

Electronic, Structural, and Optical Properties of Conjugated Polymers Based on Carbazole, Fluorene, and Borafluorene

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We present a first-principles study of the structural, electronic, and optical properties of four conjugated polymers, poly(*p*-phenylene) (PPP), poly(2,7-fluorene) (PF), poly(2,7-carbazole) (PC), and poly(2,7-borafluorene) (PBF), and of their isolated constituent molecules. All the calculations were done using density-functional theory (DFT) with a plane-wave basis set, pseudopotentials, and local exchange-correlation energy. Resemblances in the atomic structures of the systems studied allow us to make correspondences between their wave functions near the Fermi energy. The dihedral angles of the polymers under consideration are all similar, varying between 26° and 27°. In agreement with experimental data, we find smaller energy gaps for carbazole and borafluorene compared to biphenyl and fluorene, which is due to differences in the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) wave functions. However, for the polymers, the experimental gap for PC was found to be almost the same as for PPP and PF. Our calculations explain this experimental observation which is attributed to a change in the ordering of the last two valence bands between carbazole and its polymer. We also find that the energy gap of PBF, which has not been synthesized yet, should be smaller than the minimum energy gaps of the other studied polymers by ≈ 0.5 eV. The polarizations for the lowest electronic transitions are presented from the analysis of the wave functions' symmetries. We find excellent agreement between the calculated and available experimental data, validating the predictions made.

1. Introduction

The use of conjugated polymers for the development of electronic devices has been, and still is, fruitful and varied. Many applications such as organic light emitting diodes^{1–3} and even solid state organic lasers⁴ use poly(*p*-phenylene) (PPP) or its derivatives. It is interesting to consider polymers with variations of the atomic structure of PPP. The polymers based on the molecules of fluorene, carbazole, and borafluorene all possess the sequence of bonded benzene rings characteristic of the geometry of PPP. The similarity in the atomic structure of the polymers and molecules suggests a resemblance in their electronic and optical properties.

First-principles methods, for which no experimental parameters are necessary, enable us to study systems where few or no data are available. The knowledge acquired about the electronic structure gives us information on the interesting optical properties of the polymers under consideration. Many theoretical studies were done on PPP^{5–7} and some on poly(2,7-fluorene).⁸ However, we are not aware of any theoretical work on poly(2,7-carbazole), which is a very recently synthesized polymer,⁹ and poly(2,7-borafluorene), which has not been synthesized yet. We propose a comparative study of electronic and structural properties of these systems.

The majority of the studies on polymers using first-principles methods consider in fact oligomers. The general strategy is the simulation of a number of oligomers of increasing lengths such that the properties of the polymers can be inferred by extrapolating the results. The use of first-principles methods formulated in plane-waves basis enables us to directly study periodic systems such as polymers.

The density-functional theory (DFT) with a local exchange-correlation energy is the first-principles method that we chose to use for this study. Even if many properties can be evaluated accurately with DFT, some other interesting values such as the minimum energy gaps disagree with the experimental data. The use of other methods, such as the hybrid functionals CASSCF or MP2, could solve some of these problems. However, these methods require much more computational resources and are rarely used in a periodic formulation. The DFT method enables us to study larger systems and to have a good idea of the properties of the new polymers.

The computational details are discussed in section 2. In section 3, we emphasize the similarity in the atomic structure of the molecules and polymers studied by comparing some characteristic bond lengths and dihedral angles. These systems are alike, so their electronic and optical properties should be comparable. The electronic properties of the molecules obtained from density-functional theory (DFT) and time dependent DFT (TDDFT) are presented in section 4. The results for the energy spectra, as well as for the lowest transitions and their polarization, are compared with the corresponding experimental data. In section 5, we report a comparative study of the electronic properties of the polymers among themselves, and also with their constituent molecules. The comparison in the energy ordering of the wave functions of both the polymers and the molecules shows the resemblances and differences between some of their electronic and optical properties. The band structures, wave functions, and lowest transitions' polarizations of the polymers under consideration are also presented.

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2. Methods

As mentioned in the Introduction, we treat the polymer as a one-dimensional periodic system. This approach allows us to simulate the polymer as if it was an infinite system in the most efficient way. It has the advantage that our results can readily be compared to measurement on long chain polymers while keeping the simulation at a reasonable computational cost. Essentially, we need only to define the unit cell of the system which in the case of a polymer is one monomer, and the length of this monomer is the length by which the unit cell is repeated. In doing so, we are able to make use of the translational symmetries of the polymer. This symmetry of the system allows us to write the wave functions in Bloch's form

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad (1)$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a periodic function over the unit cell and \mathbf{k} is the wave vector associated with this wave function and describes the phase difference from one periodic cell to the next. Since the periodicity of the polymer is only in one dimension for an isolated chain, the only significant component of \mathbf{k} is along the axis of the polymer.

