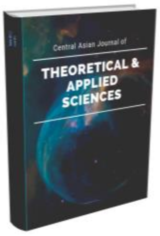

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Article

Design and Theoretical Investigation of Novel Organic Dye Sensitizers for Solar Cells: Electronic Transitions and Photovoltaic Properties

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Abstract: The present paper addresses the electronic structure of various proposed compounds derived from the anthracene molecule, intended for use in photovoltaic applications as dye-sensitized solar cells. The compounds under investigation were initially designed using the Gauss View 5.0.8 software and subsequently optimized through the B3LYP-DFT hybrid functional in conjunction with the 6-31G basis sets within the Gaussian 09 program suite, aimed at examining and analyzing the ground state and spectroscopic characteristics of these compounds. The DFT methodology wasemployed to investigate the properties of the excited states of the compounds studied**.** The findings indicated that a satisfactory relaxation was achieved for the compounds utilizing the DFT theoretical approach. The computed values for the geometrical parameters and the virial ratio of the compounds align well with experimental data and other theoretical analyses. The total energy remains unaffected by the positioning of identical subgroups within the compounds; rather, it is solely contingent upon the electron count in each compound. The calculations revealed that the compounds under study exhibit a destabilization of the LUMO and a stabilization of the HOMO, with both parameters undergoing significant alterations, suggesting that different structural configurations play crucial roles in the electronic properties. The influence of symmetry and the arrangement of aromatic rings affects the calculations of HOMO and LUMO. The results concerning the energy gap indicated that the introduction of double and triple carbon-carbon bonds between the anthracene backbone and the phenyl rings on both the donor and acceptor sides, along with the presence of electron-withdrawing NO subgroups in the compounds, leads to a reduction in the band gap of the compounds. Consequently, an increase in the conjugation length of the compounds facilitates their participation in charge transfer processes.

Keywords: Organic Dye Sensitizers, Dye-Sensitized Solar Cells (Dsscs),Density Functional Theory (Dsscs), HOMO-LUMO Energy Gap

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1. Introduction

In recent decades, energy has become one of the most pressing global challenges. The absence or insufficiency of energy resources leads to critical issues, including the lack of food, shelter, communication, and access to technology. With the rapid advancement of nanotechnology and the increasing demand for sustainable energy, the development of innovative energy systems has become essential for modern societies.Among the most promising solutions is solar energy, a clean and abundant resource that can be harnessed through various technologies. Solar cells, particularly photovoltaic (PV) cells, play a significant role in converting sunlight directly into electricity. The evolution of solar cell technology has been driven by the need for efficient, cost-effective, and adaptable systems capable of powering everything from small portable devices to large-scale power grids.

Recent research has explored both organic and inorganic semiconductor materials for use in solar cells. Initially, experimental data guided material selection, but the integration of computational and theoretical methods has enhanced the design and performance of solar technologies. Advances such as multi-junction structures and second-generation thin-film solar cells—made from materials like amorphous silicon, cadmium telluride, and copper indium gallium selenide—have significantly improved efficiency and applicability. Thin-film technologies, despite their lower efficiency (typically 3–6%), are widely used due to their flexibility, lightweight nature, and compatibility with indoor lighting conditions. These properties make them suitable for integration into everyday items like watches, calculators, and portable chargers.

The photovoltaic effect, first observed by Alexandre Edmond Becquerel in 1839, laid the foundation for the development of modern solar cells. Since then, research has produced various generations of PV technologies, including dye-sensitized solar cells (DSSCs), which offer a low-cost alternative with simple manufacturing processes and promising performance under diffuse lighting.This study focuses on the scientific foundation and technological advancements in solar cell systems, particularly in the context of material science and nanotechnology, aiming to contribute to the ongoing pursuit of efficient and sustainable solar energy solutions.

