Structural design and characterization paradigms for aqueous-compatible electroactive polymers

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Electrochemical processes in π-conjugated polymers underpin a diverse range of emergent biomedical technologies, such as low-voltage biosensors and drug pumps. Such devices require the active polymer film to undergo rapid, reversible electrochemical "doping" processes in biological milieu. Despite the mounting applied literature in the field, there remains a significant gap in fundamental knowledge regarding how to design aqueous-compatible conjugated polymers with enhanced redox capacity, stability, charge transport, and optimal device performance. Moreover, little work has probed the in situ structural and compositional consequences of electrochemical doping in saline for materials of different structures.

Using a model family of polydioxythiophenes, this study establishes a series of material design principles for aqueous-compatible conjugated polymers. We show how structural properties (e.g. side chain functionality and substitution pattern) drastically influence a polymer's electrochemical characteristics and in a saline electrolyte. Meanwhile, other factors such as side chain length and processing method appear to have minimal impact on the polymer's redox behavior, thermal properties, microstructure, and associated electrochemical device performance. We also report the first utilization of specular neutron reflectivity (NR) to track the swelling and ion transport phenomena in conjugated polymers in situ. NR contrast-matching methods reveal that ions irreversibly penetrate the conjugated polymer films upon doping, and that the extent of swelling and ion distribution in the film is polymer-dependent. Such results, which are supported by in situ electrochemical quartz microgravimetry, sets a precedent for using NR as a new tool for understanding redox dynamics in conjugated polymers in a general sense. This comprehensive study showcases the chemical, physical, and microstructural properties that do (and don't) matter for the development of electroactive polymers capable of interfacing with biological systems.