

Theoretical Investigation of the Tunable Behavior of p – n Copolymers Based on Oligothiophenes and 1,4-Bis(oxadiazolyl)-benzene

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Semiempirical calculations were carried out on several model oligomers to investigate the tunable behavior of p – n copolymers with the repeating units constructed by oligothiophenes as the π -excessive type blocks and 1,4-bis(oxadiazolyl) benzene as the π -deficient type block. The calculated evolutions of the HOMO and LUMO of the model oligomers were in good agreement with the experimental oxidation and reduction potentials of the corresponding polymers. The effect of the length of the oligothiophene on the electronic structures and optical properties was elucidated by analyzing the HOMO and LUMO spatial distribution patterns of the model oligomers. When the number of thiophene rings increases, the HOMO and LUMO are contributed mostly from the oligothiophene segments and either the introduced single positive or negative charge focuses on the oligothiophene segments. The absorption spectra of polymers were also simulated by performing calculations on the corresponding oligomers. Good matches were observed between the calculated absorption spectra and the experimental UV–vis spectra of the corresponding polymers. The study shows that the backbone modification of the p – n copolymer, that is, changing the number of thiophene unit in the p – n diblock copolymer, greatly modifies the optical properties of the polymer.

I. Introduction

Recently, application of organic polymers as the active semiconductors in light-emitting diodes (LED) has made rapid progress because of its potential in developing large-area and flexible displays.^{1–3} Prototype devices made by UNIAX and our group have met realistic specifications for some types of applications. Desired polymers for LED should have energy values of the first optical transition in the visible spectrum, high stability, and good processability.⁴ A lot of studies have been carried out both experimentally and theoretically to design new conjugated polymers as the emission layer.^{5–7}

Polythiophenes and polyoxadiazoles have long been studied for LED applications.^{8,9} Our group proposed a new molecular design and synthesis of p – n diblock conjugated copolymers^{10a,b} that can be used as molecular diodes.^{10c} Oligothiophenes, which are π -excessive (p -doped type) blocks and di(1,3,4-oxadiazole)-phenylenes, which are π -deficient (n -doped type) block segments, were alternatively incorporated into the backbone of conjugated polymers to adjust the HOMO and LUMO of the resulting polymers.^{10d} It was found that the electronic and optical properties that related to the HOMO and LUMO of the polymers

could be conveniently tuned by varying the length of the oligothiophene block in the repeating unit.^{10e}

To have a better understanding of this tunable behavior of the p – n diblock polymers, we carried out quantum chemical calculations on the oligomer representatives with the same p – n diblock structures. In this study, we presented results of semiempirical parametrization method 3 (PM3) geometry optimization and charge distribution as well as the optical properties from ZINDO/S calculation, which is a specially parametrized intermediate neglect of differential overlap (INDO) and has been used frequently in the investigation of the electronic structure of PPP,¹¹ PPV,¹² polythiophene (PT),⁸ poly(p -pyridyl vinylene) (PPyV), and poly(p -pyridine) (PPy).¹³ The theoretical results can account for the tunable redox behavior and emissive color of the polymers, explain the tunable electronic structures and optical properties on the molecular orbital level, and be helpful in the design of new conjugated systems with optimum physicochemical characteristics.

II. Theoretical Methodology

Three selected p – n copolymers discussed in this study were sketched in Figure 1. Polymers I and II have 1,4-bis(1,3,4-oxadiazolyl)benzene as the n -doped type block and thiophene(s) as the p -doped type block in the repeating unit. Polymer A has a long alkyl side chain on thiophene rings. Polymer B has extra alkoxy substitutes on the phenyl rings in comparison with polymer A. Polymer C has more thiophene units than the p -doped type block in the repeating unit. Additional descriptions of these polymers can be found in ref 10a. Oligomers I, II, A, B, and C were the corresponding model molecules in this study.

