

# Comparative Study of the Optoelectronic, Reactivity Descriptors, and Thermodynamic Properties for Derivatives of Fluorene, and its Hetero-Analogous (Si, NH, O, S, and Se) by Employing the DFT and TD-DFT Approaches

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**Abstract** A comparative study of the optoelectronic, reactivity descriptors, and thermodynamic properties for derivatives of fluorene, and its hetero - analogous (Si, NH, O, S, and Se) was performed by employing the DFT and TD-DFT approaches in the gaseous state. Based on the DFT approach, the thermodynamic properties and molecular electrostatic potential were computed while based on the TD-DFT approach, optoelectronic properties were calculated by employing the B3LYP/6-311(d,p) level. The reactivity descriptors were calculated by using an electronic property (HOMO and LUMO energies). The calculated absorption values of investigated compounds are predicted to range from 330-643nm. Comparatively, all the investigated compounds are expected used in the field of designing new types of optoelectronic materials.

**Keywords:** Fluorene, DFT and TD-DFT, optoelectronic applications.

## Introduction

Many scientific fields are continuing to focus on the exploration of conjugated organic materials for optoelectronic devices[1]. These conjugated organic materials have applications in sensors, electrochromism, organic photovoltaic devices, organic/poly light-emitting diodes (O/PLEDs), and organic field-effect transistors (OFETs)[2–7]. In organic materials, the introduction of heteroatom into conjugated organic materials has gained much attention[8]. Fused heteroatomic conjugated organic materials are those materials in which one or more of the carbons are replaced by nitrogen, oxygen, sulphur atoms, etc. [8]. Incorporating heteroatoms into the conjugated system framework is an effective method for enhancing their significant chemical and physical properties such as electronic properties, etc[9–12]. The optoelectronic and charge transport characteristics of the isomers of benzotrithiophene and its heteroatomic analogues (NH, O, and Se), such as benzotripyrrole, benzotrifuran, and benzotriselenophene, were studied by Tripathi *et al.* [13]. According to their findings, benzotripyrrole and benzotrifuran isomers show a blue shift in absorption as compared to that of the corresponding benzotrithiophene isomers leads to the destabilization of both HOMO and LUMO levels, whereas benzotriselenophene isomers showed a red shift in absorption as compared to benzotrithiophene isomers causes to the stabilization of both HOMO and LUMO levels. Among all under-study series, benzotripyrrole isomers have the least ionization potential value, and it is easy to insert a hole in them. However, compared to the other set of series under study, benzotriselenophene isomers possessed the highest values for electron affinity showing that they possess greater ability for electron injection capabilities. In another investigation, Tri *et al.* studied the optoelectronic characteristics of unsubstituted heptacene, its fluorinated derivatives, and thiophene, silol analogous[14]. Their analysis demonstrates that replacing H atoms with F atoms in unsubstituted heptacene reduces band gaps, showing a redshift (visible light) in electronic absorption. In contrast, replacing benzene rings with thiophene and

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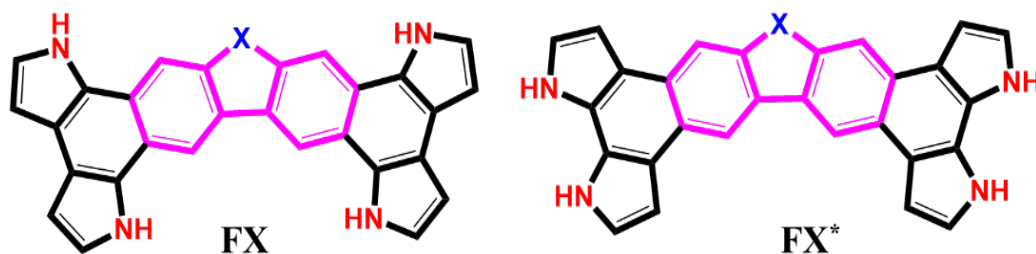
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silol units in unsubstituted heptacene raises band gaps while showing a blueshift for thiophene and a redshift for silol derivatives in electronic absorption. The outcome of incorporating heteroatoms (N and O atoms) into pentacene on its electronic structure and charge carrier injection capabilities was examined by Lin *et al.* [15]. Their findings show that HOMO (highest occupied molecular orbitals) and LUMO (lowest occupied molecular orbitals) energy levels rise and the ionization potential declines with the incorporation of the oxygen atom, which makes hole injection easier. The insertion of the nitrogen atom causes the ionization potential to rise and the HOMO and LUMO energy levels to decrease, which are favourable to the hole stability. In another study, Kumar *et al.* investigated the optoelectronic features of benzodiselenophene and benzodithiophene isomers [16]. Their findings demonstrate that the absorption wavelength of all benzodiselenophene and benzodithiophene isomers observed in the range of 290-445nm and 250-417nm. The HOMO-LUMO energy gap and HOMO for all benzodiselenophene and benzodithiophene isomers are 3.29 to 4.88 eV and -5.30 to -6.07 eV, respectively. Furthermore, their findings suggest that all benzodiselenophene and benzodithiophene isomers are planar and suitable materials for charge mobility.

From above the discussion, we conclude that the incorporation of heteroatoms (Si, NH, O, S, and Se) into the conjugated system framework has a great influence on the molecular structure, optoelectronic properties, reactivity and charge injection capabilities. In this work, a comparative study of the optoelectronic, reactivity descriptors, and thermodynamic properties for derivatives of fluorene, and its hetero-analogous (Si, NH, O, S, and Se) by employing the DFT and TD-DFT approaches was done.

## Designed Compounds

We designed twelve derivatives (Figure 1) based on fluorene, and its hetero-analogous (Si, NH, O, S, and Se) by attaching 3,4,5,6-tetrahydropyrrolo[3,2-e] indole (THPI1) and 1,4,5,8-tetrahydropyrrolo[3,2-g] indole (THPI2) units at the end cores for this comparative study of the optoelectronic, reactivity descriptors, and thermodynamic properties. Fluorene hetero-analogous (Si, NH, O, S, and Se) i.e., FHAs are usually categorized as heterocyclic derivatives of polycyclic aromatic hydrocarbons (conjugated system framework). In the FX and FX\* (where X = C, Si, NH, S and Se) compounds, fluorene, and FHAs (fluorene hetero-analogous) are situated in the central part and THPI1, THPI2 units are attached to both sides end cores in them. Attaching the THPI1 units constructs compounds FC, FSi, FNH, FO, FS, and FSe (FX where X = C, Si, NH, S, and Se), whereas attaching THPI2 units creates FC\*, FSi\*, FNH\*, FO\*, FS\* and FSe\* (FX\* where X = C, Si, NH, S and Se) that are presented in Figure 1.



X	FX	FX*
CH <sub>2</sub>	FC	FC*
Si	FSi	FSi*
NH	FNH	FNH*
O	FO	FO*
S	FS	FS*
Se	FSe	FSe*

Figure 1. Designed compounds for this comparative study

## Computational Methods

The designed compounds were optimized using molecular mechanics, semi-empirical, and density functional theory (DFT) approaches. Semi-empirical and density functional theory (DFT) approaches were implemented to optimize the structure with frequency calculations, which were then checked to ensure that the optimized structure corresponded to energy minima. As a result, the energy minima on potential energy surfaces with zero imaginary frequency were determined. The DFT-optimized geometry was used for further calculations. The entire perspective study's results were obtained using DFT and TD-DFT methods at B3LYP/6-311(d,p) levels [17,18]. All the calculations were carried out using the Gaussian software package [19]. Furthermore, thermodynamic and molecular electrostatic surfaces were measured with the help of a DFT-optimized structure at the B3LYP/6-311(d,p) levels. In contrast, optoelectronics properties were obtained at the TD-DFT/ B3LYP/6-311(d,p) levels. The result for the density of states was computed by using the Gauss Sum software [20].

## Reactivity Descriptors

The following formula is used to determine the HOMO-LUMO energy gap (HLG):

$$HLG = E_{LUMO} - E_{HOMO} = IP - EA \quad (1)$$

Ionization potential, electron affinity, electronegativity, hardness, softness, chemical index, electrophilicity index, electro-donating power, electro-accepting power, and nucleophilicity index are included in the reactivity descriptors that are measured using the following formulas.