2. Materials and Methods

A. Theoretical Foundations of Computational Chemistry and Physics:

Computational approaches have become integral in modern theoretical chemistry and physics, offering a powerful framework for understanding molecular interactions and electronic behavior at the atomic level. The utilization of mathematical models and simulations allows for the exploration of complex systems that are often inaccessible through experimental methods alone. According to Leach (2001), molecular modeling serves as a fundamental tool in computational chemistry, enabling the prediction of molecular structures, energy distributions, and reactivity profiles across various chemical systems.

Over the past few decades, computational methods have evolved significantly, with increased emphasis on simulating molecular geometries, electronic structures, charge distributions, and spectral properties such as ultraviolet (UV) absorption. These methods are applied in diverse fields including biological systems, inorganic and organometallic chemistry, polymer science, catalysis, and pharmaceutical research (Cramer, 2013).

B. Molecular Modeling Methods:

Computational chemistry commonly employs four major modeling approaches: molecular mechanics (MM), semi-empirical methods (SE), ab initio methods, and density functional theory (DFT). Each method varies in complexity, computational cost, and accuracy.

Molecular mechanics methods rely on classical physics to describe the behavior of atoms and molecules, and are often used for large systems due to their efficiency. Semi-empirical methods incorporate empirical data to simplify quantum mechanical calculations, while ab initio methods derive all necessary information from first principles without empirical parameters, offering high accuracy but at greater computational expense.

Among these, density functional theory (DFT) has gained significant prominence over the last three decades. As noted by Parr and Yang (1989), DFT provides a balance between computational efficiency and accuracy, making it a preferred tool for modeling electronic structures in organometallic and molecular systems. Numerous studies (e.g., Becke, 1993; Kohn & Sham, 1965) have confirmed the robustness of DFT in predicting structural, energetic, and electronic properties with reasonable computational resources.

C. Quantum Mechanical Foundations and Schrödinger's Equation:

At the core of theoretical and computational chemistry lies quantum mechanics, particularly the Schrödinger equation, which governs the behavior of quantum systems. First formulated by Erwin Schrödinger in 1926, the equation describes the wave-like nature of particles and provides the foundation for modern quantum theory.

The Schrödinger equation is fundamental to understanding atomic and molecular systems, serving as the theoretical basis for most computational models. Its role in quantum mechanics is analogous to Newton's laws in classical mechanics, as it allows for the prediction of system behavior at the microscopic level. Modern quantum chemistry relies heavily on solving or approximating solutions to this equation, especially for systems involving complex electron interactions.

3. Results and Discussion

Structural and Geometrical Analysis of the Designed Compounds

The structural and geometrical properties of the proposed anthracene-based dye sensitizers were investigated using Density Functional Theory (DFT) at the B3LYP/6-31G level. The relaxed structures of four selected compounds, as illustrated in Figure 1, reveal that the addition of various substituent groups to both sides of the anthracene backbone significantly influences the molecular conformation and the π-electron delocalization. All compounds exhibit nearly planar geometries with slight variations in the dihedral angles between adjacent phenyl rings, ranging between 180° and −180° Table (1) indicating the preservation of conjugation across the molecular framework. The optimization results further confirm the structural stability and, in symmetric cases, the preservation of molecular symmetry.

Moreover, the calculated bond lengths and angles were found to be in good agreement with experimental X-ray crystallography data, confirming the reliability of the computational approach. The introduction of electron-donating and electron-withdrawing groups affects the conjugation length and the distribution of electronic density, which are expected to play a significant role in the optical and photovoltaic performance of these compounds.

