

# Optical and electronic properties of crystalline poly(*para*-phenylene) by first-principles calculations and experimental results

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## Abstract

We have performed first-principles LDA band structure calculations for 1D and 3D crystalline poly(*para*-phenylene) using the LAPW and the pseudopotential method, which are based on the density functional theory. The band gap can be easily tuned through the whole visible region by varying the structural parameters. Optimized structural parameters have been determined for the orthorhombic space group *Pbam* and the 1D chain. We predict a torsion angle between two adjacent rings of 18° for the 3D structure and 27° for the 1D chain. The interchain coupling leads to band splittings of nearly 1 eV. The absorption coefficient has been calculated and compared to experimental data. The excellent agreement indicates that excitonic effects are weak. Calculations of the luminescence emission efficiency are presented.

## 1. INTRODUCTION

The fabrication of efficient light emitting diodes (LED) based on semiconducting and conducting conjugated polymers has been a breakthrough in the field of polymer electronics. The most intriguing application of poly(*para*-phenylene) (PPP) demonstrated recently [1] is the fabrication of blue light emitting diodes. An optimization of PPP-LED's in ordered structures must meet two criteria. First, the energy gap should lie in the desired (blue) frequency regime, and second, the band width of the lowest lying conduction bands or topmost valence bands should be sufficiently large, because the carrier mobility is inversely proportional to the effective mass. Bredas et al. [2] have concluded from calculations based on semi-empirical methods, that the band gap can be engineered in a wide range from red to ultraviolet by structural changes that may be realized by doping or the addition of side-chains.

In this work we present first-principles studies of structural and optical properties of single-chain (1D) and crystalline (3D) PPP and compare them to experimental data. We investigate theoretically the influence of structural modifications of PPP on the energy gap and optical properties.

We employ two different first-principles methods, namely the linearized-augmented-plane-wave (LAPW) method as well as the pseudopotential

method. Both methods are based on density functional theory where exchange and correlation effects are treated by the local density approximation (LDA). For the calculation of electronic and optical properties we employed the LAPW method using the optimized version WIEN93 of the WIEN code. [3]. The structural optimization of 1D and 3D PPP has been carried out by the pseudopotential formalism with a separable carbon pseudopotential generated by the method of Troullier and Martins [4]. Some calculations, performed by both methods, allow a critical assessment and show very good agreement between them.

LDA calculations are known to underestimate the band gap of semiconductors. Systematic LDA calculations for several polyenes have revealed that one obtains, to a very good approximation,  $E_{gap}(LDA) = 0.6 E_{gap}(experiment)$  [5]. In the present work the conduction bands include a self-energy of 1.2 eV.

Improved PPP thin films are now available, produced via precursor routes [6]. We present optical absorption data of this new PPP together with the calculated absorption coefficient.

## 2. CRYSTAL STRUCTURE OF PPP

Polyphenyls are formed by chains of phenyl rings. The structures of phenylene oligomers and crystalline

PPP have been studied extensively, but the space group and the structural parameters of crystalline PPP are still controversial. Recent diffraction experiments on crystalline PPP have been interpreted in terms of the monoclinic space group  $P2_1/n$ . The monoclinic distortion, however, seems to be small or equal to zero [7].

In this work we assume an orthorhombic space group for 3D PPP with two chains per unit cell. Each chain contains phenyl rings that are alternately twisted by some angle relative to each other. We therefore define the lattice constant  $c$  in chain direction to contain 2 phenyl rings. We assume the two chains to be unshifted against each other (space group  $Pbam$ ). Calculations for shifted chains (space group  $Pnmm$ ) do not show drastic changes in the electronic and optical properties and will be published elsewhere [8].

In the present calculations, we optimize the atomic positions in the unit cell, but take the lattice constants determined by experiments [9, 10, 11], namely  $a = 7.78$  Å,  $b = 5.52$  Å, and  $c = 8.54$  Å.

The parameters characterizing completely the geometry of the unit cell are shown in Fig. 1. Note, that adjacent phenyl rings are inequivalent in general. Their torsion angle is denoted by  $\theta$ .

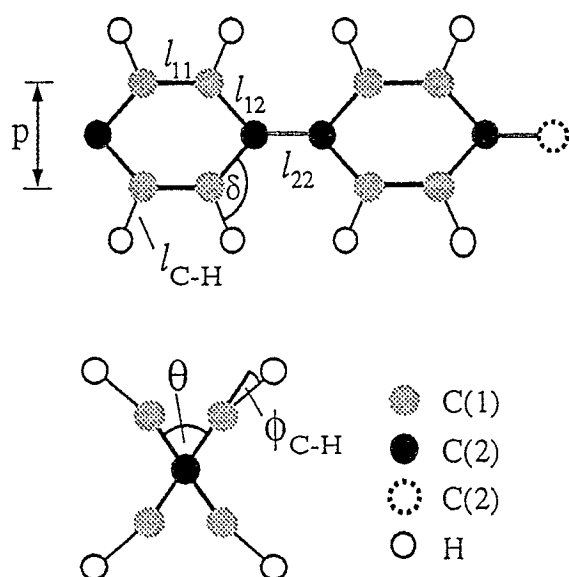


Figure 1. Repeat unit of PPP and projection of two adjacent phenyl rings rotated against each other.

