

Structural effect on the charge transfer and on the internal reorganization energy: Computational study

Mohamed Jabha^{1,2+}, Abdelah El Alaoui², Abdellah Jarid³, El Houssine Mabrouk^{1,4}

1. University of Moulay Ismail, Faculty of Sciences and Technics, Errachidia, Morocco.
2. University of Moulay Ismail, Faculty of Sciences, Meknes, Morocco.
3. University of Cadi Ayyad, Faculty of Sciences Semlalia, Marrakech, Morocco.
4. Sidi Mohamed Ben Abdellah University, Faculty of Sciences, Fez, Morocco.

+Corresponding author: Mohamed Jabha, **Phone:** +212614018410, **Email address:** m.jabha@edu.umi.ac.ma

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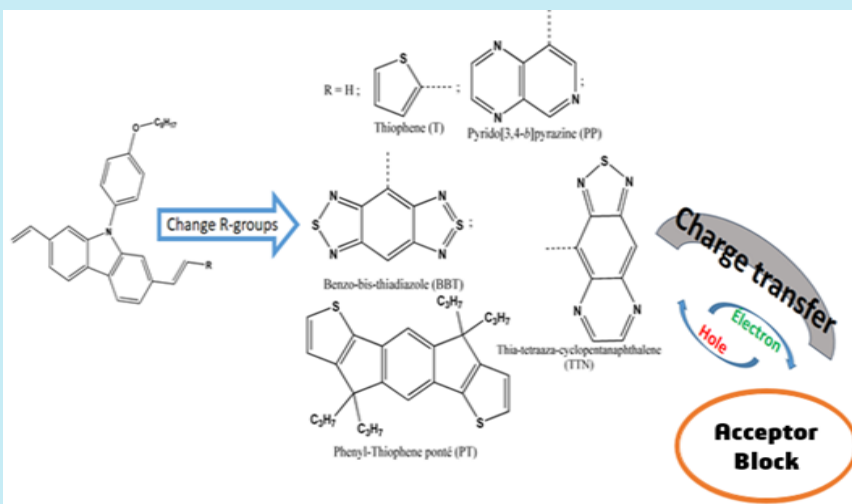
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ABSTRACT: The effects of addition of thiophene, bridged phenyl-thiophene, thia-tetra-azacyclopenta-naphthalene, benzo-bis-thiadiazole, and pyrido(3,4-b)pyrazine to 9-(4-octyloxyphenyl)-2,7-divinylcabazole on the internal reorganization energies, electronic affinity, and ionization potential were studied using density functional theory (DFT). These compounds are characterized by their charge exchange potentials (donor-acceptor), which can be applied in energy conversion devices such as photovoltaic cells. The so-called internal reorganization concerns, above all, the positions of holes and points of high electron density on the molecular skeleton.

Thus, valuable information is provided by the knowledge of the structure, the length of the desired oligomer and the nature of the radicals attached to the oligomer. Considering the available data, 2,7-divinylcarbazole (CrV-H) is the basic oligomer to carry out this theoretical study by extending the choice of ligands and length order to other oligomers while setting charge mobility as the major objective. The λ^+ of all the oligomers studied was lower than their λ^- except for the CrV-BBT oligomer, indicating a lower hole transfer cost than electron transfer cost with changes in molecular geometry during this process.



1. Introduction

The advent of organic electronics is deeply related to the development of new oligomers with high performance and reproducible properties (Muth *et al.*, 2013; Rodríguez-Monge and Larsson, 1995). Thus, the design of new oligomer architectures is a task usually accompanied by difficulties, especially the molecular stability that should generate the reproducible properties.

Oligomers based on 2,7-divinylcarbazole have been the subject of much experimental and theoretical work (Huixia *et al.*, 2017; Jabha *et al.*, 2018; 2021; Leclerc *et al.*, 2006). They have been qualified as promising compounds. Thus, taking into account the available data of this nanostructure, a theoretical approach would allow to widen the field of stakes for applications in electronics, optoelectronics and light energy-electric energy conversion. Thus, a quantum treatment by means of the density functional theory (DFT) seems to be a good way to understand the relationship between the structures and the electronic properties mentioned above.

Studies such as the one realized by Aly (2009) show that carbazole units have properties (high thermal stability, excellent physicochemical, and charge hole transport properties). Similarly, derivatives of carbazole have been analyzed by chemical modification (Jabha *et al.*, 2018).

In general, oligomers and conjugated organic polymers (Jabha *et al.*, 2021) have the same mechanism of charge transfer, their rate of hole and electron transfer mainly depends on the reorganization energy due to the geometrical relaxation that accompanies this transfer (André and Brédas, 2002). The reorganization energy is usually expressed as the sum of the internal and external contributions. The internal reorganization energy comes from the change in the equilibrium geometry of the donor and acceptor sites due to charge gain/loss during an electron transfer. The external reorganization energy comes from the electronic and nuclear polarization/decay of a surrounding medium.

In this manuscript, the strategy is the theoretical study of the structural properties of a carbazole-based oligomers series, in order to reveal the charge transfer and electronic properties of organic semiconductor materials of different natures. The effect of substitution and nature of substituent grouping on the reorganization energy for hole and electron transfer (λ^+ and λ^-) and electron affinity and ionization potential are also investigated (Schwenn *et al.*, 2011).

2. Computational details

All calculations were performed using the Gaussian 09 series (Bally *et al.*, 1991; Frisch *et al.*, 1984; Green *et al.*, 2005; Rassolov *et al.*, 2001). The ground state structure of all oligomers was fully optimized at the level of DFT theory and B3LYP functional by choosing 6-31G (d,p) basis set (Baker *et al.*, 1995; Ochterski *et al.*, 1996; Petersson and Al-Laham, 1991). The values of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), E_g levels, dihedral angles, bond lengths and energies of the minima of the compounds were determined from these optimized geometries. In the same way the charge quantities were determined at the same level and on the same optimized structures. For the ultraviolet-visible (UV-vis) spectrum as well as the oscillator power (f), excitation energies and wavelengths of the oligomers, has been chosen the TD-BP86/6-31G (d,p) method (Becke *et al.*, 1988; Burke *et al.*, 1996) for its reliability in such evaluations.

3. Results and discussion

The 9-(4-octyloxyphenyl)-2,7-divinylcarbazole (CrV-H) (Leclerc *et al.*, 2006) is the basic molecule, (Fig. 1), in which we substituted the vinyl hydrogen with heterocyclic groups (R). Figure 2 presents the different R groups studied by the DFT method to investigate the substitution effects on the electronic and optoelectronic properties of the CrV-R system (Jabha *et al.*, 2022).

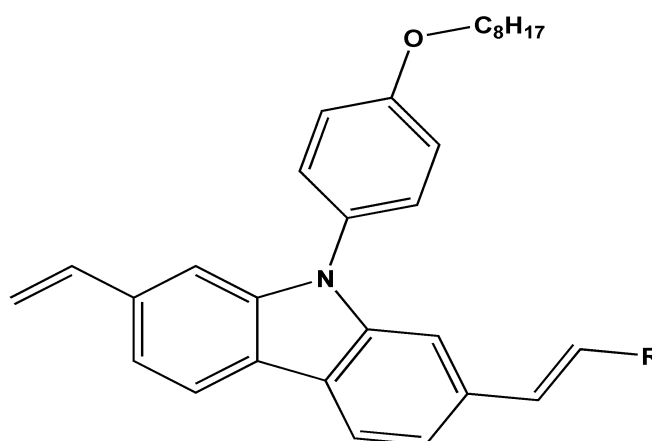


Figure 1. Structure of 9-(4-octyloxyphenyl)-2,7-divinylcarbazole (CrV-H); R=H.

