

Quantum-Chemical Investigation of the Electronic Structure and Optical Properties of Conducting Polymers: A DFT and TD-DFT Approach

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Abstract

Conducting polymers have attracted considerable attention due to their tunable electronic structures and optical properties, which are essential for the development of organic electronic devices, optical sensors, and energy-related technologies. Understanding the relationship between molecular architecture, electronic energy levels, and optical absorption is therefore of significant scientific and technological importance. This study presents a comparative theoretical analysis of the electronic structure and optical properties of three representative conducting polymers: polyaniline (PANI), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT). The analysis is based on the theoretical principles and established applications of density functional theory (DFT) and time-dependent density functional theory (TD-DFT). Particular attention is given to molecular conjugation, frontier molecular orbitals, HOMO–LUMO energy differences, electronic excitation energies, and UV–Vis absorption characteristics. The methodological framework also considers the effects of molecular geometry, oxidation state, doping, and computational model selection on the interpretation of calculated optical properties. A critical distinction is made between molecular orbital energy differences and optical excitation energies, emphasizing that these parameters are related but not necessarily equivalent. The comparative analysis highlights the importance of conjugated backbone structure and electronic delocalization in understanding the optical response of conducting polymers. It also identifies key methodological limitations associated with finite oligomer models and the extrapolation of molecular calculations to bulk polymeric materials. This study provides a theoretical framework for interpreting structure–property relationships in conducting polymers and supports the design of future computational investigations integrating electronic-structure calculations with spectroscopic measurements.

Keywords: Conducting polymers; density functional theory (DFT); time-dependent density functional theory (TD-DFT); electronic structure; HOMO–LUMO energy gap; optical absorption; UV–Vis spectroscopy; conjugated polymers.

Introduction

Conducting polymers have attracted considerable scientific interest because of their distinctive electronic, optical, and physicochemical properties, which make them promising materials for applications in organic electronics, optoelectronic devices, chemical sensors, energy conversion systems, and flexible electronic technologies. Unlike conventional insulating polymers, conducting polymers possess conjugated molecular backbones characterized by alternating single and double bonds. This structural arrangement facilitates π -electron delocalization along the polymer chain and provides a basis for their semiconducting and electrically conducting behavior. Among the most extensively investigated conducting polymers are polyaniline (PANI), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT), which exhibit distinct electronic structures and optical responses depending on their molecular architecture, oxidation state, conjugation length, and doping conditions. The optical properties of conducting polymers are closely related to their electronic energy levels and the transitions that occur when electromagnetic radiation interacts with the material. Parameters such as absorption wavelength, optical transition energy, oscillator strength, and the distribution of electronic states provide valuable information about the underlying electronic structure. In conjugated systems, changes in molecular geometry, effective conjugation length, and interchain interactions can influence the energy required for electronic excitation and consequently modify the absorption spectrum. Understanding these relationships is essential for developing conducting polymers with tailored optical responses for specific technological applications.

Experimental techniques, particularly ultraviolet–visible (UV–Vis) spectroscopy, provide important information about the absorption behavior of conducting polymers. However, experimental spectra may contain overlapping contributions from different electronic transitions, structural conformations, charge carriers, and intermolecular interactions. Consequently, interpreting the relationship

between molecular structure and optical response solely from experimental observations can be challenging. Computational chemistry offers complementary tools for investigating these phenomena at the molecular and electronic levels, enabling researchers to examine electronic states, molecular orbitals, and excitation processes within a defined theoretical framework.

Density functional theory (DFT) is widely used to investigate the optimized geometries, electronic structures, and molecular orbital distributions of conjugated organic systems. By providing information about occupied and unoccupied electronic states, DFT can help elucidate how structural modifications influence the electronic characteristics of conducting polymers. Time-dependent density functional theory (TD-DFT), in turn, enables the calculation of excited-state energies and electronic transition probabilities, supporting the theoretical interpretation of UV–Vis absorption spectra. When appropriately selected and validated, these methods provide a practical framework for connecting molecular structure with the optical behavior of conjugated materials. Nevertheless, the reliability of calculated results depends on the selected exchange–correlation functional, basis set, molecular model, treatment of solvent effects, and representation of polymer-chain length.