The ionization potential (IP) and electron affinity (EA) are determined utilizing the energies of the HOMO and LUMO orbitals:

$$IP = -E_{HOMO} \quad (2)$$

$$EA = -E_{LUMO} \quad (3)$$

Chemical hardness is determined by implementing the following formula [21]:

$$\eta = \frac{(IP-EA)}{2} \quad (4)$$

The chemical softness electronegativity and chemical potential are measured by implementing the following formula respectively [22]:

$$\xi = \frac{2}{(IP-EA)} = \frac{1}{\eta} \quad (5)$$

$$\chi = \frac{(IP+EA)}{2} \quad (6)$$

$$\mu = -\left(\frac{IP+EA}{2}\right) = -\chi \quad (7)$$

The electrophilicity index is measured by implementing the following formula [22,23]:

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

The nucleophilicity index [24–27] is measured by implementing the following formula:

$$NI = -IP \quad (9)$$

The electro-accepting power and electro-donating power are determined by implementing the following [28]:

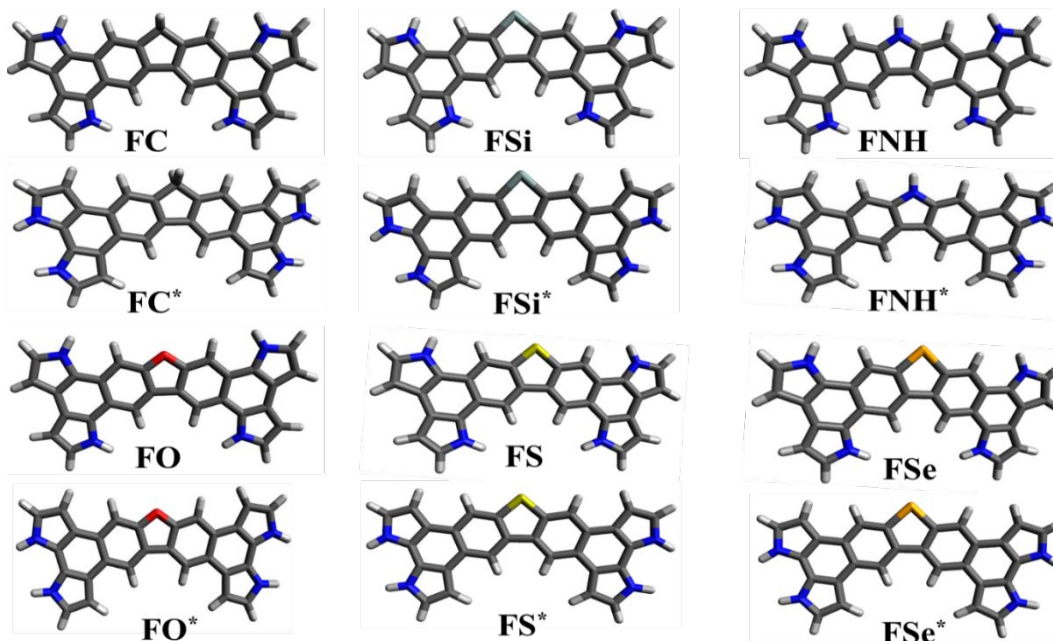
$$\omega^+ = \frac{(IP+3EA)^2}{16(IP-EA)} \quad (10)$$

$$\omega^- = \frac{(3IP+EA)^2}{16(IP-EA)} \quad (11)$$

## Results and Discussion

### Optimized Geometry and Relative Stability

Table 1 and Figure 2, respectively, show the calculated relative energy and optimized molecular structure of the examined compounds using DFT/B3LYP/6-311(d,p). Relative energies suggest that FX isomers are more stable than their respective FX\* isomers i.e order of relative stability is FC>FC\*, FSi>FSi\*, FNH>FNH\*, FO>FO\*, FS>FS\* and FSe>FSe\*.



**Figure 2.** DFT-optimized structures of studied designed compounds

**Table 1.** Relative energy for optimized structures of studied compounds

Compounds	Relative Energy (kcal.mol <sup>-1</sup> )
FC	0
FC*	4.376
FSi	0
FSi*	5.096
FNH	0
FNH*	3.883
FO	0
FO*	3.855
FS	0
FS*	3.737
FSe	0
FSe*	3.695

## Electronic Properties

Optoelectronic device usability can be explained particularly by electronic features like frontier molecular orbitals and their energy gap. The frontier molecular orbital energies for each of the proposed compounds were calculated using the TD-DFT/B3LYP/6-311(d,p.) The value of the HOMO-LUMO energy gap (HLG) is obtained using formula 1. If a compound contains a frontier molecular orbital, its energy should match the work function (WF) of the metal electrodes to improve or facilitate the hole/electron injection. At the same time, a compound's charge transfer capability is enhanced by a small HOMO-LUMO energy gap (HLG). The outcomes of the frontier molecular orbitals and their energy gap are depicted in Table 2 and Figure 3. Furthermore, Figure 4 displays the spatial distribution of the electron density of the frontier molecular orbitals for the studied compounds. The values of HOMO/LUMO are -4.903/-1.316, -4.714/-0.845, -5.049/-2.562, -4.858/-2.170, -4.747/-1.346, -4.498/-0.860, -5.014/-1.502, -4.821/-1.026, -5.025/-1.488, -4.769/-1.016, -5.014/-1.479, and -4.750/-1.007 while energy gap values are 3.587, 3.869, 2.487, 2.687, 3.402, 3.637, 3.512, 3.795, 3.537, 3.754, 3.535, and 3.742 for FC, FC\*, FSi, FSi\*, FNH, FNH\*, FO, FO\*, FS, FS\*, FSe, and FSe\* compounds respectively. The range of HOMO, LUMO and HLG lies from -4.498 to -5.049eV, -0.845 to -2.562eV and 2.487 to 3.869eV respectively. The energy of HOMOs levels for all under-studied compounds ranges from -4.498 to -5.049eV, showing a small hole injection barrier that's sufficient for hole injection; however, the energy of LUMOs levels ranges from -0.845 to -2.562eV, showing a large energy barrier that is too high for electron injection, if Au (gold) is selected as the applied electrode (WF=-5.5eV)[15]. In comparison to THPI1 units, attaching THPI2 units at the end cores of fluorene (X=CH<sub>2</sub>) and its FHAs (X=Si, NH, O, S, and Se) increase the HLG due to destabilization (increase) of HOMO and LUMO levels. If a chalcogen atom, such as an oxygen, sulphur, or selenium atom (FO/FO\*, FS/FS\*, and FSe/FSe\*), is replaced in place of carbon atom (in FC/FC\*), the LUMO energy level lowered (stabilized) due to the electrophilic ability of the oxygen (O), sulphur (S), and selenium (Se). On the other hand, if carbon replaces (in FC/FC\*) with a nitrogen atom (for FNH/FNH\*), destabilized (increases) the HOMO energy level due to the nitrogen atom's ability to donate electrons. The order of HOMO/LUMO and HLG are: FNH\* > FC\* > FNH > FSe\* > FS\* > FO\* > FSi\* > FC > FO = FSe > FS > FSi/FC\* > FNH\* > FSe\* > FS\* > FO\* > FC > FNH > FSe > FS > FO > FSi\* > FSi and FSi < FSi\* < FNH < FO < FSe < FS < FC < FNH\* < FSe\* < FS\* < FO\* < FC\* respectively. Among all the studied compounds, FSi (2.487eV) has better charge transfer capability due to its smallest HLG. As seen in Figure 4, the electron density in HOMO orbitals of all the studied compounds is located on the pi-conjugated framework or skeleton while in the LUMO orbitals are located on the core part except CH<sub>2</sub>, NH, O, S and Se. Interestingly, in FSi and FSi\* compounds, the electron density in LUMO orbitals is located on the core part as well as the silicon atom.

