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Computational study on geometric and electronic properties of 3.6-carbazole based conjugated polymers

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Abstract

In this work, we present firstly a study based on the calculation of the local spin densities of radical cations, which is known as a good measure of reactivity for coupling reactions, to obtain a theoretical basis for the one-step formation of poly(3.6-carbazole) and derivatives. Then we detail a DFT theoretical study of the geometric and electronic properties of oligomers based on carbazole and other conjugated monomers. These results will be compared with the experimental ones and with works realized by other authors

Keywords: Carbazole, DFT, Geometrics, Electronic properties

1. Introduction

Since their discovery, conjugated polymers attract continuing interest as a result of their suitability in a broad range of applications, such as batteries [1], electroluminescent devices [2], field-effect transistors [3] and photovoltaics [4]. Conjugated polymers containing carbazole moieties either in the main or side chains have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency, thermal stability and also their facile color tenability [5]. These properties depend on the degree of electronic delocalization in these materials and on the modification of chemical structure through the incorporation of charge carriers into the polymer backbone. In order to obtain materials with more predominant capability, the development of novel structures is now being undertaken following the molecular engineering guidelines.

Recently, poly(3,6-carbazole) and derivatives have been synthesized [6]. These materials form a subset of the organic materials under study for blue EL applications [7]. One of the most important factors of controlling physical properties is the bandgap, which is a current topic of research. In particular, polymers with a low and gap are desired in optoelectronic applications. Many ways have been used to modulate this parameter of polycarbazole derivatives including conjugates length control as well as the modification of chemical structure through the incorporation of charges carriers in the polymer backbone [8]. Different kinds of conjugated

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units are introduced to carbazole conjugated system such as Tao *et al.* [9] have introduced fluorine unit and achieved pure deep blue LED. Beoupre et al [10] have enhanced the coloration efficiency of the polymeric system by incorporation of thiophene.

Following these encouraging results, we decided to develop a new class of such polycarbazoles with tunable emission colors (blue, green, and red). For this purpose, different aromatic molecules can be coupled to carbazole moieties to modulate the electronic structure of the resulting polymer

Yang *et al.* [11], Suramitr *et al.* [12] have studied the geometric and electronic properties polymers containing carbazole and other conjugated monomers. They reported that the coupling of the two different monomers is done between carbon 2 of carbazole and carbon 2 of thiophene. However, they did not specify why they choose exactly the coupling between these two carbons? Their studies give us a good example to have an insight into the reaction mechanism. In this work, we present initially a study based on the calculation of the local spin densities of radical cations, which is known as a good measure of reactivity for coupling reactions. Then we detail a DFT theoretical study of the geometric and electronic properties of these oligomers based on carbazole. These results will be compared with the experimental one and with works realized by other authors.

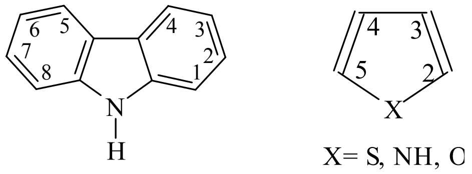


Fig. 1 Molecular structure and numbering of the carbazole derivatives

2. Methodologies

The quantum calculations were performed using Gaussian 03 program [13]. The geometries of the resulting conformers were optimized at the DFT level of three-parameter compound functional of Becke (B3LYP) [14]. The 6-31G* basis set was used for all atoms. The geometries structures of neutral molecules were optimized under no constraints. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The geometric structures of radical cations were optimized independently from the neutral molecules prior to calculation of spin densities. Radical cations were treated as open shell systems by UB3LYP /6-31G* method. The ground state energies and oscillator strengths were investigated using ZINDO method starting with the fully optimized geometries obtained at B3LYP/6-31G* levels. In fact, these calculation methods have been successfully applied to other conjugated polymers [15].

3. Results and discussion

3.1. Local spin densities and coupling reactivity

A generally accepted mechanism for the coupling reaction of conjugated monomers, which consists of two step reactions [16, 17]. The initial step is a one-electron oxidation of the monomer to form its radical cation. The second step is a coupling reaction of two radical cations to form a dihydro-dimer dication, which is followed by the elimination of two protons to form the dimer. The reactivity of this step should be closely related to the unpaired-electron spin density. Since the oxidation of dimer is easier than that of monomer, a radical cation of dimer undergoes further coupling reactions with other radical cations [18]. Fig. 2 lists the calculated total atomic spin densities of radical cations for thiophene, furane, carbazole, pyrrole, etc.

