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Tuning redox behavior and emissive wavelength of conjugated polymers by p – n diblock structures — a theoretical investigation

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Abstract

In this communication, we present the results of molecular modeling on the structural units of two series of conjugated polymers using semi-empirical MO calculations. The results confirm that the redox behavior and emissive wavelength of the polymers can be tuned by p – n diblock structures. In addition, the results obtained from parameterization method 3 (PM3) calculations performed on model compounds give good correlation with physicochemical properties observed from the corresponding polymers. The reverse trend in the calculated values of polymer A and B is analyzed with conformational study. Some of the Austin model 1 (AM1) data are also included for comparison. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tuning redox behavior; Emissive wavelength; Conjugated polymers; p – n diblock structures

1. Introduction

The application of conjugated polymers as the active emissive layer in light-emitting diodes (LED) has made rapid progress due to its potential in developing large area flat panel displays [1–3]. Prototype devices made by UNIAx and our group have met realistic specifications for some types of applications. Desired polymers for LEDs should have energy values of the first optical transition ($\Delta E = \text{HOMO} - \text{LUMO}$) in the visible spectrum, high stability, and good processability [4]. Since the discovery of the Cambridge group [5], extensive studies have been carried out both theoretically and experimentally to design and synthesize new conjugated polymers [6–8].

Polythiophenes and polyoxadiazoles have long been studied for LED applications. Their electronic structures and conformational analysis have been studied theoretically [9,10]. More recently our group developed a new molecular design and synthesis, i.e., p – n diblock conjugated co-polymers [11]. Oligothiophenes, which are π -excessive p -doped type blocks and di(1,3,4-oxadiazoly)phenylenes, which are π -deficient n -doped type blocks, were alternatively incorporated into the backbone of a

conjugated polymer to adjust the HOMO and LUMO energy levels of the resulting polymer. It was found that the electronic and optical properties, which are related to the HOMO and LUMO of the polymers, can be adjusted by varying the length of the oligothiophene block.

In order to have a better understanding of the p – n diblock system, quantum chemical calculations of monomer representatives of p – n diblock structures were carried out. In this paper, we present the results of semi-empirical PM3 (parameterization method 3) calculations. It was found that the trends derived from the theoretical study of the monomers are consistent with the properties observed from the polymers. These theoretical results account for the tunable redox behavior and emissive color of the polymers, which is helpful to the design of new conjugated systems with optimum physicochemical properties. Some results of the AM1 (Austin model 1) calculations are included for comparison.

2. Theoretical methodology

The structures of p – n diblock monomers investigated in this study are shown in Fig. 1. They correspond to polymers A–G, respectively. Actually, there are two series in these seven polymers, i.e., B, C, and D in series 1 with

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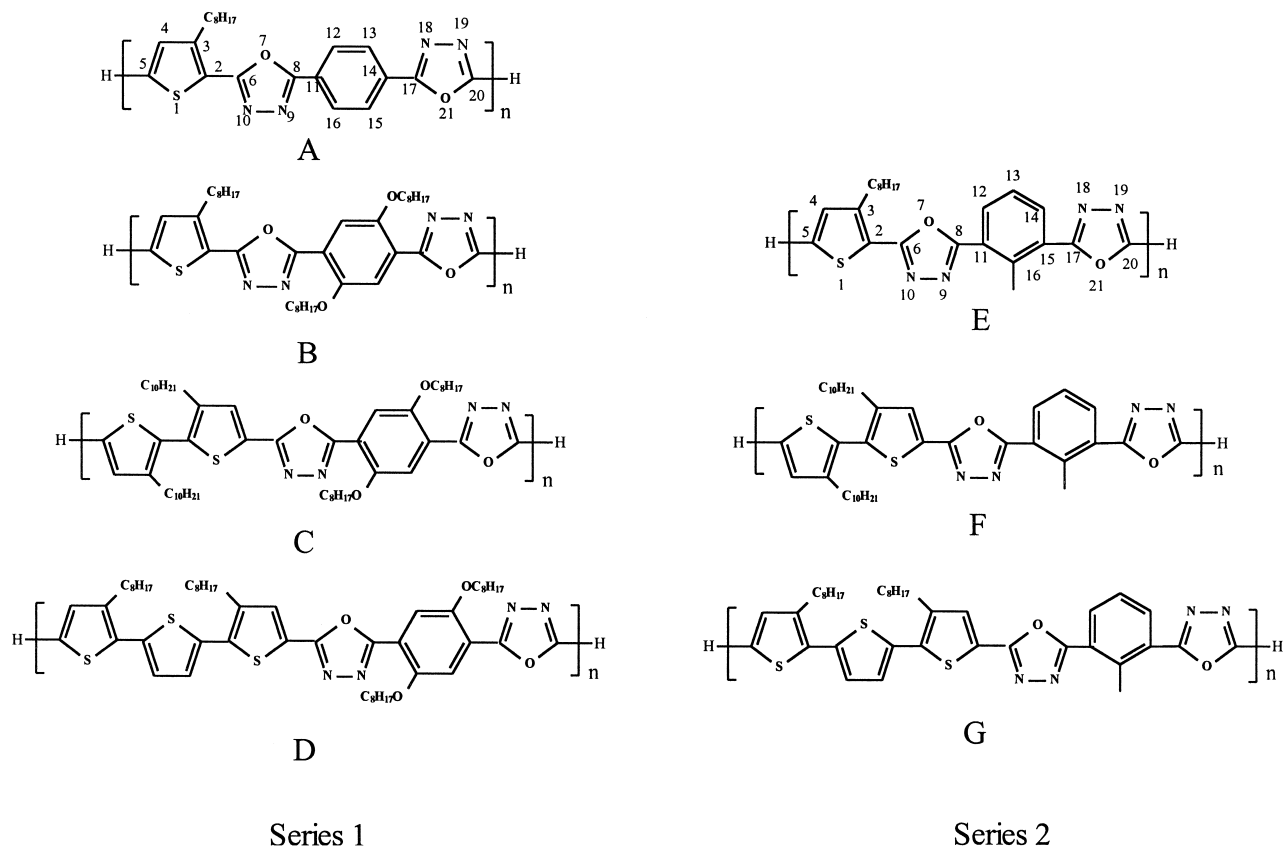