**Table 2.** Electronic properties (energy of HOMO and LUMO levels with their energy gap)

Compounds	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	HLG (eV)
FC	-4.903	-1.316	3.587
FC*	-4.714	-0.845	3.869
FSi	-5.049	-2.562	2.487
FSi*	-4.858	-2.170	2.687
FNH	-4.747	-1.346	3.402
FNH*	-4.498	-0.860	3.637
FO	-5.014	-1.502	3.512
FO*	-4.821	-1.026	3.795
FS	-5.025	-1.488	3.537
FS*	-4.769	-1.016	3.754
FSe	-5.014	-1.479	3.535
FSe*	-4.750	-1.007	3.742

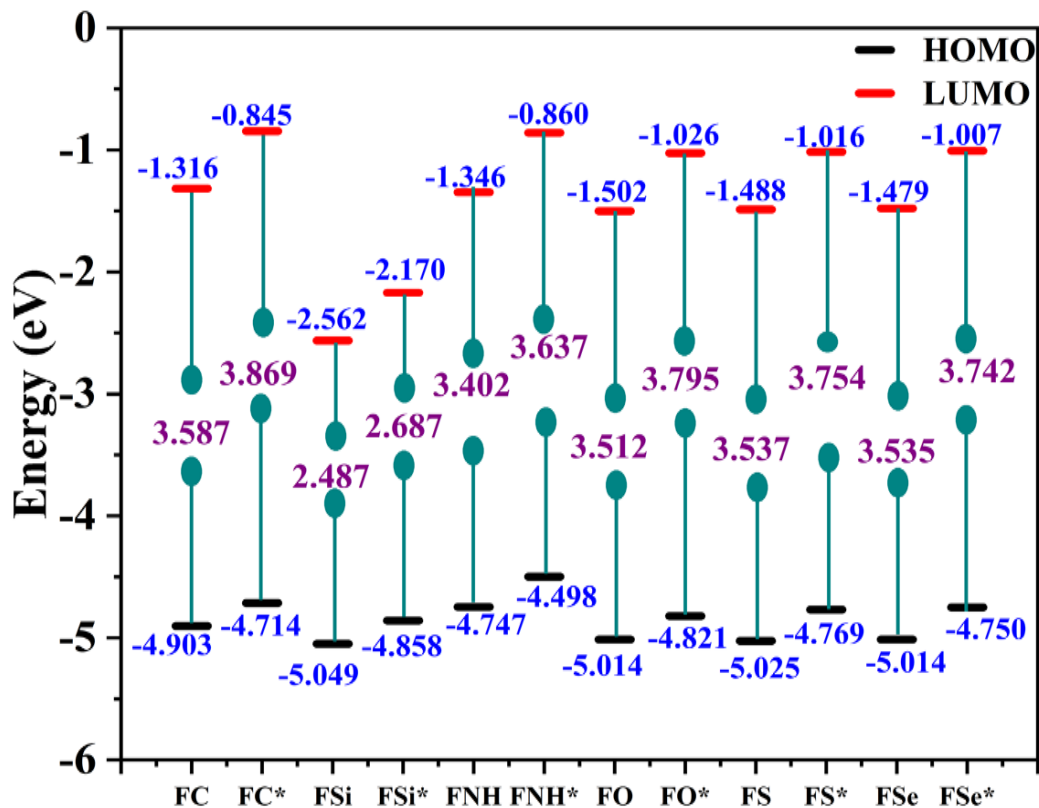


Figure 3. Electronic properties (energy of HOMO and LUMO levels with their energy gap)

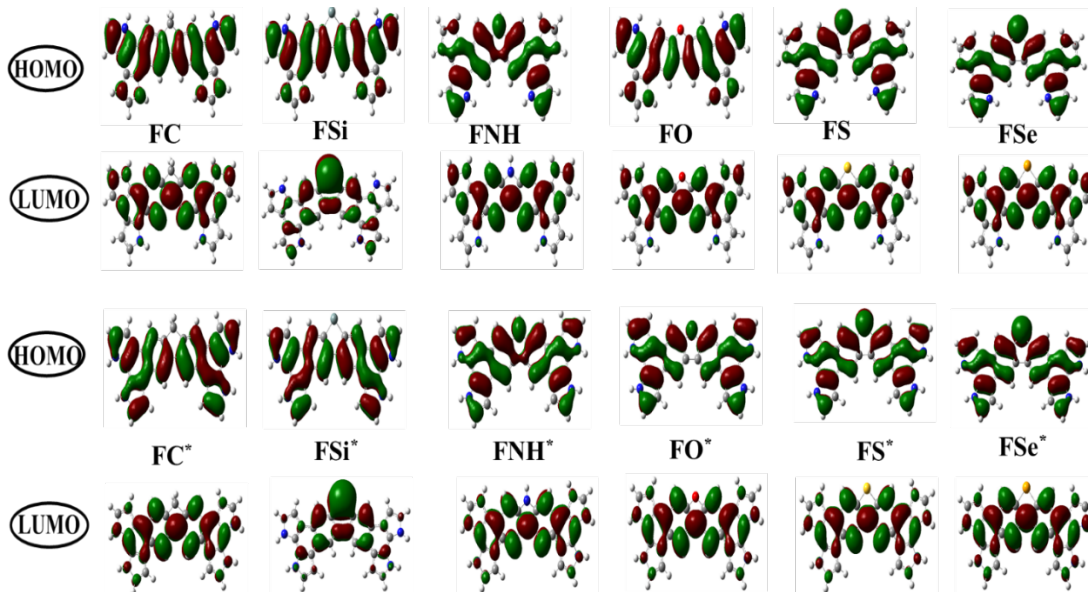


Figure 4. Spatial distribution of electron density of HOMO and LUMO orbitals of studied compounds

### Density of State

To validate the findings of the frontier molecular orbital analysis, the density of states was calculated. The contribution of the occupied (HOMO) and unoccupied (LUMO) orbitals in any electronic transitions is described by this density of states analysis. Using the Gauss Sum software [20], the density of states

for each of the proposed compounds was calculated using the TD-DFT/B3LYP/6-311(d,p) findings, as seen in Figure 5. In the DOS graph, negative values (left side) represent the valence band (HOMO), and positive values (right side) represent the conduction band (LUMO) along the x-axis while along y-axis represent the density of states. The space between the valence band (HOMO) and conduction band (LUMO), as illustrated in Figure 5, represents the energy gap. In conclusion, there is a significant correlation between the frontier molecular orbital outcomes and the analysis of DOS findings.

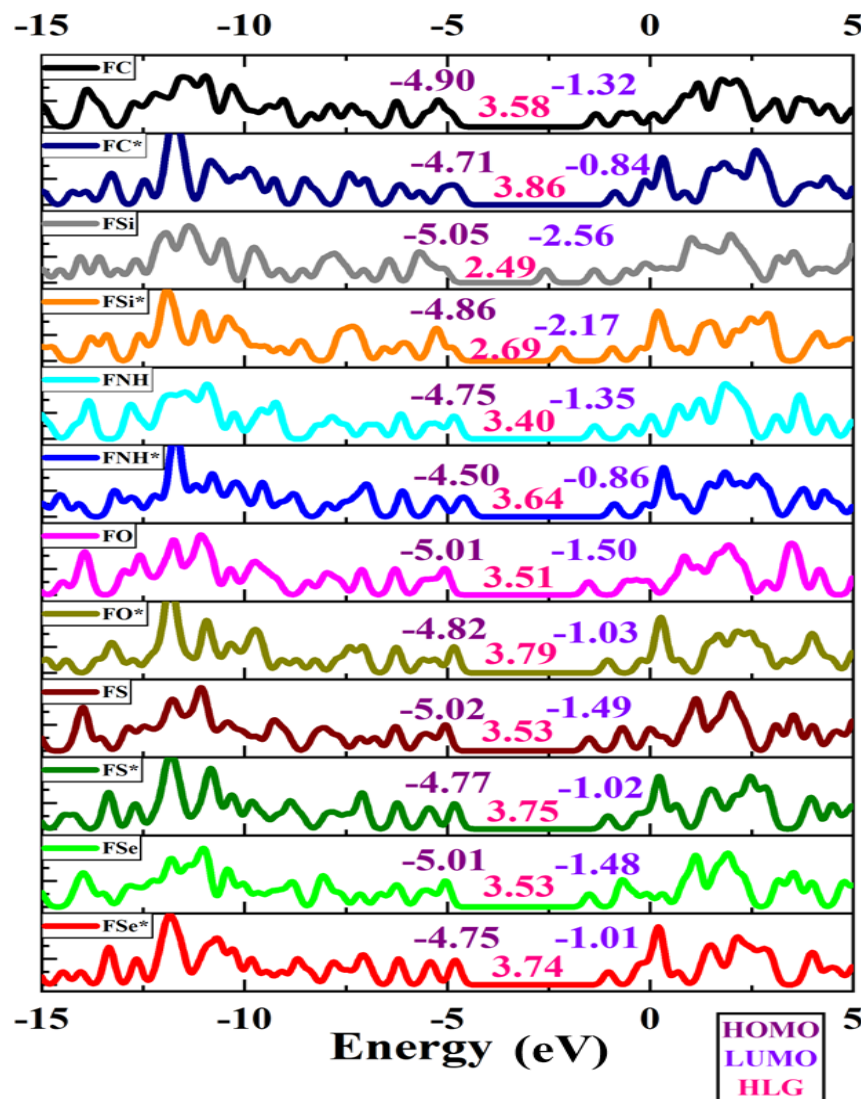


Figure 5. Density of states for studied compounds

### Chemical Reactivity Descriptors

The frontier molecular orbital energies and their energy gap are effective ways for measuring chemical reactivity descriptors that involve ionization potential, electron affinity, electronegativity, chemical potential, hardness, softness, electrophilicity index, nucleophilicity index, electron accepting power, and electron donating power.

