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DFT simulation of conductivity of the p-type doped and charge-injected cis-polyacetylene

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ABSTRACT

Semiconducting conjugated polymers (CPs) have shown great potential in organic solar cells and organic field-effect transistors (OFETs), due to their tunable electronic and optical properties. In this study, we compare computational predictions of electronic and optical properties of ensembles of cis-polyacetylene (cis-PA) multiple oligomers in two different forms (a) undoped cis-PA and (b) cis-PA doped by phosphorous fluoride (PF_6^-) via density functional theory (DFT) with hybrid functionals. The comparison of undoped cis-PA under the constraint of injected charge carrier and cis-PA doped by PF_6^- shows that either doping or injection provides very similar features in electronic structure and optical properties. Doped and injected are similar to each other and different from the pristine, undoped PA. Computed results also indicate that the injection of charge carriers and adding p-type doping into the semiconducting CP model both greatly affect the conductivity. These observations provide a better understanding and practical use of the properties of polyacetylene films for flexible electronic applications.



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Conjugated polymers (CPs); Density functional theory (DFT); p-type doping; cis-polyacetylene doped and cis-polyacetylene undoped

Introduction

Conjugated polymers (CPs) are one type of organic macromolecules that show interesting tunable electronic properties, conductive properties and their potential applications in different fields such as organic photovoltaics, soft electronics, field-effect transistors (FET), light-emitting devices, sensors, microelectronic actuators, photovoltaic cells, coatings, energy storage devices and so on [1–5]. Significant experimental and computational efforts have been devoted to studying the electronic properties of conjugated polymers using the approximation of the energies and density of states via density functional theory (DFT). However, such studies are quite complicated, because polymers do not have well-defined structures. Amorphous or semicrystalline rather than long-range crystals, there are no long-range orders and many of them are insoluble and polydisperse, and computational techniques are significantly less developed for infinite polymers than for well-defined molecules. Therefore, it is common to extrapolate oligomer properties to infinite chain lengths to estimate polymeric properties. We examine different aspects of such extrapolations in this article and discuss how their properties converge with increasing oligomer chain length. There are several CPs available that show excellent results in the molecular modification of the structure, solution processability, electrical properties and charge carrier compared to their inorganic counterpart's silicon [6].

The conductivity and the charge carrier density of CPs can be modified by adding p-type or n-type doping

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or injecting charge in the models [7]. Adding dopants or injecting charge in the CPs has the potential to control carrier mobility, electronic properties and absorption. When the charge is injected into the CPs, the electronic population is added to the lowest unoccupied molecular orbital (LUMO) and this process occurs when the doping type is 'n'. In p-type doping, the electronic population can be removed from the highest occupied molecular orbital (HOMO) [8,9]. This charge injection is occurred by withdrawing or adding electrons from the polymer or oxidising the polymer [10]. For doping, there is no chemical reaction needed. Adding a dopant or injecting a charge carrier affects the bandgap of the semiconductor CP materials [11,12]. As an example, a bandgap increases the visible light absorption in the photovoltaic cells and improves the charge carrier mobility which educates the separation between the electron-hole pair. Therefore, it is more challenging to understand the behavior of the electronic properties of CPs and the effect of adding doping or injecting charge in the system. For a better understanding of the electronic properties of the conjugated polymers, DFT can be used.

Recently, DFT calculations can be used for predicting molecular geometries, energy levels and absorption spectra of CPs [13]. DFT is one of the most common computational methods which are used to compute the electronic properties of the quantum-chemical modelling of materials [14,15]. Therefore, the local electronic density and local energy density per electron can be calculated using many DFT functionals. Performing DFT calculations on CPs is challenging due to their size (a large number of atoms); so, for better accuracy/precision, methods such as hybrid functionals, Heyd-Scuseria-Ernzerhof (HSE06) screened-Coulomb hybrid density functionals can be used. Hartree-Fock (HF) exchange energy is contributed to the HSE06 hybrid functional. These functionals employ a screened coulomb potential for exchanging the exact correlation between atomic structures using short-range HF exchange [16-19] instead of full exact exchange to avoid the computational expenses of the long-range character of HF exchange [20]. For this purpose, Heyd–Scuseria–Ernzerhof (HSE06) methods have been used to compute the electronic structures and bandgap of the CPs which are a function of DFT [20,21]. Compared to other methods of DFT, HSE06 is more relevant and provides accurate results for computing the fundamental electronic structures [22]. Though the computational cost of DFT is lower than traditional exchange-correlation methods HSE06, for this research work HSE06 methods were used because it gives exact exchange-correlation energy from other ab initio or empirical methods. HSE06 methods can be used

to explore the electronic properties and estimate the bandgap of the CPs.

