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Computational Investigation of the Structural, Vibrational, and Optoelectronic Properties of DH4T: A DFT Study

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Abstract

In this communication, the structural, vibrational, electronic, and optical properties of DH4T, a dialkyl-substituted quaterthiophene, were investigated using density functional theory. The molecular geometry was optimized at the B3LYP/6-311G(d,p) level using Gaussian 09, followed by analysis of the vibrational spectra, frontier molecular orbitals, electronic properties, and electron-density distribution. The calculated IR spectrum exhibits prominent features near 560, 1250, and 1600 cm^{-1}, while the Raman spectrum shows notable bands around 1100 and 1500 cm^{-1}. The calculated UV-visible spectrum displays a prominent absorption near 450 nm, corresponding to an optical energy of approximately 2.76 eV. The calculated HOMO and LUMO energies are -4.8232 and -1.7780 eV, respectively, giving a HOMO-LUMO separation of 3.0452 eV. Global reactivity descriptors were also evaluated to characterize the electronic behaviour of the molecule. The combined vibrational, electronic, and optical results provide a molecular-level understanding of DH4T and indicate its potential relevance for further investigation as a conjugated organic material for optoelectronic applications.

Keywords: DH4T; quaterthiophene; density functional theory; B3LYP; vibrational spectra; UV-visible spectroscopy; HOMO-LUMO; optoelectronic properties.

1. Introduction

π-Conjugated organic molecules have attracted considerable attention as functional materials because their electronic structures and optical properties can be tuned through molecular architecture and chemical substitution. In particular, oligothiophenes and quaterthiophene derivatives possess extended π-conjugated backbones that facilitate electronic delocalization and make them interesting candidates for organic electronic and optoelectronic applications. Substitution with alkyl chains can further influence molecular solubility, processability, and intermolecular interactions, thereby providing additional control over the properties of these materials [1-3].

DH4T, a dialkyl-substituted quaterthiophene, represents an interesting molecular system in which an extended thiophene framework is combined with alkyl substitution. Understanding its structural, vibrational, electronic, and optical characteristics at the molecular level is important for assessing its potential in functional organic materials. Infrared and Raman spectroscopy provide complementary information on molecular vibrations, while UV-visible spectroscopy gives insight into electronic excitations and optical absorption. Computational approaches can complement these spectroscopic investigations by relating the calculated properties to the molecular electronic structure [4,5].

Density functional theory (DFT) has become an established approach for studying the geometrical and electronic properties of organic molecules. The B3LYP functional, in combination with suitable basis sets, has been extensively employed for molecular structure, vibrational frequencies, frontier molecular orbitals, and related electronic properties [6-8]. In addition, frontier molecular orbital analysis and conceptual-DFT descriptors provide useful information about the electronic structure and chemical behaviour of molecular systems [9,10].

In this communication, we present a DFT-based investigation of DH4T focusing on its optimized molecular structure, vibrational characteristics, IR and Raman spectra, UV-visible absorption, frontier molecular orbitals, HOMO-LUMO energy separation, and global reactivity parameters. The calculated results provide a concise molecular-level description of DH4T and its electronic and optical characteristics.

2. Methodology

The molecular geometry of DH4T was optimized using density functional theory with the B3LYP hybrid exchange-correlation functional and the 6-311G(d,p) basis set, as implemented in Gaussian 09 [6,11]. The optimized geometry was used for subsequent electronic and vibrational calculations. Harmonic vibrational-frequency calculations were performed at the same level of theory to obtain the IR and Raman spectra and to characterize the normal modes of the optimized structure. The calculated vibrational frequencies were analyzed using the corresponding normal-mode displacement vectors, while molecular structures, vibrational modes, and frontier molecular orbitals were visualized using GaussView 5.0.

