Polarized ultraviolet absorption by an oriented derivative of poly(*para*-phenylene)

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We present polarized ultraviolet (UV) absorption spectra of oriented poly (9-hexyl-9-(2′-ethyl-hexyl)-fluorene-2, 7-diyl). Samples oriented by gel processing in polyethylene show polarized photoluminescence and dichroism in the near and deep UV. The spectra consist of four distinct absorption bands with characteristic polarizations. The lowest energy band, polarized parallel to the draw axis, peaks at 3.3 eV. The second transition is at 5.3 eV and polarized primarily perpendicular to the draw axis. There are two strong absorption bands in the deep UV, one at 5.7 eV with polarization parallel to the chains and the other at 6.2 eV with off-axis polarization. Electronic-structure calculations based on dimers of the poly(*para*-phenylene) repeat unit with parameters estimated from the biphenyl spectra and supplemented by inclusion of the Coulomb attraction between electrons and holes successfully predict the energies and polarizations of these spectral features. Quantitative agreement of parameters that are extracted from the data indicates that the one-electron band structure is an appropriate starting point for calculating the electronic structure of phenylene-based polymers. [S0163-1829(99)08235-1]

I. INTRODUCTION

In recent years, semiconducting (conjugated) polymers have been used successfully to make a variety of electronic devices, including light-emitting diodes (LED's),[1,2] light-emitting electrochemical cells (LEC's),[3] high sensitivity photodiodes,[4] and all-polymer integrated circuits.[5] Studies of amplified spontaneous emission in thin films[6,7] have shown that conjugated polymers offer promise as high gain laser materials. Indeed, optically pumped vertical-cavity lasers[8] and distributed feedback lasers[9] have been demonstrated using thin polymer films as the active gain material, highlighting the possibility of fabricating diode lasers with polymers as transport and emissive layers.

In parallel, theoretical studies of these polymers as quasi-one-dimensional π-electron semiconductors have focused on the achievement of a deeper understanding of their electronic structure. Starting from a tight-binding approach to the band structure, several groups[10–12] have attempted to include the Coulomb attraction between electrons and holes as well as more subtle effects such as electron-hole interaction over various length scales and the coexistence of multiple excitonic species. Quantum-chemical calculations, which explicitly include electron-electron interactions, have successfully modeled the electronic structure of oligomers.[13] By monitoring trends with oligomers with increasingly longer lengths, such quantum-chemical calculations are able to distinguish features intrinsic to the electronic structure of the polymer from those associated with chain ends.[13]

Although considerable effort has focused on the poly(*para*-phenylene vinylene) (PPV) family of polymers, the poly(*para*-phenylene) (PPP) family has a simpler molecular structure. Thus PPP and its soluble derivatives offer interesting opportunities for understanding the interaction of ring symmetries and electronic delocalization along the chain in phenylene-based conjugated polymers.

We present here a study of the polarized ultraviolet (UV) absorption of oriented poly (9-hexyl-9-(2′-ethyl-hexyl)-fluorene-2, 7-diyl) (HEH-PF), a soluble derivative of PPP. The spectra, which consist of contributions from excitonic and interband transitions in different spectral ranges, show clearly the polarization of each of the absorption bands. We use the data to quantify the parameters of two analytical models[11,12] that use different strategies to proceed beyond the one-electron band structure to include electron-electron interactions. We find that the parameters related to the bandwidth and level splittings obtained from comparing each of the models to the absorption spectra are in good agreement, indicating that the one-electron band structure is an appropriate starting point for calculating the electronic structure.

II. EXPERIMENTAL DETAILS

The HEH-PF polymer was obtained from UNIAX Corporation and used as received. The synthesis of a related polyfluorene is described by Pei *et al.*[14] Oriented HEH-PF/PE blends were prepared by tensile drawing of dried gel films at 100 °C, as previously reported for MEH-PPV.[15] The data presented here were obtained from oriented films of PE containing 15% (by weight) of HEH-PF. The oriented films had a draw ratio of 50 and exhibited polarized photoluminescence with an intensity ratio of 7:1 (parallel to perpendicular). For comparison, disordered HEH-PF films were spincast from solution in toluene (under nitrogen atmosphere) onto UV-grade silica substrates and subsequently dried under vacuum for 36 h to remove residual solvent.