Fig. 1. Chemical structures of the polymers.

1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene as the *n*-doped block, and E, F, and G in series 2 with 2,6-bis(1,3,4-oxadiazolyl)-toluene as the *n*-doped type block. Polymer A was designed for comparison with polymer B to investigate the substituent effect. The semi-empirical calculations were performed on a Silicon Graphics Octane R10000 work station using the AMPAC 6.0 program [12]. Geometries of the monomers have been fully optimized by using the semi-empirical PM3 [13,14]. Conformational analysis was done on 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene and 1,4-bis(1,3,4-oxadiazolyl)-benzene to estimate the energy barrier of optimized minimum to coplanar conformation. In the conformational study, the phenyl ring was rotated back and forth, keeping the two end rings on the same plane. The calculations were performed with fully relaxed PM3 level which may have slight difference with that of the rigid rotor approximation, i.e., the optimized geometry was kept fixed while the two ring torsion angles were changed [15,16].

3. Results and discussion

3.1. Geometry considerations

PM3 predicts nearly planar structures for monomer A. Two rings at the ends adopt a co-planar conformation with

the dihedral angle $\angle 7-6-2-3 = 1.3^\circ$ and $\angle 18-17-14-13 = -1.5^\circ$. These two planes are slightly twisted with the dihedral angle $\angle 16-11-8-9 = -9.3^\circ$. In monomer B, the co-planar assemblies are broken through side-chain disordering as two octoxy groups were introduced into the backbone. Three dihedral angles mentioned above changed to $\angle 7-6-2-3 = 51.9^\circ$, $\angle 18-17-14-13 = -133.1^\circ$, and $\angle 16-11-8-9 = -84.6^\circ$, respectively. As one more thiophene ring was added into the monomer B, it adopts a torsional conformation twisted by about 90° with the previous thiophene ring. This is consistent with the ab initio calculations (HF/3-21G*) performed on 3,3'-diethyl-2,2'-bithiophene [17] as well as semi-empirical AM1 calculation performed on 3,3'-didecyl-2,2'-bithiophene [18], both showed that there is a global minimum at the torsional angle around 100° . When three thiophene rings exist in the structure (monomer D), they adopt torsional conformation with each other at the angle around 60° , which is in reasonable agreement with the most recent conformational analysis using ab initio (HF/3-21G*) performed on 3,3'-dimethyl-2,2':5',2''-terthiophene (DMTT) [19]. It can be concluded that the combination of the oligomer thiophene rings with the *n*-doped groups has not much effect on the conformations of the oligothiophene segment. The thiophene ring conformation is related more with the side-chain groups attached to them. PM3 seems to predict a more planar conformation for the 2,6-bis(1,3,4-oxadiazolyl)-

