

Even parity states in small band gap π -conjugated polymers: polydithienothiophenes

E. Ehrenfreund^{a,b,*}, A. Cravino^a, H. Neugebauer^a, N.S. Sariciftci^a,
S. Luzzati^c, M. Catellani^c

^a *Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria*

^b *Department of Physics and Solid State Institute, Technion, Israel Institute of Technology, Haifa 32000, Israel*

^c *Institute for the Study of Macromolecules (ISMAL), National Research Council (CNR), 20133 Milan, Italy*

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Abstract

Using the photon energy induced blue shift of the resonant Raman scattering frequencies in inhomogeneous films ('RRS dispersion'), we extract the energy of the lowest even parity state of π -conjugated polymers. We show that in the small band gap (≈ 1.1 eV) poly(dithienothiophenes), the experimentally observed unusually large RRS dispersion yields for the lowest even parity state ($2A_g$) an energy, which is in the vicinity of the optically allowed state ($1B_u$).

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1. Introduction

Small band gap semiconducting π -conjugated polymers are, in principle, of considerable interest as the active media in solar cells, due to a better match of their absorption spectra to the solar emission spectrum. However, the photon to charge conversion efficiency critically depends on the charge separation mechanism following light absorption. Several competing processes, like radiative or nonradiative recombination, charge separation, or charge transfer to acceptor (donor) sites may occur. In luminescent π -conjugated polymers, interband photon absorption results in a fast radiative recombination of the photogenerated excitons, thus decreasing the efficiency for charge separation.

The photoluminescence (PL) quantum efficiency is largely determined by the relative energies of the lowest odd parity (LOP, e.g. $1B_u$ in polymers with centrosym-

metric repeating units) excited state and the lowest even parity (LEP, e.g. $2A_g$) excited state. If $E(\text{LEP}) < E(\text{LOP})$ then the PL quantum efficiency is small because of the dipole forbidden character of the lowest level, and charge separation following photoexcitation is more likely than in efficient PL π -conjugated polymers. The determination of the relative position of the LEP and LOP states, is therefore essential for the possible utilization of small band gap π -conjugated polymers in practical devices. LEP states can experimentally be directly determined using two photon absorption measurements with a powerful photon source at half the optical gap. However, for low band gap π -conjugated polymers, a photon source at half the optical gap may not be readily available.

The poly(dithienothiophene)s (PDTTs) are small band gap π -conjugated polymers with a polythiophene (PT) like chain, similar in a way to the low band gap poly(isothianaphthene) [1,2]. The optical absorption spectrum of PDTTs films is fairly broad [3], indicating a considerable inhomogeneity. It is generally believed that this inhomogeneity is caused by a conjugation length

* Corresponding author. Fax: +972-4823-5107.

E-mail address: eitane@tx.technion.ac.il (E. Ehrenfreund).

distribution. The optical absorption onset and its peak energy of the PDTTs were found to be around 1.1 and 1.6 eV, respectively [3]. Thus, the band gap of the longest conjugation length polymers was determined to be at around 1.1 eV. The very low 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 the estimations of the LEP state in low band gap π -conjugated polymers is desirable.

In previous studies [4,5], 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 π -conjugated polymers films having a distribution of optical energy gaps (E_g), the RRS frequencies are blue shifted with increasing excitation laser photon energy, E_L . This blue shift is the result of, first, the selectivity of the resonant process and, second, the sensitivity of the Raman vibrational modes to the energy gap of the polymer. First, at a given E_L , only that energy gap (out of the whole distribution) for which $E_g = E_L$ is in resonance with the exciting photons. Second, the higher is E_g the higher are the vibrational frequencies [6–8]. As a consequence, a coupled set of vibrational frequencies, ω_i , which are associated with this particular energy gap, is selected by E_L . Thus, the observed RRS frequencies are blue shifted with increasing E_L (this phenomenon is termed ‘RRS dispersion’). As was established earlier [4,5], this RRS dispersion is solely determined by the dependence of the even parity states on the conjugation length, N , rather than that of the optical gap, E_g .

In this work, we use the RRS dispersion found experimentally in PDTTs in order to estimate the LEP state. We find that in the three PDTTs investigated, the LEP energy level is in the vicinity of the optical gap.

2. Materials and experimental results

The three PDTTs studied are poly(dithieno[3,4-b:3',n-d]-thiophene) with $n=4',2',3'$ for PDTT1, PDTT2, PDTT3, respectively. Their structures are shown in Fig. 1. These PDTTs may be looked upon as

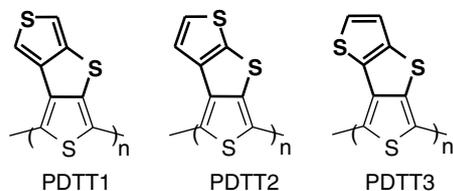


Fig. 1. Chemical structure of the three PDTTs. The bold bonds indicate the thienothiophene aromatic moieties fused onto each thiophene ring.