Equivalently, we could regard this approach as if the polymer were simulated by making a cyclic ring with a large number of monomers. A cyclic ring will permit the assignation of the eigenstates to the irreducible representation of the cyclic group. The cyclic group has N different irreducible representations where N is the number of repeated monomers. In the periodic approach, we can consider that the wave vector has the label of the representation of the cyclic group. It is simply defined as $\mathbf{k} = (2\pi/N)n$ where n is an integer from $-N/2$ to $N/2$. Therefore, the wave vector is an additional quantum number to identify to wave function. From the above definition, the range of \mathbf{k} is easily seen to be from $-\pi/a$ to π/a , and in the limit of an infinite ring, \mathbf{k} can take any value within this range. This range of values is referred as the Brillouin zone. Because of time inversion symmetry, the eigenvalues at $-\mathbf{k}$ are identical to those at \mathbf{k} , so we only have to show the eigenvalues for the range from 0 to π/a knowing that the eigenvalues in the range from $-\pi/a$ to 0 are mirror images. In condensed matter, it is customary to call the plot of the eigenvalues versus \mathbf{k} vector a band structure since each eigenstate will draw a band on this plot. It is also customary to label the $\mathbf{k} = 0$ vector as Γ and the $\mathbf{k} = \pi/a$ vector as X . We will use this representation when we will address the eigenstates of the polymers considered in section 5.

All the calculations were done with the Abinit code¹⁰ which is based on DFT and uses a plane-wave basis set. The exchange-correlation energy is introduced through the local density approximation (LDA) with the Teter–Padé parametrization which reproduces the Ceperley–Alder interpolation formula.¹¹ The core electrons were included in pseudopotentials generated by the method of Trouiller and Martins.¹² Because periodic boundary conditions are used, convergence tests were performed on the unit cell volume to ensure that the properties studied were not affected by the periodic images. The ions' positions were relaxed, with residual forces of less than 0.004 Ry/bohr, as was the lattice constant in the case of calculations involving polymers. Numerical convergence of the total energy necessitated a number of plane waves in the basis set corresponding to an energy cutoff of 70 Ry. In the case of calculations on molecules, only the Γ -point is required to sample the Brillouin zone, whereas for calculations on polymers, shifted grids of four k -points were employed. These parameters ensure that the total energy of the systems was converged to better than 0.4 mRy/atom.

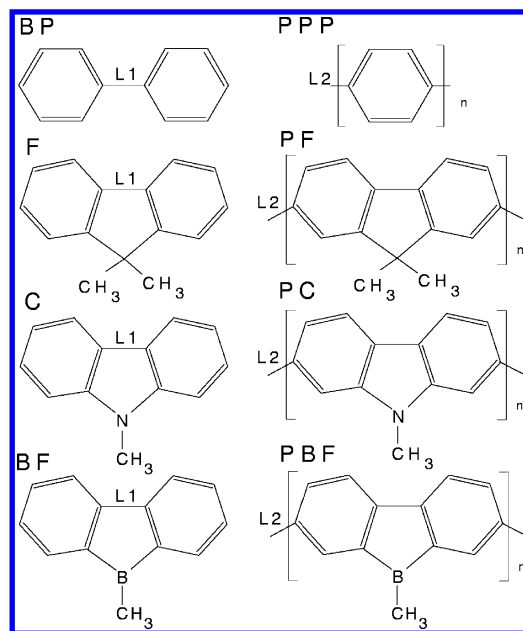


Figure 1. Atomic structures of the molecules and polymers.

The DFT methods are developed to study the ground state properties of systems. However, it is possible to consider excitation energies by evaluating the minimum energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The results obtained with this procedure are unfortunately in poor agreement with the experimental data.²⁴ Even if these gaps are not accurate, it is possible to use them to get information by comparing similar polymers or molecules.

The excitation energies of the molecules were computed using TDDFT¹³ with the Abinit code.¹⁰ Since this is a periodic code and uses a plane-wave basis, we had to use a supercell approach to make sure that the molecules are sufficiently separated such that the periodic images do not interact with each other. In the present applications, atoms on different molecules are separated by more than 10 Å. We used the method previously presented to calculate the density required by the TDDFT calculations. The excitation energies were then computed from linear response theory¹⁴ with the same LDA exchange-correlation energy. To converge sufficiently the lowest excitation energies, the number of excitation states, each represented by the combination of one valence and one conduction state, included in the calculations varied between 100 and 200 depending on the molecule. Tests were also done to ensure that the periodic images had little influence on the excitation energies. The parameters used ensure that the first excitation energies were converged to better than 0.1 eV.

