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Theoretical study on energy levels and photophysical properties of p-n block oligomers

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Recently, a novel series of oligomers consisting of thiophene as *p*-type unit and oxadiazole as *n*-type unit were successfully synthesized. In this article, we present a first-principles study of the electronic, and optical properties on *p-n* diblock and triblock oligomers systematically. Theoretical studies showed changing the number of thiophene and oxadiazole unit could effectively modulate the electronic properties of *p-n* diblock and triblock oligomers. The electronic and photophysical properties of theoretical calculation results were in consistent with observed experimental results. These results provide useful guidelines to control the band gap principle of *p-n* hereostructure oligomers systems, and fundamental insights into understanding the electronic and photophysical properties in *p-n* hereostructure oligomers systems.

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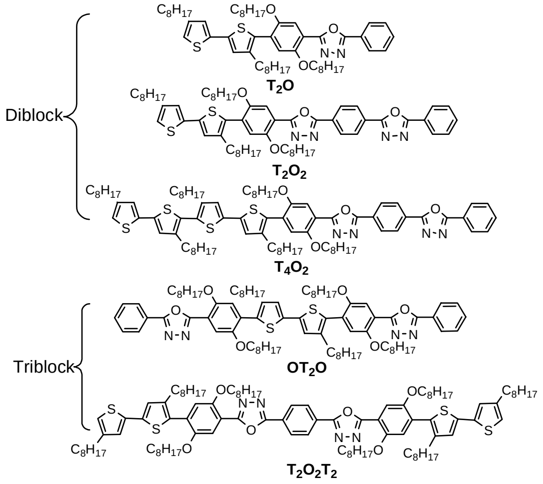
1. Introduction

Since the pioneering work of Tang and VanSlyke in the thin film OLED device, conjugated organic materials with high morphological stability have received considerable attention due to their promising potential for the industrial manufacture of light-emitting displays [1]. π-Conjugated thiophene-based polymers and oligomers have been investigated intensively in the past few decades because of their potential applications in the semiconductor devices such as thin film organic field-effect transistors (OFETs) [4], organic light-emitting diodes (OLEDs) [2], photovoltaic cells [3], etc. However, most of the organic solids used for OLED exhibit several orders higher of hole mobility than electron mobility. Therefore, the poor quantum efficiency of the OLED device can be primarily ascribed to the imbalance of electron-hole recombination in the active layer. Over the past decade, many activities have been carried out on this issue, resulting in great contributions to the molecular design for fulfilling the requirements of high electron affinity, high electron mobility, and morphology stability. Most of these applications would benefit from a full understanding of charge transport properties, which depend on the morphology of thin film and the electronic structure [5]. Therefore, developing a method to modulate the HOMO and LUMO energy levels of the elemental conjugated units to get a balance between hole mobility and electron mobility is indispensable. In our previous work, we have developed a *p-n* diblock concept and obtained a series of *p-n* diblock conjugated polymers [6,15]. The variation of the length of p and n segments in block polymer chain afforded the possibility of tuning the HOMO and LUMO energy levels and emissive wavelength. The electron deficient unit inserted into the p-type polymer chain will partially act as the hole-blocking unit due to its high electron deficiency. Vice versa, the hole-transporting unit will lower the electron mobility. Actually, the above-mentioned drawback can be resolved by the diblock oligomer with two seperate blocks, which is consisted of the p-type and n-type unit respectively. The *p-n* diblock oligomer [7], which is an idea analogous to semiconductor *p-n* junction, combined easy charge injection with current rectification properties. These polymers show improved photoluminescent (PL) and electroluminescent (EL) properties. Note that, the term, oligomer, means the polymer with less repeat units and low molecular weight compared with common polymer with several blocks. Here, we used the terms, diblock oligomer and triblock oligomer, due to the same structure of them as the diblock and triblock polymers. The only difference is the block length of the oligomer is much less than that of polymer. And moreover, in the context p-type unit and n-type unit mean electron-rich segment and electron-deficient segment, respectively. Furthermore, deep electron traps possibly occur in polymeric systems due to chain entanglements or structural defects [9].

Recently, a thiophene-thiazole diblock oligomer has been synthesized and the rectification properties have been investigated in molecular rectifier device [3,5,15]. However, the report about the systematic theoretical study for the electronic and photophysical properties of the *p-n* diblock system is still lacking. Very recently, a novel series of diblock oligomers (**T_2O**, **T_2O_2**, **T_4O_2**) consisting of electron-rich thiophene unit and electron-deficient oxadiazole unit with different unit lengths are successfully synthesized (Scheme 1) by our group [15]. In this article, the electronic properties of these oligomers are investigated systematically. The electronic and photophysical properties of theoretical calculation results are in consistent with observed experimental results. These results provide useful guidelines and fundamental insights to control the band gap of *p-n* hereostructure oligomers systems.

Scheme 1 The Chemical Structures of Diblock and Triblock Oligomers.



