

Supporting information for:

Paving the way for future Ca metal batteries through comprehensive electrochemical testing of organic polymer cathodes

Olivera Lužanin^{1,2}, Anja Kopač-Lautar¹, Tjaša Pavčnik^{1,2}, Jan Bitenc^{1,2*}

¹National Institute of Chemistry, Hajdrihova 19, 1000, Ljubljana, Slovenia

²Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000, Ljubljana, Slovenia

Corresponding author: jan.bitenc@ki.si

Salt synthesis and characterization

Synthesis and work-up were performed in an Ar-filled glovebox with water and oxygen levels below 0.1 ppm. Ca[B(hfip)₄]₂·4DME was synthesized through a previously reported procedure,¹ with a modified salt isolation method. Ca(BH₄)·2THF powder was dissolved in 10 ml of anhydrous DME. 4.5 ml of anhydrous HFIP was dropwise added over a period of 30 minutes into the stirred solution. The resulting solution was stirred at room temperature for 20 h. The DME was evaporated under reduced pressure to obtain the concentrated solution, which was added to hexane, to precipitate a solid product. Salt was filtered, and dried in vacuum at 50 °C for two days to obtain white powder. NMR and IR characterization (Figure S1) is consistent with data from the literature. Electrolyte was prepared by weighing the appropriate amount of salt into volumetric flasks and diluting it up to the mark obtaining 0.2 M Ca[B(hfip)₄]₂ in DME.

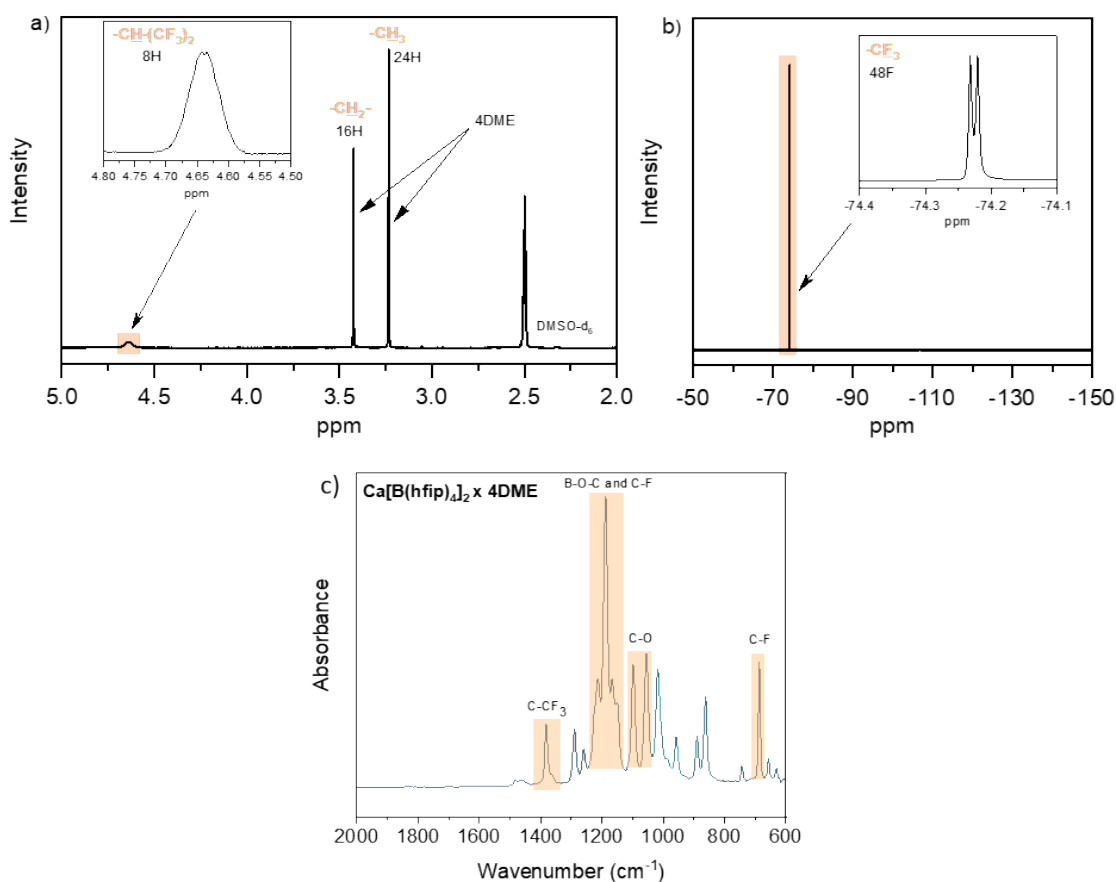


Figure S1: ^1H (a) and ^{19}F (b) NMR spectra of $\text{Ca}[\text{B}(\text{hfip})_4]_2 \cdot 4\text{DME}$ salt with peak assignment. Spectra were measured on a Bruker AVANCE NEO 600 MHz NMR spectrometer using $\text{DMSO-}d_6$ solvent. IR spectrum (c) of $\text{Ca}[\text{B}(\text{hfip})_4]_2 \cdot 4\text{DME}$ salt with peak assignment. Measurement was performed under an inert atmosphere using an ATR-IR Alpha II (Bruker) equipped with a Ge crystal.

