

Theoretical studies of the structures and optical properties of the bifluorene and its derivatives

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ABSTRACT: The ground and excited structures of the molecules are compared basis on the calculated by HF and CIS, respectively. The ionization potentials (IPs), electron affinities (EAs) and HOMO–LUMO gaps ($\Delta E_{\text{HOMO-LUMO}}$) of the oligomers are studied by the density functional theory (DFT) with B3LYP functional while the vertical excitation energies (E_g s) and the maximal absorption wavelength λ_{abs} of oligomers of bifluorene and its derivatives DFE, DFA, DFBT, FDBO, and FSCHD are studied employing the time dependent density functional theory (TD-DFT) and ZINDO. Compared with BF, the derivatives DFE, DFA, and DFBT are better conjugated, easier to give an electron or a hole, as well as get an electron or a hole. Their HOMO–LUMO gaps are narrower and they have lower vertical excitation energies. The absorption and emission spectra of them are red shifting. However, FDBO and FSCHD are in the other way round. It is important that FDBO and FSCHD are good blue emitters. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: bifluorene; structure; optical properties

INTRODUCTION

Much effort has been undertaken recently to develop flexible and tunable light-emitting diodes from conjugated polymers and oligomers.^{1–8} Organic polymers like oligomeric fluorenes, polyfluorenes, polythiophene, and poly(*p*-phenylene)vinylene pointed out to build new generations of electronic and photonic devices. Indeed, fluorenes and oligofluorenes are well known as highly fluorescent compounds.^{9–11} Fluorene-based oligomers and polymers have been intensively studied not only because they are blue-light-emitting materials, but also because they exhibit good thermal stability, high solubility and efficient fluorescence quantum yields in dilute solution as well as in the solid state. Extensive reviews of π -conjugated systems, including oligo- and polyfluorenes, have been published recently and provide comprehensive data concerning synthesis, characterization by a number of physical techniques, and applications.^{12–14} It is known that control of the band gap (E_g) of organic materials is fundamental for building devices and furthermore reducing its value is desired to enhance

the intrinsic charge carriers population and also to get a stabilization in both oxidized and reduced doped states. The oligofluorenes are generally regarded as the most promising candidates for blue OLEDs since they are processable materials and their properties can be easily chemically tailored.¹⁵ In this paper we report absorption and fluorescence spectra of bifluorene and its derivatives, seen in Fig. 1, as well as the correlation properties. The calculated values are compared with the attainable experimental data to test the theoretical methods. We discuss relation between the properties and the characteristic of the derivatives in succession.

CALCULATION DETAILS

The ground-state geometries of oligomers were fully optimized using the density functional theory (DFT), B3LYP/6-31G and HF/6-31G, as implemented in Gaussian 03. ZINDO and TD-DFT/B3LYP calculations of the vertical excitation energies and the maximal absorption wavelengths (λ_{abs}) were then performed at the optimized geometries of the ground states. All of IPs and EAs involved in this paper are the dispersion energies between the ions and molecules. The excited geometries were optimized by *ab initio* CIS/6-31G and the emission

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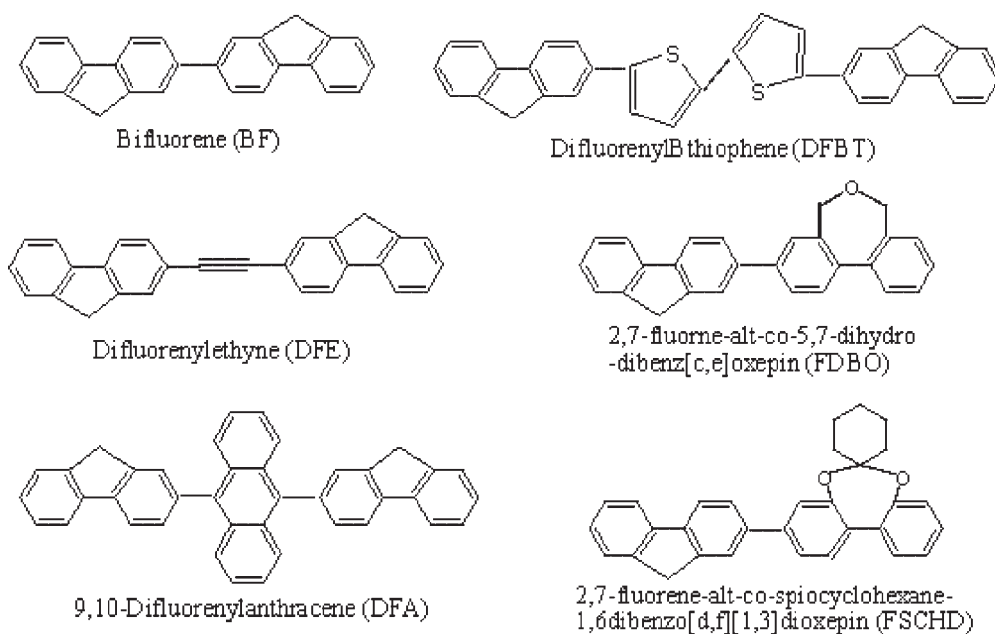


Figure 1. The sketch map of the structures of the bifluorenes

spectra were computed based on the excited geometries. All of IPs and EAs involved in this paper are the difference energies between the ions and molecules.