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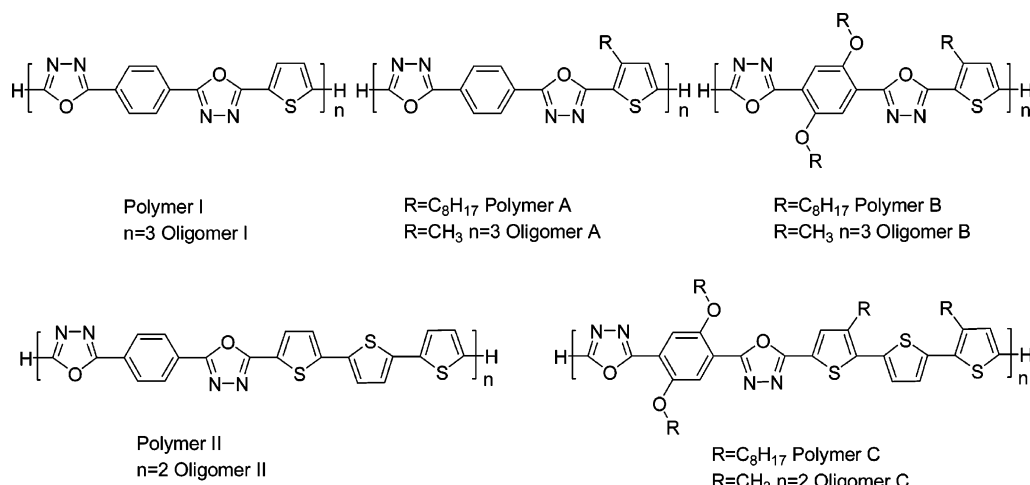


Figure 1. Sketch of the molecular structures of the polymers investigated in this work and the model oligomers.

The inter-ring twisting angles were set to zero during the optimization, considering the planar conformation in the solid state. Such conformations were supported by various torsion analyses performed on various segments.^{10b,14} Geometries of all oligomers in the ground state were optimized by semiempirical parametrization method 3 (PM3) within the restricted Hartree–Fock formalism (RHF). A previous study showed that PM3 calculated bond length and angles of thiophene and oxadiazole segments were much closer to those obtained from *ab initio* ones in comparison with AM1.^{10b} The restricted open-shell Hartree–Fock formalism (ROHF) was used to treat the singly charged species for better reproduction of the localized nature of the geometry relaxations around the charge carriers than an unrestricted Hartree–Fock formalism (UHF).¹⁵ On the basis of the geometric data, the one-electronic structures of the neutral oligomers were generated by means of the semiempirical ZINDO/S method, which is a modified INDO method parametrized to reproduce UV–visible spectroscopic transitions. The transition energy and intensity of the lowest-lying one-photo-allowed singlet excited state were then obtained by coupling the ZINDO/S to configuration interaction (CI). The CI-active space included the 24 highest occupied and 24 lowest unoccupied levels. The calculated CI properties were consistent with those of smaller CI size calculations (20 + 20). The theoretical spectra were simulated using a Gaussian broadening with the full width at half-maximum (fwhm) of 60 nm for comparison with experimental spectra.

III. Results and Discussion

A. Geometry Considerations. The optimized geometry parameters for a unit cell of polymer I obtained by PM3, AM1, and B3LYP/6-31G* were listed in Table 1. All C–C and C=C bond lengths predicted by three methods are in reasonable agreement. The major difference between PM3 and AM1 comes from the geometry of the oxadiazole ring. AM1 predicted shorter N–N bonds than C=N bonds, conflicting with the experimental geometries of such molecules extracted from X-ray data.¹⁶ PM3 made the C–O length very close to that by B3LYP/6-31G*, whereas AM1 made it too long. Significant differences between PM3 and AM1 predicted geometries were also found in the thiophene segment. PM3 gave 1.734 Å for the C–S bond, which is quite close to 1.744 Å by *ab initio* B3LYP/6-31G* and HF/3-21G*,¹⁴ whereas AM1 made this bond too short. We therefore conclude that PM3 gives more correct qualitative geometries of this *p*-*n* diblock structures than AM1.

TABLE 1: Some Bond Lengths (in Å) and Bond Angles (in Degrees) of the Repeating Unit of Polymer I Calculated from Various Theoretical Methods

