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The Effect of Substitution and Polymerization of 2,7-Divinylcarbazole-benzo-bis-thiadiazole on Optoelectronic Properties: A DFT Study

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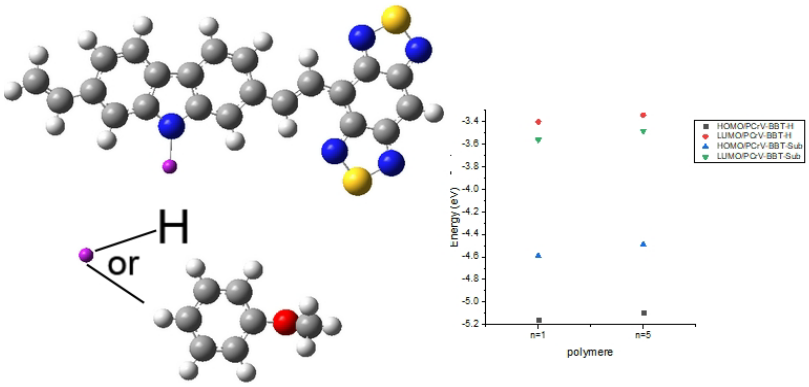
In this work, we present the study of the conjugated copolymers 2,7-divinylcabazole and benzo-bis-thiadiazole, by the DFT method using the base B3LYP/6-31G (d, p). To evaluate the properties of these systems, we performed structural optimization without geometric restriction. The NBO analysis was obtained by an energy calculation of the DFT-B3LYP method under the atomic base 6-31G (d, p) from the optimized geometries. Calculations of vibratory frequencies of all the structures studied show that they have minima (all frequencies are positive) on the TPES. In order to study the electronic and optical properties, we calculated the HOMO and LUMO energy levels as well as the band gap (Gap energy). The absorption wavelengths of each system were calculated by the TD-DFT method at the functional level WB97XD under the atomic base 6-31G (d, p).

Graphical abstract



Keywords

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1. Introduction

2,7-Carbazole derivatives [1] are organic materials with the properties of a semiconductor. These oligomers are known for their high stability due to the presence of nitrogen atoms and exhibit important physicochemical and optoelectronic properties. The addition of the methoxy-benzyl group to the nitrogen atom increases the solubility of these oligomers and facilitates their synthesis. During the last decade, conjugated donor-acceptor (D − A) copolymers have been the subject of numerous studies [2]. Among the main advantages of these hetero-junction materials, they have high flexibility and low

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weight [3–5]. The objective of this work is to show the interest of π-conjugated polymers by focusing on the electronic structure, the factors influencing the gap energy and the substitution effect of these polymers. We are interested in increasing the efficiency of the organic photovoltaic cell, by seeking to decrease the gap energy (HOMO-LUMO), in characterizing these compounds in terms of geometric and electronic structures to ensure good absorption of radiation and facilitate the charge transfer between the different compounds of our copolymer. This study was carried out on copolymers based on 2,7-divinylcabazole (PCrV) and benzo-bis-thiadiazole (BBT) (Figure 1). We were interested in the effect, on the structural, optoelectronic and photovoltaic properties of the addition of the méthoxy-benzyl group on the N atom of carbazole. This study was carried out by the DFT–B3LYP method as functional with the 6-31G (d, p) atomic base to optimize all systems, from monomer to pentamer. The structural and electronic properties have been demonstrated following this optimization, while the optical properties are obtained by the TD-DFT method at the level of the WB97XD functional and with the 6-31G base.

The LUMO level of the N-substituted copolymer is more stable than that of unsubstituted copolymer. This shows that the substitution of H by the méthoxy-benzyl group allows to decrease the energy gap of these compounds.

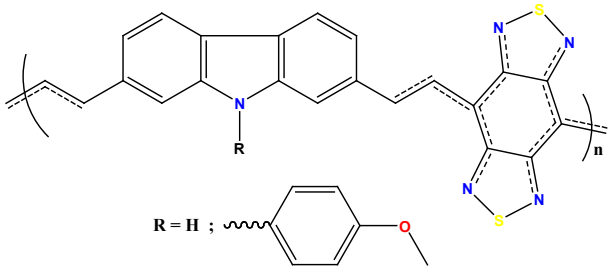


Fig. 1. the structures of the copolymers studied of 2, 7-divinyl-carbazole and Benzo-bis-thiadiazole (PCrV-BBT); N Substituted and N not Substituted.

2. Material and Methods

The optimization of the geometries of the different systems in their neutral states was performed by the DFT method with the three-parameter Becke hybrid exchange [6–9] using the Lee Yang and Parr functional (B3LYP) [10–13], under atomic basis 6-31G (d, p) [14–18] without any constraint. The structural parameters, the values of the energy levels HOMO, LUMO and the energy gap were deduced from the ground state of the optimized conformations in their neutral states.

The wavelength maxima, absorption spectra, excitation energies and oscillation forces were determined by the TD-DFT/wb97xd method with 6-31 G as the basis [19–22]. The choice of the wb97xd functional is to estimate successfully the transition energies as reported in the literature [23-27].

The NBO (Natural Bond Orbital Analysis) [28–30], the program of which is integrated in the Gaussian 09 package [31], is obtained by optimizing the molecules studied by the B3LYP/6-31g (d, p) method.

3. Results and Discussion

3.1 Structural properties

The structures of the Donor-Acceptor (DA) [32] copolymers based on 2,7-divinyl-carbazole and benzo-bis-thiadiazole (PCrV-BBT) have been optimized with the base B3LYP/6-31G (d, p) . The geometric parameters (bond lengths d_i, angles A_i and dihedral angles D_i) (Figure 2) of the most stable conformations obtained after the total optimization of the systems studied are presented in Table 1.

