

## ARTICLE

# Theoretical Study on Optical Properties of Oligofluorenes

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We present theoretical investigations on structure-property correlations in fluorenone (FLO) and benzothiadiazole (BT) substituted oligofluorenes (OFLs) derived mainly from the chain morphology, thermal vibration and conjugated extent. Both the vertical absorptions and the vibrationally-resolved absorption and fluorescence spectra have been calculated by the combination of *ab initio* and time-dependent density functional theory. By properly taking into account of the anharmonic torsion potentials in the OFLs, we have reasonably reproduced the experimentally observed spectroscopic features. Both FLO and BT on-chain chemical defects acting as charge-trapping sites for singlet excitations, are responsible for long wave absorption and emission species, and thus alter the blue light-emitting properties of OFLs. As temperature decreases, the electronic spectral lineshapes of FLO-substituted oligomers become more structured. The lineshapes of BT-substituted oligomers are always smooth and featureless because of less low collective modes resonance. A more gentle excited potential energy surface of BT-mixed molecules can enhance electronic delocalization and achieve bigger red shifts.

**Key words:** Oligofluorene, Electronic spectroscopy, Time-dependent density functional theory, Vibrationally-resolved

## I. INTRODUCTION

Conjugated polymers, also known as conducting polymers, have recently drawn considerable attention in both academic and industrial researches, because of its potential application in light-emitting diodes (LED), field-effect transistors, and photovoltaic cells [1–5]. Many  $\pi$ -conjugated polymers, such as polyacetylene, poly(p-phenylenevinylene) (PPV) [6, 7], polythiophene [8], and poly(p-phenylene) (PPP) [9, 10] have been developed and well characterized in their chemical and physical properties. Among these materials, polyfluorenes (PFs) and its derivatives get much attention for their high solid-state fluorescence quantum yields, good thermal, and chemical stability, exceptional high solubility, and color tunability within entire visible spectrum [11–13].

Emission color tuning of PFs can be achieved by incorporating an electron-deficient or narrow-band-gap monomer, such as benzothiadiazole (BT), porphyrin, into the polymer backbone. When chromophore is introduced to PF backbone, high effective energy transfer from fluorene to chromophore is completed and various colors (green, red) can be implemented. For PFs' luminescence tunable ability, they are used widely to develop new, multicolor, light-emitting materials which

are needed for full color displays. PFs and its derivatives have so many gratifying property, however, there have nevertheless been reports on the appearance of the broad and featureless red-shift component in the luminescence spectra of a range of PF homo- and copolymers in thin film [14–18]. This component usually corresponds to the green, even yellow color, with the energy around 2.2–2.4 eV (520–560 nm) [17–21]. Previously, researchers consider this phenomenon are caused by the reorganization of polymer chain and subsequent in-chain species aggregates and excimers [22, 23]. Recent extensive studies showed that isolated fluorenone (FLO) defects on PF chains, which is called keto-defect, is responsible for the green emission band [24–26].

Many theoretical investigations on electronic spectrum of fluorene (FL) related oligomer (homo- and hetero-oligomer) or polymer have been reported [27–33]. But most of these have focused only on the vertical excitation or studied the absorption and emission properties at semiempirical Hamiltonian level (AM1 or INDO/s) without the effect of Duschinsky mixing of the normal coordinate vector of two electronic states [28]. To compare experimental spectroscopies directly, vibrationally-resolved absorption and emission spectra of oligomers are indispensable. A regularly used approach to calculate the vibronic spectra is to employ the multimode Brownian oscillator (BO) [34, 35], where the Huang-Rhys factor gained by theoretical Franck-Condon analysis is introduced to evaluate the vibronic coupling.

In this work, we chose the two typical chemi-

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cal substituents for FL-based materials, FLO and BT, to investigate their electronic structures and vibronic featured absorption and emission spectroscopic properties. During the spectral calculation, Franck-Condon (FC) approximation, Duschinsky rotation, and special anharmonicity are considered. A better and deeper interpretation of spectroscopic characteristics and structure-property relationship of heterocyclic substituted oligofluorenes (OFLs) is expected to be achieved.