RESULTS AND DISCUSSION

Ground-state and excited-state geometry

In the Fig. 2 we can see the excited structures by CIS/6-31G and ground structures of these bifluorenes by HF/6-31G, except FDBO and FSCHD by 3–21 g functions, in view of the valid comparison. It is seen that all single bonds in BF, that is the bridge bond between two fluorene rings and three single bonds in each fluorene ring, are shorten in the excited structure than that in ground structure; While their neighbors, except R(A–A') and R(B–B'), are longer by some degree without broken the C_{2h} symmetry.

The middle bond R(1,1') of DFE is shortened in the excited state compared with the ground state. The single bond R(1,5), R(8,8) and the bond R(3',4'), R(3',8'), R(6',7'), R(5',6'), R(4',5') are shorter after excited, while R(2,3), R(2,3'), R(4,5), R(5,6), R(7,8), R(3,8) are longer.

The single bond on DFA, R(4,8) elongates its length after excited by about 0.005 nm. R(11,11'), R(13,12), R(13,12'), single bonds in fluorene rings, are longer in the excited structure than in ground. To the other round, the bonds R(1',1), R(3',3), R(5',5), R(7',7), R(2,3), R(5,6) in the anthracene and R(9,10), R(10,11), R(11,12), R(12,14), R(10',11'), R(9',10'), R(8',9'), R(8',14'), R(12',14'), R(11',12') in the fluorene rings are shorten by excited in some degree, while R(6,7), R(4,5), R(3,4), R(1,2) of anthracene ring and R(8,9), R(8,14) of the fluorene ring

are longer. Also the excited structure has the same symmetry, C_{2v} , to the ground structure.

It is shown that the comparisons of the excited and ground structure of DFBT. The single bonds R(1,1') and R(3,3') are shortened during the exciting, as well as the bonds R(1,2), R(2,3), R(4,5), and R(7',8), R(8,9), R(9,10), R(10,11), R(7',8'), R(7',12'), R(11',12'), R(10',11'), R(9',10'). R(3,4), R(1,5) of the thiophene rings and R(6,8), R(6,8'), R(9,9'), R(3',7), R(3',11) are longer in excited structure, compared with the ground structure.

From the comparison of excited and ground structure of FDBO, it is shown that single bonds of the five-membered ring and the seven-membered ring decrease the length after excited and the single bond R(7,7') shorten its length by 0.0046 nm. At the same time, R(2,3), R(2',3'), R(3,4), R(4,5), R(5,6), R(5',6'), R(1,2), R(1,2') and the bridge bond R(4',12) are shortened by a degree, as well as all bonds of the seven-membered ring except R(10,15). On the contrary, R(6,7), R(6',7'), R(2,7), R(2',7'), R(3',4'), R(4'5') increase their length to some extent. R(10,11), R(10'11'), R(12',13'), R(11',12'), R(13,14), R(13',14') are shortened but others in the phenyl ring which adjacent to the seven-membered ring are longer in the excited state than in the ground state.

In the excited structure of FSCHD, the single bonds R(1,2), R(1,2') and R(2,7), R(2',7'), R(6,7), R(6',7'), R(4',5'), R(3',4') increase the bonds length, as well as R(12,13), R(11,12), R(14,15), R(10,15), R(10',15'), R(8,18), R(8,18') in the twisty part. However, R(7,7'), R(15,15'), R(5,6), R(4,5), R(3,4), R(2,3), R(2',3'), R(5',6'), R(4',12), R(13,14), R(10,11), R(10',11'), R(11',12'), R(12',13'), R(13',14') are decreased the bonds length after excited and the bonds length of R(8,9) and R(8,9') shorten by 0.0023 and 0.0028 nm, respectively. Most of