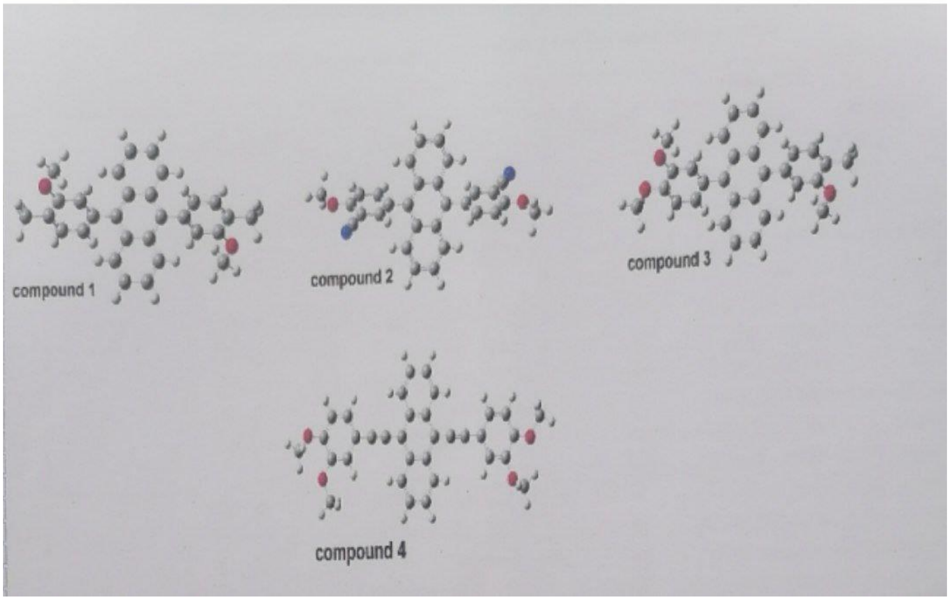

Figure 1. The Relax structure of the compounds.

Table 1. The geometrical parameters for each compound.

Compound	Bound	Length	Value Å	Angle	Bound	Value degree
1	C=C	1.45497–1.51759	C–C–C	118.34743–118.35195		
	C=C	1.40694–1.44233	C–C–H	118.53156–120.11733		
	C–H	1.08497–1.09590	C=C–H	110.89353–119.586882		
	O=C	1.40191–1.45359	C=C–H	118.89347–118.94369		
2	C=C	1.43348–1.50150	C–C–C	105.30951–111.26271		
	C–C	1.38115–1.42140	C–C–C	118.31716–118.35435		
	C–H	1.08703–1.09822	C–C–H	118.86178–121.47932		
	C=N	1.38391–1.46003	C–C–H	104.93496–115.64004		
	C=N	1.18284	C–N–C	110.37943–116.03813		
3	C=C	1.43418–1.50287	C–C–C	118.33185–118.36494		
	C=C	1.38317–1.42173	C–C–H	118.58687–119.59829		
	C–C	1.39204–1.09497	C–C–H	118.28101–119.75483		
4	C=C	1.43224–1.49992	C–C–C	118.34823–119.70793		
	C=C	1.38177–1.42060	C–C–H	118.70016–118.79499		
	C–H	1.08731–1.09022	C–C–H	103.38168–110.39000		
	C=N	1.38944–1.46732	C–H	104.60112–110.90009		

Total Energy

The total energy Ey in a.u. for the compounds under investigation was calculated and is presented in Table 2. As indicated in the aforementioned table, the Er is largely independent of the positioning of identical subgroups within the compounds; rather, it is solely dependent on the number of electrons present in the compounds. This suggests that the total energy serves as a reflection of the binding energy for each compound. Er exhibits an inverse relationship with the number of electrons, decreasing as the number of electrons in the compound increases. Figure 2 illustrates the data for the compounds studied. On the other hand, the corresponding calculated values of the virial ratio (-V/T) for the compounds listed in Table 2 demonstrate that they fall within the same range for such compounds, with the experimental value for the hydrogen atom being (V/F-2.0032) (27). The results above indicate that a good relaxation was achieved without any imaginary frequency for each of the studied compounds through the application of the DFT method.

Table 2. The total energy E_t and (-V/T) for the compounds.

