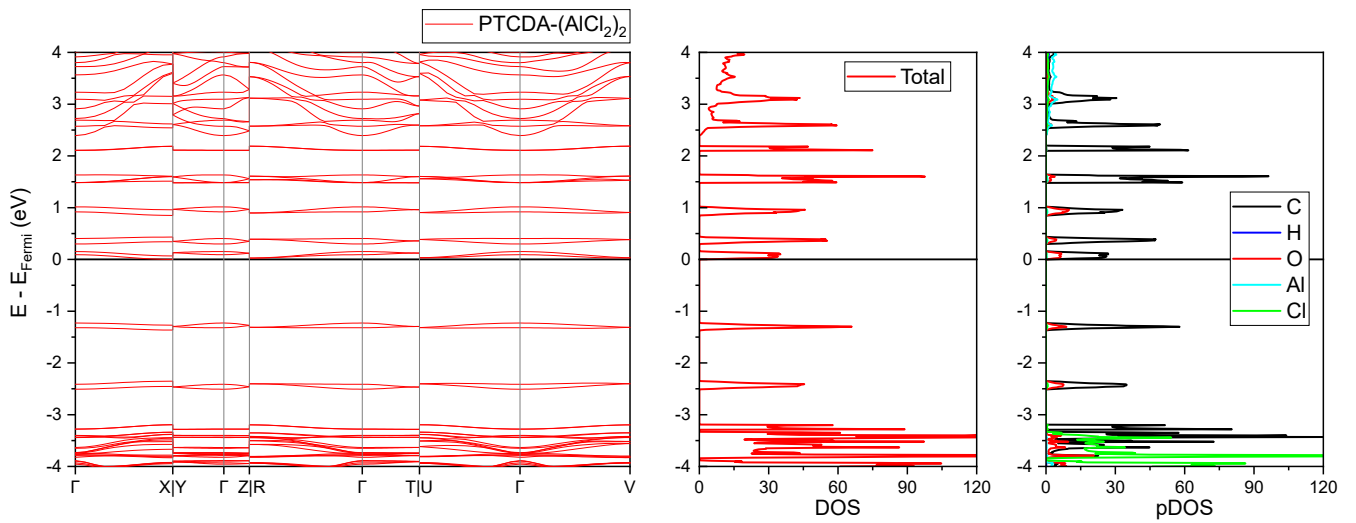


Figure S6: Band diagram, density of states (DOS) and projected density of states (pDOS) for the calculated structure of PTCDA- $(\text{AlCl}_2)_2$.