Source: Adapted from Jabha *et al.* (2022).

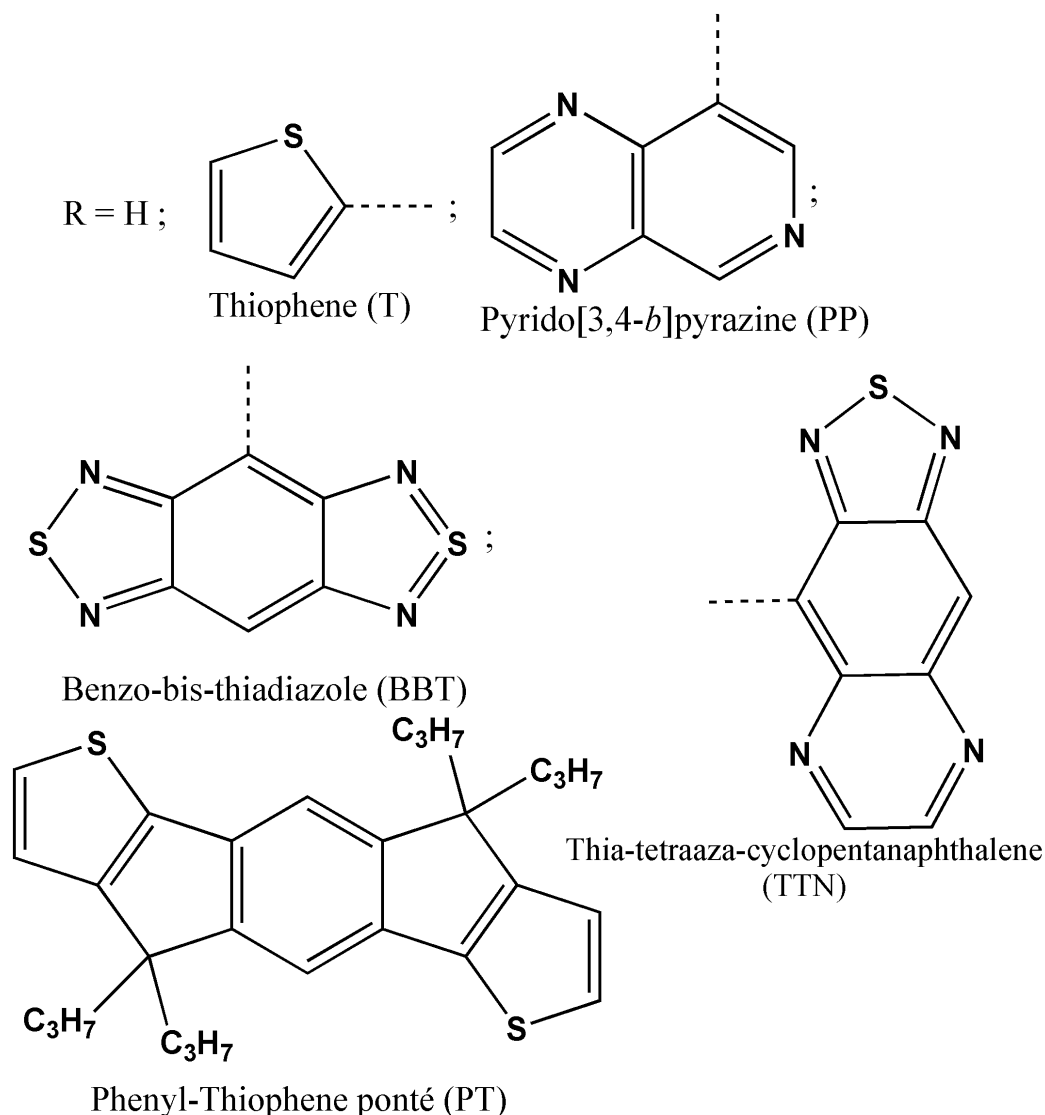


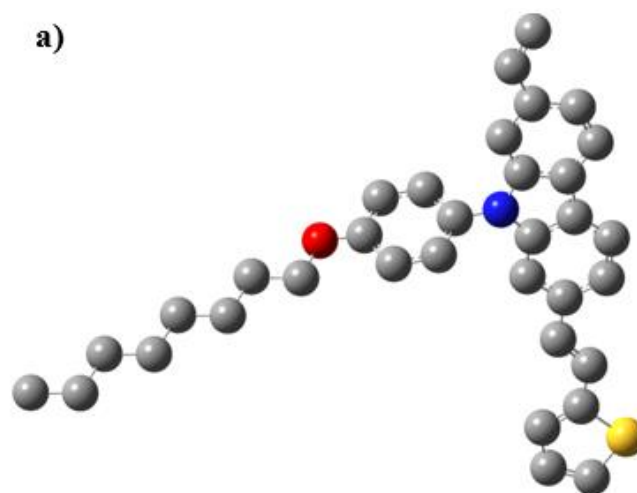
Figure 2. Schema and symbol of R groups.

Source: Adapted from Jabha *et al.* (2022).

3.1 Structural properties

All oligomers were optimized at the B3LYP/6-31G (d,p) level, and Fig. 3 represents the most stable conformations. For a credible study of the structural properties, extractions of the main structural parameters are necessary.

Based on the optimization of the systems by the DFT method at the level of the B3LYP functional under the atomic basis 6-31G (d,p), the geometrical study of the oligomers neutral and charged is completed by the calculation of the various structural parameters which depend on the geometry of the molecules, mainly the dihedral angles, the lengths of the primordial bonds between the base unit note CrV and the adjacent groups R (Fig. 4).



