

Theoretical study of the geometric, electronic structure and properties of alternating donor-acceptor conjugated oligomers: Carbazole (Cbz)-based 3,4-ethylenedioxythiophene (Edot)

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ABSTRACT

In this work the geometrical and electronic properties of (Carbazole-3,4-Ethylenedioxythiophene) (Cbz-Edot) based alternating donor-acceptor conjugated oligomers were studied by the density functional theory (DFT) at the B3LYP level with 6-31G(d) basis set. The acceptors investigated include thiazole (Z), thiadiazole (D), thienopyrazine (TP), thienothiadiazole (TD), benzothiadiazole (BT) and thiadiazolothienopyrazine (TPD). A low band gap will be expected in polymers containing donor-acceptor (D-A) repeating units. In order to predict the band gaps for guiding the synthesis of novel materials with low band gaps, we apply quantum-chemical techniques to calculate the band gaps in several oligomers. The results have been compared with those of thiophene and 3,4-ethylenedioxythiophene polymers with donor-acceptor fragment. The lowest excitation energies (E_{ex}) and the maximal absorption wavelength (λ_{abs}) are studied using the time dependent density functional theory (TD-DFT), method. The electronic transitions of the absorption spectrum derived by TD-DFT method give useful structural and electronic information for designing novel conducting organic polymer materials. The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor-acceptor conjugated copolymers. Copyright © 2012 VBRI press.

Keywords: Carbazole; 3,4-ethylenedioxythiophene; theoretical electronic properties; low band gap; DFT; donor-acceptor.



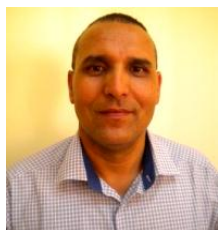
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Introduction

Recent years have seen a rapid increase of interest in solar cells from polymer materials [1]. Conjugated polymer systems with donor-acceptor architecture [2-4], including alternating copolymers, have been widely studied for applications as transparent conductors [2-4], light-emitting diodes [5, 6], thin film transistors [7, 8], and photovoltaic devices [9, 10]. The interaction between the electron donor (D) and acceptor (A) moieties in such an alternating donor-acceptor copolymer can result in the hybridization of the high-lying HOMO energy level of the donor and low-lying energy levels of the acceptor, leading to a relatively small band gap polymer semiconductor with novel electronic structure. Polymer for photovoltaic materials, such as poly(p-phenylene-vinylene) (PPV) [11-13] and polythiophene (PT) [14-16]. PT and its derivatives have been widely researched because of their environmental stability, large current density, lower band gap, and easy electrochemical preparations [17-19]. Of this family, poly(3,4-ethylenedioxythiophene) (PEDOT) showed a remarkable high stability, high electrical conductivity and a low optical band gap [20, 21], making this material to be a candidate for many industrial applications. As antistatic material, PEDOT is already being used industrially in a large scale. Several EDOT based donor-acceptor conjugated polymers with small band gaps have been reported [22-24]. On the other hand, most of recent papers are focused on the polyvinylcarbazole (PVK) [25-27], due to its important specific properties (photoconductivity, photoluminescence and hole transport properties). In fact PVK absorbs entirely in the UV region and as a consequence of its photoconductivity, its wide band gap. Conjugated polymers containing carbazole moieties either in the main or in the side chains have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency, and thermal stability. After the successful synthesis of N-alkyl-2,7-diodocarbazole [28], 2,7-functionalized carbazole became the promising candidate with more planar and well delocalized π -electron structure for the applications of organic photovoltaic [29]. However, a critical factor for block further improving the efficiency of the solar cells is that polymer photovoltaic materials mismatch the photon flux spectrum from the sun, which has a maximum flux around 700 nm. The use of low band gap polymers ($E_g < 1.8$ eV) is a viable method for better harvesting of the solar spectrum and increasing its efficiency [30-32]. The most efficient strategy has been applied to design molecules structure with alternate donor-acceptor (D-A) repeating units that are expected to have small gaps. In order to guide the synthesis of novel materials with low band gaps, quantum-chemical methods have been increasingly applied to predict the band gaps of conjugated polymers. These works provide a simple method for prediction of optoelectronic properties for the copolymers containing both electron donor and acceptor units.

