



Theoretical investigation on the effects of π -conjugation attenuation of poly(*p*-phenylenevinylene) polymers upon incorporating 2,2'-bipyridines

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Abstract

Localized-density-matrix method [Yokojima and Chen, Phys. Rev. B 59 (1999) 7259] has been employed to calculate the optical absorption of poly(*p*-phenylenevinylene) incorporated with 2,2'-bipyridines. The poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylenevinylene) (Behppv) as well as Polymer 1 and Polymer 2 whose 2,2'-bipyridyl-5-vinylene unit incorporated with one and three 2,5-bis(*n*-decyloxy)-1,4-phenylenevinylene monomer units, respectively, have been studied. The calculated results are consistent with the experimental results [Chen et al., J. Phys. Chem. A 103 (1999) 4341]. Moreover, the density matrices corresponding to first absorption peak for each of three polymers are examined and the microscopic origin of energy shifts is determined. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently Chen et al. studied the optical absorption of three polymers named Behppv, Polymer 1 and Polymer 2 (depicted in Fig. 1) in toluene solution [1]. They observed that the blue shift of absorption peaks occurred when 2,2'-bipyridine was incorporated into Behppv. The addition of 2,2'-bipyridine leads to a twist of the 2,2' single bond and thus results in the attenuation of π -conjugation length [1]. The blue shift is attributed to the π -conjugation attenuation which results in decreasing size of electron-hole pairs [1].

It is desirable to carry out numerical simulation to examine the sizes of excitons in these three materi-

als. However, the exciton sizes are expected to be 40 ~ 50 Å which are too large for conventional ab initio or semi-empirical calculations. Recently a linear scaling method, the localized-density-matrix (LDM) method [2–4], was developed to simulate the optical response of very large molecular systems. The method based on the time-dependent Hartree-Fock (TDHF) approximation [5–7] which includes all single electron excitations and partial double, triple and other multiple electron excitations. Instead of many-body wavefunctions, the reduced single-electron density matrix ρ is calculated from which the physical observables such as the charge distribution, dipole moment and photoexcitation spectrum are determined. Since the expensive calculation of a many-body wavefunction is avoided, the computational cost decreases substantially. More importantly, a truncation of reduced density matrix ρ is adopted

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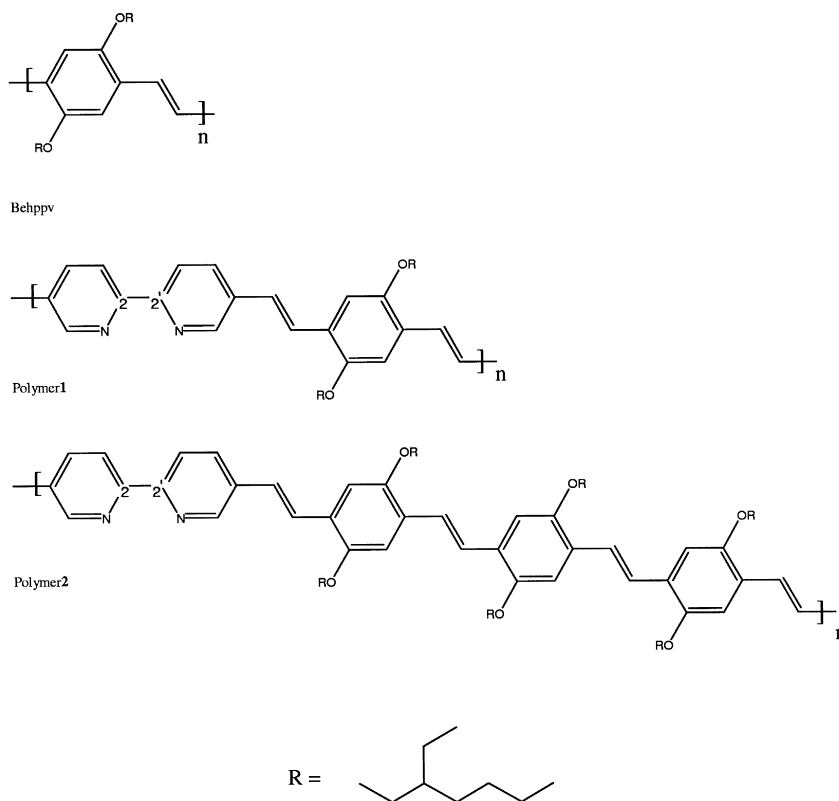