**Table 3.** Ionization potential, electron affinity, electronegativity, chemical potential, hardness, and softness of studied compounds

Compounds	IP (eV)	EA (eV)	$\chi$ (eV)	$\mu$ (eV)	$\eta$ (eV)	$\xi$ (eV <sup>-1</sup> )
FC	4.903	1.316	3.109	-3.109	1.793	0.279
FC*	4.714	0.845	2.779	-2.779	1.934	0.259
FSi	5.049	2.562	3.805	-3.805	1.243	0.402
FSi*	4.858	2.170	3.514	-3.514	1.344	0.372
FNH	4.747	1.346	3.046	-3.046	1.701	0.294
FNH*	4.498	0.860	2.679	-2.679	1.819	0.275
FO	5.014	1.502	3.258	-3.258	1.756	0.285
FO*	4.821	1.026	2.924	-2.924	1.898	0.263
FS	5.025	1.488	3.256	-3.256	1.769	0.283
FS*	4.769	1.016	2.892	-2.892	1.877	0.266
FSe	5.014	1.479	3.246	-3.246	1.768	0.283
FSe*	4.750	1.007	2.878	-2.878	1.871	0.267

**Table 4.** Electrophilicity index, nucleophilicity index, electron accepting power and electron donating power of studied compounds

Compounds	$\omega$ (eV)	Nu (eV)	$\omega_+$ (eV)	$\omega_-$ (eV)
FC	2.695	-4.903	4.210	13.801
FC*	1.997	-4.714	2.824	12.071
FSi	5.823	-5.049	8.716	16.853
FSi*	4.595	-4.858	6.945	15.067
FNH	2.728	-4.747	4.147	13.056
FNH*	1.973	-4.498	2.692	11.073
FO	3.022	-5.014	4.871	14.709
FO*	2.252	-4.821	3.353	12.893
FS	2.998	-5.025	4.839	14.743
FS*	2.229	-4.769	3.284	12.618
FSe	2.981	-5.014	4.800	14.668
FSe*	2.214	-4.750	3.245	12.509

### Ionization Potential and Electron Affinity

Ionization potential and electron affinity are the energy component values associated with removing and adding electrons in a molecule. A molecule with a high electron affinity value is a good electron acceptor, whereas with a low ionization potential value is a good electron donor. The value of the ionization potential and electron affinity are obtained using formulas 2 and 3. The outcomes of the frontier molecular orbitals and their energy gap are depicted in Table 3 and Figure 6. The values of ionization potential and electron affinity are 4.903, 4.714, 5.049, 4.858, 4.747, 4.498, 5.014, 4.821, 5.025, 4.769, 5.014, 4.750 and 1.316, 0.845, 2.562, 2.170, 1.346, 0.860, 1.502, 1.026, 1.488, 1.016, 1.479, 1.007 for FC, FC\*, FSi, FSi\*, FNH, FNH\*, FO, FO\*, FS, FS\*, FSe, and FSe\* compounds respectively. The range of ionization potential and electron affinity lies from 4.498 - 5.049eV and 0.845 - 2.562eV respectively. In comparison to THPI1 units, attaching THPI2 units at the end cores of fluorene (X=CH<sub>2</sub>) and its hetero-analogous (X=Si, NH, O, S, and Se) decrease ionization potential and electron affinity. The order of ionization potential and electron affinity are: FNH\* < FC\* < FNH < FSe\* < FS\* < FO\* < FSi\* < FC < FO = FSe < FS < FSi and FC\* < FNH\* < FSe\* < FS\* < FO\* < FC < FNH < FSe < FS < FO < FSi\* < FSi respectively. The highest value of electron affinity is found for FSi while the smallest value of ionization potential is found for FNH\* among all the studied compounds. As a result, FSi (2.562 eV) is a good electron acceptor and FNH\* (4.498 eV) is a good electron donor.



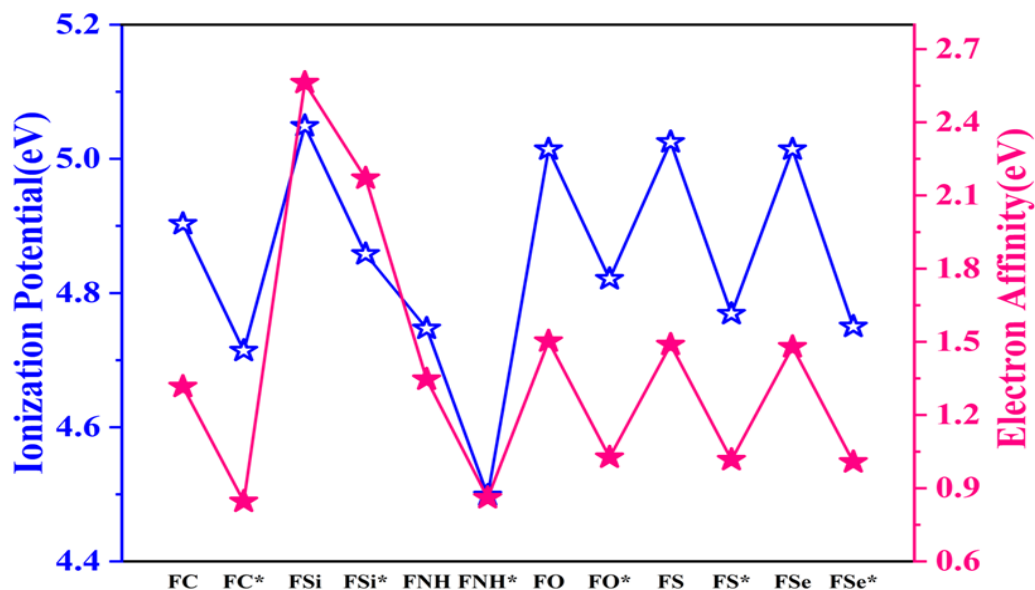


Figure 6. Ionization potential and electron affinity of studied compounds

### Hardness and Softness

The chemical hardness is proportional to the HOMO-LUMO energy gap (HLG). An increase in chemical hardness leads to the molecule being less reactive and more stable, which hinders intramolecular charge transfer. On the other hand, chemical softness has an inverse relationship to the HOMO-LUMO energy gap (HLG) or chemical hardness. An increase in chemical softness makes the molecule more reactive and less stable, which facilitates intermolecular charge transfer. The values of the chemical hardness and chemical softness are obtained using formulas 4 and 5. The outcomes of the chemical softness and chemical hardness are depicted in Table 3 and Figure 7. The values of chemical hardness are 1.793, 1.934, 1.243, 1.344, 1.701, 1.819, 1.756, 1.898, 1.769, 1.877, 1.768, and 1.871 eV while the values of chemical softness are 0.279, 0.259, 0.402, 0.372, 0.294, 0.275, 0.285, 0.263, 0.283, 0.266, 0.283 and 0.267 eV<sup>-1</sup> for FC, FC\*, FSi, FSi\*, FNH, FNH\*, FO, FO\*, FS, FS\*, FSe, FSe\* respectively. As a result, the chemical softness and chemical hardness values range from 0.259-0.402 eV<sup>-1</sup> and 1.243-1.793 eV. In comparison to THPI1 units, attaching THPI2 units at the end cores of fluorene (X=CH<sub>2</sub>) and its hetero-analogous (X=Si, NH, O, S, and Se) increase chemical hardness and decreases the chemical softness. The order of chemical hardness and chemical softness are FSi < FSi\* < FNH < FO < FSe < FS < FC < FNH\* < FSe\* < FS\* < FO\* < FC\* and FC\* < FNH\* < FSe\* < FS\* < FO\* < FC < FNH < FSe < FS < FO < FSi\* < FSi respectively. The largest value of chemical hardness is found for FC\* while the smallest value of chemical hardness is found for FSi among all the studied compounds. As a result, the FC\* compound is more stable, while FSi is more reactive and has a more probable intramolecular charge transfer feature due to its soft nature.