bond length	bond length			bond angle	bond angle		
	PM3	AM1	B3LYP/6-31G*		PM3	AM1	B3LYP/6-31G*
N2–C1	1.338	1.356	1.305	N3–N2–C1	108.7	109.2	106.5
N3–N2	1.349	1.317	1.384	C4–N3–N2	108.9	109.4	106.9
C4–N3	1.337	1.354	1.303	O5–C4–N3	107.9	108.9	111.9
O5–C4	1.379	1.408	1.370	C6–C4–N3	130.6	132.4	128.4
C6–C4	1.455	1.447	1.454	C7–C6–C4	119.0	119.6	119.1
C7–C6	1.400	1.403	1.406	C8–C7–C6	120.0	119.8	120.2
C8–C7	1.389	1.392	1.387	C9–C8–C7	120.1	120.2	120.2
C9–C8	1.399	1.403	1.406	C10–C9–C8	121.1	120.4	121.3
C10–C9	1.454	1.447	1.454	C11–C10–C9	130.6	132.4	128.5
N11–C10	1.338	1.355	1.304	N12–N11–C10	108.9	109.4	106.9
N12–N11	1.348	1.316	1.383	C13–N12–N11	108.7	109.2	106.5
C13–N12	1.338	1.356	1.304	O14–C13–N12	108.0	109.0	112.2
O14–C13	1.380	1.408	1.366	C15–C13–N12	131.5	132.7	128.5
C15–C13	1.441	1.427	1.438	C16–C15–C13	124.3	126.7	127.7
C16–C15	1.382	1.383	1.381	C17–C16–C15	112.3	111.6	112.6
C17–C16	1.422	1.429	1.414	C18–C17–C16	112.3	111.6	112.6
C18–C17	1.381	1.382	1.380	S19–C15–C13	123.5	121.7	120.1
S19–C18	1.734	1.682	1.744				

The PM3 calculated bond length changes of oligomer I from the neutral state to singly charged states were displayed in Figure 2a. When a single positive charge was introduced into the system, geometry modifications largely happened on the oxadiazole ring. And the pattern of the geometric distortions caused by the single negative charge was quite similar to that by the single positive charge. The net charge distribution of oligomer I in the neutral state shown in Figure 2b indicates that the partial negative/positive charges exist alternatively along the molecule, that is, the π -excessive thiophene rings and the phenylene rings have positive net charges and π -deficient oxadiazole rings have negative net charges. Figure 2b also showed the distribution of the excess charges calculated as the difference between the charges of the atoms in the ions and in the neutral molecules. When a positive charge was introduced into the system, the geometry distortion and the charge distribution centered on the oxadiazole ring and extended to the thiophene and phenylene rings connected to it, because oxadiazole rings have extra negative charges in the neutral molecules. Meanwhile when a negative charge was introduced, they were located mainly on the thiophene rings.

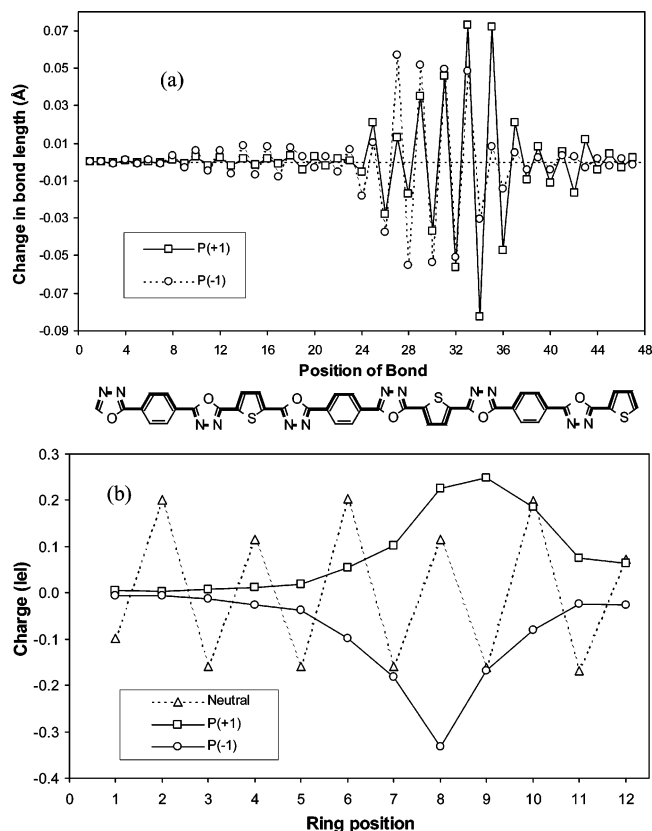


Figure 2. PM3 calculated (a) changes in bond lengths of oligomer I when going from the neutral state to the singly oxidized [P(+1)] and singly negatively charged [P(-1)] states; (b) net atomic charge distribution for neutral oligomer I and their changes to various doped states.

