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Investigations and doping effect on tetrapyrrolofluorene derivatives theoretically to produce potential semiconductor materials: Through DFT insight

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Abstract

This study examines the electronic and thermodynamic parameters of three tetrapyrrolofluorene based derivatives using the density functional theory (DFT) approach. These computations of these parameters were done using the Density Functional Theory (DFT) with B3LYP functional associated with both 6-31G (d, p) basis set. All the calculations were performed in the gas phase. The goal is to demonstrate the influence of the implantation or doping of hetero atoms (Si, S, and Se) on tetrapyrrolofluorene's electronic and thermodynamic capabilities. These characteristics lead to the introduction of silicon atom in tetrapyrrolofluorene molecule can be an efficient choice for optoelectronic purposes and produce potential semiconductors.

Keywords: DFT, tetrapyrrolofluorene, frontiers molecular orbitals, thermodynamic parameters

Introduction

Shirakawathe, MacDiarmid, and Hedger received the Nobel Chemistry Prize in 2000 for the recognition of some organic molecules with semiconductor characteristics^[1], which piqued the scientific interest in organic semiconductors and identified an area known as "organic electronics"^[2]. The field of organic electronics has substantial possibilities for expanding the scope of classic semiconductor sectors and achieving services that are practically unattainable to implement with standard semiconductors. Conjugated organic molecules have been rigorously studied and applied in a variety of fields of organic electronic uses such as solar cells, organic light-emitting diodes, field-effect transistors, and photovoltaic devices^[3-6], etc. because of their versatility, ease of manufacture, and low cost. The optoelectronic features of these electronics are influenced by a variety of parameters, including electron density on frontier molecular orbitals (FMOs), frontier molecular orbital energies and their energy gap, appropriate charge carriers, molecule structural features, and so on^[7]. The energies of the frontier molecular orbitals (FMOs) and their energy gap, the electron density on the frontier molecular orbitals (FMOs), appropriate charge carriers, the structural characteristics of molecules, and other parameters are related to the optoelectronic features of these electronic devices^[7]. On the other hand, recently a lot of theoretical study has been done to anticipate the attributes of organic materials. The optical and electronic properties of organic semiconductor materials can be adjusted as needed, making the design of novel materials simpler and more affordable. The energy gap of organic semiconductors can be predicted theoretically, and the optoelectronic properties of organic semiconductor materials can be adjusted as needed, making the creation of novel materials simpler and more cost-effective. Many studies have proved that the DFT and TD-DFT theories provide accurate findings for π -conjugated systems.

Over the past few years, there has been a lot of interest in a novel strategy such as incorporating heteroatoms into π -conjugated systems. This involves substituting various heteroatoms, like silicon (Si), oxygen (O), sulphur (S), selenium (Se), and nitrogen (N), in place of carbon atoms. Ting Qi *et al.* synthesized a series of carbazole or fluorene-based and dicyanovinyl-capped oligomers containing thiophene or benzene portions and studied their physical characteristics^[8].

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Their findings suggest that these kinds of materials have appropriate HOMO and LUMO energy levels, while the compounds that attached thiophene segments have lower LUMO energy levels. These materials also exhibit good thermal stability. Their study concluded that these organic compounds are potential candidates for n-channel semiconductors. Qi *et al.* conducted an extensive theoretical analysis on heteroatom-bridged heterofluorenes built up with a double heteroatom bridge of biphenyl to demonstrate the impact of highly inserted heteroatoms on the molecular framework and π -conjugation for various optoelectronic capabilities^[9]. Their analysis demonstrated that all the studied compounds showed intriguing potential optoelectronic capabilities due to their extensively fused molecular arrangement with substantial π -conjugation. However, they

conclude that introducing various kinds and proportions of heteroatoms would lead to varying capabilities.

The approach of introducing heteroatoms to create or design extremely flexible π -conjugated materials or systems may be applied to offer a fresh perspective on the fabrication of innovative small molecules for high-performance optoelectronic uses. This work provides a theoretical investigation of electronic and thermodynamic parameters for tetrapyrrolofluorene (TPF) and its derivatives based on the introduction (doping) of heteroatoms (Si, S, and Se) such as tetrapyrrolo-dibenzosilole (TPDBSi), tetrapyrrolo-dibenzothiophene (TPDBT), tetrapyrrolo-dibenzoselenophene (TPDBSe). The structure of the designed molecules is displayed in Figure 1. The molecules proposed or designed in this study have not been previously reported, studied, or synthesized.