In this paper, we report a theoretical study of the structural and optoelectronic properties of (Cbz-Edot)-based alternating donor-acceptor conjugated oligomers.

The molecular structures are shown in Fig. 1. Six copolymers were investigated, corresponding to six different electron acceptors. The electron acceptors can be grouped in the following structures: Thiazole (Z), Thiadiazole (D), Thienopyrazine (TP), Thienothiadiazole (TD), Benzothiadiazole (BT) and Thiadiazolothienopyrazine (TPD). The series of six acceptors provide a basis for a comprehensive understanding of the effects of the heteroatom, and fused rings on the geometric and electronic properties of the study copolymers. The geometric structures and electronic properties were investigated by the density functional theory (DFT) at the B3LYP level and 6-31G(d) basis set. The effects of the acceptor strength on the electronic properties, including the HOMO level, LUMO level, band gap and the maximal absorption wavelength (λ_{abs}) were also studied. In addition, we analyzed the effects of the electronic properties of the conjugated copolymers due to long-side chains.

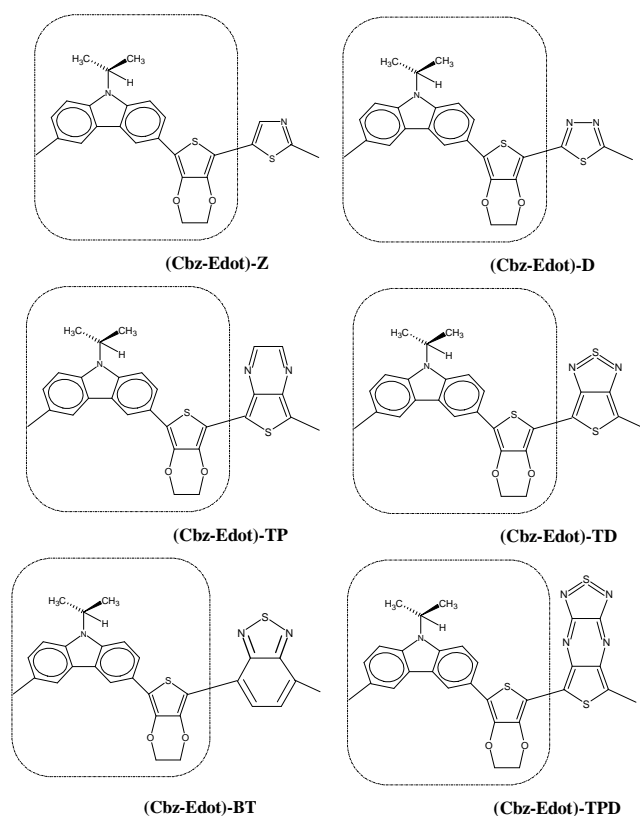


Fig. 1. Structures of the studied molecules.

Computational method

All the calculations were performed with the Gaussian 03 program [33]. The geometries of the oligomers (Cbz-Edot)-acceptor were optimized at B3LYP [34] level using 6-31G(d) basis set. DFT-B3LYP/6-31G(d) has been found to be an accurate formalism for calculating the geometrical, electronic structures and optical properties of many organic molecules [35-37]. The HOMO, LUMO and gap (HOMO-LUMO) energies were also deduced for the stable structures. Electronic transition energies of the

oligomers were obtained by using the time dependent density functional theory (TD-DFT) [38]. According to the calculated results, the UV-Vis absorption spectrum was simulated using a Gaussian convolution program with the model described by S.I. Gorelsky [39, 40].

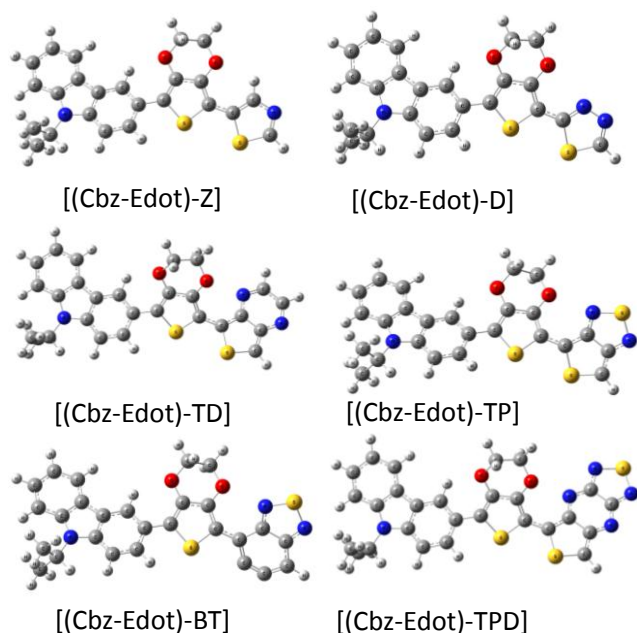


Fig. 2. Optimized Molecular structures obtained by B3LYP/6-31G(d) of the studied compounds.