The geometric modifications and the charge distributions of oligomer II were displayed in Figure 3a and b. Either the introduced single positive charge or the single negative charge focuses on the oligothiophene segment because of the large destabilization of HOMO and stabilization of LUMO by the strong conjugation effect of the oligothiophene segments. The different charge distribution between oligomers I and II indicates that the charge modifications of the *p*-*n* diblock structure are quite dependent on the arrangement of rings of different characteristics. The geometry deformations and charge distributions corresponded very well for the single negative and positive charge in the two oligomers.

B. Electronic Structures. The ZINDO/S calculated energies of HOMO, LUMO, and the energy difference between them (ΔE) of various oligomers were shown in Figure 4. Because of the electron-donating effect of methyl and methoxy groups,¹⁷ the HOMOs of oligomers A and B are destabilized slightly in comparison with the unsubstituted oligomer I. This substitute effect of methyl and methoxy groups is comparable with the theoretical results obtained on other systems with similar methods.¹⁸ Comparing oligomer I to II, the introduction of thiophene ring clearly causes a large destabilization of HOMO level but does not have much effect on the LUMO energy level. Experimentally, polymer B has the HOMO and LUMO of -6.15 and -2.57 eV, respectively, whereas polymer C has -6.70 and -2.61 eV, respectively, as measured by cyclic voltammetry (CV).^{10e} The calculated trend for oligomers A-C is in good agreement with the experimental observation of the corresponding polymers. Their oxidation potentials (related with HOMO) are reduced especially with increasing the thiophene ring number in the oligothiophene segments, but the reduction potentials

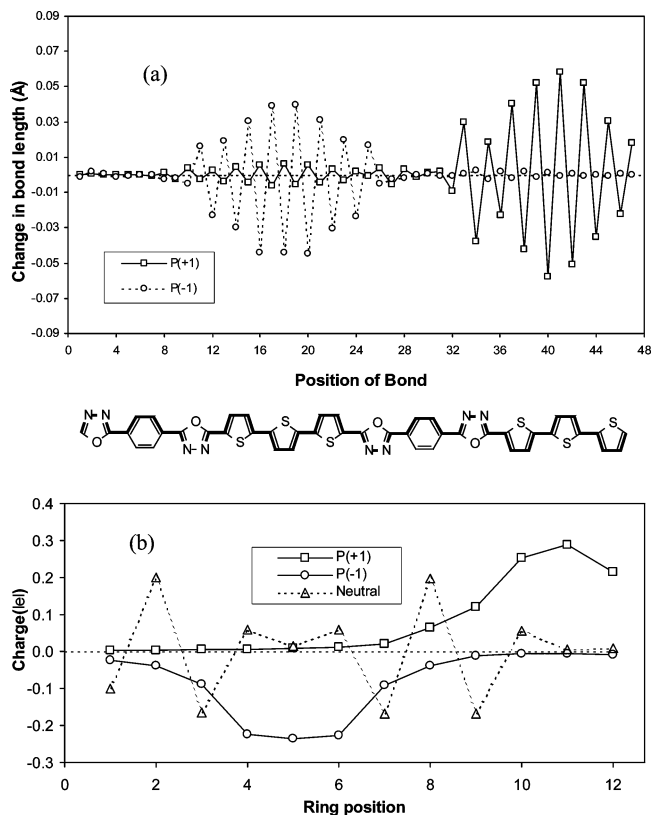


Figure 3. PM3 calculated (a) changes in bond lengths of oligomer II when going from the neutral state to the singly oxidized [P(+1)] and singly negatively charged [P(-1)] states; (b) net atomic charge distribution for neutral oligomer II and their changes to various doped states.

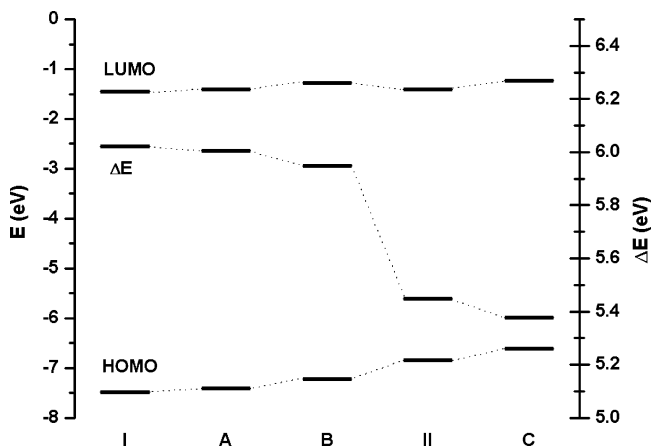


Figure 4. ZINDO/S calculated evolution of the energy (*E*) of the HOMO and LUMO energy levels of various oligomers and the energy difference (ΔE) between them.

