

# Resonant Raman scattering dispersion in poly(dithieno[3,4-b:3',4-d]-thiophene): $2A_g$ spectroscopy

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## Abstract

Small band gap semiconducting  $\pi$ -conjugated polymers may, in principle, be more efficient as the active media in solar cells, due to their better adaptability to the solar spectrum. In luminescent  $\pi$ -conjugated polymers, interband photon absorption results in the radiative recombination of the photogenerated excitons, which competes with charge separation. The photoluminescence (PL) quantum efficiency is largely determined by the relative energies of the optically allowed lowest odd parity (LOP, e.g.  $1B_u$ ) excited state and the optically forbidden lowest even parity (LEP, e.g.  $2A_g$ ) excited state. If  $E(\text{LEP}) < E(\text{LOP})$ , the quantum efficiency is small and charge separation following photoexcitation is more likely than in efficient PL polymers. The determination of the relative position of LEP and LOP states is therefore essential for the possible utilization of small band gap  $\pi$ -conjugated polymers in practical devices. It was previously shown that resonant Raman scattering dispersion might serve as a spectroscopic tool for the determination of the LEP states, since the dispersion is solely determined by the dependence of the LEP state on the conjugation length, rather than that of the optical gap, or LOP state. In this work, we use the Raman spectra measured in poly(dithieno-thiophene) (PDTT1) in order to estimate the LEP energy level. We find that the LEP energy level is in the vicinity of the optical gap.

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## 1. Introduction

The relative order of the lowest even parity (LEP) and lowest odd parity (LOP) states in conjugated polymers is relevant for light emitting and photovoltaic devices. If  $E(\text{LEP}) < E(\text{LOP})$  then light emission efficiency is small because of the dipole forbidden transition to the lowest level, and charge separation following photoexcitation is more likely than in efficient photoluminescent (PL)  $\pi$ -conjugated polymers. In principle, LEP states can experimentally be directly determined using two-photon absorption measurements with a powerful photon source at half the optical gap.

However, for a low band gap  $\pi$ -conjugated polymer, a photon source at half the optical gap may not be readily available.

Poly(dithieno[3,4-b:3',4-d]-thiophene) (PDTT1) is a member of the poly(dithieno-thiophene)s (PDTTs) family of small band gap  $\pi$ -conjugated polymers. They consist of a polythiophene (PT) like chain where an aromatic thienothiophene moiety is fused onto each thiophene ring (see inset, Fig. 1, for the structure of PDTT1). Using optical absorption [1], the band gap was determined at around 1.1 eV. The LEP states were not measured yet, since the very low optical band gap in this series makes the direct experimental determination of the LEP state by two-photon absorption a prohibitive task. Therefore, an alternative experimental method, for estimating the LEP state in low band gap  $\pi$ -conjugated polymers, is desirable.

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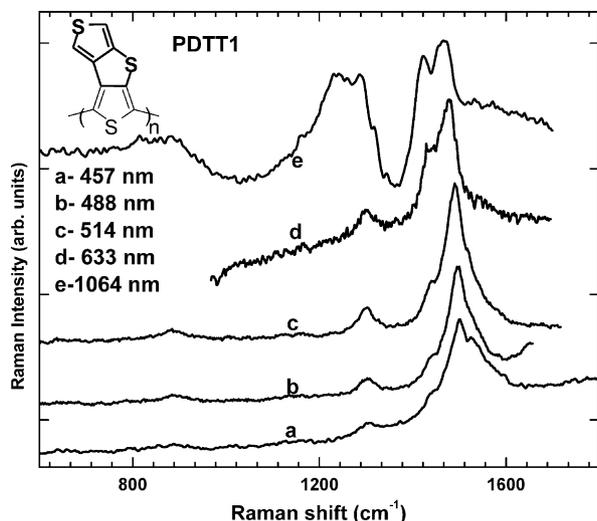


Fig. 1. Raman spectra of pristine PDTT1, excited at  $E_L = 2.71$  eV (a), 2.54 eV (b), 2.41 eV (c), 1.96 eV (d) and 1.16 eV (e) (from Ref. [6]). The inset shows the chemical structure of PDTT1.

In previous studies [2,3], it was shown that the position of the LEP state determines the resonant Raman scattering (RRS) frequencies of the  $A_g$  vibrational modes. In particular, in inhomogeneous films made of  $\pi$ -conjugated polymers having a distribution of optical energy gaps ( $E_g$ ) due to, say, a conjugation length distribution, the RRS frequencies are blue shifted with increasing excitation photon energy,  $E_L$ . This blue shift is the result of the selectivity of the resonant process and the sensitivity of the Raman vibrational modes to the energy gap of the polymer. First, the exciting photon energy,  $E_L$ , selects only that conjugation length for which  $E_g = E_L$ . Second, the higher is  $E_g$  the higher are the vibrational frequencies [9]. As a consequence, a coupled set of vibrational frequencies, which are associated with this particular energy gap, is selected by  $E_L$ , causing these frequencies to blue shift with increasing  $E_L$  (this phenomenon is termed “RRS dispersion”). As was established earlier [2,3], this RRS dispersion is solely determined by the dependence of the even parity states on the conjugation length, rather than that of  $E_g$ , or the odd parity states.

In this work, we report on our results for PDTT1. We use the RRS dispersion measured in PDTT1 in order to estimate the LEP state. We find that the LEP energy level is in the vicinity of the optical gap.

