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The Effects of A Single Atom Substitution and Temperature on Electronic and Photophysical Properties F8t2 Organic Material

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Abstract: The electronic and photophysical features of F8T2 organic semiconductor-based on a single atom substitution and temperature have been carried out by the self-consistent charge density-functional based tight-binding (SCC-DFTB) which is based on the density functional theory (DFT) and molecular dynamics (MD) methods. First of all, the heat treatment was carried out on the F8T2 from 50 K to 600 K. After that, the optoelectronic features of F8T2 by substitution of some nonmetallic single atoms, such as Fluorine (F), Bromine (Br) and Iodine (I) was studied. Herein, the dipole moments, HOMO, LUMO, bandgap and Fermi energies were searched. Also, the absorbance has been examined by time-dependent (TD)-DFTB. The obtained results of F8T2 were compared to experimental results. The HOMO value was found as -5.045 eV, which is compatible with its experimental value (-5.44 eV); the LUMO value was found -2.729 eV, which is coherent with the experimental LUMO value (-2.95 eV). Similarly, the bandgap of F8T2 (2.32 eV) was found to be compatible with measured result (2.49 eV). The bandgap for F8T2 increased from 2.32 eV (at 0 K) to 3.03 K (at 663.38 K) which is about 0.71 eV wide than that of F8T2 at 0 K. The maximum absorbance is found as 437 nm which is very well matched with experimental value (465 nm).

Keywords: F8T2, Absorbance, Electronic structure, TD-DFTB.

1. Introduction

Recently, organic semiconductors have been of significant attention in many applications such as electronic and photonic applications (Cheng, et al. 2019; Zhang, et al. 2018). Among them, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-bithiophene] (F8T2) which has high ionization potential (5.5 eV), is a significant category in organic field-effect phototransistors as the active material (Whang, et al. 2010; Sirringhaus, et al. 2000). Besides, the transistors demonstrate a highly stable and reproducible response when exposed to temperature (Whang, et al. 2010).

The photophysical features of materials are highly tunable with a change in temperature and an atom doped on it (Kurban, 2018; Kurban, et al. 2016). Herein, the electronic structure and photophysical features of organic F8T2 semiconductor have been studied by the self-consistent charge density-functional based tight-binding (SCC-DFTB) which is based on the density functional theory (DFT) and molecular dynamics (MD) methods in this study (Aradi, et al. 2007; Elstner, et al. 1998). First of all, the heat treatment was carried out on the F8T2 from 50 K to 600 K. After that, the properties mentioned above of F8T2 by substitution of some nonmetallic single atoms, such as Fluorine (F), Bromine (Br) and Iodine (I), was performed. The dipole moments to understand the interactions in F8T2 molecule, as well as, HOMO, LUMO, bandgap energies and Fermi energies were investigated. Also, the absorbance spectra were carried out time-dependent (TD)-DFTB.

2. Material and Method

The electronic and photophysical properties of undoped and Br-, I- and F-doped F8T2 have been examined using SCC-DFTB implemented in DFTB+ code (Aradi, et al. 2007) with the 3ob/3ob-

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3-1 (Gaus, et al. 2013; Kubillus, et al. 2015) set of Slater Koster parameters. On the other hand, DFTB approximates a Taylor series expansion of the total energy density functional theory (DFT). The SCC-DFTB includes a self-consistent charge step, optimizing the (Mulliken) charges, thus it improves very much the accuracy of the DFTB method. MD method was used to search temperature dependence properties in the frame of DFTB+ code. Besides, the absorption spectra were calculated by the TD-DFTB method based on Casida's approach (Andersen, 1980).

3. Results

The different views obtained from the optimized geometry of F8T2 organic molecule are indicated in Fig. 1.