## II. THEORY AND MODELS

For an easier comparison with the experiment and the obtaining vibrationally resolved absorption and fluorescence spectra, the nuclear motion has to be taken into account properly. It is well known that vibronic absorption across section  $\alpha(\omega)$  and emission across section  $\beta(\omega)$  are related to the dipole-dipole autocorrelation function as,

$$\alpha(\omega) \propto \omega \int_{-\infty}^{\infty} dt \exp(i\omega t - \gamma|t|) C_a(t) \quad (1)$$

$$\beta(\omega) \propto \omega^3 \int_{-\infty}^{\infty} dt \exp(-i\omega t - \gamma|t|) C_e(t) \quad (2)$$

$$C_{a(e)}(t) = \frac{Tr}{Tr \exp[-\beta H_{g(e)}]} \left\{ \exp[-\beta H_{g(e)}] \cdot \exp\left[\frac{iH_{g(e)}t}{\hbar}\right] \mu \exp\left[\frac{-iH_{e(g)}t}{\hbar}\right] \mu \right\} \quad (3)$$

where subscripts  $a$  and  $e$  correspond to absorption and emission respectively,  $\gamma$  represents the damping factor, and  $H_g$  and  $H_e$  are the nuclear Hamiltonians of electronic ground and excited states. The detailed solution of  $C_{a(e)}(t)$  with Green's function approach under Condon approximation can be found in Refs.[36–38]. Under harmonic potential approximation, we write the Hamiltonians as

$$H_g^h(q) = \frac{1}{2} \sum_i^n \omega_i^g (p_i^{g2} + q_i^{g2}) \quad (4)$$

$$H_e^h(q) = \frac{1}{2} \sum_i^n \omega_i^e (p_i^{e2} + q_i^{e2}) + \omega_{eg} \quad (5)$$

here  $\omega_{eg}$  is energy gap between two electronic states with the zero-point energy correction. The dimensionless nuclear coordinates  $\mathbf{q}_g$  and  $\mathbf{q}_e$  are related by

$$\mathbf{q}_e = S\mathbf{q}_g + \mathbf{D} \quad (6)$$

$\mathbf{D}$  is the displacement and  $S$  is the Duschinsky rotation matrix which allows the ground state and the excited state to have different coordinate systems. It is well known, strong electron-photon coupling in organic  $\pi$ -conjugated molecules gives rise to structure

distortions upon photo-excitation. Different Born-Oppenheimer potential energy surfaces (PES) are possessed by the ground and excited state, and the mirror image symmetry in the optical absorption/emission spectra of organic molecules break down [37–39]. As a result, simple Franck-Condon picture with full harmonic oscillator approximation becomes invalid and a method including both Duschinsky rotations and anharmonic effect needs to be exploited [39–43]. When the coupling among the harmonic and anharmonic oscillators is weak or these oscillators have different time scale, the Hamiltonians can be approximately divided into two parts

$$H = H^h + H^t \quad (7)$$

where  $H^h$  defines all the vibrational motion under harmonic approximation and the  $H^t$  represents the torsional motion. The Hamiltonians of two electronic states can be respectively written as,

$$H_g^t = -\frac{\hbar^2}{2I^t} \frac{\partial^2}{\partial^2 \phi} + V_g(\phi) \quad (8)$$

$$H_e^t = -\frac{\hbar^2}{2I^t} \frac{\partial^2}{\partial^2 \phi} + V_e(\phi) \quad (9)$$

here,  $\phi$  corresponds to the torsion angle,  $I^t$  is a reduced moment of inertia,  $V_g(\phi)$  and  $V_e(\phi)$  are the torsion PES of ground state and excited state respectively. In this case, the dipole correlation function can be factorized into

$$C_a(t) = C_a^t(t) C_a^h(t) \quad (10)$$

The  $C_a^h(t)$  and  $C_a^t(t)$  have been given in Refs.[36, 37].

