Long-Range Excitons in Optical Absorption Spectra of Electroluminescent Polymer Poly(paraphenylenvinylene)

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Abstract

The component of photoexcited states with large spatial extent is investigated for poly(paraphenylenvinylene) using the intermediate exciton theory. We find a peak due to long-range excitons at the higher-energy side of the lowest main feature of optical spectra. The fact that the onset of long-range excitons is located near the energy gap is related to the mechanisms of large photocurrents measured in such energy regions. We show that a large value of the hopping integral is realistic for characterizing optical excitations.

KEYWORDS: excitons, electroluminescent polymer, poly(paraphenylenvinylene), electron-electron interactions, optical absorption, photocurrents, theory
The remarkable electroluminescent properties of poly(\textit{para}-phenylenevinylene) (PPV)\textsuperscript{1)} have prompted physical and chemical research activities. The polymer structure is shown in Fig. 1. The onset of the photocurrent occurs at an excitation energy between 3.0 eV and 4.0 eV,\textsuperscript{2}–\textsuperscript{4)} which is significantly larger than both of the optical absorption edge at about 2.0 eV and the lowest peak energy at 2.4 eV. The experiments have been interpreted theoretically in terms of excitonic effects which have been taken into account by the single excitation configuration interaction (single-CI) method\textsuperscript{5,6)} and also by the density matrix renormalization group method.\textsuperscript{7)}

The binding energy of excitons is about 0.9 eV, as estimated using the single-CI theory.\textsuperscript{5)}

The spatial extent of excitons, in other words, the distance between electrons and holes, depends on their photoexcitation energies. If an exciton is strongly bound, its extent can be smaller than the region of the PPV monomer unit and thus the exciton becomes Frenkel-like, as observed in molecular crystals. If the binding is weak, the photoexcited electron-hole pair tends to distribute over several monomer units, like the charge-transfer exciton in molecular systems. The main purpose of this study is to characterize the extent of photoexcited states of the PPV using the single-CI theory recently developed by Shimoi and Abe.\textsuperscript{6)} The polymer backbone structure is treated using a tight binding model Hamiltonian with electron-phonon interactions, and attractions between electrons and holes are taken into account by long-range Coulomb interactions. When the distance between an electron and a hole is shorter than the spatial extent of the monomer, we call the exciton a “short-range” exciton. When the exciton width is larger than the extent of the monomer, we call it a “long-range” exciton. We will characterize each photoexcited state as “short range” or “long range” by calculating the probability that the photoexcited electron and hole exist on different PPV monomer units. A similar characterization method has also been used in recent investigations of charge-transfer excitons in \(C_{60}\) cluster systems.\textsuperscript{8–10)}

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

\[
H = H_{\text{pol}} + H_{\text{int}}, 
\]

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

\[
H_{\text{int}} = U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{n_{e\uparrow}}{2}) (c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{n_{e\downarrow}}{2}) + \sum_{i,j} W(r_{i,j}) \left( \sum_{\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - n_{e\sigma} \right) \left( \sum_{\tau} c_{j,\tau}^\dagger c_{j,\tau} - n_{e\tau} \right). 
\]

In eq. (1), the first term \(H_{\text{pol}}\) is the tight binding model along the PPV polymer backbone (shown in Fig. 1) 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 is a measure of the magnitude of the 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 \( y_{i,j} \) 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) describes the Coulomb interaction among electrons. Here, \( n_{el} \) is the average number of electrons per site; \( r_{i,j} \) is the distance between the \( i \)th and \( j \)th sites; and \( W(r) = 1/\sqrt{(1/U)^2 + (r/aV)^2} \) 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 \( a = 1.4 \text{Å} \) is the mean bond length. We use the long-range interaction because the excited electron and hole are spread over a fairly large region of the system considered. The parameter values used in this paper are \( \alpha = 2.59t/\text{Å}, K = 26.6t/\text{Å}^2, U = 2.5t, \) and \( V = 1.3t \) (ref. 6). 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 (HF) approximation followed by the single-CI method. This method has been used in the optical spectra of the PPV chain,\(^5,6\) and \( \text{C}_{60} \) (\( \text{C}_{70} \)) molecules and solids.\(^8-11\) The optical absorption spectra become anisotropic with respect to the electric field of light, as expected from the polymer structures. Anisotropy effects are considered by applying an electric field in the direction parallel to the chain axis (shown in Fig. 1) as well as in the perpendicular directions.