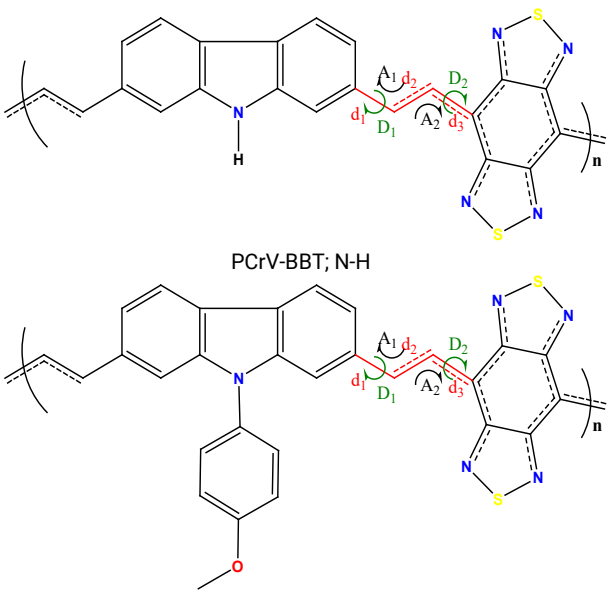


Fig. 2. The structures of the copolymers studied (of 2,7-divinyl-carbazole and benzo-bis-thiadiazole (PCrV-BBT; NH), and PCrV-BBT; N-Sub (with the addition of methoxy - benzyl on the N atom of carbazole).

Table 1. The structural parameters of the copolymers; d_i: inter-cyclic distances, A_i: normal angles, D_i: dihedral angles.

	Parameters	(PCrV-BBT; N-H)n					(PCrV-BTT; N-sub)n				
		n=1	n=2	n=3	n=4	n=5	n=1	n=2	n=3	n=4	n=5
inter-cyclic distance (Å)	d_1	1.455	1.454	1.454	1.454	1.454	1.455	1.454	1.454	1.453	1.453
	d_2	1.360	1.362	1.36	1.362	1.362	1.360	1.360	1.362	1.363	1.363
	d_3	1.440	1.436	1.436	1.436	1.436	1.439	1.435	1.435	1.435	1.435
normal angles (°)	A_1	117.65	117.74	117.81	117.75	117.74	117.7	117.68	117.68	117.63	117.71
	A_2	127.15	127.65	127.68	127.66	127.63	127.36	127.68	127.67	127.59	127.49
dihedral angles (°)	D_1	180.01	179.99	179.93	179.96	180.04	179.72	179.52	179.23	179.56	179.92
	D_2	179.99	180.0	179.98	179.98	180.02	179.89	179.88	179.95	179.86	179.80

The values of the inter-cyclic bonds (d_i), the values of the normal angles (A_i) and the values of the dihedral angles (D_i) of the copolymers based on PCrV-BBT with the substituted carbazole nitrogen atom (PCrV-BBT; N-sub) are generally very similar to those of the copolymers based on PCrV-BBT unsubstituted in N carbazole (PCrV-BBT; NH) (Table 1).

The lengths of the inter-cyclic bonds (d_i, i=1-3) of all the copolymers remain almost constant going from monomer to

pentamer while maintaining the double and single bond alternation, i.e. an increase of the length of the conjugation with the extension of the carbon chain. Thus, the lengths of the bonds d_1 and d_3 have values close to the length of the single bond C-C (1.465 Å) and the value of R2 is close to that of the length of double bond C = C (1.361 Å) [33-35].

From the values mentioned in Table 1, it is observed that the values of the dihedral angles of the systems studied are generally porches of 180 °. This indicates that the two benzo-bis-thiadiazole and 2,7-vinyl-carbazole moieties are found in the same plane in all systems (from n = 1 through n = 5). On the other hand, the pentamer has a planar structure with dihedral angle values very close to 180°. This flatness, confirmed by the values of the normal angles (A_i; i = 1, 2) close to 120°, reflects SP2 hybridization.

These results show a good improvement in flatness and an increase in electron conjugation p. This facilitates the possibility of delocalization of electrons along the molecular skeleton.

3.2 Optimized structures

In the Figure 3 we present the optimized structures of the different copolymers using the B3LYP functional under the atomic basis 6-31G (d, p).

