Abstract of the doctoral thesis

"Thiophene polymers with tailored break of π-conjugated bond featuring tuneable electrochromic properties"

Paulos Asefa Fufa (M. Sc.)

This doctoral dissertation presents the design, synthesis, and comprehensive electrochemical and spectroscopic investigation of thiophene-based oligomers incorporating deliberately introduced π-conjugation-break spacers. The objective of this work is to establish clear structure–property relationships and to understand how controlled interruption of π-conjugation influences redox behaviour, charge localization, and electrochromic response. Three systematic series of oligothiophene systems were synthesized: (i) alkyl-substituted methylene-bridged quaterthiophenes, (ii) oligothiophenes of varying conjugation length connected through methylene bridges, and (iii) quaterthiophene units separated by methylene, ethylene, and propylene spacers. In addition, selected model compounds were synthesized to support mechanistic interpretation and structure–redox correlation.

The molecular structures of all synthesized monomers were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The UV–Vis spectroscopic properties of the monomers were investigated to evaluate the effectiveness of π-conjugation interruption in the ground state and to assess electronic communication between thiophene segments. Electrochemical behaviour was examined using cyclic voltammetry to analyze first oxidation processes and structure-dependent follow-up reactions. UV–Vis–NIR spectroelectrochemical measurements were performed on electrogenerated films across all three series to monitor electronic-state evolution during controlled doping and dedoping cycles. Electron paramagnetic resonance (EPR) spectroelectrochemical analysis was conducted for compound 3 to directly confirm the formation of spin-active radical species.

The results demonstrate that oxidation proceeds predominantly through stepwise one-electron processes strongly influenced by bridge substitution, thiophene conjugation length, and spacer length. Spectroelectrochemical analysis confirms the formation of localized polaronic species, with limited long-range charge delocalization due to the presence of conjugation-break spacers. Increasing spacer length progressively reduces electronic coupling between conjugated segments and modulates redox reversibility and optical response. The observed spectral changes during oxidation directly correlate spacer architecture with electrochromic behaviour, demonstrating that controlled conjugation interruption provides a molecular strategy for tuning color transitions and redox stability.

Overall, this work establishes a mechanistically coherent framework linking molecular structure, oxidation pathways, charge localization, and electrochromic properties in conjugation-broken thiophene systems. The findings provide fundamental insight into spacer-engineered organic semiconductors and contribute to the rational design of tunable electrochromic and redox-active materials.