The electronic properties were analyzed through the HOMO and LUMO energies and their energy separation. The ionization potential and electron affinity were estimated from the frontier-orbital energies, and the global reactivity descriptors were calculated using the conventional conceptual-DFT relationships [9,10]:

$$I = -E_{HOMO}, A = -E_{LUMO}, \chi = \frac{I+A}{2}, \mu = -\chi, \eta = \frac{I-A}{2}, S = \frac{1}{2\eta}, \text{and } \omega = \frac{\mu^2}{2\eta}$$

The optical properties were evaluated from the calculated electronic transitions. The resulting excitation wavelengths and oscillator strengths were used to analyze the UV-visible absorption characteristics of DH4T. The calculated spectral and electronic parameters were subsequently correlated with the extended π-conjugated molecular framework to provide an integrated description of its structural, vibrational, and optoelectronic properties.

3. Result and discussion

The molecular geometry of DH4T was optimized using the B3LYP/6-311G(d,p) method. The optimized structure is shown in Fig. 1. DH4T consists of an extended quaterthiophene framework in which four thiophene units form the principal conjugated backbone, while the alkyl substituents provide additional molecular flexibility and can influence the solubility and processing characteristics of the molecule. The optimized geometry was subsequently used for the vibrational, electronic, and optical calculations.

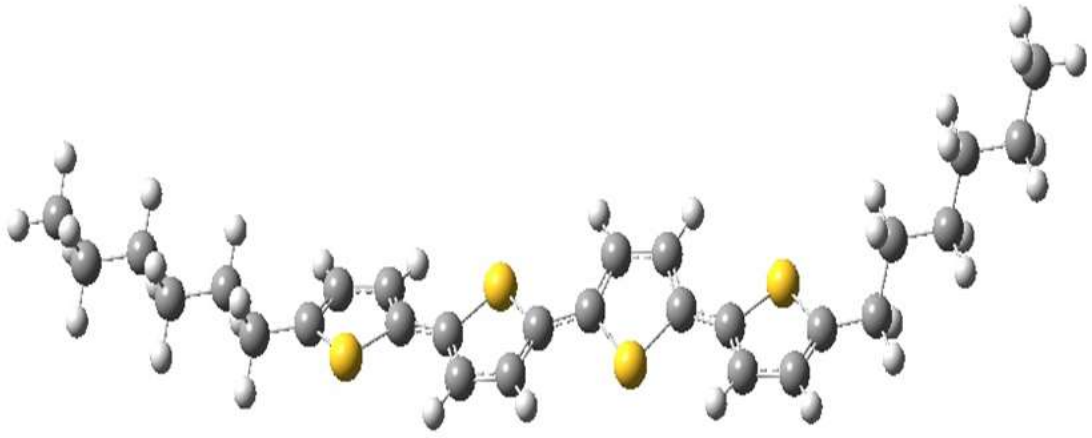


Fig (1) Optimized structure of DH4T molecule.

3.1 IR spectra

The calculated infrared (IR) spectrum of DH4T is presented in Fig. 2. The spectrum provides a characteristic vibrational fingerprint of the optimized molecular structure. Several prominent bands are observed in the calculated spectrum, with notable features occurring near 560, 1250, 1600, 3000, and 3240 cm^{-1}.

The bands in the lower- and middle-frequency regions are mainly associated with skeletal and deformation modes of the conjugated molecular framework, whereas the higher-frequency region is associated with C–H stretching vibrations. In particular, the calculated mode at 3046.10 cm^{-1} is assigned to C–H stretching of the conjugated framework. The calculated vibrational modes listed in the manuscript range from 231.73 to 3046.10 cm^{-1}.