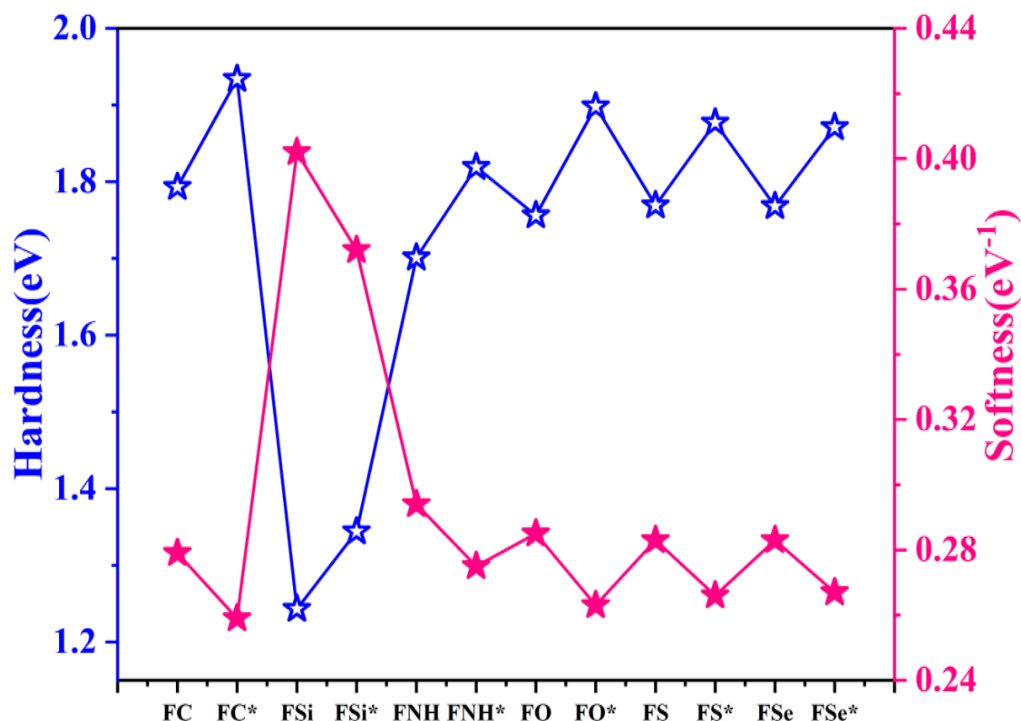


Figure 7. Hardness, and softness of studied compounds

### Electronegativity and Chemical Potential

The ability of a molecule to attract and release electrons is referred to as electronegativity and chemical potential. An electron can escape from a molecule having a low chemical potential value. On the other hand, a high electronegativity outcome shows substantial charge flow and a great ability to attract electrons. Formulas 6 and 7 are used to determine the electronegativity and chemical potential values. Table 3 and Figure 8 show the results of the electronegativity and chemical potential. The values of electronegativity are 3.109, 2.779, 3.805, 3.514, 3.046, 2.679, 3.258, 2.924, 3.26, 2.892, 3.246, and 2.878 eV while the values of chemical potential are -3.109, -2.779, -3.805, -3.514, -3.046, -2.679, -3.258, -2.924, -3.26, -2.892, -3.246, and -2.878 eV for FC, FC\*, FSi, FSi\*, FNH, FNH\*, FO, FO\*, FS, FS\*, FSe, FSe\* respectively. The electronegativity and chemical potential values range from 2.679-3.805 eV and -3.805 to -2.679 eV. In comparison to THPI1 units, attaching THPI2 units at the end cores of fluorene (X=CH<sub>2</sub>) and its hetero-analogous (X=Si, NH, O, S, and Se) increase the chemical potential and decreases the electronegativity. The order of electronegativity and chemical potential are: FNH\* < FC\* < FSe\* < FS\* < FO\* < FNH < FC < FSe < FS < FO < FSi\* < FSi and FNH\* > FC\* > FSe\* > FS\* > FO\* > FNH > FC > FSe > FS > FO > FSi\* > FSi respectively. The highest value of electronegativity is found for FSi while the smallest value of chemical potential is found for FSi among all the studied compounds. Overall, a high electronegativity FSi (3.805 eV) compound shows it has substantial charge flow and a great ability to attract electrons while FSi (-3.805 eV) has a better ability to escape electrons.

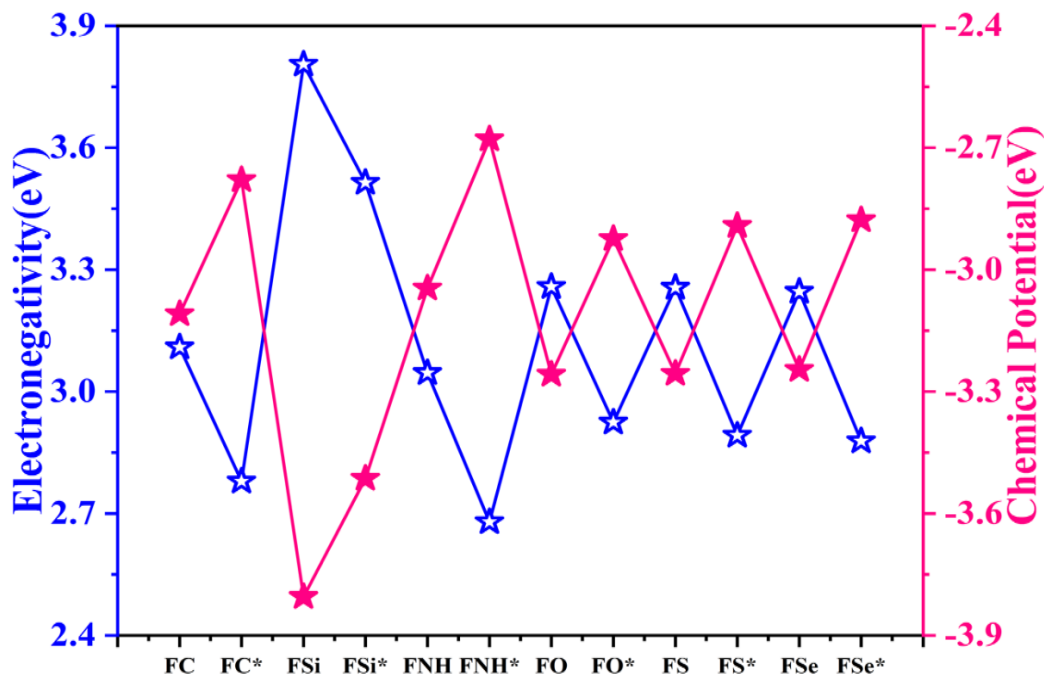
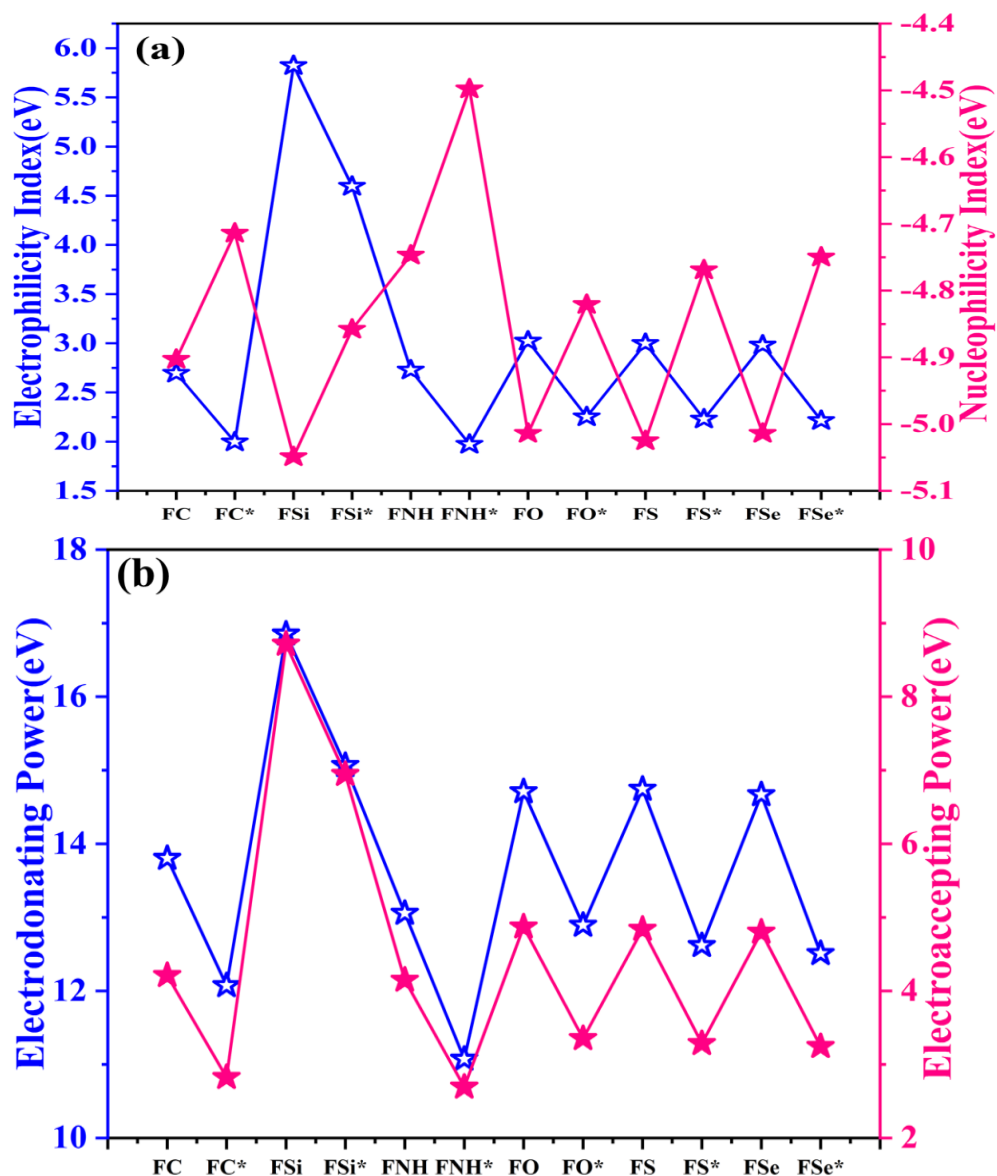