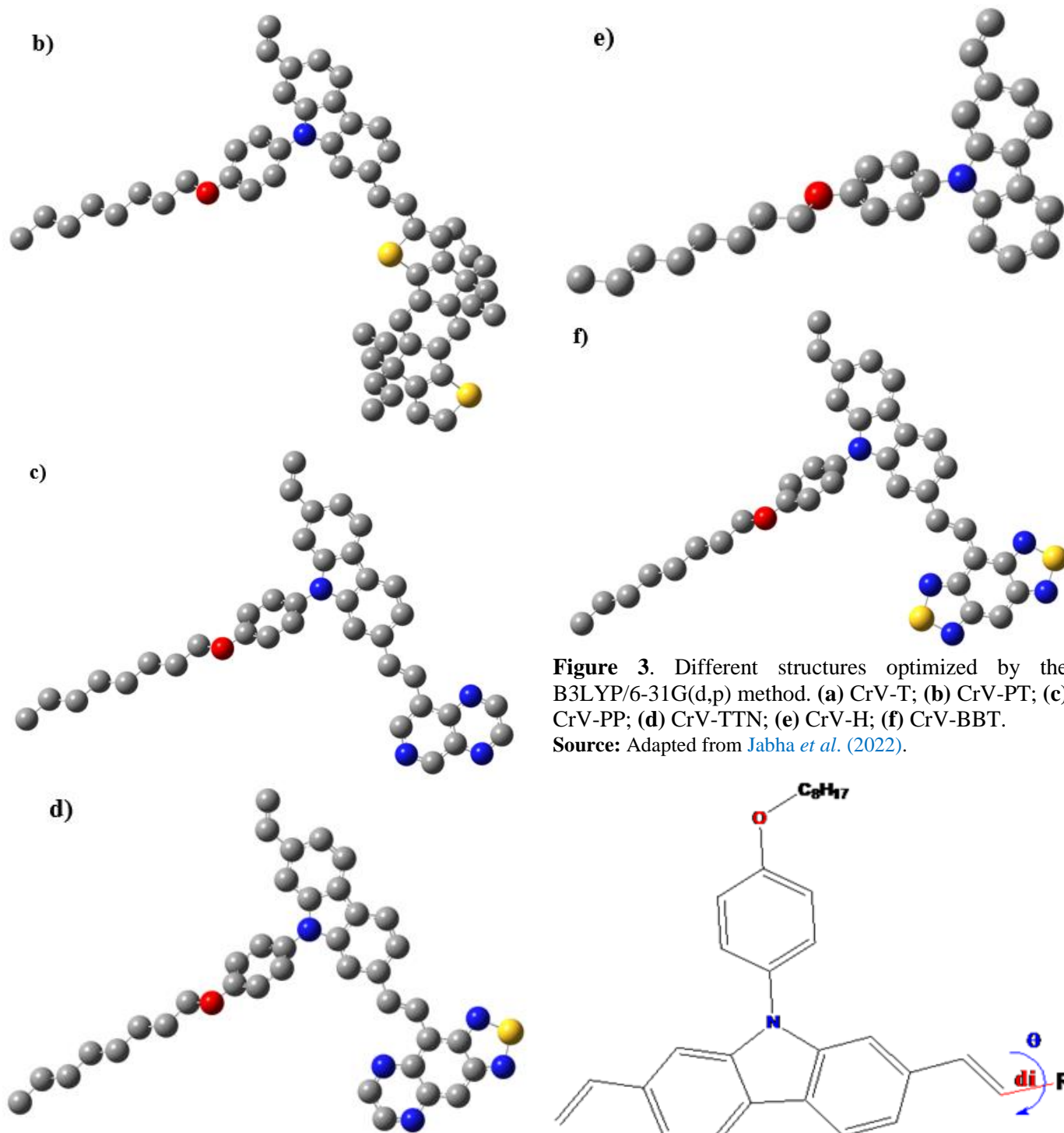


Figure 3. Different structures optimized by the B3LYP/6-31G(d,p) method. (a) CrV-T; (b) CrV-PT; (c) CrV-PP; (d) CrV-TTN; (e) CrV-H; (f) CrV-BBT.

Source: Adapted from Jabha *et al.* (2022).

In the theory of Marcus *et al.* (1989), the charge transfer integral is important for electron transfer because it is one of the factors for calculating the mobility of a material. The other factor is the reorganization energy. The higher the charge transfer

integral and the lower the reorganization energy, the higher the charge transfer rate and mobility. The charge transfer integral represents for exchange electrons between molecules, and strongly affected by the intermolecular and/or intramolecular (interatomic) distance, the shorter the distance, the stronger the orbital overlaps. Figures 5 and 6 illustrate the main structural parameters, especially the intramolecular distances and the dihedral angles of the studied systems.

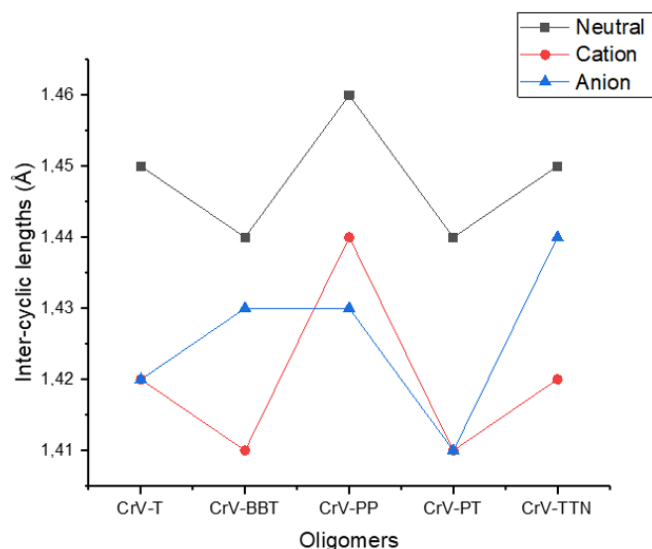


Figure 5. Inter-cyclic lengths (Å) obtained by the B3LYP/6-31G method (d,p).

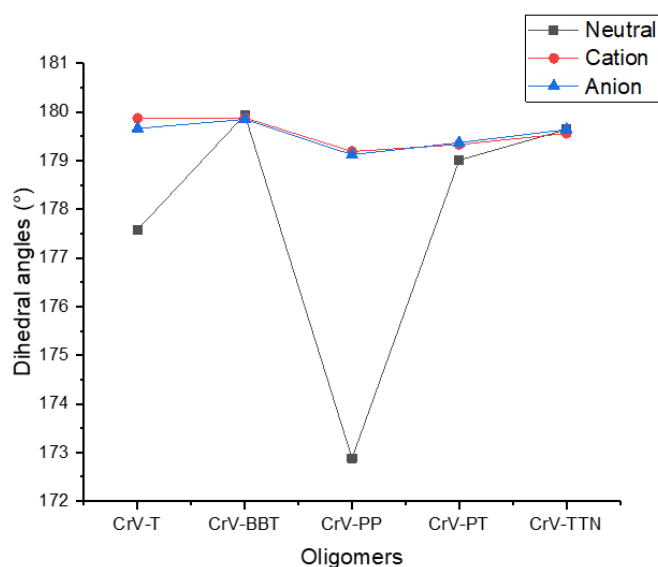


Figure 6. Dihedral angles obtained by the B3LYP/6-31G method (d,p).

The dihedral angles between the blocks of conjugated oligomers contribute significantly to the determination of the reorganization energy (λ_{tot}) and the charge

transport process. Thus, comparison of the dihedral angles between charged and neutral counterparts is crucial in the optoelectronic study of these oligomers. The values of the dihedral angles of the neutral and charged forms of all the studied oligomers (Fig. 6) are generally close to 180° , which would allow to conclude that the structures are nearly planar, especially the CrV-BBT based compounds, whose values are 179.94° , 179.88° , and 179.85° for the neutral, cationic and anionic structure, respectively. It is concluded that the neutral states tend towards flat and rigid structures.

In addition, a dramatic reduction of the bond length from the neutral to the anionic or cationic state was observed in Fig. 5. As well as the introduction of the groups containing nitrogen atoms at the terminal of the vinyl, would give more flatness to the molecular skeleton, so all the bonds are kept short of about 1.44 \AA between oligomer CrV-BBT and the vinyl unit. This shortening is attributed to the size and electronegativity of the nitrogen atom, as well as influencing the electron density distribution.

Dipole moments can explain charge transport properties. Thus, Fig. 7 indicates that the dipole moment of oligomers with planar structures is higher than that of other oligomers in the neutral state. This means that CrV-BBT and CrV-TTN, which show high dipole moments, indicate the presence of significant charge transfer.