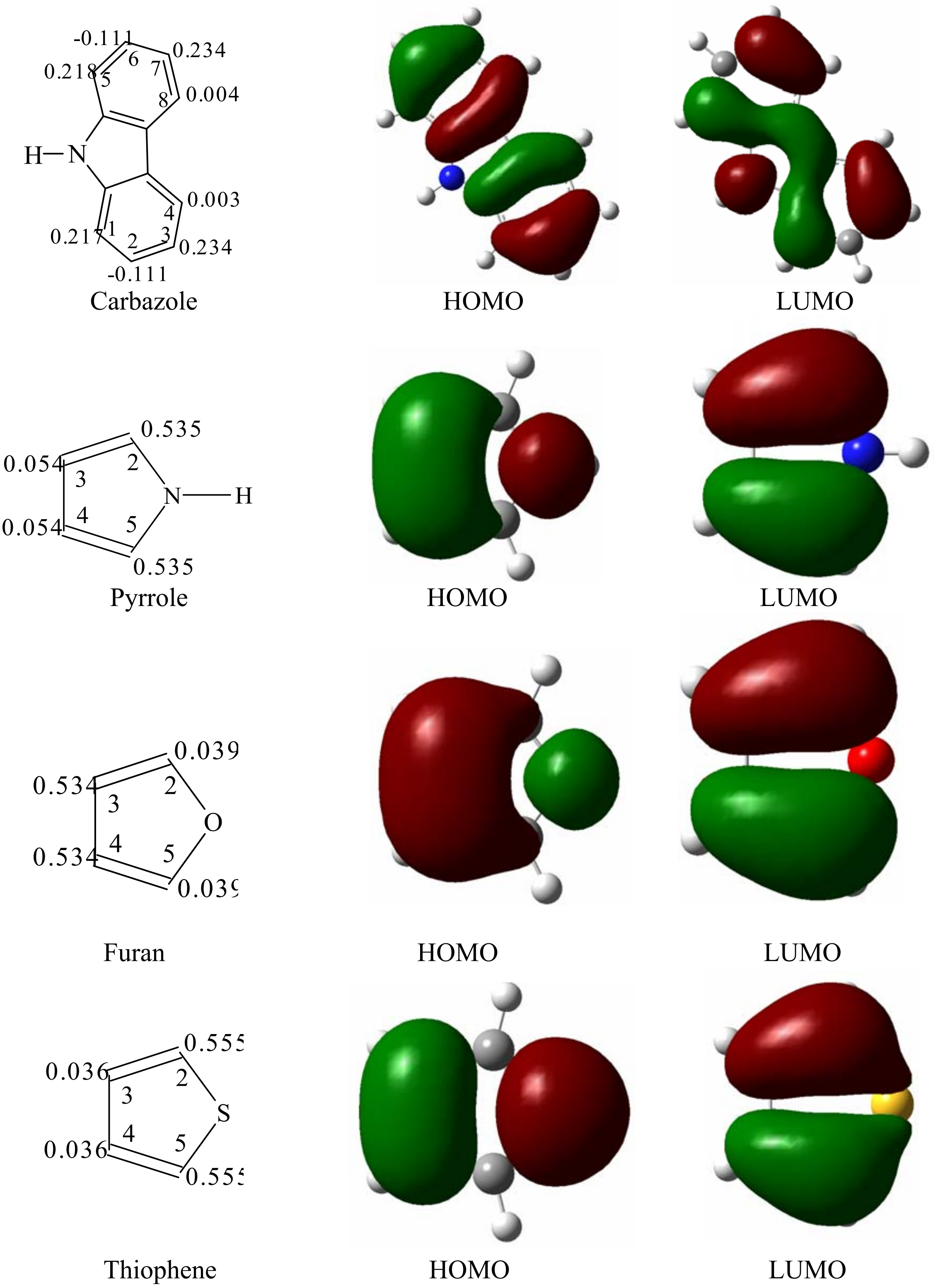


Fig. 2 Calculated total atomic spin densities of radical cations for thiophene, furane, carbazole, pyrrole

The highest spin densities are observed at C-2 of the rings for thiophene, pyrrole, and furrane. In addition, high spin densities are located on the 4-carbons of carbazole. These facts indicate that the reactivity for the propagation reactions of the radical cations can be elucidated from the difference between the spin densities at C-2 and C-5 (Fig.3).