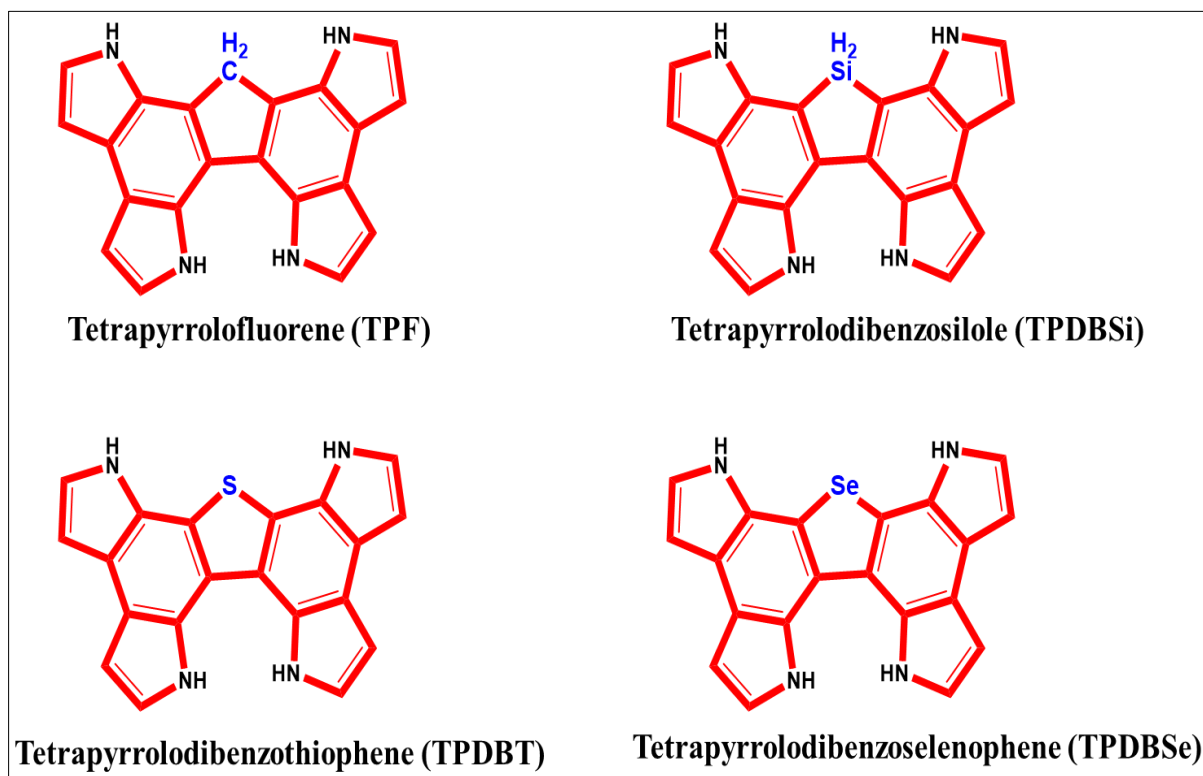


Fig 1: Structure of the designed tetrapyrrolofluorene (TPF) and its derivatives

Computational method

Gaussian 09 software package^[10] was used for computational calculations. Density functional theory (DFT) with B3LYP functional^[11-14] and basis set 6-31G (d, p)^[15] was applied to optimize structures of the designed tetrapyrrolofluorene (TPF) and its derivatives. The gaseous phase was used for conducting all the calculations. To confirm that the structures are fully optimized, vibration frequencies at the same level of theory were also calculated. Further, DFT calculations were used at the same levels of theory to calculate the energy of frontier molecular orbitals with their electronic distribution, HOMO-LUMO energy gap, and thermodynamic parameters.

Results and Discussion

Initially, the geometry of the TPF and its derivatives

was optimized using the molecular mechanics approach and then reoptimized through a semi-empirical methodology with the PM6 functional. Furthermore, these structures were again optimized using the density functional theory approach with B3LYP functional and basis set 6-31G (d, p). To confirm the potential energy minima for the geometry of TPF, and its derivatives were tested using frequency calculations. The zero imaginary frequencies proved that the geometry of the TPF and its derivatives was entirely or fully optimized. All the calculations were carried out in the gaseous phase. The DFT-optimized structures of the TPF and its derivatives are shown in (Figure 2). Moreover, the energy of border molecular orbitals and their electronic distribution, HOMO-LUMO energy gap, and thermodynamic parameters were determined using DFT computations at the same levels of theory.