3. Structural Properties

Since the properties of the polymers depend greatly on their constituent monomers, we begin by studying the properties of the four molecules that will form the repeated unit of the polymers under consideration. These molecules are biphenyl (BP), fluorene (F), carbazole (C), and boronfluorene (BF). Their atomic structures are depicted in Figure 1. All these molecules are composed of two benzene rings bonded together. In biphenyl, only one bond, labeled L1 in Figure 1, links the benzene rings, leaving a torsional degree of freedom. The dihedral angle, used to quantify the torsion, is defined as the angle between the planes formed by the two benzene rings. The ground state configuration of biphenyl has a dihedral angle of

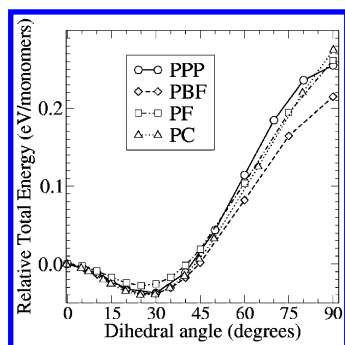


Figure 2. Dependence of the total energy on the dihedral angle for different polymers. The calculations were done with an LDA exchange-correlation functional. The zero energy corresponds to the energy of the planar polymers.

34° according to our calculations. This result is smaller but comparable to the angle of 44.6° obtained with MP2¹⁷ or to the experimental value observed in the vapor phase^{15,16} at $\approx 44^\circ$. The discrepancies in these results can be explained by the small energy difference obtained when varying the dihedral angle. In fact, the variation of the total energy evaluated between the relaxed and planar conformation is only 0.07 eV per inter-ring bond. For this reason, the calculated torsion angle will depend strongly on the choice of the exchange-correlation functional used.

Unlike biphenyl, the atomic structure of the other molecules is forced to be planar by additional bonds linking the benzene rings together through an added atom. In this study, the group of atoms added in these lateral chains is always a methyl.

The polymers studied, all of which are made of the previously stated molecules, are poly(*p*-phenylene) (PPP), poly(2,7-fluorene) (PF), poly(2,7-carbazole) (PC), and poly(2,7-borfluorene) (PBF). Their atomic structures are presented in Figure 1. The polymers all possess the same backbone structure made of a linear sequence of linked benzene rings. The bond linking the monomers, L2 in Figure 1, is a single bond connecting two benzene rings such as the bond L1 in biphenyl. The calculated length of this bond in biphenyl is 1.47 Å compare to 1.46 Å for the bond L2 in PPP and 1.47 Å for the corresponding bond in the other polymers.

The total energy of these polymers depends on the dihedral angle, which in this case describes the twisting between the monomers. We study this dependence by calculating the total energy for systems of fixed atomic coordinates describing different dihedral angles. As for the evaluation of the dihedral angle in biphenyl, the variations in energy involved are very small and the results will depend considerably on the choice of the exchange-correlation functional. Our results, obtained with an LDA functional, only give a trend for the dihedral angles. However, since the angles of the polymers are all obtained with the same functional, it gives us some qualitative information on their relative behavior. To obtain accurate dihedral angles, methods requiring more computational resources should be used. The torsional energy dependence on the dihedral angle is shown in Figure 2 with respect to the energy of the planar configuration. As seen from these results, we can affirm that the polymers studied have similar behaviors relative to this degree of freedom.

This can be explained by similar contributions of the two principal mechanisms defining the torsion angle in these polymers: steric hindrance and delocalization. Since the local geometry around the intermonomer bond (L2) is almost the same in each of the polymers considered, the steric hindrance, due to the electrostatic repulsion between the hydrogen atoms near this bond, contributes approximately equally in each case. The

TABLE 1: Calculated Torsion Angles and Total Energy Differences between the Planar and Relaxed Configurations for Biphenyl and the Polymers Considered^a

	BP	PPP	PF	PC	PBF
torsion angle (deg)	34	27	26	26	27
$\Delta E_{p,r}$ (eV)	0.07	0.04	0.03	0.04	0.04

^a The differences in energy are given per torsional degree of freedom (i.e., per bond which allows torsion).

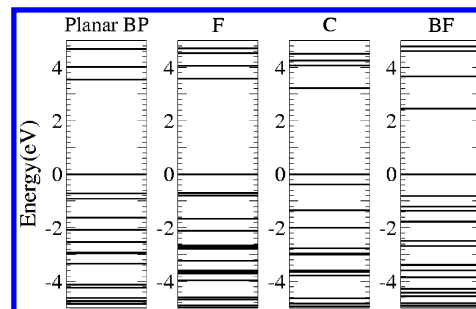


Figure 3. Calculated energy levels of biphenyl, fluorene, carbazole, and borfluorene. The zero energy is set to be the HOMO energy.