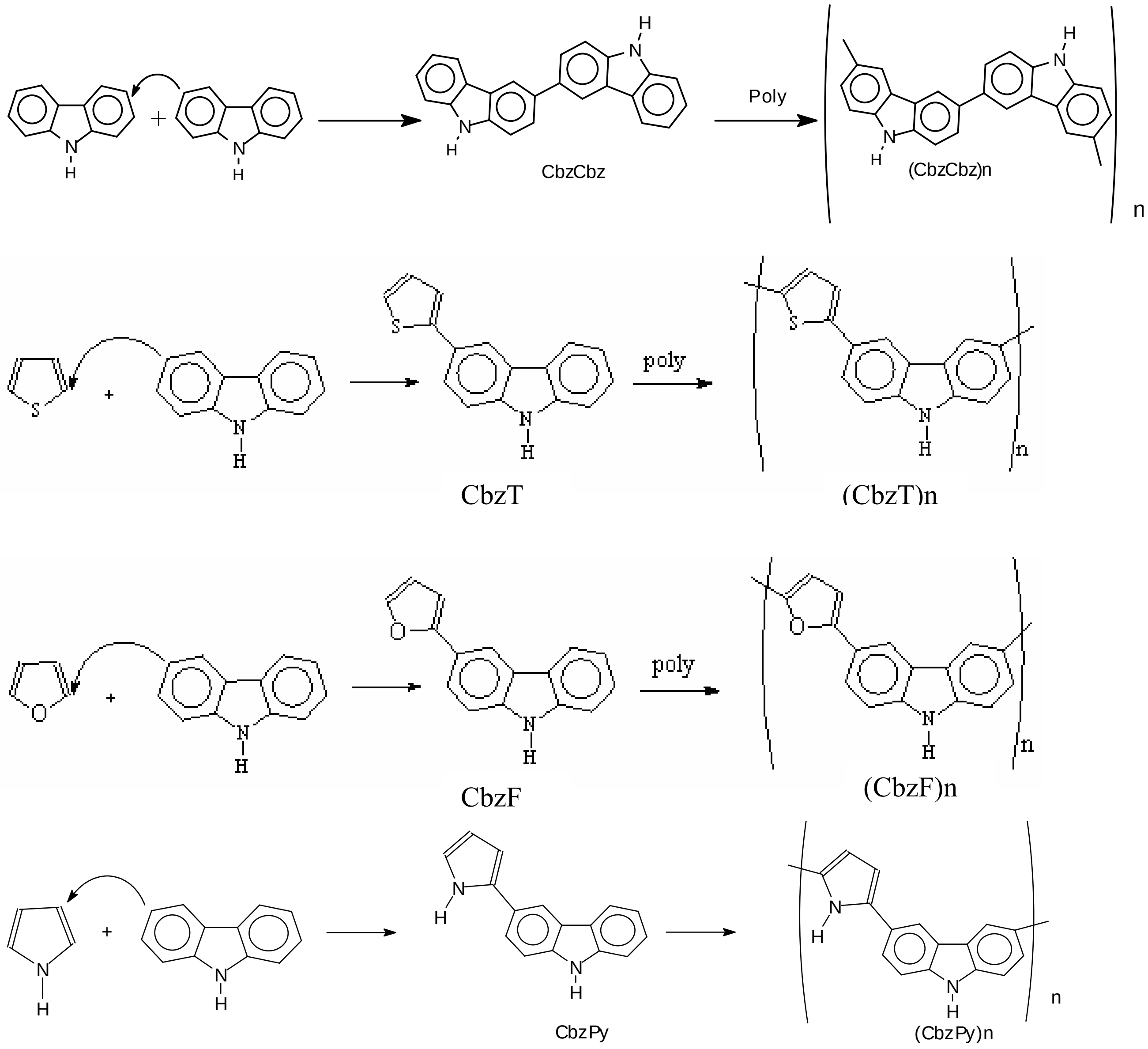
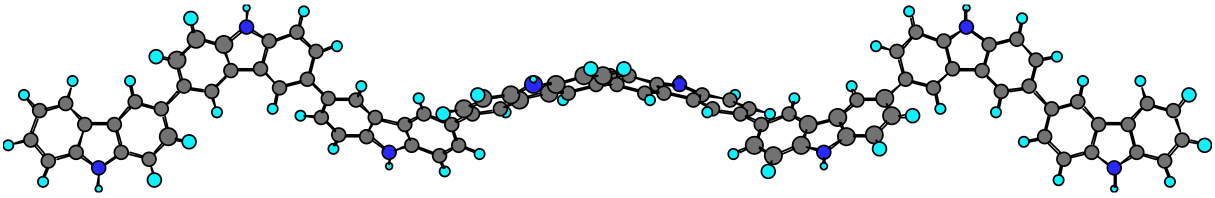