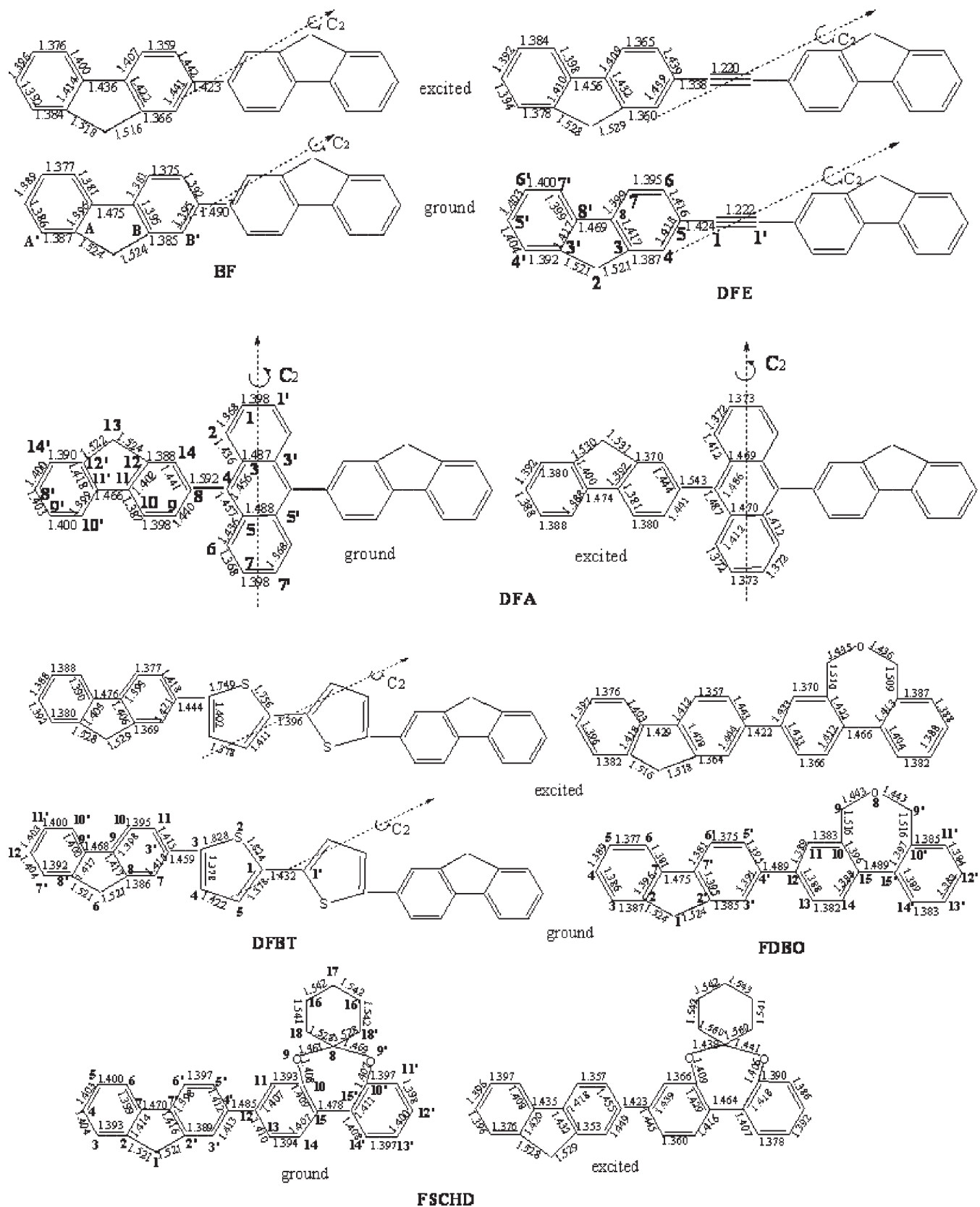


Figure 2. The excited and ground structure

the bonds of the saturated six-membered ring change slightly except that R(8,18) and R(8,18') increase the bonds length by 0.0032 nm after excited.

Compared with others, FDBO and FSCHD are dramatically twisted in the ground structures and they both tend to be plane in the excited structures, which also take place in other bifluorenes. As to FDBO, the dihedral angle $\Phi(2,7,7',2')$ is 0.142° in ground state but 0.0091° in the excited state, with the difference of 0.05° . Moreover, $\Phi(3',4',12,13)$ changed from 35.97° to 7.772° during the exciting, that is, the dihedral angle dwindled by 28.202° . $\Phi(10,15,15',10')$ from 42.65° X-ray datum is 43° to 39.148° dwindled by 3.5° . For FSCHD, $\Phi(2,7,7',2')$ reduced from 0.195° to 0.012° , $\Phi(3',4',12,13)$ from 34.885° to 2.163° , $\Phi(10,15,15',10')$ from 38.693° X-ray datum is 35° to 33.961° , respectively.

Characters of the frontier orbitals

It will be useful to examine the highest occupied orbitals (HOMO) and the lowest unoccupied orbitals (LUMO) for molecules to provide the framework for the excited state. Furthermore, the relative ordering of the occupied and virtual orbitals provides a reasonable qualitative indication of the excitation properties.¹⁶ The HOMOs and LUMOs of the molecules and their energies are shown in Fig. 3.