Compound	E_t a.u	-V/T
1	-1309.11299	2.0058
2	-1414.92708	2.0058
3	-1384.30205	2.0057
4	-1611.62170	2.0056

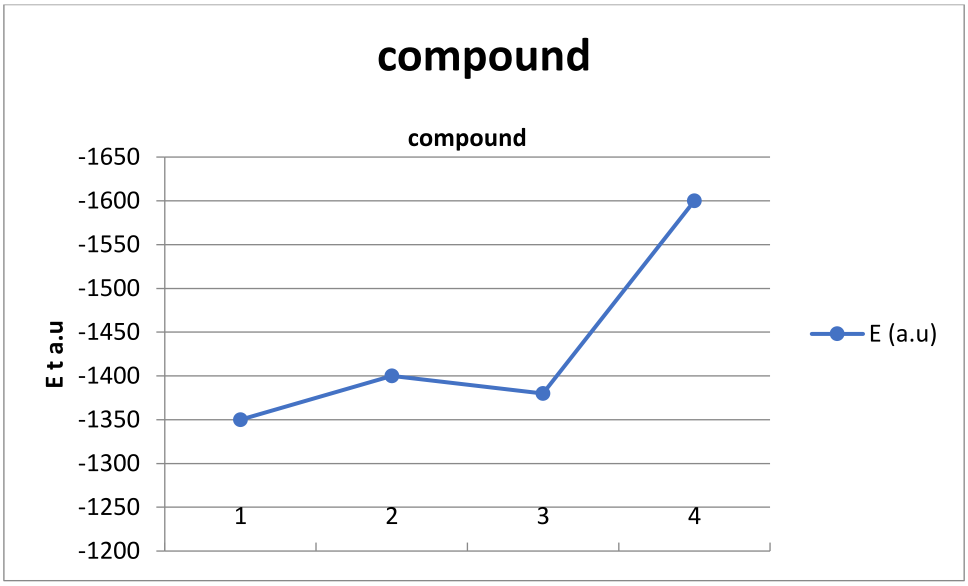

Figure 2. Total Energy of the compounds.

Electronic States and Energy Gap

To interpret and understand the behavior of the absorption spectra of the compounds, it is essential to study the electronic structures of the compounds under investigation. Table 3 presents the calculated frontier orbital energies, specifically the High Occupied Molecular Orbital (HOMO) and the Low Unoccupied Molecular Orbital (LUMO), along with the LUMO-HOMO energy gap (Egap) for each compound. The results displayed in Table 3 indicate that all the compounds examined exhibit a destabilization of the LUMO and a stabilization of the HOMO when compared to the HOMO and LUMO of compound 8. The energies of the HOMO and LUMO for the compounds studied have changed significantly, as shown in Table 3 The results indicate that the HOMO and LUMO differ slightly, suggesting that varying structures have a considerable impact on electronic properties, enhancing electron-accepting capabilities. Furthermore, the influence of symmetry and the arrangement of aromatic rings on the energies of the HOMO and LUMO should not be overlooked. The ranking of LUMO energy is as follows:

2< 4 < 1< 3

The results revealed the presence of electron-attracting NO subgroups within the compounds, leading to a decrease in the LUMO and, as a result, a reduction in the energy gap. Additionally, the existence of both triple and double C-C bonds plays a role in lowering the LUMO and diminishing the energy gap due to the destabilization of both HOMO and LUMO energies; this finding aligns with the experimental data. Figure 3 illustrates the HOMO and LUMO energies of the compounds under examination**.**

The energy gap Eipop for the compounds analyzed was calculated as the difference between LUMO and HOMO energy using B3LYP/6-31G-DFT calculations**.**

The significance of the frontier molecular orbitals (FMO) is paramount in defining the charge-separated states of the compounds under investigation. Figure 5 depicts the electronic structures of the HOMO and LUMO of the compounds studied. As shown, all the organic dyes examined display notable charge-separated states. The distribution of HOMO and LUMO in Figure 5 indicates that strong localization of the HOMO occurs on the phenyl donor subunits of the compounds' backbone, while significant delocalization of the LUMO is noted on the bridges connecting the subunits, thereby confirming the flow of electron density along the compounds' backbone. The electron density of the LUMO is predominantly localized on the acceptor units, suggesting that the electronic transitions of the compounds from HOMO to LUMO may promote intra-molecular charge transfer from the donor units to the acceptor units via the conjugated bridge linking both sides**.**

Table 3 presents the comprehensive data of the energy of the frontier orbital for the compounds studied, with PCBM included for comparative analysis. The results imply that structural modifications influence the HOMO/LUMO energies in accordance with their electron donor/acceptor characteristics. To assess the potential for electron transfer from the studied compounds to the conductive band of PCBM, the HOMO and LUMO levels were compared.:

Voc EHOMO (Donor) | |ELUMO (Acceptor) -0.3

The theoretical values of the open circuit voltage Voc / PCBM of the studied compounds range from 1.68 eV to 2.219 eV. These values are sufficient for a possible effective electron injection.