In order to isolate the effect of the crystalline packing on the structure of the phenyl chains, we have also studied isolated chains of PPP, setting the lattice constant  $c$  equal to the crystalline value and optimizing all other structural parameters. One-dimensional chains were treated using sufficiently large supercells to render interchain interactions negligible. We found lattice

constants  $a = b = 7$  Å perpendicular to the chain axis to be sufficient.

The optimized geometries for the 1D chain and the 3D space group  $Pbam$  have been determined with the pseudopotential approach and verified by the LAPW method for a few sets of structural parameters. We find a torsion angle between two adjacent rings of  $18^\circ$  for the 3D structure and  $27^\circ$  for the 1D chain to be most stable.

### 3. BAND GAP

We have studied theoretically the variation of the energy gap for several structural modifications of the phenyl rings in PPP. Experimentally, these modifications can only be achieved by introducing additional side-chains or other methods of synthesis that are likely to alter several properties of PPP simultaneously. However, the present studies provide guidelines for gap variations that can be expected in real systems. In this paper we focus on the change of the band gap with torsion angle.

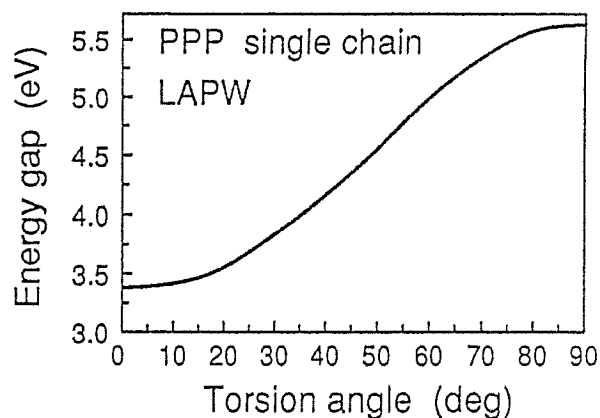


Figure 2. Energy gap of one chain with two rings rotated in opposite sense as a function of the torsion angle  $\theta$ .

These calculations have been carried out for single chains of PPP, using the experimental structural parameters. Fig. 2 shows the energy gap as a function of the torsion angle between neighboring phenyl rings. We predict the energy gap to increase with increasing torsion angle since the inter-ring coupling between the C- $\pi$  orbitals becomes weaker. Accordingly, the band width decreases for increasing torsion angle. Analogously it can be shown that the band gap can even be tuned within the visible region by changing the interatomic bond lengths within one ring or by changing the distance between two adjacent rings.

#### 4. BAND STRUCTURE

Fig. 3 shows the band structure of 3D PPP with space group Pbam. The most interesting feature in this band structure is the pronounced energy dispersion from the Brillouin-zone center  $\Gamma$  to the X-point which is of the order of 0.5 eV. Since this dispersion occurs perpendicular to the chain, this result indicates a substantial interaction across the chains. In fact, the same qualitative effect has been found previously in crystalline *trans*-(CH)<sub>x</sub> [12] and in crystalline poly(p-phenylene vinylene) (PPV) [13]. The physical origin of this interchain-coupling is the electron-ion interaction between carbon atoms on neighboring chains mediated by hydrogen *p*-states. There is a small anisotropy in  $k_x$  and  $k_y$  that is related to the lattice constant  $a$  being larger than  $b$ . The lowest conduction band state at  $k=Y$  has a lower energy than at X and  $\Gamma$ , whereas the highest valence band state occurs at the center of the Brillouin zone  $\Gamma$ . Thus, the energy gap of crystalline PPP is slightly indirect and lower by 0.24 eV than the direct band gap at  $\Gamma$ .

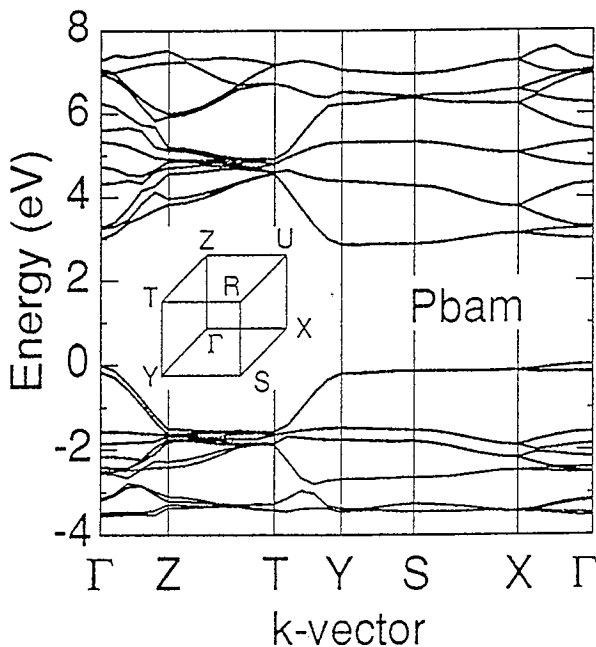


Figure 3. Band structure of 3D crystalline PPP with Pbam symmetry.