Usually, there are tense electronic clouds in the bonding bonds, while the density of the electronic clouds light in the antibonding bond. Therefore, when the bonding ones turn into antibonding ones the bond length will increase, *vice versa*. In Fig. 3, it is shown that the HOMO and LUMO of BF are localized predominantly on the phenyl rings. The bonds R(1,2) and R(3,3) are bonding in HOMO, while antibonding in LUMO. Compared with Fig. 2, it is obvious that they are longer in the excited structure than in the ground structure by 0.046×10^{-10} m and 0.050×10^{-10} m, respectively. The electronic clouds of HOMO centralize on the benzene rings and the triple bond in DFE, while the single bonds have little. However, the tense electronic clouds in the LUMO are the bridge bond between benzene rings and the single bond between the triple bond and fluorene rings. The HOMO and LUMO of DFA are focus on the anthracene ring, on the contrary, the tense of the electronic on the fluorine ring light. The bridge bonds between the anthracene ring and fluorine rings have tense electronic clouds at LUMO but light at HOMO. The electronic clouds of the frontier orbital of DFBT are mainly located in the thiophene rings and their neighbor benzene rings, while less located in the outboard benzene rings. At sulfur atom, there is less on HOMO but more on LUMO. For FDBO, the HOMO and LUMO are localized predominantly on the phenyl rings. There is antibonding between the bridge atoms and there is bonding between the bridge carbon atom and its conjoint atoms in the

same benzenes in the HOMO. On the contrary, there are bonding in the bridge single bond and the antibonding between the bridge atom and its neighbor in the same phenyl ring in the LUMO. The electronic cloud distributing in the frontier orbitals in benzene on the left side of the seven-membered ring is distributed less than that of other benzenes in FDBO. Furthermore, the seven-membered ring is bonding relaxation compared with the fluorene ring from the electronic cloud picture. The electronic cloud of FSCHD is mostly located on the benzenes but hardly on the saturated six-membered ring. The single bonds between the benzenes in fluorene ring and in the seven-membered ring are antibonding, as well as the bridge bond of the fluorene ring and the distorted part in HOMO, while bonding in LUMO. To DFE, DFA, and DFBT, their framework atoms are mostly on the same plane, so they have higher degree of conjugation, compared with FDBO and FSCHD.

Ionization potentials and electron affinities

Additional information derived from our calculations provides insight into the interrelationship of structure and electronic behavior, in particular the response of the molecule to the formation of a hole or the addition of an electron. Table 1 contains the ionization potentials (IPs), electron affinities (EAs), both vertical (*v*; at the geometry of the neutral molecule) and adiabatic (*a*; optimized structure for both the neutral and charged molecule), and extraction potentials (HEP and EEP for the hole and electron, respectively) that refer to the geometry of the ions.^{17,18}

It is easy to see that FDBO and FSCHD have higher IP(*v*)s and IP(*a*)s than BF, while DFE, DFA, and DFBT are lower than BF in IPs. The maximum data of HEP in these molecules is the value of BF. Also FDBO and FSCHD are slightly lower than BF by 0.01 and 0.02 eV. So FDBO and FSCHD are easier to give out electron than others in the table to do. FDBO and FSCHD have lower EAs energy compared with DFE, DFA, and DFBT, especially EA(*v*)s. BF has the lowest energy in EA(*v*) and EEP. In other words, DFE, DFA, and DFBT are prone to take in electron because of the high EAs. In all cases, the energy cost to create a hole in these molecules is about 6.5 eV, that to extract an electron from an anion requires ~ 1.3 eV. The EAs calculated here, namely, binding energy of the injected electron, cannot be simply obtained by experiment. These calculations are also used to estimate self-trapping energies of positive and negative charges in the materials. Indeed, the traps that characterize the electron transport in the material were identified as the states in which the injected electron is self-trapped in the individual molecules as a consequence of structural relaxation. Besides the IPs and EAs, we also report the data of the correct energy what in our scheme is the