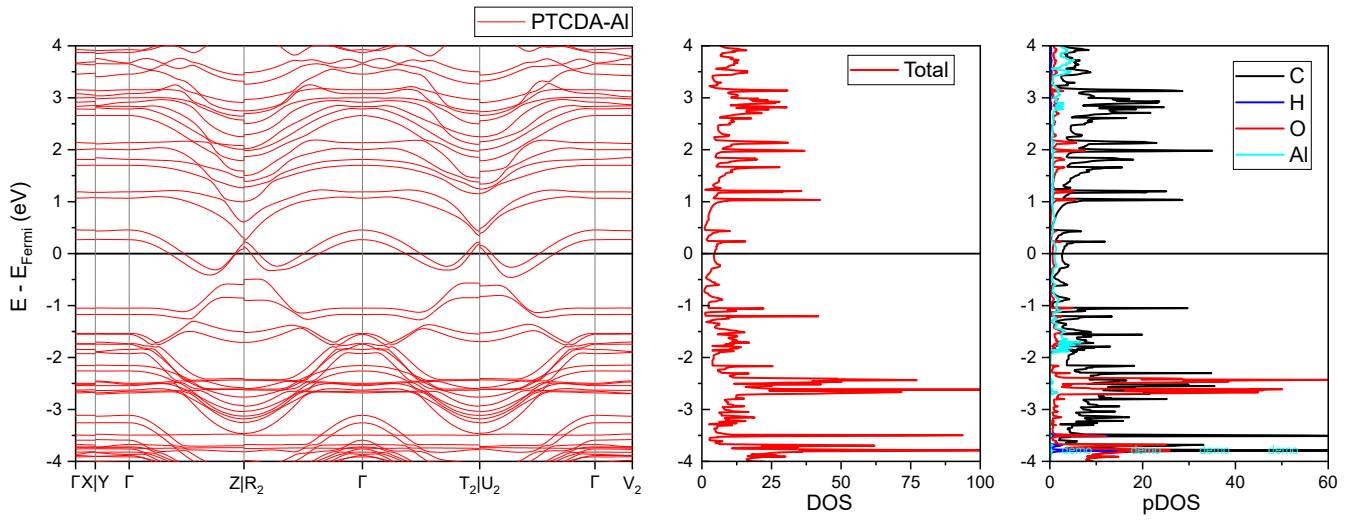


Figure S7: Band diagram, density of states (DOS) and projected density of states (pDOS) for the calculated structure of the partially intercalated structure PTCDA-Al.

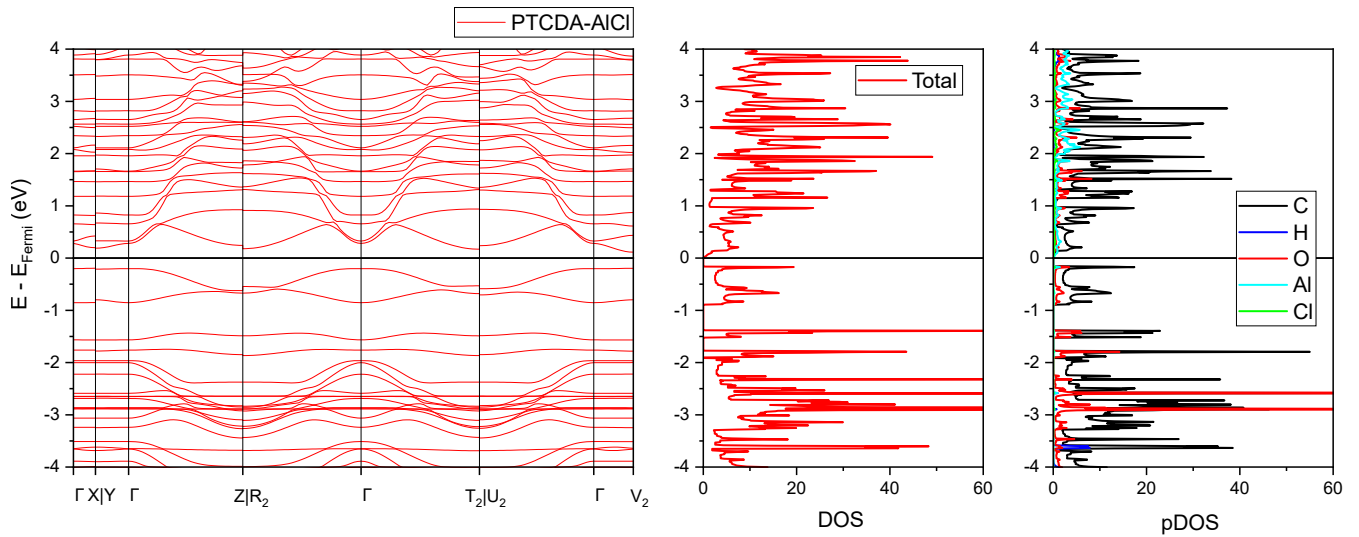


Figure S8: Band diagram, density of states (DOS) and projected density of states (pDOS) for the calculated structure of the partially intercalated structure PTCDA-AlCl.