All the parameters, such as equilibrium structure, energies, dipole moments and frequency analysis which is used to construct Hamiltonian and dipole correlation function are prepared by quantum chemistry calculation. The optimized structure of both ground and excited states, electronic excitation and PES of oligomer-models are performed on TURBOMOLE software package [44]. B3LYP exchange-correlation functional with a SV(P) basis set, which is comparable with the 6-31G(d) Gaussian basis set, is implemented. The calculated vibrational frequencies are scaled by a factor of 0.89. Only the molecular orbitals (MOs) of oligomers were calculated on the Gaussian 03 program package [45] at B3LYP functional using 6-31G(d) level.

## III. RESULT AND DISCUSSIONS

Two and three blocks of FLO and BT substituted OFLs (as seen in Fig.1), named as FLFLO/FLFLOFL and FLBT/FLBTFL, are chosen to study their influences on OFLs' optical properties. The visual optical excited states of those four molecules, which are

TABLE I Calculated vertical excited states' properties of FLFLO, FLFLOFL, FLBT, and FLBTFL molecules and compared with oligofluorenes. H denotes the HOMO and L denotes LUMO respectively.

	FLFLO				FLBT			(FL) <sub>2</sub>	
	E/eV	OS <sup>a</sup>	MO		E/eV	OS <sup>a</sup>	MO	Cal. [37, 38]	Exp. [46]
S <sub>1</sub>	2.81	0.10	H→L	S <sub>1</sub>	2.89	0.23	H→L	3.76	3.79
S <sub>4</sub>	3.80	0.67	H→L+1	S <sub>5</sub>	4.20	0.60	H→L+1		
	FLFLOFL				FLBTFL			(FL) <sub>3</sub>	
	E/eV	OS <sup>a</sup>	MO		E/eV	OS <sup>a</sup>	MO	Cal. [37, 38]	Exp. [46]
S <sub>1</sub>	2.65	0.25	H→L	S <sub>1</sub>	2.59	0.56	H→L	3.41	3.57
S <sub>4</sub>	3.53	1.40	H→L+1	S <sub>5</sub>	3.79	1.10	H→L+1		

<sup>a</sup> OS is oscillator strength.

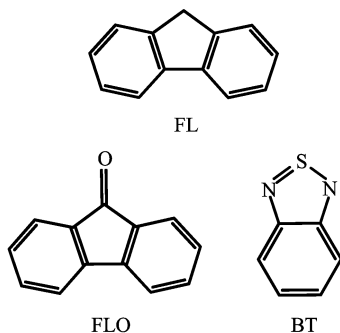


FIG. 1 Structure of fluorenes (FL), fluorenone (FLO), and benzothiadiazole (BT).

calculated by time-dependent density functional theory method, are listed in Table I. It is obvious that the lowest-lying singlet state is no more the sole main transition-allowed excited state in mixed OFLs among visible region, although it is always the fact in the pure (FL)<sub>n</sub>. The two excited states of FLFLO are 2.81 eV with 0.10 oscillator strength and 3.80 eV with 0.67 oscillator strength, respectively. Compared with FLFLO, a small red shift can be found in three block FLFLOFL, in which S<sub>1</sub> and S<sub>2</sub> excited energies are 2.65 and 3.35 eV with larger amplitudes 0.25 and 1.40, respectively. To understand the two states clearly, related frontier orbitals of molecules are investigated and the FLFLO's HOMO, LUMO, and LUMO+1 frontier orbitals are displayed in Fig.2. It is clear that the lower first excited state S<sub>1</sub>, which comes from HOMO to LUMO, is a fluorene ring π orbital to local FLO ring transition. Instead, the second state S<sub>2</sub>, mostly contributed by the HOMO to LUMO+1, is the normal fluorene ring π-π\* transition. By comparing excited energies with (FL)<sub>n</sub> [46], we can also identify the S<sub>2</sub> is the fluorene ring transition. For example, the second state S<sub>4</sub> with 3.79 eV of FLFLO is close to the calculated value 3.76 eV and experimental 3.79 eV. Through orbital analysis, it means the specie FLO is responsible for the long-wave absorption part. This matches up the others' experimental and theoretical results [24–26].