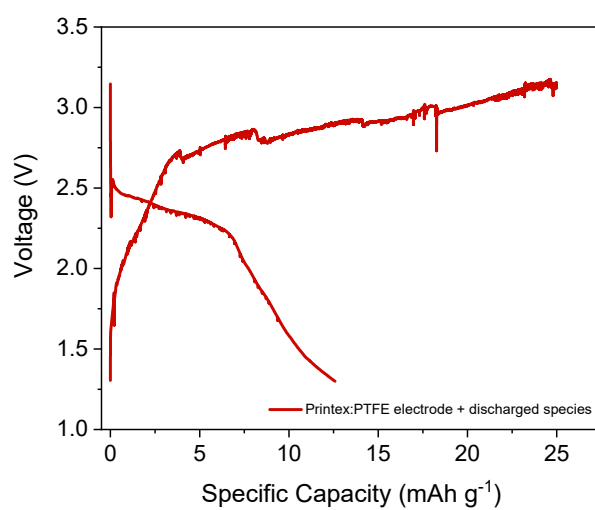


Figure S2. Galvanostatic curve of Printex:PTFE electrode in electrolyte with added dissolved NTCD discharge species obtained at 10 mA g^{-1} .

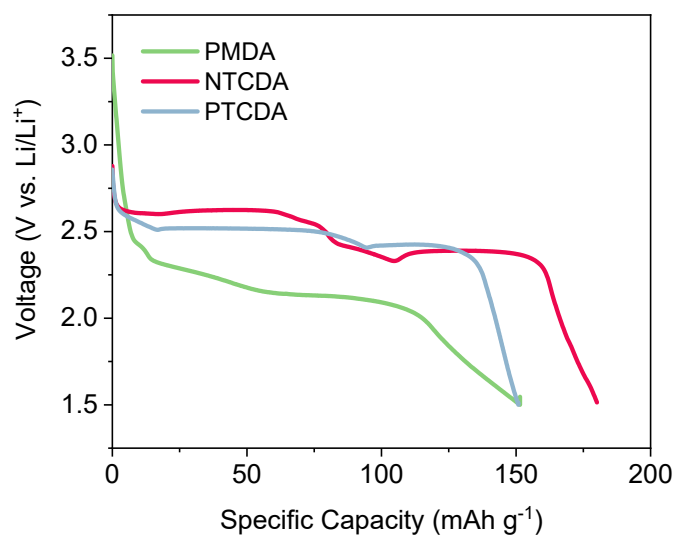


Figure S3. Galvanostatic discharge curves of PMDA (green), NTCDA (red), and PTCDA (blue) in 1 M LiTFSI (DOL:DME, 1:1, v/v) at the current density of 50 mA g⁻¹.

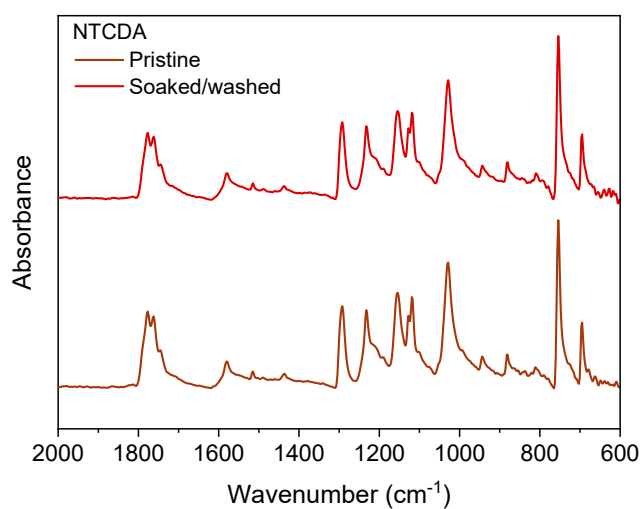


Figure S4. Infrared spectra of pristine NTCDA electrode and NTCDA electrode that has been soaked in 0.2 M Ca[B(hfip)₄]₂/DME for 12 h and then washed in DME, demonstrating that washing and soaking do not affect the material's structure.