PT-like chains in which a thienothiophene aromatic moiety is fused onto each thiophene ring [9,10]. These aromatic moieties reduce the dimerization along the PT chain, resulting in the reduction of the optical band gap, which is directly proportional to the dimerization. Indeed, the band gaps reported for these three polymers are around 1.1 eV [3], compared with ≈ 2 eV for PT, or 1.8 eV for regio-regular PT.

The RRS spectra, for each of the PDTTs discussed here, were measured and reported previously [11,12]. In Fig. 2 we depict, as an example, the RRS spectra for PDTT3 taken at various excitations. The main feature, which is relevant to the present Letter, is the RRS dispersion (or equivalently, Raman frequency blue shift) 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 PDTT1 and PDTT2. Below, we quantify the intensity redistribution and the apparent amount of RRS dispersion by a parameter D , whose magnitude is proportional to the (normalized square) frequency blue shift with increasing E_L . We show that in the PDTTs D is much larger than in the simpler PT or poly(alkylthiophene)s.

We mention here that, except for a weak featureless background observed for 1064 nm excitation, no PL background was observed in the range of the Raman probe at all excitations, at room temperature.

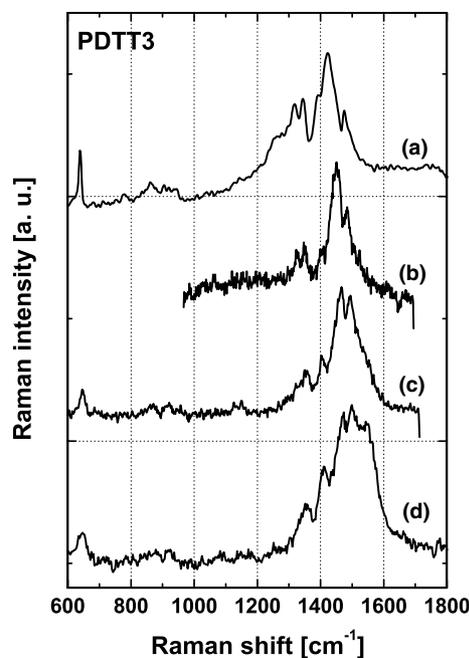


Fig. 2. Raman spectra of pristine PDTT3, excited at $E_L = 1.16$: (a) 1.96; (b) 2.41; (c) 2.71 eV; (d) (From [11]).

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, ω_i^L (at a given E_L),

$$P(E_L) \equiv \prod_i^m (\omega_i^L / \omega_i^0)^2, \quad (1)$$

where ω_i^0 are the RRS frequencies at $E_L = E_{L0}$ (to be defined below). $P(E_L)$, defined in Eq. (1), is proportional to the ‘renormalization coupling parameter’, $\tilde{\lambda}$, introduced previously in the amplitude modes theory [8,13,14]. This quantity was shown [13] 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, N , $P(E_L)$ can be written as [4,5]

$$P(E_L) = 1 + C(\chi_{N_0} - \chi_N), \quad (2)$$

where C is a constant independent on the conjugation length, N . In Eq. (2), χ is the electronic susceptibility associated with the staggered bond order, introduced by Girlando and co-workers [15–18],

$$\chi(N) = \frac{8}{N} \sum_n |\langle n | \sum_j (-1)^j p_j | 0 \rangle|^2 / E_n \equiv \sum_n a_n^2 / E_n, \quad (3)$$

where p_j is the π bond order operator between sites $j+1$ and j , and $|0\rangle$ and $|n\rangle$ are the ground and excited π electron states with energies 0 and E_n , respectively. N_0 (Eq. (2)) is the longest conjugation length, beyond which the decrease of the energy gap and the vibrational frequencies is negligible. The frequencies ω_i^0 in Eq. (1) are then the RRS frequencies for conjugation lengths $N \geq N_0$, with an energy gap $E_g^0 = E_{L0}$. It was pointed out earlier [4] that when the parity of the ground state is even ($1A_g$), as is the case for *trans*-polyacetylene, PT and other centro-symmetric π -conjugated polymers, then χ is solely determined by the even parity electronic states, nA_g . Consequently, the RRS dispersion does not depend explicitly on the dispersion of the odd parity nB_u states; and in particular not directly on $1B_u$ (which is the optical gap, E_g). It is therefore evident that the RRS dispersion results only from the *distribution* of the even parity states, caused by inhomogeneities in the π -conjugated polymer films. Specifically, for an inhomogeneity which arises from conjugation length distribution in a centro-symmetric π -conjugated polymer, we write the even and odd parity excited state energies as: $E_{nA_g}(N) = E_{nA_g}^0 + \beta_n/N$ and $E_g(N) = E_g^0 + \beta/N$, respectively (β, β_n are constants independent of N). Under resonant conditions and for relatively weak variations of

the energy gap with N , it was shown [4] that the product $P(E_L)$ can be written in the form

$$P(E_L) \equiv \prod_{i=1}^m (\omega_i^L / \omega_i^0)^2 = 1 + D(E_L - E_g^0), \quad (4)$$

where the ‘dispersion coefficient’, D , is an explicit function of the even parity energies,

$$D = C \sum_{n \geq 2} \frac{\beta_n a_n^2}{\beta (E_{nA_g}^0)^2}. \quad (5)$$

The product $P(E_L)$ (Eq. (4)) is thus linearly dependent on the exciting photon energy.