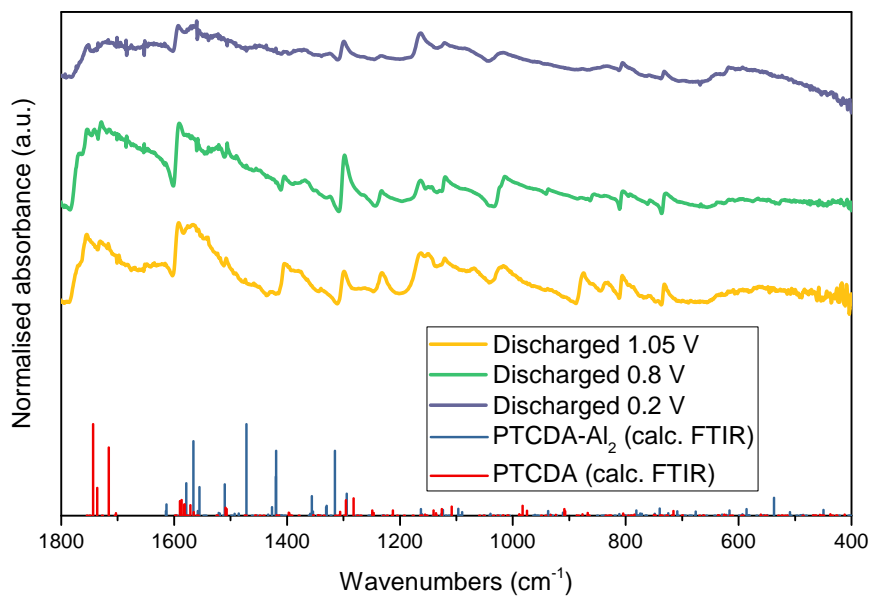


Figure S9: Predicted FT-IR spectra for PTCDA and PTCDA-Al₂, compared with the experimental FT-IR spectra of the PTCDA cathode discharged at different voltages. Although some of the experimental peaks can be attributed to the pristine PTCDA material, the predicted spectrum for PTCDA-Al₂ shows poor agreement with the acquired data, thus further disproving the intercalation of Al³⁺ as the redox mechanism.

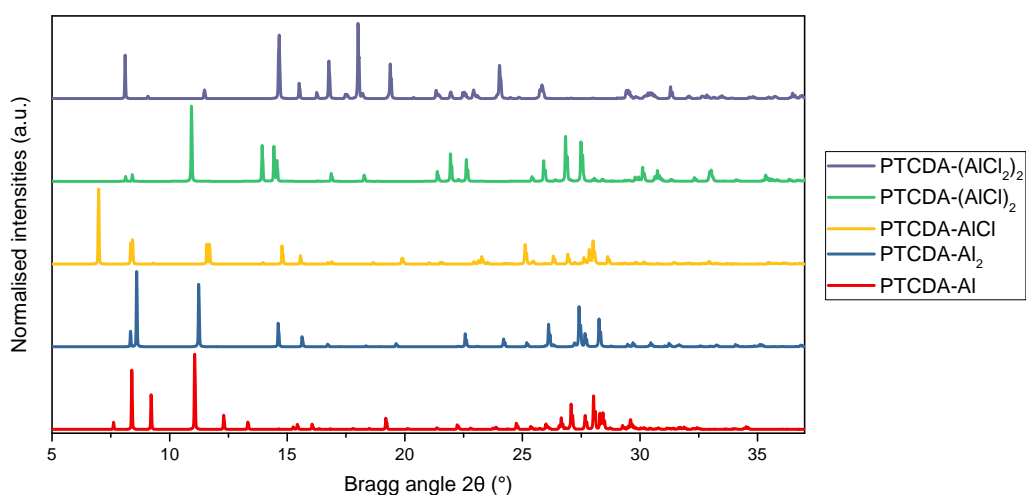


Figure S10: Predicted X-ray diffractograms for the intercalated PTCDA structures.