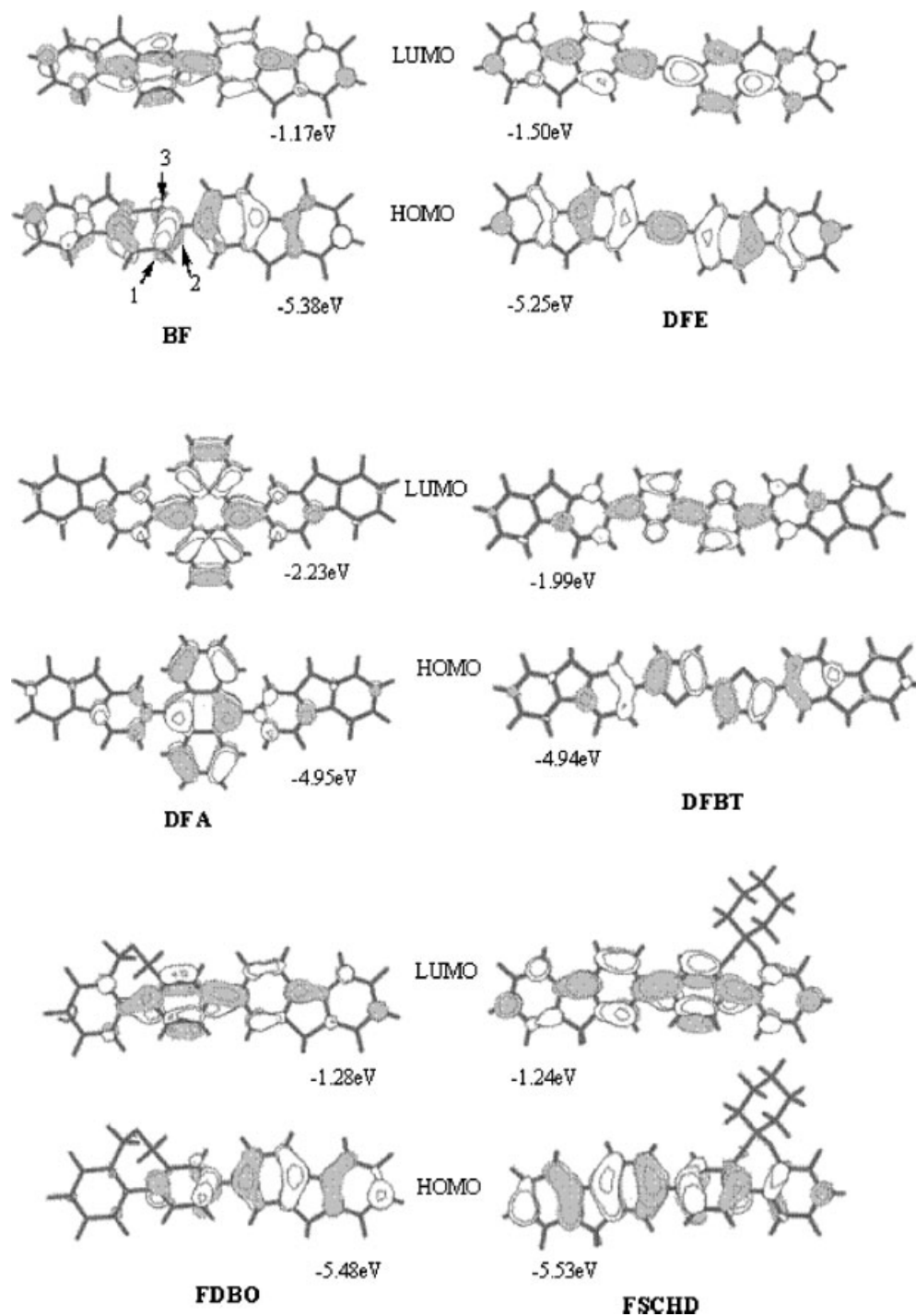


Figure 3. The HOMO and LUMO orbitals of the bifluorenes

energy gain of the excess electron due to structural relaxation, the difference $EA(a) - EA(v)$ and $IP(a) - IP(v)$, as the “small-polaron” stabilization energy, $SPE(e,h)$. Our values of $SPE(e)$ and $SPE(h)$ are $0.05 \sim 0.15$ eV and $0.10 \sim 0.20$ eV, respectively. FSCHD has both the highest $SPE(e)$ and $SPE(h)$ in the table, that is, its structure will change more dramatically than others when it traps an electron or a hole.

Energy gaps and vertical excitation energies

We can get energy gap from calculating the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Here, the HOMO–LUMO gaps are calculated by DFT, which function is widely accepted.^{19,20} But it is difficult to obtain the correct these data by experiment due to the

Table 1. Ionization potentials, electron affinities, extraction potentials, and extraction potentials for bifluorenes (in eV)

eV	IP (v)	IP (a)	HEP	EA (v)	EA (a)	EEP	SPE(h)	SPE(e)
BF	6.64	6.51	6.51	-0.07	0.10	0.27	0.13	0.17
DFE	6.45	6.36	6.26	0.33	0.44	0.54	0.09	0.10
DFA	6.06	5.98	5.88	1.12	1.22	1.30	0.08	0.10
DFBT	6.02	5.90	5.78	0.91	1.02	1.14	0.12	0.12
FDBO	6.88	6.83	6.49	0.05	0.24	0.44	0.05	0.19
FSCHD	6.77	6.62	6.48	0.03	0.23	0.42	0.15	0.20

The suffixes (v) and (a), respectively, indicate vertical and adiabatic values.

experimental condition limit, such as interchain interactions, solvent effects, and other environmental effects. The experiment energy gap is usually observed by two methods, the maximal wavelength in the spectra and the onset from CV-UV. They are valid when the lowest singlet excited state can be described by only one singly excited configuration in which an electron is promoted from HOMO to LUMO and the experimental condition limit can be neglected.^{21,22} The experimental data we quoted in the table are obtained from the onset of CV-UV. Interestingly, all molecules we studied here the maximal excitation is from HOMO to LUMO. The theoretical quantity for direct comparison with experimental energy gap should be the transition (or excitation) energy from the ground state to the first dipole-allowed excited state. In order to compare with the experiment data we also calculate the lowest excitation energies of the oligomers by Time-dependent DFT (TD-DFT) and ZINDO. The excitation energies calculated by TD-DFT with the current exchange-correlation functions are not reliable when the calculated excitation energies are higher than the negative of the HOMO energies ($-\epsilon_{\text{HOMO}}$).²³ In order to check the validity of the excitation energies by TD-DFT, we display $-\epsilon_{\text{HOMO}}$ in the table to convenient for comparisons.