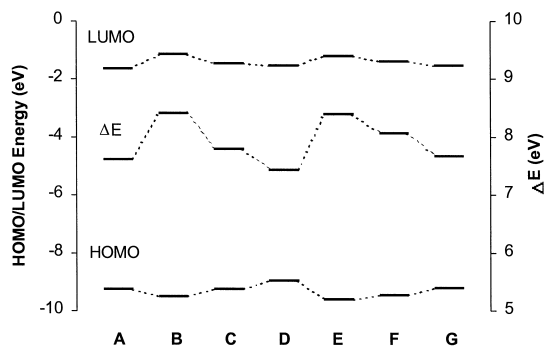


Fig. 2. Sketch of the PM3 calculated energies of the HOMO, LUMO and the differences between them.

toluene moiety than that for the 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene moiety. As a comparison with monomer B, the dihedral angles in monomer E are $\angle 7-6-2-3 = -18.3^\circ$, $\angle 16-11-8-9 = 19^\circ$, and $\angle 18-17-15-14 = -42.4^\circ$, respectively.

3.2. One-electron structure

The PM3 calculated energies of HOMO, LUMO and the energy difference (ΔE) between them of the studied monomers are shown in Fig. 2. There is a systematical change of the HOMO, LUMO energies as the number of thiophene ring increased in both series. Introducing thiophene ring causes destabilization of HOMO and stabilization of LUMO, with the first being the most affected. This is in good agreement with the experimental observation obtained from polymers series. For both series 1 and 2, the oxidation potential (related with HOMO) reduced with increasing the thiophene ring number in the oligothiophene segments, while the reduction potentials (related to LUMO) are not sensitive to variation of the thiophene ring number. The calculated energy differences (ΔE) between LUMO and HOMO show a systematical decrease for both series as the number of thiophene ring increases. This may include the effect of increment in the conjugation length. Also, the calculations were performed on the corresponding monomers, the derivation of ΔE from absorption wavelength observed from the polymer films is reasonable [20,21]. We want to stress that the PM3 calculations performed on the *p-n* diblock monomers predict that the tunable trend of the redox and optical properties observed from the polymers mainly comes from the destabilization of the HOMO by the thiophene segments. These calculations on monomer models provide a good understanding of various properties of the corresponding polymers in future studies.

3.3. Conformation consideration

It is interesting to compare the calculated values on monomers A and B with observations from polymers A

and B. The experimental values show that the reductive potential does not change much as octoxy groups were introduced into phenylene ring, while the oxidative potential decreases remarkably, and the UV–VIS absorption shifts to longer wavelengths (from polymer A to B). However, the PM3 calculations on the corresponding monomers A and B give a reverse trend. There is large destabilization in LUMO, stabilization in HOMO and consequently large increase in the energy difference (ΔE) between them from monomers A to B.

Introducing side-chain to the phenylene ring can affect the electronic structure in two ways, i.e., by withdrawing or donating charge carriers thereby lowering or raising the energy bands, and by steric hindrance induced ring torsion thereby changing the conjugating length [22,23]. We first analyze the HOMO and LUMO spatial distribution patterns for monomer B. Its HOMO shows a large contribution from the octoxy groups, basically $\sigma-\pi$ donor effect in nature. This is the main effect inducing changes in oxidative potential and shift of absorption wavelength observed from polymer A to B. The derivation of calculated trend with the observed ones probably comes from the estimation of the torsion angles. The calculated torsion angle became very large as the octoxy groups were introduced into the phenylene ring as mentioned above. Note that the calculations were performed in the gas phase, while the properties were measured in the solid state, it is possible for polymers with large torsion angles yet with small barriers towards coplane, to be driven into a more coplanar configuration in films by solid state packing, decreasing torsion angles and hence decreasing the band gap thus affecting absorption maximum [15]. Taking this into consideration, torsion analysis was performed on 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene to estimate the energy barrier of the optimized minimum to the co-planar conformation. The potential energy curves of these two structures are shown in Fig. 3 and Fig. 4. For 1,4-bis(1,3,4-oxadiazolyl)-benzene segment, the torsion potential curve in the region from 0° to 15° is quite flat. As mentioned above, the calculated dihedral angles in monomer A are very small, the structure is likely to be

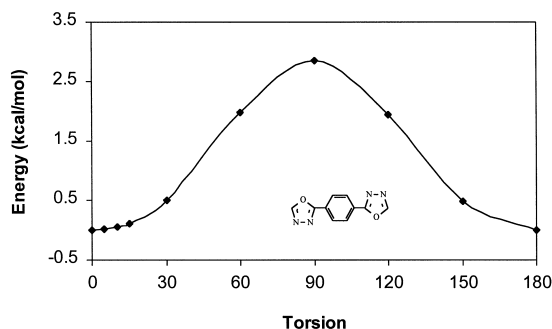


Fig. 3. Potential energy curves associated with torsion of the middle phenylene ring in 1,4-bis(1,3,4-oxadiazolyl)-benzene segment.

