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Structurally Engineered EDOT–Porphyrin Electropolymers for Stable and High-Performance Pseudocapacitive Energy Storage

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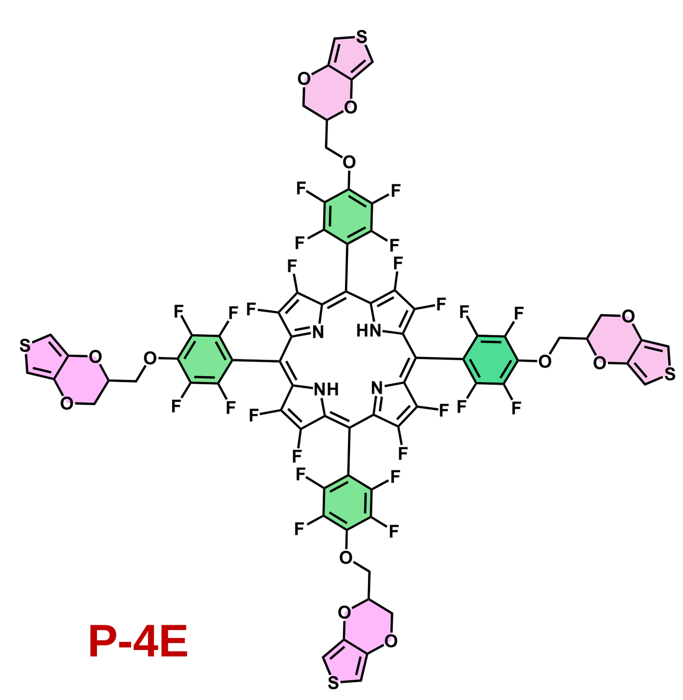
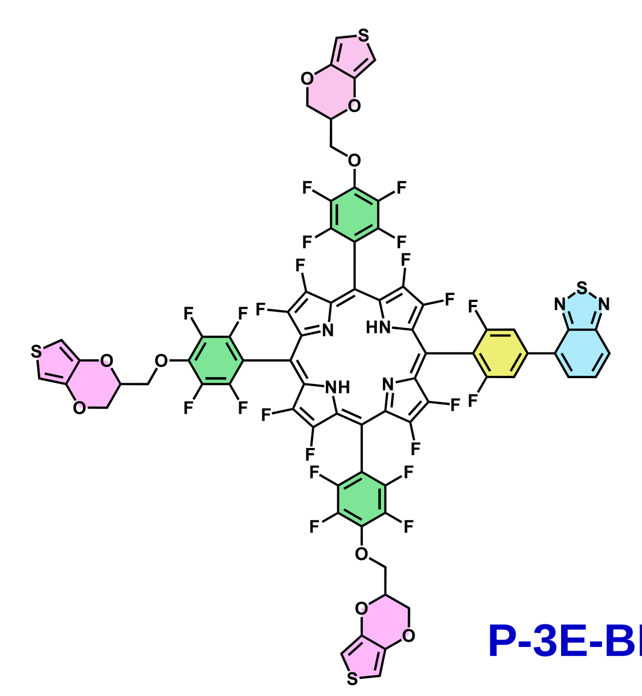
INTRODUCTION & AIM

The development of electrode materials combining high energy and power density with long-term stability remains a key challenge in electrochemical energy storage. Organic pseudocapacitive materials are promising due to their fast redox kinetics, structural tunability, and compatibility with solution-based processing. In this context, electropolymerized conjugated polymers enable the direct formation of binder-free electroactive films with controlled thickness and strong electrical contact.

Porphyrins are particularly attractive redox-active building blocks because of their extended π-conjugation and multielectron redox properties. Fully fluorinated porphyrins offer enhanced electrochemical stability, while functionalization with conjugated units allows their integration into conductive polymer networks. Here, we compare two fluorinated porphyrin monomers, **P-4E** and **P-3E-BDT**, to investigate how the nature and distribution of conjugated substituents affect electropolymer growth, stability, and pseudocapacitive behavior.