In Table 2, it shows that in all cases the TD-DFT excitation energies are below the negative of HOMO energies and thus may be numerically reliable. The lowest excitation energy values by both ZINDO and TD-DFT are

better than the HOMO-LUMO gaps when the experimental energy gap values are taken into consideration, although they are all in good agreement with the experimental data. For BF and DFE, the deviations are about 0.1 eV by ZINDO and less than 0.05 eV by TD-DFT. The FDBO and FSCHD have bigger deviations between calculated and experimental data, 0.76 and 0.1 eV between ZINDO and experimental data, 0.52 and 0.22 eV between TD-DFT and experimental data. The experimental data of FDBO and FSCHD are obtained by their polymers. That is, the interchain interactions and conjugation of neighbor units should responsible for the error.^{24,25} Although, the orbital energy difference between HOMO and LUMO is only an approximate estimation to the transition energy since the transition energy also contains significant contributions from some two-electron integrals, it is desirable to obtain the useful information in the nature of the lowest singlet excited state when treating larger systems because of easiness.²⁶⁻²⁹ TD-DFT with the B3LYP functional is expected to be a relatively reliable tool for evaluating the excitation energies of low-lying excited states for small- and medium-sized molecules. But unlike HOMO-LUMO gap, TD-DFT is computationally expensive and difficult to treat even larger systems. As the table shown, data even by the reliable tool of calculation, TD-DFT, deviate from the experimental ones. These may attribute to several factors. First, the calculations have some approximate

Table 2. HOMO-LUMO gaps ($\Delta E_{\text{HOMO-LUMO}}$) and the lowest excitation energies (E_g) and the negative of HOMO energies ($-\epsilon_{\text{HOMO}}$) of the molecules

	$\Delta E_{\text{LUMO-HOMO}}$ eV	E_g/eV		$-\epsilon_{\text{HOMO}}$ eV	Expl. eV
		ZINDO	TD-DFT		
BF	4.21	3.79	3.87	5.38	3.56 ^a , 3.86 ^c
DFE	3.74	3.40	3.45	5.25	3.47 ^b
DFA	2.72	2.94	2.50	4.95	—
DFBT	2.95	2.85	2.70	4.94	3.46 ^c
FDBO	4.31	4.20	3.96	5.48	3.44 ^d
FSCHD	4.29	3.80	3.92	5.53	3.70 ^d

^a Solution in CH_3Cl , seen in Ref. [30].

^b Seen in Ref. [31].

^c Seen in Ref. [32].

^d Seen in Ref. [33].

^e Solution in cyclohexane, seen in Ref. [26].

corrections. Second, the predicted energy gaps are for isolated gas-phase molecules, while experimental data are measured in the condensed phase where environmental effect may be significant. Third, the experimental data are the average of multi-structures, while the calculated data are of only one structure. Additionally, the methods of calculation and experiment have fault in themselves. In all cases, both the lowest excitation energies, by ZINDO and TD-DFT, and the HOMO–LUMO gaps convey the same information that DFE, DFA, and DFBT have more narrow energy gaps than BF, while FDBO and FSCHD have broader energy gaps.

Absorption spectra

The absorption spectrums of these molecules are calculated on the basis of the optimized geometry. The data of absorption wavelengths (λ_{abs}) and oscillator strengths (f) by ZINDO and TD-DFT are shown in Table 3. In order to compared with the experimental data, it is listed the gainable observed values in the right tier.

As it is shown that their main electronic transitions are the $S_0 \rightarrow S_1$, that is, the maximal absorption of these molecules are mainly from HOMO to LUMO. Of the importance, oscillator strengths in the maximal absorption of these oligomers are strong enough. All the oscillator strengths are more than 0.7. The calculated maximal absorption wavelengths of DFE, DFA, and DFBT are

longer than that of BF, while that of FDBO is shorter than that of BF, both by ZINDO and TD-DFT. The maximal absorption wavelength of FSCHD is close to that of BF by ZINDO, which difference is only 0.2 nm, and shorter than that of it by TD-DFT. The calculated wavelengths of PCM(CHCl_3), which in solution of CHCl_3 , are shorter than those of TD-DFT. The experimental data in the table are from different sources. The experimental data of a, b, and c are observed by the same structures as the calculated molecules. However, the experimental data of d are observed by the polymers which unit structures are same to the calculated ones. Therefore, the data from d have some larger difference to the calculated data. Because of the conjugation the bigger of the molecules are the longer absorption wavelengths of the molecules. So the polymer has longer absorption wavelength than the oligomer when they have the same unit.