Table 3. The HOMO, LUMO, and Egab for the compounds.

Compound	HOMO (eV)	LUMO (eV)	Egap (eV)	Voc (eV)
1	-5.2351	-1.7839	3.4511	1.715
2	-5.6451	-2.2059	3.4391	2.219
3	-5.2149	-1.7760	3.4389	1.688
4	-4.7703	-2.1706	2.5997	1.244

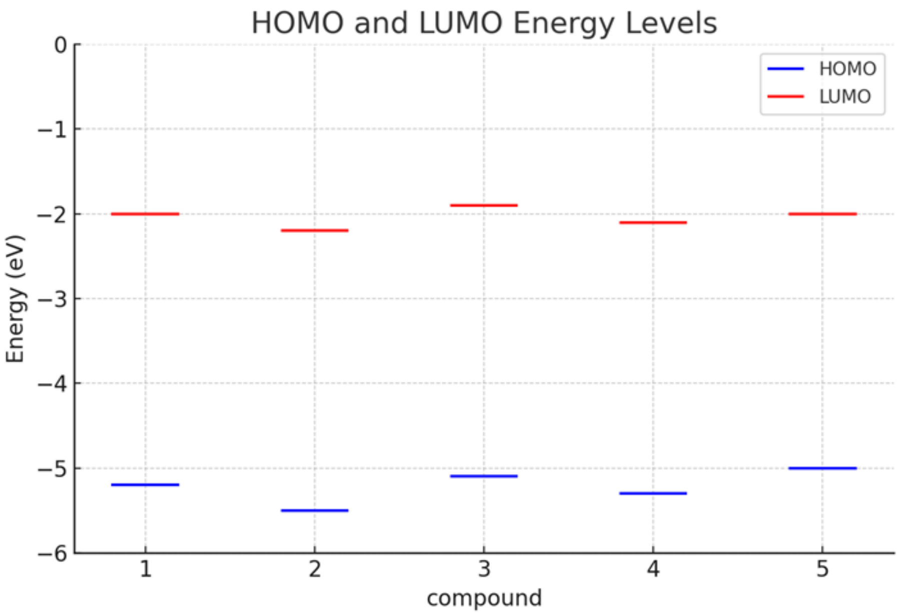

Figure 3. Eomo and ELMO of the compounds.

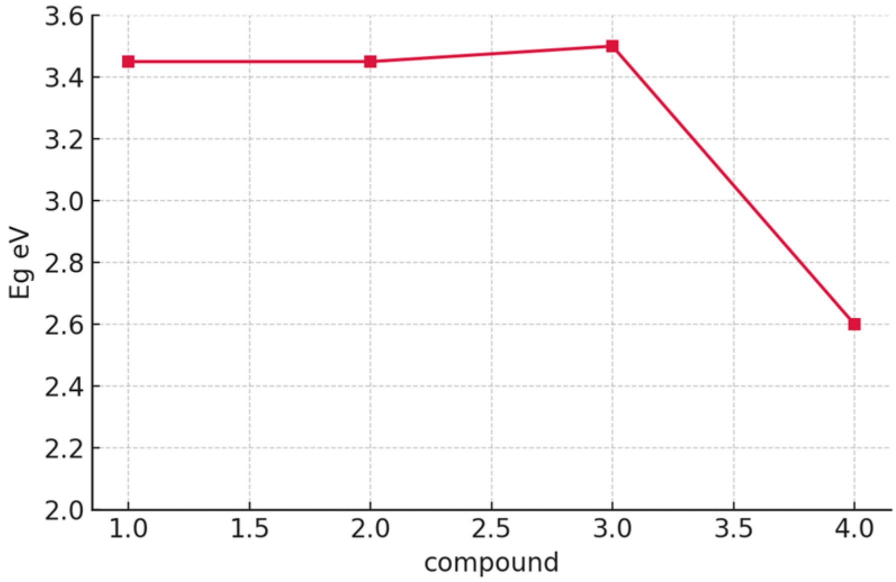

Figure 4. Energy gaps of the compounds.