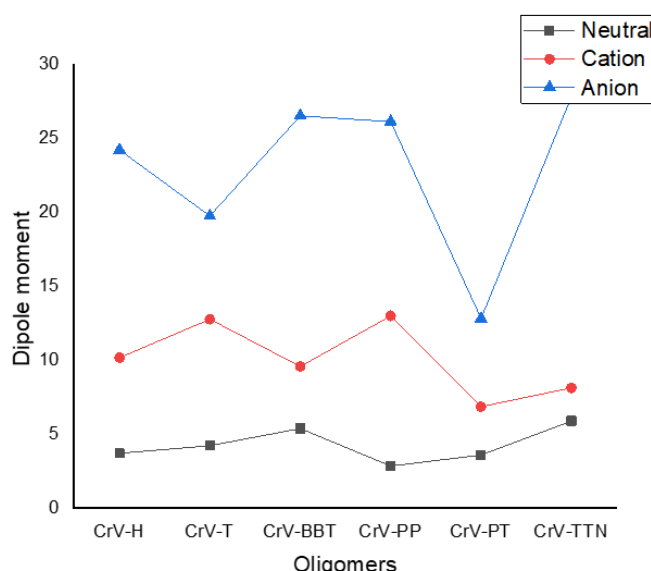


Figure 7. Dipole moment of oligomers in the neutral and charged state obtained by B3LYP/6-31G (d,p).

When the ground states are excited a sharp change in dipole moment takes place which would have a change in the degree of intermolecular charge transfer. The dipole moment of the oligomers in the neutral and charged states were calculated. The values are presented

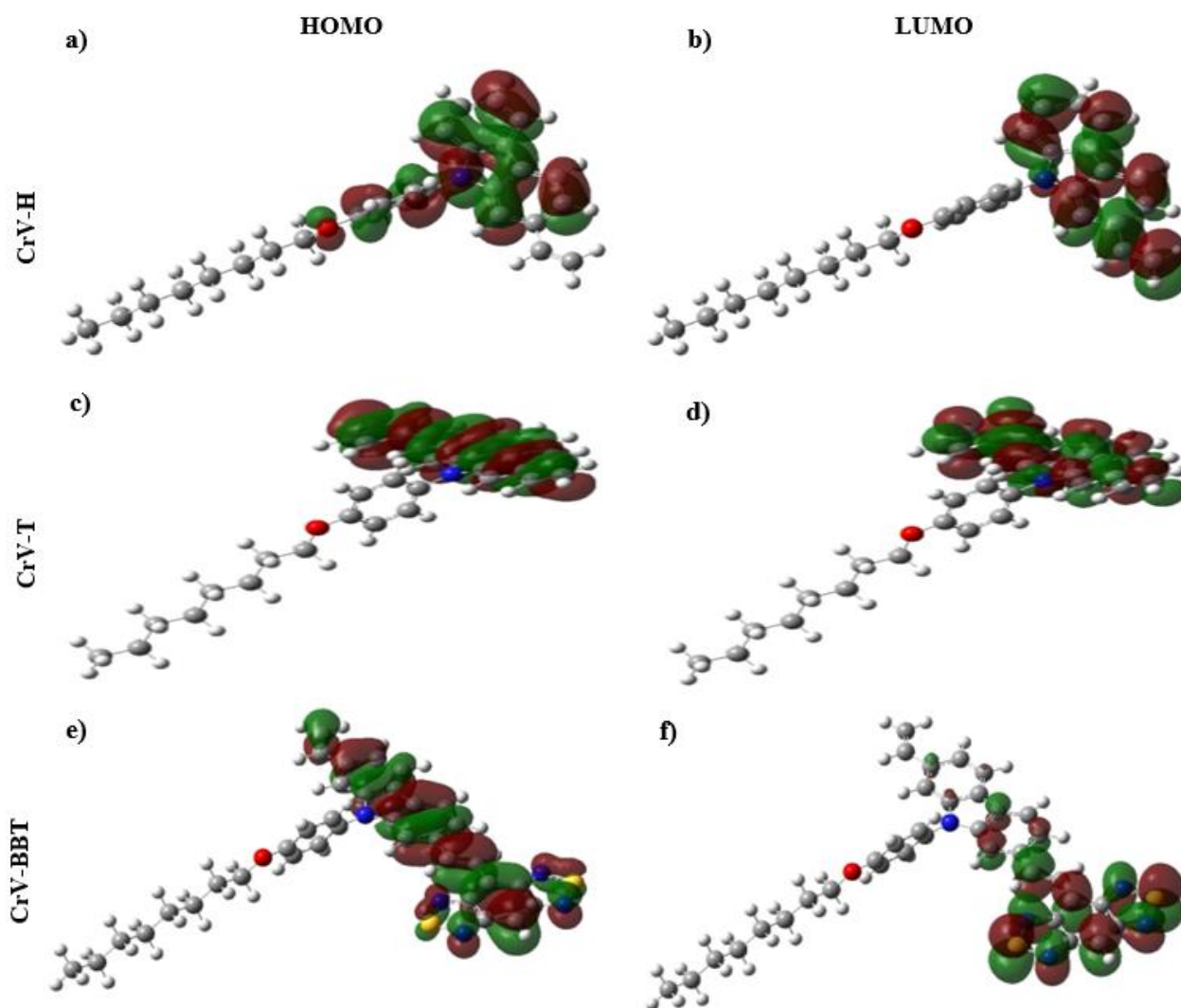
in Fig. 7. It is clear that CrV-BBT and CrV-TTN have the highest values of the dipole moments, which make their excited states highly polarized and facilitate the charge transport. These results agree with the reorganization energy. In the excited state, the negative charge tends to localize on the acceptor unit (A) while the positive charge tends to localize on the donor (D). The large separation between the negative and positive charges after excitation reduces the D-A binding energy which facilitates exciton dissociation and transport.

Conversely, the recombination rate is high and fast in compounds with low dipole moment, which indicates

that electrons and holes are more bound in compounds with high dipole moment value namely CrV-BBT and CrV-TTN than in other compounds with low dipole moment.

3.2 The boundary orbitals

Figure 8 presents the electronic density of the HOMO and LUMO orbitals of the studied oligomers, which give a qualitative and rational indication of the electronic properties of the studied oligomers.