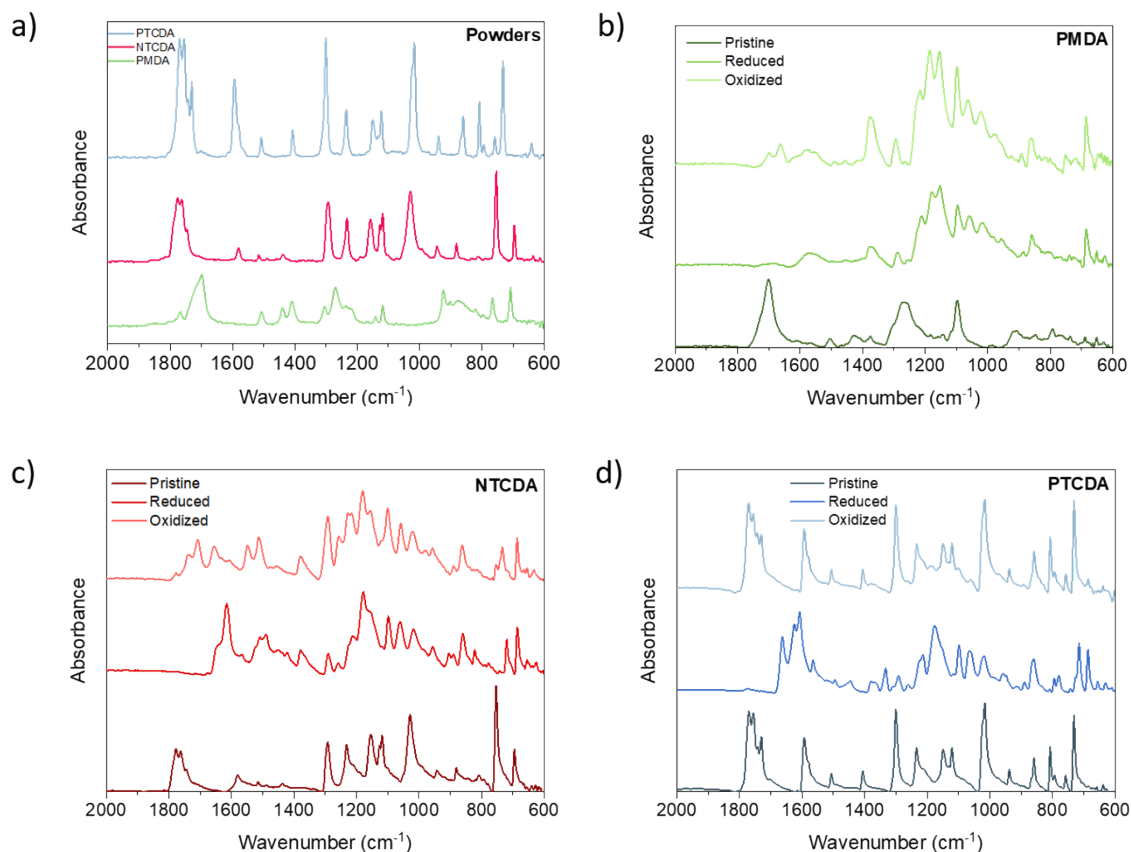


Figure S5. Infrared spectra of PMDA (green), NTCDA (red), and PTCDA (blue) active materials (a). Recorded FTIR spectra of pristine, discharged, and charged electrodes for PMDA (b), NTCDA (c), and PTCDA (d).

P-NTCDA and P-PTCDA synthesis and characterization

Polymers were synthesized according to the previously published procedure.² Imidazole (17.7 g) and the anhydride (1.0 mmol) were added to the round-bottom flask. After the solids, amine (1.0 mmol) was added to the flask. The reaction flask was sealed and the mixture was heated to 130 °C and stirred for 24 h. After cooling down, the solid was diluted with 300 ml of deionized water and centrifuged. The solid residue was additionally rinsed two times with 300 ml of acetone. After drying at 80 °C overnight, Soxhlet purification was performed in chloroform for three days. The solid was then dried in vacuum at 120 °C overnight.

