

SAC–CI theoretical investigation on electronic structure of fluorene–thiophene oligomers

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Abstract

The excited states of the fluorene–thiophene compounds whose polymers are useful as a light-emitting diode were studied by SAC–CI method. The effect of the torsional angle on the excited state was examined for the FT and FMT monomers in details. The first three excited states were calculated for the conformers of several torsional angles. These three excited states were found to change their characters by varying the torsional angle from 0 to 90°. The accurate absorption spectra were simulated by taking the thermal average for the conformers of torsional angle from 0 to 90°. The absorption spectra of dimer and trimer were also calculated at the equilibrium structure. It was found that the oscillator strength of *S*1 states of the dimer and trimer was very high and the red shift occurs due to the π -conjugation. The equilibrium structures are planar for both FT and FMT, and the calculated emission energies are in consistent agreement with the experiment. The effect of applying the electric fields to these molecules was examined.

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1. Introduction

Recent research has shown that fluorene derivatives emerging as a very promising candidate to develop flexible and tunable light-emitting diode (LEDs) [1–5]. These polymers are soluble in organic solvents and their structure can be controlled to obtain the desired electro–optical properties. Previously, many theoretical works only investigated the structures and electronic properties in the ground state of these polymers or their segments. Therefore, theoretical information for the excited states of these molecules are limited. The RCIS/6-31G* calculations were performed to determine the structures of the *S*1 state and excitation energies of fluorene oligomers by Tirapattur et al. [6]. It is not only the structure of the excited state of

conjugated polymer which is an important investigation but the optical non-linearities and spectral characteristics are also a major problem in the research. The time-dependent density functional theory (TDDFT) is only one tool to determine the excitation energy, therefore, it was widely common used to investigate the excitation energy of the conjugated system [7–9]. Recently, the electronic spectra of thiophene–fluorene π -conjugated derivatives was interpreted using ZINDO/s by Lukes et al. [10]. In their work the influence of conformation effect on the electronic spectra was studied and Boltzman's distribution was taken into account to simulate the average electronic absorption spectra. Belletete et al. [11] reported the important work on the optical properties of monomers; they observed the absorption and fluorescence spectra of fluorene derivatives and characterized the excited states by ZINDO/s calculations. For the optical properties of 2-(9,9-dioctylfluorene-2-yl)thiophene and 2-(9,9-dioctylfluorene-2-yl)-3-methylthiophene, they concentrated on the vertical transition for the absorption spectra in their theoretical treatment. Many conjugated polymers, such as thiophene

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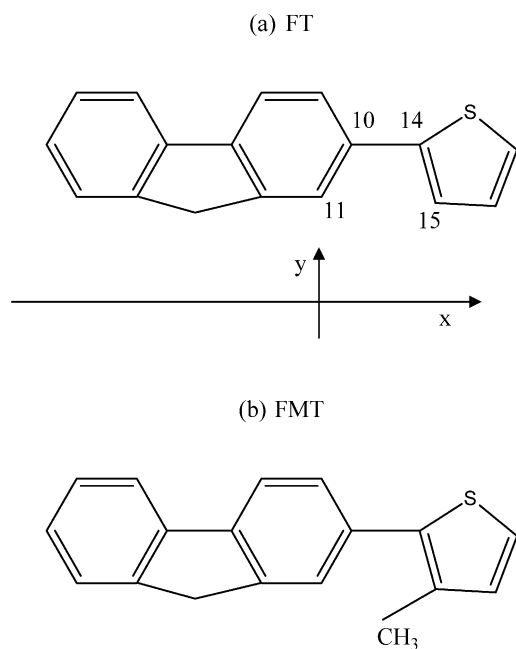


Fig. 1. Structures of FT and FMT.

and its cyano derivative oligomers and carbazole-based dydads were also studied by CIS [12,13].

