

MOLECULAR CONJUGATION AND DOPING EFFECTS ON THE OPTICAL RESPONSE OF CONDUCTING POLYMERS: INSIGHTS FROM QUANTUM CHEMISTRY

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Abstract

Conducting polymers represent an important class of functional materials whose optical properties can be modified through molecular design, changes in conjugation length, and controlled doping. These characteristics make them promising candidates for applications in organic optoelectronics, optical sensing, flexible electronic devices, and energy-conversion systems. This thesis examines the relationship between molecular conjugation, chemical structure, doping, and optical absorption in three representative conducting polymers: polyaniline (PANI), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT). Particular emphasis is placed on the application of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) to interpret electronic structure and excited-state behavior. The analysis indicates that optical properties cannot be explained solely by the chemical composition of a polymer; molecular conformation, effective conjugation length, oxidation state, and charge-carrier formation must also be considered. Doping may introduce additional electronic states associated with polarons and bipolarons, thereby modifying absorption features and extending the optical response into different spectral regions. Nevertheless, the magnitude and direction of these changes depend on the polymer system and its chemical environment. The thesis highlights the importance of combining quantum-chemical modeling with UV-Vis and, where appropriate,

near-infrared spectroscopy to obtain a more comprehensive understanding of structure–property relationships in conducting polymers.

Keywords: Conducting polymers; molecular conjugation; doping; optical absorption; density functional theory; TD-DFT; polyaniline; polythiophene; PEDOT.

Introduction

Conducting polymers have attracted increasing attention because their electronic and optical characteristics can be adjusted through chemical modification, oxidation, doping, and control of molecular architecture. Unlike conventional insulating polymers, conjugated polymers contain alternating single and double bonds that facilitate π -electron delocalization along the molecular backbone. This electronic structure provides the foundation for their characteristic absorption behavior and their potential use in optoelectronic and electrochemical technologies.

The optical response of these materials is strongly influenced by the relationship between molecular structure and electronic excitation. Changes in conjugation length, backbone planarity, and electronic charge distribution can modify the energies and intensities of optical transitions. Doping introduces additional complexity by changing the electronic state of the polymer and, in many cases, generating mobile or partially localized charge carriers. Understanding these effects is important for interpreting experimental spectra and designing materials with specific optical characteristics.

Quantum-chemical calculations provide a useful approach for examining these mechanisms. Density functional theory (DFT) can be applied to investigate molecular geometries, frontier orbitals, and charge distributions, while time-dependent density functional theory (TD-DFT) can help interpret electronic excitation energies and calculated absorption spectra. The combined use of these methods offers a theoretical framework for investigating how structural and chemical changes influence the optical behavior of conducting polymers.

Molecular Conjugation and Optical Absorption

Conjugation is one of the principal structural factors governing the electronic properties of conducting polymers. The overlap of adjacent p orbitals facilitates π -electron delocalization and influences the distribution of occupied and unoccupied electronic states. In general, changes in effective conjugation length can alter the energies of electronic transitions, although the precise behavior depends on molecular geometry, chemical substitution, and the theoretical model employed.

Polythiophene provides a useful example of the relationship between conjugation and optical response. Its thiophene-based backbone supports electronic delocalization, but deviations from planarity can reduce effective orbital overlap. Consequently, two molecular structures with the same number of repeating units may exhibit different electronic characteristics if their conformations differ. Calculations on oligothiophenes can therefore help clarify the influence of molecular length and geometry on electronic excitation, provided that finite-chain and end-group effects are considered.

Polyaniline presents a different structural situation because its electronic properties depend strongly on the oxidation and protonation states of the nitrogen-containing backbone. Changes in chemical state can modify charge distribution and the availability of electronic transitions. As a result, interpreting its optical spectrum requires a clear distinction between the relevant forms of the polymer rather than treating polyaniline as a single, invariant electronic system.