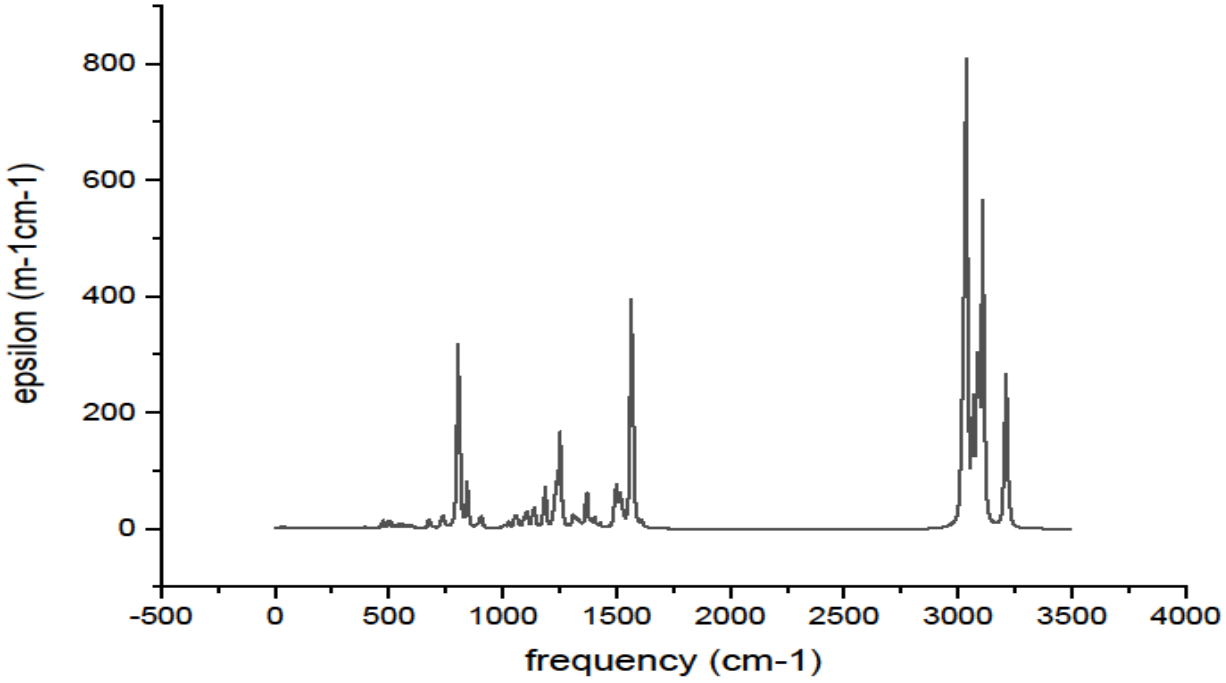


Fig (2) Calculated infrared spectrum of DH4T showing the characteristic vibrational absorption bands of the molecule.

The prominent feature around 1250 cm^{-1} can be associated with vibrational motions involving the C–H/C–C framework, while the band near 1600 cm^{-1} occurs in a region characteristic of skeletal stretching vibrations within the conjugated system. However, individual normal modes may involve coupled atomic motions; therefore, detailed assignments should be based on the corresponding calculated normal-mode displacement vectors rather than frequency values alone.

3.2 Modes of vibrations

The calculated vibrational frequencies of DH4T were analyzed by examining the corresponding normal-mode displacement vectors. The lower-frequency region is predominantly associated with skeletal deformations and collective motions of the conjugated quaterthiophene framework, whereas the intermediate-frequency modes mainly involve C–C and C–H bending and ring deformation. The band at 3046.10 cm^{-1} is assigned to C–H stretching vibrations of the aromatic/thiophene framework. The calculated frequencies provide a characteristic vibrational fingerprint of the optimized DH4T molecule tabulated in table 1.

Table 1: Modes of vibration in DH4T molecule.

S.N.	Frequency	Modes of vibrations
1	451.16	Bending between C-H bond
2	551.81	Symmetric stretching between C-H bond
3	845.36	Scissoring between C-C bond
4	1053.27	Bending in C-C thiopene ring
5	1221.84	Rocking in C-H thiopene ring
6	1238.81	Scissoring between carbon of two ring

7	1251.56	Rocking in C-H bond
8	1429.62	Wagging C-H bond
9	3046.10	Asymmetric stretching C-H bond

3.3 UV-Vis spectra

The calculated UV–visible spectrum of DH4T is shown in Fig. 3. The spectrum exhibits a prominent absorption band at approximately 450 nm, which lies in the visible region. This absorption is associated with an electronic excitation involving the extended π-conjugated quaterthiophene framework of DH4T. The presence of a visible-region absorption band reflects the ability of the conjugated molecular backbone to undergo relatively low-energy electronic excitation.