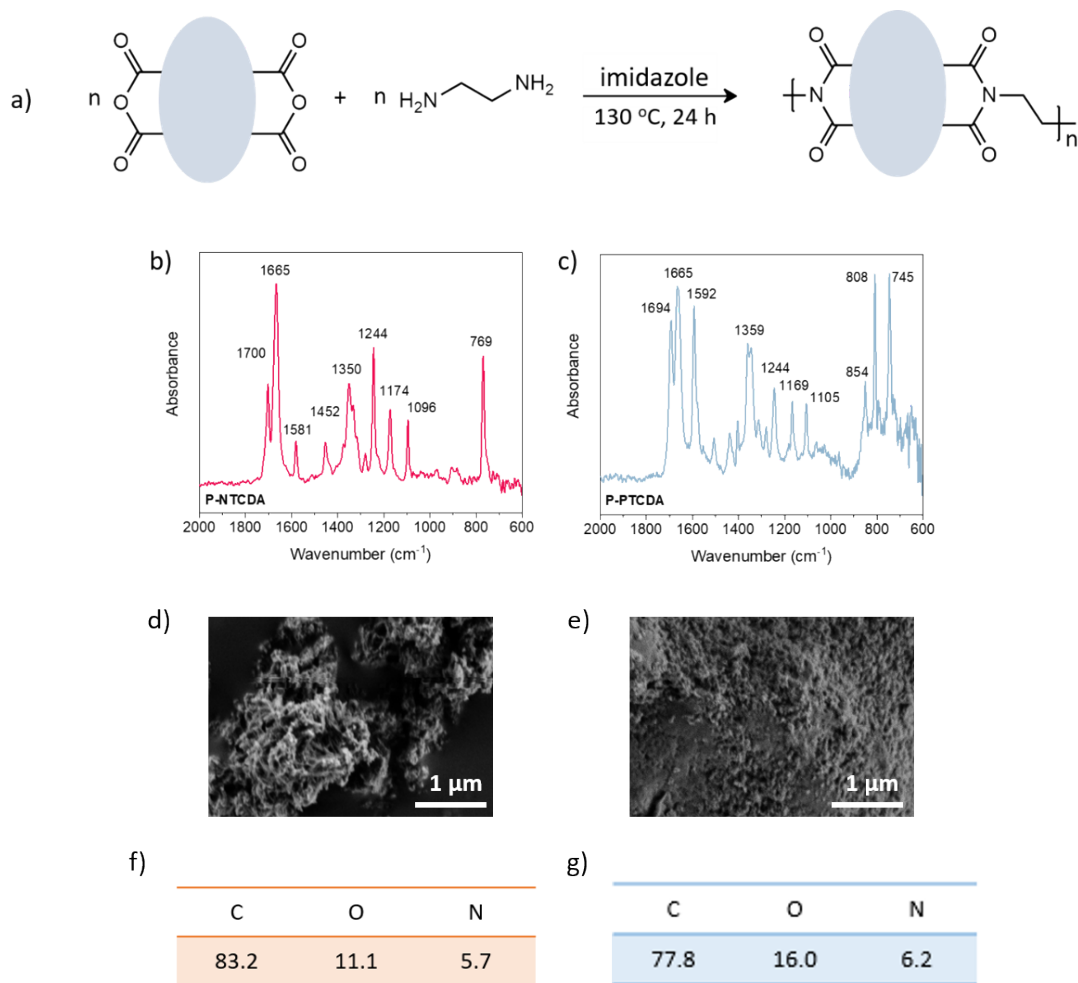


Figure S6. General synthetic scheme of imide polymers (a). Infrared spectra of P-NTCDA (b) and P-PTCDA (c) powders. SEM images of P-NTCDA (d) and P-PTCDA (e) powders. Atomic percentages obtained from EDS analysis on P-NTCDA (f) and P-PTCDA (g) powders.