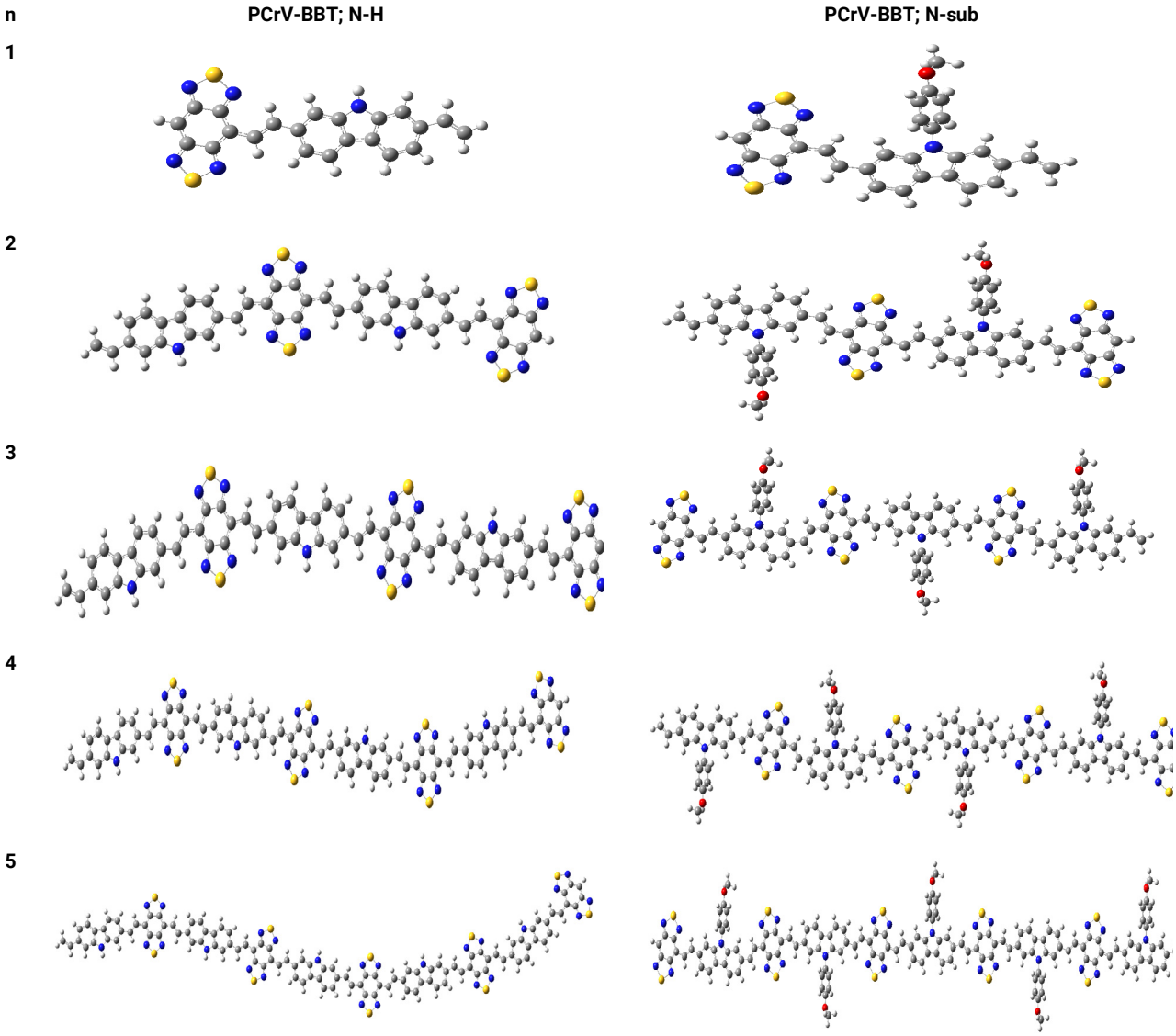


Fig. 3. Structures optimized by B3LYP / 6-31G (d, p).

Figure 3 shows that the systems adopt planar structures with the addition of the methoxy-benzyl group on the carbazole nitrogen (PCrV-BBT; N-sub). The length of conjugation increases from monomer to pentamer and the delocalization of electrons p between aromatic units appears to be easier with increasing flatness of these systems. The addition of methoxy-benzyl group decreases the length of the d_3 bond compared to those of unsubstituted systems (Table 1) and increases the p character of these bonds.

3.3 Electronic properties

The study of electronic properties mainly concerns the determination of energy levels HOMO, LUMO and the band gap (energy gap). This determination makes it possible to validate the candidacy of the molecules studied for use in the electronic field. The calculation of the HOMO, LUMO and Energy Gap levels was carried out after the optimization of the systems by the B3LYP/6-31g (d, p) method.

From Table 2, we note that the gap values decrease going

from monomer to pentamer. We also note that the addition of the methoxy-benzyl group on the nitrogen atom of the carbazole causes the gap to decrease by an average of 0.02 eV. This decrease due to a good stability of the energy levels is clearly illustrated in Figure 4. This decrease in the gap is in agreement with the improvement in the flatness of these systems.

Table 2. The values of the energies of the HOMO and LUMO levels and of the energy gap of the copolymers.

Polymers	PCrV-BBT; N-H			PCrV-BBT; N-Sub		
	HOMO (eV)	LUMO (eV)	GAP Energy (eV)	HOMO (eV)	LUMO (eV)	GAP Energy (eV)
n=1	-5.16	-3.40	1.76	-5.09	-3.34	1.75
n=2	-4.77	-3.49	1.28	-4.68	-3.42	1.26
n=3	-4.66	-3.53	1.13	-4.58	-3.46	1.12
n=4	-4.61	-3.54	1.07	-4.53	-3.47	1.06
n=5	-4.59	-3.56	1.03	-4.49	-3.48	1.01