In our previous work [14], structure and energetic properties of fluorene–thiophene copolymer was investigated, based on quantum chemical calculations. It was found that the energy gap of this copolymer as estimated by TDDFT (B3LYP/6-31G*) was in well agreement with experimental data. Unfortunately, there are no theoretical works that examined the effect of the torsional angle between the fluorene and thiophene units on the optical properties of these compounds, though the rotational barrier has been proven to be very small. Since the LUMO of FT has the bonding character between these units, it is anticipated that the excitation spectrum depends on the torsional angle. For this reason, reliable theoretical work is necessary to elucidate the mechanism of the optical properties.

The SAC (symmetry adapted cluster) [15]/SAC–CI (configuration interaction) method [16,17] has been established as a reliable and useful method for investigating a wide variety of molecular spectroscopy through many successful applications [18–26]. Recently, the SAC–CI method is emerging in the Gaussian03 [27] to be the useful method for studying molecular excited states. This method has clarified the details of the excited states of the π -conjugated system and transition metal complex [28]. In relation to the present study, the excitation spectrum of thiophene has been accurately investigated [26].

The purpose of this paper are to investigate the excited-state electronic structures and optical properties of 2-(fluorene-2-yl)thiophene (FT) and 2-(fluorene-2-yl)-3-methylthiophene (FMT) which are the model unit compounds of the light-emitting diodes by using SAC–CI

calculations. We studied the effect of torsional angle on the absorption spectra and gave the accurate absorption spectra of monomer, dimer and trimer. We also addressed the emission spectrum of monomer through the calculation and the accurate characterizations of the excited states are provided.

2. Computational details

Structures of FT and FMT studied in the present work are demonstrated in Fig. 1. The ground-state potential energy curves of FT and FMT monomers along the torsion angle (11–10–14–15) were calculated by using B3LYP/6-31G* [29,30] level. In the calculation, the torsional angle was changed by 15° , whereas all the other geometrical parameters were fixed.

The SAC–CI SD-R calculations were performed for the excitation spectra of FT and FMT at each torsional angle. Double zeta basis set of Huzinaga–Dunning [4s 2p/2s] were adopted [31,32]; the valence excited states were investigated and the consistent calculations up to trimer can be possible with this basis set. In the preliminary calculations, it was found that only the low lying three excited states are important for the first absorption peak in the experimental spectrum. Therefore, we present the results of these three excited states, although we also calculated higher excited states. In the SAC–CI calculation, 1s orbital of C and 1s, 2s, 2p orbitals of S were taken as the frozen core MOs and their counterparts were excluded from the active space. For monomer, the resultant SAC–CI active space consist of 43 occupied and 125 unoccupied MOs. For dimer and trimer, the active space is 129 occupied and 247 unoccupied MOs and 193 occupied MOs and 256 unoccupied MOs, respectively.

To reduce the computational requirements, the perturbation selection procedure was adopted [21]. LevelTwo accuracy in SAC–CI Gaussian03 [27] was adopted as follows. The threshold of the linked terms for the ground state was set to $\lambda g = 5.0 \times 10^{-6}$. The unlink terms were described as the product of the important linked terms whose SDCI coefficient were larger than 0.005. For excited state, the thresholds of the linked doubles were set to $\lambda e = 5.0 \times 10^{-7}$. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC–CI method were 0.05 and 0.0 for the *R* and *S* operators, respectively. For the trimer, LevelOne accuracy was adopted.

3. Results and discussion

3.1. Ground state of FT and FMT

The ground-state potential energy curves of FT and FMT monomers along the torsion angle were calculated by using B3LYP/6-31G* level. The calculations were performed for

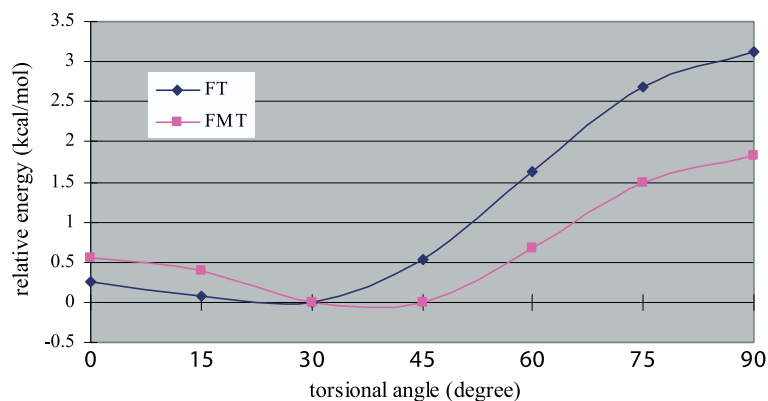


Fig. 2. The ground state potential energy curves of FT and FMT monomers.

the conformers of the torsional angle (11-10-14-15) $\theta=0-90^\circ$, with the grid of $\Delta\theta=15^\circ$, whereas all the other geometrical parameters were fixed. The potential energy curves of FT and FMT are shown in Fig. 2.