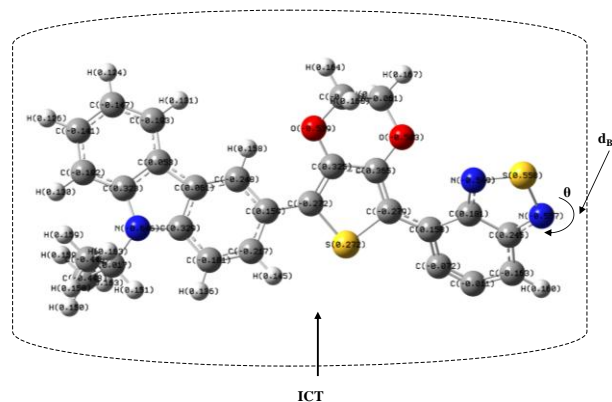


Fig. 3. Optimum geometry (torsional angle θ in ($^{\circ}$) and bridge length d_B in (\AA) and Mulliken charge distribution ICT (e) of the model compound [(Cbz-Edot)-BT].

Results and discussion

Geometrical parameters and property analyzed of the studied compounds

The optimized structures of the all molecules obtained with the B3LYP/6-31G(d) level, are presented in **Fig. 2**. **Fig. 3** shows the definition of torsional angle (θ), intramolecular charge transfer (ICT) and bridge length (d_B), using compound [Cbz-Edot)-BT] as an example. Torsional angle is the deviation from coplanarity between the donor and acceptor and the (d_B) is the bond length

between the donor and acceptor. Intramolecular charge transfer (ICT) was calculated as the average of the summation of Mulliken charge distribution of the donor and acceptor. For example, the ICT is a summation of all charges for the (Cbz-Edot) unit (0.049 e), as shown in **Fig. 2**. The torsional angle (θ), intramolecular charge transfers (ICT) and bridge length are listed in **Table 1**. As shown in **Table 1**, the almost model compounds have a syn-gauche conformation ($\theta \approx 40^{\circ}$) calculated from DFT/B3LYP/6-31G(d) level, the large torsional angle of the (Cbz-Edot)-TP, (Cbz-Edot)-BT, (Cbz-Edot)-TD and (Cbz-Edot)-TPD model compounds suggest that strong steric hindrance exist between the donor and acceptor moieties. The fact that dihedral angles of (Cbz-Edot)-Z (4.68°) and (Cbz-Edot)-D (3.22°) are the smallest of all the model compounds indicates that thiazole and thiadiazole rings are coplanar between (Cbz-Edot) unit. The bond length between the donor and acceptor (d_B) decreases with the acceptor strengths: (Cbz-Edot)-TPD < (Cbz-Edot)-D < (Cbz-Edot)-TP < Cbz-Edot)-BT < (Cbz-Edot)₂. The order on the ICT obtained from the Mulliken charge distribution is: (Cbz-Edot)-TPD > (Cbz-Edot)-D > (Cbz-Edot)-TD > (Cbz-Edot)-TP > (Cbz-Edot)-Z > (Cbz-Edot)-BT > (Cbz-Edot)₂. The trend of the intramolecular charge transfer is similar to that of the acceptor strength except in the case of (Cbz-Edot)-D. The unusually large ICT of (Cbz-Edot)-D backbone is probably a result of the two adjacent imine nitrogen atoms with high electronegativity in the thiadiazole ring, which could localize electrons while the adjacent (Cbz-Edot) localize a hole. Furthermore, the intramolecular charge transfer significantly enhances the π -electron delocalization and thus decreases the d_B of the model compounds. The same observations are obtained for (Edot-TPD) and (Edot-TD) [41].