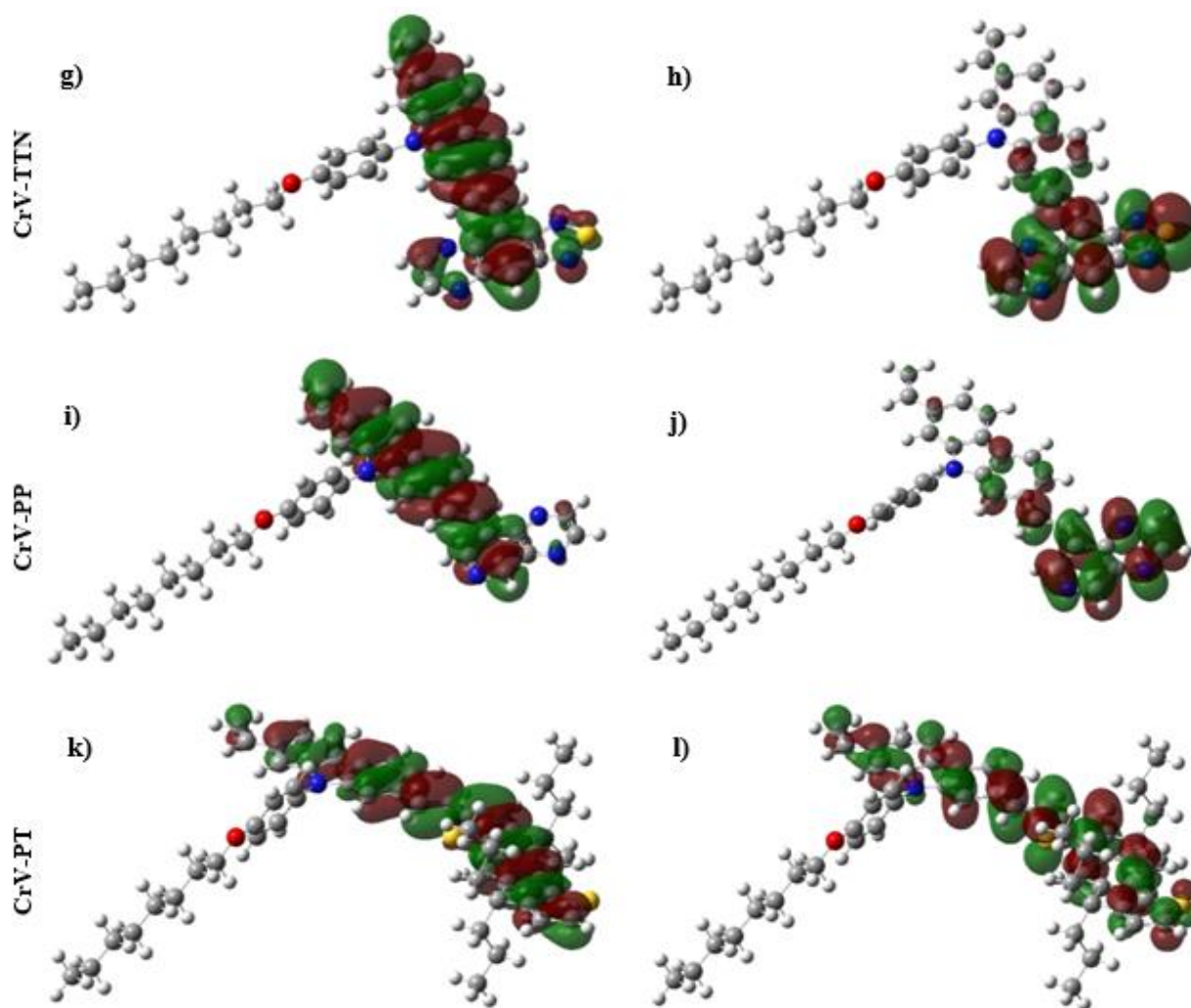


Figure 8. The contour plots of HOMO (a, c, e, g, i, k) and LUMO (b, d, f, h, j, l) orbitals of the studied oligomers by DFT/B3LYP 6-31G (d,p).

Source: Adapted from Jabha *et al.* (2022).

The propagation of the electron density appears very clearly in Fig. 8. The electron density of the LUMO is stronger around the nitrogenous group, on the other hand the systems related to groups possessing the thiophene are characterized by electron densities spread out on the whole carbon skeleton. Thus, at the HOMO level, the electron density is spread over the whole skeleton of the system. It is important to notice the absence of electron density on the chain linked to the carbazole nitrogen (N). Thus, this chain does not present any optical effect. It plays, perhaps, a role of solubilization and stability of the system.

3.3 Electronic properties

The electronic properties are of fundamental importance for the study of this type of molecules. Thus, the knowledge of the energy levels of the HOMO and

LUMO orbitals is fundamental for the study of the properties and feasibility of these oligomers to be used as base materials of the active layer of organic solar cells (Dufil *et al.*, 2018; Jabha *et al.*, 2018).

Figure 9 groups the energy levels of the systems optimized by the DFT method at the level of the B3LYP functional with the base 6-31G (d,p). The values of E_g show that the oligomers having a group different from hydrogen, has a semiconductor character, mainly the CrV-BBT by the smallest value of gap energy ($E_g = 1.75$). This value allows a good exciton creation, i.e., excitation of the electrons from the HOMO to the LUMO, thus the recombination rate decreases.

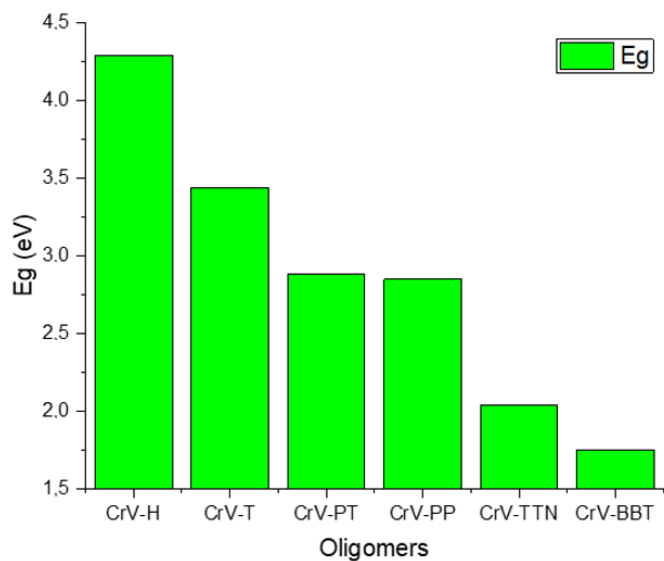


Figure 9. Gap energies (E_g) calculated by the DFT/B3LYP/6-31G(d,p) method.

Figure 10 shows that the LUMO values become lower when moving from CrV-H to CrV-BBT while the HOMO varies slightly and remains stable. The decrease in energy of the LUMO of CrV-BBT (donor) approaches that of the acceptor unit here Bis-PCBM as shown in Fig. 11.

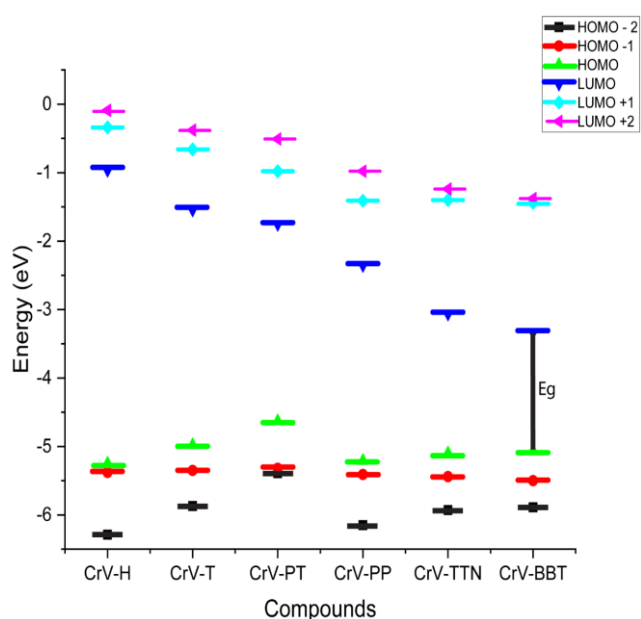


Figure 10. Evolution of energy levels with respect to the added R group.