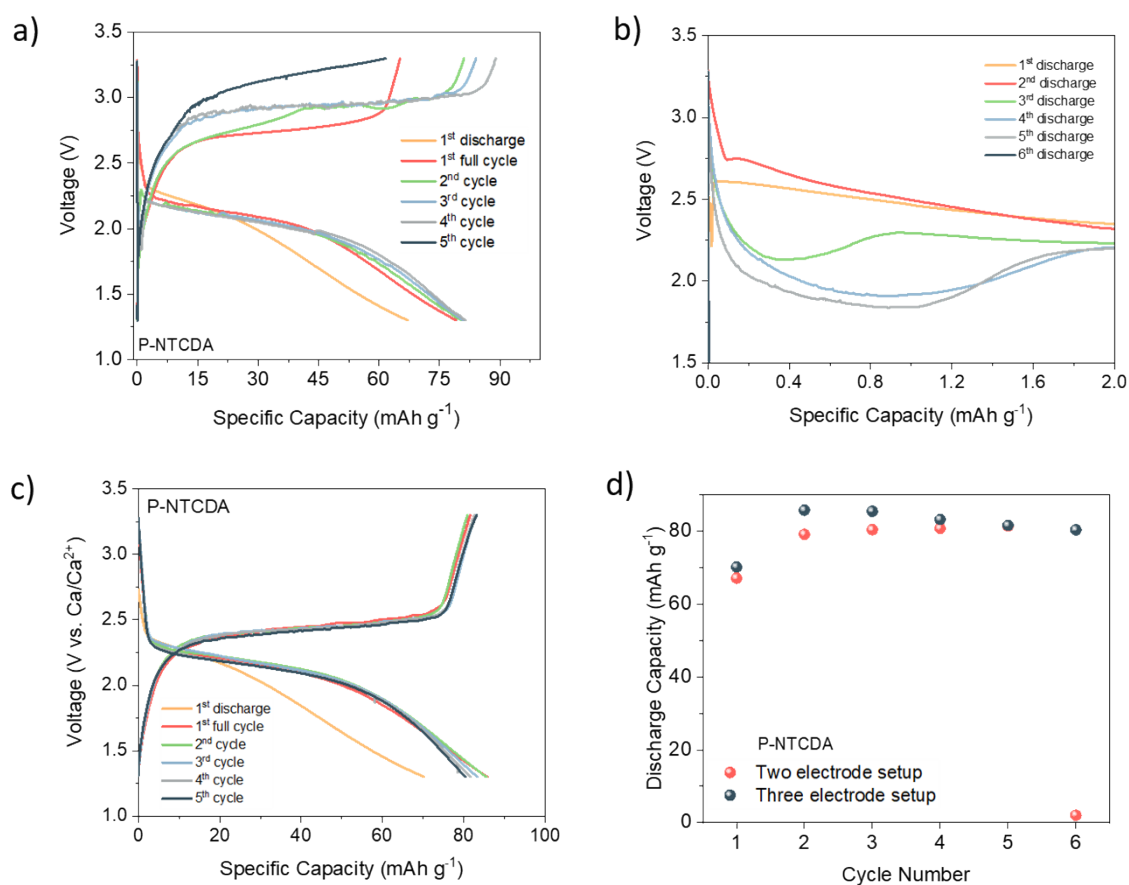


Figure S7. Galvanostatic cycling of P-NTCDA in two-electrode setup (a). Voltage dip at the beginning of discharge half-cycle in two electrode cell (b). Cells were cycled with a current density of 50 mA g⁻¹. Galvanostatic cycling in three-electrode setup (c). Discharge capacity evolution with the cycle number for two- and three-electrode cells (d).

Electrochemical performance of polyimides in 1 M LiTFSI

LiTFSI (Sigma-Aldrich, 99.95%) was dried overnight under a vacuum at 180 °C. An appropriate amount of salt was dissolved in a 1:1 volume ratio of 1,3-dioxolane (DOL) (Acros, 99.8%) and 1,2-dimethoxyethane (DME) (Honeywell). Both solvents were dried for several days with 4 Å molecular sieves, then refluxed with Na/K alloy (ca. 1 ml l⁻¹) overnight, and then distilled and stored under an Ar atmosphere. The final water content was below 1 ppm, determined by Karl-Fischer titration.

Electrochemical testing was performed in the Swagelok-type cells. One glassy fiber GF/A (13 mm) and one Celgard 2400 (25 μm, 13 mm) were used as separators. Lithium (110 μm, FMC) was rolled until fine shine and cut into 12 mm discs. Cycling was done in the electrochemical window from 1.5 to 3.5 V with a current density of 50 mA g⁻¹.