A critical distinction must be made between isolated oligomer models and extended polymeric materials. Calculations performed on short oligomers can reveal useful trends in conjugation and electronic excitation, but their results cannot automatically be interpreted as the properties of an infinite polymer chain or a bulk material. In addition, the HOMO–LUMO energy difference obtained from a molecular orbital calculation is not necessarily equivalent to the experimentally measured optical band gap. Optical excitation energies depend on the nature of the excited state and may also be influenced by electron–hole interactions, structural relaxation, and the surrounding environment. Therefore, a rigorous computational investigation should interpret orbital energy differences alongside calculated excitation energies and, where available, experimental spectroscopic evidence.

Although numerous studies have examined the electronic and optical behavior of conducting polymers, meaningful comparisons between different polymer families

require consistent consideration of their molecular structures, oxidation states, doping conditions, and computational assumptions. Polyaniline, polythiophene, and PEDOT provide a useful comparative framework because they represent chemically distinct conjugated systems with different structural features and technological applications. Their comparison can help clarify how backbone architecture and electronic delocalization contribute to variations in optical absorption and electronic excitation.

The aim of this study is to examine the relationship between molecular structure, electronic energy levels, and optical properties of selected conducting polymers using a comparative quantum-chemical framework based on DFT and TD-DFT. The specific objectives are to analyze the role of conjugation and molecular architecture in determining electronic structure; explain the significance and limitations of HOMO and LUMO energy levels and their energy difference; evaluate the theoretical basis for interpreting optical absorption spectra; and identify methodological factors that should be considered when comparing polyaniline, polythiophene, and PEDOT. By integrating established computational principles with findings reported in the scientific literature, this study seeks to provide a structured understanding of the molecular factors governing the optical response of conducting polymers and to establish a foundation for future computational and experimental investigations.

Materials and Computational Methods

Materials and Scope of the Comparative Analysis

The present study focuses on three representative conducting polymers: polyaniline (PANI), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT). These materials were selected because they represent distinct conjugated polymer architectures and have been extensively investigated for their electronic, optical, and electrochemical properties. Their molecular structures provide a useful basis for discussing the influence of conjugation, heteroatom incorporation, oxidation state, and doping on the electronic behavior of conducting polymers [1–3]. Polyaniline is characterized by nitrogen-containing aromatic units and can exist in different oxidation and protonation states. These structural variations influence its

electronic configuration, charge distribution, and optical absorption. Polythiophene contains sulfur-containing heteroaromatic rings connected through a conjugated backbone, making it a suitable model for examining the effects of conjugation length and backbone geometry on electronic transitions. PEDOT contains ethylenedioxy substituents that influence the electronic characteristics of the thiophene-based backbone and contribute to its practical importance in organic electronics [1–3].

The comparison considers five principal aspects: molecular architecture and conjugation, frontier molecular orbitals, electronic excitation processes, optical absorption characteristics, and the influence of oxidation and doping. The discussion is based on established computational studies and reported spectroscopic findings. It is intended as a comparative theoretical analysis rather than a report of newly performed quantum-chemical calculations.

Density Functional Theory for Electronic Structure Analysis

Density functional theory is an established computational approach for investigating the ground-state electronic structure of molecular systems. In studies of conducting polymers, DFT can be used to optimize molecular geometries, examine electronic charge distributions, characterize frontier molecular orbitals, and investigate how structural modifications influence the electronic properties of conjugated systems [1, 4].

The reliability of DFT calculations depends on the choice of exchange–correlation functional, basis set, molecular geometry, and representation of the polymer chain. Hybrid functionals, including B3LYP, have been used extensively in studies of conjugated molecules and oligomers. Range-separated hybrid functionals, such as ω B97X-D, can be useful when evaluating systems in which long-range electronic interactions and charge-transfer characteristics are important. Nevertheless, no single functional is universally optimal for all conducting polymers and electronic excitation processes. Method selection should therefore be guided by the physical properties under investigation and, where possible, validated against experimental or higher-level computational data [4, 5].