During the last few decades, many researchers have worked on the electronic conductivity of polyacetylene, and it gets great attention particularly because of the possibility of increasing its electrical conductivity by doping [23-25]. Heeger and co-workers suggested that solitons played a fundamental role in the charge-transfer doping mechanism [26]. Yamabe et al. studied the conducting mechanism in the direction perpendicular to the chains for lightly doped PA [27]. Based on their model, the charged soliton was helped to hop between the PA chains due to the vibrational motion of the dopant. However, most earlier models for conducting mechanisms were one-dimensional (1D) models, and not suited to the electrical anisotropy of the PA system. Detailed experiments have shown that the doped oriented-polyacetylene shows conductivity anisotropy in directions parallel and perpendicular to the oriented direction of the film [28,29]. Makoto Kuwabara et al. numerically investigated the interchain hopping of solitons and polarons in polyacetylene and observed that charge solitons can hop to the opposite chain by forming bipolarons [30]. R. R. Chance et al. studied the interchain hopping of bipolarons of doped polyacetylene which was discussed as a mechanism for spinless conductivity. They observed that this mechanism can account for the observed dopantconcentration dependence of the conductivity in transpolyacetylene and the observation of anomalously low magnetic susceptibilities in the highly conducting regime of several doped polymers [31]. Several researchers investigated that polyacetylene showed remarkable electronic properties in the films doped and undoped PA. It is important to explore the research on the conductivity of the conjugated polymer like cis-PA at the ground state and understand the influence of the electronic structure of the semiconducting CPs after adding doping or injection of charge carriers. The electronic properties, charge carrier density, and conductivity of the conjugated polymer can be improved by adding p- or n-type doping (charge injection) after adding those things to the CPs, the conductivity of the semiconducting material can be changed or modified [9].

In this current study, we investigate the groundstate properties of the polyacetylene (PA) using HSE06 which is an organic conjugated polymer. PA consists of a long chain of carbon and hydrogen atoms, this long chain of carbon atoms bonded using single or double bonds between them. Because of the geometry, PA which consists of double bonds can be named cispolyacetylene (cis-PA) or trans-polyacetylene (trans-PA). By changing the temperature of the cis-PA or trans-PA, the isomer of the polymer can be controlled. One

may note that a favourable comparison with experiments and wavefunction-based methods, was reported for Vinylene-linked conjugated polymer systems by use of 'full hybrid' functional such as B3LYP [32,33]. A model of an isolated PA oligomer was studied in our previous work [34] to explore excitonic effects by TDDFT with B3LYP functional and patterns of relaxation in absence of neighbour oligomers, as a reference point. Multiple oligomers model processed by B3LYP is expected to demonstrate similar correction as for a single oligomer, in respect to other functionals [34]. Therefore, a consideration of excitonic effects in models with multiple oligomers would be a natural continuation of this research. Multi-oligomer models are expected to show certain difference to a single oligomer model as a function of the oligomer length. The shorter oligomers behaving like molecules are expected to show similarity between single-and multi-oligomer models. In contrast, longer oligomers are expected to show different trends: singleoligomer models are expected to demonstrate confinement and exciton effects, while multi-oligomer models are expected to demonstrate saturation, where the gap is defined not by the length of the oligomer but interoligomer hoping. So, we have selected the small enough oligomer that allows to analyse interchain hopping. Also, we are bound by our recently published reference point work [34].

The main goal of this work is to control the conductivity of the conjugated polymer which can be hypothetically controlled by doping or injecting charge carrier. Therefore, the charge carrier density and conductivity of conducting conjugated polymers can be modified either by charge injection or via p- or n-type doping [35]. Most of the conducting polymers are the p-doped type because the Fermi level in the electrodes on the metal/polymer interface is typically aligned with the valence band of polymer, which favours the hole injection [22].