π orbital involved in the intermonomer bond, causing delocalization, works against the steric hindrance to favor a planar geometry. Since the effect of delocalization is also similar between the polymers studied, their dihedral angles should be similar.

The similarity is confirmed by the calculated dihedral angles that vary between 26° and 27° depending on the polymer (see Table 1).¹⁸ The experimental dihedral angle of these isolated polymers is unknown. However, the angles for crystalline oligomers of PPP¹⁹ should be comparable to the value for isolated PPP chains, the major difference probably due to the packing effects which tend to decrease the dihedral angle. The observed values between 20° and 30° are in agreement with our results. The total energy difference between the planar and relaxed polymers are also alike, varying between 0.03 and 0.04 eV per intermonomer bond. These values are below the 0.07 eV per inter-ring bond obtained for biphenyl. This difference is due to the stronger delocalization of the π orbitals in the polymers, which favors a more planar form. The dihedral angles of the polymers are also slightly below the angle of 34° computed for biphenyl because of the stronger delocalization of the polymers.

4. Molecular Electronic and Optical Properties

DFT calculations give access to the wave functions of the systems studied,²⁰ providing information about the electronic density associated with each energy level, the atomic orbitals involved, and the bonding and antibonding structures. The molecular orbitals that most determine the optical and electronic properties are those near the Fermi energy. The energy spectra near the Fermi level are shown in Figure 3 for the molecules considered, and the isosurfaces of their wave functions are shown in Figure 4. Even if the atomic structure of the molecules is different, a correspondence can be made between the wave functions involving the same atomic orbitals. For example, the HOMO of biphenyl (BP(H)) corresponds to the HOMO of fluorene (F(H)) and of borfluorene (BF(H)) and to the previous occupied molecular orbital (HOMO - 1) of carbazole (C(H - 1)).

The same comparison can be done for the LUMO of biphenyl (BP(L)) that is similar to the LUMO of fluorene (F(L)) and of carbazole (C(L)) and to the LUMO + 1 for borfluorene (BF-

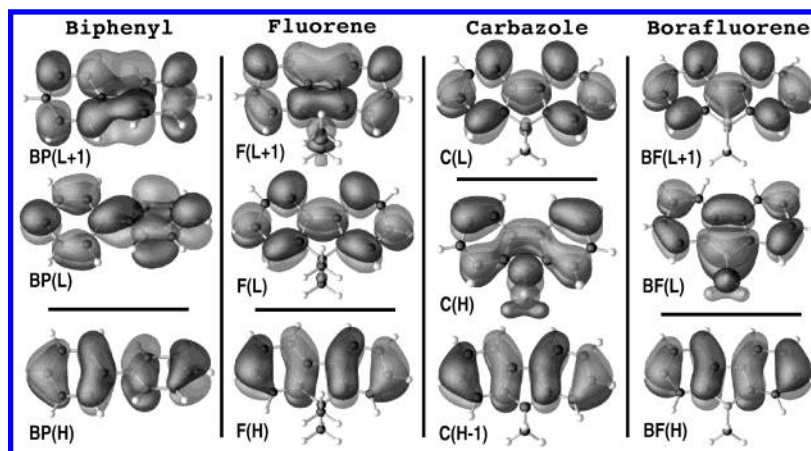


Figure 4. Calculated wave functions of biphenyl, fluorene, carbazole, and borafluorene. Depicted are two isosurfaces of equal values but opposite sign. The valence and conduction wave functions are, respectively, under and over the horizontal lines.

($L + 1$)). This suggests that fluorene and biphenyl should have similar characteristics for their lowest excitation since they have the same wave functions involved in that transition. Consequently, the different HOMO of carbazole and LUMO of borafluorene indicate different characteristics for the transitions of carbazole and borafluorene. The ordering and electronic configurations of the wave functions calculated agrees with previous theoretical studies for biphenyl,²¹ fluorene,²² and carbazole.²³ However, no previous study has been done on borafluorene.

It is a well-known fact that energy gaps computed with DFT using local exchange-correlation energy underestimate the experimental values,²⁴ and the same will be true for the molecules considered in this study. However, because the atomic structures of the molecules are alike and almost only carbon atoms are involved in their wave functions near the Fermi energy, the hypothesis can be made that the difference between the theoretical and experimental gaps will be similar for all molecules. Using this assumption, we find that the relative differences between the calculated gaps of molecules agree with the differences between their experimental gaps.