The torsional angle of the most stable conformation of FT was $\theta=27^\circ$. The energy barrier towards co-planar conformation was calculated to be only 0.25 kcal/mol, while the barrier to the perpendicular conformation was about

3.1 kcal/mol. This very low rotational energy barrier indicated that it allows a wide range of non-planar conformations at the room temperature. In the case of FMT, the torsional angle of the most stable conformation was $\theta=43^\circ$. The energy barrier to co-planar conformation is higher than that of FT due to the steric interaction between the methyl group and the hydrogen atom at the C₁₁ position of the fluorene unit. FMT is much more stable in the

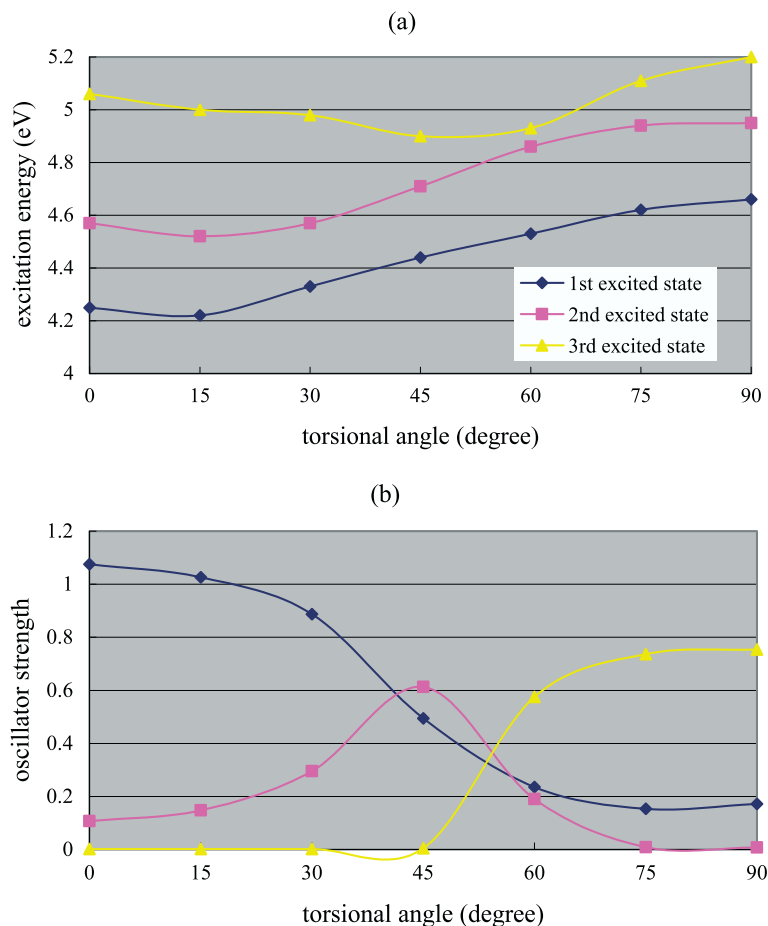


Fig. 3. The SAC-CI (a) excitation energy and (b) oscillator strength of FT versus torsional angle.