In this work, we want to check which mechanism provides better improvement to conductivity: doping or charge injection into the conjugated polymer. We utilised Vienna Ab initio Simulation Package (VASP) to study the optical, electronic, and conductive properties of the $PF_6^$ doped cis-PA and undoped cis-PA conjugated polymers at the fundamental atomic level. DFT with HSE06 hybrid functional has been used to understand such properties such as bandgap and absorption spectra. We add a few PF_6^- groups serving as p-dopants inside the cis-PA model as an attempt to control the conductivity of the polymer. First principles calculations are used to prove a hypothesis that upon adding dopants or injecting charge into the conjugated polymer, several polymer properties experience a change, such as the bandgap getting smaller. We organise computational evidence of conversion of the considered models from semi-conductor to conductive range. A comparison of the DOS and absorption spectrum of the undoped and PF_6^- doped models help to understand the trends in the conductive materials and how they change upon doping. The results indicate that the energy offset between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies are decreased greatly, as explained in detail in the result and discussion section.

Methods

This paper presents theoretical method based on groundstate DFT calculations. In this research, the electronic structure of atomic model is determined by using DFT which is implemented in the VASP software. The atomic model is defined by the initial positions of each ion, set of coordinates for nuclei $\{\vec{R}_I\}$ and number of electrons N_{el} . Kohn–Sham equations are employed to self-consistent DFT functions to get better approximation. The main equation is a fictitious one-electron Kohn–Sham equation [36,37]:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \nu([\rho(\vec{r})], \vec{r}) \right) \varphi_i^{KS}(\{\vec{R}_I\}, \vec{r})$$

= $\varepsilon_i(\{\vec{R}_I\}) \varphi_i^{KS}(\{\vec{R}_I\}, \vec{r})$ (1)

where the first term corresponds to kinetic energy Tand uses the symbol of gradient $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$. In Equation (1), we find a set of one-electron orbitals $\varphi_i^{KS}(\{\vec{R}_I\}, \vec{r})$ and their energies ε_i . The orbitals are combined with orbital occupation function f_i for constructing the total density of electrons.

$$\rho(\vec{r}) = \sum_{i=1}^{N_{el}} f_i \varphi_i^{KS^*}(\vec{r}) \varphi_i^{KS}(\vec{r})$$
(2)

$$f_i = \begin{cases} 1, & i \le HOMO \\ 0, & i \ge LUMO \end{cases}$$
(3)

where HOMO and LUMO stand for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. The total density determines the potential,

$$\nu[\rho] = \delta/\delta\rho(E^{tot}[\rho] - T[\rho])$$
(4)

The potential energy is defined in terms of a functional derivative of the total energy with respect to variation of the total density and includes interactions of electrons with ions and three electron interactions: Coulomb, correlation and exchange. Rectangular brackets symbolise functional. Equations (1)-(4) are solved in the iterative,

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self-consistent manner by using hybrid functionals which gives us approximate exchange-correlation results.

In this article, the HSE06 (Heyd–Scuseria–Ernzerhof) functionals are used to improve the computational efficiency of the systems. The HSE06 functional calculated from the fraction of Fock exchange, *a*, at zero electron separation and a length scale, ω^{-1} , where the short-range Fock exchange is computed as follows [34,38]:

$$E_{Xc}^{HSE} = aE_X^{HF,SR}(\omega) + (1-a)E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_c^{PBE}(\omega)$$
(5)

where $E_X^{HF,SR}(\omega)$ is the component of Hartree–Fock exact exchange functional, $E_X^{PBE,LR}(\omega)$ and $E_X^{PBE,SR}(\omega)$ are the long and short-range elements of the PBE (Perdew–Burke-Ernzerhof) exchange functional and $E_c^{PBE}(\omega)$ is used to compute the correlation of the PBE functional. The above $E_X^{HF,SR}(\omega)$ is computed through the spinful Kohn–Sham density matrix $\rho\sigma, \sigma'(r, r')$, which is given below:

$$E_X^{HF,SR}(\omega) = -\frac{1}{2} \sum_{\sigma,\sigma'} \int dr \, dr' \frac{\operatorname{erfc}(\omega|r-r'|)}{|r-r'|} \times |\rho\sigma,\sigma'(r,r')|^2 \tag{6}$$

Though this function accuracy was achieved which was equal to PBE0, the value of a = 0.25 exchange fraction was limited. Therefore, for improving the accuracy reparametrised the HSE06 function which was based on ω not *a* [34,39,40].