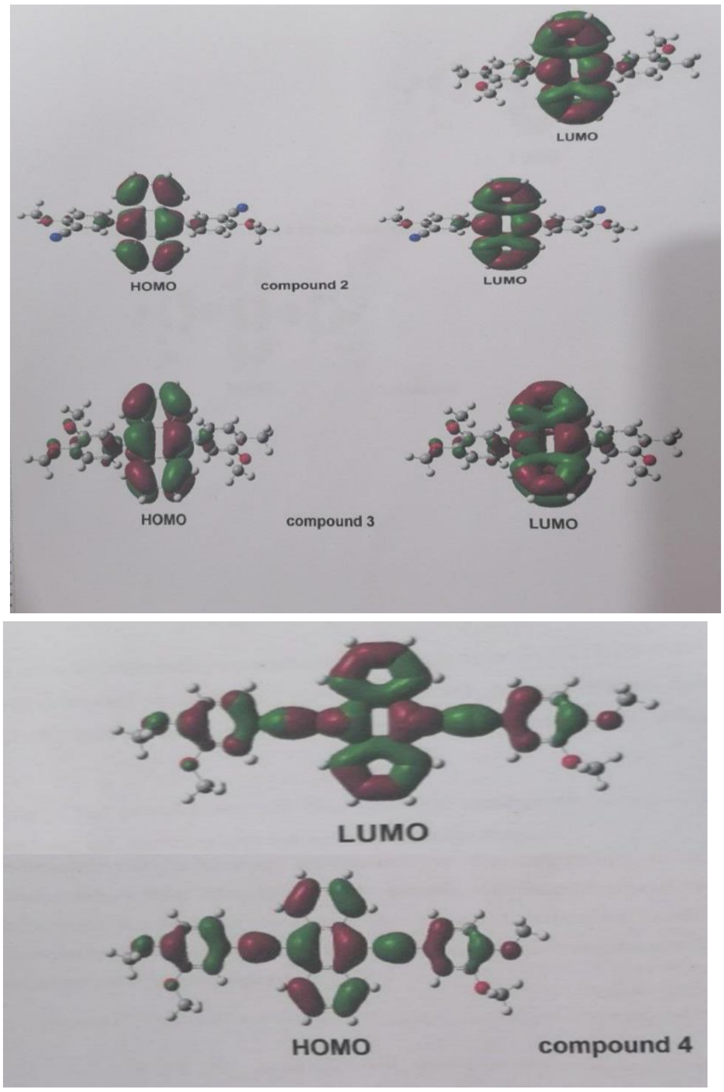

Figure 5. HOMO and LUMO distribution of the compounds.

4. Conclusion

a. Good relaxation was obtained for the studied compounds by using the B3LYP-DFT with a suitable 6-13G basis set. The calculated values of geometrical parameters and virial ratio of the compounds are in a good agreement with experimental data and other theoretical studies.

b. The total energy is independent on the position of the same subgroup in the compounds, it depends only on the number of electrons in cach compound.

c. Approximately, all the studied compounds show destabilization of LUMO and stabilization of HOMO, they both changed importantly to propose different structures play significant roles in electronic properties. The effect of symmetry and distribution of aromatic rings has an influence on the calculation of HOMO and LUMO,

d. Inserting the double and triple carbon-carbon bonds between the backbone anthracene molecule and and the phenyl rings in both donor and acceptor sides, and the presence of an electron attracting NO, subgroups in the compounds reducing the band gap of the compound.

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