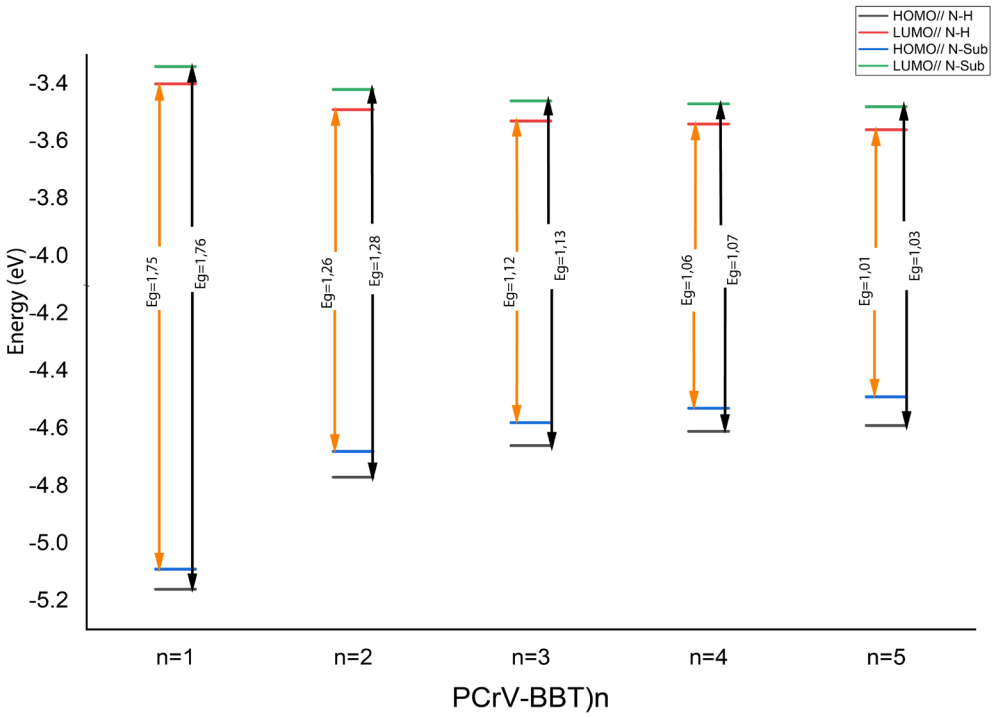


Fig. 4. Illustration of the HOMO, LUMO, and Eg levels of the monomer to the pentamer obtained by B3LYP/6-31G (d, p).

The change from monomer to pentamer shows a general reduction in the gap with a strong stability of the LUMO level compared to the HOMO level, which seems a little destabilized (see Figure 4). We also observe that the LUMO levels of PCrV-BBT-N-substituted are more stable than those of unsubstituted PCrV-BBT-N-H. This clearly shows that the substitution of the H atom by the methoxy-benzyl group allows a reduction in the gap of these copolymers.

Concerning the electronic densities of the HOMO and LUMO border molecular orbitals of the copolymers studied, they are presented in Figure 5.

This Figure shows that the electron density at the level of HOMO orbitals is distributed along the conjugation chain. In contrast, at LUMO orbitals, the electron cloud is mainly located on the electron acceptor unit (BBT). This phenomenon is due to the Puch-Pull properties of type polymers (D-A). It should be noted that the addition of the methoxy-benzyl group to the nitrogen of the carbazole promoting the flatness of these systems, allows the total displacement of the electron density towards the acceptor unit (Figure 5) and plays an important role at the level of the solubility and stability of the systems [4, 36]. It is also important to note that the transfer of electrons from the HOMO orbital to the LUMO orbital in the N-substituted copolymer is more efficient compared to other N-unsubstituted copolymers and therefore results in energy low gap.