P-4E



P-3E-BDT

METHOD

Synthesis of Monomers
P-4E / P-3E-BDT

Electropolymerization (CV)
3-electrode configuration:
- Working (GC/Pt/ITO)
- Pt counter | Ag quasi-ref
- 0.10 M $TBAPF_6$ / DCM
- 0.1 V s^{-1}

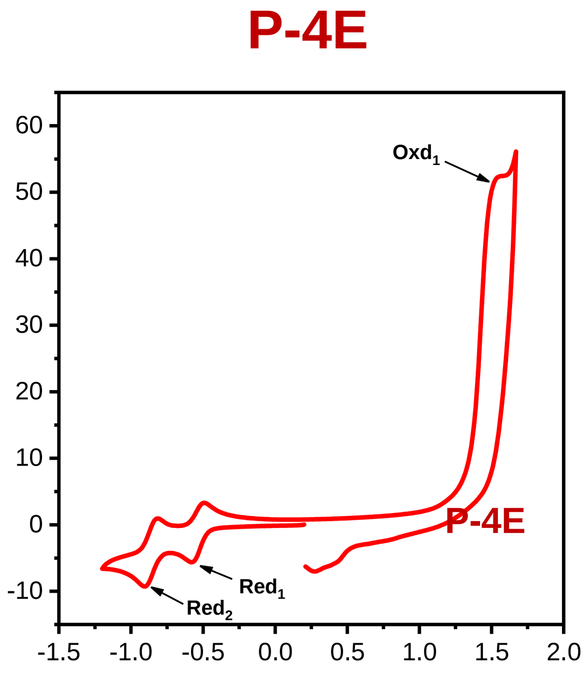
Polymer Films
poly-P-4E / poly-P-3E-BDT
on GC / Pt / ITO

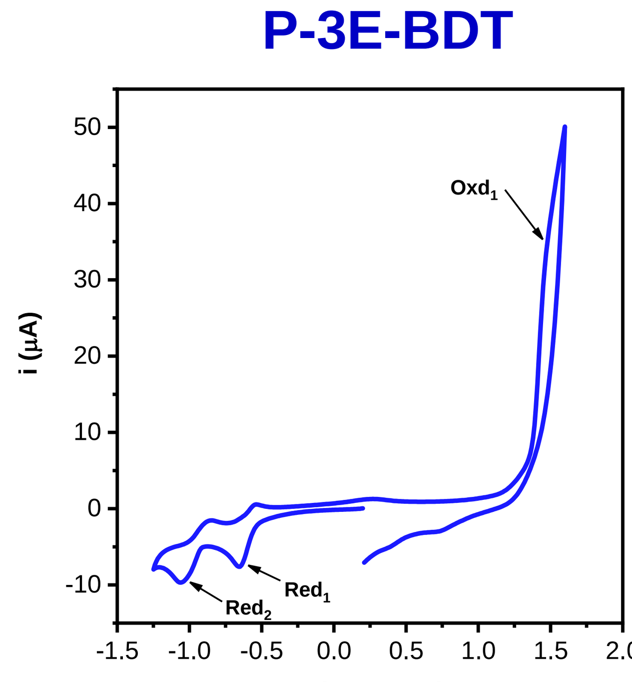
- **Characterization:**
- Redox processes
- UV–Vis Spectroelectrochemistry
- SEM / AFM
- EQCM (mass determination)
- EIS
- GALVANOSTATIC C-D