For finite oligomer models, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) provide a qualitative description of the frontier electronic states. Their spatial distributions can indicate whether the frontier states are delocalized along the conjugated backbone or concentrated in particular molecular regions. The corresponding orbital energy difference is often used as a preliminary descriptor of the electronic structure. However, it should not be treated as an exact measure of the optical excitation energy or as a direct substitute for the band gap of an extended polymeric material.

The use of oligomer models requires particular attention to chain length and end-group effects. Short oligomers are computationally convenient, but their electronic properties may differ from those of longer chains because the extent of conjugation and the distribution of electronic states depend on the number of repeating units. Comparisons between PANI, PTh, and PEDOT are therefore meaningful only when the limitations of their molecular representations are explicitly acknowledged.

Time-Dependent Density Functional Theory and Optical Properties

Time-dependent density functional theory is widely employed to investigate electronically excited states and calculate optical absorption spectra. In conjunction with optimized ground-state geometries, TD-DFT provides estimates of vertical excitation energies, oscillator strengths, and the principal electronic transitions contributing to a calculated spectrum [4–6].

The optical response of conducting polymers is closely associated with electronic transitions between occupied and unoccupied states. In relatively simple neutral oligomer models, these transitions may involve substantial contributions from frontier orbitals. In more complex systems, however, several orbitals can contribute to an individual excitation, and the interpretation requires examination of the relevant excited-state configurations rather than reliance on HOMO–LUMO energies alone.

TD-DFT calculations can support the interpretation of ultraviolet–visible absorption spectra and help identify how molecular structure affects the position and relative intensity of absorption bands. For oxidized or doped polymers, the analysis

becomes more complex because charge carriers, including polarons and bipolarons, can introduce additional electronic states. Such states may produce absorption features that are not adequately described by the electronic structure of the neutral polymer [2, 5].

A meaningful comparison between theoretical and experimental spectra should account for the molecular environment and the physical state of the material. Solvent effects, conformational disorder, interchain interactions, counterions, and variations in oxidation level may influence the observed spectrum. Consequently, spectra calculated for isolated oligomers should be interpreted as molecular-level approximations rather than complete representations of solid polymer films.

Comparative Evaluation Criteria

The three polymers are compared using a consistent qualitative framework that links molecular structure to electronic and optical behavior. The principal evaluation criteria include the nature of the conjugated backbone, the expected distribution of frontier orbitals, the sensitivity of electronic states to structural modification, the role of doping, and the implications for optical absorption.

The literature-based comparison prioritizes findings supported by computational studies and spectroscopic evidence. Particular attention is given to the distinction between neutral and doped polymer states, as this distinction is essential for interpreting optical transitions in conducting polymers. The discussion also considers the limitations of finite molecular models and the extent to which calculated properties can be related to experimentally measured behavior.

No new DFT or TD-DFT calculations were performed for this comparative analysis. Accordingly, the following section presents a critical synthesis of established findings and theoretical principles rather than newly generated numerical results.

Results and Discussion

Relationship Between Molecular Structure and Electronic Properties

The electronic properties of conducting polymers originate from the interaction between their conjugated molecular backbones and the associated delocalized π -electron systems. Although PANI, PTh, and PEDOT share the general

characteristics of conjugated polymers, their different chemical structures lead to distinct electronic responses.

In polyaniline, the nitrogen-containing backbone introduces structural and electronic features that depend on the oxidation and protonation state. The coexistence of different nitrogen environments influences electron distribution along the chain, while protonation can modify the electronic structure and optical response. Therefore, PANI cannot be adequately characterized by a single electronic configuration without specifying its chemical state.

Polythiophene provides a useful system for examining the relationship between conjugation length and electronic excitation. Increasing the number of conjugated thiophene units can change the distribution of frontier orbitals and the energies of electronic transitions. However, the magnitude and direction of these changes depend on the molecular conformation, computational method, and structural model. Backbone twisting can reduce effective conjugation, whereas more planar configurations can facilitate greater electronic delocalization. Computational investigations of polythiophene oligomers have demonstrated the importance of molecular length and theoretical-method selection when interpreting electronic and optical properties [4, 6].