2. Theoretical calculations

Calculations on electronic ground states described in this paper were performed at the ab initio HF and DFT levels of theory as implemented within the Gaussian 03 software package [10,18]. Recent studies show that density functional theory calculations are remarkably successful in predicting a wide variety of problems in organic chemistry. Here, gradient optimizations were carried out using the 6-31G* basis set for C and H atoms [10,18,21]. The electronic structures of all oligomers were investigated using density functional theoretical method B3LYP at the 6-31G* basis sets calculations of GAUSSIAN 03 program [10,18,21-24]. The structures of the model systems were optimized in the first singlet excited state (S_1) and triplet excited state (T_1) using configuration interaction with all singly excited determinants (CIS) [16]. On the basis of ground and excited state optimization, a time-dependent density functional theory (TD-DFT) approach was applied to investigate the excited state electronic properties of these oligomers at the B3LYP/6-31G* level. Applications of TD-DFT have become reliable approaches for the theoretical treatment of electronic excitation processes and recent works demonstrate the good accuracy for a wide range of organic systems [22-24].

Table 1. HOMO/LUMO energy levels and gap △E calculated by DFT method (B3LYP/6-31G).*

Oligomer	HOMO	LUMO	ΔE	E_g (eV)
T_2O	-5.18	-1.69	3.49	2.98
T_2O_2	-5.23	-2.11	3.12	2.90
T_4O_2	-5.04	-2.12	2.92	2.77

[a] Optical band gap derived from the UV-vis absorption spectra of oligomer solutions from Ref.[15].

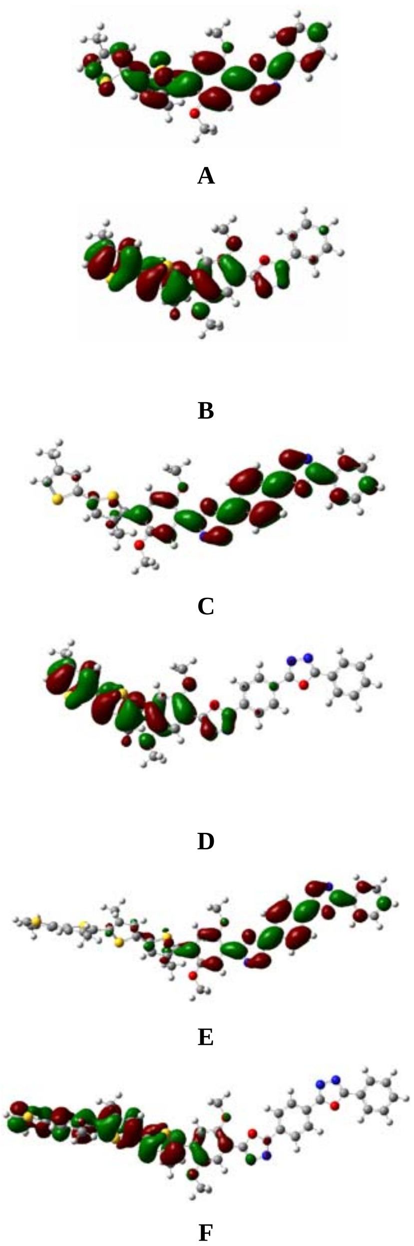


Fig. 1. Molecular orbital contours of the LUMO (A) and HOMO (B) for T_2O molecule, LUMO (C) and HOMO (D) for T_2O_2 molecule, LUMO (E) and HOMO (F) for the T_4O_2 molecule.

3. Results and discussion

The calculated band gap of these oligomers derives from the difference between the HOMO and LUMO energy levels. As expected, **T_2O** has the biggest band gap of the series. The relatively smaller band gap of **T_2O_2** with respect to **T_2O** ascribes to much lower LUMO energy level of **T_2O_2**. **T_4O_2** has the smallest band gap of the series due to the highest HOMO energy level. The calculated energy band gap of triblock oligomers (**OT_2O** and **$T_2O_2T_2$**) lies between those of **T_2O** and **T_4O_2**. The reason why **T_4O_2** has a larger band gap than the regioisomer **$T_2O_2T_2$** is due to much lower HOMO level of **T_4O_2** with respect to **$T_2O_2T_2$**. In the same way, the higher LUMO level of **T_2O_2** with respect to that of **OT_2O** contributes to the relatively larger HOMO-LUMO gap of **T_2O_2**. However, we find that the band gap of the triblock **$T_2O_2T_2$** is larger than that of the simple diblock **T_2O_2**. Furthermore, the contours of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the diblock oligomers are plotted in **Figure 1**. We can see that HOMO and LUMO of the diblock **T_2O** are delocalized among the whole molecule. With the increasing number of thiophene or oxadiazole ring of the **T_2O_2** and **T_4O_2** systems, the HOMO and LUMO tend to be localized on thiophene and oxadiazole moieties of the systems respectively. These results demonstrate that HOMO and LUMO energy levels of **T_2O_2** and **T_4O_2** can be modulated independently by thiophene and oxadiazole moiety. However, the HOMO and LUMO of triblock oligomers (**OT_2O** and **$T_2O_2T_2$**) are delocaliazed to some degree among the whole molecule. Another important characteristic of the electronic structure that we are interested in is the energy gap between the HOMO and LUMO. The trend of the calculated HOMO and LUMO energy levels and the energy gap (ΔE) correlates well with that obtained from the electrochemical measurement and optical band gap (**TABLE 1**). This indicates that our calculation can be used to predict the electronic structures of the system. Calculated data for the diblock oligomers shows that, as expected, the LUMO level increases with the increase of the length of oxadiazole unit, and the HOMO level increased with increase of the length of thiophene unit. We conclude that strong electronic interaction between two adjacent oxadiazole rings exists. And the results suggest that the LUMO of those materials can be effectively adjusted by changing the oxadiazole ring number and molecular regiochemistry. It is concluded that the HOMO level of the diblock oligomers could be effectively adjusted by changing the thiophene number.

