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DFT and TD-DFT Investigation of the Electronic and Optical Properties of halogenated C60 Fullerene for Photonic and Laser Applications

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Abstract

Fullerene-based nanomaterials have attracted considerable attention owing to their unique electronic and optical characteristics and their potential applications in photonic and optoelectronic technologies. In the present study, the influence of chlorine functionalization on the electronic structure and optical behavior of C60 fullerene was investigated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Geometry optimization was performed at the B3LYP/6-31G(d) level, followed by frontier molecular orbital, global reactivity, density of states (DOS), and electronic circular dichroism (ECD) analyses. The calculated HOMO and LUMO energies of chlorinated C60 were −8.28 and −3.55 eV, respectively, yielding an energy gap of 4.73 eV. The derived global reactivity descriptors revealed enhanced electron-accepting ability and favorable charge-transfer characteristics after chlorination. Frontier molecular orbital analysis showed a redistribution of electron density between the occupied and unoccupied states, indicating improved electronic responsiveness. DOS analysis confirmed the semiconducting nature of the modified fullerene and demonstrated the formation of additional electronic states near the frontier orbital region. Furthermore, ECD calculations revealed a significant red shift in the first electronic excitation from 552.01 nm for pristine C60 to 1128.47 nm for chlorinated C60, accompanied by an extension of the optical response into the near-infrared region. The obtained results demonstrate that chlorine functionalization effectively modifies the electronic and optical properties of C60 fullerene, leading to enhanced optical activity and broader spectral responsiveness. These findings suggest that chlorinated fullerene derivatives may serve as promising candidates for future photonic, optoelectronic, and laser-related applications.

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1. Introduction

Fullerenes represent an important class of carbon nanomaterials that have attracted considerable attention due to their unique structural, electronic, and optical properties. Among them, C60 fullerene is one of the most extensively studied nanostructures because of its highly symmetric cage-like geometry, remarkable electron-accepting ability, and potential applications in optoelectronics, photovoltaics, sensors, and photonic devices [1-3]. The delocalized π-electron system of C60 enables efficient charge transport and electronic excitation processes, making it a promising candidate for advanced functional materials.

In recent years, chemical functionalization has emerged as an effective strategy for tailoring the physicochemical properties of fullerene-based systems. The introduction of heteroatoms or functional groups onto the fullerene surface can significantly modify the electronic structure, alter the frontier molecular orbital energies, and improve the optical response of the material. Among various functionalization approaches, halogen incorporation has received increasing interest because halogen atoms can influence charge distribution, molecular symmetry, and excited-state behavior, leading to enhanced optical and electronic performance [4-6].

Understanding the effect of halogen functionalization on the electronic and optical characteristics of fullerene derivatives is essential for the rational design of materials intended for photonic and laser-related applications. Computational chemistry methods, particularly density functional theory (DFT) and time-dependent density functional theory (TD-DFT), provide powerful tools for investigating these properties at the molecular level and for predicting the influence of structural modifications on electronic transitions and optical activity [7-10].

Therefore, the present study aims to investigate the electronic structure and optical properties of pristine C60 and chlorinated C60 fullerene using DFT and TD-DFT calculations. Particular attention is given to frontier molecular orbital characteristics, global reactivity descriptors, density of states distributions, and electronic circular dichroism spectra in order to evaluate the impact of chlorine functionalization on the optical behavior of the fullerene cage and its potential suitability for photonic and laser-related applications.

2. Computaional models

The computational models investigated in this study comprise pristine C60 fullerene and its chlorinated derivative (C60–Cl). Molecular structures were initially constructed and visualized using GaussView 6.0, while all quantum chemical calculations were performed using the Gaussian 16 software package [11-12]. Geometry optimizations and electronic structure evaluations were carried out within the framework of Density Functional Theory (DFT) at the B3LYP/6-31G(d) level of theory. This specific hybrid functional was chosen for its well-established reliability in accurately describing the structural, electronic, and optical properties of carbon-based nanomaterials.

Using the fully optimized geometries (illustrated in Figure 1), we determined key electronic parameters and frontier molecular orbital energies. These include the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, energy gap, ionization potential, electron affinity, electronegativity, chemical hardness, chemical softness, and the electrophilicity index. To probe the excited-state profiles and electronic transitions of both systems, time-dependent density functional theory (TD-DFT) calculations were executed at the same level of theory. Finally, a comparative analysis was performed to evaluate how chlorine functionalization modulates the electronic structure and optical response of the fullerene cage, assessing its viability for advanced photonic, optoelectronic, and laser-related technologies.