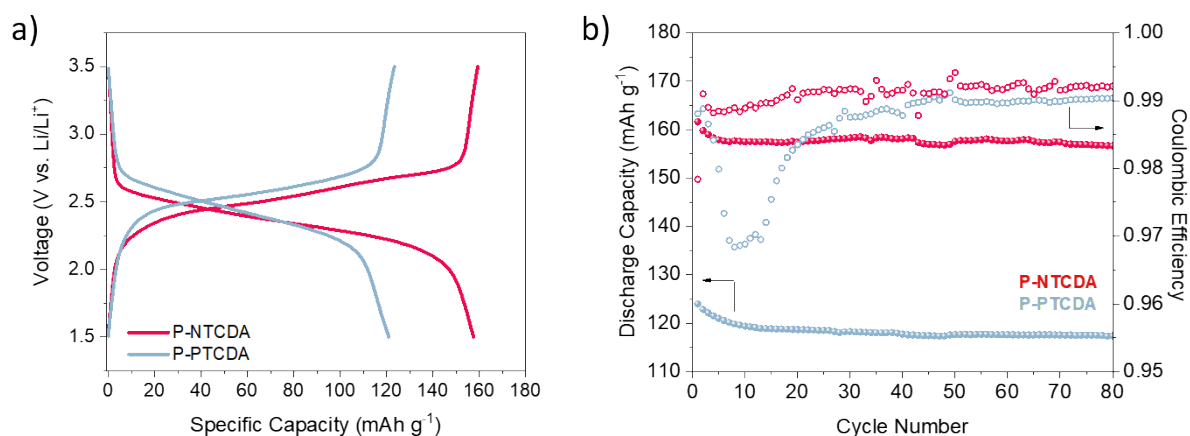


Figure S8. Galvanostatic profiles of P-NTCDA and P-PTCDA Li half-cells obtained at 50 mAh g⁻¹ (5th cycle shown) (a). Capacity retention and Coulombic efficiency at 50 mAh g⁻¹ in 1 M LiTFSI DOL:DME (1:1, v/v) (b).

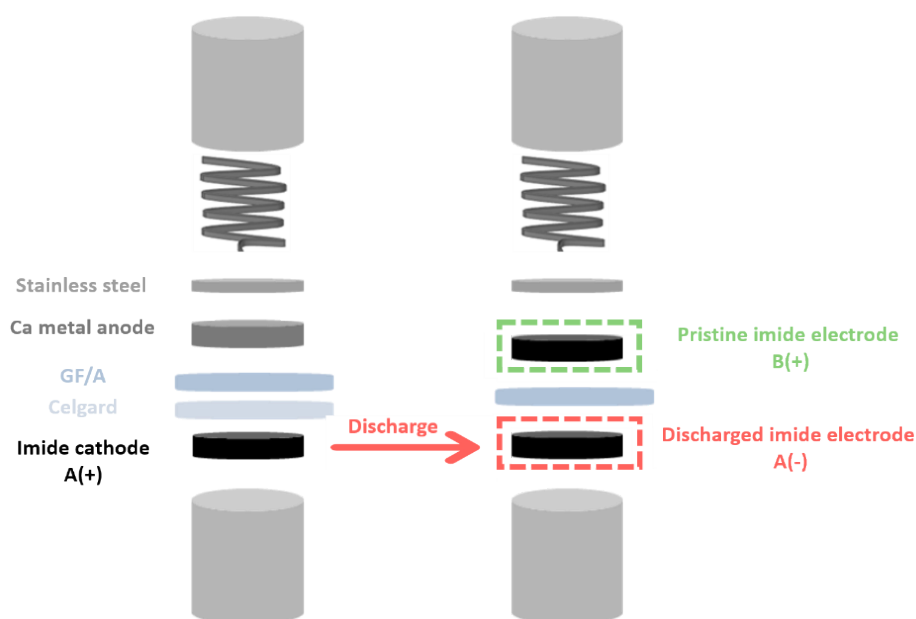


Figure S9. Schematics of symmetric cell assembly.

Symmetric cells were subjected to rate capability tests (C/5, C/2, 1C, 2C, 5C, 10C, 20C, 50C) and stability test (100 cycles at C/2).

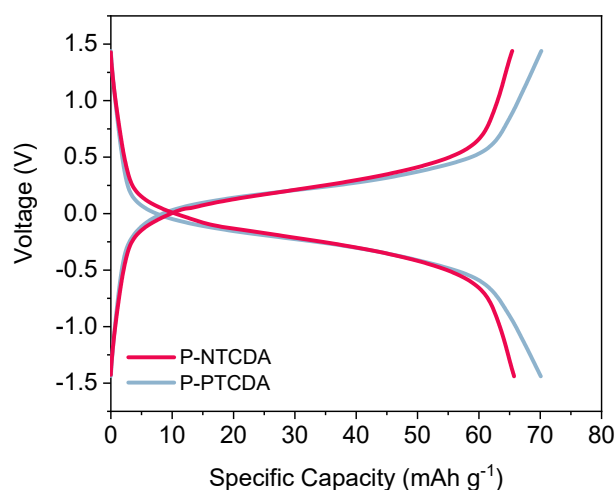


Figure S10. GCPL curves (5th cycle) for P-NTCDA (red) and P-PTCDA (blue) polymers obtained at C/2 in symmetric cell setup in 0.2 M Ca[B(hfip)₄]₂/DME.

Infrared spectra of soaked and carbon black electrodes

To exclude any peaks potentially coming from carbon black or PTFE binder, we have performed FTIR measurements under the same conditions as for composite electrodes with electrode containing carbon black and PTFE binder in a mass ratio of 3:1. The spectrum shows an elevated baseline, but no peaks stemming from these materials in the span from 2000-600 cm⁻¹.