Table 1

The excitation energy (ΔE), oscillator strength, excitation character, and dipole moment of FT at torsional angle 0, 30, and 60°

Torsional angle	State	ΔE (eV)	Oscillator strength (f)	Excitation character	Dipole moment
0°	1st	4.25	1.08	0.91(H→L)	0.65
	2nd	4.56	0.11	0.73(H→nL)	0.58
	3rd	5.06	0.00	0.56(nH→L)	0.57
30°	1st	4.32	0.89	0.83(H→L)	0.65
	2nd	4.57	0.30	0.69(H→nL)	0.60
	3rd	4.98	0.00	0.56(nH→L)+0.50(nH→L+3)	0.58
60°	1st	4.53	0.24	0.62(H→nL)	0.64
	2nd	4.86	0.19	0.48(H-2→L)+0.47(H→L+3)	0.76
	3rd	4.93	0.58	0.68(H→L)	0.45

conformation of large angle than FT; the energy of the conformer of $\theta=90^\circ$ is 1.9 kcal/mol relative to the most stable conformer of $\theta=43^\circ$. Therefore, the energy barrier along the torsion angle is very small for both FT and FMT proving conformers of wide range of torsion angles can exist at room temperature as will be shown later.

3.2. Excited states; effect of torsional angle

The SAC-CI/D95 was used to calculate the first three excited states of FT, which are responsible for the first band observed experimentally. The excitation energy (ΔE) and the oscillator strength (f) of FT as the function of torsional angle are shown in Fig. 3. Excitation energy, oscillator strength, and excitation characters of these three excited states for the conformer of 0, 30 and 60° are summarized in Table 1.

The present calculation shows that the excitation energies of 1st and 2nd excited states increase when the planarity between fluorene unit and thiophene unit reduces. It was also found that the excitation character of the excited states of the FT depend on the torsional angle, for instance, the S1 state of FT at torsional angle 0° is characterized as the excitation from HOMO to LUMO, while the S1 state at torsional angle 90° is from HOMO to next LUMO. The

avoided crossing occurs between the 1st and 3rd states in the region of $\theta=45-60^\circ$ as also seen in the oscillator strength of Fig. 3(b). Namely, the excitation characters are represented as follows;

	Torsional angle 0°	Torsional angle 90°
1st excited state	H→L	H→nL
2nd excited state	H→nL	H-2→L
3rd excited state	nH→nL	H→L

From the oscillator strength and the excitation character of the excited states, it can be concluded that the excitation of HOMO–LUMO mainly contributes to the absorption of the 1st peak of the FT and FMT, however, it was found that the excitation to the higher states does not contribute to the 1st peak. The next higher excited states occur higher than 5.5 eV with small oscillator strength, whereas the first absorption bands of FT and FMT are centered at 3.09 eV and 4.04 eV, respectively [11].

The SECI (single excitation configuration interaction) results of FT are shown in Fig. 4 for comparison. The SECI excitation energies of these three excited states were calculated to be much higher than those of the SAC-CI method. Significantly, the SECI gave wrong picture for these excited states. The excitation character of the S1 state is not dependent on the torsional angle; it is characterized as

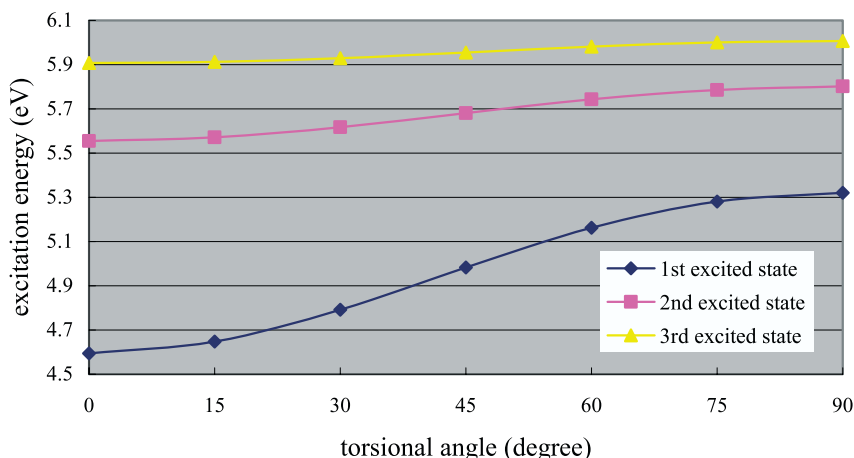


Fig. 4. The SECI excitation energy of FT monomer versus torsional angle.