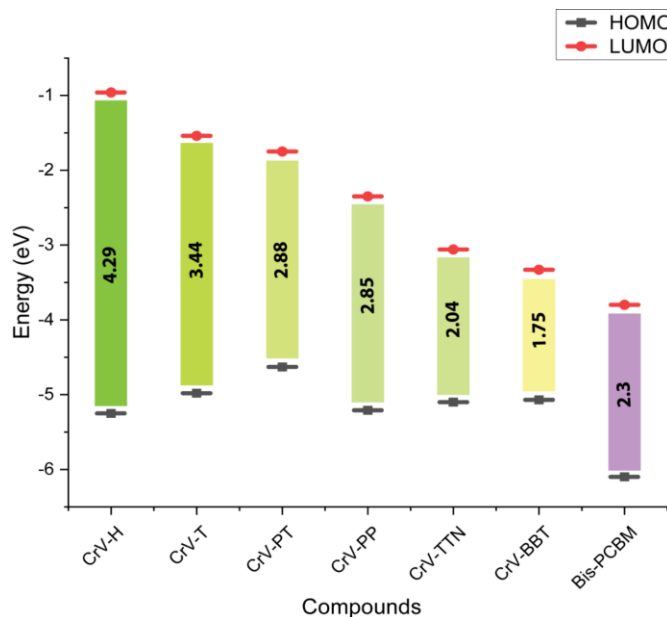


Figure 11. Position of the energy levels of oligomers (D) relative to oligomer A (Bis-PCBM) studied at the B3LYP level.

The HOMO energy of CrV-BBT is high compared to the other oligomers, with the lowest band gap energy indicating that the BBT groups in this molecule have significantly improved the properties of the hole carrier, thus the better stability of the LUMO level gives this oligomer a lower HOMO-LUMO gap. As a result, there should be higher carrier mobility and low kinetic stability. As well as the hole acceptor character accompanied by the decrease of the ionization potential (IP) increases. This phenomenon is accompanied by an increase in the conjugation length and the flatness of the structure. These findings are confirmed by the structural parameters (Figs. 5 and 6).

3.4 Reorganization energy

In general, conjugated organic oligomers and polymers undergo charge transfer phenomena via a jump-type mechanism. However, organic oligomers are mainly p-type. Therefore, in this case, the charge transfer process is essentially a hole transfer process. The hole transport in organic semiconductor materials between adjacent molecules depended on the reorganization energy. The rate of hole transfer mainly depends on the reorganization energy (λ) due to the geometric relaxation accompanying the charge transfer and the electronic coupling matrix element (V) between the two D-A semiconductors. However, V is related to the bandwidth in conventional solid-state descriptions (Camara, 2011;

Khoudir *et al.*, 2000; Koh *et al.*, 2008; Liu *et al.*, 2019; Provencher *et al.*, 2014).

The hole/electron transfer rate for higher temperature mainly depends on the reorganization energy (λ) due to geometric relaxation (Camara, 2011). The importance of λ in charge transfer processes has been widely studied in the context of Marcus *et al.* (1989) and Baran *et al.* (2017) theories.

Some reorganization energy studies have been performed on isolated molecules (Khoudir *et al.*, 2000; Marcus *et al.*, 1989). The reorganization energy is usually expressed as the sum of the internal and external contributions. The internal contribution consists of two terms related to the relaxation of the geometry from the neutral to the charged state and from the charged to the neutral state (Liu *et al.*, 2019). On the other hand, the external reorganization energy represents the effect of the external environment on the charge transfer. The calculated values of the external reorganization in pure organic phases are negligible in front of the internal reorganization energy values (Camara, 2011). Therefore, an estimate of the internal reorganization energy can give accurate and important information about the charge mobility in organic semiconductor materials (Koh *et al.*, 2008). Internal reorganization energies for hole (λ^+) and electron (λ^-) transfer, adiabatic electron affinity, and potential are also discussed.

The reorganization energy for electron (λ^-) and hole (λ^+) of the oligomers was predicted from energetic calculations at the B3LYP/6-31G(d,p) level based on the optimized neutral, cationic, and anionic geometries at the B3LYP/6-31G(d) level. Thus, the reorganization energies for λ^+ and λ^- transfer are determined by Eqs. 1 and 2 (Berlin *et al.*, 2003; Cheung *et al.*, 2010; Sun *et al.*, 2017):

$$\lambda^+ = [E^+(M) - E^+(M^+)] + [E(M^+) - E(M)] = IP_v - HEP \quad (1)$$

$$\lambda^- = [E^-(M) - E^-(M^-)] + [E(M^-) - E(M)] = EA_v - EEP \quad (2)$$

where $E(M)$, $E^-(M^-)$, and $E^+(M^+)$ are the energy of the neutral state, anion, and cation in their optimized structures, respectively. $E^+(M)$ is the total energy of the cation in the neutral geometry, $E(M^+)$ is the total energy of the neutral state in the cation geometry, $E^-(M)$ is the total energy of the anion in the neutral geometry, and $E(M^-)$ is the total energy of the neutral in anion geometry.

The values of the adiabatic (EAa) and vertical (EA_v) electron affinity and the adiabatic (IPa) and vertical (IP_v) ionization potential of the molecules are calculated from according to Eqs. 3–6:

- **Electronic affinity:**

$$EA_a = E(M) - E^-(M^-) \quad (3)$$

$$EA_v = E(M) - E^-(M) \quad (4)$$

- **Ionization potential:**

$$IP_a = E^+(M^+) - E(M) \quad (5)$$

$$IP_v = E^+(M) - E(M) \quad (6)$$

The electron extraction potential (EEP) and hole extraction potential (HEP) are calculated by the Eq. 7 and 8:

$$EEP = E(M^-) - E^-(M^-) \quad (7)$$

$$HEP = E^+(M^+) - E(M^+) \quad (8)$$

Figures 12–14 show several parameters related to the studied oligomers: the adiabatic ionization potential, vertical ionization potential and hole extraction potential (Fig. 12), adiabatic electron affinity, vertical electron affinity and electron extraction potential (Fig. 13) and oligomer hole/electron reorganization energy (Fig. 14).

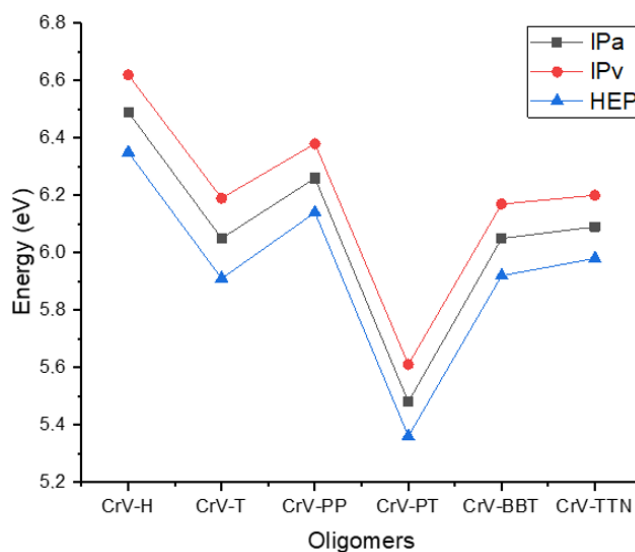


Figure 12. Adiabatic ionization potential (IPa), vertical ionization potential (IPv), hole extraction potential (HEP) of oligomers (eV) calculated by B3LYP/6-31G(d,p).