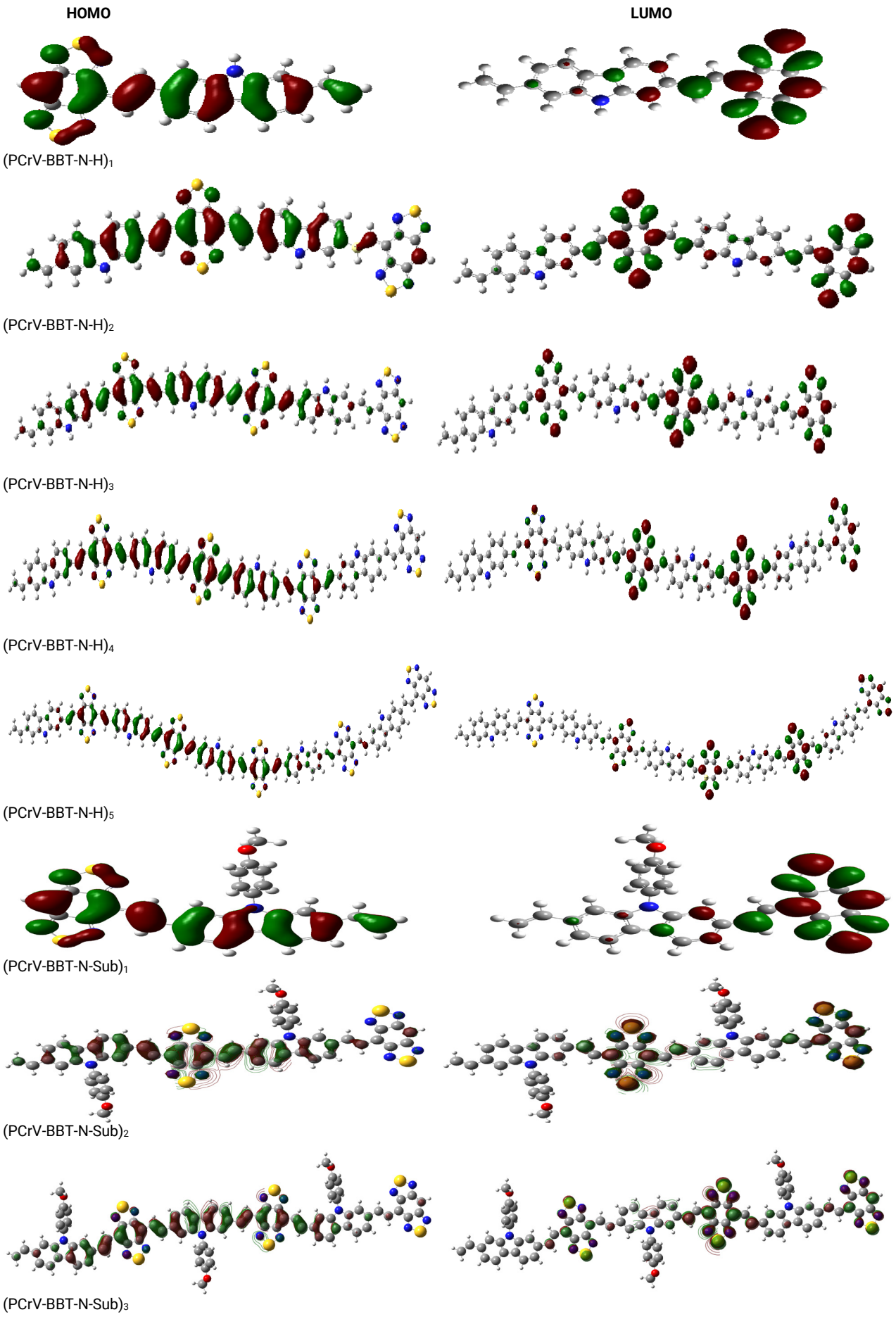
3.4 Photovoltaic properties

Bulk-heterojunction (BHJ) solar cells have better efficiency compared to other types of organic solar cells [37, 38] and therefore, the efficiency of converting solar energy into electrical energy by this type of cell is significantly improved [38]. To study the photovoltaic properties of our copolymers, we calculated the maximum open circuit voltage (VOC) using equation (1). We also calculated the parameter a (difference between the LUMO energy levels of the acceptor and the donor) to have an aid on the delocalization of the electrons. The factors related to this parameter are calculated from equation (2) [39, 40].

The energy levels of the different systems were optimized by the DFT-B3LYP method under the atomic base 6-31 G (d, p). The chosen acceptor is (Bis-PCBM).

◆ Voc = | E HOMO (donor) | - | E LUMO (acceptor) | - 0.3 (1)

◆ α = | E LUMO (acceptor) | - | E LUMO (donor) (2)


HOMO
LUMO
(PCrV-BBT-N-H)1
(PCrV-BBT-N-H)2
(PCrV-BBT-N-H)3
(PCrV-BBT-N-H)4
(PCrV-BBT-N-H)5
(PCrV-BBT-N-Sub)1
(PCrV-BBT-N-Sub)2
(PCrV-BBT-N-Sub)3

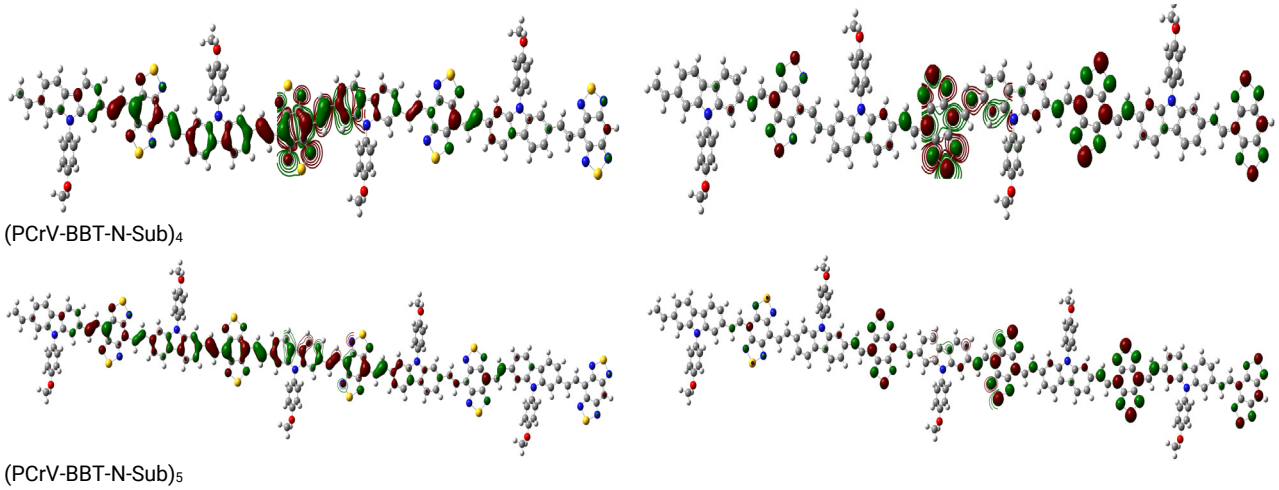


Fig. 5. Illustration of the border orbitals HOMO, LUMO of the copolymers without group (PCrV-BBT; N-H), and with methoxy-benzyl group (PCrV-BBT; N-Sub).

Table 3. Theoretical values of the voltage of the open circuits Voc (eV) and α (eV).

Polymers	PCrV-BBT ; N-H				PCrV-BBT ; N-Sub			
	HOMO (eV)	LUMO (eV)	VOC (eV)	α (eV)	HOMO (eV)	LUMO (eV)	VOC (eV)	α (eV)
n=1	-5.16	-3.40	1.06	0.4	-5.09	-3.34	0.99	0.46
n=2	-4.77	-3.49	0.67	0.31	-4.68	-3.42	0.58	0.38
n=3	-4.66	-3.53	0.56	0.27	-4.58	-3.46	0.48	0.34
n=4	-4.61	-3.54	0.51	0.26	-4.53	-3.47	0.43	0.33
n=5	-4.59	-3.56	0.49	0.24	-4.49	-3.48	0.39	0.32
BisPC61BM	-6.1	-3.8	-----	-----	-6.1	-3.8	-----	-----

The Voc values vary very little with the lengthening of the carbon chain, as well as the passage from the monomer to the pentamer shows a decrease in the value of α, this suggests that the transfer of electrons p from the donor compound to the semiconductor Bis-PC61BM is facilitated.

On the other hand, we notice that the LUMO levels of all the copolymers studied are placed above the LUMO level of Bis-PC61BM. We deduce that all the compounds studied are likely to be injected in the excited state and in particular the pentamer is the most favored given the position of its LUMO relative to that of Bis-PC61BM.

3.5 Optical properties and electronic transitions

UV-visible absorption spectra, wavelengths and excitation energies of the copolymers studied were calculated using the TD-DFT-WB97XD/6-31G method, from the optimized geometries of the copolymers. The corresponding values of excitation energies (Eex), wavelengths (lmax), and light harvesting efficiency (LHE) (expressed by equation (3)) [41], are gathered in Table 4.