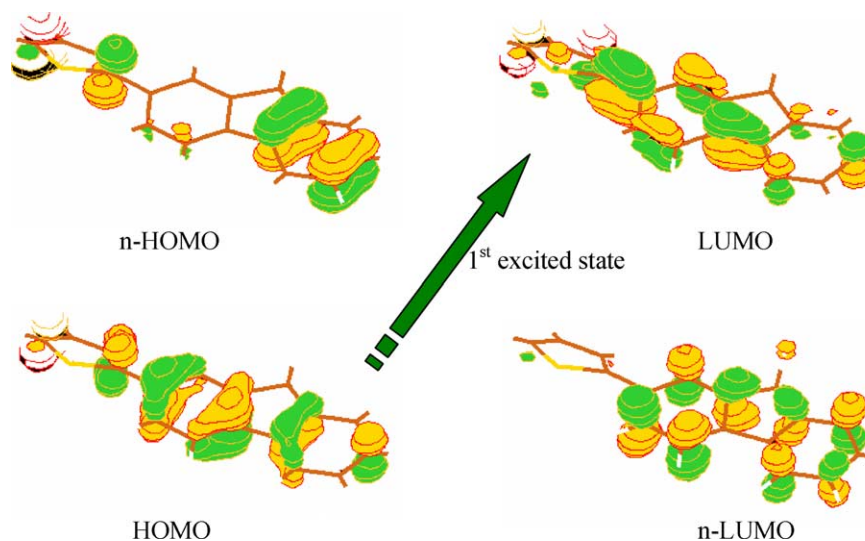


Fig. 5. Schematic representation of MOs of FT monomer ($\theta=30^\circ$).

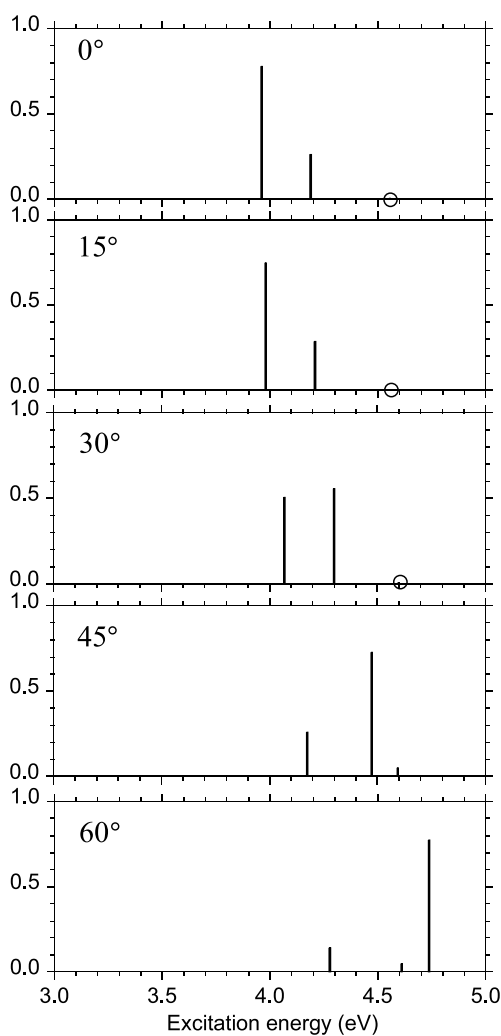


Fig. 6. The calculated absorption spectra of FT at torsional angle 0, 15, 30, 45 and 60°.

the excitation from HOMO to LUMO in all torsional angles and the S_1 state is located apart from other two states.

Next, the MOs which are important for these excited states are analyzed. From the SAC–CI results, these excited states are mainly described by the linear combination of the transitions from next HOMO and HOMO to LUMO and next LUMO. These four orbitals of FT at torsional angle 30° are displayed in Fig. 5.