Figure 8. Electronegativity and chemical potential of studied compounds

### Electrophilicity and Nucleophilicity

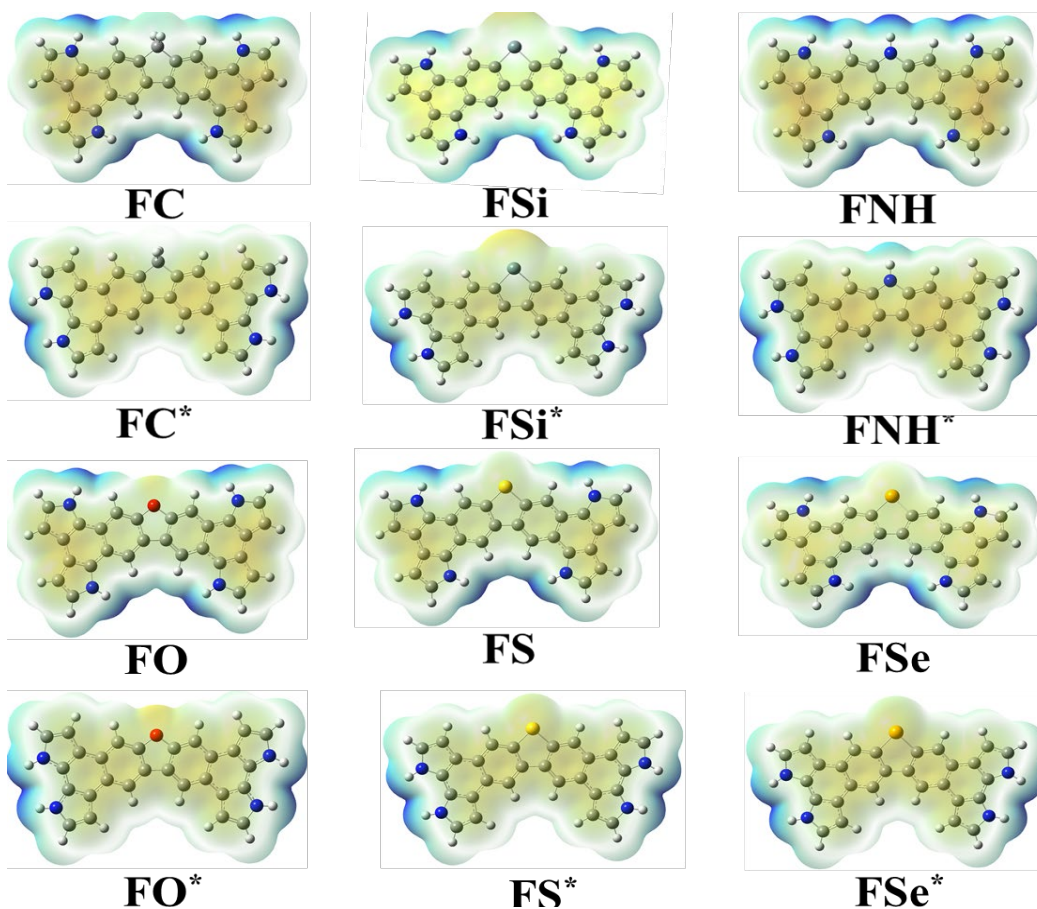
The electrophilicity index and nucleophilicity index measure the capability to accept and donate electrons in a molecule. A molecule with a high value of electrophilicity index has a good electrophilic character and with a high nucleophilicity index value has a good nucleophilic character. The electro-accepting and electron-donating power examined the accepting and donating power of a molecule. Formulas 8,9,11 and 12 are used to determine the values electrophilicity index, nucleophilicity index, electron-accepting and electron-donating power. Table 4 and Figure 9(a,b) show the obtained results of the electrophilicity index, nucleophilicity index, electron-accepting and electro-donating power. The values range of electrophilicity index, nucleophilicity index, electron-accepting and electro-donating power from 1.973-5.823 eV, -4.498 to -5.049 eV, 2.824-8.716 eV and 12.071-16.853 eV respectively. In comparison to THPI1 units, attaching THPI2 units at the end cores of fluorene (X=CH<sub>2</sub>) and its hetero-analogous (X=Si, NH, O, S, and Se) increases nucleophilicity index while decreasing the electrophilicity index, electron-accepting and electron-donating power. The order of nucleophilicity index and electrophilicity index is: FNH\* > FC\* > FNH > FSe\* > FS\* > FO\* > FSi\* > FC > FO = FSe > FS > FSi and FNH\* < FC\* < FSe\* < FS\* < FO\* < FC < FNH < FSe < FS < FO < FSi\* < FSi respectively while electron-accepting and electro-donating power are FNH\* < FC\* < FSe\* < FS\* < FO\* < FNH < FC < FSe < FS < FO < FSi\* < FSi and FNH\* < FC\* < FSe\* < FS\* < FO\* < FNH < FC < FSe < FO < FS < FSi\* < FSi respectively. As a result, FSi compound has good electrophilic character (5.823 eV), and electro-accepting (16.853 eV) power while FNH\* has a good nucleophilic character (-4.498 eV) and electro-donating power (2.824 eV).



**Figure 9.** (a) Electrophilicity index and nucleophilicity index, (b) Electroaccepting power and electrodonating power of studied compounds

### Molecular Electrostatic Potentials

The molecular electrostatic potential surface is a useful measure to represent electron density. It offers a better knowledge of molecular characteristics like electronegativity, hydrogen bonding, dipole moment, charge distribution, and intermolecular charge transfer characteristics. The molecular electrostatic potential surface is constructed using distinct colours that represent a molecule's electron density. The following colours depict the molecule's electrostatic potential surface: red, electron-rich site, partially negative charge; yellow, slightly electron-rich site; blue, electron-deficient site, partially positive charge; light blue, slightly electron-deficient site; and green, neutral site. An electrophilic attack favours a red colour site on the molecule's electrostatic potential surface, whereas a nucleophilic attack prefers a blue colour site. The surface of molecule electrostatic potential for investigated compounds is shown in Figure 10. The blue colour is located mainly on the attaching THPI1 and THPI2 units at the end cores in all studied compounds. Additionally, in FNH and FNH\* blue colour is also located on the hydrogen atom attached to the nitrogen. On the other hand, the light red colour is located on the Si and O atoms in the case of FSi/FSi\* and FO/FO\*.