To understand the evolution of the short-circuit current density (Jsc), we studied the LHE energy which depends on Jsc according to equation (4) [42]. We notice that large values of LHE lead to high values of Jsc. This therefore improves the efficiency of electronic devices.

- LHE = 1− 10-f (3)
- Jsc= ∫λ LHE(λ) ϕ(inject) η(collect) dλ (4)

With: ϕ(inject): Efficiency of electron injection.

η(collect): The efficiency of the collection of charges. f: oscillation force.

From the data in Table 4, we have three types of same-spin (S→S) excitation from the lowest occupied molecular orbitals and the highest void levels. In regard to lmax, these increases going from the monomer to the pentamer. In addition, the addition of the methoxy-benzyl group contributes to increasing the values of maximum absorption lengths. This indicates that these copolymers are good candidates for absorbing the maximum of incident light radiation and therefore further increasing the photoelectric conversion efficiency of the corresponding solar cell from this type of material.

The absorption spectra (Figures 6 and 7) show an increase in the magnitude of epsilon directly related to the absorbance of light. This implies very good absorption of light radiation going from the monomer to the pentamer. The value of l_{max} increases until it reaches the far IR zone. In other words, it only takes a gentle incident light radiation to have a very good excitation of the electrons. We also find that the width of the excitation plug increases when the methoxy-benzyl group is substituted on the N atom of the carbazole. This is favorable to good absorption of the light ray.

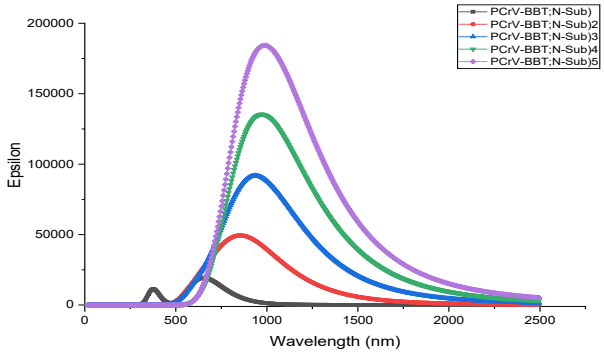


Fig. 6. Data of wavelength according to absorbance of copolymers with the methoxy-benzyl group on N of carbazole obtained at DFT-WB97XD/6-31G.

Table 4. Types of excitation, excitation energies, wavelengths and LHE, obtained by the TD-DFT/WB97xd-6-31G method.