The corresponding photon energy can be estimated from

$$E = \frac{hc}{\lambda} \approx 2.76\ eV$$

This value represents the energy corresponding to the 450-nm optical absorption and should not be identified directly with the calculated HOMO-LUMO energy separation. In the present calculation, the HOMO and LUMO energies are -4.8232 and -1.7780 eV, respectively, giving a frontier-orbital separation of 3.0452 eV. These quantities describe different aspects of the electronic structure: the HOMO-LUMO difference is an orbital-energy descriptor, whereas the wavelength-derived value corresponds to the optical transition energy.

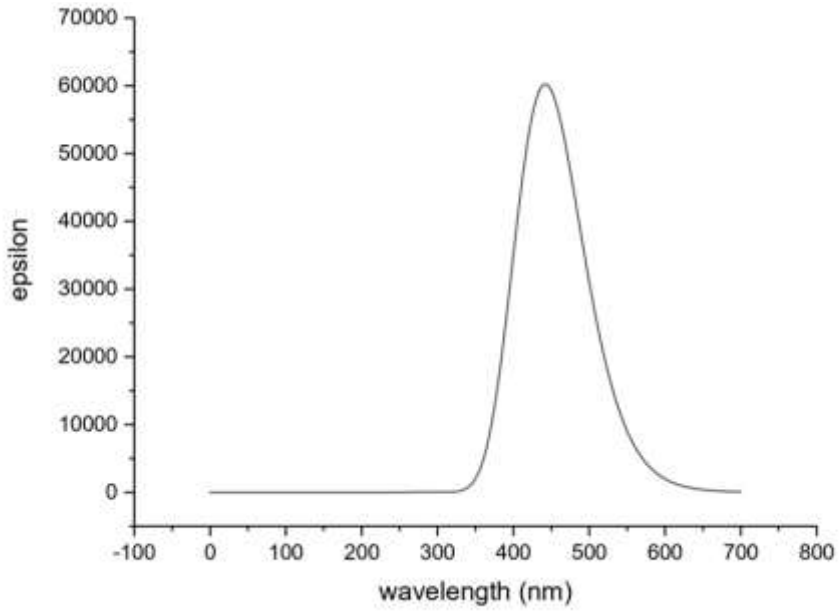


Fig (3) Calculated UV-visible absorption spectrum of DH4T showing the prominent absorption band near 450 nm.

The calculated absorption therefore provides useful information about the optical response of DH4T and, together with the frontier molecular orbital analysis, indicates the influence of its extended π-conjugated framework on its electronic properties. A definitive assignment of the 450-nm band to a particular orbital transition, such as HOMO→LUMO, should be made only from the corresponding excited-state calculation and molecular-orbital contributions.

3.4 Raman Activity

The calculated Raman spectrum of DH4T is presented in Fig. 4. Raman spectroscopy provides complementary information to the IR spectrum because Raman-active vibrations are associated with changes in molecular polarizability. The calculated spectrum of DH4T exhibits prominent Raman features near 1100 and 1500 cm^{-1}, as observed in the simulated spectrum.

The Raman bands in this region can be attributed to vibrational motions involving the conjugated molecular framework, including coupled C–C stretching and skeletal deformation modes of the thiophene units and their substituents. The calculated feature near 1100 cm^{-1} is particularly associated with vibrations involving the carbon framework, while the band around 1500 cm^{-1} occurs in a region characteristic of vibrations of the conjugated backbone. Since individual normal modes can involve coupled atomic motions, the detailed assignments should be confirmed from the corresponding calculated normal-mode displacement vectors.