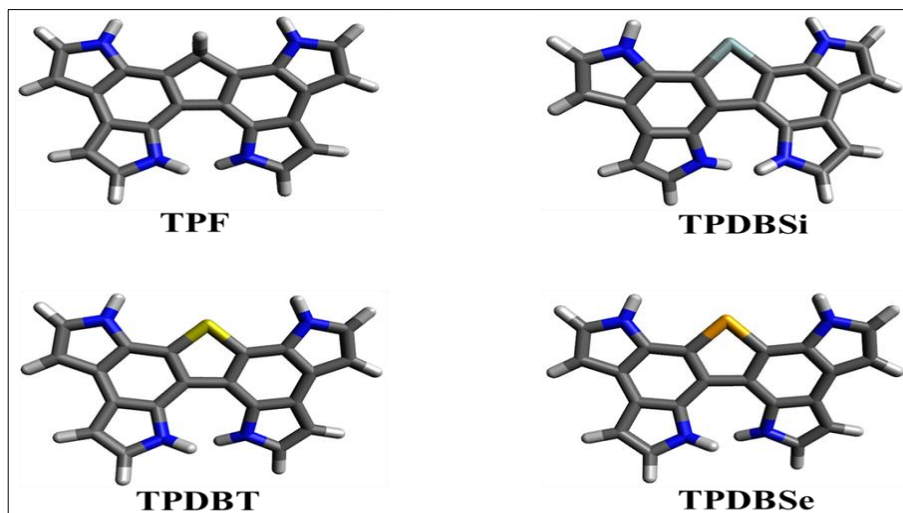


Fig 2: DFT-optimized structures of the TPF, TPDBSi, TPDBT, and TPDBSe

Frontier molecular orbitals

To look into the optoelectronic characteristics, frontier molecular orbital energy levels, HOMO-LUMO energy gaps in eV, and frontier molecular orbital's electronic patterns were calculated for the TPF, TPDBSi, TPDBT, and TPDBSe (Figure 3). We determined the frontier molecular orbital energies and their electronic patterns of the TPF, TPDBSi, TPDBT, and TPDBSe through the DFT approach with B3LYP hybrid functional and a 6-31 G (d, p) basis set. Table 1 summarises the energies of frontier molecular orbitals and their energy gaps. The incorporation of silicon (Si), sulphur (S), and selenium (Se) atoms in the TPF molecule lowers (stabilized) the HOMO and LUMO levels. Introducing the Si atom in the TPF molecule greatly stabilized the LUMO level. TPDBT and TPDBSe have low LUMO levels due to the electrophilic nature of their S, and Se atoms. The HOMO-LUMO gap, which is the energy difference between HOMO and LUMO levels, is an extremely important designation to explain reactivity parameters for molecular frameworks. A system that is more chemically reactive and softer due to a smaller HOMO-LUMO gap. The systematic trend of the HOMO-LUMO gap is as TPDBT (3.972eV) > TPDBSe

(3.908eV) > TPF (3.715eV) > TPDBSi (2.050eV). We discovered that the TPDBSi molecule (incorporation of silicon in TPF) has a smaller band gap than the other TPF, TPDBSi, and TPDBT, indicating that it is more reactive. Overall, TPDBSi is more chemically reactive and softer due to a smaller HOMO-LUMO gap. The smaller HOMO-LUMO gap of TPDBSi (silicon substituted derivatives of TPF) explores and better tailors the electro-optical characteristics. Furthermore, in the case of the HOMO level, electron density delocalized on the entire molecule except the C, Si, S, and Se atoms present in a central five-membered ring, whereas delocalized electron density in case of LUMO on the core part of TPF, TPDBSi, TPDBT, and TPDBSe, according to the electronic distributions of frontier molecular orbitals (Fig 3).

Table 1: Energies of HOMO and LUMO with their energy gap (in eV) for TPF, TPDBSi, TPDBT, and TPDBSe

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
TPF	-4.319	-0.604	3.715
TPDBSi	-4.493	-2.443	2.050
TPDBT	-4.600	-0.628	3.972
TPDBSe	-4.602	-0.693	3.908