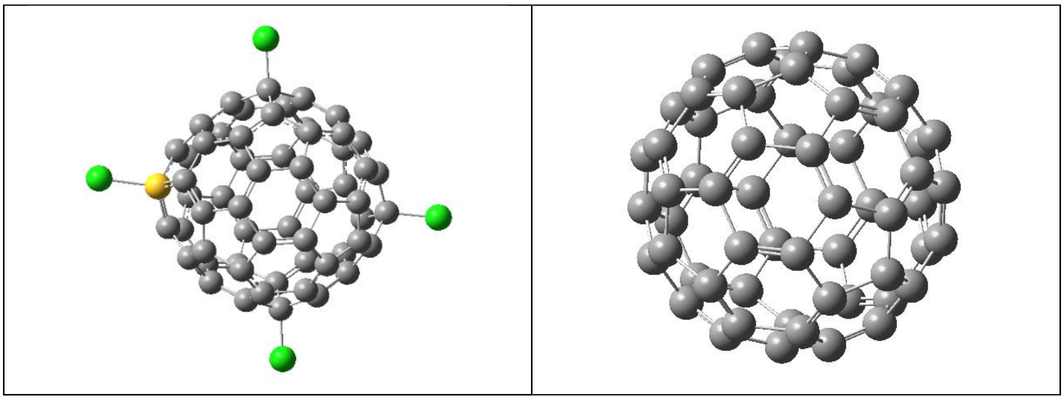


Fig 1: Optimized structures of pristine C60 and halogenated C60 fullerene.

3. Results and discusssions

3.1. Global reactivity

The calculated frontier molecular orbital parameters of the doped, halogenated C60 fullerene give us clear insights into its electronic structure and chemical reactivity [13-15]. As shown in Table 1, the HOMO and LUMO energies are −8.28 and −3.55 eV, respectively, which results in a moderate energy gap (ΔE) of 4.73 eV. This gap shows that the modified fullerene is electronically stable while remaining fully capable of participating in electronic excitation processes. Additionally, this narrower HOMO–LUMO separation compared to pristine fullerene proves that heteroatom doping and halogen functionalization successfully alter the electronic distribution and make charge-transfer interactions much easier. Its ionization potential (IP) of 8.28 eV and electron affinity (EA) of 3.55 eV indicate that the system strongly holds onto its own electrons, yet still maintains a solid capacity to accept additional electronic charge. The electronegativity value ($\chi = 5.92$ eV) highlights the strong electron-attracting nature of the modified fullerene surface, while its chemical hardness ($\eta = 2.36$ eV) points to a stable electronic setup with moderate resistance to charge shifting. Conversely, its chemical softness ($S = 0.424$ eV^{-1}) demonstrates the system's flexibility to undergo electronic polarization and form intermolecular interactions. Furthermore, the electrophilicity index ($\omega = 7.43$ eV) reveals a highly electrophilic character, meaning the doped fullerene can efficiently draw in electron density from surrounding molecules. This trait is incredibly valuable for applications involving charge-transfer processes, optoelectronic devices, and photonic materials. Ultimately, these quantum chemical descriptors confirm that the doped halogenated C60 fullerene boasts enhanced electronic responsiveness and great physicochemical traits, making it a highly promising candidate for advanced optical and laser technologies.

Table 1: Quantum chemical parameters of halogenated C60 fullerene calculated from frontier molecular orbital energies.