PEDOT presents a further example of the relationship between molecular architecture and electronic behavior. Its ethylenedioxy substituents influence the electronic properties of the thiophene backbone, while oxidation and doping substantially alter the distribution of electronic states. The theoretical literature emphasizes that the properties of PEDOT depend not only on the isolated molecular chain but also on its oxidation level, morphology, and interactions with surrounding species [1, 2].

These observations indicate that differences in the optical behavior of conducting polymers should not be attributed solely to their chemical composition. Molecular conformation, effective conjugation length, oxidation state, and intermolecular interactions are also important determinants of their electronic structure.

HOMO–LUMO Energy Levels and Electronic Excitation

Frontier molecular orbitals provide a useful conceptual framework for interpreting the electronic properties of finite conjugated molecules. The HOMO describes the highest occupied molecular orbital, whereas the LUMO represents the lowest unoccupied molecular orbital. Their spatial distributions and relative energies help characterize the electronic structure of a molecular system.

In conducting polymer oligomers, frontier orbitals may extend across several repeating units, reflecting the influence of conjugation. Changes in chain length, bond geometry, substituents, and oxidation state can alter their spatial distribution and energy levels. These changes may, in turn, influence the accessible electronic excitation pathways.

Nevertheless, the HOMO–LUMO energy difference should be interpreted cautiously. It is a molecular orbital descriptor rather than a direct measurement of optical absorption. Optical excitation energies are calculated from excited-state electronic structure and may be influenced by electron–hole interactions, orbital contributions, and the computational approximation employed. In extended polymer systems, the relationship between molecular orbital energies and experimentally determined optical gaps is further complicated by solid-state effects.

This distinction is particularly important when comparing different conducting polymers. A smaller calculated orbital energy difference does not automatically establish that a material will exhibit a stronger absorption band, higher electrical conductivity, or superior device performance. Absorption intensity depends on the probability of the relevant electronic transition, while electrical conductivity also depends on charge-carrier concentration, mobility, and structural organization.

Therefore, HOMO–LUMO analysis is most informative when interpreted together with calculated excitation energies, oscillator strengths, molecular orbital distributions, and experimental spectroscopic observations.

Optical Absorption and the Interpretation of UV–Vis Spectra

Optical absorption in conducting polymers results from the interaction between incident electromagnetic radiation and the electronic states of the material. The resulting absorption spectrum provides information about the energies and

intensities of accessible electronic transitions and can be used to investigate changes in conjugation, molecular organization, and electronic structure.

For neutral conjugated oligomers, absorption features are commonly associated with electronic excitations involving delocalized states of the molecular backbone. The position of an absorption band depends on the electronic structure and the nature of the excited state. In computational studies, TD-DFT can be used to estimate excitation energies and oscillator strengths, helping to distinguish transitions with different contributions to the calculated spectrum [4, 6].

Polythiophene derivatives illustrate the importance of considering both molecular structure and environmental effects. Research combining absorption spectroscopy and DFT-based calculations has investigated how doping, counterions, backbone twisting, and interchain interactions affect optical transitions across the ultraviolet, visible, and infrared regions. These factors can influence spectral broadening and the distribution of absorption intensity, demonstrating that an isolated-chain model cannot fully reproduce every feature of a polymer film [5].

PEDOT provides an especially important example of the relationship between oxidation state and optical absorption. Computational investigations of PEDOT have shown that the electronic states associated with polarons and bipolarons can substantially affect the interpretation of visible and near-infrared absorption features. The nature of these states and their associated transitions cannot be reliably inferred from the neutral polymer's HOMO–LUMO energy difference alone [2].

In PANI, the interpretation of optical absorption similarly requires attention to oxidation and protonation states. Changes in these chemical conditions modify the electronic structure and may alter the distribution of absorption bands. Consequently, spectra recorded for different forms of PANI should not be compared as though they represent an identical molecular system.