Fig. 3 Reactivity of the studied compounds and chemical structures of oligomers (CbzCbz)n, (CbzT)n, (CbzPy)n, (CbzF)n (n=1 – 4)

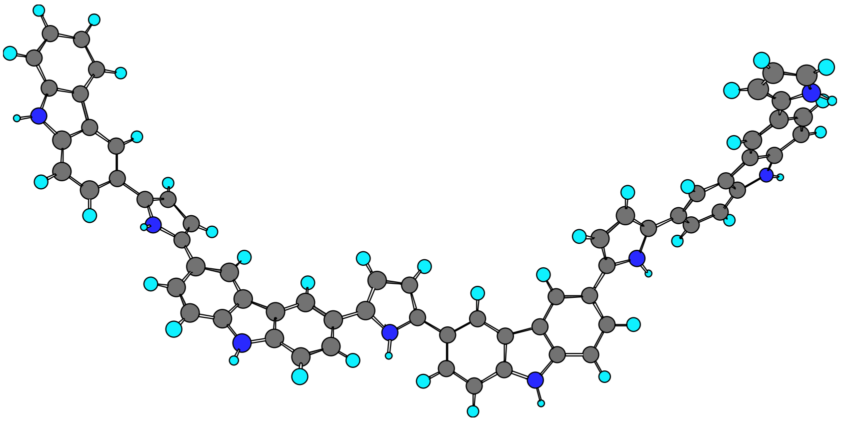
3.2. Ground state geometries

The chemical structures of **(**CbzCbz)n, (CbzT)n, (CbzPy)n and(CbzF)n are depicted in Fig. 3 and optimized ground state geometries of **(**CbzCbz)4, (CbzT)4, (CbzPy)4 and (CbzF)4 obtained at the B3LYP/6-31G(d) level are given in Fig. 4. The optimized dihedral angles between the subunits and the inter-ring bond lengths are summarized in Table 1 and Table 2.

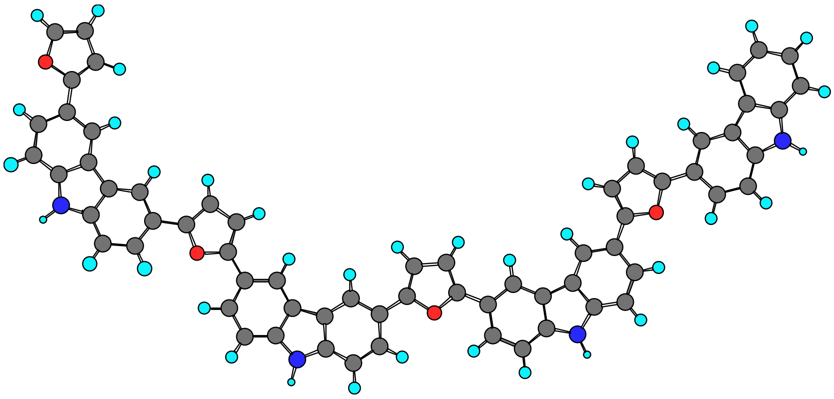
The dihedral angle of CbzCbz 39° and an inter-ring distance of 1.486 Å are computed for this molecule. The computed torsional angles of CbzT and CbzPy are slightly smaller than that of CbzCbz (see table 1 and 2). Accordingly, the inter-ring distances are slightly shorter (1.469 Å for CbzT, 1.465 Å for CbzPy and 1.459 Å for CbzF). As expected, five-membered aromatic rings create less steric hindrance than six-membered rings [19]. Upon a first glance over the numbers, we note the are no significant differences among the dihedral angles and the inter-ring bond lengths in all oligomers (CbzCbz)n. The same results were obtained for oligo-para-phenylenes [20].



