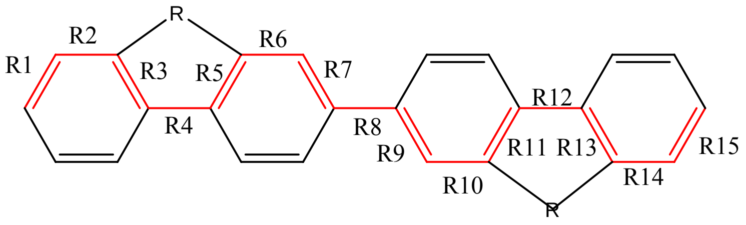
Understanding on Absorption and Fluorescence Electronic Transitions of Carbazole-Based Conducting Polymers

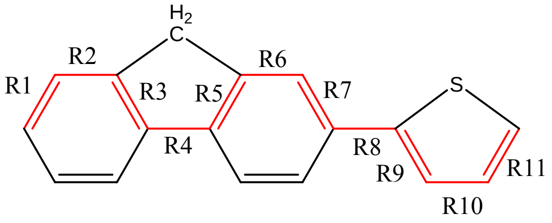
1. Ground and Excited States Structural Properties

The structures and the atomic numbering scheme of carbazole-dimer $(Cz)_2$, carbazole-co-fluorene (Cz-co-Fl) and carbazole-co-thiophene (Cz-co-Th) are depicted in Figure 40. The optimized structures by B3LYP/SVP, B3LYP/TZVP and RI-CC2/SVP methods of calculation of $(Cz)_2$, Cz-co-Fl and Cz-co-Th are reported in Table 21. In the ground state, the B3LYP/TZVP distances are slightly shorter (about 0.006) than the B3LYP/SVP ones. The RI-CC2 approach leads to practically the same bond distances as obtained with B3LYP/SVP. These qualitative trends are also reflected by the RI-CC2/SVP approach. Therefore, we can conclude that the B3LYP/SVP geometry optimization method is considered to be the most suitable approach to calculate the ground state geometry, and it was employed to investigate the details of the different states of electronic transitions.

In Table 21, it is found that the optimized structures of $(Cz)_2$, Cz-co-Fl and Cz-co-Th are nonplanar in their ground electronic states. The results of the optimized structures for the oligomeric of $(Cz)_2$ and Cz-co-Fl molecules show that the bond lengths and angles lead to only small changes. The dihedral angles of bicarbazole $(Cz)_2$ and carbazole-co-fluorene (Cz-co-Fl) between the monomer units are about 140 degrees and the bond distance of the fluorene monomer leads to a shortening of R8 bond by about 0.001 Å. Whereas, Cz-co-Th has more difference with structure of $(Cz)_2$. Because of Cz-copolymerized with thiophene unit has lower steric than six-membered aromatic ring monomers.



(a) Carbazole-dimer and carbazole-co-fluorene



(b) carbazole-co-thiophene

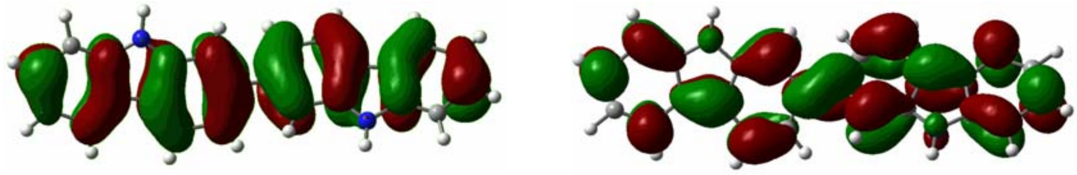
Figure 40 Structure and numbering scheme of (a) carbazole-dimer and carbazole-co-fluorene and (b) carbazole-co-thiophene.

For excited state geometry, it is well known that until now the standard for calculating excited-state equilibrium properties of larger molecules is the configuration interaction singles (CIS) method. However, because of the neglect of electron correlation, CIS results are not accurate enough in many applications. In this study, TD-B3LYP/SVP and TD-B3LYP/TZVP optimizations were performed in the lowest excited state as well.

The bonds R4, R6, R8, R10, R12 and R14 of $(Cz)_2$ and Cz-co-Fl molecules are shortened while bonds R1, R3, R5, R7, R9, R11, R13 and R15 are elongated. Bond distances of Cz-co-Th are similar to those of $(Cz)_2$ and Cz-co-Fl molecules. The bonds R4, R6, R8, and R10 are shortened while bonds R1, R3, R5, R7, R9, and R11 are elongated for the case of Cz-co-Th molecule. These results were shown that the electronic excitation leads to formation of a quinoide-type structure.