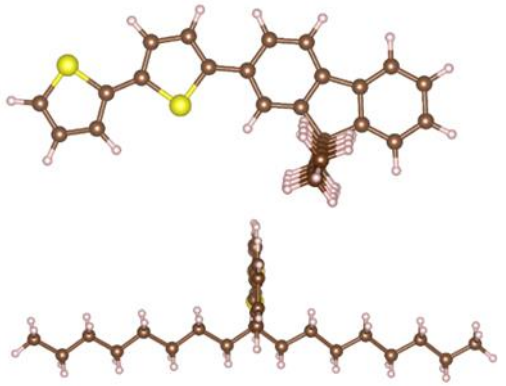

Figure 1. Different views obtained from the optimized geometry of F8T2 organic molecule. (Yellow is Sulfur, purple is Hydrogen and brown is Carbon).

To get more information on electronic states in undoped F8T2 organic semiconductor, firstly, a deep analysis has been performed on the electronic total DOS at different temperatures and doped single atoms (see Fig. 2). The density of localized states decreases in terms of an increase in temperature where the greatest contribution comes from F8T2 at 0 K and Br-doped F8T2. These oscillating behaviors progressively continue based on the increase in temperature, but there is a shift in energy values. The density of localized states shows a sharp increase between -8 and -7 eV. Besides, the DOS analysis demonstrates that F8T2 have the bandgap, so, all the nanoparticles show semiconductor character. There is an increase in HOMO, and a decrease in LUMO and Fermi energy is slightly increasing with increasing temperature in the range of 0-600 K.

The HOMO value for F8T2 organic semiconductor is -5.04 eV wide, i.e., about 0.40 eV smaller than the experimental data (-5.44) (Kettner, et al. 2016), which is more reactive, while being less stable than F8T2 at high temperatures (see Fig. 3). Fermi energies are in the middle of the valence and conduction band. The HOMO-LUMO energy gap of F8T2 is 2.31 eV, which increases from 2.31 to 3.03 eV in the range of 0-600 K (see Fig. 4), because of the interatomic spacing increases. It is clear then that a rise in the temperature contributes to the stabilization of F8T2 because of an increase in the bandgap. The total energy (per/atom), which is the sum of potential and kinetic energy, also increases under heat treatment (see Fig. 4).

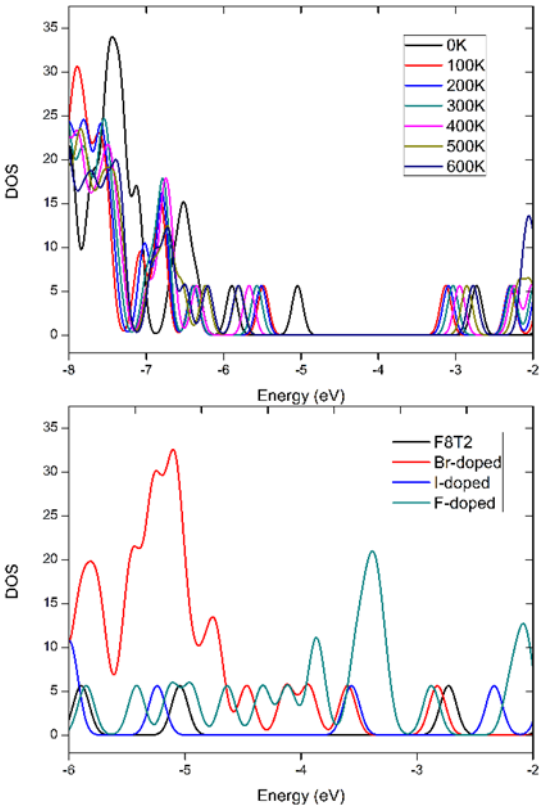

Figure 2. The total density of states (DOS) under heat treatment and atom doped F8T2.

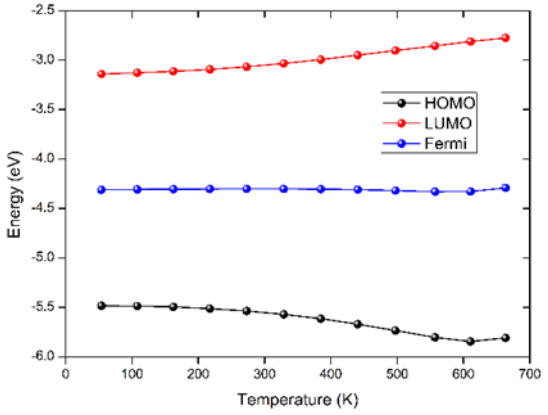

Figure 3. The HOMO, LUMO and Fermi energy levels of F8T2 under heat treatment.