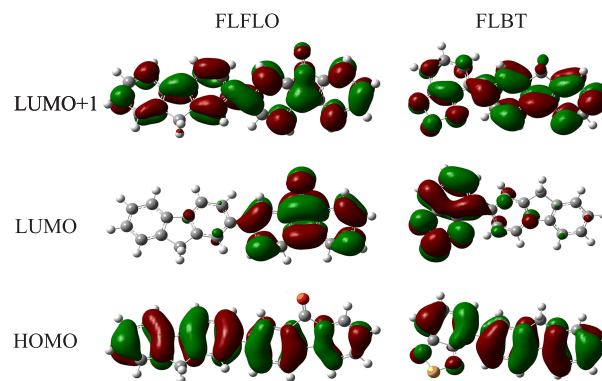


FIG. 2 Frontier orbitals of FLFLO and FLBT.

With regard to BT blends, similar absorption features can be found. The two states of FLBT are 2.89 eV (0.23 oscillator strength), 4.20 eV (0.60 oscillator strength), and those of FLBTFL are 2.59 eV (0.56 oscillator strength), 3.79 eV (1.10 oscillator strength), respectively. Combined with the orbital analysis in Fig.2, the lower excited state S<sub>1</sub> mainly comes from local BT specie and the other state comes from whole conjugated backbone chain. Besides, electronic structure calculation in Table I shows that the amplitudes of excited states S<sub>1</sub> of BT-doped blends are larger than those of FLO-mixed molecules. For example, the oscillator strength of FLFLO's S<sub>1</sub> is 0.10 and that of FLBT's is 0.23, the oscillator strength of FLFLOFL's S<sub>1</sub> is 0.25 and that of FLBTFL's is 0.56. This means that more complete energy transfer process occurs in BT-substituted molecules than that in FLO-containing ones. It can be regarded as one reason why people consider BT species as a nice color tuning candidate and FLO as an impurity.

Past theoretical studies of OFLs showed that the anharmonic effect of torsion degree between different blocks has significant impact on electronic spectra [38, 39]. For example, anharmonic torsional motion can lead to the breakdown of symmetrical feature between absorption and emission spectra, and therefore should be

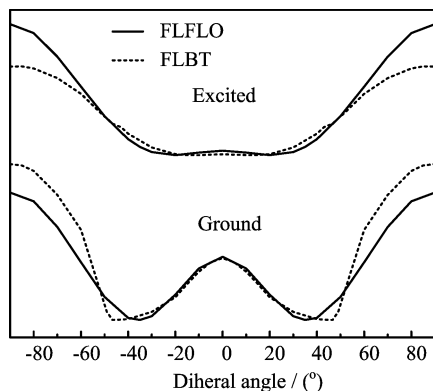


FIG. 3 Ground and excited torsional potential energy surface of FLFLO and FLBT molecules.

considered in simulating electronic spectra of fluorene-related oligomers. In this work, this special torsional motion is also been taken over in our vibrationally resolved spectra calculation.