The oriented samples were mounted between plates of UV-grade silica, which shows no absorption in the relevant spectral range. Surface scattering was reduced by index-matching the samples with *n*-decane (Aldrich), which also shows no UV absorption below 6.5 eV. Decane is an ideal index-matching fluid for polyethylene, since it is an oligomer with the same repeat unit. Encapsulated samples were mounted on a rotating stage at the focus of the optics. Parallel orientation was defined as the orientation that maximized the absorption in the lowest energy peak. The optical axis was observed to coincide with the mechanical draw axis to within ~2°.

Light from a deuterium lamp was collimated and then polarized by Brewster angle reflection from UV-grade silica. The light, polarized vertically with respect to the optical table, was then sent through a McPherson monochromator equipped with a UV-blazed diffraction grating, mechanically chopped and focused onto the sample. Light was then collected and focused onto a McPherson photomultiplier tube and measured with a lock-in amplifier. Quantitative analysis of the polarization is presented elsewhere;[16] the importance of each of the following was emphasized: (a) polarization by reflection, (b) polarization by the monochromator, (c) reflective optics, and (d) scattering of light by the sample.

The parallel polarized absorption and luminescence spectra, together with the molecular structure of HEH-PF, are shown in Fig. 1.

III. RESULTS AND DISCUSSION

In Fig. 2(a), we present the polarized absorption spectra of the oriented HEH-PF blend. The absorption spectrum of a spin-cast film is shown for comparison. The lowest energy absorption band onsets sharply at 3 eV and peaks at 3.3 eV. It is strongly polarized parallel to the draw direction with a dichroic ratio of 7:1 at 3.3 eV, i.e., comparable to the polarization anisotropy of the luminescence. We assign this lowest energy transition to the $D1$-$D1^*$ transition involving initial and final states which are delocalized over several monomers.

Since the polarization of the absorption and luminescence are comparable, the perpendicular absorption could result from a small fraction of incompletely aligned chains (the most likely explanation; see below), an off-axis dipole moment for a single transition or a second, weaker transition with a dipole moment perpendicular to the chain axis. Indeed, a transition in this spectral region polarized perpen-
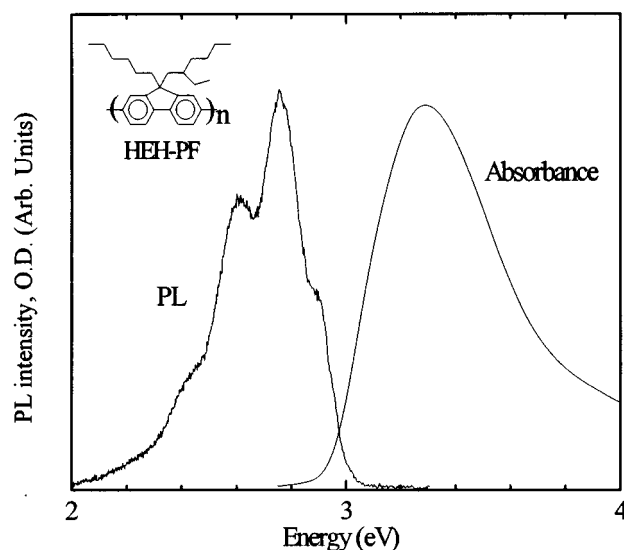

FIG. 1. Parallel polarized absorption and luminescence spectra of oriented HEH-PF.

dicular to the chain was predicted by Kirova *et al.*[17] as an intrinsic feature of the spectrum associated with an excitonic absorption between delocalized ($D1$ or $D1^*$) and localized (L^* or L) electronic bands. Another possible mechanism for perpendicular absorption is the formation of aggregates in which intermolecular transitions arise due to interactions of π electrons on neighboring chains.[18,19] We note, however, that the onset of parallel and of perpendicular absorption, shown in Fig. 2(b) is identical to within the resolution of our measurements (0.05 eV). Furthermore, the peak of the perpendicular absorption is slightly blueshifted from the parallel feature, just as seen in oriented PPV-type polymers which have significantly higher polarization anisotropies for their luminescence.[16] Based on these observations, we conclude that the perpendicular absorption is dominated by the same transition as the parallel absorption, but the former involves shorter, more disordered chain segments, resulting in a blueshifted absorption peak.