Emission spectra

On the basis of the option of CIS, ZINDO, and TD-DFT are used to calculate the emission spectra of these molecules. The maximal emission wavelengths (λ_{emi}) of these molecules are listed in the Table 4, as well as the oscillator strength (f) and the gained experimental emission wavelengths.

As the table shown, the emission properties are correlative with their absorption properties. The maximal

Table 3. Absorption wavelengths (λ_{abs} in nm), oscillator strengths (f) and electronic transitions computed at the ZINDO, TD-DFT methods and solution in CHCl_3

	Electronic transitions	ZINDO λ_{abs} /nm (f)	TD-DFT λ_{abs} /nm (f)	PCM (CHCl_3) λ_{abs} /nm (f)	Expl./nm
BF	$S_0 \rightarrow S_1$	325.8 (1.40)	320.4 (1.65)	308.1 (1.36)	347 ^a , 321 ^e
DFE	$S_0 \rightarrow S_1$	365.7 (1.35)	358.9 (1.94)	399.6 (1.70)	349 ^b
DFA	$S_0 \rightarrow S_1$	421.1 (1.07)	494.9 (0.93)	409.8 (1.16)	—
DFBT	$S_0 \rightarrow S_1$	435.8 (1.87)	460.0 (2.08)	381.5 (1.89)	350 ^c
FDBO	$S_0 \rightarrow S_1$	293.8 (0.79)	313.2 (1.28)	271.5 (1.05)	353 ^d
FSCHD	$S_0 \rightarrow S_1$	326.0 (0.77)	315.8 (1.29)	267.4 (1.16)	328 ^d

^a Solution in CH_2Cl_2 , seen in Ref. [30].

^b Seen in Ref. [31].

^c Seen in Ref. [32].

^d Seen in Ref. [33].

^e Solution in cyclohexane, seen in Ref. [26].

Table 4. Emission wavelengths (λ_{emi} in nm), oscillator strengths (f) computed at the ZINDO, TD-DFT methods

	ZINDO λ_{emi} /nm (f)	TD-DFT λ_{emi} /nm (f)	PCM (CHCl_3) λ_{emi} /nm (f)	Expl./nm
BF	374.4 (1.23)	374.3 (1.63)	330.1 (1.45)	390 ^a , 364 ^e
DFE	394.4 (1.46)	387.7 (2.07)	430.3 (1.83)	375 ^b
DFA	454.1 (1.17)	547.5 (0.97)	475.6 (1.17)	—
DFBT	481.9 (1.84)	496.3 (2.17)	435.7 (1.89)	—
FDBO	340.7 (1.59)	366.1 (1.54)	321.7 (1.37)	397 ^d
FSCHD	368.5 (1.56)	376.5 (1.58)	332.4 (1.41)	368 ^d

^a Solution in CH_2Cl_2 , seen in Ref. [30].

^b Solution in chloroform, seen in Ref. [31].

^d Polymer, seen in Ref. [33].

^e Solution in cyclohexane, seen in Ref. [26].

emission wavelengths of DFE, DFA, DFBT are longer than that of BF by both methods and the maximal emission wavelengths of FDBO, FSCHD are shorter than it by ZINDO. As far as to the TD-DFT is concerned, the maximal emission wavelength of FDBO is shorter than that of BF but that of FSCHD is slightly longer than that of BF. Also the calculated data are in good agreement with the experimental data. There are several reasons caused the difference between the experimental data and the calculated data. Besides the foregoing reasons, the compounds are in their gaseity when calculated but in liquid state or solid state when observed. The interaction of the molecules cannot be ignored in the liquid or solid. However, the theoretical methods can give experiments the guidance in the right direction because they take the necessary effects into account and this guidance is importance to the experimentation.

CONCLUSIONS

The excited structures of BF and its derivatives have a strong coplanar tendency than the ground structures. The conjugation chains are broken at the twisted parts in FDBO and FSCHD, while ethyne, anthracene and thiophene enhance the conjugation of bifluorene. Therefore, the twisted derivatives FDBO and FSCHD are easy to add an electron and difficult to ionize, while DFE, DFA, and DFBT are easy to ionize, compared with BF. To be precise, it results in broader energy gap and shorter maximal absorption and emission wavelengths in the spectra of FDBO and FSCHD than BF, that is, they are blue shifting. On the contrary, DFE, DFA, and DFBT are red shifting to some extent.