As shown in Fig. 5, the HOMO and LUMO delocalized over the molecule, while the next LUMO localized in the fluorene unit. The HOMO shows inter-ring anti-bonding character between the two subunits and the LUMO shows inter-ring bonding character. The HOMO to LUMO transition is destabilized as the torsion angle becomes large, because of the bonding character of LUMO. On the other hand, HOMO to next LUMO transition does not change along the torsional angle. This situation gives rise to the interchange of the excited states.

Next, we discuss the dipole moment of FT in the three excited states. It was found that the dipole moments of three excited states are not significantly different at torsional angle 0 and 30°. On the other hand, dipole moment at torsional angle 60° is different for the 2nd and 3rd excited states.

3.3. Absorption spectra of FT and FMT

The SAC–CI absorption spectra of FT for the torsional angles 0–60° are displayed in Fig. 6. These three excited states shift into high energy region for the conformer of large θ and the oscillator strength of the 3rd excited state becomes large in $\theta=60^\circ$.

The ground state potential energy surface is flat along the torsion angle, therefore, in order to simulate the absorption spectra, the Boltzmann distribution of the conformers should be considered. The absorption spectra were

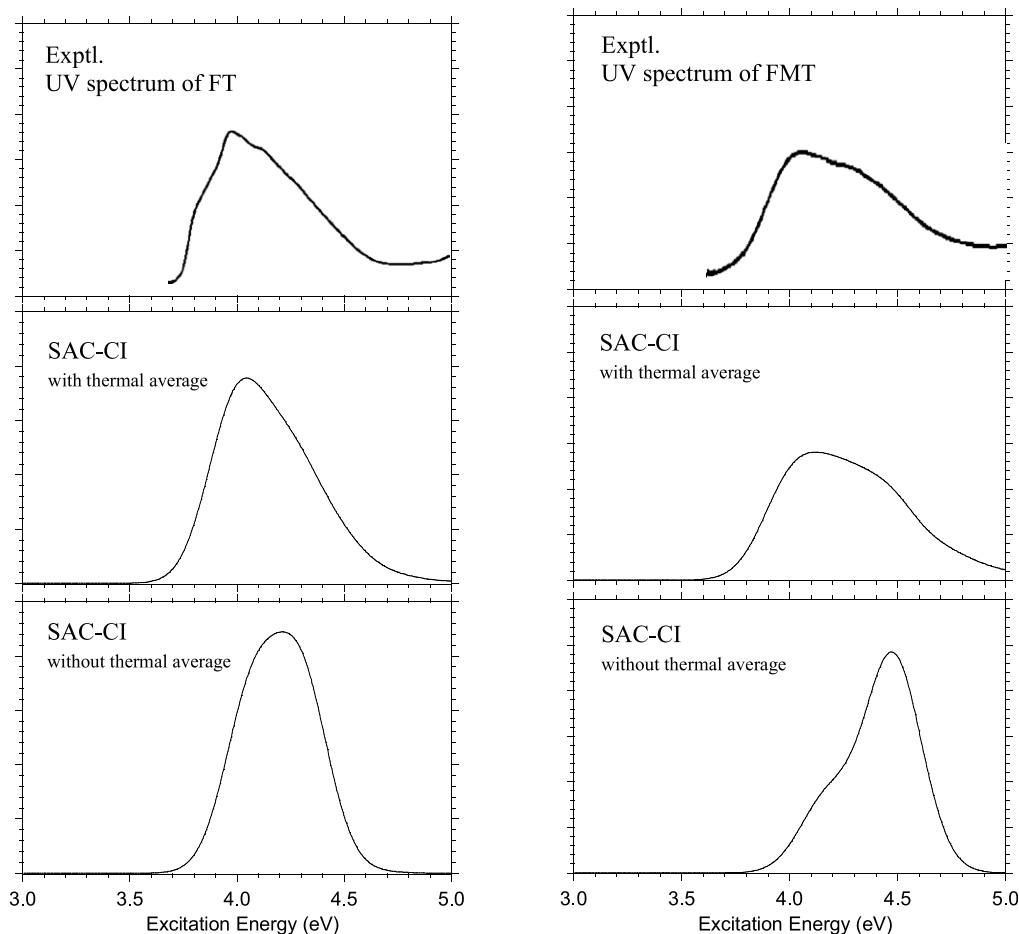


Fig. 7. Experimental [11] and SAC-CI absorption spectra of FT and FMT. Theoretical spectra with and without thermal average are shown.