Figure 3 shows the FLFLO's torsional PESs of both ground state and first excited state, which are scanned with TDDFT method. As shown in Fig.3, the two states show different PES shapes, with the ground state being a "W" type and the excited state being almost a "U" type. The energy minimal torsion angle of ground state is  $36.5^\circ$  and that of first excited state is  $20.9^\circ$ . The difference between the dihedral torsion angles of ground and excited state leads to significantly different Born-Oppenheimer potential energy curves and definitely influences the features of electronic spectra. The vibrationally resolved absorption and emission spectra of FLFLO, are shown in Fig.4. At room temperature 300 K, the emission spectrum has vibrational structure, while the absorption band curve is smooth and featureless. The maximum of absorption at 300 K is 2.71 eV and the two peaks of emission are 2.38 and 2.25 eV. The two peaks can be assigned to the 0-0 and 0-1 vibrational transition, respectively. The broadening of the absorption is explained by the presence of a distribution of site energies associated with different conjugated lengths [39, 47, 48]. When the temperature changes from 300 K to 110 K, both absorption and emission spectra become more structured. Emission band's vibrational transitions become sharp and the peaks' location almost has no change. While, absorption spectrum gets vibrational feature, with an additional shoulder peak 2.58 eV except the maximum 2.71 eV peak. The reason is when the temperature changes, thermal population of vibration level is redistributed relatively.

The calculated vibrationally resolved absorption ( $S_0 \rightarrow S_1$ ) and emission spectra of FLFLOFL are shown in Fig.5. At ambient temperature, the absorption band energy is 2.54 eV and remains the featureless structure, while the yellow-green emission exhibits well-resolved vibronic feature with bands at 2.05 and 2.17 eV. This long-wave absorption and green emission spectra data

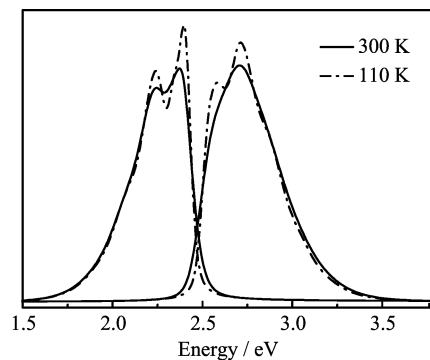


FIG. 4 Vibrationally resolved absorption and emission spectra of FLFLO at different temperature.

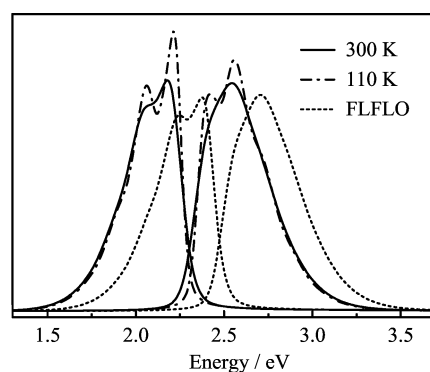


FIG. 5 Vibrationally resolved absorption and emission spectra of FLFLOFL at different temperature.

agree well with Wegner's experimental results [49]. In Wegner's work, the long-wave absorption energy band is around 2.71 eV and the two peaks of low-energy fluorescence spectrum are 2.08 and 2.12 eV at room temperature in chloroform (fluorene unit concentration is 0.01 mmol/L). This harmony between experiment and theoretical calculation further supports the responsibility of fluorenone unit in the low green-yellow emission of PFs. When the temperature changes to 110 K, the broad absorption band splits into 2.56 and 2.42 eV peaks similarly to FLFLO. From Fig.5, it can be seen that the whole spectra band have a red shift from FLFLO to FLFLOFL. For example, absorption maximum shifts 0.17 eV and the emission spectrum shifts 0.14 eV at 300 K, respectively. This is due to the larger  $\pi$ -conjugated length of three block than that of two block.