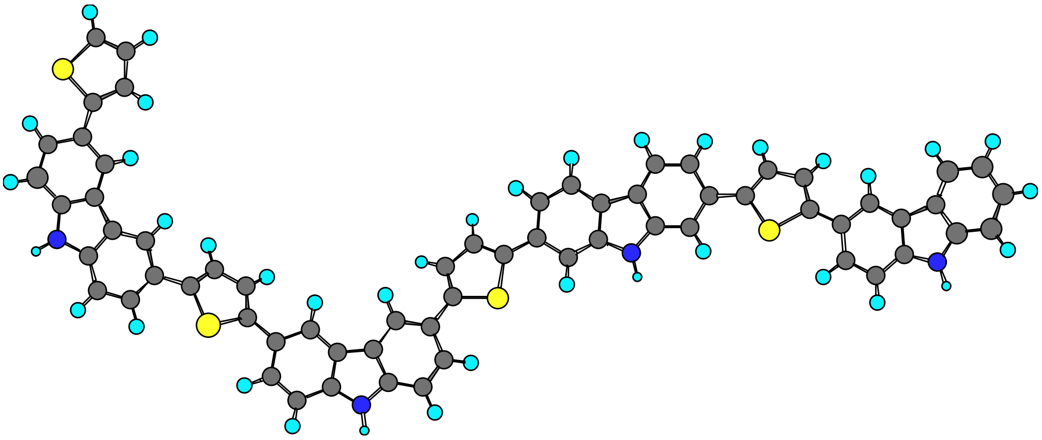
Optimized structure of (CbzCbz)4



Optimized structure of (CbzPy)4



Optimized structure of (CbzF)4



Optimized structure of (CbzT)4

Fig. 4 Optimized structures obtained at the B3LYP/6-31G(d) level for (CbzCbz)4, (CbzT)4, (CbzPy)4 and (CbzF)4

Table 1
Dihedral angles (θi) of (CbzCbz)n, (CbzT)n, (CbzPy)n and(CbzF)n obtained by B3LYP/6-31G(d)

	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7
(cbzpy)n							
1	30.00						
2	29.11	26.84	29.65				
3	27.50	28.00	28.94	28.70	29.50		
4	27.61	27.44	28.08	28.33	28.22	28.38	29.70
(cbzF)n							
1	0.00						
2	0.00	0.00	0.00				
3	0.00	0.00	0.00	0.00	0.00		
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
(cbzT)n							
1	31.76						
2	28.94	28.83	30.67				
3	28.66	28.13	29.08	28.75	30.41		
4	28.35	29.38	28.65	28.98	29.14	27.38	30.28
(cbz-cbz)n							
1	39.00						
2	40.00	39.15	39.00				
3	39.70	-39.38	39.50	39.8	39.86		
4	39.30	-40.05	40.44	39.62	40.45	40.05	39.31

Table 2
Inter-ring bond lengths (di) of (CbzCbz)n, (CbzT)n, (CbzPy)n and(CbzF)n obtained by B3LYP/6-31G(d)

	d_1	d_2	d_3	d_4	d_5	d_6	d_7
(cbzpy)n							
1	1.465						
2	1.463	1.463	1.465				
3	1.463	1.463	1.464	1.464	1.465		
4	1.463	1.463	1.464	1.464	1.464	1.464	1.465
(cbzF)n							
1	1.459						
2	1.457	1.456	1.459				
3	1.457	1.456	1.457	1.456	1.459		
4	1.457	1.456	1.456	1.456	1.547	1.457	1.459
(cbzT)n							
1	1.469						
2	1.468	1.468	1.469	1.468			
3	1.468	1.468	1.468	1.468	1.469		
4	1.468	1.468	1.468		1.467	1.467	1.469
(cbz-cbz)n							
1	1.486						
2	1.486	1.486	1.486	1.486			
3	1.486	1.486	1.486	1.486	1.486		
4	1.486	1.486	1.486		1.486	1.486	1.486

Finally, as expected, Table 1 shows that the oligomers (CbzF)n are completely planar (θi = 0.00°). This can be explained by the smaller steric effect caused by the oxygen atom, which is smaller than the sulfur atom and the better electron donor–acceptor effect between carbazole and furan. A similar observation has been found by Leclerc *et al.* [21] for examining the properties of dimers with HF/6-31G(d).