First, we show the total absorption spectra, and discuss the effects of the boundary conditions and anisotropic effects with respect to the directions of the electric field of light. Figures 2 (a) and 2 (b) show the calculated spectra with periodic and open boundaries, respectively. It seems that the number of PPV monomer units, \( N = 20 \), gives the spectral shape which is almost independent of the chain length. The optical spectra strongly depend on the system size when the number \( N \) is less than 10, but they become almost independent of the size when \( N \) is near 20. Also, the difference in the spectral shapes of the two boundaries is small. This is related to the saturated behavior of the spectral shape.

There are four features at 1.2\( t \), 2.1\( t \), 2.4\( t \), and 3.0\( t \), in the total absorption spectra in Fig. 2. Anisotropy effects with respect to the electric field are clearly seen. The first and third features are larger when the field is parallel to the polymer axis, while the second and fourth features are larger when the field is perpendicular to the axis. In the literature,\(^5-7\) there are two different schemes of theoretical assignment of absorption peaks.
Here, we have applied both schemes using $t = 2.0$ eV (ref. 6) and $t = 2.3$ eV (refs. 5 and 7). The results are shown in Table I with the experimental absorption values of the chemically improved PPV reported in ref. 3. The degree of agreement between experiment and theory is comparable for the two schemes in terms of the optical excitation energies. However, the recent measurement of anisotropy$^{12}$ favors the assignment with $t = 2.3$ eV. The feature at around 4.7 eV shows reverse anisotropy from that of the lowest feature around 2.5 eV. The assignment of the experiment with $t = 2.3$ eV is consistent with the anisotropy shown in Fig. 2. Therefore, we find that the larger value of the hopping integral, $t = 2.3$ eV, is realistic for optical excitations of the neutral PPV chain.

Next, we look at the origins of the main features in relation to the band structure. Figure 3 shows the band structure obtained through the HF approximation. The branches of the valence (conduction) band are labeled as $VB_j$ ($CB_j$) ($j = 1 \sim 4$) from the energy gap to the band edges. The bands $VB_2$ and $CB_2$ almost lack dispersion. This is due to the fact that the amplitudes at atoms A and D are nearly zero, and the wavefunctions are localized at atoms B, C, B', and C'. Therefore, these two bands are nearly flat. In the parallel electric field case, the dominant first and third features are mainly given by the transitions from $VB_1$ to $CB_1$ bands and from $VB_2$ to $CB_2$ bands, respectively. In the perpendicular electric field case, the large second and fourth features originate from transitions from $VB_1$ ($VB_2$) to $CB_2$ ($CB_1$) bands and from $VB_2$ ($VB_3$) to $CB_3$ ($CB_2$) bands, respectively.

The long-range component is defined as below. First, we calculate the probability that the photoexcited electron and hole exist on different PPV monomer units. This probability is $1 - 1/N$ for the system with $N$ monomer units, when the electron and hole are distributed uniformly. If it is less than $1 - 1/N$, the electron and hole tend to localize in a single monomer unit, and the excited state resembles a Frenkel exciton, which is typical for molecular crystals. If the probability is higher than $1 - 1/N$, the electron and hole preferably separate into different monomer units, and the excited state has characteristics resembling those of a charge-transfer exciton in molecular crystals. We call such an excited state the “long-range” component. We can determine the contribution to the optical spectra from the long-range component by taking the sum over such states only.