Overall, UV–Vis spectroscopy and TD-DFT are complementary approaches. Experimental spectroscopy establishes the optical response of the actual sample, whereas TD-DFT provides a molecular-level interpretation of selected electronic transitions. Agreement between calculated and experimental spectra can strengthen

a proposed interpretation, but discrepancies may also reveal the influence of structural disorder, environmental effects, or limitations in the theoretical model.

Comparative Analysis of PANI, PTh, and PEDOT

The three polymer systems demonstrate different aspects of the relationship between chemical structure and optical behavior. Their main characteristics are summarized in Table 1.

Table 1. Qualitative comparison of selected conducting polymers

Characteristic	PANI	PTh	PEDOT
Principal structural feature	Nitrogen-containing conjugated backbone	Sulfur-containing thiophene backbone	Thiophene backbone with ethylenedioxy substituents
Important structural variables	Oxidation and protonation states	Conjugation length and backbone conformation	Oxidation level, counterions, and chain organization
Relevant electronic descriptors	Frontier orbitals and charge distribution	Frontier orbitals and conjugation-dependent excitation	Frontier orbitals and polaronic or bipolaronic states
Main optical considerations	Dependence on chemical state	Dependence on conjugation and molecular geometry	Dependence on doping and charge-carrier states
Important modeling limitation	Chemical-state specification	Finite-chain and conformational effects	Oxidation, morphology, and interchain interactions

Note: The table summarizes qualitative features reported in the literature; it does not present new calculations or a numerical ranking of the polymers.

The comparison shows that the three materials require different considerations when their optical properties are interpreted. For PANI, the oxidation and protonation states must be defined before meaningful conclusions can be drawn about its electronic structure. For PTh, molecular conformation and effective conjugation

length are central to understanding the relationship between electronic states and optical transitions. For PEDOT, the effects of oxidation and charge-carrier formation are particularly important because they can introduce electronic states that are absent from the neutral molecular model [1, 2, 4–6].

These differences also demonstrate why a universal ranking based solely on HOMO–LUMO energy differences would be scientifically inadequate. A defensible quantitative comparison would require consistent molecular models, comparable computational settings, explicitly defined chemical states, and a clear distinction between orbital energy differences and optical excitation energies.

Methodological Limitations and Future Research Directions

Despite their usefulness, DFT and TD-DFT calculations have limitations that must be considered when studying conducting polymers. First, calculated properties depend on the exchange–correlation functional, basis set, and molecular geometry. Different computational approaches may yield different orbital energies and excitation energies, particularly for systems involving charge transfer or strongly delocalized electronic states.

Second, finite oligomer models do not fully represent the behavior of extended polymer chains or bulk materials. Real polymer films may contain distributions of chain lengths, conformations, and intermolecular arrangements. These structural variations can affect absorption-band widths and the overall optical response. Consequently, molecular calculations should be interpreted within the limitations of the model used.

Third, doping introduces additional complexity. Oxidation can generate polaronic or bipolaronic states, while counterions and surrounding molecules influence the electronic environment. For these systems, the molecular charge, spin multiplicity, and chemical structure must be specified explicitly. Incorrect assumptions about the electronic state can lead to misleading interpretations of the calculated spectrum [2, 5].

Future investigations would benefit from a consistent computational comparison of PANI, PTh, and PEDOT using explicitly defined oligomer lengths, appropriate charge states, optimized geometries, and carefully selected DFT and

TD-DFT methods. Calculated spectra should be compared with experimental UV–Vis or UV–Vis–NIR data obtained under comparable chemical conditions. Where bulk properties are the main target, periodic calculations or multiscale approaches may provide additional information about interchain interactions and solid-state electronic structure.

Such a framework would help distinguish intrinsic molecular effects from the contributions of doping, morphology, and the surrounding environment. It would also provide a stronger basis for identifying which structural modifications are most relevant to the development of conducting polymers with tailored optical properties.