As seen also in Fig. 2(b), the perpendicular spectrum appears to have a broad, weak absorption feature with an onset near 4 eV. The maximum of this feature is difficult to identify with precision, but it lies between 4.2 and 4.8 eV, or 0.5–1.1 eV below the next absorption band. This energy difference is comparable to the binding energy of a one-dimensional, hydrogenic exciton of a localized hole (electron) and a delocalized electron (hole), as proposed by Kirova *et al.*[17] However, since this absorption is weak compared to all the other features of the spectrum, we will not consider it further. Studies of other polymers are needed to provide insight into the origin of this weak, broad absorption.

The second strong absorption band is at 5.3 eV, and is polarized primarily perpendicular to the chain axis. Since the 5.3-eV absorption is observed as a shoulder on the stronger peak at 5.7 eV, it is difficult to quantify the off-axis nature of the polarization. However, the 5.3-eV feature is absent in the parallel absorption spectrum but clearly observed in the spectrum obtained from an unoriented spin-cast film. This feature bears a striking resemblance to the perpendicular absorption observed at 4.6 eV in oriented PPV's.[16,20,21] Thus, we assign it to the analogous $D1$-L^*/L-$D1^*$ transition in-
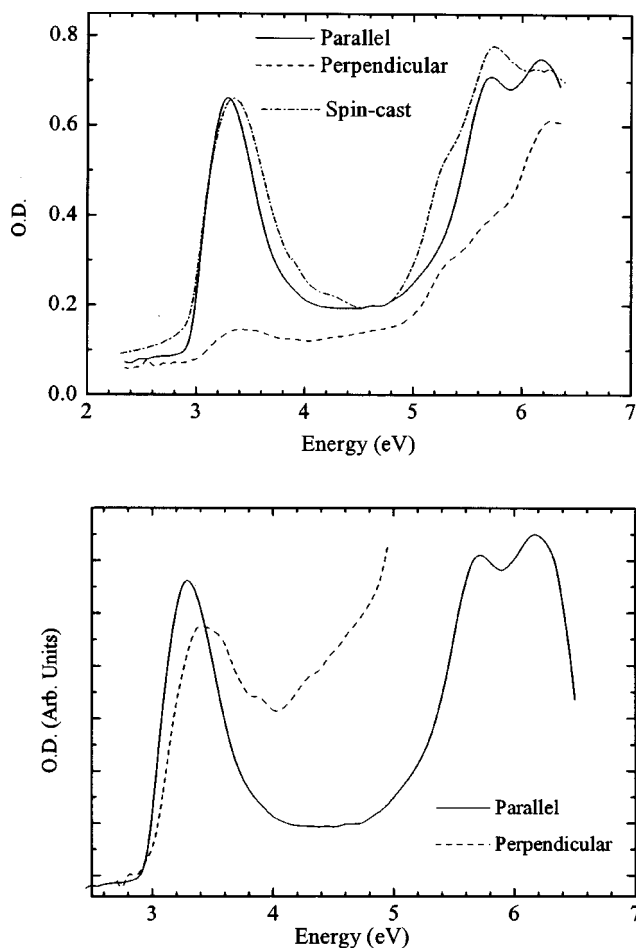
FIG. 2. Parallel and perpendicular UV absorption spectra of oriented HEH-PF. (a) Spectra plotted on an absolute scale. The absorption spectrum of a spin-cast film of the same material is shown for reference. (b) The same polarized spectra as in (a), but with the perpendicular absorption rescaled to show that the onset of absorption coincides with that of the parallel polarized spectrum.
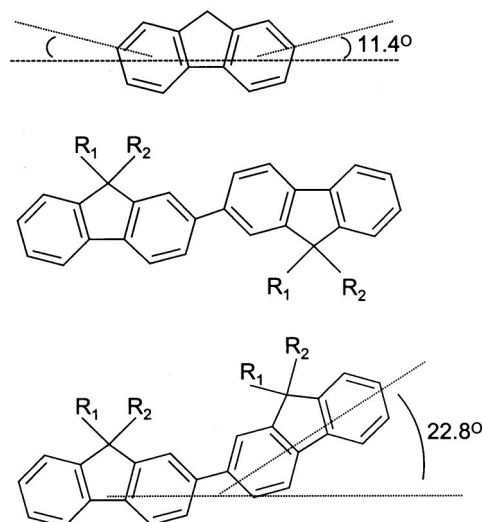

FIG. 3. Geometry of the fluorene molecule. (a) The molecule is planar, and the *para* axes make angles of 11.4° with the molecular axis. (b) *Trans*-configuration of bifluorene. Molecular axes of the fluorene monomers are parallel. (c) *Cis*-configuration of bifluorene. Molecular axes of the fluorene monomers define a 22.4° angle.

volving a state delocalized over several monomers and a state localized on a single ring. Whether this transition is excitonic or interband in nature is a point of dispute based on published estimates of transition energies.[17,22] The various predictions related to this peak will be compared and discussed in Sec. IV.