First-principles methods offer the opportunity to study particular configurations of a molecule. Therefore, it is possible to study the planar form of biphenyl, which is closer to the geometry of the other studied molecules. We also know from experiments that biphenyl is almost planar in the crystalline phase.^{25,26} The data on crystalline biphenyl can then be seen as an approximation of the observations on planar biphenyl. The difference of 0.29 eV between the calculated energy gap of relaxed and planar biphenyl agrees with the experimental difference of 0.26 eV found between the free and crystalline phases of biphenyl (Table 2). The HOMO–LUMO gap of planar biphenyl is of 3.55 eV. The energy differences between the wave functions of the other molecules that correspond to the HOMO and LUMO of biphenyl ($F(H) - F(L)$; $C(H - 1) - C(L)$; $BF(H) - BF(H + 1)$) is 3.58 eV for fluorene, 3.60 eV for carbazole, and 3.65 eV for borafluorene as shown in Figure 3. The similarity between these results shows the resemblance in the electronic structures of the molecules.

We stated previously that the HOMO wave functions of biphenyl and fluorene correspond to the HOMO $- 1$ wave function of carbazole. Still, the difference in energy between the HOMO $- 1$ and the LUMO of carbazole has nearly the same value as the energy gaps in fluorene and planar biphenyl. Thus, the different wave function for the HOMO of carbazole has the effect of decreasing the gap relative to planar biphenyl and fluorene. In fact, the difference of 0.36 eV found between

TABLE 2: Calculated and Experimental First Excitation Energies and Polarizations of Biphenyl, Fluorene, Carbazole, and Borafluorene

	excitation energy				polarization ^h	
	vapor (eV)	crystal (eV)	DFT (eV)	TDDFT (eV)	exptl	DFT
biphenyl	4.37 ^a	4.11 ^b	3.84	4.46	L ^b	L
fluorene	4.19 ^c	4.07 ^d –4.10 ^e	3.58	4.24	L ^{d,e}	L
carbazole	3.81 ^c	3.618 ^f	3.22	3.66	S ^f	S
borafluorene	3.02 ^g		2.46	2.78		L

^a Supersonic jet spectroscopy.¹⁶ ^b Absorption spectrum at 4.2 K.²⁷ ^c Absorption spectrum.³¹ ^d Absorption spectrum at 90 K.²⁹ ^e Absorption spectrum at 15 K.²⁸ ^f Absorption spectrum at 90 K.³⁰ ^g Absorption spectrum in solution.^{32,33} No data are available in either the vapor or crystalline phases. ^h The symbols for the polarization refer to the long (L) and the short (S) molecular axis.

the gaps of fluorene and carbazole with DFT agrees very well with the difference of 0.38 eV between the gaps obtained experimentally (Table 2). As for carbazole, the energy spectra of borafluorene has an added energy level in comparison to biphenyl and fluorene. The different wave function becomes the LUMO. The decrease in the gap, calculated to be 1.12 eV relative to fluorene and planar biphenyl, is even more important than for carbazole.

For molecules, it is also possible to calculate the excitation energies using TDDFT. The application of TDDFT gives quantitative results for the first singlet excitation energies that agree very well with the experimental data (Table 1), the biggest difference being ≈ 0.24 eV for borafluorene. Even if the difference is more important in that case, the general characteristics of the absorption spectra are well reproduced by TDDFT calculations. For instance, we calculated a difference in energy of 0.85 eV between the first and second excitations, in excellent agreement with the experimental data.³² These results show that TDDFT is a good predictive tool for the first excitation energy of molecules. However, this method cannot yet be used to study extended systems represented by periodic boundary conditions because of a too strong decrease in the asymptotic behavior of the functionals.³⁴

From the symmetry group of the molecules and the irreducible representations of the wave functions, it is possible to obtain the polarization of the allowed electric dipole transitions by analyzing the matrix elements, proportional to $|\langle \phi_v | \mathbf{r} | \phi_c \rangle|$, where \mathbf{r} is defined as the position operator, ϕ_v as a valence wave function and ϕ_c as a conduction wave function. The fluorene molecule has the C_{2v} symmetry group. If we neglect the methyl group of carbazole and borafluorene, they also possess the C_{2v}

symmetry group. The planar form of biphenyl satisfies the larger D_{2h} symmetry group. We can consider this geometry to study the polarization of biphenyl since it is almost planar in the crystalline phase used to obtain the polarization properties.^{25,26} The coordinate system is defined so that the yz plane is placed in the molecular plane with the y axis parallel to the long molecular axis. The z axis then corresponds to the axis of the C_2 rotation included in the C_{2v} group, and the x axis is perpendicular to the molecular plane.

To complete the analysis of the polarization, it is necessary to know which energy levels are involved in the lowest energy transitions. The results obtained with TDDFT show that for carbazole and borafluorene the pair HOMO–LUMO gives the major contribution, 91% and 97% of the transition, respectively. It is a good approximation to consider in these two cases that the lowest transition corresponds to the HOMO–LUMO transition.