simulated with the simple model: contributions of the conformer of $\theta=0-90^\circ$ with the interval of $\Delta\theta=15^\circ$ were averaged with the statistical weights at the room temperature. From the Boltzmann weight, the excitation which has the high oscillator strength at torsional angle 0, 15, 30, 45 and 60° contributed mainly to the absorption spectra of the FT and FMT. The calculated absorption spectra of FT and FMT in which Boltzmann distribution was taken into account are shown with the experimental spectra in Fig. 7. The spectra without the thermal average correction are also displayed for comparison. For FT, the Boltzmann weights at torsion angle 0, 15, 30, 45 and 60° are 22, 29, 33, 13 and 2%,

respectively, and for FMT, they are 12, 15, 30, 30 and 9%, respectively.

For FT the contributions of the conformer whose torsional angle is up to $\sim 30^\circ$ are dominant and the asymmetric spectra are obtained. In the case of FMT, the strong shoulder was observed in the higher energy side of the peak at about 4.3 eV. This absorption can be mainly attributed to the 2nd excited state of the conformer of $\theta=30-45^\circ$.

3.4. Effect of electric field

The effect of the electric field is examined for the conformer of $\theta=0$ and 60° . The results for applying the electric field of $E=0.01$ a.u. in the x direction (E_x) are given in Table 2. By applying the electric field, all three excited states are stabilized and the excitation energy becomes small. In particular, the HOMO-LUMO transition is stabilized. Since the 1st excited state of the conformer $\theta=0^\circ$ is described as HOMO-LUMO transition, the spectrum shape does not change. However, the 1st excited states of the conformer $\theta=60^\circ$ is characterized as HOMO-LUMO transition under the electric field. Therefore, the oscillator strength of the 1st excited state becomes large compared to that without electric field (Table 1).

Table 2
Excited states of FT in the electric field ($E_x=0.01$ a.u.)

Torsional angle	State	ΔE (eV)	f	Excitation character
0°	1st	3.59	0.89	0.91(H→L)
	2nd	4.14	0.12	0.82(H→nL)
	3rd	4.74	0.01	0.58(H→L+3)
60°	1st	3.89	0.5	0.89(H→L)
	2nd	4.48	0.02	0.81(H→L+2)
	3rd	4.89	0.29	0.89(H→nL)