A strong absorption band polarized primarily parallel to the chain axis is observed at 5.7 eV. However, since the dichroic ratio is only approximately 2:1 at 5.7 eV (much lower than that of the 3.3-eV peak), the polarization is not coincident with the chain axis. The 5.7-eV transition is expected to involve only localized states (L-L^*) and be a molecular (Frenkel) exciton localized on a single phenyl ring. The dipole moment of the L-L^* transition is expected to be strongly along the axis connecting the *para* linkage sites.

Since this transition is much more localized than the $D1$-$D1^*$ transition, it can be taken as a probe of the distribution of *local* ring axes in polyfluorene. With this assumption, the average angle θ between the local ring axis and the mechanical axis can be estimated; $\langle \mathrm{arccot}^2\,\theta \rangle = 2$ or $\langle \theta \rangle = 35°$. Fluorene, shown in Fig. 3(a), has a planar configuration, with angle of 11.4° between the long molecular axis

and the *para* axes of the respective phenyl rings.[23] Hence each monomer can be thought of as a ''bend'' in the chain of approximately 22.8°. Figures 3(b) and 3(c) show the two possibilities for monomer-monomer bonding. In the *trans*-type bonding [Fig. 3(b)], neighboring monomers have their bridges on opposite sides, and the angles cancel, leaving the molecular axes parallel. In the *cis*-type bonding [Fig. 3(c)], however, the bridges are on the same sides, and the angles add. Single-crystal absorption measurements on fluorene have shown that the lowest electronic transition is polarized parallel to the long molecular axis with a dichroic ratio greater than 30,[24] so for *trans*-bifluorene, the analogous transition may still be highly polarized. However, the dichroism of localized transitions will likely be weakened due to the angle between the individual *para* axes and the molecular axis.

Alternatively, the lower dichroism of this peak could result from an off-axis component to the transition dipole moment for the L-L^* exciton as a result of mixing of transitions (D-D^*,D-L^*,L-L^*). Mixing of transitions in luminescent polymers has been proposed[11,13,25,26] to explain polarization and spectral positions of other absorption bands, particularly in PPV derivatives.

Finally, the absorption band at 6.2 eV is nearly unpolarized. Since this band has a markedly different polarization than the 5.7-eV band, it has a distinct physical origin. Kirova *et al.*[17] suggested that in polyfluorenes, the 6.2-eV absorption results from the dimerization of the phenyl rings and the associated halving of the first Brillouin zone. Within this picture, Kirova *et al.* assigned the 6.2-eV peak to the transition from the highest occupied delocalized band ($D1$) to the second unoccupied delocalized band; they did not comment on the polarization. The second unoccupied band in the dimerized polyfluorenes is derived from the upper half of the PPP $D1^*$ band [Fig. 4(b)] by folding the Brioullin zone (the unit-cell length is doubled).
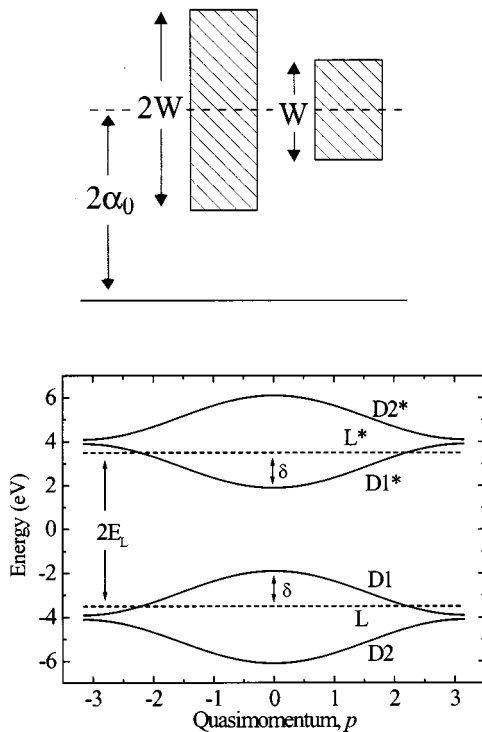
FIG. 4. Electronic energy levels of undimerized PPP. (a) Schematic diagram of the one-electron states involved in the low-energy, dipole allowed transitions in the model of Rice and Gartstein. (b) Schematic band diagram for PPP. The dimerized polyfluorenes will have ten bands instead of six, with the L and L^* bands being doubly degenerate. The energies $2E_L$ and δ for the model of Brazovskii and Kirova are illustrated.