Parameter (eV)	Eq	Value
EHOMO	--	−8.28
ELUMO	--	−3.55
ΔE	ΔE = ELUMO − EHOMO	4.73
IP	IP = −EHOMO	8.28
EA	EA = −ELUMO	3.55
χ	$\chi = (IP + EA)/2$	5.92
η	$\eta = (IP - EA)/2$	2.36
S (eV^{-1})	$S = 1/\eta$	0.424
ω	$\omega = \chi^2/(2\eta)$	7.43

3.2. Frontier Molecular Orbital

The frontier molecular orbital analysis gives us a clear look into how electrons behave within the doped, halogenated C60 fullerene [16-17]. As shown in Figures 2, the electron density of the HOMO is mostly concentrated around specific areas of the fullerene cage especially near the dopant and functionalized sites which tells us that these spots serve as the main electron-donating centers. The LUMO orbital is much more spread out across the fullerene framework, drawing significant contributions from both the carbon cage and the dopant region, which points to a stronger ability to accept electrons. This striking contrast between where the HOMO and LUMO sit spatially shows that when electronic excitation happens, it triggers an internal charge transfer from the electron-rich zones to the electron-deficient ones. This shifting of charges clearly highlights how heavily doping and halogen functionalization impact the electronic structure of C60, reshaping its frontier orbital traits and boosting its overall electronic responsiveness. These findings perfectly back up the calculated HOMO–LUMO energy gap and prove that the modified fullerene has excellent charge-transfer properties that can elevate its performance in optical, photonic, and optoelectronic devices.

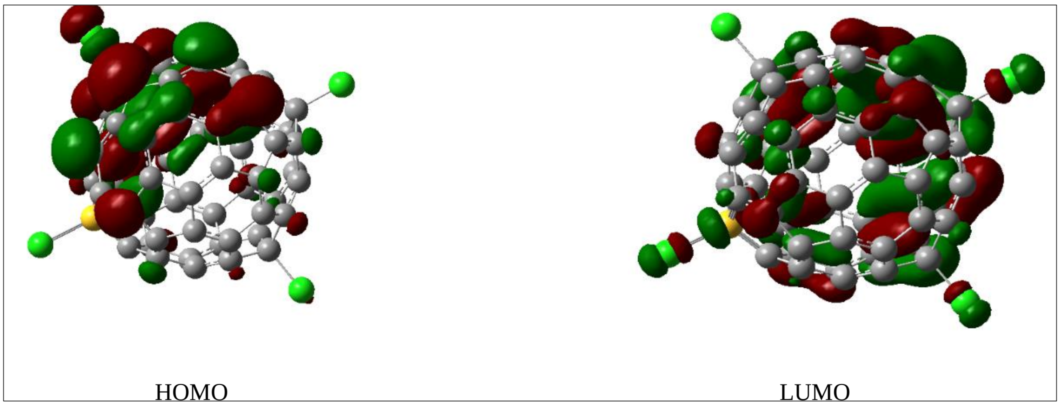


Fig 2: HOMO and LUMO orbitals of the halogenated fullerene.

3.3. The density of states (DOS)

The density of states (DOS) spectrum of the doped, halogenated C_{60} fullerene offers key insights into the distribution of electronic states and how doping alters the electronic structure [18]. As illustrated in Figure 3, the occupied molecular orbitals are predominantly clustered within the -20 to -8 eV energy range, whereas the virtual (unoccupied) orbitals emerge around -3.5 eV and extend up to the Fermi region. A distinct energy gap separates the highest occupied and lowest unoccupied states, confirming the semiconducting behavior of this modified fullerene system. The appearance of multiple intense DOS peaks in the occupied region reflects a high density of available electronic states, which stem from the π-conjugated carbon framework and the direct contribution of the dopant atoms. Additionally, the emergence of electronic states near the frontier orbital region indicates that doping combined with halogen functionalization successfully modulates the electronic structure, thereby facilitating electronic transitions. This narrowed separation between the occupied and virtual states aligns with the calculated HOMO–LUMO energy gap of 4.73 eV, pointing to enhanced electronic responsiveness and charge-transfer efficiency. Ultimately, these tailored characteristics promote optical excitation processes, highlighting the strong potential of this doped fullerene for applications in photonic, optoelectronic, and laser-based technologies.