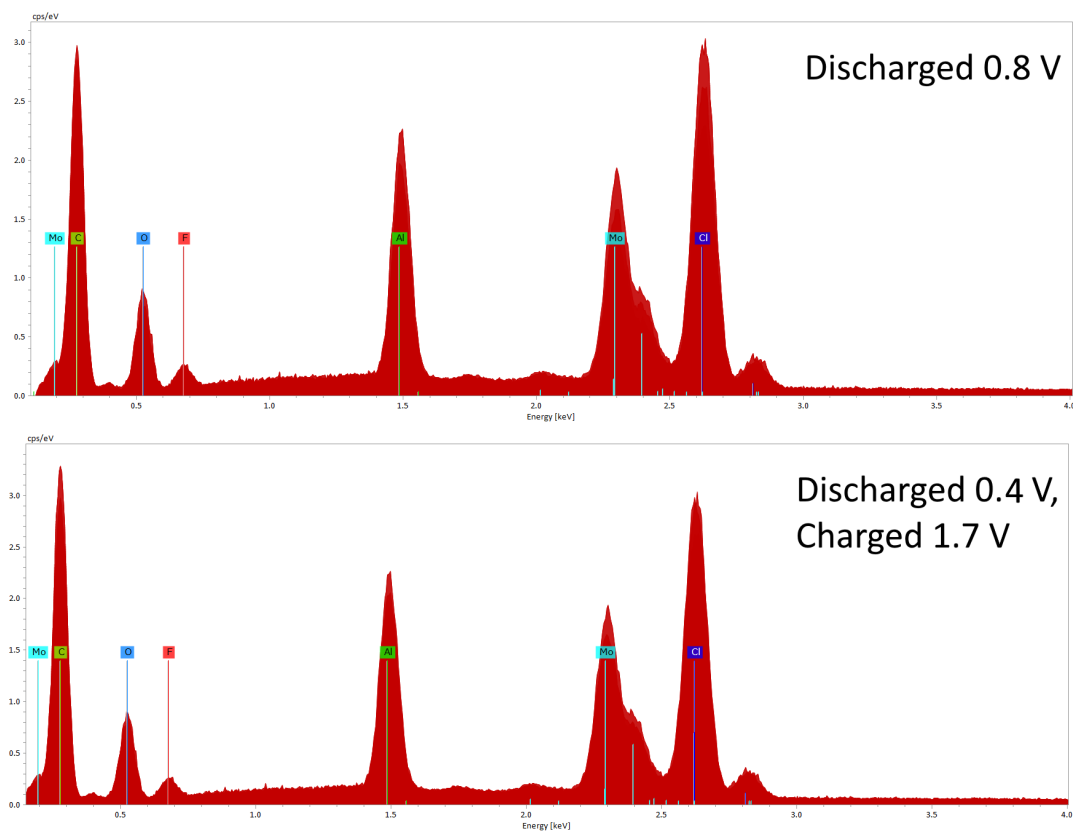


Figure S11: EDX spectra for partially discharged and discharged-charged PTCDA cathodes. the Mo and F peaks are relative to the metallic current collector and the fluorinated binder polymer, respectively.

Sample	C:Al ratio	Al:Cl ratio
Discharged 0.8 V	35.3:1	1:2.08
Discharged 0.4 V	27.3:1	1:1.58
Discharged 0.4 V, Charged 1.7 V	47.7:1	1:1.98

Table S1: EDX Atomic ratios of the cycled PTCDA cathodes. The C:Al ratio is consistent with a progressive increase of Al content in the cathode as discharge progresses, and a decrease upon re-charge. The Al:Cl ratio is consistent with the presence of residual chloroaluminate ions, resulting in a value larger than 1.

References

- [1] K. Tojo and J. Mizuguchi, "Refinement of the crystal structure of -3,4:9,10-perylenetetracarboxylic dianhydride, C₂₄H₈O₆, at 223 K," *Zeitschrift für Kristallographie - New Crystal Structures*, vol. 217, pp. 253–254, June 2002. Publisher: De Gruyter (O).
- [2] J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan, and W. Yang, "NCI-PLOT: A Program for Plotting Noncovalent Interaction Regions," *Journal of Chemical Theory and Computation*, vol. 7, pp. 625–632, Mar. 2011. Publisher: American Chemical Society.