IV. RESOLUTION OF THE SPECTRA WITH THEORETICAL PREDICTIONS

We attempt a detailed analysis of the spectra in terms of the predictions of Kirova et al. and Rice et al. Kirova et al.[17] predicted an interband transition in polyfluorene at 4.3 eV with an associated exciton as part of the lowest energy absorption band. Rice et al.,[11] on the other hand, constructed a modified band model which incorporated parameters estimated from spectra of crystalline biphenyl to predict polarized spectra for PPP, their results are strikingly similar to the data shown in Fig. 1 for HEH-PF (in which the repeat unit is a phenyl dimer).

To predict the energies of the optical transitions, one must correctly compute the relative positions of the interband absorption edges, the binding energies of the associated excitons, and the transition dipole moments between the ground and excited states. We focus the discussion on the position of the band edges and the binding energies of the various excitons. A band calculation for conjugated polymers begins with a Huckel-type tight-binding Hamiltonian[10,11,25,27] supplemented by additional terms which are intended to account for lattice distortion, molecular symmetries, and electron-electron Coulomb interactions. In the one-electron band-structure approximation for phenylene-based polymers, there are three evenly spaced optical transitions[11] at energies between 2 and 6.5 eV. The positions of the interband transitions are largely determined by the hopping integral, t, used in the Huckel Hamiltonian.

The principal differences between the Rice-Gartstein (RG) model and the Brazovskii-Kirova (BK) model are (a) the strategy for incorporating Coulomb and symmetry effects and (b) the method of computing exciton binding energies. RG assumes that an excited electron-hole pair on a single phenyl ring will have an interaction energy which depends on the symmetry of the state. The four interaction energies, U_n ($n=1,2,3,4$), associated with the four possible electron-hole symmetry combinations, are included in the Hamiltonian before the eigenenergies are calculated. The U_n and the hopping integral, t, determine the different binding energies of the excitons at the various band edges. BK (Ref. 12) assumes instead that the one-electron bands can be treated as eigenstates with effective masses that are calculated from the band curvature; the binding energies (with respect to the interband edge) of the one-dimensional, hydrogenic excitons are then calculated by treating the Coulomb attraction between an electron and a hole. The Coulomb interaction and ring symmetries are accounted for in the one-electron band structure by shifting the center of gravity of the bands from their zeroth-order position.

To compare the predictions of these two models, we must first identify the analogous parameters and then use the spectra to compute the parameters which define the two models.

(i) In the RG model, the one-electron transition energies are defined in terms of the Huckel L-L^* (localized) transition energy ($2\alpha_0$) and the electronic bandwidth (W). The one-electron UV transitions are then at energies of $2\alpha_0$ (for L-L^*), $2\alpha_0$-$W/2$ (for $D1$-L^*), and $2\alpha_0$-W (for $D1$-$D1^*$).

(ii) In the BK model, since the shifting of the bands is essential, we define the parameters $2E_L$ (analogous to $2\alpha_0$), where E_L is the energy difference between the midgap Fermi level and the energy of the localized electronic band, and δ is the energy difference between the L band and the $D1$ band at the center of the Brillouin zone. With these parameters, the single-electron excitation energies are $2E_L$ (for L-L^*), $2E_L$-δ (for $D1$-L^*), and $2E_L$-2δ (for $D1$-$D1^*$).

In Fig. 4, we show schematically the relevant features of the one-electron energy diagrams from the RG and BK models. Figure 4(a) shows the bands for optically allowed transitions in the RG model. Figure 4(b) shows schematically the one-electron bands for PPP and the energies $2E_L$ and δ in the BK model. The dimerized polyfluorenes will have ten bands instead of six, with the L and L^* bands being doubly degenerate; the splittings resulting from the dimerization are not shown in Fig. 4(b). Each of the three transitions described above have associated excitons with binding energies labeled as follows: E_{B3} (L-L^* exciton), E_{B2} ($D1$-L^* exciton), and E_{B1} ($D1$-$D1^*$ exciton). Table I summarizes the expressions for the various transitions from RG (Ref. 22) and from BK,[12] together with the peak positions observed in Fig. 2. We note that the value of the $D1$-$D1^*$ interband transition (3.6 eV) is estimated using an exciton binding energy of 0.3 eV as calculated by Kirova et al.,[17] This is a typical value in the literature for PPP, with its electronic bands somewhat narrower than those of PPV.