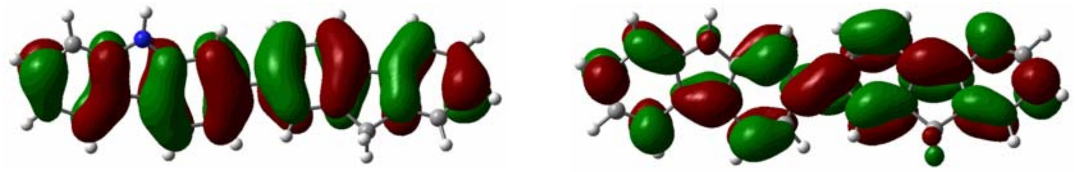
Table 21 Optimized geometries in electronic ground (GS) and lowest excited state (ES) for the (Cz)$_2$, Cz-co-Fl and Cz-co-Th molecules. All distances are in Å and torsional angles are in degree.

	GS			ES	
parameters	B3LYP/ SVP	B3LYP/ TZVP	RI-CC2/ SVP	TD-B3LYP/ SVP	TD-B3LYP/ TZVP
(Cz)$_2$: 1	1.396	1.389	1.400	1.404	1.397
2	1.400	1.393	1.404	1.395	1.387
3	1.425	1.418	1.426	1.440	1.433
4	1.451	1.447	1.447	1.425	1.419
5	1.423	1.416	1.426	1.440	1.434
6	1.398	1.390	1.402	1.379	1.371
7	1.405	1.397	1.407	1.445	1.439
8	1.488	1.484	1.481	1.441	1.433
9	1.405	1.397	1.407	1.445	1.439
10	1.398	1.390	1.402	1.379	1.371
11	1.423	1.416	1.427	1.440	1.434
12	1.451	1.447	1.447	1.425	1.419
13	1.425	1.418	1.426	1.440	1.433
14	1.400	1.393	1.404	1.395	1.387
15	1.396	1.389	1.400	1.404	1.397
Torsional	*140.5*	*140.1*	*139.9*	*170.2*	*167.3*
Cz-co-Fl: 1	1.396	1.389	1.399	1.402	1.396
2	1.400	1.393	1.404	1.396	1.388
3	1.425	1.418	1.427	1.441	1.434
4	1.451	1.447	1.445	1.425	1.419
5	1.423	1.416	1.426	1.437	1.431
6	1.398	1.390	1.402	1.380	1.372
7	1.406	1.398	1.406	1.446	1.441
8	1.487	1.483	1.478	1.441	1.433
9	1.412	1.405	1.413	1.444	1.439
10	1.391	1.383	1.396	1.373	1.365
11	1.413	1.406	1.416	1.437	1.431
12	1.470	1.466	1.466	1.437	1.432
13	1.414	1.407	1.416	1.431	1.424
14	1.394	1.386	1.398	1.388	1.380
15	1.403	1.396	1.405	1.409	1.402
Torsional	*142.1*	*141.9*	*136.3*	*170.7*	*168.5*
Cz-co-Th: 1	1.396	1.389	1.399	1.398	1.393
2	1.400	1.392	1.399	1.402	1.391
3	1.425	1.418	1.428	1.451	1.440
4	1.451	1.446	1.445	1.426	1.417
5	1.424	1.416	1.427	1.430	1.428
6	1.397	1.389	1.401	1.376	1.370
7	1.406	1.399	1.407	1.460	1.451
8	1.471	1.466	1.466	1.421	1.409
9	1.382	1.372	1.392	1.418	1.413
10	1.427	1.422	1.421	1.403	1.393
11	1.373	1.363	1.385	1.394	1.388
Torsional	*28.6*	*1.4*	*37.5*	*0.2*	*0.1*



HOMO LUMO

(a)