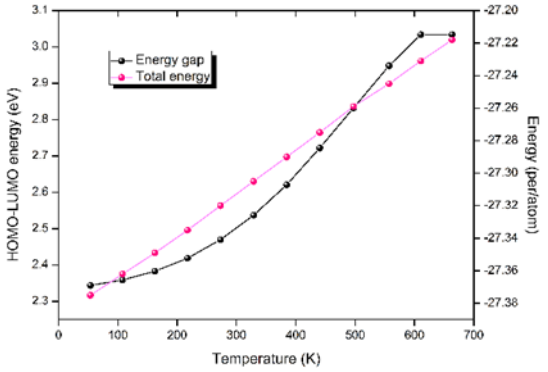

Figure 4. The variations of the HOMO-LUMO energy gap and total energy (per/atom) of F8T2 under heat treatment.

On the other hand, the energetic properties of Br, I and F doped-F8T2 have been investigated. The HOMO, LUMO, bandgap and Fermi energies were given in Table 1. The bandgap of pure F8T2 are in the following decreasing order: F8T2> I-doped F8T2> F-doped F8T2> Br-doped F8T2 (see Table 1). The experimental energy gap value of F8T2 is 2.49 eV wide (Kettner, et al. 2016), i.e., about 0.17 eV greater than that of DFTB calculations which are very compatible with experimental data. The HOMO value for Br-doped F8T2 organic semiconductor is -3.78 eV wide, i.e., about 1.26 eV smaller than that of undoped F8T2 (-5.04 eV). The HOMO value for I-doped F8T2 is -5.17 eV wide, i.e., about 0.12 eV greater than undoped F8T2. This also indicates that the transfer of the electrons from HOMO to LUMO for Br-doped F8T2 is easier that of undoped and I and F-doped F8T2.

Table 1. The HOMO (H), LUMO(L), Energy gap (Eg) and Fermi Energy (EF) of undoped and Br-, I- and F-doped F8T2.

Structures	H	L	E_g	E_F
F8T2-DFTB	-5.04	-2.72	2.31	-3.88
F8T2-Exp.	-5.44	-2.95	2.49	-
I-doped	-5.17	-3.49	1.67	-4.33
F-doped	-4.79	-3.13	1.66	-3.96
Br-doped	-3.78	-2.68	1.09	-3.23

The dipole moment (D_M) is related to differences in electronegativity. The bigger D_M corresponds to stronger intermolecular force. Herein, the D_M in x-, y- and z-directions as a function of temperature was shown in Fig. 5. Our results show that the *Dx* (-0.48 Debye) at 0 K for F8T2 causes the largest negative charge separation in the x-direction. D_M decreases in terms of temperature along x-directions; it increases along y and z directions. After 500 K, it started increasing up to almost 663 K. When it comes to Br, I and F doped F8T2, the biggest component of DM for Br-doped F8T2 is found to be along the x-axis (-1.39 Debye) which

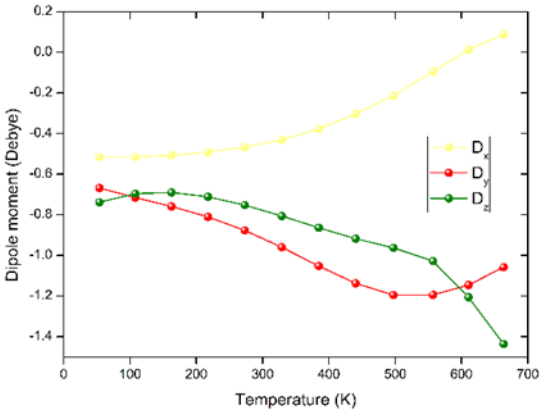

Figure 5. The variations of dipole moments of F8T2 in different x, y, z directions under heat treatment.