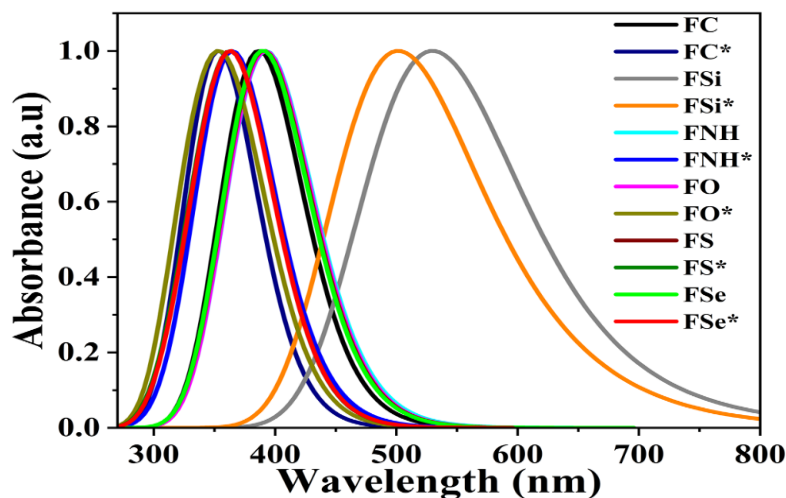
**Figure 10.** Molecular electrostatic potential surfaces of studied compounds

### Optical Properties

The optical properties which include the absorption wavelength, oscillation strength, electronic transition energy, and main transition with their percentage contribution were determined using TD-DFT/B3LYP/6-311(d,p) method which is listed in Table 5. The absorption spectra are shown in Figure 11. Large visible absorption properties (small electronic transition energy) are important to have a good optoelectronic application and devices due to it enhancing the intermolecular charge transfer process. From the findings of TD-DFT/B3LYP/6-311(d,p) investigation, the calculated absorption wavelength(nm)/electronic transition energy(eV) for the FC compound is found at 387/3.205, 374/3.319, and 372/3.337 with the oscillating strength 0.625, 0.007, and 0.006, due to major transition of these excitation H to L(94%), H-1 to L(93%), and H-2 to L(83%), respectively. For the compound FC\*, the calculated absorption wavelength(nm)/electronic transition energy(eV) is found at 359/3.451, 349/3.553, and 336/3.685 with the oscillating strength 0.349, 0.039, and 0.123 respectively. The absorption maximum wavelength is observed at 359nm due to the major transition of H to L (96%), while the other weaker transitions are observed at 349 and 336nm absorption wavelength due to H-1 to L (94%), and H-2 to L (71%) transitions, respectively. The introduction of heteroatom (X=Si, NH, O, S, and Se) in FC/ FC\*(X=CH<sub>2</sub>), the absorption wavelength is found towards the longer wavelength (red shift) and decline in the electronic transition energy due to their corresponding major transition (Table 5) which improve the intramolecular charge transfer process. In comparison to THPI1 units, attaching THPI2 units at the end cores of fluorene (X=CH<sub>2</sub>) and its hetero-analogous (X=Si, NH, O, S, and Se) increases the electronic transition energy while decreasing the oscillating strength and absorption wavelength (blue shift observed). The calculated absorption values, oscillating strength and excitation transition energy of investigated compounds are 330-643nm, 0.006-0.655 and 1.929-3.761eV respectively. The FSi compound has the longest absorption maximum wavelength or the smallest electronic transition energy, indicating the most likely charge transfer, according to the TD-DFT/B3LYP/6-311(d,p) study analysis.

**Table 5.** Optical properties (absorption wavelength  $\lambda_{max}$  (nm), oscillation strength  $f$ , electronic transition energy  $E_{ex}$  (eV), and main transition MT with their percentage contribution %C<sub>i</sub>) of investigated compounds

Compounds	$\lambda_{max}$ (nm)	$f$	$E_{ex}$ (eV)	MT(%C <sub>i</sub> )
FC	387	0.625	3.205	H → L (94%)
	374	0.007	3.319	H-1 → L (93%)
	372	0.006	3.337	H-2 → L (83%)
FC*	359	0.349	3.451	H → L (96%)
	349	0.039	3.553	H-1 → L (94%)
	336	0.123	3.685	H-2 → L (71%)
FSi	643	0.015	1.929	H → L (97%)
	528	0.245	2.347	H-1 → L (93%)
	523	0.011	2.373	H-4 → L (100%)
FSi*	582	0.04	2.13	H → L (87%)
	527	0.012	2.353	H-3 → L (100%)
	494	0.221	2.508	H-2 → L (85%)
FNH	429	0.016	2.889	H → L (96%)
	394	0.521	3.151	H-1 → L (91%)
	370	0.05	3.151	H-2 → L (95%)
FNH*	397	0.036	3.126	H → L (95%)
	366	0.284	3.392	H-1 → L (92%)
	333	0.049	3.727	H-2 → L (82%)
FO	407	0.015	3.044	H-1 → L (95%)
	394	0.655	3.148	H → L (94%)
	374	0.092	3.316	H-2 → L (94%)
FO*	376	0.044	3.293	H → L (95%)
	367	0.342	3.379	H-1 → L (95%)
	332	0.29	3.73	H-2 → L (89%)
FS	413	0.01	2.999	H → L (95%)
	393	0.479	3.157	H-1 → L (92%)
	369	0.069	3.361	H-2 → L (90%)
FS*	384	0.029	3.225	H → L (94%)
	367	0.244	3.382	H-1 → L+2 (94%)
	330	0.08	3.761	H-2 → L (80%)
FSe	415	0.01	2.99	H → L (95%)
	392	0.48	3.164	H-1 → L (92%)
	369	0.064	3.358	H-2 → L (88%)
FSe*	387	0.026	3.202	H → L (95%)
	366	0.241	3.385	H-1 → L (94%)
	330	0.071	3.756	H-2 → L (78%)



**Figure 11.** Absorption spectra of investigated compounds

## Thermodynamic Properties

The DFT/B3LYP/6-311(d,p) approach was employed for determining the thermodynamic properties which include zero-point vibrational energies (ZPVE in kcal.mol<sup>-1</sup>), thermal energies ( $E_T$  in kcal.mol<sup>-1</sup>), heat capacity at constant volume ( $C_v$  in cal./mol. kelvin), entropy ( $S$  in cal./mol. kelvin), enthalpies ( $H$  in kcal.mol<sup>-1</sup>) and Gibbs free energies ( $G$  in kcal.mol<sup>-1</sup>) of studied compounds at 1 atm pressure and 298.15K temperature. The findings of the thermodynamic properties are summarised in Table 6. Heat capacity at constant volume, entropy, enthalpies, and Gibbs free energies are increased while decreasing the zero-point vibrational energies and thermal energies when THPI2 units are attached to the end cores of fluorene ( $X=CH_2$ ) and its hetero-analogous ( $X=Si, NH, O, S,$  and  $Se$ ) in comparison to THPI1 units. The replacement of the carbon atom ( $X=CH_2$ ) with heteroatoms ( $X=Si, NH, O, S,$  and  $Se$ ) decreases the zero-point vibrational energies, thermal energies, enthalpies, and Gibbs free energies. Further, the incorporation of a heteroatom ( $X=Si, NH, S,$  and  $Se$ ) in place of a carbon atom increases the heat capacity at constant volume and entropy while the inserting of an oxygen atom in place of a carbon atom declines the heat capacity at constant volume and entropy.

**Table 6.** Thermodynamic properties of investigated compounds

Compounds	ZPVE (kcal.mol <sup>-1</sup> )	$E_T$ (kcal.mol <sup>-1</sup> )	$C_v$ (cal./mol. kelvin)	$S$ (cal./mol. kelvin)	$H$ (kcal.mol <sup>-1</sup> )	$G$ (kcal.mol <sup>-1</sup> )
FC	248.233	262.946	99.544	160.360	-837649.273	-837697.084
FC*	247.976	262.871	100.065	161.580	-837644.972	-837693.147
FSi	230.954	245.976	100.082	163.780	-994640.401	-994689.232
FSi*	230.689	245.918	100.687	165.311	-994635.364	-994684.651
FNH	240.791	255.658	100.090	161.083	-847728.122	-847776.149
FNH*	240.636	255.632	100.451	161.798	-847724.266	-847772.505
FO	233.257	247.776	98.157	158.957	-860200.691	-860248.084
FO*	233.091	247.742	98.564	159.618	-860196.871	-860244.461
FS	231.284	246.217	100.100	162.340	-1062876.675	-1062925.076
FS*	231.067	246.158	100.555	163.497	-1062872.997	-1062921.744
FSe	230.710	245.897	100.729	165.424	-2319986.456	-2320035.777
FSe*	230.511	245.855	101.175	166.581	-2319982.802	-2320032.468