#### 5. OPTICAL ABSORPTION AND LUMINESCENCE

The interband absorption coefficient is given by

$$\alpha_i(\omega) = \sqrt{2} \frac{\omega}{c} \sqrt{|\epsilon_i| - \text{Re}\epsilon_i} \quad (1)$$

where  $\epsilon_i$  is the *i*-th component of the complex dielectric tensor in the long wave-length limit. Since the space

group is orthorhombic, the dielectric tensor is diagonal. We note that  $\epsilon$  takes into account the nonlocality of the self-energy which is contained in the conduction band energies [14]. The interband absorption coefficient  $\alpha_z$  ( $z \parallel c$ ) calculated from the energy bands shown in Fig. 3 is displayed in Fig. 4 and compared to experimental data. The very good overall agreement between theory and experiments may be an indication that excitonic effects do not play a dominant role in extended PPP. Correspondingly, it has recently been argued that excitonic binding energies in PPV are only of the order of  $k_B T$  [16]. Thus excitonic energies may also be very small in PPP.

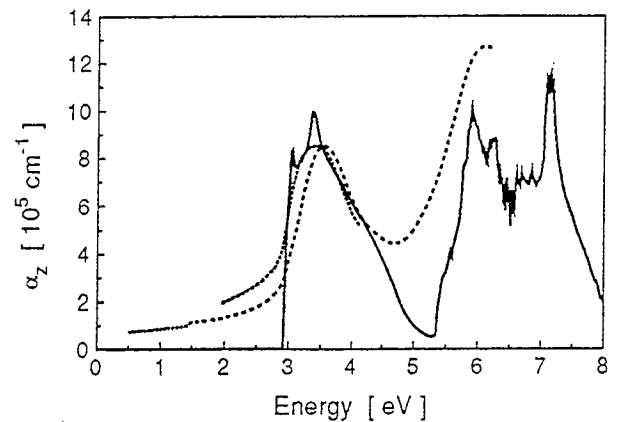


Figure 4. *z*-component of the absorption coefficient of crystalline PPP (full line) compared to experimental data taken from Tieke et al. [15] (dotted line) and this work (dashed line).

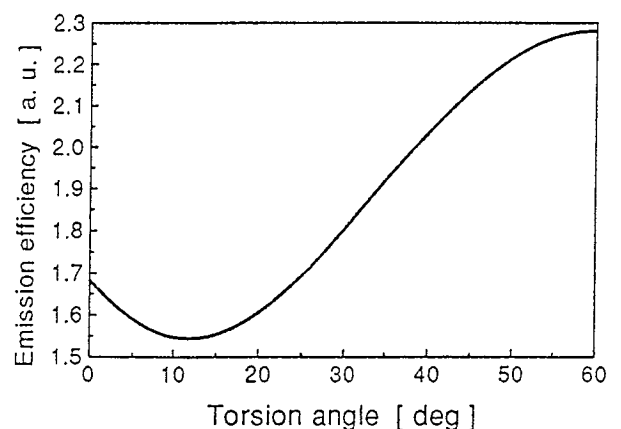


Figure 5. Emission efficiency versus torsion angle  $\theta$  for the 1D PPP chain.

Since the luminescence efficiency is a very important parameter for our polymer optoelectronic devices, we study the quantum yield as a function of the torsion angle  $\theta$ . The spontaneous emission rate per energy in-

terval, time and volume is given by [17]

$$dr/d(\hbar\omega) \propto \hbar\omega \frac{P^2}{m} e^{-\hbar\omega/kT} \sqrt{\mu} \frac{1}{\sqrt{\hbar\omega - E_{gap}}} \quad (2)$$

where  $P$  is the momentum matrix element between the uppermost valence band and the lowest conduction band,  $\mu$  is the reduced mass, and  $\hbar\omega$  the excitation energy. The expression  $\frac{P^2}{m} \sqrt{\mu}$  has been calculated for the 1D PPP chain for angles up to  $60^\circ$  and is plotted in Fig. 5. We predict a minimum at approximately  $12^\circ$  and an increase for larger angles for a fixed excitation energy  $\hbar\omega$ . Since the energy gap is increasing with the torsion angle (Fig. 2), it should be noted that this effect is enhanced by the factor  $1/\sqrt{\hbar\omega - E_{gap}}$ , especially for excitation energies near the band gap.

## 6. CONCLUSIONS

We have shown that the band gap of PPP systems can be easily tuned through the whole visible region. The large interchain interaction causes the band edge states to have a three-dimensional character which destabilizes polarons. This coupling seems to be a universal feature of conjugated polymers. A band calculation of optical properties gives very good agreement with experimental data, indicating that excitonic effects do not play a dominant role in crystalline bulk PPP. The prediction of an increase of the photoluminescence quantum yield with increasing torsion angle is a very encouraging result for the application of PPP systems in electroluminescence devices with improved performance.

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