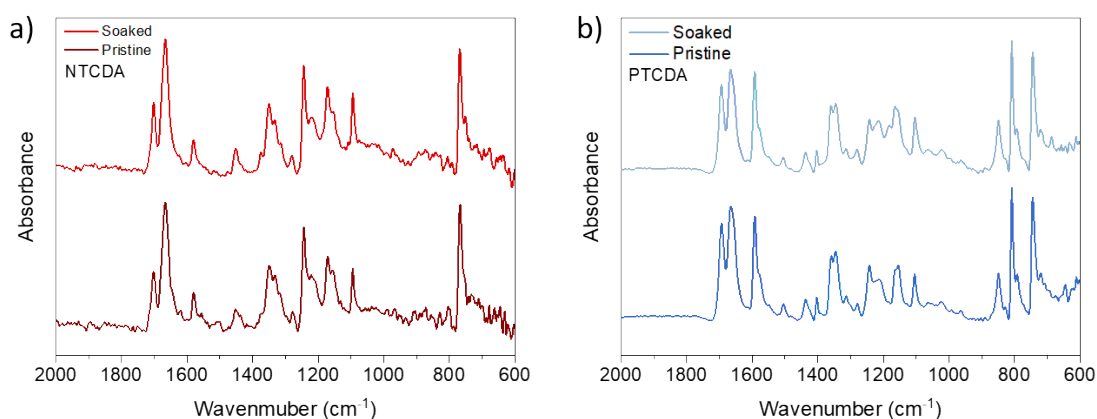


Figure S11. FTIR spectra of pristine and soaked P-NTCDA (a) and P-PTCDA electrodes (b).

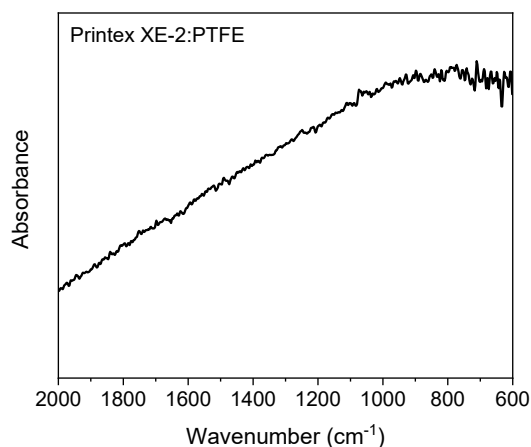


Figure S12. FTIR spectrum of the electrode containing Printex and PTFE binder in ratio 3:1.

To demonstrate that the soaking alone doesn't bring any detectable changes, we have soaked P-PTCDA and P-NTCDA electrodes in 0.2 M $\text{Ca}[\text{B}(\text{hfi})_4]_2/\text{DME}$ overnight. After soaking, electrodes were washed two times in DME, to remove the residual salt and then dried for 2 hours inside the glovebox. A comparison of infrared spectra of pristine and soaked electrodes shows no significant differences.