FLBT and FLBTFL molecules (see Fig.1) have been chosen to study the effect of BT on the absorption and fluorescence properties. The ground and first excited torsional PES of FLBT are shown in Fig.3. The PES shapes of FLBT are very similar to FLFLO, and the torsional angles of ground and excited states' minimal points are  $44.5^\circ$  and  $14.2^\circ$ , respectively. However, both absorption and the emission spectrum show featureless character of BT-substituted blends, which is different

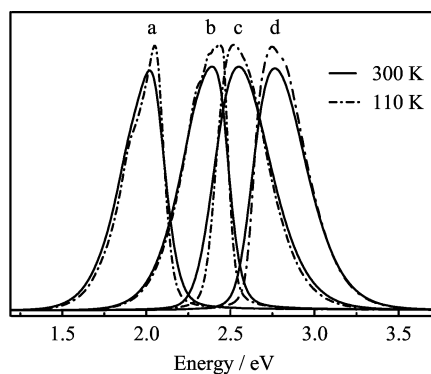


FIG. 6 Vibrationally resolved emission and absorption spectra of FLBTFL (a and c) and FLBT (b and d) at different temperature.

from keto defect containing models but is identical to experimental result [50].

Figure 6 shows vibrationally resolved emission and absorption spectra of FLBT and FLBTFL at different temperature. At 300 K, the maximum values of absorption and emission of FLBT are 2.76 and 2.39 eV, respectively. When the temperature changes from 300 K to 110 K, the spectra of FLBT retain nearly featureless with small fluctuation at the top. In conjugated molecules' spectral study [51], the vibrational structure of electronic spectra are mainly determined by several intramolecular collective modes, such as ring breathing/stretching modes [52, 53]. Here, except oxidation of "9-", the FLO ring keeps most FL ring structure character while the BT unit is totally another species. It means that the activated collective modes of FLO-mixed blends can find resonance more easily than those of BT-mixed blends. Difference of low collective modes between FLO- and BT-substituted OFLs can lead to different spectral lineshapes despite they have similar PES. It should be noted again that here is not contrary to the above PES's role. Without considering torsional anharmonic effect, totally mirror imaged and sharply vibrational structured absorption and emission spectra are obtained [38]. The spectral red shifts from FLBT to FLBTFL can also be found and they are larger than those from FLFLO and FLFLOFL. The average absorption and emission shift values of BT contained models are 0.21 and 0.38 eV at 300 K, respectively. For the perspective of chemical bond, the lone pair electrons in "9-" oxygen in FLO unit play the key role in electronic localization of  $S_1$  state. In BT unit, two nitrogen atoms aside sulfur atom can share the lone pair electrons of sulfur and this, in a manner, is beneficial to electronic delocalization. Besides, it can be seen in Fig.3 that the  $S_1$  equilibrium torsional angle of FLBT ( $14.2^\circ$ ) is smaller than that of FLFLO ( $20.9^\circ$ ). This better coplanarity of BT-substituted molecule definitely gives rise to larger conjugated length.

#### IV. CONCLUSION

We have studied the electronic structure and the optical properties of two important defects (FLO and BT) mixed OFLs through the combination of *ab initio* and time-dependent density functional theory. The theoretical calculation shows that both FLO and BT species in oligo- or poly- fluorene phase are responsible for long-wave absorption band and emission spectra. Theoretical vibrationally-resolved electronic spectra of oligomers agree well with experiments both in lineshape and peaks. We also do a systemic and detailed discussion on the relationship between structure and spectral properties. Due to different Born-Oppenheimer torsional potential energy surfaces of the ground and excited states of oligomers, mirror symmetric character between absorption and emission spectra breaks down. With the temperature changing from 300 K to 100 K, vibrational thermal population can be redistributed and result in more structured electronic spectra of FLFLO and FLFLOFL molecules. Due to the  $\pi$ -conjugated length increasing, obvious red shifts can be found from two units to three units both in FLO and BT blends. Excepting anharmonic torsion motion, harmonic low collective modes, which are determined by the whole molecular structure, can also influence spectral lineshape. That is why although FLBT has similar torsion PES to FLFLO, but more smoother and featureless electronic spectra are obtained. The good chain planarity of emission state of BT-substituted oligomers can enhance electronic delocalization and achieve larger red shift.

#### V. ACKNOWLEDGMENTS

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