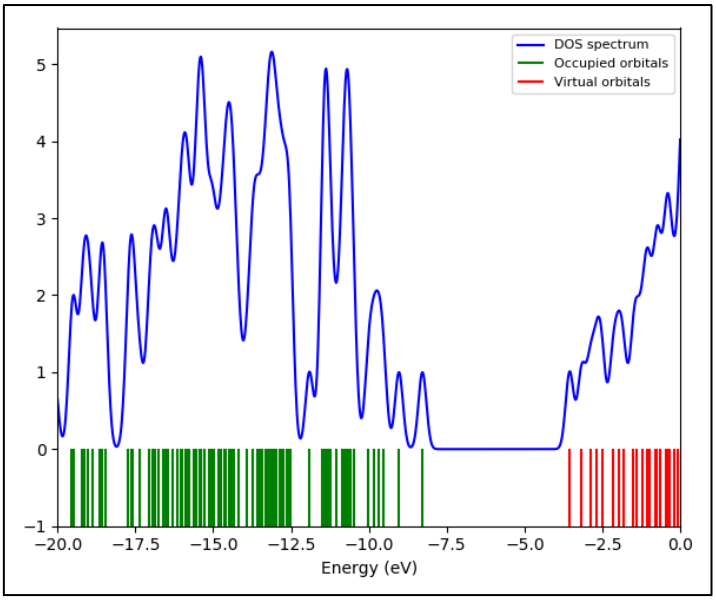
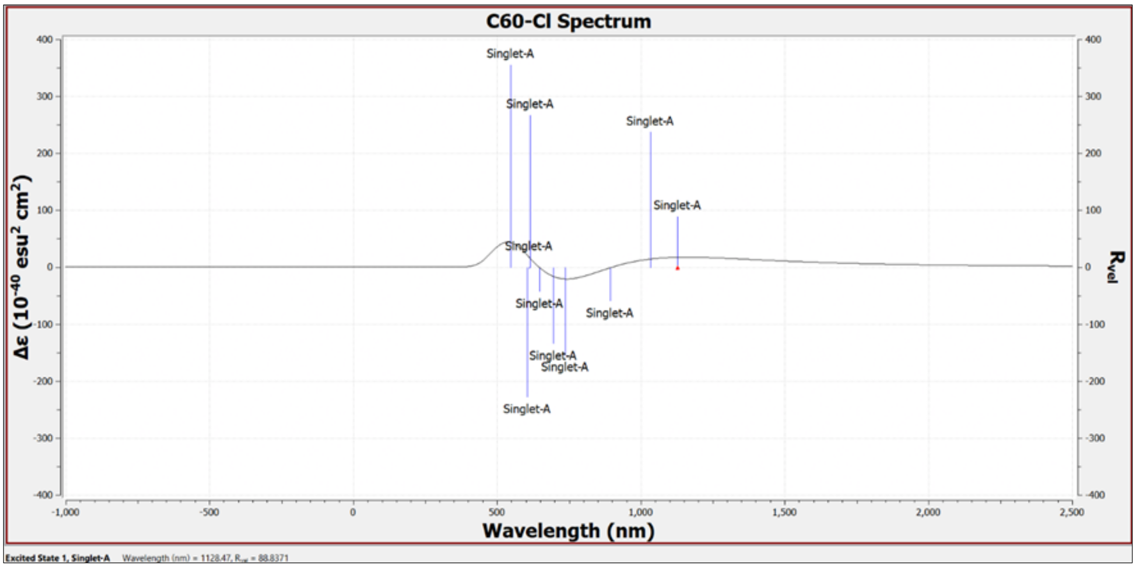


Fig 3: Density of states (DOS) spectrum of the doped halogenated C60 fullerene showing the distribution of occupied and virtual molecular orbitals and the electronic states surrounding the frontier orbital region.

3.4. Electronic Circular Dichroism (ECD)

The electronic circular dichroism (ECD) spectra of pristine and chlorinated (C60) provide clear evidence of how chlorine functionalization modulates the excited-state electronic structure and optical behavior of the fullerene cage [19-20]. As illustrated in Figures 4, pristine (C60) displays limited electronic transitions primarily confined to the visible region, with its first excited state appearing at approximately 552.01 nm. This spectrum is characterized by weak optical activity and a narrow spectral distribution a direct consequence of the fullerene's highly symmetric structure, which restricts the number of allowed electronic transitions and reduces overall transition probabilities. Conversely, chlorination significantly alters the fullerene framework, driving remarkable changes in the ECD profile. The first electronic excitation undergoes a pronounced red shift to 1128.47 nm (a net shift of approximately 576.46 nm relative to the pristine cage). Furthermore, the emergence of several new transitions across both the visible and near-infrared (NIR) regions confirms the creation of novel electronic states induced by chlorine incorporation. The coexistence of positive and negative rotational strengths reflects a substantial redistribution of electron density during excitation, stemming from the broken molecular symmetry. By perturbing the (pi)-electron system of the cage, the chlorine substituents lower the excitation threshold and facilitate efficient charge-transfer transitions.