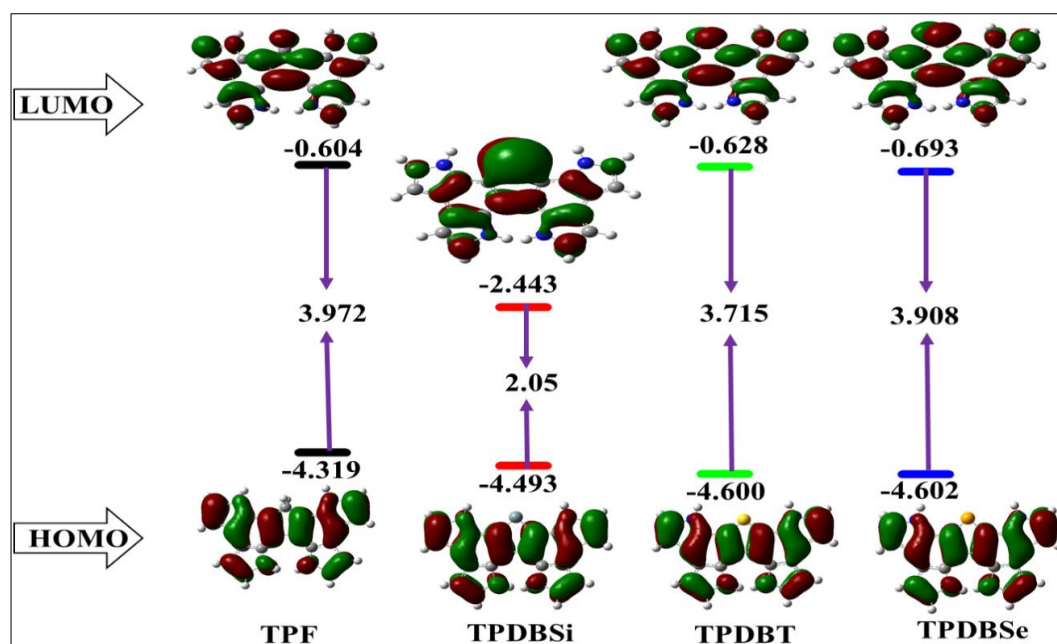


Fig 3: Energies of HOMO and LUMO with their electronic distribution and HOMO-LUMO energy gap for TPF, TPDBSi, TPDBT, and TPDBSe

Thermodynamic parameters

The thermodynamic parameters of the TPF, TPDBSi, TPDBT, and TPDBSe were measured at 1 atm pressure and 298.15 kelvin temperature using DFT/B3LYP/6-31(d, p) methodology. These properties included zero-point vibrational energies (ZPVE in kcal.mol⁻¹), enthalpies (H in kcal.mol⁻¹), Gibbs free energies (G in kcal.mol⁻¹), entropy (S in cal./mol. kelvin), thermal energies (E_T in kcal.mol⁻¹), and heat capacity at constant volume (C_v in cal./mol. kelvin). The outcomes of thermodynamic parameters are listed in Table 2.

Table 2: Thermodynamic parameters of the TPF, TPDBSi, TPDBT, and TPDBSe

Compounds	ZPVE (kcal.mol ⁻¹)	G (kcal.mol ⁻¹)	E _T (kcal.mol ⁻¹)	S (cal./mol. Kelvin)	C _v (cal./mol. Kelvin)	H (kcal.mol ⁻¹)
TPF	191.337	-644740	202.377	131.921	74.906	-644701
TPDBSi	174.136	-801726	185.404	134.421	75.165	-801686
TPDBT	174.69	-869959	185.903	133.562	75.077	-869919
TPDBSe	174.634	-2125727	185.975	135.637	75.055	-2125686

Conclusion

The influence of injecting the heteroatoms (Si, S, and Se) in the tetrapyrrolofluorene (TPF) molecule on the energies of frontier molecular orbitals with their energy gap and thermodynamic parameters was investigated in this work. This investigation was conducted with the 6-31 G (d, p) basis set and the DFT approaches at the B3LYP levels of the theory. This study revealed that the electronic and thermodynamic parameters are systematically affected by the doping of heteroatoms (Si, S, and Se). The incorporation of silicon (Si), sulphur (S), and selenium (Se) atoms in the TPF molecule lowers (stabilized) the HOMO and LUMO levels. TPDBSi (silicon substituted derivatives of TPF) has a narrower HOMO-LUMO gap, which allows for greater exploration and tailoring of electro-optical features. The zero-point vibrational energies, Gibbs free energies, enthalpies, thermal energies, and heat capacity at constant volume decreased as the Si, S, and Se atoms were incorporated into the TPF molecule, while the entropy increased. The mentioned characteristics point out that the TPDBSi molecule is a promising option for optoelectronic applications.

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Introducing the Si, S, and Se atoms in the TPF molecule declined the ZPVE, G, H, E_T, and C_v. On the other hand, entropy is increased, when Si, S, and Se atoms are incorporated into the TPF molecule. We interpret that the entropy of the doped materials (insertion of the heteroatom in TPF) is larger as compared to the TPF molecule, indicating that the charge movement of the doped molecules is greater than the parent tetrapyrrolofluorene molecule (TPF). Overall, TPDBSi has the most probable charge movement or carriers, suggesting an improvement in the electro-optical properties.

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