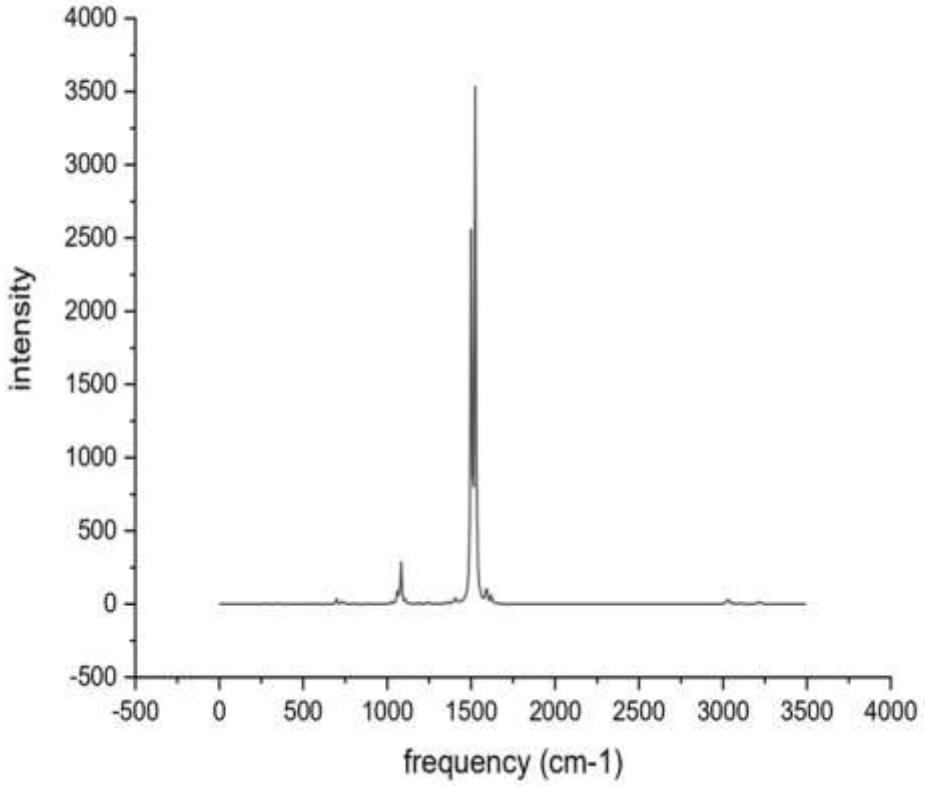


Fig (4) Calculated Raman spectrum of DH4T showing prominent vibrational features near 1100 and 1500 cm^{-1}.

The calculated Raman spectrum therefore provides complementary information to the IR spectrum and further characterizes the vibrational behaviour of DH4T. The predicted Raman features may also serve as useful reference points for future experimental spectroscopic investigations of the molecule.

3.5 Frontier molecular orbital analysis

The frontier molecular orbital (FMO) distribution of DH4T is shown in Fig. 5. The calculated HOMO and LUMO energies are -4.8232 eV and -1.7780 eV, respectively, giving a HOMO-LUMO energy separation of 3.0452 eV.

The HOMO and LUMO distributions provide information about the electronic structure of the conjugated DH4T framework. The spatial distribution of these orbitals can be used to identify the regions of the molecule that are predominantly involved in electron donation and electron acceptance. For a π-conjugated molecule such as DH4T, the frontier orbitals are particularly relevant to understanding its electronic excitation and optical response.

The calculated HOMO-LUMO separation of 3.0452 eV represents the difference between the corresponding Kohn-Sham orbital energies. A relatively substantial orbital separation indicates that an appreciable amount of energy is required to alter the frontier-orbital electronic configuration. However, the HOMO-LUMO gap should be regarded as an electronic-structure descriptor rather than directly equated with the optical excitation energy obtained from the UV-Vis calculation.