Note that number of electrons N_{el} is a critical parameter, which affects the occupation of orbitals, shape of orbitals and total energy. Total number of electrons is

$$N_{el} = \iiint dx dy dz \rho(\vec{r}) \tag{7a}$$

For restricted DFT singlets, the number of occupied orbitals reads

$$HO^{neutral} = \frac{N_{el}^{neutral}}{2}, LU^{neutral} = \frac{N_{el}^{neutral}}{2} + 1 \quad (7b)$$

A change in the number of electrons results in redefinition of the number of occupied orbitals. Specifically, for anions and cations, the indices of HO and LU Kohn–Sham orbitals differ from those in neutral models. Therefore, absolute values of indices of frontier orbitals are changed as follows:

$$HO^{anion} = \frac{N_{el}^{neutral}}{2} + 1 = LU^{neutral},$$
$$LU^{anion} = \frac{N_{el}^{neutral}}{2} + 2 = LU^{neutral} + 1$$
(7c)

$$HO^{\text{cation}} = \frac{N_{el}^{neutral}}{2} - 1 = HO^{neutral} - 1,$$
$$LU^{\text{cation}} = \frac{N_{el}^{neutral}}{2} = HO^{neutral}$$
(7d)

A band gap of a material in a neutral configuration is defined as an offset between the energies of the lowest unoccupied Kohn–Sham orbital and the highest occupied Kohn–Sham orbital.

$$\Delta E_{gap}^{neutral} = \varepsilon_{LU}^{neutral} - \varepsilon_{HO}^{neutral} \tag{8}$$

The definitions of the bandgap of anion and cation use the energy difference of specific pairs of orbitals defined in Equations 7(c)-7(d). The electron density of states (DOS) describes the number of states per interval of energy. One uses DOS to characterise electronic structures of the studied models. DOS is defined as

$$n(\varepsilon) = \sum_{i} \delta(\varepsilon - \varepsilon_i) \tag{9}$$

where the Dirac delta function was approximated with a finite width Gaussian function. One of the parameters obtained from the DFT calculation is the oscillator strength representing probability that a model, which absorbs a photon will undergo an electronic transition. Thus the oscillator strength is related to the rate of absorption and is defined as

$$f_{ij} = \frac{4\pi m_e \omega_{ij}}{3he^2} |\vec{D}_{ij}|^2 \tag{10}$$

where $\omega_{ij} = \frac{\varepsilon_i - \varepsilon_j}{\hbar}$ is the angular frequency required to excite an electron from state *i* to state *j*.

 $\vec{D}_{ij} = e \int d\vec{r} \, \varphi_i^*(\vec{r}) \cdot \vec{r} \cdot \varphi_j(\vec{r})$ is the transition dipole moment for transition from state *i* to state *j*, and m_e , *h* and *e* are fundamental constants. The spectral density of absorption was calculated analogously to the DOS using [34]

$$\alpha(\omega) = \sum_{i \le HO} \sum_{j \ge LU} f_{ij} \delta(\hbar \omega - \hbar \omega_{ij})$$
(11a)

Here, two sums run over pairs of orbitals. Each delta function is weighted by the oscillator strength corresponding to the transition so that the more probable transitions are given greater weight in the total absorption spectrum. Delta function is approximated by the finite width function with a width parameter corresponding to spectral line broadening due to the Heisenberg uncertainty principle and thermal fluctuations. There is a strong relationship between absorption spectrum and conductivity. They are closely related to each other. Generally, the conductivity is equivalent to the absorption of the conjugated polymer at zero frequency [41]

$$\sigma = \alpha(\omega = 0) \tag{11b}$$

Maximal conductivity is expected in case an intense absorption peak is found at zero transition energy.