## 2. Materials and experimental results

The structure of poly(dithieno[3,4-b:3',4-d]-thiophene) is shown in the inset of Fig. 1. PDTT1, as well as PDTT2 and PDTT3, may be looked upon as PT-like chains in which a thienothiophene aromatic moiety is fused onto each thiophene ring [4,5]. These aromatic moieties reduce the dimerization along the PT chain, resulting in the reduction of the

optical band gap. Indeed, the band gap reported is around 1.1 eV [1], compared with  $\approx 2$  eV for PT.

The RRS spectra of films of PDTT1 were measured and reported previously [6,7]. In Fig. 1, we show the RRS spectra for PDTT1 taken at various excitation energies. The main feature, which is relevant to the present paper, is the RRS dispersion with increasing laser photon energy,  $E_L$ . Starting with the lowest  $E_L$ , it is seen that the rich spectrum observed for  $E_L = 1.16$  eV undergoes an intensity redistribution, while the whole redistributed pattern is blue shifted as  $E_L$  increases. Similar intensity redistribution and RRS dispersion is observed also in PDTT2 and PDTT3. The intensity redistribution and the apparent amount of RRS dispersion in these  $\pi$ -conjugated polymers is considerably more noticeable here than in the simpler PT or poly(alkyl-thiophene)s, where the observed RRS dispersion is much weaker (see below).

## 3. Discussion

Since individual Raman frequencies blue shift with increasing  $E_L$  by a different amount, we quantitatively describe the RRS dispersion of a given polymer by the normalized product square of all the observed RRS frequencies,  $\omega_i^L$  (at a given  $E_L$ ):

$$P(E_L) \equiv \prod_i^m \left( \frac{\omega_i^L}{\omega_i^0} \right)^2, \quad (1)$$

where  $\omega_i^0$  are the RRS frequencies at  $E_L = E_{L_0}$ , the smallest optical energy gap (i.e. the optical energy gap of the longest conjugation length).  $P(E_L)$ , defined in Eq. (1), is proportional to the “renormalization coupling parameter”, introduced previously in the amplitude modes theory [8,9]. This quantity was shown [8] to be an “electronic property” rather than a “vibrational property” of the coupled Raman active vibrations. More quantitatively, assuming that the RRS dispersion arises from a distribution in conjugation length,  $P(E_L)$  can be written as [2,3],

$$P(E_L) = 1 + D(E_L - E_{g_0}), \quad (2)$$

where  $D = C/E_{2A_{g_0}}^2$  is the “dispersion coefficient”, which depends on the lowest even parity state energy,  $E_{2A_{g_0}}$ , and  $C$  is a constant independent on the exciting photon energy. In writing Eq. (2), it is implicitly assumed that the contribution of the higher lying even parity states to both the electronic susceptibility [10,11] and the dispersion coefficient,  $D$ , can be neglected. The product  $P(E_L)$  (Eq. (2)) is thus linearly dependent on the exciting photon energy.

In Fig. 2 we show the product  $P(E_L)$ , extracted from the observed RRS spectra, as a function of  $E_L$  for PDTT1.  $E_{g_0}$  was chosen as 1.16 eV, the lowest exciting photon energy applied here, since it is very close to the intrinsic energy gap of these polymers ( $\approx 1.1$  eV) [1]. It is clearly seen that the normalized product shows a linear dependence on  $E_L$ , as

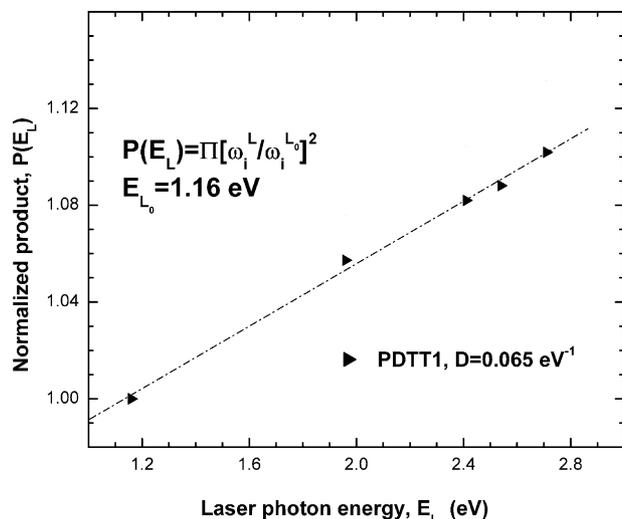


Fig. 2. The normalized product square of the observed RRS frequencies,  $P(E_L)$ , (full symbols) and linear fit (line) as a function of the resonant laser photon energy  $E_L$  for PDTT1. The slope of the linear fit is marked as  $D$ .

predicted by Eq. (2). Furthermore, the dispersion coefficient extracted from the data of Fig. 2 is  $D = 0.065 \text{ eV}^{-1}$ , which is relatively large, compared with the larger band gap polymer PT, for which  $D \approx 0.02 \text{ eV}^{-1}$  [2,3]. The relatively large value of  $D$  for PDTT1 strongly indicates that the LEP state,  $2A_g$ , is much lower than that in PT ( $E_{2A_g} \approx 2.1\text{--}2.3 \text{ eV}$ , see Ref. [12]) possibly as low as the PDTT1 optical energy gap. Similar large values of  $D$  were extracted for PDTT2 and PDTT3 [13].

#### 4. Conclusions

We have shown that in low band gap  $\pi$ -conjugated polymers, for which experimental techniques to measure directly the energy of the even parity states are not readily applicable, RRS can alternatively be used to experimentally estimate the lowest  $2A_g$  even parity state. In particular, the RRS dispersion, defined as the normalized square of the product of the

RRS frequencies, in the  $\pi$ -conjugated polymer PDTT1, is found to increase with a relatively high rate of change,  $D$ , as the photon excitation energy increases. The high value of  $D$  indicates a very low even parity  $2A_g$  state.

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