HOMO LUMO

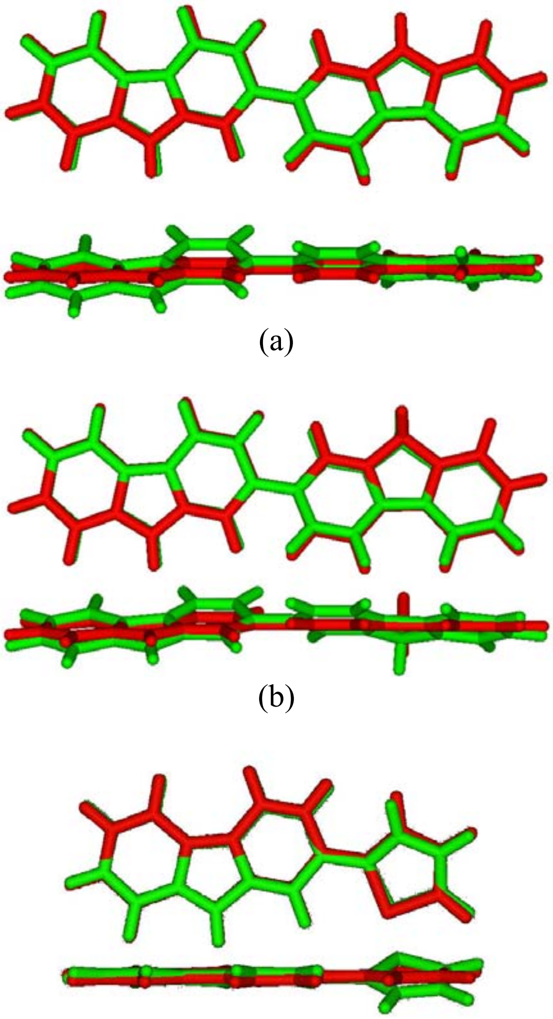
(b)

HOMO LUMO

(c)

Figure 41 HOMO and LUMO of $(Cz)_2$, (Cz-co-FL) and (Cz-co-Th) oligomers. Depicted are two isosurfaces of equal values but opposite sign.

We can predict the differences in the bond lengths between the ground (GS) and lowest singlet excited state (ES) from MO nodal patterns. Because the lowest singlet state corresponds to an excitation from the HOMO to the LUMO in all of the considered oligomers, we explore the bond-length variation by analyzing the HOMO and LUMO. By comparing Figure 40 and Figure 41, we can see that the HOMO has nodes across the R3, R5, R7, R9, R11 and R13 bonds in all molecules, but the LUMO is bonding in these regions. Therefore, one would expect a contraction of these bonds; the data in the Figure 41 shows that these bonds are in fact considerably shorter in the excited state. However, the bond length will increase when the bonding changes to antibonding. The dihedral angle between the two adjacent units shortened from 140° to 170° in $(Cz)_2$ and Cz-co-Fl molecules. Whereas the dihedral angle of Cz-co-Th shortened from 28° to nearly 0°. It is obvious that the excited structure has a strong coplanar tendency in all molecules; that is, the conjugation is better in the excited structure (see in Figure 41). In this Figure we can see that the geometries of excited state are more planar than ground state.



(a)

(b)

(c)

Figure 41 The comparing of optimized geometries in ground state (green color) and lowest excited state (red color) for the (a) carbazole-dimer, (b) carbazole-co-fluorene and (c) carbazole-co-thiophene molecules

2 Absorption and Fluorescence Transitions

For absorption transition, the results have calculated the energy of the first three singlet-singlet electronic transitions of the three carbazole-based oligomers using the TD-B3LYP/SVP method performed on B3LYP/SVP optimized geometries. It was found that TDDFT calculations provide the best overall agreement between the energies and the corresponding optical transitions obtained from the absorption 0–0 peaks measured in dichloromethane. Table 22 lists the absorption $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transition energies and oscillator strengths (*f*) computed at the TD-B3LYP/SVP//B3LYP/SVP level of theory.

From the data in Table 22, it was found that for Cz-dimer and Cz-co-Fl, the S_1 excitation corresponds mainly to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (H→L) as indicated by large oscillator strengths, f = 0.969 and 1.465, respectively. On the other hand, the S_2 and S_3 electronic transitions of each compound possess very small oscillator strengths and therefore, these can be considered as forbidden transitions. In contrast, for Cz-co-Th, the first S_1 electronic transition is almost forbidden (f = 0.025), while the S_2 electronic transition has a larger oscillator strength (f = 0.714). Moreover, the $S_0 \rightarrow S_1$ excitation corresponds mainly to the promotion of an electron from the highest occupied (HOMO) to lowest unoccupied (LUMO) delocalized p molecular orbitals. On the other hand, the $S_0 \rightarrow S_2$ electronic transition of each derivative possesses much larger oscillator strength. The excitation to the S_2 state is mainly described by the promotion of one electron from the HOMO-1 to the LUMO. Relying on the fact that the oscillator strength is proportional to the square of both the charge and the average distance over which the charge is delocalized (squared of the electronic transition moment), it is reasonable that the $S_0 \rightarrow S_2$ transition shows a large f value when it is delocalized throughout the whole molecule. Comparing to experimental excitation energies available for Cz-dimer, Cz-co-Fl and Cz-co-Th (3.85, 3.83 and 3.84 eV, respectively (Belletete, 2003 and 2004)), it can be seen that TD-B3LYP/SVP calculation give excellent prediction of the excitation energies for the S_1 transition (3.84, 3.79 and 3.89 eV, respectively).