In this research, we explore a response of the properties of the conjugated polymer models to adding or removing charge. Adding or removing charge corresponds to experimental setups with charge injection to intrinsic model or by functionalisation of the models by doping. Specifically, we focus on $C_{32}H_{32}$ oligomers functionalised by electron-withdrawing dopants PF_6^- composed of P (phosphorous) and F (fluoride). All modellings are performed by the first principles treatment. Practically, after adding and removing electrons from the conjugated polymer, we are trying to see that how material reacts, and which material shows more conductivity behaviour. This conductivity behaviour can be interpreted most efficiently based on the absorption spectrum analysis. Additional insight into the mechanism of conductivity can be obtained from the analysis of orbitals. The orbitals computed by Equation (1) are visualised and interpreted in form of 3D iso-surfaces of partial charge density, for selected orbital $|\varphi_i^{KS}(\vec{r})|^2$ or by 1D distributions [34]

$$\rho_i(z) = \iint dx dy |\varphi_i^{KS}(x, y, z)|^2 \tag{12}$$

$$\rho_i(y) = \iint dx dz |\varphi_i^{KS}(x, y, z)|^2 \tag{13}$$

Computational details

The atomistic model of the different conjugated polymers is shown in Figure 1. For this study, two types of conjugated polymer have been used: Figure 1(a) intrinsic cis-PA without any doping and (b) cis-PA doped by phosphorous and fluoride. In Figure 1(a), the size of the oligomer is $36 \text{ Å} \times 5.7 \text{ Å} \times 19.6 \text{ Å}$ and Figure 1(b) the size of the oligomer is $20 \text{ Å} \times 5.7 \text{ Å} \times 36 \text{ Å}$. Figure 1 shows the geometrically optimised structure of the polymer model. We carefully inject the positive and negative charge carriers, i.e. holes and electrons respectively and add some p-type dopants (Figure 1b) which is a fundamental pre-requisite for high quantum electroluminescence efficiencies, which markedly affect the performances of conjugated polymer. In this work, we investigated the conductivity of the cis-PA using DFT-based computational approach. We want to demonstrate that dopant and injection of charge are showing equivalent influence on changes of the band gap and so that any decrease in the band gap is equivalent to an increase in conductivity. It is a lower computational cost to form a periodic box filled with shorter/longer oligomers, as

a possible extension of this work. The general trends reported in this work are expected to hold for a periodic box filled with oligomers longer than those used here. An exploration of periodic models filled with shorterlength oligomers is expected to show lower values of computed conductivity for the following reason, quantum confinement in the shorter oligomers would increase gaps and sub gaps and subsequently decrease conductivity. Oligomers of conjugated polymers demonstrate the formation of bound excitons of finite size, due to the electron-hole interaction. In short-length oligomers, electrons and holes experience confinement due to the limited size of the oligomer. In long-length oligomers, the transition energies are defined by exciton size and do not depend on an additional increase in length. Although a size of exciton is specific for each conjugated polymer, there are common trends for this class of materials. Kraner et al. reported a uniform increase of the exciton size when molecules with π system sizes between 10 and 40 Å. When molecules size larger than 40 Å, there was no significant additional increase observed in the excitation size [42]. Stefanie A. Mewes et al. showed that TDDFT functions were dominated by the nonlocal orbital exchange in terms of asymptotic exciton size limits. The exciton size of the polymer changes with length size of the oligomer and for TDDFT/PBE functional, author showed that exciton size increases when the oligomers size increasing in the range from 10 - 30 Å. Upon reaching the oligomers length above 30 Å, no significant change was observed in exciton size [43]. For our work, we choose shorter oligomers. So, our qualitative analysis is expected to remain valid for short-range and long-range oligomers.

Figure 1(c) schematically shows the energy gap of the undoped model in the uncharged, positive and negative charge configurations which gives an idea about how occupied (HOMO) and unoccupied (LUMO) orbital get affected when withdrawing or adding charge from the model. After losing electrons from the model, the HOMO–LUMO gap gets smaller. Losing electrons corresponds to the model receiving a positive charge, thus forming cations. Due to HOMO–LUMO gaps that are small, electrons can jump easily from higher energy levels to lower energy levels. The energy gap between HOMO and LUMO of the anion is comparatively smaller than the neutral state. The energy level of the HOMO of the anion significantly decreases and electrons go from lower energy levels to higher energy levels.