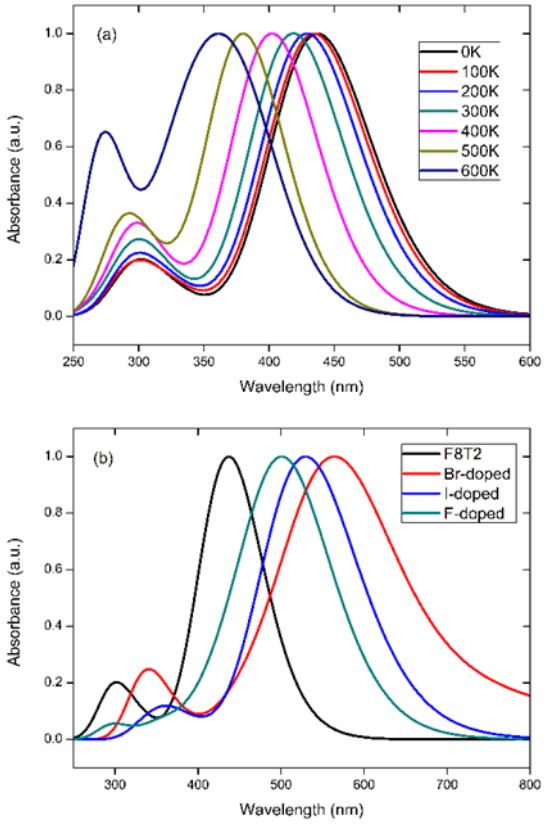

Figure 6. Absorbance spectra of (a) undoped F8T2 under heat treatment and (b) atom doped F8T2.

means large negative charge separation in the x-direction.

The biggest value of DM for Br-doped F8T2 corresponds to the stronger interaction among the atoms in the molecule. These results are compatible with the bandgap because the lowest bandgap of Br-doped F8T2 infers that electrons easily jump from HOMO to LUMO. Herein, there is a correlation between DM and the bandgap of the undoped and doped FT82. Thus, it can be expressed that the large DM has small bandgap.

Absorbance spectra of F8T2 at different temperatures and Br, I and F-doped F8T2 were depicted in Fig. 6 (a, b). The F8T2 exhibits the maximum peaks 2.84 eV (436 nm) for undoped F8T2 corresponds to the ultraviolet (UV) region, which is very well matched with experimental data 2.66 eV (465 nm) (Kettner, et al. 2016). The absorbance spectrum of F8T2 decreases concomitantly with an increase in temperature where the maximum spectra of F8T2 (361 nm; 3.43 eV) are smallest at 600K. The absorption peaks are getting narrower and have smaller magnitude from 0 K to 600 K. It is also clear from the spectra that the structures are shifted towards higher energy in going from 0 K to 600 K. Absorbance spectra of Br-, I- and F-doped F8T2 are 2.20 eV (563 nm), 2.34 eV (529 nm) and 2.38 eV (501 nm), respectively. The obtained results show that a single atom substitution significantly improves the photophysical properties of F8T2.

4. Discussion and Conclusions

The electronic and photophysical properties of F8T2 organic semiconductor-based on a single atom substitution and temperature have been researched by the DFTB approach. The predicted HOMO (-5.045 eV) and LUMO (-2.729 eV) energies were compatible with measured HOMO (-5.44 eV) and LUMO (-2.95 eV) energies. Besides, the bandgap (2.32 eV) is compatible with measured result (2.49 eV). The bandgap of F8T2 increased from 2.32 eV (at 0 K) to 3.03 K (at 663.38 K) which is about 0.71 eV wide than that of F8T2 at 0 K. The biggest component of dipole moment for Br-doped F8T2 is along the x-axis (-1.39 Debye), thus there is a large negative charge separation in the x-direction. Besides, there is a correlation between D_M and the energy gap of the undoped and doped FT82. The maximum absorbance is 437 nm which is very well matched with experimental value (465 nm). Br-, I- and F- were doped on F8T2; such doping procedure significantly improves the photophysical properties of F8T2.

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