

# Optical excitations in electroluminescent polymers: poly(*para*-phenylenevinylene) family

(Running head: *Optical excitations in PPV family*)

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(Received )

## Abstract

Component of photoexcited states with large spatial extent is investigated for optical absorption spectra of the electroluminescent conjugated polymers by using the intermediate exciton theory. We calculate the ratio of oscillator strengths due to long-range excitons with respect to sum of all the oscillator strengths of the absorption as a function of the monomer number. The oscillator strengths of the long-range excitons in poly(*para*-phenylene) are smaller than those in poly(*para*-phenylenevinylene), and those of poly(*para*-phenylenedivinylene) are larger than those in poly(*para*-phenylenevinylene). Such relative variations are explained by the differences of the number of vinylene units. The oscillator strengths of long-range excitons in poly(*di-para*-phenylenevinylene) are much larger than those of the above three polymers, due to the increase of number of phenyl rings. We also find that the energy position of the almost localized exciton is nearly the same in the four polymers.

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PACS numbers: 78.66.Qn, 73.61.Ph, 71.35.Cc

# 1. Introduction

The observation of remarkable electroluminescent properties of the polymer poly(*para*-phenylenevinylene) (PPV) [1] has attracted physical and chemical research activities. An important recent development is the observation of stimulated emission and lasing from a PPV layer incorporated within an optical cavity [2]. Lasing has been also proposed in order to explain the band-narrowing observed on high intensity photoexcitation of a composite film of a PPV derivative and nanoparticles of TiO<sub>2</sub> [3]. Therefore, understanding of structures of photoexcited states in PPV and related polymers containing phenyl rings is one of interesting research topics.

In the PPV polymer, the onset of the photocurrents locates at the excitation energy between 3.0 eV and 4.0 eV [4,5,6], and this energy is significantly larger than both of the optical absorption edge at about 2.0 eV and the lowest peak energy at 2.4 eV. In the previous study [7,8], we have characterized the extent of photoexcited states of the PPV by using the intermediate exciton theory. When the distance between an electron and a hole is shorter than the spatial extent of the monomer, we have called the exciton as a “short-range” exciton. When the exciton width is larger than the extent of the monomer, we have called the exciton as a “long-range” exciton. We have characterized each photoexcited state as “short-range” or “long-range”. We have shown that a long-range exciton feature starts at the energy in the higher energy side of the lowest feature of the optical absorption of PPV. The energy position is nearly the same as that of the semiconducting energy gap which has been interpreted as the onset of the large photocurrents observed in experiments. Therefore, the presence of photoexcited states with large spatial extent is essential in mechanisms of remarkable photocurrents observed in PPV.

The purpose of this paper is to look at contributions from long-range excitons, which make large effects on photoconduction properties in PPV-related polymers: poly(*para*-phenylene) (PPP), poly(*para*-phenylenedivinylene) (PPD), and poly(*di-para*-phenylenevinylene) (PDV). The structures of these polymers, namely, PPV family, are illustrated in Fig. 1. These polymers are composed of phenyl rings and vinylene CH-dimers. The names of the two polymers and

their abbreviations, PPD and PDV, are pseudonyms (tentative names) in this paper, because current common names of these polymers have not been known at present. The long-range excitons are characterized as we have done for PPV in the previous study [7,8].

In the next section, the theoretical formalism is explained, and the characterization method of long-range excitons is given. The calculated results are reported in §3, and the paper is concluded with a summary in §4.

## 2. Model

We consider the following model with electron-phonon and electron-electron interactions.

$$H = H_{\text{pol}} + H_{\text{int}}, \quad (1)$$

$$H_{\text{pol}} = - \sum_{\langle i,j \rangle, \sigma} (t - \alpha y_{i,j}) (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) + \frac{K}{2} \sum_{\langle i,j \rangle} y_{i,j}^2, \quad (2)$$

$$H_{\text{int}} = U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{n_{\text{el}}}{2}) (c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{n_{\text{el}}}{2}) + \sum_{i,j} W(r_{i,j}) (\sum_\sigma c_{i,\sigma}^\dagger c_{i,\sigma} - n_{\text{el}}) (\sum_\tau c_{j,\tau}^\dagger c_{j,\tau} - n_{\text{el}}). \quad (3)$$