Table 1. The optimum geometry results (θ , d_B and ICT) for model compounds calculated by B3LYP/6-31G(d) level.

Model compound	$\theta(^{\circ})$	$d_B(\text{\AA})$	ICT(e)
(Cbz-Edot) ₂	25.18	1.464	0.000
(Cbz-Edot)-Z	4.68	1.443	0.053
(Cbz-Edot)-D	3.22	1.441	0.137
(Cbz-Edot)-TP	42.72	1.443	0.070
(Cbz-Edot)-BT	33.29	1.444	0.049
(Cbz-Edot)-TD	34.18	1.436	0.092
(Cbz-Edot)-TPD	40.01	1.436	0.139

The dipole moments of (Cbz-Edot)-Z, (Cbz-Edot)-D, (Cbz-Edot)-TP, (Cbz-Edot)-BT, (Cbz-Edot)-TD, and (Cbz-Edot)-TPD are 4.22, 5.54, 3.13, 4.40, 4.21 and 6.11 Debye, respectively, indicating that the insertion of the thiadiazole ring of the acceptor moiety enhances the polar molecules. The values of quadrupole moments for the model compounds are listed in Table 2, where the average of the diagonal quadrupole moment tensor elements Q_{ii} and unique quadrupole moment Q are defined as follows:

$$Q_{ii} = \frac{(Q_{xx} + Q_{yy} + Q_{zz})}{3} \quad (1)$$

$$Q = Q_{xx} - Q_{yy}$$

As shown in **Table 2**, all the diagonal elements of the quadrupole moment tensor for the model compounds are negative, indicating that the negative charge distribution is farther removed from the molecular center of the nuclear charges. The values of the off-diagonal elements Q_{xz} and Q_{yz} of the molecules are relatively lower, which can be attributed to its symmetric plane nearly perpendicular to the z-axis. It is noteworthy that the dipole and quadrupole moment values of (Cbz-Edot)-TPD and (Cbz-Edot)-TD are larger than those of (Cbz-Edot)-Z, (Cbz-Edot)-D and (Cbz-Edot)-TP, revealing that the thiadiazole group is indeed a stronger electron donor. The same observations are obtained for diphenylaniline and 4-diphenylamino-diphenylaniline as donor moiety [42].

Table 2. Quadrupole moments (in Debye.Å) of the model compounds, calculated by B3LYP/6-31G(d) method.

Model compound	Q_{xx}	Q_{yy}	Q_{zz}	Q_{xy}	Q_{xz}	Q_{yz}	Q_i	Q
(Cbz-Edot)-Z	-189.21	-157.04	-190.33	13.26	-1.48	0.36	-178.86	-32.17
(Cbz-Edot)-D	-193.23	-156.00	-188.73	3.41	-2.92	0.21	-179.32	-37.23
(Cbz-Edot)-TP	-192.65	-180.59	-209.86	-20.60	-0.22	0.16	-194.37	-12.06
(Cbz-Edot)-BT	-199.11	-181.69	-210.27	17.75	-3.88	-2.62	-197.02	-17.42
(Cbz-Edot)-TD	-205.03	-181.50	-211.48	15.32	-5.65	-1.27	-199.34	-23.53
(Cbz-Edot)-TPD	-229.13	-205.63	-229.84	17.60	7.91	5.49	-221.53	-23.50

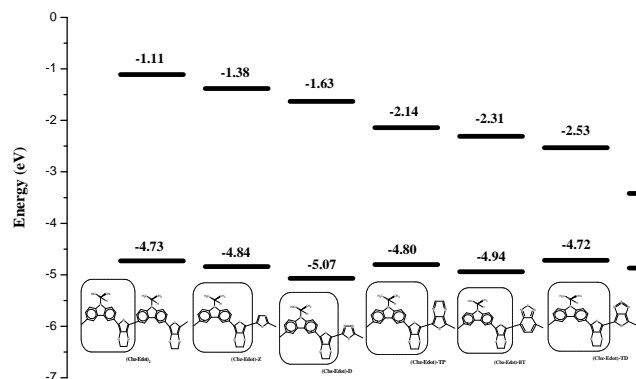


Fig. 4. HOMO and LUMO energy levels of the model compounds by DFT/B3LYP/6-31G(d) basis set.