	Type of excitement	Eex (eV)	l (nm)	LHF	Attributions
(PCrV-BBT; N-Sub	S0→S1	1.8983	653.13	0.6651	H-2→L (11%); H → L (88%)
	S0→S2	3.1570	392.73	0.0355	H-5 → L1 5(3%); H-1 → L (86%); H→L+1 (6%)
	S0→S3	3.3028	375.39	0.4563	H-8→L (2%); H-4→L (24%); H-2→L (59%); H-1→L (2%); H→L (7%); H→L+1 (3%)
(PCrV-BBT; N-Sub)2	S0→S1	1.3976	887.09	0.9244	H-1→L+1(4%); H-→L (77%); H→L+1 (14%)
	S0→S2	1.8953	654.16	0.6036	H-5→L+1 (3%); H-4→L+1 (4%); H-1→L (22%); H-1→L+1(49%); H→L+1 (19%)
	S0→S3	2.8687	432.20	0.0059	H-8→L (6%); H-8→L+1 (2%); H-5→L (9%); H-4→L (24%); H-4→L+1 (6%); H-3→L (2%); H-1→L (32%); H-1→L+1 (9%)
(PCrV-BBT; N-Sub)3	S0→S1	1.3107	945.93	0.9938	H-2→L+2 (3%); H-1→L (3%); H-1→L+1 (21%); H-1→L+2 (8%); H→L (54%); H→L+1(6%)
	S0→S2	1.4693	843.82	0.0243	; H-1→L (34%); H-1→L+2 (5%); H→L+1 (38%) H→L+2 (14%)
	S0→S3	1.8973	653.49	0.6033	H-7→L+2 (2%); H-2→L (11%); H-2→L+1 (19%); H-2→L+2 (38%); H-1→L+1 (3%); H-1→L+2 (12%); H→L+2 (7%)
(PCrV-BBT; N-Sub)4	S0→S1	1.2684	977.48	0.9994	H-2→L+2 (14%);; H-2→L+3 (6%); H-1→L+1 (17%); H-1→L+2 (3%); H→L (44%); H→L+1 (4%)
	S0→S2	1.4041	883.05	0.0212	H-2→L+1 (12%); H-2→L+2 (2%); H-1→L (27%); H-1→L+2 (10%); H-1→L+3 (9%); H→L+1 (26%); H→L+2 (5%);
	S0→S3	1.4957	828.95	0.2504	H-2→L (25%); H-2→L+1 (3%); H-1→L+1 (19%); H-1→L+2 (3%); H→L+2 (26%); H→L+3 (13%)
(PCrV-BBT; N-Sub)5	S0→S1	1.2492	992.49	0.9999	H-3→L+2 (2%); H-3→L+3 (6%); H-3→L+4 (8%); H-2→L+1 (3%); H-1→L+2 (9%); H-2→L+3 (3%); H-1→L (5%); H-1→L+1 (12%); H-1→L+2 (5%); H→L(32%); H→L+1 (8%);
	S0→S2	1.3543	915.48	0.0076	H-3→L+1 (2%); H-3→L+2 (6%); H-3→L+3 (3%); H-2→L (3%); H-2→L+1 (7%); H-2→L+3 (4%); H-2→L+4 (8%); H-1→L (23%); H-1→L+2 (6%); H→L+3 (4%); H→L+1 (20%); H→L+2 (5%);
	S0→S3	1.4491	855.60	0.3458	H-3→L+1 (7%); H-3→L+2 (4%); H-2→L (18%); H-2→L+2 (4%); H-2→L+3 (3%); H-1→L+1 (13%); H-1→L+3 (5%); H-1→L+4 (11%); H→L+2 (18%); H→L+3 (5%);
PCrV-BBT; N-H	S0→S1	1.9137	647.86	0.6744	H-2→L (11%); H→L (88%);
	S0→S2	3.3145	374.07	0.4419	H-6→L (2%); H-3→L (23%); H-2→L (55%); H-1→L (8%); H→L (7%);
	S0→S3	3.3758	367.28	0.0744	H-4→L (5%); H-2→L (5%); H-1→L (79%); H-1→L+1 (6%);
(PCrV-BBT; N-H)2	S0→S1	1.4144	876.58	0.9259	H-1→L+1(4%) ; H→L (78%) ; H→L+1 (13%) ;
	S0→S2	1.9089	649.50	0.5977	H-5→L+1 (3%) ; H-2→L+1 (4%) ; H-1→L (22%) ; H-1→L+1 (49%) ; H→L+1 (19%) ;
	S0→S3	2.8812	430.31	0.0341	H-6→L (6%) ; H-6→L+1(2%) ; H-5→L (10%) ; H-2→L (25%) ; H-2→L+1 (6%) ; H-1→L (33%) ; H-1→L+1 (9%) ;
(PCrV-BBT; N-H)3	S0→S1	1.3283	933.38	0.9943	H-2→L+2 (3%) ; H-1→L (3%) ; H-1→L+1 (22%) ; H-1→L+2 (8%) ; H→L (54%) ; H→L+1 (6%) ;
	S0→S2	1.4920	830.97	0.0561	H-1→L (35%) ; H-1→L+1 (4%) ; H→L+1 (38%) ; H→L+2 (14%) ;
	S0→S3	1.9109	648.82	0.5951	H-7→L+2 (2%) ; H-2→L (11%) ; H-2→L+1 (19%) ; H-2→L+2 (38%) ; H-1→L+1 (3%) ; H-1→L+2 (12%) ; H→L+2 (7%)
(PCrV-BBT; N-H)4	S0→S1	1.2846	965.15	0.9994	H-2→L+1 (3%) ; H-2→L+2 (12%) ; H-2→L+3 (7%) ; H-1→L (4%) ; H-1→L+1 (15%) ; H-1→L+2 (4%) ; H→L (42%) ; H→L+1 (7%) ;
	S0→S2	1.4199	873.21	0.0043	H-2→L+1 (10%) ; H-2→L+2 (3%) ; H-1→L (26%) ; H-1→L+2 (10%) ; H-1→L+3(9%) ; H→L+1 (25%) ; H→L+2 (5%) ;
	S0→S3	1.5178	816.86	0.2333	H-2→L (24%) ; H-2→L+1 (4%) ; H-1→L+1 (18%) ; H-1→L+2(3%) ; H→L+1 (2%) ; H→L+2 (26%) ; H→L+3 (13%) ;
(PCrV-BBT; N-H)5	S0→S1	1.2600	983.96	0.9999	H-3→L+2 (3%) ; H-3→L+3 (8%) ; H-3→L+4 (6%) ; H-2→L+1 (4%) ; H-2→L+2 (9%) ; H-2→L+3 (3%) ; H-1→L (5%) ; H-1→L+1 (11%) ; H-1→L+2 (5%) ; H→L (32%) ; H→L+1 (8%) ;
	S0→S2	1.3689	905.75	0.2034	H-3→L+1 (2%) ; H-3→L+2 (6%) ; H-3→L+3(2%) ; H-2→L (3%) ; H-2→L+1 (7%) ; H-2→L+3 (5%) ; H-2→L+4 (7%) ; H-1→L (22%) ; H-1→L+2 (6%) ; H-1→L+3 (4%) ; H→L+1 (20%); H→L+2 (6%) ;
	S0→S3	1.4661	845.69	0.4410	H-3→L+1 (7%) ; H-3→L+2 (3%) ; H-2→L (18%) ; H-2→L+2 (4%) ; H-2→L+3 (2%) ; H-1→L+1 (13%) ; H-1→L+3 (6%) ; H-1→L+4 (10%) ; H→L+1 (2%) ; H→L+2 (17%) ; H→L+3 (6%) ;

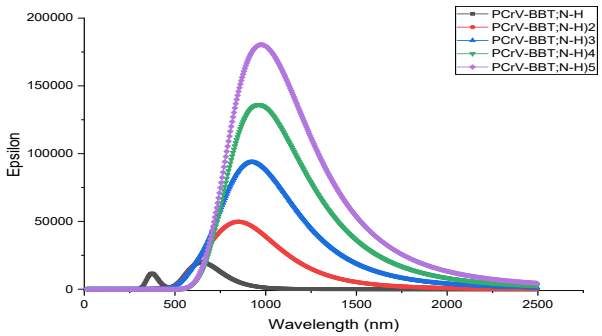


Fig. 7. Data of wavelength according to absorbance of copolymers with the H on N of carbazole obtained at DFT-WB97XD/6-31G.

3.6 NBO analysis and charge transfer

From the optimized geometries of the copolymers, we fragmented the systems into donor fragments and other acceptors. Then we carried out the energy calculation by the DFT-B3LYP/6-31G (d, p) method.

NBO analysis [28–30] is an efficient method to study the interaction between intra and intermolecular bonds. It also allows the study of charge transfer in the molecular system.