Result and discussion

In this paper, the hybrid HSE06 functional is used to understand the electronic configurations of the groundstate of the electronic structure and predict the bandgap



Figure 1. Optimised geometry of ensemble of oligomers of (a) undoped cis-polyacetylene (cis-PA) model and (b) PF_6 -doped cis-polyacetylene (cis-PA) model. Each ensemble is composed of six oligomers terminated by methyl groups, under periodic boundary conditions. Note that the size of the periodic box is smaller than the length of a single oligomer. Oligomers are labelled 1 through 6 in the direction of increasing z-coordinate. All models are oriented along Z-axis, so that all models can be translated along Z-axis. The atomic structure of the undoped cis-PA and PF_6 -doped cis-PA is $C_{184}H_{208}$ and $C_{184}H_{208}F_{12}P_2$. (c) illustrates a schematic diagram of the band gap of the undoped model in the uncharged, positive and negative charge configurations.

of the system. The bandgap of conjugated polymer (Table 1) helps to predict the behaviour of the system whether it is behaving like semiconductor materials or conductor materials. The density of states (DOS) representing the band structures of different electronic configurations of the cis-PA undoped, and PF_6^- doped cis-PA models are reported in Figure 2. Figure 2(a) shows the DOS of the uncharged (neutral) cis-PA undoped model where the computed bandgap of the system is 0.9059 *eV*. In case one creates anions and cations by removing/adding literally one electron, the total spin configuration would change from singlet to doublet and would require spin-polarised calculations. However, we change the charge by adding or removing two electrons,

Table 1. Band gap for all models. In all considered models, in all considered configurations, the number of electrons is even. All electrons are paired.

Model	Band gap	Total no. of electrons
Undoped (neutral)	0.9059 eV	944
Undoped (cation)	0.0662 eV	942
Undoped (anion)	0.0989 eV	946
PF ₆ -doped (p-type) (neutral)	0.0925 eV	1038

in purpose to keep the singlet configuration, for simplicity, as a first step. In the same analogy, the doping agents were added by a pair of PF_6^- ions. Consequently, all models and configurations are legitimate to be treated as singlets. Figure 2(b) and (c) show the energy gap of the injection of the positive charge and negative charge carriers. It is expected that the results of the injection of the positive charge carriers will show similar behaviour to the cis-PA PF_6^- doped model. After withdrawing two electrons from the cis-PA undoped model, the original HOMO is affected. Because of the removing electrons, labelling of the orbital changes (i.e. shown in Figure 1c). This creates space inside the HOMO and generates the new LUMO which is shown in Figure 1(c). Then the initial bandgap is reduced to 0.0662 eV. This decrease of the bandgap indicates that after injecting a positive charge into the system, the system behaves like a conductive material, or it helps to improve the conductivity of the system. Figure 2(c) shows that after the injection of two electrons, the energy gap of the undoped model is decreased from its initial bandgap which is 0.0989 eV. This bandgap tends to decrease the bandgap of the cis-PA undoped model and the original LUMO is also



Figure 2. The density of states (DOS) of the polymer model is calculated by DFT using the HSE06 hybrid function method. Green-shaded regions represent the occupied orbitals and unshaded regions indicate unoccupied orbitals. Four frontier orbitals near the bandgap are labelled. (a) DOS of the neutral (uncharged) undoped cis-polyacetylene model, (b) DOS of cation (positively charged) undoped cis-polyacetylene model, (c) DOS of the anion (injecting charge or negatively charge) undoped cis-polyacetylene model, and (d) DOS of neutral PF₆-doped- (p-doping, positive polaron) cis-polyacetylene model. A, B, C, and D refer to HO, HO-1, LU and LU+1 respectively.

populated. Similarly, after adding doping (p-type) in the model (PF_6^- doped), we can see occupied and unoccupied orbitals are in the same energy level (Figure 2d). p-doping creates hole in the model which initiates the LUMO level and HOMO level should be closely aligned with each other. Figure 2(d) indicates the band gap (0.0925 eV) of the PF_6^- doped cis-PA model (neutral) which is almost the same as the energy gap of the injecting negative electron into the cis-PA undoped system. In both cases Figure 2(c) and (d), the original LUMO is populated which intends to decrease the bandgap of the system and influence the behaviour of the materials.