Figure 12 shows the lowest value of ionization potential carried by the CrV-PT molecule, which gives this molecule the character of an electron donor, as well as the values of the CrV-BBT molecule are also slightly small, i.e., this oligomer has an electron donor character.

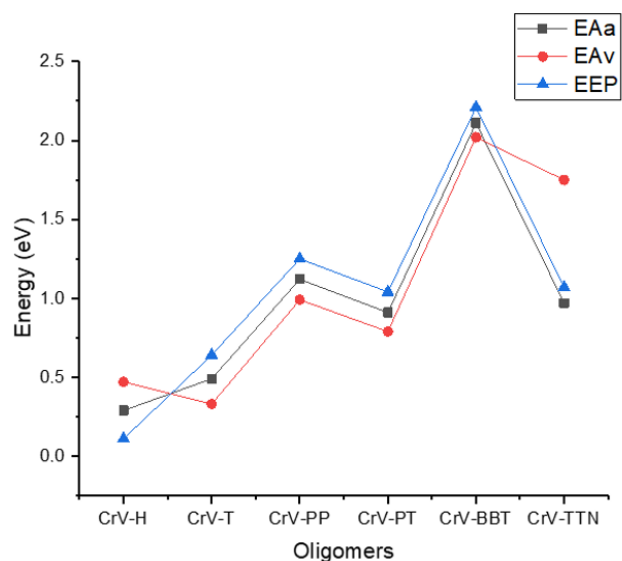


Figure 13. Adiabatic electron affinity (EAa), vertical electron affinity (EAν), electron extraction potential (EEP) of oligomers (eV) calculated by B3LYP/6-31G (d,p).

In Fig. 13, the higher value of electron affinity of the CrV-BBT molecule makes this molecule more stable and electron rich, which confirms that this molecule is a strong electron donor.

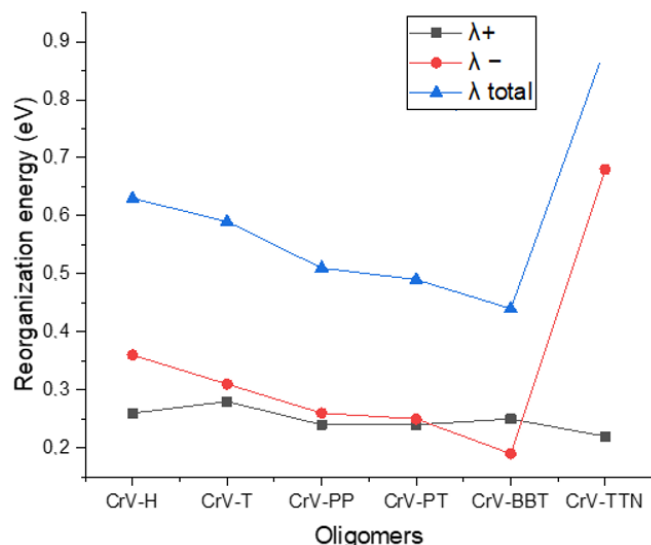


Figure 14. Oligomer hole/electron reorganization energy (eV) calculated by B3LYP/6-31G(d,p).

The oligomer with the BBT moiety has at the lowest value of λ reorganization energy (0.4431 eV). This indicates that the transport of electrons gives the materials based on this compound is favored, likewise this compound to the greatest value of EAa. Therefore, the greater the electron affinity the better the electron capture ability.

The IP values for the molecules with R groups are all lower than the value of the CrV-H oligomer, which can be attributed to the inductive and negative resonance effects of R groups.

From the values of EA and IP, it is believed that the systems with R groups can be used as a better organic semiconductor material, for D- π -A-A type devices.

As shown in Fig. 14, the λ^+ of all the studied oligomers was lower than their λ^- , except for the CrV-BBT oligomer, indicating a lower hole transfer cost than electron transfer cost with changes in molecular geometry during this charge transfer.

3.5 Excitation state calculation

The OSC (oligomer semi-conductor) coefficient of the studied molecules was obtained by DFT-B3LYP/6-31G (d,p) method and the maximum absorption wavelength (λ_{\max}), oscillator strengths (f) and excitation energy values Eex (eV) were obtained. The knowledge of the UV-visible absorptions of the studied oligomers contributes to their evaluation as potential materials in photovoltaic applications.

Taking the optimized structures at the level B3LYP/6-31G (d,p), we calculated the UV-Visible spectra of the oligomers at the level TD-DFT-BP86/6-31G(d,p) (Burke *et al.*, 1996).

3.5.1 Electronic transition, excitation energy and oscillation strength

The calculated electronic absorption spectra of the studied oligomers are shown in Fig. 15. Table 1 presents the λ_{\max} , oscillation strengths (f), and excitation energy values Eex (eV).

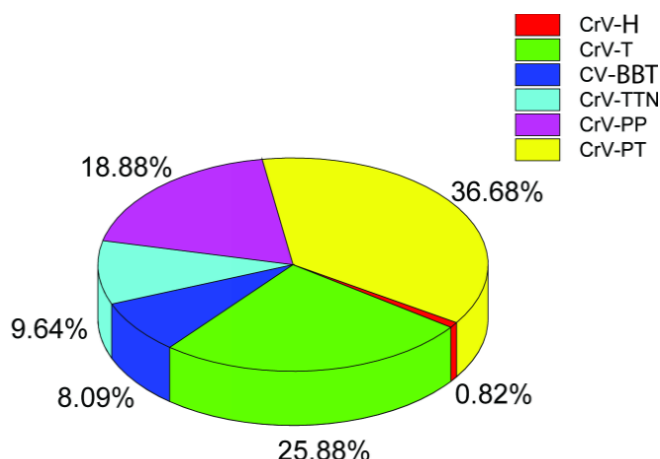


Figure 15. Percent of OSC of the molecules studied by the DFT-B3LYP/6-3G method (d,p).

Table 1. Electronic transition data obtained by TD-DFT-BP86/6-31G (d, p) calculation for all oligomers models.

Compound	DFT-BP86/6-31G (d,p)			λ_{\max} 'exp' (nm)*
	E _{ex} (eV)	f	λ_{\max} (nm)	
CrV-H	3.1182	0.0354	397.62	436
	3.5174	0.0051	352.49	
	3.6101	0.0006	343.44	
CrV-T	2.6142	0.0222	474.28	466
	2.8195	1.2246	439.74	
	3.0152	0.0061	411.20	
CV-BBT	1.1671	0.0027	1062.34	
	1.3509	0.3658	917.77	
	1.8504	0.0098	670.04	
CrV-TTN	1.2660	0.0028	979.37	
	1.4403	0.3549	860.84	
	2.0194	0.0317	613.96	
CrV-PP	1.7405	0.0036	712.35	
	1.8352	0.2258	675.59	
	2.5562	0.0051	485.02	
CrV-PT	2.2100	1.9128	561.02	
	2.3550	0.0102	526.47	
	2.4545	0.0408	505.13	

*Leclerc *et al.* (2006)

As presented in Tab. 1, the maximum absorption wavelength λ_{\max} of the reference oligomers (CrV-H, CrV-T) (397.62 and 474.28 nm) correlates perfectly with the available experimental values (of 436 and 466 nm, respectively) (Leclerc *et al.*, 2006), suggesting that TD-BP86/6-31G (d,p) was a suitable level to predict the evolution of the optoelectronic properties of the oligomers.