3.3. Electronic properties

For a better understanding of the electronic properties of carbazole-based molecules, we present in Table 3 the calculated HOMO and LUMO energies, gap (= LUMO-HOMO) and the absorption λmax of these carbazole derivatives.

Table 3
Calculated HOMO (eV), LUMO (eV) and Eg (eV) energies

	HOMO (eV)	LUMO (eV)	Eg (eV)
(cbzpy)n			
1	-4.842	-0.714	4.602
2	-4.493	-0.763	3.727
3	-4.416	-0.766	3.650
4	-4.376	-0.763	3.613
∞	-	-	3.300
(cbzF)n			
1	-5.023	-0.726	4.297
2	-4.626	-0.852	3.774
3	-4.548	-0.943	3.602
4	-4.513	-0.979	3.533
∞	-	-	3.270
(cbzT)n			
1	-5.218	-0.793	4.425
2	-4.887	-0.980	3.907
3	-4.813	-1.059	3.754
4	-4.779	-1.101	3.678
∞	-	-	3.370
(cbz-cbz)n			
1	-5.027	-0.663	4.364
2	-4.869	-0.666	4.203
3	-4.827	-0.665	4.162
4	-4.813	-0.661	4.152
∞	-	-	4.020

We note that calculations were performed in isolated state, while the properties were measured in the liquid state. The theoretical band gaps calculated for isolated chains are expected to be about 0.2 eV larger than condensed phase values [22]. When taking into consideration this difference, the B3LYP/6-31G* method has the particularity to reproduce gap values similar to those of the experience [23]. The B3LYP/6-31G* calculated HOMO, LUMO and Gap energies of the studied oligomers are shown in Fig 5.

There is systematical decrease of the electronic calculated Gap of (CbzCbz)n, (CbzT)n, (CbzPy)n and(CbzF)n oligomers as the number of chain length increased. These results indicate that the chain length of polymers have more effect on electronic transition.

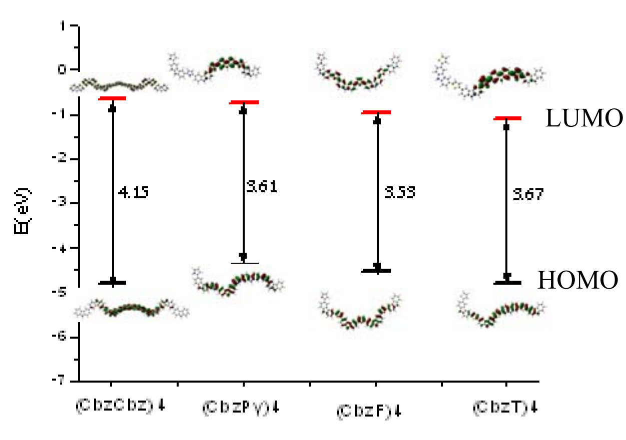


Fig. 5 Sketch of B3LYP/6-31G* calculated energies HOMO, LUMO levels of the studied oligomers

When we compare the various values of calculated Gap of the longest oligomer, we can noted that, the energy gaps in (CbzT)4 (3.67 eV) , (CzPy)4 (3.61 eV) and (CzF)4 (2.47 eV) are dramatically lower than that in (CbzCbz)4 (4.15 eV), suggesting that additive conjugated monomers allow modulate the band gaps and facilitate the decreasing of the energy gaps. These agree well the experimental results [23]. On the other hand, comparing the calculated λmax of (CbzCbz)n, (CbzT)n, (CbzPy)n and(CbzF)n oligomers, we can find the superiority of carbazole-based polymers and the influence of the introduction of charge carriers (Table 4).