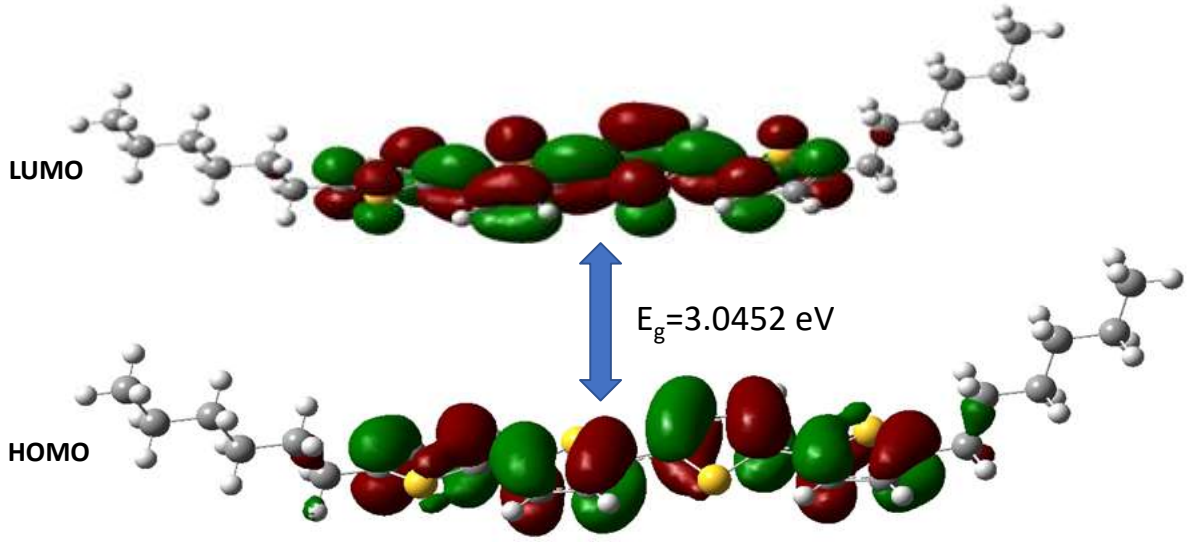


Fig (5) Spatial distributions of the HOMO and LUMO of DH4T calculated at the B3LYP/6-311G(d,p) level, showing a HOMO-LUMO energy separation of 3.0452 eV.

The FMO analysis, together with the calculated absorption near 450 nm, provides complementary information about the electronic and optical behaviour of DH4T. The combined results demonstrate the influence of the extended π-conjugated framework on the frontier electronic structure of the molecule.

3.6 Global reactivity parameters

The global reactivity descriptors were calculated from the HOMO and LUMO energies to assess the electronic characteristics of DH4T. The calculated ionization potential and electron affinity are 4.8232 and 1.7780 eV, respectively. The corresponding electronegativity and chemical potential are 3.3006 and -3.3006 eV. The chemical hardness is 1.5226 eV, while the corresponding softness is 0.3284 eV^{-1}. The positive hardness value indicates a moderate resistance of the molecule toward changes in its electronic distribution, whereas the softness value provides a complementary measure of its electronic flexibility. The calculated electrophilicity index is approximately 3.58 eV, indicating the electron-accepting character of the molecule within the adopted conceptual-DFT framework. The HOMO-LUMO energy gap of 3.0452 eV further characterizes the electronic structure of DH4T.

Table 2: Global reactivity parameters of DH4T molecule.

Global reactivity parameters	**DH4T**
HOMO (eV)	-4.8232
LUMO (eV)	-1.7780
IP	4.8232
EA	1.7780
Electronegativity	3.3006
Chemical potential	-3.3006
Hardness	1.5226
Softness	0.6568
Electrophilicity index	3.5800
Energy gap	3.0452

3.7 Electron-Density Analysis

The calculated electron-density distribution of DH4T is presented in Fig. 6. Electron density provides information about the spatial distribution of electrons within the molecule and therefore helps in understanding the distribution of electronic charge across the molecular framework.

The calculated distribution reflects the electronic character of the conjugated quaterthiophene framework and provides a visual representation of the regions with different electron densities. The distribution is influenced by the molecular geometry, conjugated π-electron system, and the presence of the substituent groups. Such an analysis complements the frontier molecular orbital results by providing additional information about the overall electronic distribution of the molecule.