In eq. (1), the first term  $H_{\text{pol}}$  is the tight binding model along the polymer backbone with electron-phonon interactions which couple electrons with modulation modes of the bond lengths, and the second term  $H_{\text{int}}$  is the Coulomb interaction potentials among electrons. In eq. (2),  $t$  is the hopping integral between the nearest neighbor carbon atoms in the ideal system without bond alternations;  $\alpha$  is the electron-phonon coupling constant that modulates the hopping integral linearly with respect to the bond variable  $y_{i,j}$  which measures the magnitude of the bond alternation of the bond  $\langle i,j \rangle$ ;  $y_{i,j} > 0$  for longer bonds and  $y_{i,j} < 0$  for shorter bonds (the average of  $y_{i,j}$  is taken to be zero);  $K$  is the harmonic spring constant for  $y_{i,j}$ ; and the sum is taken over the pairs of neighboring atoms. Equation (3) is the Coulomb interactions among electrons. Here,  $n_{\text{el}}$  is the average number of electrons per site;  $r_{i,j}$  is the distance between the  $i$ th and  $j$ th sites; and

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/aV)^2}} \quad (4)$$

is the parametrized Ohno potential. The quantity  $W(0) = U$  is the strength of the onsite interaction;  $V$  means the strength of the long-range part ( $W(r) \sim aV/r$  in the limit  $r \gg a$ ); and  $a = 1.4\text{\AA}$  is the mean bond length. The parameter values used in this paper are  $\alpha = 2.59t/\text{\AA}$ ,  $K = 26.6t/\text{\AA}^2$ ,  $U = 2.5t$ , and  $V = 1.3t$ . They have been determined by comparison with experiments of PPV, and have been used in [7,8]. Most of the quantities in the energy units are shown by the unit of  $t$  in this paper.

Excitation wavefunctions of the electron-hole pair are calculated by the Hartree-Fock approximation followed by the single excitation configuration interaction method. This method, which is appropriate for the cases of moderate Coulomb interactions – strengths between negligible and strong Coulomb interactions – is known as the intermediate exciton theory in the literatures [7,8]. We write the singlet electron-hole excitations as

$$|\mu, \lambda\rangle = \frac{1}{\sqrt{2}}(c_{\mu,\uparrow}^\dagger c_{\lambda,\uparrow} + c_{\mu,\downarrow}^\dagger c_{\lambda,\downarrow})|g\rangle, \quad (5)$$

where  $\mu$  and  $\lambda$  mean unoccupied and occupied states, respectively, and  $|g\rangle$  is the Hartree-Fock ground state. The general expression of the  $\kappa$ th optical excitation is:

$$|\kappa\rangle = \sum_{(\mu,\lambda)} D_{\kappa,(\mu,\lambda)} |\mu, \lambda\rangle. \quad (6)$$

After inserting the relation with the site representation  $c_{\mu,\sigma} = \sum_i \alpha_{\mu,i} c_{i,\sigma}$ , we obtain

$$|\kappa\rangle = \frac{1}{\sqrt{2}} \sum_{(i,j)} B_{\kappa,(i,j)} (c_{i,\uparrow}^\dagger c_{j,\uparrow} + c_{i,\downarrow}^\dagger c_{j,\downarrow}) |g\rangle, \quad (7)$$

where

$$B_{\kappa,(i,j)} = \sum_{(\mu,\lambda)} D_{\kappa,(\mu,\lambda)} \alpha_{\mu,i}^* \alpha_{\lambda,j}. \quad (8)$$

Thus,  $|B_{\kappa,(i,j)}|^2$  is the probability that an electron locates at the  $i$ th site and a hole is at the  $j$ th site.

We shall define the following quantity:

$$P_\kappa = \sum_{i \in M} \sum_{j \in M} |B_{\kappa,(i,j)}|^2, \quad (9)$$

where  $M$  is a set of sites within a single monomer, in other words, a set of carbon sites included in the brackets of each polymer shown in Fig. 1. When  $P_\kappa > 1/N_m$  ( $N_m$  is the number of monomers used in the calculation of periodic polymer chains), the electron and hole favor to have large amplitudes in the same single monomer. Then, this excited state is identified as a short-range exciton. On the other hand, when  $P_\kappa < 1/N_m$ , the excited state is characterized as a long-range exciton. This characterization method is performed for all the photoexcited states  $|\kappa\rangle$ , and a long-range component in the optical absorption spectrum is extracted from the total absorption. In the next section, numerical results are to be reported and discussion will be given.