RESULTS & DISCUSSION

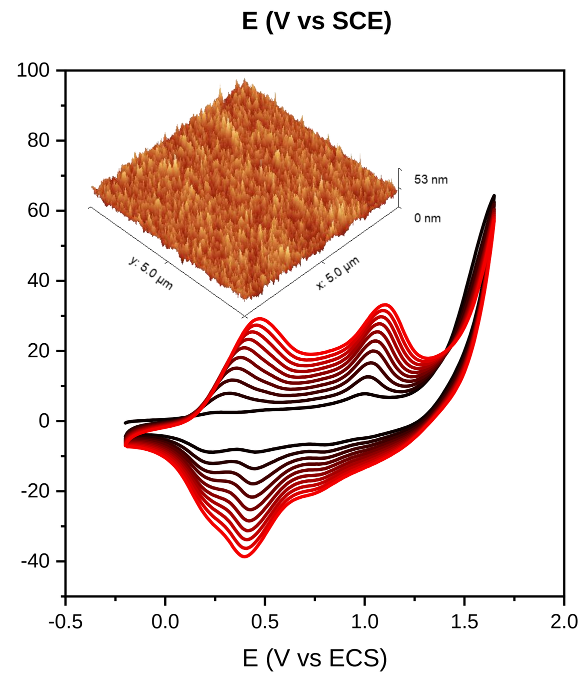
P-4E | P-3E-BDT

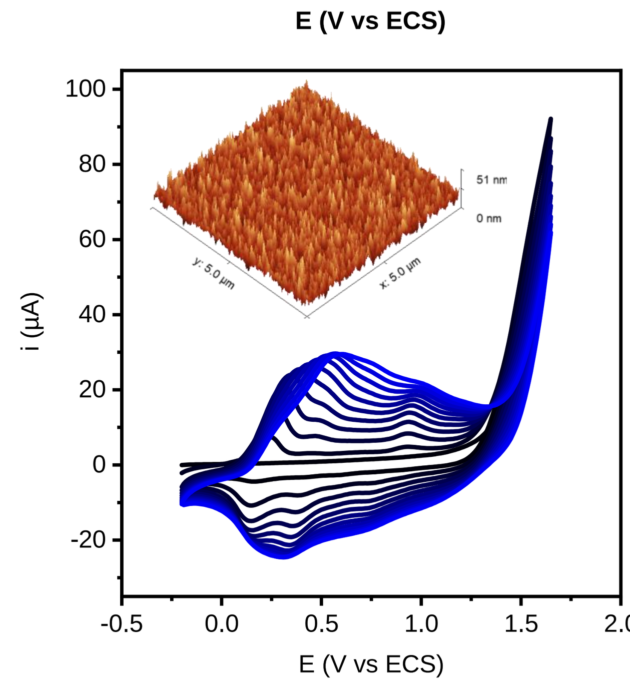
MONOMERS CHARACTERIZATION





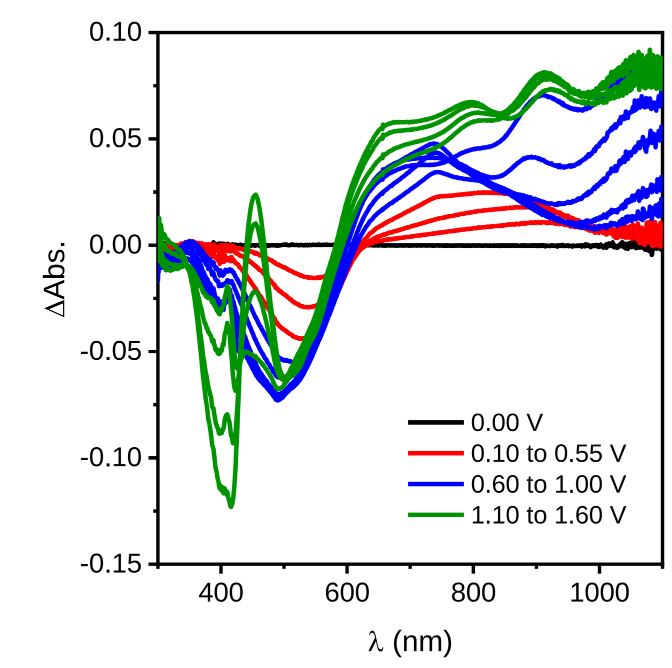
POLYMERS SYNTHESIS

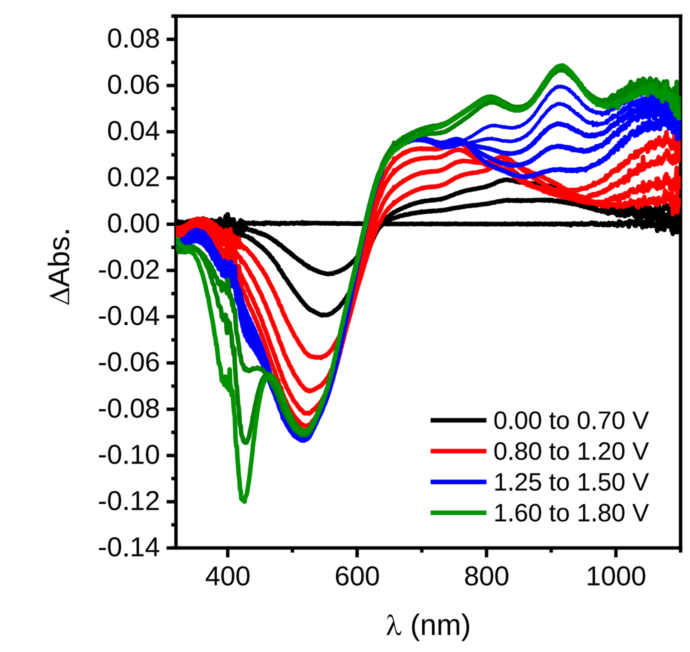




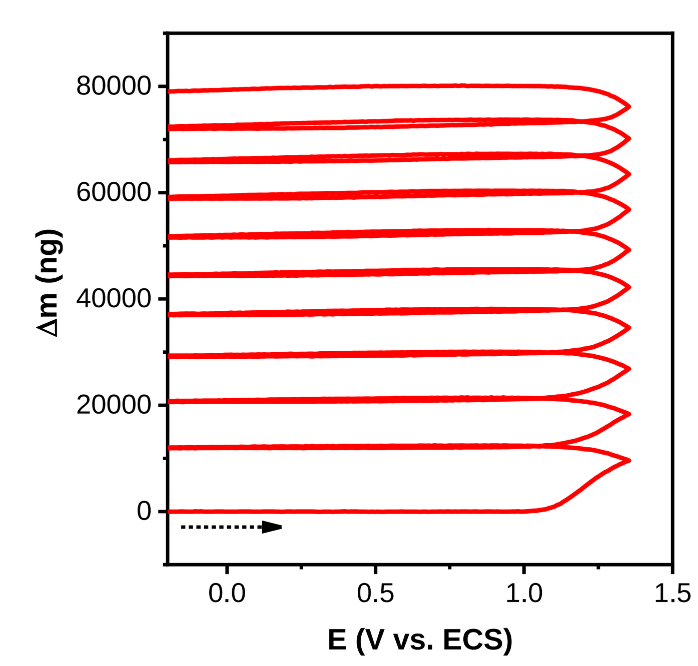
poly-P-4E | poly-P-3E-BDT