Table 3. The theoretical electronic properties (HOMO, LUMO and E_g) of model compounds calculated by B3LYP/6-31G(d).

Model compound	HOMO(eV)	LUMO(eV)	E_g (eV)
(Cbz-Edot) ₂	-4.73	-1.11	3.62
(Cbz-Edot)-Z	-4.84	-1.38	3.46
(Cbz-Edot)-D	-5.07	-1.63	3.44
(Cbz-Edot)-TP	-4.80	-2.14	2.66
(Cbz-Edot)-BT	-4.94	-2.31	2.63
(Cbz-Edot)-TD	-4.72	-2.53	2.19
(Cbz-Edot)-TPD	-4.87	-3.42	1.45

Calculation of the HOMO, LUMO and band gaps energies

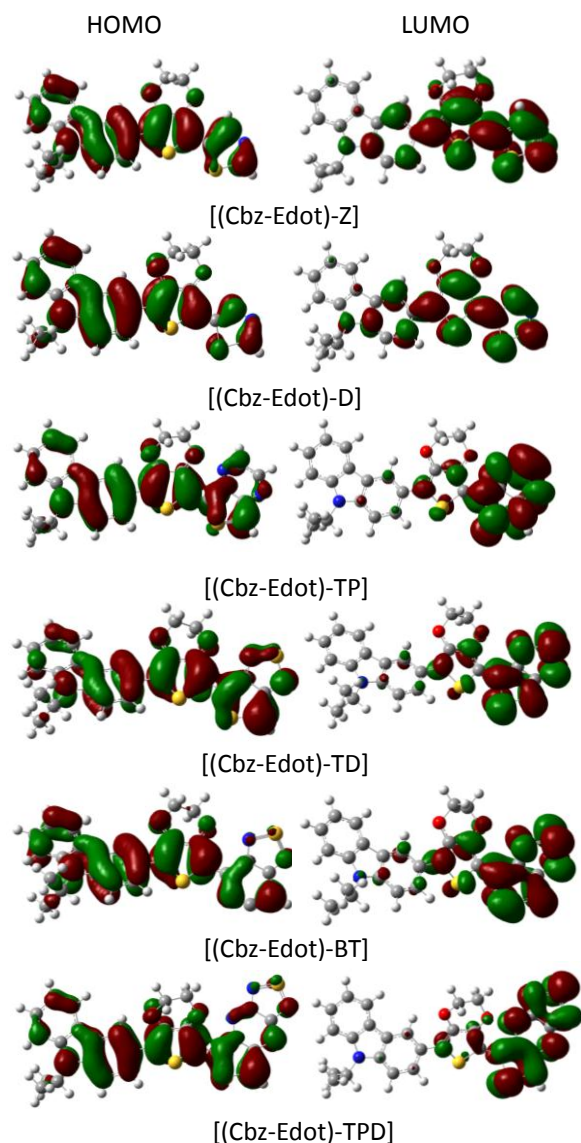
The band gaps in conjugated polymers are governed by their chemical structures. All HOMO, LUMO and band gaps energies were obtained by DFT (B3LYP/6-31G(d)) calculations with the Gaussian-03 program. **Fig. 4** shows the HOMO and LUMO energy levels of the model compounds calculated from the 6-31G(d) basis set. The calculated HOMO level, LUMO level, and E_g are summarized in **Table 3**. A significant deviation is observed for the LUMO energy level of the model compounds fused with the thiadiazole ring. As shown in the **Fig. 4**, the LUMO energy level of model compounds decreases in the order: (Cbz-Edot)₂ > (Cbz-Edot)-Z > (Cbz-Edot)-D > (Cbz-Edot)-TP > (Cbz-Edot)-BT > (Cbz-Edot)-TD > (Cbz-Edot)-TPD, which is the same order as the acceptor strength. However, the HOMO energy level of these compounds is almost unchanged, being -4.72 to -5.07 eV. We note that the LUMO levels of the Z, D, TP, TD, and TPD moieties obtained from the 6-31G level are -1.049, -1.669, -2.518, -3.415, and -4.136 eV, respectively [41].