For fluorescence transition, the optimized (relaxed) S_1 state geometries, the $S_1 \rightarrow S_0$ transition energies were derived by means of the TDDFT approach and the results are complied in Table 22. For $(Cz)_2$, Cz-co-Fl and Cz-co-Th, it is observed that, after relaxation (optimization) of the S_1 excited state, the energy of the first electronic transition significantly decreases (Tables 22). This transition should correspond to the emission energy. Indeed, the absorption of a photon excites the molecules to the S_1 Franck-Condon state, which should possess the ground state (S_0) geometry. After the excitation, the molecules should relax to their most stable geometry before the emission process could occur to reach the S_0 Franck-Condon state, which possess the S_1 relaxed geometry. As observed for excitation energies, emission energy becomes lower with increasing molecular length and with incorporation of extra alkyl chains. Moreover, TDDFT calculations give small Stokes shift, as a consequence of the similar geometries in the S_0 and S_1 states (Table 22). In order to characterize the fluorescence transitions, it is useful to examine the highest occupied (HOMO) and the lowest unoccupied (LUMO) orbitals. The excitation of the $S_0 \rightarrow S_1$ state is mainly described by the promotion of one electron from the HOMO to the LUMO as indicated by large oscillator strengths. On the other hand, the S_2 and S_3 electronic transitions of each compound possess very small oscillator strengths and therefore, these can be considered as forbidden transitions. Comparing to experimental available for Cz-dimer, Cz-co-Fl and Cz-co-Th (3.20, 3.20 and 3.21 eV, respectively), it can be seen that TD-B3LYP/SVP calculation gives a good prediction of the excitation energies for the S_1 transition (3.24, 3.20 and 3.35 eV, respectively). Therefore, the B3LYP/SVP calculation is considered to be the most suitable approach to estimate the absorption energy and fluorescence energy, and it is employed to investigate the details of the different states of electronic transition.

Table 22 Excitation energies (E_{ex}(eV)), oscillator strengths (*f*), and wave function composition for the lowest singlet electronic states of $(Cz)_2$, Cz-co-Fl and Cz-co-Th molecules computed by TD-B3LYP/SVP calculation.

Electronic transitions	E_{ex}	*f*	Expt.[a]	Wave function composition
	$(Cz)_2$			
Absorption				
$S_0 \rightarrow S_1$	3.84	0.969	3.85	H→L(88.4%), H-2→L(6.6%)
$S_0 \rightarrow S_2$	3.85	0.006	-	H-1→L(90.6%)
$S_0 \rightarrow S_3$	3.86	0.158	-	H-2→L(84.4%), H-1→L+1(7.8%)
Fluorescence				
$S_1 \rightarrow S_0$	3.24	1.465	3.20	H→L(97.5%)
$S_2 \rightarrow S_0$	3.47	0.000	-	H-1→L(90.4%)
$S_3 \rightarrow S_0$	3.58	0.047	-	H-2→L(93.5%)
	Cz-co-Fl			
Absorption				
$S_0 \rightarrow S_1$	3.79	1.004	3.83	H→L(82.9%), H-1→L(13.2%),
$S_0 \rightarrow S_2$	3.80	0.232	-	H-1→L(78.4%), H→L(14.6%),
$S_0 \rightarrow S_3$	4.33	0.006	-	H→L+1(54.4%), H→L+2(26.6%)
Fluorescence				
$S_1 \rightarrow S_0$	3.20	1.490	3.20	H→L(98.1%)
$S_2 \rightarrow S_0$	3.48	0.029	-	H-1→L(92.0%)
$S_3 \rightarrow S_0$	3.97	0.013	-	H→L+1(66.2%), H+2→L(16.5%)
	Cz-co-Th			
Absorption				
$S_0 \rightarrow S_1$	3.82	0.027	-	H-1→L(90.6%)
$S_0 \rightarrow S_2$	3.91	0.714	3.84	H→L(94.1%)
$S_0 \rightarrow S_3$	4.72	0.050	-	H→L+1(73.3%), H-2→L(12.5%)
Fluorescence				
$S_1 \rightarrow S_0$	3.36	0.758	3.21	H→L(89.3%), H-1→L(7.5%)
$S_2 \rightarrow S_0$	3.54	0.159	-	H-1→L(84.4%), H→L(7.7%)
$S_3 \rightarrow S_0$	4.31	0.016	-	H→L+1(74.1%), H-2→L(13.3%)

[a](Belletete *et al.*, 2004)