### 3. Long-range excitons in PPV family

#### 3.1 PPP and PPV

We discuss properties of photoexcited states in PPP [Fig. 1 (a)] and PPV [Fig. 1 (b)] in this subsection. Numerical results of PPV have been shown in refs. [7,8] already, but they are shown again comparing with the results of PPP. Figures 2 and 3 show optical absorption spectra and long-range component of the oscillator strengths for PPP, and Figs. 4 and 5 show results of PPV.

Figures 2 (a) and (b) show anisotropies of the optical absorption of PPP. The electric field of light is parallel and perpendicular to the polymer axis in Figs. 2 (a) and (b), respectively. The thin lines show the contributions from long-range excitons. In Fig. 2 (a), there are two features centered around about  $1.4t$  and  $2.5t$ . The former comes from optical excitations between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO have certain magnitudes of dispersions near the Brillouin zone center, and therefore the excitons near the energy  $1.4t$  have an appreciable long-range component. In fact, we observe a peak due to long-range excitons around the energy  $1.8t$ . On the other hand, the feature around  $2.5t$  is due to transitions between spatially localized band

states [9]. So, this feature does not have an appreciable long-range component in the higher energy side of the peak. Next, we discuss the case with perpendicular electric field shown in Fig. 2 (b). There is a feature at  $2.2t$ , whose long-range exciton component exists at the higher energy side. In higher energies than this feature, several transitions are mixed, and the long-range component is dominant in energies larger than  $3.0t$ . Figure 2 (c) shows the absorption spectra where the direction of the electric field of light is orientationally averaged. We find that two features around  $1.4t$  and  $2.5t$  in the parallel electric field case give the central two peaks in the spectra. The features in the perpendicular field case overlap with the lower and higher energy sides of the dominant feature around  $2.5t$ .

Figure 3 summarizes the long-range component of the oscillator strengths of PPP. It is shown as a function of the PPP monomer number  $N_m$ . The squares are for the total absorption. The circles and triangles indicate the data for the cases with the electric field parallel and perpendicular to the polymer axis, respectively. Generally, the long-range component of the perpendicular electric field case is larger than that of the parallel field case. It seems that the long-component of the orientationally averaged spectra saturates at approximately 7 % near  $N_m = 20$ . Note that the small fluctuation of the plots with respect to  $N_m$  is due to the numerical calculation errors, and is not an intrinsic behavior. Such numerical fluctuations have also been seen in our previous work of PPV [7,8]. Readers are suggest to look at the overall variations of the long-range component with respect to  $N_m$ .

Next, we compare the results of PPP with those of PPV. Numerical absorption spectra are shown in Fig. 4, and their long-range component is shown in Fig. 5. The results have been already reported in [7,8], but they are shown again in order to compare with results of the other polymers. Comparing Fig. 2 with Fig. 4, we observe that peak structures of PPP and PPV are similar at the first glance. However, there is a quantitative difference: the oscillator strengths of the lowest excitation in Figs. 4 (a) and (c) are larger in PPV than those of PPP. The long-range component of the lowest exciton is larger in PPV, too. This fact reflects in the larger saturated value of the total long-range component of PPV shown in Fig. 5 than that of

PPP shown in Fig. 3.

As noted in ref. [9], the lowest optical excitations of PPP and PPV have characters like those of excitons in a simple prototype polymer: *trans*-polyacetylene. The band structures of polyacetylene are well described by the Su-Schrieffer-Heeger (SSH) model [10]. The quasiparticle band structures have finite dispersions at the top (bottom) of the valence band (conduction band). Therefore, the lowest exciton owing to these dispersive bands has apparent long-range component at the higher energy side after taking into account of Coulomb interactions among electrons. The lowest excitons of PPP and PPV have just the similar characters, and thus Figs. 2 (a) and 4 (a) show the dominant contributions of long-range excitons with respect to the lowest band-to-band optical excitations.