Fig. 1. The molecular structures of Behppv, Polymer 1 and Polymer 2.

for its elements when the distance between the two atomic orbitals involved is beyond a critical length. This truncation reduces the number of reduced density matrix elements to be determined from N^2 to $O(N)$ where N is the number of atomic orbitals in the system, and leads subsequently to the linear-scaling of the computational time versus the system size. The LDM method has been applied to the systems containing hundreds or thousands of atoms, for instance, polyacetylene oligomers, carbon nanotubes and poly(*p*-phenylenevinylene) aggregates [2–4,8–12].

In this work, we employ the LDM method to simulate the optical response in the above three polymers. In particular, we examine the characteristics of different excitations in three polymers, in particular, the sizes of various excitons. The manuscript is organized as follows. In Section 2, we describe the computational procedure. In Section 3, the calculated absorption spectra of three polymers

are presented. The characters of excitons are examined through their density matrix contour plots. The relationship between the exciton size and structure is illustrated for three polymers. Comparison to the experiment is made. In Section 4, the conclusion is given.

2. Method

The structures of three polymers, Behppv, Polymer 1 and Polymer 2 are determined as follows. First, the structures of small oligomers, three repeating units for Behppv, one unit for Polymer 1 and one unit for Polymer 2 are determined by Austin Model 1 (AM1) [13] geometry optimization. Secondly, these structures are used to construct larger oligomers by simple duplication. No further geometry optimization is performed. Among the three, Behppv is almost planar. The 2,2'-bipyridine groups are non-planar

and result in the non-planar structures for Polymer **1** and Polymer **2** [14]. The non-planar structures reduce the conjugation length of π electrons [15].

In our LDM calculation, CNDO/S Hamiltonian [16,17] is used to describe the valence electrons in the systems. The segment-molecular-orbital (SMO) representation [8] is employed to improve the calculation efficiency. The calculations consist of two steps: the HF ground state calculation and the LDM calculation for the absorption spectrum. In the HF ground state calculation, no truncation of reduced density matrix is introduced while a cutoff length of 40 Å is employed for calculating absorption spectra. The largest sizes of Behppv, Polymer **1** and Polymer **2** oligomers studied are 118, 112 and 123 Å, respectively. The electric field is polarized along the polymer chain. The atoms are indexed from one end to another along the chain.

Calculations are carried on four different sizes of oligomers for each of the three polymers. Referred to Fig. 1, $n = 6, 9, 12$ and 18 are employed for Beh-

ppv; for Polymer **1**, $n = 2, 3, 5$ and 7; and for Polymer **2**, $n = 1, 2, 3$ and 4.

3. Results

The optimized 3D structure of Behppv is nearly planar. The distortion is attributed to the side chains at 2,5 positions of each ring, as the steric effect would cause a certain extent of distortion from planar conformation. For Polymer **1** and Polymer **2**, as 2,2'-bipyridine groups are present in their structures, they are distorted from planar by a much larger extent. For the three polymers, the dihedral angles for Behppv between adjacent repeating units range from 0° to 20°. On average, it is around 10°. For Polymer **1** and Polymer **2**, the dihedral angle between the two pyridine planes for each polymer is 55° and 52°, respectively. This is because that the 2,2'-C–C bond shown in Fig. 1 is allowed to rotate due to its small rotational potential barrier [1].