Figure 2 practically supports the features sketched in Figure 1(c). Specifically, in Figure 2, panel (a) corresponds to the first segment of the schematic diagram

in Figure 1(c), labelled as 'neutral'. In this situation, the bandgap is open, and the computed HOMO–LUMO offset is substantial, around 0.9059 eV. Figure 2, panel (b) corresponds to the middle segment of the schematic diagram in Figure 1(c), labelled as 'cation'. There, both HOMO and LUMO belong at the top of the valence band. Their energy offset is vanishing as indicated by a solid blue bar in Figure 1(c) and as computed 0.0662 eV. Figure 2, panel (c) corresponds to the rightmost segment of Figure 1(c), labelled as 'anion', and corresponds to the situation when both HOMO and LUMO are found at the bottom of the conduction band as indicated by solid red bar in Figure 1(c). On one hand, the value of the broadening parameter is chosen to be of the order of the room temperature thermal quantum kT. On the other hand, the gap for doped/cation models is smaller or comparable to the room temperature thermal quantum kT. In such situation, the broadening is larger than the gap and the peaks look unresolved.

Figure 3 shows the absorption spectra of the undoped and PF_6^- doped cis-PA models. Absorption at the transition energy value approaching zero corresponds to the conductivity of the sample [44]. Green circle, orange diamond, purple triangle, and pink square indicate the value of absorption in the limit of zero transition energy for each of the models. The violet triangle corresponds to $\Delta \varepsilon = 0 \, eV$ absorption of the neutral undoped cis-PA model, the green circle corresponds to $\Delta \varepsilon = 0 \, eV$ absorption of the cation undoped cis-PA model, the orange diamond corresponds to $\Delta \varepsilon = 0 \, eV$ absorption of the neutral undoped cis-PA model, and the pink square corresponds to $\Delta \varepsilon = 0 \, eV$ absorption of the neutral $PF_6^$ doped cis-PA model. Both linear and log scale plots are needed in Figure 3 for a better understanding of the properties of materials. The absorption/conductivity at the optical/near-infrared frequency range is convenient to analyse in the linear plot. However, the degree of absorption/conductivity at the transition energy approaching zero differs by several orders of magnitude. The linear plot shows zero value for both neutral undoped (violet line) and the neutral PF_6^- cis-PA (pink line) models, while in log scale one can focus on theoretical differences among the absorption/conductivity values of all models. The main idea under this approximation is that when voltage creates current, an electron is being accelerated via promotion between orbitals. Smaller gap, intense transitions across the gap correspond to better conductivity. The green circle and orange diamond indicate the high-intensity region of the absorption spectra. These values for the green circle and the pink square, are in the range between 0.1 and 1 eV and correspond to a conducting material (doped and injected). The purple triangle and the orange diamond illustrates absorption values in the range between 10^{-8} , which is 8 orders of magnitude smaller and correspond to an insulator.

Figures 4 and 5 demonstrate the delocalisation of orbitals over several oligomers, which have no direct chemical bond. Such delocalisation corresponds to a conductivity mechanism involving 'hopping' of charge carriers between oligomers. Figure 4 shows the charge density of the positively charged cis-PA undoped model which indicates the calculation of the iso-surfaces where the iso-surface values are computed using HSE06 functional. The conductivity of the material is greatly influenced by two components. One is the charge mobility of the system and another one is the energy gap between the given charge carriers. In this paper, both parameters affect the charge density of the system, so this paper



Figure 3. Calculated ground state absorption spectra as a function of transition energy. The Violet line refers to the neutral undoped cis-PA model, the green line indicates the cation undoped cis-PA model, the red line states anion undoped cis-PA model and the pink line shows neutral PF_6^- doped cis-PA model.

focuses on both contributions of the system and discussed the results accordingly. In the HOMO-1 orbital shown in Figure 4(a), the maximum amount of charge density appears in the fifth and sixth chains, and those chains are mostly localised. That means the localised orbital is not conductive. For the HOMO orbital shown in Figure 4(b) where all most all chains are mostly localised, and the maximum amount of the charge density appears on those sections. However, those chains are localised, they mostly affected the behavior of the conductive material. Figure 4(c) shows the LUMO demonstrates a maximal value of the squared/charge density on all chains. Figure 4(d) specifies the absolute value squared/charge density of the orbital LUMO+1 in which most of the chains are delocalised. The localised and delocalised nature of this orbital is greatly influencing the conductivity behavior of the polymer. Those orbitals are delocalised which means that orbitals behave like a conductive material and those orbitals are localised which indicates that orbitals behave like non-conductive material and incomplete delocalisation refers to that orbitals behave like partially conductive materials. Therefore, we can say that the HOMO-1 orbital behaviour like partially conductive material, the HOMO orbital is non-conductive, the LUMO orbital is also non-conductive and the LUMO+1 orbital behaves like a conductive material. Figure 5 indicates the calculation of the iso-surfaces of the PF_6^- doped cis-PA model where the iso-surface values are computed using HSE06 functional. The conductivity of the material is greatly influenced by three components. One is the charge mobility of the system and the second one is the energy gap between the given charge carriers and the third one is adding doping or materials. In this paper, both parameters affect the charge density of the system, so this paper focuses on both



