ELUCIDATING THE CHARGE TRANSPORT OF A RADICAL SYSTEM FROM A COMBINED EXPERIMENTAL AND COMPUTATIONAL APPROACH

ABSTRACT

Radical polymers bearing open-shell moieties at their pendant sites offer potential advantages in processing, stability, and optoelectronic properties compared to conventional doped conjugated polymers. The rapid development of radical-containing polymers has occurred across various applications in energy storage devices and electronic systems. However, significant gaps still exist in understanding the key structure-property-function relationships governing charge transport phenomena in these materials. Most reported radical conductors primarily rely on (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radicals, which raises fundamental questions about the ultimate limits of charge transport capabilities and the impact of radical chemistry choice on material deficiencies. Moreover, an understanding gap persists when it comes to connecting the computable electronic features of individual units and the charge transport behavior of these materials in condensed phases. This dissertation seeks to address these gaps by developing a molecular understanding of charge transport in radical-bearing materials through a combined computational and experimental approach.

The initial stage of this dissertation investigated the impact of dimeric orientations and interactions on charge transport by conducting a density functional theory (DFT) study on a diverse set of open-shell chemistries relevant to radical conductors. The results revealed the anomalously high reorganization energies of the TEMPO radical due to strong spin-localization, which may result in inefficient charge transfer. Additionally, a significant mismatch was identified between dimeric conformations favored by intermolecular interactions and those maximizing charge transfer. This study provided new insights into the impact of steric hindrance and spin delocalization on elementary charge transfer steps and suggests opportunities for exploiting directing interactions to enhance charge transport in these materials.

Building upon these findings, we established a direct relationship between the molecular architecture and intrinsic charge transport properties. To accomplish this, single-molecule characterization methods (i.e., break junction techniques) were implemented to study the nanoscale charge transport properties of radical-containing oligomeric nonconjugated molecules. Temperature-dependent measurements and molecular modeling revealed that the presence of radicals improves tunneling at the nanoscale. Integrating open-shell moieties into nonconjugated molecular structures significantly enhances charge transport, thereby characterizing charge transport through radicals at the individual level and opening new avenues for implementing molecular engineering in the field of nanoelectronics.

To further connect the electronic properties of repeat units with the condensed-phase charge transport behavior of radical polymers, a quantum chemical study was carried out to explicitly evaluate the interplay between polymer design, open-shell chemistries, and intramolecular charge transport. After comprehensive conformational sampling of the configurational space of radical polymers, we determined their anticipated intrachain charge transport values by utilizing graph-based transport metrics. We show that charge transport in radical polymers primarily hinges on the choice of radical chemistry, which in turn affects the optimal selection of backbone chemistry and spacer group to ensure proper radical alignment and prevent undesired trap states. These findings highlight the potential for a substantial synthetic exploration in radical polymers for radical conductors.

In summary, this dissertation provides compelling evidence of radical-mediated charge transport and suggests potential design guidelines to enhance the charge transfer behavior of radical-containing polymer materials. Furthermore, these findings inform future research directions in fine-tuning molecular engineering and modular design to enable the development of radical-based materials and their end-use applications in organic electronics.