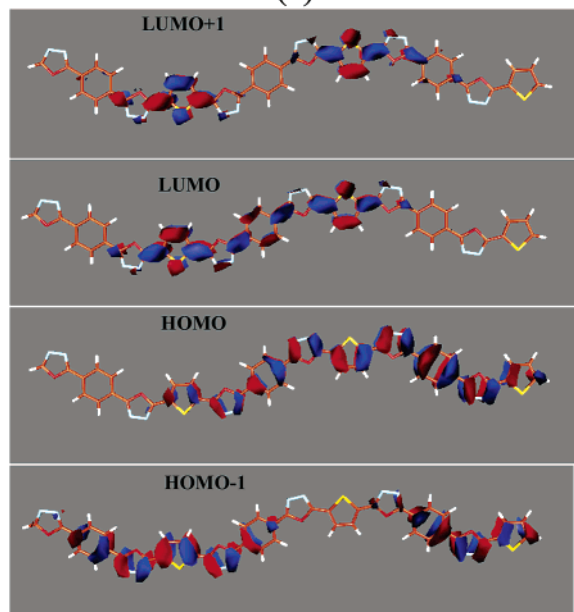
(related to LUMO) are not sensitive to the variation of the thiophene ring number. The calculated trend in ΔE is also in good agreement with the experimental observations.^{10(e)}

C. Mechanism of Tunability. The PM3 and ZINDO/S calculated HOMO, LUMO, and ΔE were listed in Table 2. The two methods predicted the same trends of the evolution of HOMO, LUMO, and ΔE . To elucidate the difference between oligomers with different numbers of thiophene rings, the frontier orbitals of oligomers I and II are displayed in Figure 5a and b, respectively. The orbital contributions of the segments of oxadiazole, phenylene, and thiophene can be revealed by comparing the spatial distribution patterns of the oligomers and the segments in HOMOs and LUMOs. The LUMO and

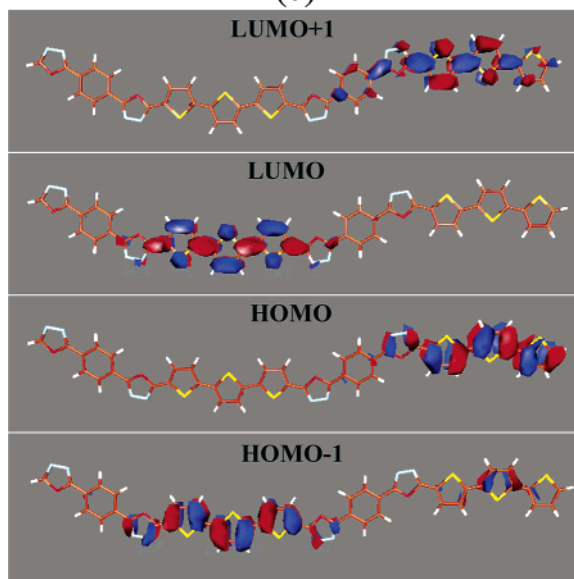
TABLE 2: Comparison of ZINDO/S and PM3 Calculated Energy (in eV) of HOMO, LUMO, and the Difference between Them (ΔE)

oligomer	ZINDO/S			PM3		
	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
I	−7.477	−1.457	6.020	−9.195	−2.210	6.984
A	−7.409	−1.404	6.005	−9.138	−2.165	6.972
B	−7.219	−1.271	5.948	−8.833	−1.999	6.834
II	−6.851	−1.401	5.449	−8.766	−2.152	6.614
C	−6.614	−1.236	5.378	−8.541	−1.978	6.564

(a)



(b)