Figure 4. Charge density of the frontier molecular orbitals of undoped cis-PA (injecting negatively charge) model at the ground state via HSE06 hybrid functionals: (a) orbital of 472, HO-1, (b) orbital of 473, HO, (c) orbital of 474, LU, and (d) orbital of 475, LU+1. Shaded areas specify the electron density. The iso-value of 0.0045 is used for plotting the iso-surfaces.



Figure 5. Charge density of the frontier molecular orbitals of PF_6^- doped cis-PA (neutral) model at the ground state via HSE06 hybrid functionals: (a) orbital of 518, HO-1, (b) orbital of 519, HO, (c) orbital of 520, LU, and (d) orbital of 521, LU+1. Shaded areas imply the electron density. The iso-value of 0.0045 is used for plotting the iso-surfaces.

contributions of the system and discussed the results accordingly. The localised and delocalised nature of this orbital is greatly influencing the conductivity behavior of the polymer. Those orbitals are delocalised which means that orbitals behave like a conductive material and those orbitals are localised which indicates that orbitals behave like non-conductive material and incomplete delocalisation refers to that orbitals behave like partially conductive materials. In the HOMO-1 orbital shown in Figure 5(a), the first and second oligomers are mostly localised, and the rest of the oligomers are delocalised. Those oligomers' localisation and delocalisation depend on the position of the doping. Where doping is added to the chain, those chain/oligomers are not localised. So, the HOMO-1 orbital is partially conductive. For the HOMO orbital shown in Figure 5(b) where the third and fourth oligomers are mostly localised, and the maximum amount of the charge density appears on those sections and other oligomers are delocalised because of the doing position. Therefore, we can say that HOMO orbital behaviour is like a partially conductive material. Figure 5(c) indicates the LUMO orbital which demonstrates a maximal value of the squared/charge density on the first, fourth, fifth and sixth oligomers of the $PF_6^$ doped cis-PA uncharged. So, this orbital is behaving like non-conductive material. Figure 5(d) specifies the absolute value squared/charge density of the orbital LUMO+1 in which most of the chains are localised. However, we can say that the LUMO+1 orbital behaves like a nonconductive material.

Conclusion

In this research, we explore the conductivity of the cispolyacetylene CPs which is studied using the DFT-based computational approach. The band gap, absorption spectrum and charge density of ground state have been studied using the HSE06 hybrid functional. The properties of the cis-PA can be manipulated by injecting charge or introducing a dopant. This paper explores the hypothesis that p-doping and charge injection provide the same increase in the conductivity of the polymer. Manipulation of the value of the bandgap in a range between fractions of an eV to a few eV changes conductivity by several orders of magnitude. From presented results, one can conclude that the bandgap becomes smaller after injecting charge or adding dopant. This trend is made evident via the DOS graph, it is visually illustrated via occupied orbitals overlap with the unoccupied orbitals. Upon injecting charge, the bandgap of the undoped cis-polyacetylene becomes 0.0989 eV which is equivalent to the bandgap of the neutral PF_6^- (phosphorus fluoride)-doped (0.0925 eV) cis-PA. From this study, one can understand that injection of charge or adding a dopant can both effectively reduce the band gap of the cis-PA. After analysing the DOS results, one can conclude that dopant and injection of charge are equivalent in their influence on changes in the band gap, so any decrease in the band gap is equivalent to increase in conductivity. The absorption spectra analysis showed that upon injecting charge, the energy of the lowest transition in the absorption spectrum is redshifted from its original energy range above 1eV to a smaller values and the undoped cis-PA behaves more like a conductive material. However, the PF_6^- doped cis-PA at a neutral state also behaves like a conductive material which is useful in the development of microelectronics; diodes and triodes (transistors).

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