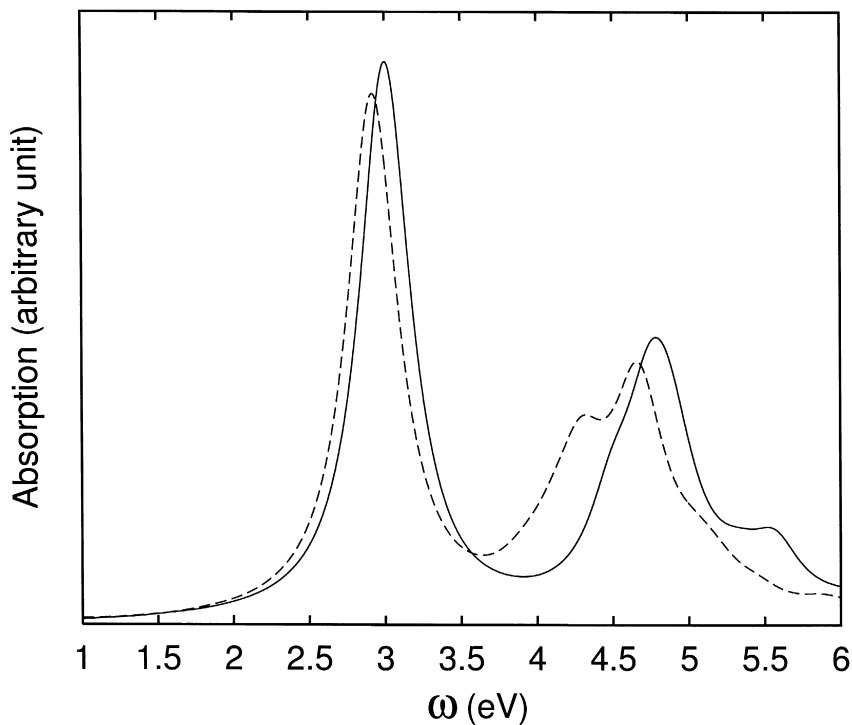


Fig. 2. The absorption spectra of Behppv ($n = 2$). Solid line: hydrogen atom; dashed line: side chains R = 2-ethyl-hexyl.

Table 1

Calculated and experimental optical gaps in unit of electron volt (eV). n is the number of repeating units.

	Behppv	Polymer 1	Polymer 2
Calculated	2.49 ^a	2.67 ^a	2.59 ^a
	2.42 ^b	2.62 ^b	2.51 ^b
	2.39 ^c	2.57 ^c	2.46 ^c
	2.36 ^d	2.56 ^d	2.45 ^d
	Experimental	2.43	2.85

^a Behppv ($n = 6$); Polymer 1 ($n = 2$); Polymer 2 ($n = 1$).

^b Behppv ($n = 9$); Polymer 1 ($n = 3$); Polymer 2 ($n = 2$).

^c Behppv ($n = 12$); Polymer 1 ($n = 5$); Polymer 2 ($n = 3$).

^d Behppv ($n = 18$); Polymer 1 ($n = 7$); Polymer 2 ($n = 4$).

For Behppv, as it has near planar structure, its π -conjugation length is longest so that it should have the lowest energy excitation as compared to Polymer 1 and Polymer 2. For Polymer 1, it has more

2,2'-bipyridine groups than the others, and is thus twisted to the largest extent so that it should have the highest energy excitations. For Polymer 2, its structure is between those of Behppv and Polymer 1, we expect that its optical gap is between those of Behppv and Polymer 1 as well.

In Fig. 2, we plot the absorption spectrum (dashed line) for a Behppv oligomer with $n = 2$. To investigate the effects of side chains, we replace the side chains with hydrogen atoms, and calculate again the absorption spectrum (solid line) of the resulting structure. As shown in Fig. 2, the first peak of the Behppv oligomer with side chains red shifts a little and the peak height is suppressed. It can be attributed to the fact that the excited electron-hole pair delocalizes to a larger extent due to the side chains. However, the shift is less than 0.1 eV. To simplify