Figure 4 shows the calculated optical absorption spectra for the periodic boundary case. The bold lines show the total absorption spectra, and the thin lines the spectra from the long-range component of excitons. Figures 4 (a) and 4 (b) show the absorption with the parallel and perpendicular electric field cases, respectively. In
Fig. 4 (a), there is a broad peak around the energy 1.7$t$ at the higher-energy side of the feature at 1.2$t$. At the higher-energy side of the 2.4$t$ feature, the oscillator strengths of the long-range component are very small, and this is consistent with the origin of the 2.4$t$ feature wherein the VB2 and CB2 bands in Fig. 3 are almost free of dispersions. The optical excitations of this feature tend to localize on a single PPV monomer. In Fig. 4 (b), there are two peaks of the long-range component around the energies, 2.3$t$ and 3.6$t$, at the higher-energy side of the two main features at 2.1$t$ and 3.0$t$. Figure 4 (c) shows the orientationally averaged spectra. The spectral shape of the long-range component is very broad and extends from 1.5$t$ to about 2.5$t$. The threshold of the long-range component is 1.566$t$, which is slightly smaller than the energy of the HF energy gap 1.581$t$. Such long-range excitons might play a part in the mechanisms of large photoconduction which has been measured in the energy region larger than the HF energy gap 1.581$t$. The oscillator strengths of the long-range component are larger when the electric field is perpendicular to the chain axis.

Finally, we calculate the ratio of the sum of oscillator strengths of the long-range excitons with respect to that of the total absorption, in other words, the ratio of the area below the thin line with respect to the area below the bold line in Fig. 4. The quantity is calculated for each case of the electric field direction, and the results are shown as a function of $N$ in Fig. 5. The ratio strongly depends on the number of monomer units when $N$ is smaller than 10, due to the finite system size. However, the size dependence becomes smaller as $N$ increases. The ratio seems to be almost constant at about 0.08 near $N = 20$. The ratio is anisotropic with respect to the direction of the electric field of light. The numerical data for the parallel and perpendicular electric field cases are also shown in Fig. 5. The ratio for the perpendicular field case is slightly larger than that for the parallel field case. This is related to the fact that the 2.4$t$ feature in Fig. 4 (a) has a very small long-range component and the electron and hole around this feature tend to localize on a single PPV monomer.

In summary, we have investigated the component of photoexcited states with large spatial extent in the PPV chain. The energy position of long-range excitons is nearly the same as the HF energy gap. This finding is related to the mechanisms of large photoconduction measured in such energy regions. Next, we calculated the ratio of oscillator strengths due to long-range excitons with respect to the sum of all the oscillator strengths of the absorption as a function of the PPV monomer number. The ratio strongly depends on the system size when the monomer number is small, but becomes almost constant when the monomer number is more than 10 and near 20.
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Table I. The excitation energies of the main four features. The energy value is not the onset of each feature, but the peak energy. The experimental values are taken from the optical spectra of the chemically improved PPV in ref. 3.

|         | experiment (ref. 3) | theory \((t = 2.0 \text{ eV})\) | theory \((t = 2.3 \text{ eV})\) |
|---------|---------------------|-------------------------------|-------------------------------|
| 2.5 (eV)| 2.4 (eV)            | 2.8 (eV)                      |
| 3.8     | 4.2                 | –                             |
| 4.7     | 4.8                 | 4.8                           |
| 5.8     | 6.0                 | 5.5                           |
| –       | –                   | 6.9                           |
Figure Captions

Fig. 1. The structure of the PPV chain. The direction of the polymer chain axis is indicated by the arrow. The eight carbon sites, not equivalent to each other, are labeled A-F, B’, and C’.

Fig. 2. Optical absorption spectra of the PPV for (a) periodic and (b) open boundaries. The number of PPV units $N$ is 20. The bold line indicates the total absorption. The thin (dotted) line indicates the absorption where the electric field is along (perpendicular to) the polymer axis. The Lorentzian broadening of $\gamma = 0.15t$ is used.

Fig. 3. The band structure of the PPV in the Hartree-Fock approximation. There are four branches (VB$j$, $j = 1 - 4$) in the valence band, and four (CB$j$, $j = 1 - 4$) in the conduction band. Only the wavenumber region $0 < k < \pi$ is shown because of symmetry. The lattice constant of the unit cell is taken as unity.

Fig. 4. Optical absorption spectra of the PPV with periodic boundary. 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 along the $z$-axis in (b). The orientationally averaged spectra are shown in (c). The number of PPV units $N$ is 20. The bold line indicates the total absorption. The thin line indicates the absorption of the long-range component. The Lorentzian broadening of $\gamma = 0.15t$ is used.

Fig. 5. Long-range component of the optical absorption spectra as a function of the PPV unit number $N$ for the case with periodic boundary. 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.