## Conclusion

In this work, a comparative study of the optoelectronic, reactivity descriptors, and thermodynamic properties for derivatives of fluorene, and its hetero - analogous (Si, NH, O, S, and Se) have been investigated by employing the DFT and TD-DFT approaches at B3LYP/6-311(d,p) in the gaseous state. Modifying the chemical structure of the investigated compounds such as the introduction of different heteroatoms and attaching 3,4,5,6-tetrahydropyrrolo[3,2-e] indole (THPI1) and 1,4,5,8-tetrahydropyrrolo[3,2-g] indole (THPI2) units at the end cores may significantly adjust the optoelectronic, reactivity descriptors, thermodynamical properties which are also studied. The compounds under investigation show absorbance values, oscillation strengths, and excitation transition energies of 330–643 nm, 0.006-0.655, and 1.929–3.761 eV, respectively. It is found that all understudied compounds have the energy of HOMOs levels ranging from -4.498 to -5.049 eV, indicating a small hole injection barrier that is adequate for hole injection, however, the energy of LUMOs levels ranges from -0.845 to -2.562 eV, indicating a large energy barrier that is too high for electron injection; if Au (gold) is chosen as the applied electrode. FSi (2.487eV) has the best charge transfer capability among all the investigated compounds due to its smallest HLG. FSi (2.562 eV) is an excellent electron acceptor, while FNH\* (4.498 eV) has a good electron donor propensity. Additionally, FSi compound has good electrophilic character (5.823 eV), and electro-accepting (16.853 eV) power while FNH\* has a good nucleophilic character (-4.498 eV) and electro-donating power (2.824 eV). The outcome of this study can help find the theoretical evidence for designing a new type of pi-conjugated framework organic materials that enhance optoelectronic applications.

## Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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## References

- [1] Forrest, S. R., & Thompson, M. E. (2007). Introduction: Organic electronics and optoelectronics. *Chemical Reviews*, 107(4), 923–925.
- [2] Thomas, S. W., Joly, G. D., & Swager, T. M. (2007). Chemical sensors based on amplifying fluorescent conjugated polymers. *Chemical Reviews*, 107(4), 1339–1386.
- [3] Beaujuge, P. M., & Reynolds, J. R. (2010). Color control in  $\pi$ -conjugated organic polymers for use in electrochromic devices. *Chemical Reviews*, 110(1), 268–320.
- [4] Sonmez, G., Shen, C. K. F., Rubin, Y., & Wudl, F. A. (2004). Red, green, and blue (RGB) polymeric electrochromic device (PECD): The dawning of the PECD era. *Angewandte Chemie*, 116(12), 1524–1528.
- [5] Martín, N., Sánchez, L., Herranz, M. Á., Illescas, B., & Guldi, D. M. (2007). Electronic communication in tetrathiafulvalene (TTF)/C60 systems: Toward molecular solar energy conversion materials? *Accounts of Chemical Research*, 40(10), 1015–1024.
- [6] Grimsdale, A. C., Leok Chan, K., Martin, R. E., Jokisz, P. G., & Holmes, A. B. (2009). Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chemical Reviews*, 109(3), 897–1091.
- [7] Katz, H. E., & Huang, J. (2009). Thin-film organic electronic devices. *Annual Review of Materials Research*, 39, 71–92.
- [8] Wang, C., Dong, H., Hu, W., Liu, Y., & Zhu, D. (2012). Semiconducting  $\pi$ -conjugated systems in field-effect transistors: A material odyssey of organic electronics. *Chemical Reviews*, 112(4), 2208–2267.
- [9] Ji, L., Friedrich, A., Krummenacher, I., Eichhorn, A., Braunschweig, H., Moos, M., Hahn, S., Geyer, F. L., Tverskoy, O., Han, J., Lambert, C., Dreuw, A., Marder, T. B., & Bunz, U. H. F. (2017). Preparation, properties, and structures of the radical anions and dianions of azapentacenes. *Journal of the American Chemical Society*, 139(44), 15968–15976.
- [10] Richter, M., Schellhammer, K. S., Machata, P., Cuniberti, G., Popov, A., Ortmann, F., Berger, R., Müllen, K., & Feng, X. (2017). Polycyclic heteroaromatic hydrocarbons containing a benzoisindole core. *Organic Chemistry Frontiers*, 4(5), 847–852.
- [11] Wang, Z., Gu, P., Liu, G., Yao, H., Wu, Y., Li, Y., Rakesh, G., Zhu, J., Fu, H., & Zhang, Q. (2017). A large pyrene-fused N-heteroacene: Fifteen aromatic six-membered rings annulated in one row. *Chemical Communications*, 53(55), 7772–7775.
- [12] Mateo-Alonso, A. (2014). Pyrene-fused pyrazaacenes: From small molecules to nanoribbons. *Chemical Society Reviews*, 43(17), 6311–6324.
- [13] Tripathi, A., & Chetti, P. (2020). Enhanced charge transport properties in heteroatomic (NH, O, Se) analogs of benzotrithiophene (BTT) isomers: A DFT insight. *Molecular Simulation*, 46(7), 548–556.
- [14] Tri, N. N., Duong, L. V., & Nguyen, M. T. (2020). Optoelectronic properties of heptacene, its fluorinated derivatives and silole, thiophene analogues. *Materials Today Communications*, 24, 101054.
- [15] Lin, P.-P., Qin, G.-Y., Zhang, N.-X., Fan, J.-X., Hao, X.-L., Zou, L.-Y., & Ren, A.-M. (2020). The roles of heteroatoms and substituents on the molecular packing motif from herringbone to  $\pi$ -stacking: A theoretical study on electronic structures and intermolecular interaction of pentacene derivatives. *Organic Electronics*, 78, 105606.
- [16] Kumar, V., Tripathi, A., Koudjina, S., & Chetti, P. (2023). Benzodithiophene (BDT) and benzodiselenophene (BDSe) isomers' charge transport properties for organic optoelectronic devices. *Journal of Sulfur Chemistry*, 44(4), 462–478.
- [17] Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*, 98(7), 5648–5652.
- [18] Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37(2), 785–789.
- [19] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, J., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, R., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Jr., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, R. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., & Ortiz, J. V. (2009). *Gaussian09*. Wallingford, CT: Gaussian, Inc.



- [20] O'Boyle, N. M., Tenderholt, A. L., & Langner, K. M. (2008). CCLib: A library for package-independent computational chemistry algorithms. *Journal of Computational Chemistry*, 29(5), 839–845.
- [21] Oyeneyin, O. E. (2017). Structural and solvent dependence of the electronic properties and corrosion inhibitive potentials of 1,3,4-thiadiazole and its substituted derivatives—a theoretical investigation. *Physical Sciences International Journal*, 16(2), 1–8.
- [22] Khan, M. F., Rashid, R. B., Hossain, M. A., & Rashid, M. A. (2017). Computational study of solvation free energy, dipole moment, polarizability, hyperpolarizability and molecular properties of betulin, a constituent of *Corypha taliera* (Roxb.). *Dhaka University Journal of Pharmaceutical Sciences*, 16(1), 1–8.
- [23] Srivastava, K. K., Srivastava, S., & Alam, T. (2014). Theoretical study of the effects of solvents on the ground state of TCNQ. *Pelagia Research Library*, 5(1), 288–295.
- [24] Contreras, R., Andres, J., Safont, V. S., Campodonico, P., & Santos, J. G. (2003). A theoretical study on the relationship between nucleophilicity and ionization potentials in solution phase. *Journal of Physical Chemistry A*, 107(29), 5588–5593.
- [25] Cedillo, A., Contreras, R., Galván, M., Aizman, A., Andrés, J., & Safont, V. S. (2007). Nucleophilicity index from perturbed electrostatic potentials. *Journal of Physical Chemistry A*, 111(12), 2442–2447.
- [26] Jaramillo, P., Pérez, P., Contreras, R., Tiznado, W., & Fuentealba, P. (2006). Definition of a nucleophilicity scale. *Journal of Physical Chemistry A*, 110(26), 8181–8187.
- [27] Campodonico, P., Santos, J. G., Andres, J., & Contreras, R. (2004). Relationship between nucleophilicity/electrophilicity indices and reaction mechanisms for the nucleophilic substitution reactions of carbonyl compounds. *Journal of Physical Organic Chemistry*, 17(4), 273–281.
- [28] Gázquez, J. L., & Cedillo, A. (2007). Vela, A. Electrodonating and electroaccepting powers. *Journal of Physical Chemistry A*, 111(10), 1966–1970.