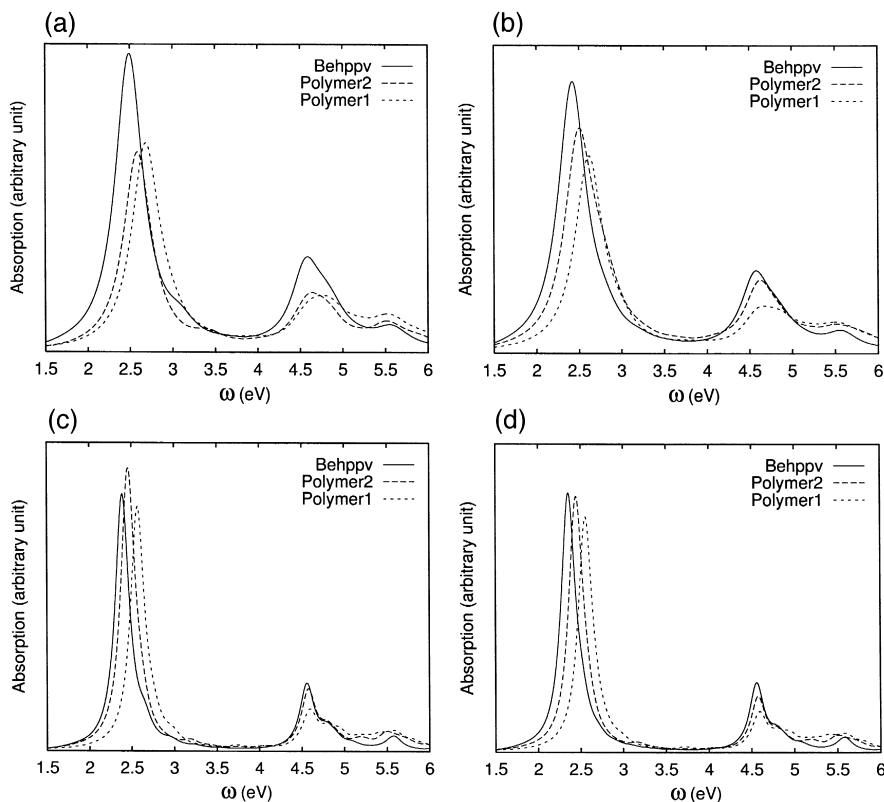


Fig. 3. The absorption spectra for different sizes of oligomers. (a) Behppv: $n = 6$, Polymer 2: $n = 1$, Polymer 1: $n = 2$, dephasing = 0.2 eV; (b) Behppv: $n = 9$, Polymer 2: $n = 2$, Polymer 1: $n = 3$, dephasing = 0.2 eV; (c) Behppv: $n = 12$, Polymer 2: $n = 3$, Polymer 1: $n = 5$, dephasing = 0.1 eV; (d) Behppv: $n = 18$, Polymer 2: $n = 4$, Polymer 1: $n = 7$, dephasing = 0.1 eV. Solid line: Behppv; dotted line: Polymer 1; and dash line: Polymer 2.

the calculations, we replace all the side chains with the hydrogen atoms in calculating absorption spectrum thereafter.

From Table 1 and the absorption spectra in Fig. 3, we find that the calculated results are overall consistent with the experimental results. Experimentally, the blue shift of absorption peaks for Polymer 1 and Polymer 2 relative to that of Behppv in solution is 0.39 and 0.18 eV, respectively. Our calculation results were 0.21 and 0.09 eV. Although the values are not the same as the experimental one, the trend of changes is consistent. The deviation of the peak positions may be accounted for by the fact that different conditions are used for the calculation and

experiment. In our calculation, the solvent effect is not considered which may lead to further the distortion of the conformation. When the structures are distorted, the π conjugation would be shortened which leads to larger exciton energy. The structures used for the calculations are optimized in gas phase so that the other effects, such as intermolecular interactions and solvent effect are ignored. Note that the HOMO to LUMO transition is the largest component contributed to the first peak in the absorption spectrum. Its amplitude in percentile are 0.72%, 0.66% and 0.64% for Behppv, Polymer 1 and Polymer 2, respectively. Near the HOMO and LUMO, the contributions of other transitions are also signifi-