The calculated band gap E_g of the studied model compounds increases in the following order (Cbz-Edot)-TPD < (Cbz-Edot)-TD < (Cbz-Edot)-BT < (Cbz-Edot)-TP < (Cbz-Edot)-D < (Cbz-Edot)-Z < (Cbz-Edot)₂. The much lower E_g of (Cbz-Edot)-BT, (Cbz-Edot)-TD and (Cbz-Edot)-TPD compared to that of (Cbz-Edot)₂ indicates a significant effect of intramolecular charge transfer. However, the E_g values of (Cbz-Edot)-Z and (Cbz-Edot)-D are smaller than that of (Cbz-Edot)₂. In both (Cbz-Edot)-Z and (Cbz-Edot)-D, the lowering of the LUMO level by the presence of the acceptor moiety is more than compensated by the lowering of the HOMO level. A likely origin of this effect is that the backbone nitrogen atom localizes electrons and breaks the symmetry of the structures with consequent widening of the band gap of the two model compounds [43]. When we compare the gap energy of (Cbz-Edot)-TP (2.66 eV) with the reported experimental E_g of (Edot-TP) (2.72 eV) [24], we conclude that the introduction of carbazole in the structure influence considerably the electronic properties of the copolymers.

The frontier molecular orbital (MO) contribution is very important in determining the charge-separated states of the model oligomers. To create an efficient charge-separated state, the highest occupied MO (HOMO) must be localized on the extended donor moiety and the lowest unoccupied MO (LUMO) on the acceptor moiety. The isodensity plots of the model compounds are shown in **Fig. 5**. The HOMO state density is distributed entirely over the conjugated molecules, while the electron density of LUMO is mainly localized on the acceptors moiety. It is interesting to note that a significant contribution to the LUMO of the electron accepting groups (Cbz-Edot)-BT, (Cbz-Edot)-TD, and (Cbz-Edot)-TPD. This result implies that the decrease in the bandgap of these compounds is due to the introduction of the thiadiazole segment, in accordance with the change in the calculated absorption spectra.

Table 4. Electronic transition data obtained by the TD/DFT-B3LYP/6-31G(d) calculation for all model compounds.

Electronic transitions	λ_{abs} (nm)	E_{ex} (eV)	O.S	MO/character	Coeff
(Cbz-Edot)-Z					
$S_0 \rightarrow S_1$	383.71	3.23	0.8926	HOMO \rightarrow LUMO	0.65
$S_0 \rightarrow S_2$	350.11	3.54	0.0171	HOMO \rightarrow LUMO+1	0.65
$S_0 \rightarrow S_3$	322.97	3.84	0.0073	HOMO \rightarrow LUMO+2	0.65
(Cbz-Edot)-D					
$S_0 \rightarrow S_1$	394.21	3.15	0.8209	HOMO \rightarrow LUMO	0.65
$S_0 \rightarrow S_2$	344.10	3.60	0.0197	HOMO \rightarrow LUMO+1	0.52
$S_0 \rightarrow S_3$	325.44	3.81	0.0478	HOMO-1 \rightarrow LUMO	0.53
(Cbz-Edot)-TP					
$S_0 \rightarrow S_1$	490.05	2.54	0.1227	HOMO \rightarrow LUMO	0.68
$S_0 \rightarrow S_2$	396.18	3.13	0.0021	HOMO-4 \rightarrow LUMO	0.66
$S_0 \rightarrow S_3$	373.05	3.32	0.0069	HOMO-1 \rightarrow LUMO	0.56
(Cbz-Edot)-BT					
$S_0 \rightarrow S_1$	530.47	2.34	0.4232	HOMO \rightarrow LUMO	0.65
$S_0 \rightarrow S_2$	598.80	2.07	0.0004	HOMO \rightarrow LUMO+1	0.66
$S_0 \rightarrow S_3$	415.97	2.98	0.0038	HOMO-1 \rightarrow LUMO+1	0.40
(Cbz-Edot)-TD					
$S_0 \rightarrow S_1$	646.18	1.92	0.2932	HOMO \rightarrow LUMO	0.63
$S_0 \rightarrow S_2$	467.91	2.65	0.0093	HOMO-1 \rightarrow LUMO	0.65
$S_0 \rightarrow S_3$	427.87	2.90	0.0021	HOMO-2 \rightarrow LUMO	0.56
(Cbz-Edot)-TPD					
$S_0 \rightarrow S_1$	1070.10	1.16	0.1602	HOMO \rightarrow LUMO	0.61
$S_0 \rightarrow S_2$	659.53	1.88	0.0085	HOMO-1 \rightarrow LUMO	0.65
$S_0 \rightarrow S_3$	585.57	2.12	0.0013	HOMO-2 \rightarrow LUMO	0.53