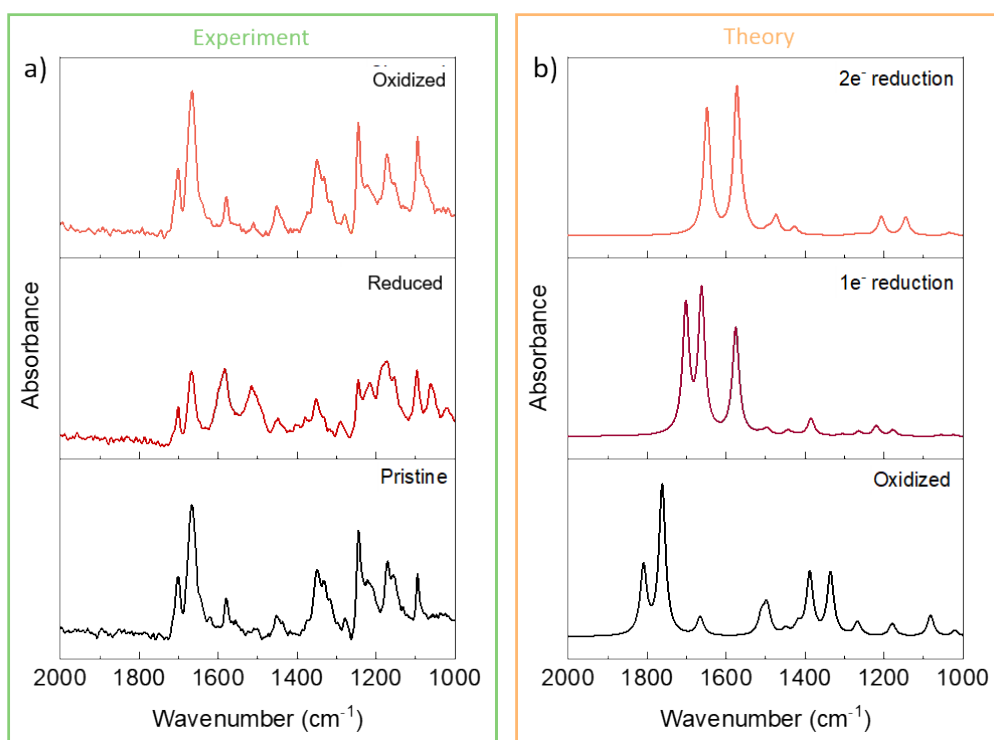


Figure S13. Experimental (a) and theoretical (b) spectra of P-NTCDA.

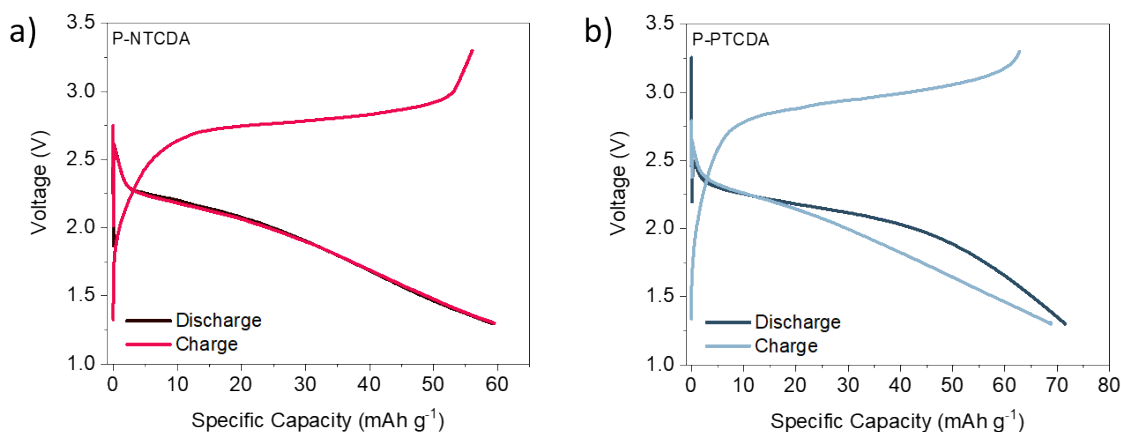


Figure S14. Galvanostatic profiles of P-NTCDA (a) and P-PTCDA (b) electrodes used for SEM/EDS analysis.

EDS analysis of discharged cathode should be considered as a qualitative tool for the rough assessment of coordinating species rather than an absolute quantitative approach. The approach presented here is based on two premises:

- 1) Complete insolubility of all electrode components will be presumed.
- 2) In the discharged electrode, we assume the presence of only three species – P-NTCDA, $\text{P-NTCDA}^{2-}\text{-Ca}^{2+}$, and $\text{P-NTCDA}^{2-}\text{-}2[\text{Ca}(\text{B}(\text{hfip})_4)^+]$. The same goes for the P-PTCDA compound.

In the polyimide electrodes, there is 60% of active material and 40% of inactive components (Printex XE2 and PTFE binder).

$$M(\text{P-NTCDA}) = 292 \text{ g mol}^{-1}$$

$$M(\text{P-NTCDA}^{2-}\text{-Ca}^{2+}) = 332 \text{ g mol}^{-1}$$

$$M(\text{P-NTCDA}^{2-}\text{-}2[\text{Ca}(\text{B}(\text{hfip})_4)^+]) = 1730 \text{ g mol}^{-1}$$

$$M(\text{P-PTCDA}) = 416 \text{ g mol}^{-1}$$

$$M(\text{P-PTCDA}^{2-}\text{-Ca}^{2+}) = 456 \text{ g mol}^{-1}$$

$$M(\text{P-PTCDA}^{2-}\text{-}2[\text{Ca}(\text{B}(\text{hfip})_4)^+]) = 1854 \text{ g mol}^{-1}$$

References

- 1 J. Bitenc, A. Scafuri, K. Pirnat, M. Lozinšek, I. Jerman, J. Grdadolnik, B. Fraise, R. Berthelot, L. Stievano and R. Dominko, *Batter. Supercaps*, 2021, **4**, 214–220.
- 2 C. N. Gannett, J. Kim, D. Tirtariyadi, P. J. Milner and H. D. Abruña, *Chem. Sci.*, 2022, **13**, 9191–9201.