The first excitation of carbazole hence involves the C(H) and C(L) wave functions which both possess the B_1 representation of the C_{2v} group.³⁵ The product of these representations is equivalent to A_1 which transforms as z . In that case, the only nonzero component of $|\langle\phi_v|\mathbf{r}|\phi_c\rangle|$ will be along the z axis. If it was the only contribution to the transition, the polarization would be exactly parallel to the short axis of the molecule. However, even if their contributions are small, the other pair of wave functions involved might not be polarized in that direction. It is therefore only possible to say that the lowest electric dipole transition of carbazole is polarized to a major extent in the short axis of the molecule according to our analysis, in agreement with the experimental observations presented in Table 2. For borafluorene, the representations involved are A_2 and B_1 , and their product transforms as y . The polarization is mainly along the long axis of the molecule, but as for carbazole, other minor contributions might give some component along the other axis.

For fluorene and biphenyl the analysis of the polarization is more complicated. According to the TDDFT results, the lowest energy transition is no longer formed by the HOMO–LUMO pair. For biphenyl the two significant contributions come from the pair (HOMO – 1)–LUMO and HOMO–(LUMO + 1) and add up for 99% of the transition. We must consider both these pairs in the analysis. For fluorene, the two pairs are (HOMO – 2)–LUMO and HOMO–(LUMO + 1), but they are responsible for only 78% of the transition. The analysis still can give the principal orientation of the polarization in the latter case.

Fortunately, all the transitions mentioned for fluorene and biphenyl are polarized in the same direction. For fluorene, both the HOMO and HOMO – 2 have the A_2 representation, while B_1 is the representation of both the LUMO and LUMO + 1. The two major parts of the transition transform as y which corresponds to a transition polarized along the long axis of the molecule. For biphenyl, the representations involved are in correspondence with those of fluorene but for the D_{2h} symmetry group. The analysis stays the same: the polarization is mainly oriented along the long axis of the molecule.

5. Electronic and Optical Properties of Polymers

As was the case for the molecules, the electronic and optical properties of the polymers can be compared by studying their wave functions. The geometry of the monomers and molecules being almost identical, there is a correspondence between their wave functions near the Fermi energy. To represent correctly the degree of freedom due to torsion, the periodic calculations must be done with a primitive cell including two monomers.

Because there are two monomers in the primitive cell, there are two polymer wave functions associated with each molecular

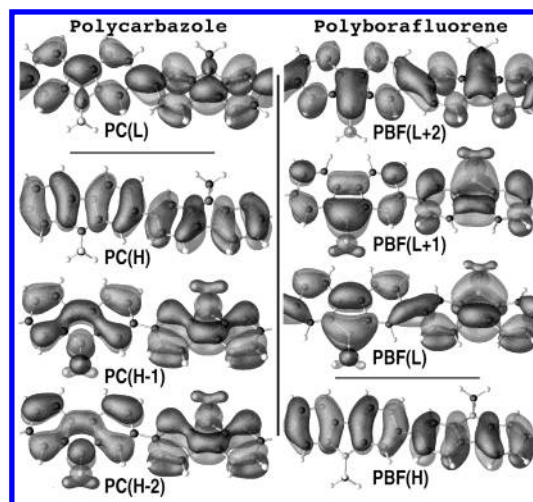


Figure 5. Calculated wave functions of poly(2,7-carbazole) (PC) and poly(2,7-borafluorene) (PBF). Depicted are two isosurfaces of equal values but opposite sign. The valence and conduction wave functions are, respectively, under and over the horizontal lines.

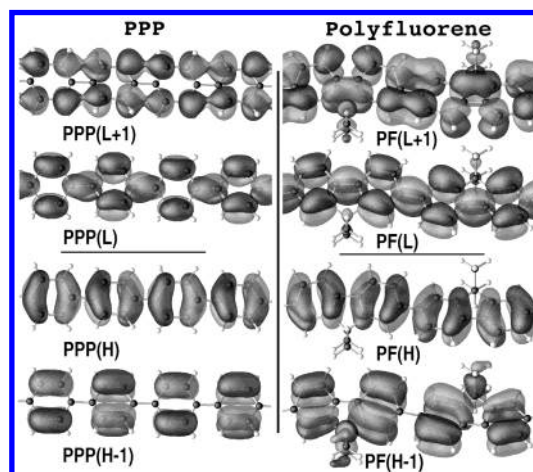


Figure 6. Calculated wave functions of poly(*p*-phenylene) (PPP) and poly(2,7-fluorene) (PF). Depicted are two isosurfaces of equal values but opposite sign. The valence and conduction wave functions are, respectively, under and over the horizontal lines.

wave function. The two polymer wave functions correspond to the combination of the same molecular wave function with either the bonding or antibonding configuration. The wave functions PC(H – 2) and PC(H – 1) of Figure 5 show the two possible combinations of the molecular orbital C(H) at the Γ -point, $\mathbf{k} = 0$, of the reciprocal space. The PC(H – 2) orbital represents the bonding form that is lower in energy than the antibonding form of the orbital PC(H – 1). This phase difference can influence the ordering of the polymers' bands relative to the molecular energy levels.