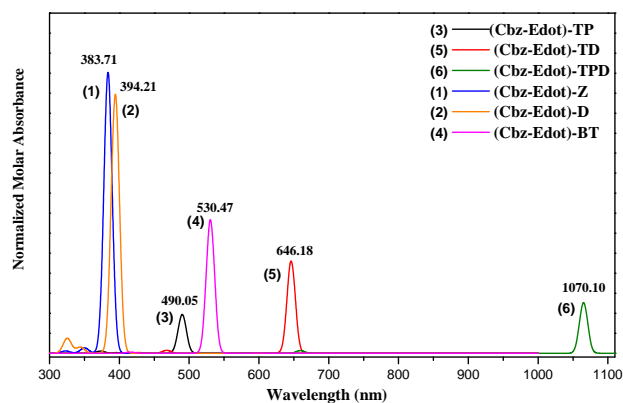
**Fig. 5.** Isodensity plots of the frontier orbitals of the model oligomers obtained by B3LYP/6-31G(d).

Absorption properties

How the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. On the basis of the optimized ground-state structures, we present in **Table 4** the vertical excitation energy E_{ex} (eV), calculated absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of the oligomers (Cbz-Edot)-Z, (Cbz-Edot)-D, (Cbz-Edot)-TP, (Cbz-Edot)-TD, (Cbz-Edot)-BT and (Cbz-Edot)-TPD. These values are calculated by TD-DFT method starting with optimized geometry obtained by B3LYP/6-31G(d) level. The calculated UV-Vis absorption of the studied compounds was obtained of the Gaussian shaped bands using the formula [39, 40]:

$$\varepsilon(\omega) = 2.174 * 10^8 \sum_i \frac{f_i}{\Delta_{1/2}} \exp\left(-2.773 \frac{(\omega - \omega_i)^2}{\Delta_{1/2}^2}\right) \quad (2)$$

where ε is the molar absorbance ($\text{mol}^{-1} \text{L cm}^{-1}$), ω is the wavelength (nm), $\Delta_{1/2}$ is the half-bandwidths (nm) and f is the oscillator strengths (O.S).

**Fig. 6.** Simulated absorption spectra of the model compounds: (1) (Cbz-Edot)-Z, (2) (Cbz-Edot)-D, (3) (Cbz-Edot)-TP, (4) (Cbz-Edot)-BT, (5) (Cbz-Edot)-TD and (6) (Cbz-Edot)-TPD, obtained by TD-DFT level.

The simulated absorption spectra of the studied model compounds (the half-wave width is 12 nm) are shown in **Fig. 6**. The calculated wavelength λ_{abs} of the studied compounds decreases in the following order (Cbz-Edot)-TPD > (Cbz-Edot)-TD > (Cbz-Edot)-BT > (Cbz-Edot)-TP > (Cbz-Edot)-D > (Cbz-Edot)-Z, which is the same order of the reduction of the acceptor strength. The largest oscillator strengths (O.S) originate from $S_0 \rightarrow S_1$ electronic transition. Excitation to the S_1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. As in the case of the oscillator strengths, the absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increase of the conjugation lengths. The bands signed at 383.71, 394.21, 490.05, 530.47, 646.18 and 1070.10 nm corresponds to the HOMO-LUMO transition and is of ICT (intramolecular charge transfer) character thus possessing high transition intensity. In comparison with the maximum absorption of (Cbz-Edot)-Z (383.71 nm), there

is a difference about 687 nm for (Cbz-Edot)-TPD (1070.10 nm), which is attributed to the stronger ICT.