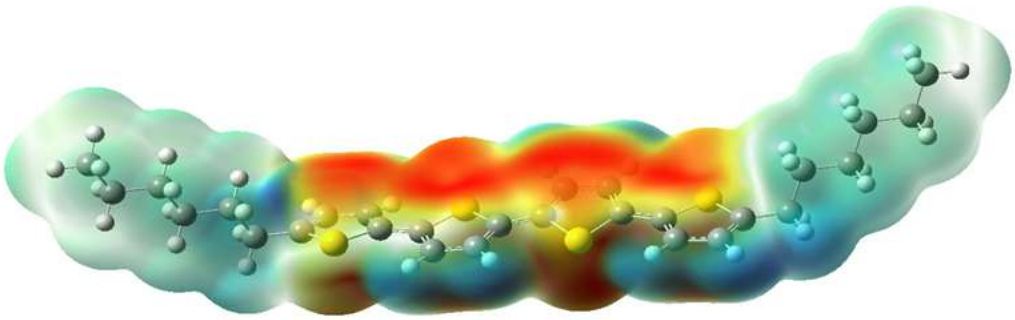


Fig (6) Calculated electron-density distribution of DH4T showing the spatial distribution of electronic charge over the molecular framework.

The electron-density surface should be interpreted carefully in relation to the quantity actually plotted. If the surface in Fig. 6 is an electrostatic-potential (ESP/MEP)-mapped electron-density surface, the colour regions represent variations in electrostatic potential rather than electron density itself. Therefore, the colour scale should be described according to the legend of the calculated surface rather than simply assigning red to "high electron density" and blue to "low electron density." The present manuscript describes the figure in terms of red and blue electron-density regions, but the exact plotted quantity should be verified from the Gaussian/GaussView calculation.

Conclusion:

In the present study, the structural, vibrational, electronic, and optical properties of DH4T were investigated using density functional theory. The optimized molecular structure and calculated vibrational spectra provide useful insight into the characteristic features of this conjugated quaterthiophene system. The calculated IR spectrum shows prominent bands in the low-, mid-, and high-frequency regions, including notable features around 1250 and 1600 cm^{-1}, while the Raman spectrum exhibits strong features near 1100 and 1500 cm^{-1}. These vibrational characteristics reflect the different stretching and bending motions of the conjugated molecular framework.

The calculated UV-Vis spectrum shows a prominent absorption band around 450 nm, corresponding to an optical transition energy of approximately 2.76 eV. The frontier molecular orbital analysis gives HOMO and LUMO energies of -4.8232 and -1.7780 eV, respectively, resulting in a HOMO-LUMO energy separation of 3.0452 eV. The calculated global reactivity descriptors further provide information about the electronic character and chemical response of DH4T. The molecule also exhibits a dipole moment of 0.3912 Debye, indicating a relatively low overall molecular polarity.

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References

1. Roncali, J. Conjugated poly(thiophenes): synthesis, functionalization, and applications. Chemical Reviews 1992, 92, 711–738.
2. McCullough, R. D. The chemistry of conducting polythiophenes. Advanced Materials 1998, 10, 93–116.
3. Handbook/review reference specifically describing substituted oligothiophenes/quaterthiophenes should be added here if DH4T's experimental application is being discussed.
4. Banwell, C. N.; McCash, E. M. Fundamentals of Molecular Spectroscopy, 4th ed.; McGraw-Hill, 1994.
5. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 6th ed.; Wiley, 2009.
6. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.
7. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 1988, 37, 785–789.
8. Andersson, M. P.; Uvdal, P. New scale factors for harmonic vibrational frequencies using the B3LYP density functional method with the triple-ζ basis set 6-311+G(d,p). J. Phys. Chem. A 2005, 109, 2937–2941.
9. Parr, R. G.; Pearson, R. G. Absolute hardness: companion parameter to absolute electronegativity. J. Am. Chem. Soc. 1983, 105, 7512–7516.
10. Parr, R. G.; Szentpály, L. v.; Liu, S. Electrophilicity index. J. Am. Chem. Soc. 1999, 121, 1922–1924.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.