There is a correspondence between bands near the Fermi energy for the different polymers (Figures 5 and 6). The LUMOs at Γ are similar for PPP (PPP(L)), poly(2,7-fluorene) (PF(L)), and poly(2,7-carbazole) (PC(L)) but different for poly(2,7-borafluorene) (PBF(L)) as was the case for the molecules. However, the HOMOs, still at Γ , are now all similar (PPP(H), PF(H), PC(H), PBF(H)), in contrast with the molecular case where the HOMO of carbazole does not correspond to the other HOMOs. The HOMO of poly(2,7-carbazole) (PC(H)) is analogous to the HOMO – 1 (C(H – 1)) of the molecule, and the HOMO of carbazole (C(H)) corresponds to the HOMO – 1 and HOMO – 2 of poly(2,7-carbazole) (PC(H – 1), PC(H –

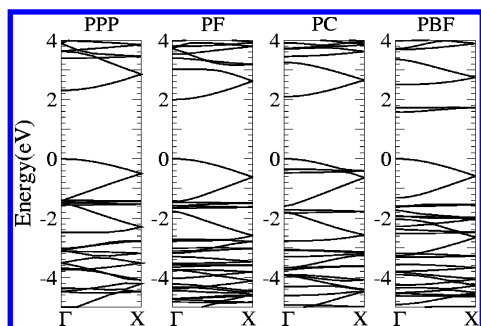


Figure 7. Calculated LDA band structure of PPP, poly(2,7-fluorene) (PF), poly(2,7-carbazole) (PC), and poly(2,7-boraffluorene) (PBF) with four benzene rings in the periodic cell. In each case, the zero energy is set at the maximum of the HOMO band.

2)). Hence, our calculations predict an inversion in the order of the last occupied bands in the polymer.

This change is explained by the dispersion in energy of the bands $PC(H-1)$ and $PC(H)$ which is characterized by the energy difference between the bonding and antibonding configurations of these bands. If the electronic weight of the carbon atoms involved in the intermonomer π bond is important ($PC(H)$), the energy difference between the bonding and antibonding configurations will be significant, causing a large dispersion. The difference in energy between the two mentioned configurations for the $PC(H)$ wave function is 1.6 eV, as can be seen in the band structure shown in Figure 7. However there is almost no electronic density on the intermonomer carbon atoms of the $PC(H-1)$ and $PC(H-2)$ bands, indicating a very weak dispersion of 0.2 eV between the bonding and antibonding configurations. Because of the dispersion's effects, the relative energies of the bands are modified, provoking an inversion in the order of the two last occupied bands of carbazole in the polymer at Γ , the reciprocal vector where the minimum energy gap is situated.

Since the intermonomer π bond is stronger for planar configuration, the dispersion is influenced by the dihedral angle. At a dihedral angle of 65° , the dispersion is not strong enough to invert the last two occupied bands. This is well above the relaxed angle of 26° . On the basis of this analysis, our results indicate quite different electronic properties between poly(2,7-carbazole) and carbazole. It is also possible to infer that even if the electronic properties of the molecules of carbazole and fluorene were different, those of their polymers should be similar.

For the molecules under consideration, the relative differences between the experimental and DFT-LDA energy gaps showed excellent agreement, even if there are discrepancies in the direct comparison of the gaps. The same disparities are observed for the polymers where DFT-LDA generally underestimates the experimental gaps.⁶ Since the atomic structure and wave functions of the polymers studied are essentially the same as for molecules, we can again assert that the DFT-LDA errors are similar for all the considered polymers, justifying the analysis of the relative differences in the energy gaps of the polymers. Moreover, the recent study of Rohlfing and Louie,³⁶ where they have done more sophisticated calculations on a simpler polymer, indicates that although the ground state wave functions obtained within DFT-LDA do not reproduce the excitation spectrum correctly, the wave functions themselves and their ordering are accurate. For this reason, we can use this information on the present polymers considered to deduce the properties of the polarization of the excitation transitions.