PEDOT also demonstrates the importance of molecular architecture. Its ethylenedioxy substituents influence the electronic properties of the thiophene-based backbone, while its oxidation state and interactions with surrounding species can affect its optical response. These examples indicate that the relationship between conjugation and optical absorption must be understood in the context of the complete molecular and chemical environment.

Influence of Doping on Electronic and Optical Properties

Doping is an important mechanism for modifying the electronic characteristics of conducting polymers. Depending on the polymer and the doping process, oxidation or reduction may alter the occupation of electronic states and generate charge carriers associated with polaronic or bipolaronic configurations. These changes can introduce additional electronic transitions and substantially modify the absorption spectrum.

In PEDOT, the relationship between doping and optical response is particularly important because the electronic structure of the oxidized material differs from that of a neutral molecular chain. Polaronic and bipolaronic states can contribute to absorption features in the visible and near-infrared regions. Theoretical studies of PEDOT have demonstrated that interpreting these features requires consideration of the polymer's electronic state rather than relying exclusively on the frontier orbital energies of a neutral model (Zozoulenko et al., 2019).

In polyaniline, protonation and oxidation can produce distinct electronic configurations, influencing both charge transport and optical absorption. Therefore, differences between measured spectra may reflect changes in chemical state as well as differences in molecular structure. A meaningful comparison requires the preparation conditions and chemical forms of the samples to be documented.

For polythiophene derivatives, doping can modify electronic states and introduce transitions associated with charge carriers. Experimental spectroscopy combined with density functional theory has been used to investigate these effects and the influence of side-chain chemistry and molecular structure on absorption behavior (Sahalianov et al., 2020).

These observations demonstrate that doping should not be regarded merely as a method of increasing electrical conductivity. It can also alter the optical characteristics of conducting polymers. However, the resulting response depends on the doping level, chemical environment, molecular organization, and type of charge carrier formed.

Contribution of DFT and TD-DFT to Optical Analysis

DFT and TD-DFT provide complementary information for understanding the relationship between molecular structure and optical response. Ground-state DFT calculations can be used to investigate optimized geometries, frontier molecular orbitals, and electronic charge distribution. Such information helps explain how conjugation, molecular twisting, and chemical substitution influence the electronic structure.

TD-DFT extends this analysis by estimating excited-state energies and electronic transition intensities. These calculations can support the interpretation of UV–Vis absorption spectra and provide insight into the electronic transitions responsible for individual absorption features. When the molecular model and computational method are appropriately selected, the calculated results can be compared with experimental spectra to assess the proposed interpretation.

Nevertheless, computational limitations must be acknowledged. Results depend on the selected exchange–correlation functional, basis set, oligomer length, molecular conformation, and treatment of the surrounding environment. In doped polymers, the charge state and spin multiplicity must also be represented appropriately. Furthermore, calculations on isolated oligomers cannot fully reproduce interchain interactions, structural disorder, or all solid-state effects.

For these reasons, a reliable investigation should distinguish molecular orbital energy differences from calculated optical excitation energies. The former are descriptors of the ground-state electronic structure, whereas the latter describe transitions to excited electronic states. Their relationship is informative but not necessarily direct or identical.

Conclusion

The optical properties of conducting polymers are determined by a combination of molecular conjugation, backbone conformation, chemical composition, oxidation state, and doping. Polythiophene illustrates the importance of effective conjugation length and molecular geometry, while polyaniline demonstrates the influence of

oxidation and protonation. PEDOT further highlights the role of charge-carrier formation and the associated changes in electronic transitions.

DFT and TD-DFT provide complementary theoretical tools for investigating these relationships. DFT supports the analysis of molecular structure and electronic states, whereas TD-DFT enables the interpretation of electronic excitations and optical absorption. However, calculated molecular properties must be interpreted with due consideration of model limitations, particularly when extrapolating from isolated oligomers to bulk polymeric materials.

The integration of quantum-chemical calculations with UV–Vis and near-infrared spectroscopy can improve the understanding of structure–property relationships and help guide the development of conducting polymers for specific optical applications. Future research should prioritize consistent computational models, explicitly defined doping states, and systematic comparison with experimental measurements.

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