Effects of the long-side chains on the electronic properties

Table 5 lists the calculated HOMO, LUMO and gap (E_g) energies of the alternating donor-acceptor conjugated copolymers ($n = 3$), obtained by DFT (B3LYP/6-31G(d)). As shown in **Fig. 7**, the HOMO and LUMO energy levels of polymers [(Cbz-Edot)-Z]₃, [(Cbz-Edot)-D]₃, [(Cbz-Edot)-TP]₃, [(Cbz-Edot)-BT]₃, [(Cbz-Edot)-TD]₃ and [(Cbz-Edot)-TPD]₃ show a clear trend with that of the acceptor strength and chain length. The order of the calculated E_g (eV) (**Table 5**) is: [(Cbz-Edot)-TPD]₃ (1.00) < [(Cbz-Edot)-TD]₃ (1.72) < [(Cbz-Edot)-BT]₃ (2.27) < [(Cbz-Edot)-TP]₃ (2.28) < [(Cbz-Edot)-Z]₃ (2.96) < [(Cbz-Edot)-D]₃ (3.07). The calculated band gap E_g of the studied molecules decreases with the chain length and the acceptor strength according to the reduction in the electronic delocalization π . The small E_g values of [(Cbz-Edot)-TPD]₃ and [(Cbz-Edot)-TD]₃ is due to the large intramolecular charge transfer and may have potential applications as photovoltaic materials since their absorption spectra could extend to the near-infrared region. The large E_g value of [(Cbz-Edot)-D]₃ is due to the backbone nitrogen atom localizes electrons.

Table 5. The HOMO, LUMO and gap energies E_g obtained by B3LYP/6-31G(d) calculation for all polymers.

Polymer E_g (eV)	HOMO(eV)	LUMO(eV)	E_g (eV)
[(Cbz-Edot)-Z] ₃	-4.53	-1.57	2.96
[(Cbz-Edot)-D] ₃	-4.87	-1.80	3.07
[(Cbz-Edot)-TP] ₃	-4.46	-2.18	2.28
[(Cbz-Edot)-BT] ₃	-4.63	-2.36	2.27
[(Cbz-Edot)-TD] ₃	-4.34	-2.62	1.72
[(Cbz-Edot)-TPD] ₃	-4.48	-3.48	1.00

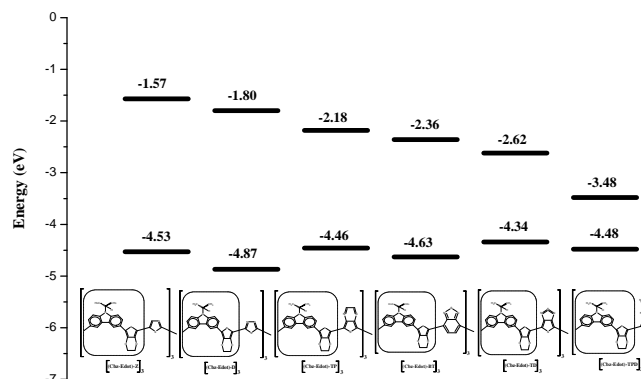


Fig. 7. HOMO and LUMO energy levels by DFT/B3LYP/6-31G(d) basis set of alternating donor-acceptor conjugated copolymers ($n = 3$).

Conclusion

In order to guide the synthesis of novel materials with low band gaps, the geometric, electronic structures and

properties of (Cbz-Edot) based alternating donor-acceptor conjugated oligomers have been computed using 6-31G(d) basis set at density functional B3LYP level. The UV-Vis absorption spectra have been simulated by TD-DFT calculations. The calculated geometries indicate that the strong conjugate effects are formed in (Cbz-Edot)-TPD, (Cbz-Edot)-TD, (Cbz-Edot)-BT and (Cbz-Edot)-TP, which is beneficial to the intramolecular charge transfer. The HOMO level, LUMO level, and band gap of the model compounds were well controlled by the acceptor strength. (Cbz-Edot)-TPD and (Cbz-Edot)-TD have E_g smaller than 1.45 and 2.19 eV respectively and large intramolecular charge transfer 0.139 and 0.092 e. Hence, these two molecules could have potential applications in transparent conductors and photovoltaic devices. The substitution of nitrogen atoms on the backbone of (Cbz-Edot)-Z, and (Cbz-Edot)-D lowers the LUMO energy but results in the large band gaps due to electron localization. The calculated absorption bands are assigned to the HOMO-LUMO transition. The calculated band gap E_g of the studied polymers decreases with the chain length and the acceptor strength, [(Cbz-Edot)-TD]₃ and [(Cbz-Edot)-TPD]₃ have the smaller gap energy 1.72 and 1.00 eV respectively. The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor-acceptor conjugated copolymers. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for organic solar cells.

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