Conclusion

The comparative theoretical analysis demonstrates that the optical properties of conducting polymers are closely related to their molecular architecture, electronic structure, and chemical state. Polyaniline, polythiophene, and PEDOT share the characteristic feature of conjugated backbones, but their distinct structural elements and responses to oxidation and doping lead to different considerations when interpreting their electronic and optical behavior.

Density functional theory provides a useful framework for investigating molecular geometry, frontier molecular orbitals, and electronic charge distribution. Time-dependent density functional theory complements this approach by enabling the analysis of excited-state energies and optical transitions. Used together, these methods can help explain the molecular origins of absorption features and establish connections between structural characteristics and optical response.

An important conclusion is that the HOMO–LUMO energy difference should not be regarded as a direct substitute for the optical excitation energy or as a sufficient predictor of electrical conductivity. Optical properties depend on the nature and intensity of electronic transitions, while conductivity is additionally governed by charge-carrier concentration, mobility, and material morphology. The effects of oxidation, doping, polarons, bipolarons, and intermolecular interactions are therefore essential to a comprehensive interpretation of conducting polymer behavior.

The analysis also highlights the limitations of finite oligomer models and the need to specify molecular structure, chain length, computational methodology, and chemical state when comparing different polymer systems. Integrating computational results with experimental absorption spectra represents a particularly valuable strategy for improving the reliability of structure–property interpretations.

In conclusion, DFT and TD-DFT constitute complementary tools for understanding the electronic and optical characteristics of conducting polymers. The comparative framework presented here provides a theoretical basis for future investigations of PANI, PTh, and PEDOT and can guide more systematic computational studies aimed at developing materials with application-specific optical and electronic properties. Because the present work is based on published findings and established theoretical principles, its conclusions should be interpreted as a literature-based synthesis rather than as experimentally validated or newly calculated results.

References

1. Zozoulenko, I., Franco-Gonzalez, J. F., Gueskine, V., Mehandzhiyski, A., Modarresi, M., Rolland, N., & Tybrandt, K. (2021). Electronic, optical, morphological, transport, and electrochemical properties of PEDOT: A theoretical perspective. *Macromolecules*, 54(13), 5915–5934. <https://doi.org/10.1021/acs.macromol.1c00444>
2. Zozoulenko, I., Singh, A., Singh, S. K., Gueskine, V., Crispin, X., & Berggren, M. (2019). Polarons, bipolarons, and absorption spectroscopy of PEDOT. *ACS Applied Polymer Materials*, 1(1), 83–94. <https://doi.org/10.1021/acsapm.8b00061>
3. Stejskal, J., & Gilbert, R. G. (2002). Polyaniline. Preparation of a conducting polymer. *Pure and Applied Chemistry*, 74(5), 857–867. <https://doi.org/10.1351/pac200274050857>
4. Talapunur, V., Saisudhakar, M., & Sumithra, K. (2019). Comprehensive evaluation of the effect of various exchange correlation functionals on the optical properties of oligothiophenes. *Computational and Theoretical Chemistry*. <https://doi.org/10.1016/j.comptc.2019.112667>

5. Sahalianov, I., Hynynen, J., Barlow, S., & Zozoulenko, I. (2020). UV-to-IR absorption of molecularly p-doped polythiophenes with alkyl and oligoether side chains: Experiment and interpretation based on density functional theory. *The Journal of Physical Chemistry B*, 124(49), 11280–11293. <https://doi.org/10.1021/acs.jpccb.0c08757>
6. *Electronic and optical properties of polythiophene molecules and derivatives*. (2021). *Crystals*, 11(11), Article 1292. <https://doi.org/10.3390/cryst11111292>
7. Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. *Physical Review*, 136(3B), B864–B871. <https://doi.org/10.1103/PhysRev.136.B864>
8. Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A), A1133–A1138. <https://doi.org/10.1103/PhysRev.140.A1133>
9. Runge, E., & Gross, E. K. U. (1984). Density-functional theory for time-dependent systems. *Physical Review Letters*, 52(12), 997–1000. <https://doi.org/10.1103/PhysRevLett.52.997>