Using the polarized absorption data, we have assigned the 5.3-eV peak to the $D1$-L^* transition due to its distinctive polarization and its similarity to the 4.6-eV peak seen in PPV derivatives.[16,20] BK's original assignment of the $D1$-L^* transition to a weak feature at 4.3 eV in a similar polyfluo-

TABLE I. Transition energies as defined in RG and BK models.

Type of excitation	RG model	BK model	Experimental value
L-L^* interband	$2\alpha_0$	$2E_L$	7 eV
L-L^* exciton	$2\alpha_0 - E_{B3}$	$2E_L - E_{B3}$	5.7 eV
$D1$-L^* interband	$2\alpha_0 - W/2$	$2E_L - \delta$	5.3 eV
$D1$-L^* exciton	$2\alpha_0 - W/2 - E_{B2}$	$2E_L - \delta - E_{B2}$	4.2–4.8 eV (?)
$D1$-$D1^*$ interband	$2\alpha_0 - W$	$2E_L - 2\delta$	~3.6 eV [for $E_{B1} \sim 0.3$ eV (Ref. 17)]
D-D^* exciton	$2\alpha_0 - W - E_{B1}$	$2E_L - 2\delta - E_{B1}$	3.3 eV

rene is not consistent with our data. The binding energy of the $D1$-L^* exciton derived from the parameters of the RG model is a small fraction of an eV,[11] whereas the binding energy from the BK model was estimated to be ~1 eV. In the limit of a small binding energy, the exciton absorption merges with the interband absorption.

From Table I, we use the spectral positions of the lowest two absorption features together with the estimate of E_{B1} = 0.3 eV (Ref. 17) to compute $\delta = 1.7$ eV in the BK model. This parameter is analogous to ($W/2$) in the RG model, and the value we extract from the data is in good agreement with RG's estimate of $W = 3$ eV from fits to biphenyl spectra.[22] We also extract the energy of the L-L^* interband transition: $2E_L = E_{D1\text{-}L^*} + \delta = 7$ eV, in agreement with RG's value for $2\alpha_0$.[22] This energy is, in the RG model, the fundamental energy scale for electronic-structure calculations of phenylene-based polymers.

The final question concerns the $D1$-L^* exciton and its binding energy. Fits of the RG model to the data seem to indicate that the binding energy should be less than ~0.3 eV, in which case it would be seen to merge with the interband $D1$-L^* transition. Binding energies small compared to the bandwidth are typical of the lowest π-π^* (i.e., $D1$-$D1^*$) absorption in luminescent polymers, and the merging of the exciton and interband absorption is seen in the present data as the single lowest energy peak. The BK model, on the other hand, predicts a significantly higher binding energy (~1 eV) for the $D1$-L^* exciton as a result of the large effective mass of the localized carrier. This exciton seemed to be a robust explanation for the strong 3.7-eV absorption band in PPV's,[12,16] but in the present case, the absorption

band in the 4.2–4.8-eV spectral range is much less pronounced than the band in PPV's. A redistribution of oscillator strength to the interband transition might explain the different spectral shape. Recently, BK have suggested that within an interband transition, the oscillator strength is redistributed toward higher energies as a result of the energy dependence of the transition matrix element.[25]

V. CONCLUSION

We have presented polarized UV absorption spectra for a highly oriented derivative of PPP and analyzed the data in terms of two models of the electronic structure. The polarization of the different absorption bands provides the information needed to assign them to the various excitonic and interband transitions expected within the π-electron system. The energies of the absorption bands allow us to quantitatively compute the electronic bandwidth and one-electron level splittings in the BK model. The parameters from this analysis are in good agreement with the values estimated by RG by fitting biphenyl absorption spectra. Generally, the exciton binding energies are relatively small (<0.3 eV). We conclude from this consistency that a one-electron band structure is a good starting point for calculating the electronic structure of phenylene-based polymers.

ACKNOWLEDGMENTS

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