TABLE 3: Calculated and Experimental Energy Gaps and Polarizations of the First Excitation of PPP, poly(2,7-fluorene), poly(2,7-carbazole), and poly(2,7-boraffluorene)

	excitation energy		polarization ^f	
	exptl (eV)	DFT (eV)	exptl (eV)	DFT (eV)
PPP	3.27 ^a –3.43 ^b	2.3		L
poly(2,7-fluorene)	3.25 ^c –3.3 ^d	2.0	L ^e	L
poly(2,7-carbazole)	3.24 ^e	2.1		L
poly(2,7-boraffluorene)		1.6		L

^a Absorption spectra of films.³⁷ ^b Absorption spectra of films made of ≈ 16 unit chains.³⁸ ^c Absorption spectra in the liquid-crystalline state.³⁹ ^d Absorption spectra and polarization of films.⁴⁰ ^e Absorption spectra of films.³ ^f The symbol for the polarization refers to the polymer long (L) axis.

The HOMO and LUMO bands of PPP, poly(2,7-fluorene), and poly(2,7-carbazole) have the same electronic configuration, similar dependence on the reciprocal vector, and consequently similar dispersion (Figure 7). Their minimum energy gaps are nearly the same, always at the Γ -point, and vary between 2.0 and 2.3 eV (Table 3). The experimental results also show small differences for the gaps, observed between 3.2 and 3.5 eV for these polymers. As predicted from the analysis of the wave functions, poly(2,7-carbazole) and poly(2,7-fluorene) have similar gaps and dispersion unlike their constituent molecules, carbazole and fluorene, which differ by their electronic properties. The minimum energy gap of poly(2,7-boraffluorene), still at Γ , is considerably smaller in comparison with the other polymers because of the different LUMO. The two different bands ($PBF(L)$, $PBF(L+1)$) decrease the gap by 0.7 eV in comparison to PPP. This smaller value of the gap could be interesting for technological applications, but a very low dispersion of less than 0.2 eV in the first conduction band indicates a heavy effective mass for the conduction electrons. In comparison, the bandwidths for the LUMO of PPP are around 1.6 eV, and those of poly(2,7-fluorene) and poly(2,7-carbazole) are around 1.0 eV.

The dihedral angle of the polymers is smaller in their film or crystalline phase.¹⁹ If we neglect the torsion so that the short molecular axes in the plane of the monomers are aligned in order to define the short axis of the polymers correctly, it is possible to apply the analysis of symmetry done for molecules to the electric dipole transitions of the polymers. With this approximation, the polymers all possess the same symmetry group as their constituent molecule, if we neglect the methyl group of poly(2,7-carbazole) and poly(2,7-boraffluorene). The axes x , y , and z are defined as for the molecules. In opposition with the molecule, the wave functions involved in the lowest energy transition of the polymers are not known. We suppose that in each case it corresponds to the HOMO–LUMO transition.

We find that the representations involved in the lowest transition of PPP are the same as for the two pairs of wave functions of the planar biphenyl. The polarization should be along the axis of the polymer. The HOMO and LUMO wave functions of poly(2,7-fluorene) and poly(2,7-carbazole) are almost the same as for PPP. Consequently, the polarization of their lowest transition is in the polymer axis. This agrees with the experimental results found for poly(2,7-fluorene) (Table 1). For poly(2,7-boraffluorene), the LUMO wave function is different, but the representations involved are the same as for the other polymers. The symmetry of the bands then allows the lowest transition along the polymer axis.

6. Conclusion

Calculations of structural, electronic, and optical properties for isolated biphenyl, fluorene, carbazole, and borafluorene and for isolated conjugated polymers chains based on these molecules have been carried out with first-principles methods. The DFT and TDDFT schemes employed use a plane-wave basis set, pseudopotentials, and local exchange-correlation energy.

Available experimental data for torsion angles, differences between the energy gaps, and polarizations for the lowest electric dipole transitions show excellent agreement with our results. The calculated wave functions for biphenyl, fluorene, and carbazole are in accordance with other theoretical studies. Even though these molecules and polymers are made of different atoms, we find many common features, such as their wave functions. The good comparison of the calculated gap differences with the available data added to the similarity in the electronic structure of the systems support the estimate made for the gap of poly(2,7-borafluorene).

The electronic properties of PPP and poly(2,7-fluorene) were similar as was the case for their associated constituents, biphenyl and fluorene. Calculations showed that the electronic properties of carbazole are different from those of fluorene and biphenyl. In contrast, the dispersion effects in poly(2,7-carbazole) provoke an inversion of the last two occupied bands of carbazole in the polymer that establishes the similarity of its electronic properties to poly(2,7-fluorene) and PPP. All these analyses are in accordance with the experimental data.

As found experimentally, the calculated gap of borafluorene is smaller than the gap of carbazole. An even more important decrease should happen for the gap of its conjugated polymer, not yet synthesized, in comparison to poly(2,7-carbazole). A very weak dispersion of the first unoccupied band also differentiates poly(2,7-borafluorene) from the other polymers.

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