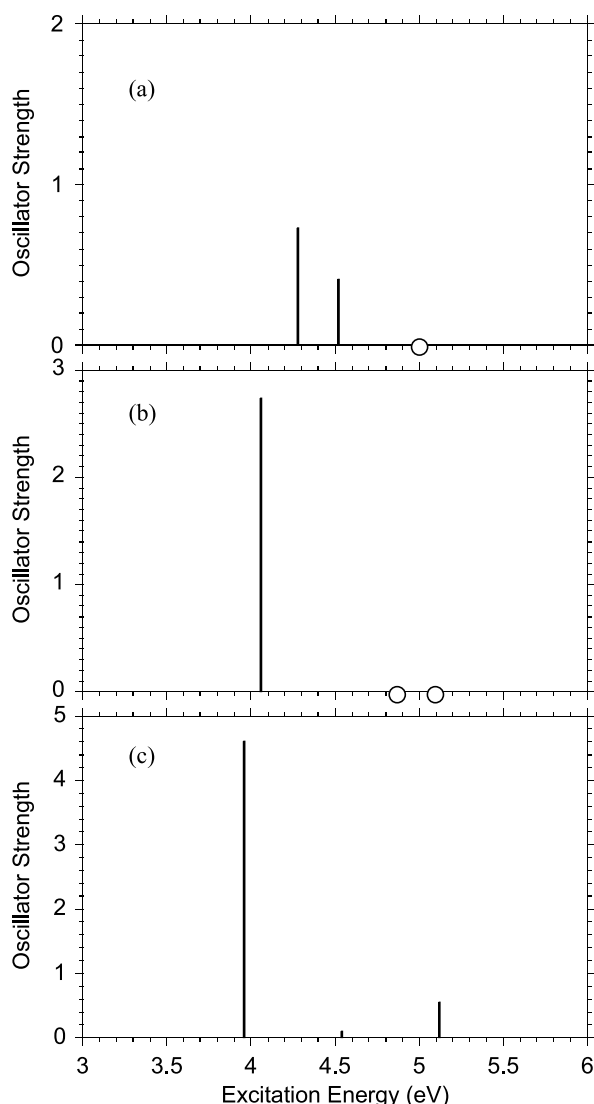


Fig. 8. The calculated absorption spectra of FT; (a) monomer, (b) dimer, and (c) trimer.

3.5. Absorption spectra of dimer and trimer

The absorption spectra of dimer and trimer were calculated at their ground-state optimized structures. These spectra are compared with that of the monomer as shown in Fig. 8. The excitation energies, oscillator strength and the excitation character of three excited states for dimer and trimer are also summarized in Table 3. In the case of

Table 3

The excitation energy (ΔE), oscillator strength (f), and character of FT monomer, dimer, and trimer at the optimized geometry

Excited state	Monomer			Dimer			Trimer		
	ΔE (eV)	f	Character	ΔE (eV)	f	Character	ΔE (eV)	f	Character
1st	4.28	0.73	H→L	4.07	2.74	H→L	3.96	4.61	H→L
2nd	4.52	0.41	H→nL	4.88	0.00	H→nL	4.54	0.10	H→nL + nH→L
3rd	4.92	0.00	nH→L	5.09	0.01	nH→L	5.12	0.55	nH→nL

Table 4

The emission energy (eV) of FT and FMT monomers

Monomer	SAC-CI	Exptl. ^a
FT	3.73	3.52
FMT	3.69	3.48

^a Ref. [11].

dimer and trimer only the 1st excited state contributes to the absorption spectrum with the large oscillator strength. Other two states have small oscillator strength. It is also characteristic that the energy separations between the 1st and the other excited states are wider than that of monomer. Since the conjugation length increases in the dimer and trimer, red shift occurred for the first excited state. It can be concluded that the 1st excited state contributes the absorption spectra not only for the dimer and trimer but also in the case of polymer.

3.6. Emission spectra for FT and FMT

We studied the emission spectra from the 1st excited state of FT and FMT. Equilibrium geometries of the 1st excited state were calculated by CIS/6-31G*. It was found that the structures of the 1st excited state of FT and FMT are almost planar. This is because the 1st excited state is HOMO–LUMO transition and the LUMO has the π -bonding character between the fluorene and thiophene units. The emission energies of FT and FMT are given in Table 4 with the experimental values. Since the stable structures in the 1st excited state are planar for both FT and FMT, the emission energies of these molecules are almost identical.

4. Summary

FT and FMT monomers are most stable in the non-planar structures in their ground states. However, the rotational energy barriers to co-planar and perpendicular conformations are well below 3 kcal/mol. This indicates that it allows a wide range of non-planar structure. The excitation energies of 1st and 2nd excited states increase when the planarity between fluorene and thiophene unit reduces. From the oscillator strength, the component of HOMO–LUMO transition mainly contributes to the absorption of the 1st peak of the FT and FMT. It was found that the excitation

energy of the HOMO–LUMO transition along the torsional angle changes caused the interchange of the character between the 1st and 3rd excited states. This was found to be because the HOMO has an inter-ring anti-bonding character between the two subunits, while the LUMO has inter-ring bonding character. The absorption spectra of FT and FMT in which Boltzmann distributions are taken into account are in common agreement with the experimental spectra.

For dimer and trimer, only the 1st excited state contributes to the absorption spectra with the large oscillator strength, the other two states have very small oscillator strength. This tendency must be valid for the polymer of these compounds.

The stable structures in the 1st excited state were predicted to be nearly planar for both FT and FMT. The calculated emission energies of these molecules are almost the same and also in common agreement with the experiment.

Therefore, using the SAC–CI method, fine analysis of the excited states of the FT and FMT, which are important fragments of the light-emitting devices, have been achieved.

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