Table 4

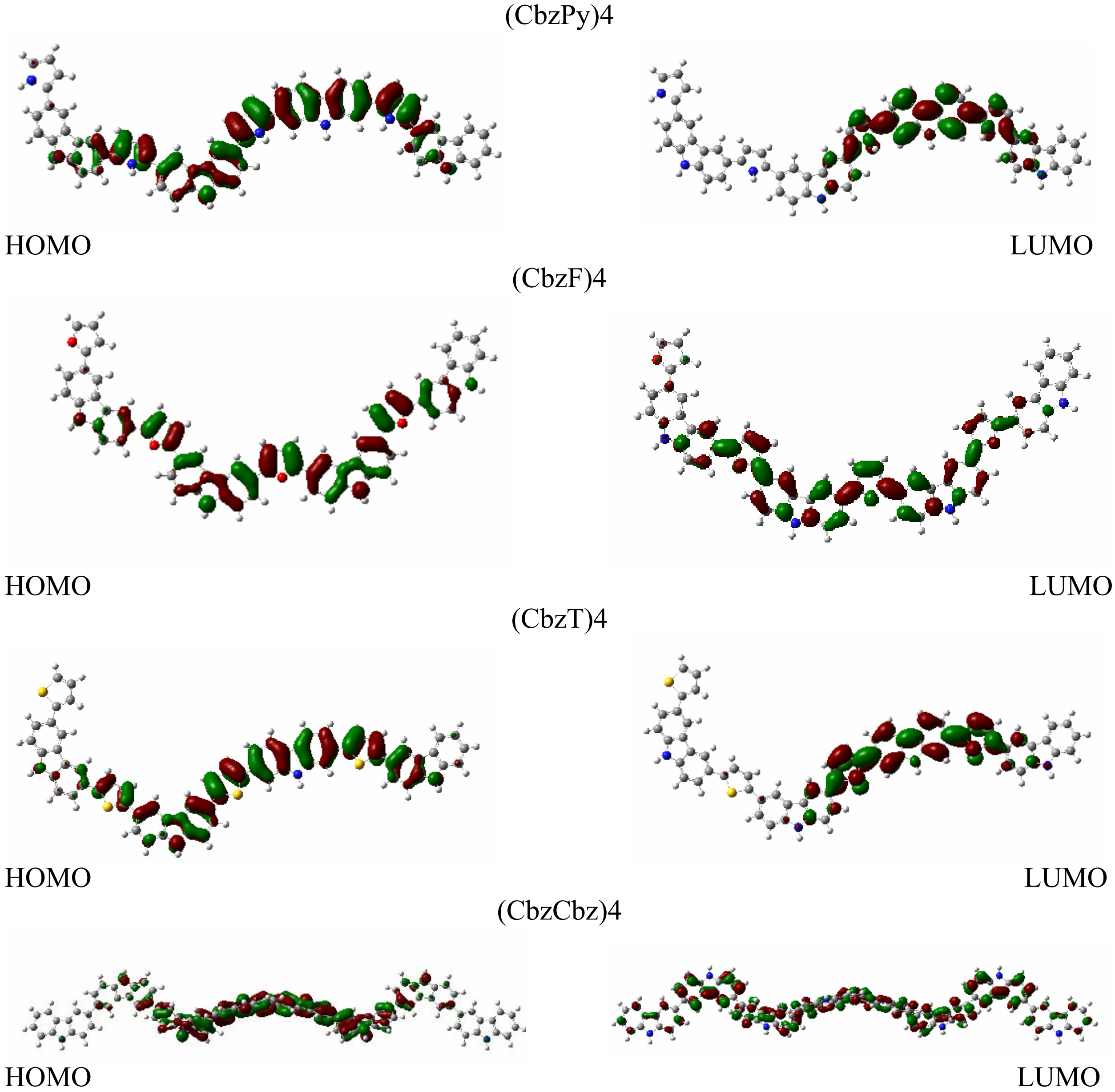
Calculated absorption λ_{max}(nm), transition energy (eV) and oscillation straight (f) for (CbzCbz)n, (CbzT)n, (CbzPy)n and(CbzF)n oligomers