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REFERENCES

1. Horst W, Susanne S, Stefan J, Alexander VU, Axel HEM. *Macromolecules* 2003; **36**: 3374–3379.

2. Mushrush M, Facchetti A, Lefenfeld M, Katz HE, Marks TJ. *J. Am. Chem. Soc.* 2003; **125**: 9414–9423.
3. Bredas JL, Silbey R, Boudreaux DS, Chance RR. *J. Am. Chem. Soc.* 1983; **105**: 6555–6559.
4. Tavan P, Schulten K. *J. Chem. Phys.* 1986; **85**: 6602–6609.
5. Beljonne D, Shuai Z, Cornil J, dos Santos DA, Bredas JL. *J. Chem. Phys.* 1999; **32**: 267–276.
6. Lahti PM, Obrzut J, Karasz FE. *Macromolecules* 1987; **20**: 2023–2026.
7. Burrows HD, Seixas de Melo J, Serpa C, Arnaut LG, Miguel M da G, Monkman AP, Hamblett I, Navaratnam S. *J. Chem. Phys.* 2002; **285**: 3–11.
8. Scheinert S, Schlieffe W. *Synthetic metals* 2003; **139**: 501–509.
9. Winokur MJ, Slinker J, Huber DL. *Phys. Rev. B* 2003; **67**: 184106. (pp. 1–11).
10. Anne DB, Isabelle L, Ye T, Marie D, Serge B, Pierre B, Maxime R, Jimmy B, Mario L. *Chem. Mater.* 2000; **12**: 1931–1936.
11. Zeng G, Yu WL, Chua SJ, Huang W. *Macromolecules* 2002; **35**: 6907–6914.
12. James RS, Antoniadis H, Hueschen M, Leonard W, Niller H, Moon R, Roitman D, Stocking A. *Science* 1996; **273**: 884–888.
13. Wohlgenannt M, Tandon K, Mazumdar S, Ramasesha S, Vardeny ZV. *Lett. Nat.* 2001; **409**: 494–498.
14. Burrows PE, Shen Z, Bulovic V, McCarty DM, Forrest SR, Cronin JA, Thompson ME. *J. Appl. Phys.* 1996; **79**: 7991–8006.
15. Wong KT, Chien YY, Chen RT, Wang CF, Lin YT, Chiang HH, Hsieh PY, Wu CC, Chou CH, Su YO, Lee GH, Peng SM. *J. Am. Chem. Soc.* 2002; **124**: 11576–11577.
16. De Oliveira MA, Duarte HA, Pernaut JM, De Almeida WB. *J. Phys. Chem. A* 2000; **104**: 8256–8262.
17. Curioni A, Andreoni W. *IBM J. Res. Dev.* 2001; **45**: 101–113.
18. Curioni A, Boero M, Andreoni W. *Chem. Phys. Lett.* 1998; **294**: 263–271.
19. Hay JP. *J. Phys. Chem. A* 2002; **106**: 1634–1641.
20. Wang JF, Feng JK, Ren AM, Liu XD, Ma YG, Lu P, Zhang HX. *Macromolecules* 2004; **37**: 3451–3458.
21. Curioni A, Andreoni W, Treusch R, Himpfel FJ, Haskal E, Seidler P, Heske C, Kakar S, van Buuren T, Terminello LJ. *Appl. Phys. Lett.* 1998; **72**: 1575–1577.
22. Sung YH, Dong YK, Chung YK, Hoffmann R. *Macromolecules* 2001; **34**: 6474–6481.
23. Ma J, Li SH, Jiang Y-S. *Macromolecules* 2002; **35**: 1109–1115.
24. Wu CC, Liu TL, Hung WY, Lin YT, Wong RT, Chen YM, Chien YY. *J. Am. Chem. Soc.* 2003; **125**: 3710–3711.
25. Menzel H, Mowery MD, Cai M, Evans CE. *J. Phys. Chem. B* 1998; **102**: 9550–9556.
26. Belletete M, Beaupre S, Bouchard J, Blondin P, Leclerc M, Durocher G. *J. phys. Chem. B* 2000; **104**: 9118–9125.
27. Rogero C, Pascual JJ, Gomez-Herrero J, Baro AM. *J. Chem. Phys.* 2002; **116**: 832–836.
28. Wang JL, Wang GH, Zhao JJ. *Phys. Rev. B* 2001; **64**: 205411 (pp. 1–5).
29. Cabrera-Trujillo JM, Robles J. *Phys. Rev. B* 2001; **64**: 165408 (pp. 1–6).
30. Irene W, Estelle BA, Olivier S, Alain I, Baldeck PL. *J. Opt. A: Pure Appl. Opt.* 2002; **4**: S258–S260.
31. Lee SH, Nakamura T, Tsutsui T. *Org. Lett.* 2001; **3**(13): 2005–2007.
32. Meng H, Bao Z, Andrew JL, Wang BC, Anthony MM. *J. Am. Chem. Soc.* 2001; **123**: 9214–9215.
33. Lu P, Zhang HQ, Shen FZ, Yang B, Li D, Ma YG, Chen XF, Li JH, Tamai N. *Macromolecular Chem. Phys.* 2003; **204**(18): 2274–2280.