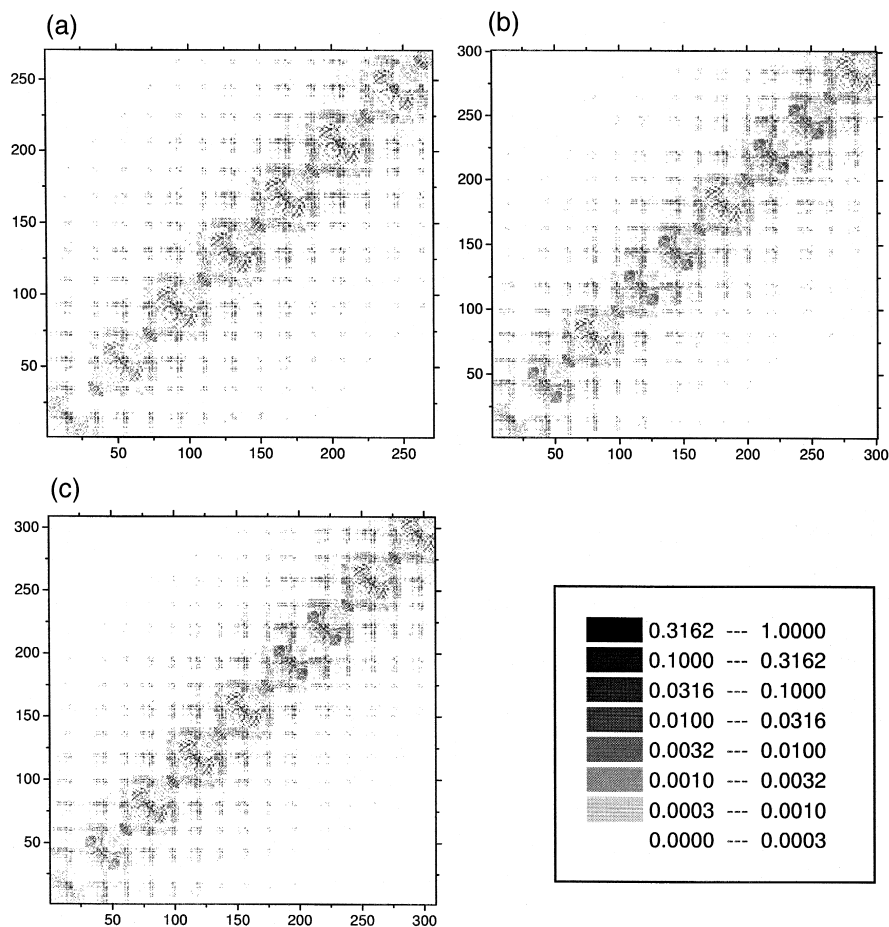


Fig. 4. The contour plots of density matrices for first peak of each polymer. (a) Behppv at 2.36 eV, (b) Polymer 1 at 2.56 eV, and (c) Polymer 2 at 2.45 eV.

cant for first peak. The excitations among other molecular orbitals account for other peaks in the spectra.

In Table 1, the saturation of optical gap can be seen clearly as the size increases. Similarly the linear polarizability $\chi^{(1)}$ saturates as the size increases. The saturation lengths are about 80 Å for three polymers. When the electric field is applied, electron–hole pairs are created. The exciton length can be defined as the distance between the hole and electron.

In Fig. 4 the reduced density matrix at first absorption peak is shown for each polymer. The x – y axes represent the indices of orbitals in the SMO representation [8]. The diagonal part is the electron occupation number of each orbital and the off-diagonal part represents the electron–electron coherence. The larger the density matrix element, the darker the corresponding dot. We may compare the relative exciton sizes for the three polymers by examining the widths of the dark stripes or bandwidth in the density matrix contour plots.

It is clear that the bandwidth for Behppv is the widest, Polymer 2 is next, and Polymer 1 has the smallest width. This observation is another evidence that Polymer 1 has smallest exciton size.