The difference in the polymer structures of PPP and PPV in Figs. 1 (a) and (b) is that a vinylene bond is added between phenyl rings of PPP. This is related with the property that electronic structures near the energy gap of PPV have more dispersive characters than those of PPP, and thus the optical excitations owing to these bands will more resemble with those of *trans*-polyacetylene described by the SSH model. Therefore, the relative oscillator strengths of the lowest excitons of PPV [Fig. 4 (a)] are larger than those of PPP [Fig. 2 (a)]. Also, total long-range component (about 8 %) of PPV (Fig. 5) is larger than that (about 7 %) of PPP (Fig. 3). We could say that optical excitations of PPV will have photoconductive properties which are stronger than those of PPP.

## 3.2 PPD

In PPD shown in Fig. 1 (c), there are two vinylene bonds between the neighboring phenyl rings. In this subsection, we look at the optical properties resulting from electronic structures and excitonic effects of PPD.

Figure 6 shows the optical absorption spectra, when the electric field of light is parallel to the polymer axis [Fig. (a)], perpendicular to the polymer [Fig. (b)], and is averaged over orientations [Fig. (c)]. Long-range exciton contributions are also shown in these three figures.

When the electric field is along with the polymer axis [Fig. 6 (a)], the oscillator strengths of the lowest exciton around the energy  $1.2t$  are dominant. This feature has its long-range component at the higher energy side. There is a small feature around the energy  $2.5t$ . The oscillator strengths of this feature becomes relatively smaller than those of PPV shown in Fig. 4 (a). The lowest exciton feature becomes larger than that of Fig. 4 (a). This comes from the larger number of vinylene units in PPD than that of PPV. When the electric field is perpendicular to the polymer [Fig. 6 (b)], the overall spectral shape is similar to that in Fig. 4 (b). Figure 6 (c) shows the orientationally averaged spectra. The lowest exciton feature becomes more dominant from PPP [Fig. 2 (c)], PPV [Fig. 4 (c)], to PPD. The three peak structure from  $\sim 2t$  to  $\sim 3t$  is commonly seen in these three polymers, but their oscillator strengths become relatively weaker.

Figure 7 shows the long-range component of PPD as a function of the monomer number  $N_m$ . The maximum number of  $N_m$  is 12. The saturation behavior is seen at smaller  $N_m$  than that of PPV, due to the larger dimension of the monomer unit. The long-range component of the perpendicular field case is larger than that of the parallel field case. The long-range component of the orientationally averaged case saturates at  $N_m \sim 10$  with the value of approximately 11 %. This polymer will be more photoconductive than PPV.

### 3.3 PDV

In previous subsections, we have considered the series: PPP, PPV, and PPD, where number of vinylene bonds increases in each monomer unit. There would be another series: PPP, PPV, and PDV [shown in Fig. 1 (d)], where number of phenyl rings increases in the monomer units. We consider optical properties of PDV in this subsection.

Figure 8 (a) shows the optical absorption spectra of the parallel electric field case. There are two main features: the lowest exciton peak around  $1.0t$  and the almost localized exciton feature around  $2.5t$ . They are commonly seen in polymers considered in this paper. The broad structure from  $\sim 3t$  to  $\sim 4t$  is due to mixing of high energy transitions among molecular orbitals with large energies in the presence of more phenyl rings. Figure 8 (b) is the spectra where the

electric field is perpendicular to the polymer. In contrast to the parallel field case, the spectral shape is rather similar to that of the other polymers. The long-range exciton contributions are remarkable in this case. Figure 8 (c) shows the averaged spectra. The overall shape is like that of PPV shown in Fig. 4 (c). There is a distinct lowest feature at around  $1.0t$ , and three small peaks are present in higher energies. However, the long-range component is larger than that of PPV. This polymer will show the largest photoconductive properties among polymers considered in this paper.

Finally, Fig. 9 shows the long-range component as a function of the number of monomer units. The long-range component of the perpendicular field case is larger than that of the parallel field case, as clearly seen in Fig. 8 (b). The saturated value of the orientationally averaged spectra is approximately 17 %. This is due to the complex molecular orbital structures of PDV. Table I summarizes the long-range component of the four polymers before closing this section.