Molecules with gap energies below 2.87 eV absorb light in the visible range and CrV-TTN and CrV-BBT oligomers absorb in the infrared, so with low excitation

energy (1.16–1.26 eV) one can excite electrons from HOMO to LUMO.

Figure 15 shows that all the substituted molecules have an important proportion of OSC, compared to that of the basic oligomer (CrV-H), which implies an increase of the rate of excitation in these molecules, as well as the transfer of charge from the HOMO level to LUMO will be easier, with a low energy of excitation.

3.5.2 Absorption spectrum

Figure 16 shows UV-vis spectra of all oligomers calculated at DFT-B3LYP/6-31G(d,p) level.

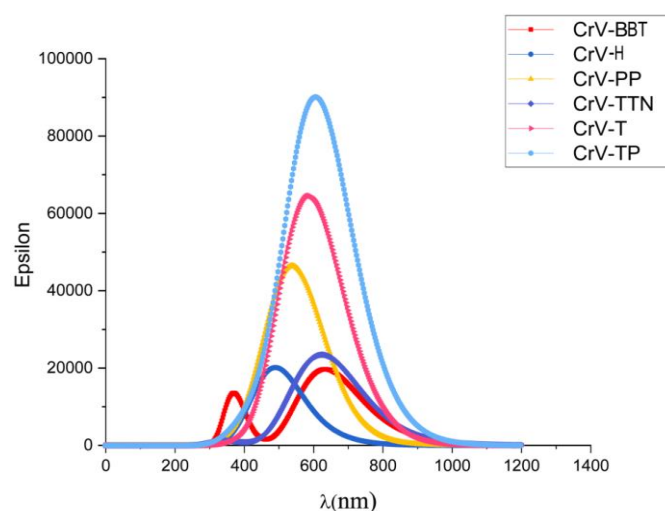


Figure 16. Data of UV-vis spectra of all oligomers calculated at DFT-B3LYP/6-31G(d,p) level.

Source: Adapted from Jabha *et al.* (2022).

All the studied oligomers have absorption spectral bands obtained by DFT method that can be attributed to the intermolecular transfer charge in the structures of these molecules. This indicates that these organic materials could absorb the maximum incident light radiation. The energy range for all the structures studied is generally in the visible and near infrared, however the CrV-BBT oligomer has a dual excitation band, one of which is broad like that of the reference oligomer (CrV-H).

3.5.3 Photovoltaic properties

Theoretically the open circuit voltage (V_{oc}) and α were calculated from Eqs. 9 and 10 (Jabha *et al.*, 2018):

$$V_{oc} = |E_{HOMO}(\text{Donor})| - |E_{LUMO}(\text{Acceptor})| - 0.3 \quad (9)$$

$$\alpha = |E_{\text{LUMO}}(\text{Acceptor})| - |E_{\text{LUMO}}(\text{Donor})| \quad (10)$$

The Voc is obtained when the current through the cell is zero. In the case of organic solar cells, the Voc is linearly dependent on the HOMO level of the donor material and the LUMO level of the acceptor material (Brabec *et al.*, 2001). In addition, charge losses at the material-electrode interfaces can also affect the Voc value (Günes *et al.*, 2007). Finally, this value decreases with temperature and varies little with light intensity (Oukachmih, 2003). The energy levels, Voc and α of the studied systems obtained by the DFT method are shown in Fig. 17.

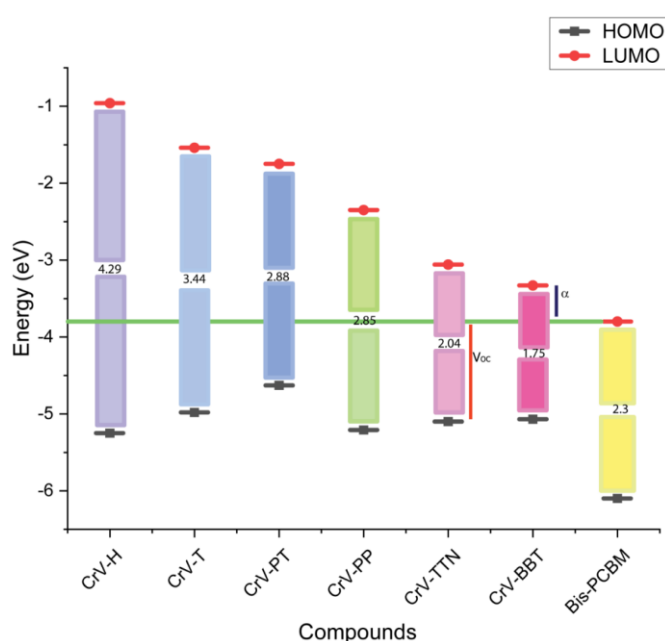


Figure 17. Illustration of the energy levels and Voc and α of the studied systems obtained by the DFT method.

The theoretical values of the Voc of the studied systems are ranked from 0.53 to 1.15 eV taking Bis-PCBM within the solar cell as the semiconductor acceptor. The CrV-PP, CrV-TTN, and CrV-BBT systems exhibit large open-circuit voltage values and low α values. Consequently, the lower the α values the greater the electron transfer from the donor LUMO levels to the acceptor LUMO levels.

4. Conclusions

In this work, the addition of R = T, PT, PP, TTN, and BBT radical to CrV to improve the electronic properties for uses in solar energy conversion devices was analyzed. Thus, the result of long conjugated chain structures, a decrease in gap energy and a high dipole

moment, has a considerable influence on a charge transfer which is the main link of this conversion.

However, this study shows that systems with a smaller energy gap, precisely for the oligomers CrV-BBT, CrV-TTN, are able to absorb sunlight in the visible range and the conversion into electricity is thus ensured. This property allows these systems (CrV-BBT, CrV-TTN) to be used to produce and manufacture electronic devices such as photovoltaic cells. Considering the EA – (electron affinity) and IP (ionization potential) values, it is believed that the systems with R = BBT, TTN groupings can be used as better organic semiconductor materials, for donor- π -acceptor-acceptor (D- π -A) type devices.

Authors' contribution

Conceptualization: Jabha, M.; Elalaoui, A.; Jarid A.

Data curation: Jabha, M.

Formal Analysis: Jabha, M.

Funding acquisition: Not applicable

Investigation: Jabha, M.; Mabrouk, E. H.

Methodology: Jabha, M.; Elalaoui, A.; Jarid, A.

Project administration: Elalaoui, A.

Resources: Not applicable

Software: Not applicable

Supervision: Elalaoui A.; Jarid A.

Validation: Elalaoui, A.; Jarid A.; Mabrouk, E. H.

Visualization: Elalaoui, A.; Jarid, A.

Writing – original draft: Jabha, M.

Writing – review & editing: Jabha, M.; Jarid, A.

Data availability statement

All data sets were generated and analyzed in the current study.

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