Another way to estimate the exciton size is as follows. Summing up the matrix elements along the direction of the diagonal of the plots using the following equations,

$$\begin{aligned} \sum_{n=1} |\delta \rho_{n,n}| &= I_1 \\ \sum_{n=1} |\delta \rho_{n,n+1}| &= I_2 \\ &\vdots \\ \sum_{n=1} |\delta \rho_{n,n+(k-1)}| &= I_k \\ &\vdots \\ \sum_{n=1} |\delta \rho_{n,n+(N-1)}| &= I_N \end{aligned}$$

where $\delta \rho$ is the induced density matrix, n is the specified orbital, N is the total number of orbital. In Fig. 5, $\log(I_k)$ versus the index k in the SMO representation is plotted. $n = 18, 7$ and 4 are used for Behppv, Polymer 1 and Polymer 2, respectively. k within about 50 Å is shown in the figure for each polymer. The zigzag shape of the graphs can be

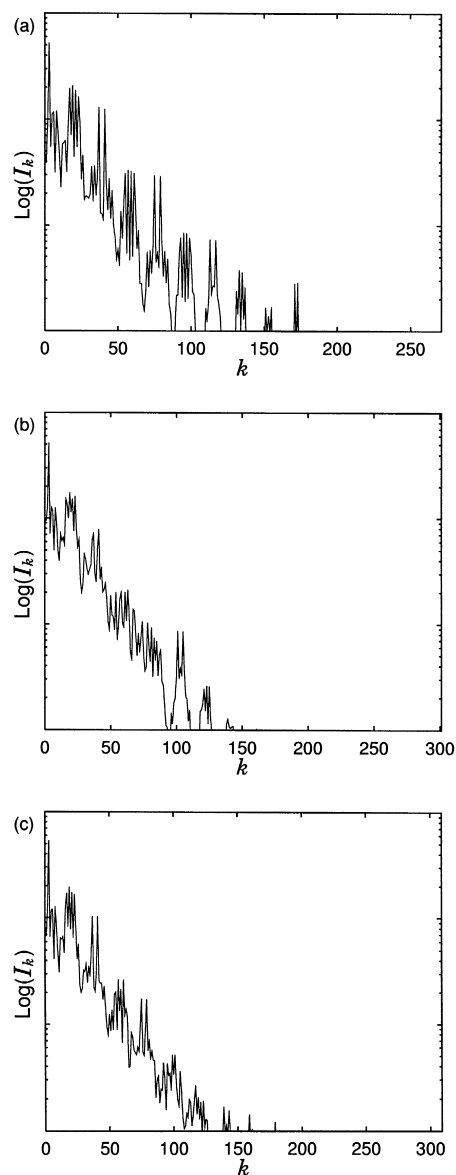


Fig. 5. The plot of I_k versus orbital index k of each polymer. (a) Behppv, (b) Polymer 1, (c) Polymer 2.

explained by the fact that the orbitals other than π are included. However, the general trend is consistent with our expectation. The higher peaks in the plot refer to the electron localized in the p_π orbitals which form the π conjugation along the main chain and the lower peaks refer to other orbitals such as s and p_σ orbitals. It is clear that the excitons are not localized at particular site.

The bandwidth of density matrix contour plots is approximated by the value of index k_0 where $I_{k_0} \approx 0$. $k_0 \approx 170$, 140 and 170 are found for Behppv, Polymer 1 and Polymer 2, respectively, and the corresponding lengths are 31.8, 23.9 and 28.9 Å. Since the exciton length is proportional to the bandwidth of corresponding reduced density matrix, this implies that the exciton has largest size in Behppv while the smallest size in Polymer 1. This π conjugation attenuation as a result of ring torsion and its effects on absorption spectrum have been investigated by small CI [1] or simpler model calculations [18,19], similar conclusion was reached.

4. Conclusion

The physical properties of excitons in Behppv, Polymer 1 and Polymer 2 are investigated by the LDM calculations with CNDO/S Hamiltonian. In particular, the absorption spectra of large oligomers of three polymers are calculated and the corresponding density matrices are examined. All valence electrons are included and the largest oligomer is 123 Å in size. Results show that the introduction of 2,2'-bipyridine groups in Polymer 1 and Polymer 2 distorts the original planar structure of Behppv. Our LDM calculation demonstrates directly that this distortion reduces the π -conjugation lengths and results subsequently in shorter exciton size and larger exciton energy. These observations are consistent with the experimental findings and explanations by Chen et al. [1].

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