These spectral modifications demonstrate that chlorination not only amplifies the optical activity of (C60) but also extends its spectral responsiveness deep into the NIR domain. This behavior is driven by the modification of frontier molecular orbitals and the increased contribution of low-energy excited states born from the interaction between the chlorine atoms and the carbon framework. Ultimately, these ECD findings confirm that chlorine functionalization is an effective strategy for tuning the optical traits of (C60) yielding enhanced light harvesting, optimized excitation dynamics, and broader spectral coverage. These enhanced features underscore the strong potential of chlorinated fullerene derivatives in advanced photonics, optoelectronics, nonlinear optics, and NIR laser technologies.



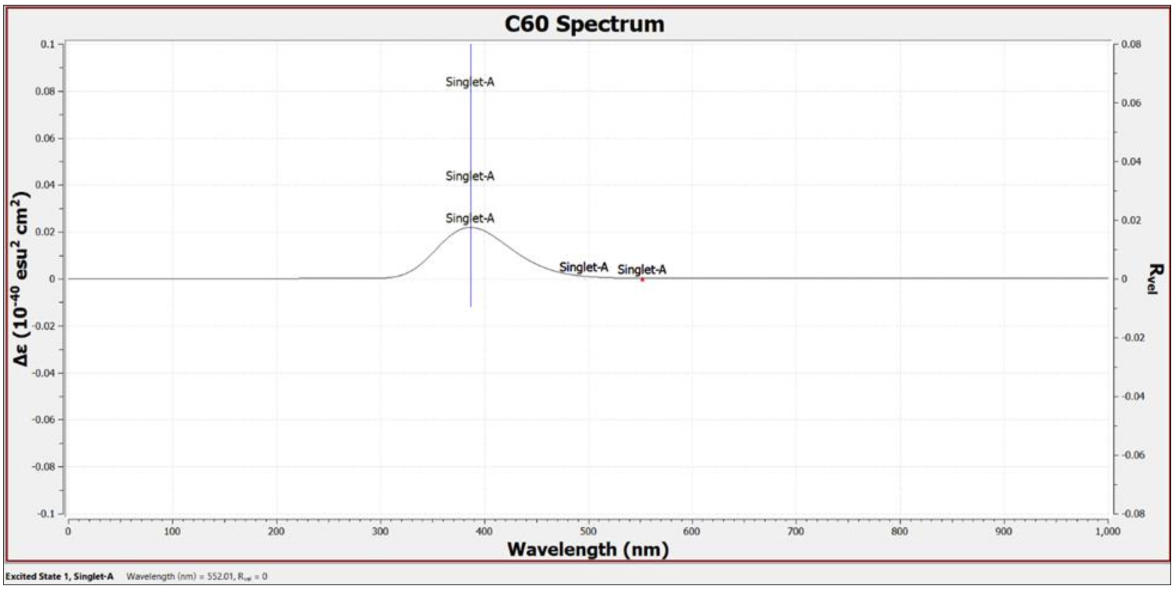


Fig 4: ECD spectra of pristine C60 and chlorinated C60 showing the effect of chlorination on the optical transitions and spectral response.

5. Conclusion

In this study, the electronic and optical properties of pristine and chlorinated C60 fullerene were investigated using DFT and TD-DFT calculations. The results demonstrated that chlorine functionalization significantly modifies the electronic structure of the fullerene cage, leading to changes in frontier molecular orbital energies and global reactivity descriptors. The calculated HOMO–LUMO energy gap of 4.73 eV confirmed the semiconducting nature and electronic stability of the chlorinated system. Frontier molecular orbital and DOS analyses revealed enhanced charge-transfer characteristics and improved electronic responsiveness following chlorination. Furthermore, ECD calculations showed a pronounced red shift in the first electronic excitation from 552.01 to 1128.47 nm, indicating an extension of the optical response into the near-infrared region. The obtained findings demonstrate that chlorine functionalization is an effective approach for tuning the electronic and optical behavior of C60 fullerene and highlight the potential of chlorinated fullerene derivatives for photonic, optoelectronic, and laser-related applications.

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