At this stage, we would like to discuss the fluorescence ($S_1 \rightarrow S_0$) emission energies of these oligomers employing TDDFT calculation described in Section 2. Photophysical investigations of the excited state properties of these oligomers have been undertaken experimentally [6,8,15]. And spectroscopic properties of the oligomers have been investigated with the UV-vis absorption and fluorescence emission [15]. . The absorption bands at the range of longer wavelength (above 360 nm) come from the thiophene units [12,15], and the remarkable enhancement of the absorption intensity in **T_4O_2** relative to **T_2O_2** reflects the corresponding increases in the number of thiophene unit in the oligomers. Another absorption bands of **T_2O_2**, **T_4O_2** and **$T_2O_2T_2$** (around 300 nm) come from the π–π* transition of oxadiazole groups [13,15]. We found that the solvatochromism may result from intramolecular charge transfer (ICT) in their excited states [14,15]. Furthermore, the intramolecular charge transfer (ICT) in **T_2O_2** and **$T_2O_2T_2$** are more effective than that in **T_2O** and **OT_2O**. For all oligomers, it is worth noting that no absorption bands are observed at longer wavelength region (450-600 nm), which would correspond to the charge transfer from the electron-rich thiophene unit to the electron-efficient oxadiazole unit. This implies that the electronic interactions between the oxadiazole units and thiophene units are rather limited in their ground states, as illustrated in **Figure 1**.

The lowest energy absorption peak with $S_0 \rightarrow S_1$ transition is found prominent red-shifted in thin film [15]. This reveals that the extent of π conjugation is increased in thin film. And, detailed TDDFT calculations also predict a decreasing red shift of $S_0 \rightarrow S_1$ transition in oligomers as conjugation increases. This indicates that the first optical absorption transition in oligomers the arising from the promotion of one electron from the HOMO to the LUMO is delocalized over about several repeat units. The relatively large Stokes shift reveals that intermolecular aggregation would exist[25,26].

***Table 2**. Calculated fluorescence ($S_1 \rightarrow S_0$) emission energies of oligomers employing TDDFT calculation on the basis of CIS optimized excited states.*

Oligomer	ΔE /λ (nm)	E_g (eV)[a]
T_2O	2.82/445	2.98
T_2O_2	2.66/467	2.90
T_4O_2	2.53/492	2.77

[a] Optical band gap derived from the UV-vis absorption spectra of oligomer solutions from Ref.[15].

Table 2 presents calculated maximal emission wavelengths in the S_1 state for oligomers. The prediction on fluorescence is in excellent agreement with the results of optical emission measurements of these oligomers in CH_2Cl_2. However, a discrepancy was found between theoretical calculation and experimental measurement where a greater degree of delocalization in the oligomer excited state was inferred from the red shift of experimental oligomer. Without exclusion of the limit of the quantum approach, the main possible reason for this difference is that in contrast to gas phase calculations our spectra were measured in the condensed phase, which may result in strong interchain interactions due to aggregate formation[25,26]. From TABLE 2, we conclude that the band gap of $\mathbf{T_2O_2}$ is smaller with respect to that of $\mathbf{T_2O}$, indicating a greater delocalization of electronic states in $\mathbf{T_2O_2}$. In the same way, the relatively smaller band gap of $\mathbf{T_4O_2}$ with respect to $\mathbf{T_2O_2}$ ascribes to two more thiophene rings in $\mathbf{T_4O_2}$ compared with $\mathbf{T_2O_2}$. These results further indicate that changing the length of thiophene and oxadiazole units as well as altering the molecular regiochemistry could effectively modulate the band gaps of these *p-n* block oligomers.

4. Conclusions

In conclusion, a novel series of oligomers consisting of thiophene as *p*-type unit and oxadiazole as *n*-type unit were theoretically investigated. Based on theoretical calculations, the *p-n* diblock oligomers exhibited excellent band-gap controlling properties. Changing the number of thiophene and oxadiazole unit could effectively modulate the electronic and photophysical properties of these oligomers. Density functional theory provided direct evidence for the observed electronic properties. And, we conclude that changing the thiophene or oxadiazole ring number could independently tune the HOMO or LUMO energy level in the *p-n* diblock oligomers. Besides, the diblock oligomers were more effective to adjust the HOMO/LUMO energy levels than the triblock oligomers. These results provide useful guidelines to control the band gap principle of *p-n* hereostructure oligomers systems, and fundamental insights into understanding the electronic and photophysical properties in *p-n* hereostructure oligomers systems.

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