	λ_{max} / nm	Et / eV	f
(cbzpy)n			
1	322.64	3.843	0.564
2	372.64	3.327	1.349
3	681.25	3.252	2.032
4	386.23	3.210	2.381
(cbzF)n			
1	338.23	3.666	0.606
2	384.19	3.227	1.698
3	411.01	3.017	2.068
4	416.64	2.975	2.472
(cbzT)n			
1	332.65	3.727	0.548
2	384.21	3.227	1.312
3	394.66	3.141	1.743
4	399.94	3.100	2.099
Exp*	419		
(cbz-cbz)n			
1	326.90	3.793	0.083
2	332.52	3.729	0.060
3	332.89	3.725	0.083
4	339.67		0.084
Exp*	380		

* λ_{max} in chloroform at room temperature in ref [23]

As in the case of the oscillator strength (f), the absorption wavelengths arising from S0/S1 electronic transition increase progressively with the conjugation lengths increasing. It is reasonable, since HOMO/LUMO transition is predominant in S0/S1 electronic transition and as analysis above that with the extending molecular size, the HOMO–LUMO gaps decrease. It is obvious that the absorption maximum of the longest oligomeric chains exhibit red-shift going from PCbz, PCbzT, PCbzPy and PCbzF, which is consistent with the estimation from the energy gap. Since the first allowed transitions are also the absorption maximum, they have the same variation trend.

It is important to announce that the values of the Eg found during our study are larger than those obtained by Yang *et al.* [11]. This is explained by the region-chemistry of coupling. Indeed, it was shown that in spite of the important reactivity of carbons 3 and 6 in the carbazole unit, the 2.7-substituted carbazole compounds have a high level of conjugaison than their 3.6-disubstituted counterparts [24]. On the other hand, it will be useful to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and the ability of electron hole transport.



(CbzPy)4

HOMO LUMO

(CbzF)4

HOMO LUMO

(CbzT)4

HOMO LUMO

(CbzCbz)4

HOMO LUMO

Fig. 6 The contour plots of HOMO and LUMO orbitals of (CbzCbz)4, (CbzT)4, (CbzPy)4 and(CbzF)4

As expected, the number of nodal planes is less for HOMO than LUMO, in general, as plotted in Fig. 6, the HOMO possesses an antibonding character between the consecutive subunits. On the other hand, the LUMO of all oligomers generally shows a bonding character between the subunits. From these figures, it can be observed how the frontier electronic levels of the carbazole monomer are affected by the incorporation of different monomer units.

As is usual in π-conjugated systems, with the increasing conjugation lengths the HOMO energies increase, whereas the LUMO energies decrease in all series. For the HOMO energies of the longest oligomer are (−4.77 eV) for (CbzT)4 , (−4.37 eV) for (CbzPy)4 and (−4.54 eV) for (CbzF)4, these values are slightly higher than that of (CbzCbz)4 (−4.81 eV), suggesting that the introduction of electron-donating conjugated unit will both slightly lift the HOMO of pristine polycarbazole

For of the LUMO levels, the LUMO of (CbzCbz)4 is generally stabilized by about 0.55 0.10 eV and 0.28 eV with respective to ((CbzT)4, −1.10 eV), ((Cbzpy)4, −0.76 eV) and ((CbzF)4, -0.943 eV) respectively. This result indicates that the introduction of charge carriers will both lower the LUMO energies. Since the LUMO shows inter-ring bonding character, the variation of torsional angles should have larger effects on LUMO. The decreasing in the dihedral angles between the two adjacent subunits induced by the presence of the electron-donating moiety thiophene, pyrrole or furrane should enhance the electron conjugation over the whole molecule and thus stabilize the LUMOs.

4. Conclusion

In this work, theoretical results are investigated in order, firstly, to describe a first step of polymerization mechanism of conjugated copolymers based on carbazole, and then to determine the geometric and electronic properties of these materials. Firstly, we have demonstrated that the coupling occurs primarily between the C4 of carbazole and C2 of the five membred aromatic rings (thiophene, furrane and pyrrole). Then, we have shown on the basis of DFT study of the geometric and electronic properties of several oligomers based on carbazole that the incorporation of different conjugated monomers in the carbazole backbone affects the physical properties. In addition to the modification of geometric parameters, the addition of monomers units to the carbazole conjugated system affects the electronic structure by lowering the energy band gap and raising conjugation length.

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