Figure 8 represents the different fragments of the two types of copolymers studied, we chose to fragment the structure according to the copolymer compositions, then we performed the NBO analysis, the results obtained are grouped together in Table 5.

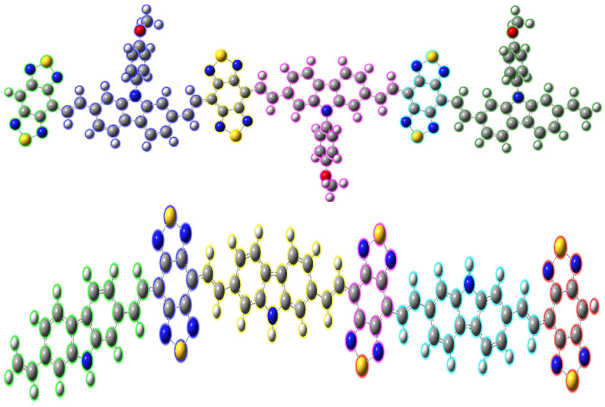


Fig. 8. Structures of the fragmented systems studied by NBO of copolymers without and with methoxy-benzyl group.

Table 5. The electronic charge and the type of fragments of the copolymers obtained by B3LYP/6-31G (d, p).

		PCrV-BBT ; N-H		PCrV-BBT ; N-Sub	
PCrV-BBT) n	**Fragments**	**Charges**	**types**	**Charges**	**types**
n = 1	Frag1	0.50	Donor	0.50	Donor
	Frag2	-0.50	Acceptor	-0.50	Acceptor
n = 2	Frag1	-0.15	Acceptor	0.13	Donor
	Frag2	0.13	Donor	-0.24	Acceptor
	Frag3	-0.23	Acceptor	0.26	Donor
	Frag4	0.25	Donor	-0.15	Acceptor
n = 3	Frag1	0.82	Donor	-0.15	Acceptor
	Frag2	0.13	Donor	0.26	Donor
	Frag3	-0.24	Acceptor	-0.24	Acceptor
	Frag4	0.24	Donor	0.25	Donor
	Frag5	-1.20	Acceptor	-0.24	Acceptor
	Frag6	0.25	Donor	0.13	Donor
n = 4	Frag1	0.24	Donor	0.19	Donor
	Frag2	0.13	Donor	-0.35	Acceptor
	Frag3	-0.24	Acceptor	0.36	Donor
	Frag4	-0.24	Acceptor	-0.36	Acceptor
	Frag5	0.24	Donor	0.37	Donor
	Frag6	-0.24	Acceptor	-0.35	Acceptor
	Frag7	0.25	Donor	0.38	Donor
	Frag8	-0.15	Acceptor	-0.25	Acceptor
n = 5	Frag1	0.13	Donor	-0.15	Acceptor
	Frag2	-0.14	Acceptor	0.26	Donor
	Frag3	0.25	Donor	-0.24	Acceptor
	Frag4	-0.24	Acceptor	0.25	Donor
	Frag5	0.24	Donor	-0.24	Acceptor
	Frag6	-0.24	Acceptor	0.25	Donor
	Frag7	0.24	Donor	-0.25	Acceptor
	Frag8	-0.24	Acceptor	0.24	Donor
	Frag9	0.24	Donor	-0.25	Acceptor
	Frag10	-0.24	Acceptor	0.13	Donor

NBO analysis of the various fragments of the copolymer highlights the role of the interaction of intermolecular orbitals and charge transfer in the system. It is carried out by taking into account all the possible interactions between filled donors and empty acceptors and by estimating their energetic importance by the theory of second order disturbances.

Each positively charged NBO represents a donor (i) and each negatively charged NBO is linked to an acceptor moiety (j). The stabilization energy E associated with electronic delocalization between donor and acceptor is estimated by equation (5) [43, 44].

◆ $E = qi\ (Fi.j)2/\ \varepsilon j - \varepsilon i$ (5)

With: qi: is the occupation of the i orbital, εj , εi are diagonal elements, Fi. j is the o-diagonal NBO Fock matrix element.

From Table 5, it is observed that the change from

monomer to pentamer leads to the location of charges in the middle of the system; the charge values of the middle fragments are higher than those of the end fragments. The addition of the methoxy-benzyl group further increases the absolute value of charge compared to that of copolymers without a group (PCrV-BBT; N-H).

4. Conclusions

The conjugated copolymers based on 2,7-divinylcabazole (PCrV) and benzo-bis-thiadiazole (BBT) have been studied by suitable quantum methods. It emerges from this study that the electronic and optoelectronic properties are intimately linked to the molecular structure. In this sense, the electron donor and electron acceptor motif alternation approach is an effective strategy for modulating these properties.

The LUMO level of the N-substituted copolymer is more stable than that of unsubstituted copolymer. This shows that the substitution of H by the méthoxy-benzyl group allows to decrease the energy gap of these compounds.

The data obtained from the energy levels of the different molecules indicate that the LUMO and HOMO levels, as well as the values of the energy of gap Eg, vary according to the length of the carbon chain. The majority of the copolymers studied exhibit a high quality P-type semiconductor character. Electronic transitions in this type of material require low energy light radiation. For all the reasons mentioned above, these molecules are good candidates for a good application in photovoltaic systems.

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Author Contributions

Conceptualization, Mohamed JABHA, Abdellah ELALAOUI; Methodology, Mohamed JABHA, Abdellah ELALAOUI, Abdellah JARID, Writing - preparation of the original draft, Mohamed JABHA, Writing - revision and editing, Mohamed JABHA, EL Houssine MABROUK; Supervision, Abdellah ELALAOUI, Abdellah JARID; Administration of the project, Abdellah ELALAOUI; All the authors have read and accepted to the published version of the manuscript.

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