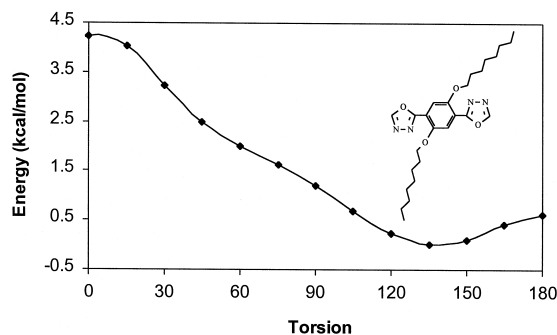


Fig. 4. Potential energy curves associated with torsion of the middle phenylene ring on 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene segment.

driven into a coplanar conformation in films by the solid state packing but the electronic properties do not change much due to the small torsion angles. For 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene segment, the energy barrier to the co-plane is also very small, but the calculated torsion angle to co-plane (180°) is very large ($\sim 50^\circ$), and this conformation is quite similar with that calculated in monomer B as mentioned earlier. The segment is likely to be driven into a co-planar conformation in films by solid state packing due to the low energy barrier towards 180° torsion, and the electron properties will have a large change due to the large torsion angle towards 180° .

3.4. Comparison with AM1

To compare with the PM3 calculated results, AM1 [24] calculations performed on the system is included using the same AMPAC 6.0 program package. The calculated HOMO, LUMO energy levels and the difference between them are shown in Fig. 5. It seems that AM1 cannot predict the correct trend that exists between polymers C and D. The optimized bond lengths for the ring structures of oligomer A obtained by both PM3 and AM1 are listed in Table 1. The major difference between PM3 and AM1 comes from the geometry of the oxadiazole ring. In very good agreement with the result of Brocks and Tol [10],

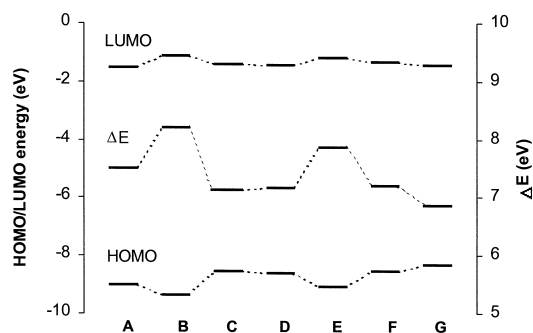


Fig. 5. Sketch of the AM1 calculated energies of the HOMO, LUMO and the differences between them.

Table 1

Optimized bond lengths (in Å)

Bond length	PM3	AM1	Bond length	PM3	AM1	Bond length	PM3	AM1
C2–C3	1.384	1.394	C8–N9	1.336	1.353	C16–C15	1.400	1.403
C3–C4	1.435	1.431	O7–C8	1.381	1.403	N18–C17	1.335	1.352
C4–C5	1.367	1.381	C12–C11	1.398	1.403	N19–N18	1.358	1.324
C5–S1	1.745	1.687	C13–C12	1.388	1.392	C20–N19	1.326	1.342
N10–C6	1.339	1.360	C14–C13	1.399	1.403	O21–C20	1.383	1.411
N9–N10	1.349	1.316	C15–C14	1.399	1.403			

AM1 makes N–N bonds too short and C–N and C–O bonds too long. It is noticed that the PM3 bond lengths lie between those of DFT and AM1. Another significant difference between the results of PM3 and AM1 is the bond length of C–S bond in the thiophene ring. PM3 gives 1.745 Å for this bond, which is quite close to 1.735 Å suggested by the ab initio (HF/3–21G*) [19], while AM1, which overestimates the strength of this bond, gives 1.687 Å. We therefore conclude that PM3 can give more correct qualitative geometries of *p*–*n* diblock structures compared to AM1.

4. Conclusions

Geometries of several *p*–*n* diblock oligomers were calculated using the semi-empirical PM3 method. The conformations of the thiophene rings (*p*-doped block) are quite close with those from oligomer thiophenes. The good correlation between the tunable redox and emissive wavelength of polymers and the calculated HOMO and LUMO energy levels, shows not only the possibility of *p*–*n* diblock monomers to model conjugated polymers but also the ability of PM3 to predict correct structures of the system. The reverse in the trend of A and B between the calculated values of monomers and the observed values from polymers is attributed to the solid state packing, through the conformational analysis performed on 1,4-bis(1,3,4-oxadiazolyl)-benzene and 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene, respectively. Some data from AM1 calculations are also included for comparison. It is concluded that PM3 calculated results are closer to those obtained from ab initio ones.

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