## 4. Summary

We have considered optical excited states of the electroluminescent polymers which are related with the most famous polymer PPV. We have paid attention to the long-range component of the optical excitations using the intermediate exciton theory. The following is the main conclusions of this paper:

- (1) As we go from PPP, PPV, to PPD, the oscillator strengths of the long-range excitons become larger. Such the relative variation is explained by the difference of number of the vinylene bonds in each monomer unit.
- (2) The oscillator strengths of long-range excitons in PDV are much larger than those of the above three polymers, due to the increase of number of phenyl rings.
- (3) The energy position of the almost localized exciton is nearly the same ( $\sim 2.5t$ ) in the four polymers considered in this paper. The excitation energy of the almost localized exciton is just

$2.0t$  in a free electron model [9] for all the polymers. The enhancement about  $0.5t$  originates from the Coulomb interaction part of our model.

## **Acknowledgements**

Useful discussion with Y. Shimoi, S. Abe, S. Kobayashi, K. Murata, and S. Kuroda is acknowledged. Helpful communications with S. Mazumdar, M. Chandross, W. Barford, D. D. C. Bradley, R. H. Friend, E. M. Conwell, and Z. V. Vardeny are much acknowledged.

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TABLE I. The component of long-range excitons in four kinds of polymers for which we calculated.

polymer	long-range component
PPP	7 %
PPV	8 %
PPD	11 %
PDV	17 %

## Figure Captions

Fig. 1. Lattice structures of the electroluminescent polymers studied in this paper. The abbreviations, PPD and PDV, are pseudonyms.

Fig. 2. Optical absorption spectra of the PPP. The polymer axis is in the  $x$ - $y$  plane. The electric field of light is parallel to the chain and in the direction of the  $x$ -axis in (a), and it is perpendicular to the axis and is along with the  $z$ -axis in (b). The orientationally averaged spectra are shown in (c). The number of the PPP units is  $N_m = 19$ . The bold line is for the total absorption. The thin line indicates the absorption of the long-range component. The Lorentzian broadening  $\gamma = 0.15t$  is used.

Fig. 3. Long-range component of the optical absorption spectra as a function of the PPP unit number  $N_m$ . The squares are for the total absorption. The circles and triangles indicate the data for the cases with the electric field parallel and perpendicular to the polymer axis, respectively.

Fig. 4. Optical absorption spectra of the PPV. The polymer axis is in the  $x$ - $y$  plane. The electric field of light is parallel to the chain and in the direction of the  $x$ -axis in (a), and it is perpendicular to the axis and is along with the  $z$ -axis in (b). The orientationally averaged spectra are shown in (c). The number of the PPV units is  $N_m = 20$ . The bold line is for the total absorption. The thin line indicates the absorption of the long-range component. The Lorentzian broadening  $\gamma = 0.15t$  is used.

Fig. 5. Long-range component of the optical absorption spectra as a function of the PPV unit number  $N_m$ . The squares are for the total absorption. The circles and triangles indicate the data for the cases with the electric field parallel and perpendicular to the polymer axis,

respectively.

Fig. 6. Optical absorption spectra of the PPD. The polymer axis is in the  $x$ - $y$  plane. The electric field of light is parallel to the chain and in the direction of the  $x$ -axis in (a), and it is perpendicular to the axis and is along with the  $z$ -axis in (b). The orientationally averaged spectra are shown in (c). The number of the PPD units is  $N_m = 12$ . The bold line is for the total absorption. The thin line indicates the absorption of the long-range component. The Lorentzian broadening  $\gamma = 0.15t$  is used.

Fig. 7. Long-range component of the optical absorption spectra as a function of the PPD unit number  $N_m$ . The squares are for the total absorption. The circles and triangles indicate the data for the cases with the electric field parallel and perpendicular to the polymer axis, respectively.

Fig. 8. Optical absorption spectra of the PDV. The polymer axis is in the  $x$ - $y$  plane. The electric field of light is parallel to the chain and in the direction of the  $x$ -axis in (a), and it is perpendicular to the axis and is along with the  $z$ -axis in (b). The orientationally averaged spectra are shown in (c). The number of the PDV units is  $N_m = 9$ . The bold line is for the total absorption. The thin line indicates the absorption of the long-range component. The Lorentzian broadening  $\gamma = 0.15t$  is used.

Fig. 9. Long-range component of the optical absorption spectra as a function of the PDV unit number  $N_m$ . The squares are for the total absorption. The circles and triangles indicate the data for the cases with the electric field parallel and perpendicular to the polymer axis, respectively.