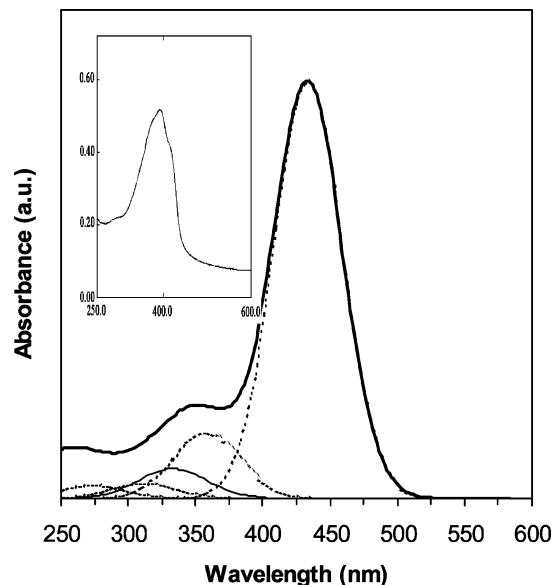
**Figure 5.** (a) PM3 frontier orbitals of oligomer I. (b). PM3 frontier orbitals of oligomer II.

LUMO+1 of the oligomers are composed of LUMOs of oxadiazole (−0.258 eV), phenylene (0.396 eV), and thiophene (−0.198 eV). Although their HOMO and HOMO−1 are composed of HOMOs of oxadiazole (PM3: −10.921 eV) and phenylene (−9.751 eV) segments and HOMO−1 of thiophene segments (−9.867 eV) as required by the symmetry, because the HOMO and HOMO−1 of the oligomers are generated from the π orbital but the HOMO of thiophene is the n orbital of the

TABLE 3: ZINDO/SCI Calculated Wavelengths (in nm), Experimental Wavelengths (in nm), Oscillator Strength (arb units), and CI Descriptions of the Lowest Two Absorption of Oligomers A–C

oligomer	excited state	calculated wavelength	experimental wavelength ^a	oscillator strength	CI description
A	S ₁	436.3	393, 416	3.67	−0.50H → L
	S ₂	364.2		0.51	−0.32H → L + 2
B	S ₁	443.9	360, 420, 443	3.55	−0.50H → L
	S ₂	372.7		0.60	0.33 H → L + 2
C	S ₁	501.8	439, 494	3.62	−0.36H → L, −0.48H − 1 → L
	S ₂	461.4		0.54	−0.52H → L + 1

^a The maximum absorption and shoulders of the corresponding polymers from ref 10a.

**Figure 6.** ZINDO/SCI simulated UV–vis spectrum of oligomer A. The experimental spectrum of polymer A is shown in the inset.

sulfur atom. In oligomer I, HOMO disperses on different segments in a large range with similar contribution from all kinds of rings, whereas the LUMO located mainly on thiophene rings and the contributions from the oxadiazole and phenylene are small. In oligomer II, both the HOMO and LUMO are contributed mainly by the oligothiophene segments, and the contribution from the oxadiazole segment is greatly reduced especially in HOMO compared with that of oligomer I. This is the main reason for the HOMO increase from oligomer I to II. The LUMO has little change because the LUMOs of the oxadiazole (−0.258 eV) and thiophene (−0.198 eV) are quite close.

D. Optical Properties. The ZINDO/SCI predicted first and second absorption wavelength, and the oscillator strength of the corresponding excited states were listed in Table 3. The calculated first transition wavelength of oligomers A–C were longer than the wavelength of the maximum absorption of the corresponding polymers. Many investigations show that ZINDO is a good tool for predicting the absorption spectra of the extended systems.¹⁹ However, this method overestimates the absorption spectra when studying this complicated *p*–*n* diblock system. This overestimate has also been observed in other conjugated systems²⁰ with the red shift up to 120 nm.

The ZINDO/SCI calculated UV–vis spectra of oligomers A–C were displayed in Figures 6–8, respectively. Each transition was represented by a dashed line, and the sum of them gave the overall absorption spectrum. Good similarities with the corresponding experimental spectra^{10a} (insets of Figures)

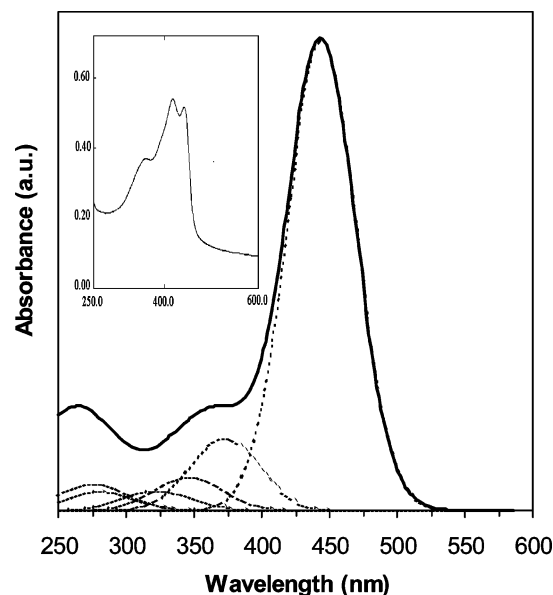


Figure 7. ZINDO/SCI simulated UV-vis spectra of oligomer B. The experimental spectrum of polymer B is shown in the inset.