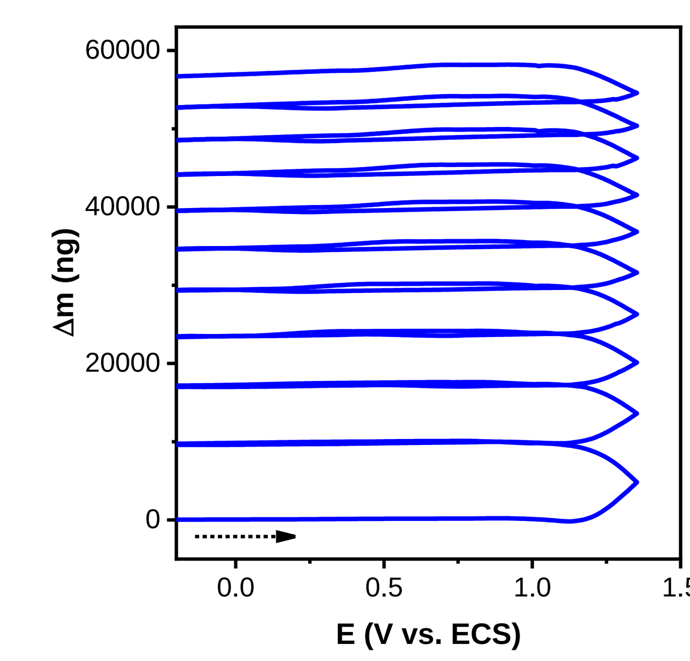
SPECTRO-ELECTROCHEMISTRY



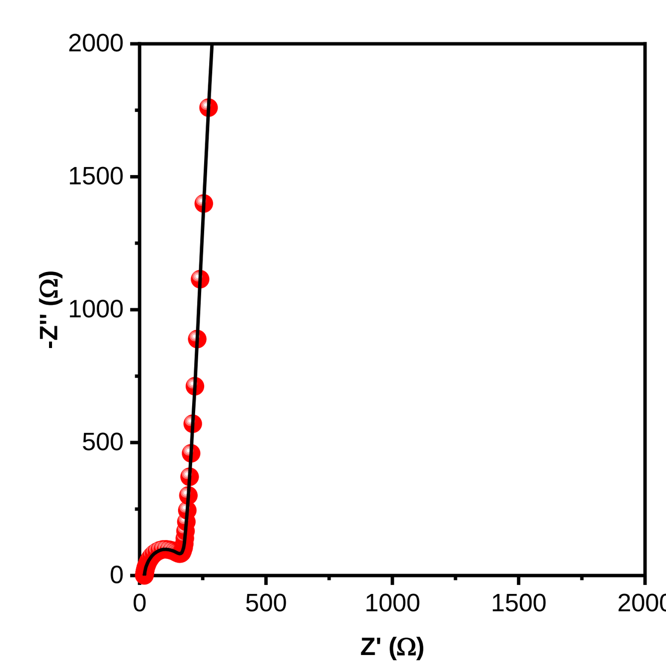


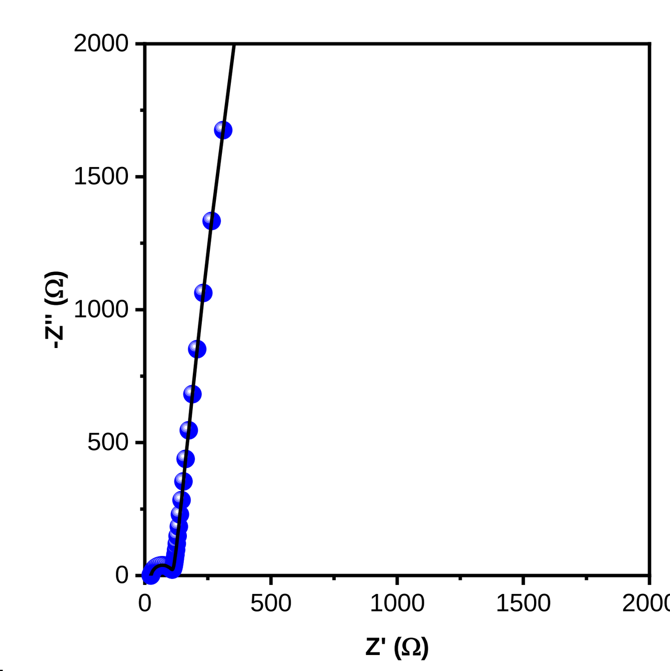
EQCM MASS DETERMINATION





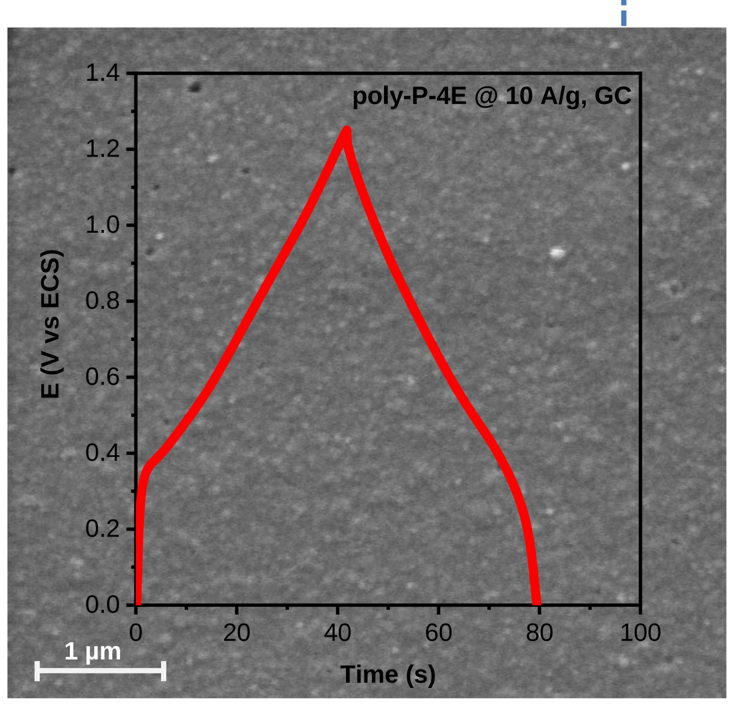
EIS IMPEDANCE SPECTROSCOPY

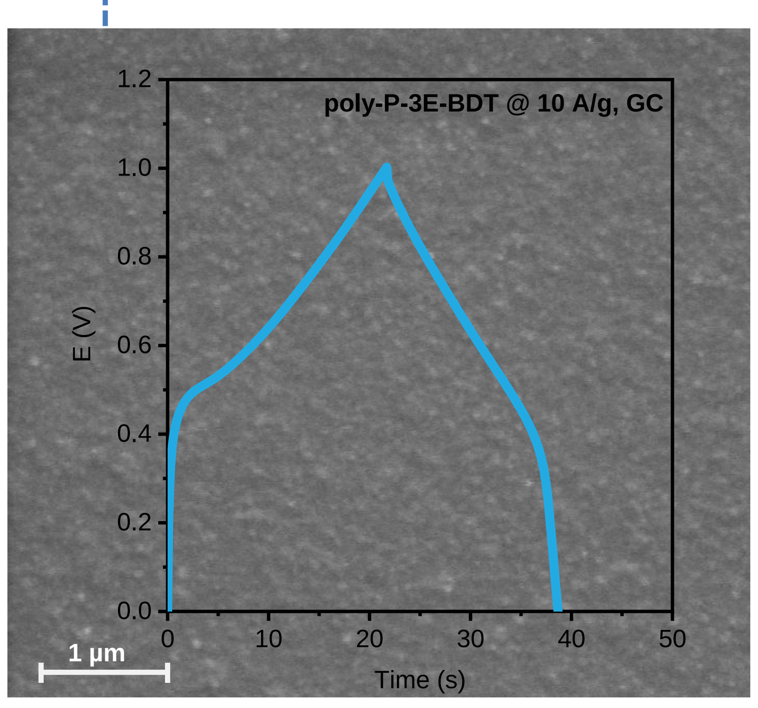




SEM

GALVANOSTATIC CHARGE-DISCHARGE





Polymer	C_{GCD} [a] (F g^{-1})	C_{ret} [b] (%)	C_{EIS} (F g^{-1})	R_S (Ohm)	R_{CT} (Ohm)
poly-P-4E/GC	317	89.7	303	20	176
poly-P-3E-BDT/GC	238	40.3	217	23	102

[a] Performed at 10 A g^{-1}. [b] After 3000 GCD cycles.

CONCLUSION

- Molecular engineering of fluorinated porphyrin electropolymers enables stable, high-performance pseudocapacitive materials.
- EDOT–porphyrin networks show reversible redox behavior and efficient charge storage with good cycling stability.
- The polymer with higher EDOT content (poly-P-4E) exhibits superior gravimetric capacitance and stability.
- Molecular architecture is key, highlighting these systems as promising organic electrode materials for energy storage.