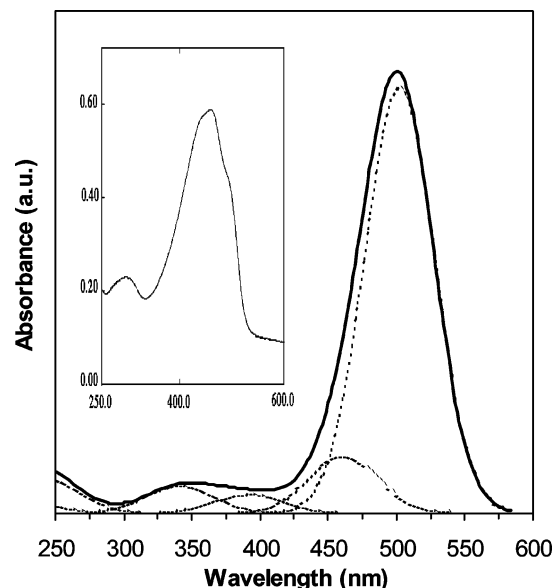


Figure 8. ZINDO/SCI simulated UV-vis spectra of oligomer C. The experimental spectrum of polymer C is shown in the inset.

were found because of the good prediction in the relative positions of the first few peaks in each spectrum. For the spectra of oligomers A and B, the separation of the first two peaks is quite large. The CI description of the two peaks showed that the first peak arises mainly from the transition of HOMO to LUMO, which is the usual case for most of the conjugated polymers, whereas the second absorption peak arises from the transition of HOMO to LUMO+2 with a large separation between the first peak (see Table 3). The ZINDO/SCI results of oligomers A and B are very similar because they have the same backbone structure. However, the experimental spectra of their corresponding polymers are markedly different, mainly because of the spatial hindrance of alkoxy substituents, which hinder the inter-ring rotation and influence the UV-vis spectrum. As for the calculated spectrum of oligomer C, the separation of the first two peaks was largely reduced. The peak around 290 nm in the experimental spectrum of polymer C is not attributed to the second transition, which is largely merged into the first peak. The CI description of oligomer C showed quite a

difference from those of oligomer A and B. Its first transition is from HOMO \rightarrow LUMO mixing with HOMO-1 \rightarrow LUMO, whereas its second transition corresponds to the excitation of HOMO \rightarrow LUMO+1. As a result, the backbone modification, that is, changing the number of thiophene unit in the p - n diblock structure, largely changes the optical transition character.

IV. Conclusions

To study the electronic and optical properties of polymers that have p - n diblock structure in the repeating unit, we carried out semiempirical PM3 and ZINDO/SCI calculations on several oligomer model molecules. The good correlation between the tunable redox properties and absorption wavelength of the polymers with the calculated values shows the possibility of modeling the complicated polymer systems with suitable oligomer models. PM3 gives more correct qualitative geometries of the p - n diblock structures compared to AM1 and was made on the investigation of the positive and negative charge distribution and the frontier orbital pattern. In oligomer I, oxadiazole, thiophene, and phenylene have similar contributions to the HOMO, whereas thiophene has larger contributions to the LUMO, but when a single positive or negative charge is introduced into oligomer I geometry modifications largely happen on oxadiazole ring. When the number of thiophene rings increases as in oligomer II, the HOMO and LUMO are contributed mostly from the oligothiophene segments with the remarkably reduced contributions from oxadiazole and phenylene segments, and either the introduced single positive or negative charge focuses on the oligothiophene segments. The introduction of thiophene ring causes a large destabilization of the HOMO level but not much effect on the LUMO energy level, which is in good agreement with the experimental observation of the corresponding polymers. The simulated absorption spectra also match well with the experimental UV spectra of the corresponding polymers. This study indicates that the backbone modification of changing the number of thiophene units in the p - n copolymer greatly changes the optical properties of the polymer.

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