In Fig. 3 we show the product $P(E_L)$, extracted from the observed RRS spectra, as a function of E_L for the small band gap π -conjugated polymers, PDTT1, PDTT2 and PDTT3. 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 (≈ 1.1 eV) [3]. In order to estimate the error bar associated with each data point in Fig. 3, we note the following. Since $P(E_L)$ is given by the product $\prod_{i=1}^m (\omega_i^L / \omega_i^0)^2$, the uncertainty in its value is proportional to the sum of the relative uncertainties, $\Delta\omega_i^L / \omega_i^L$, in the determination of ω_i^L , times the relative blue shift $|\omega_i^L - \omega_i^0| / \omega_i^L$ of each Raman line. Taking $\Delta\omega_i^L \simeq \Delta\omega_i^0 \simeq 5 \text{ cm}^{-1}$ and the actual measured values of $|\omega_i^L - \omega_i^0|$, we find for the uncertainty in $P(E_L)$, $\Delta P(E_L) \leq 5 \times 10^{-4}$. Thus the error bar associated with each of the data points in Fig. 3 is within the symbol size shown in the figure. It is then clearly evident that the normalized products show linear dependence on E_L , supporting thus the above discussion and approximation. The accuracy of the dispersion coefficient, D , extracted from these data, is of the order of a

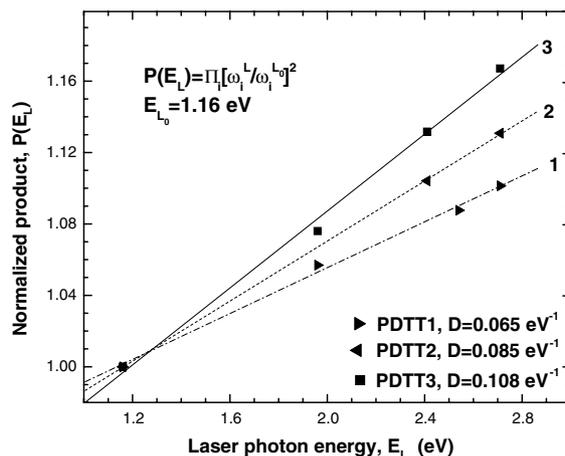


Fig. 3. The normalized product square of the observed RRS frequencies, $\prod_i (\omega_i^L / \omega_i^0)^2$, (full symbols) and linear fits (lines, marked 1, 2, 3) as a function of the resonant laser photon energy E_L for PDTT1, PDTT2, PDTT3, respectively. The slopes of the respective linear fits are marked as D .

Table 1

The dispersion coefficients, D (row 1), the relative position of the LEP state (row 2) and the LEP level, E_2 (row 3) for PDTTs, PT and *trans*-polyacetylene (PAC)

		PDTT1	PDTT2	PDTT3	PT	PAC
1	D (eV ⁻¹)	0.065	0.085	0.11	0.02 ^a	0.19 ^a
2	$E_2(\text{PDTTs})/E_2(\text{PDTT1})$	1	0.88	0.77	–	–
3	E_2 (eV)	1.2–1.4	1.1–1.2	0.9–1.1	2.2–2.5 ^b	1.1 ^c

^a Ref. [4].

^b Ref. [19].

^c Ref. [20].

percent. In Table 1 (row 1), we list the values of D found here, along with the values found for PT (a weak PL polymer) and *trans*-polyacetylene (a non-PL polymer). It is clearly seen that: (a) the D values are significantly higher in PDTTs than in PT; (b) the D values among the PDTTs increase by as much as 70% on going from PDTT1 to PDTT3. We thus conclude that the higher values of D found for PDTT2 and PDTT3 point towards lower values of the $2A_g$ level, relative to PDTT1. This conclusion is based on the expectation that the thienothiophene aromatic moiety fused into each thiophene ring in the PDTTs changes only slightly the matrix elements $a(2A_g)$ in Eq. (3) and the coefficients β_n and β in Eq. (5) within the series. Assuming further that D is dominated by the LEP level, $2A_g$, we list in Table 1 (row 2) the $2A_g$ state in PDTT2 and PDTT3, relative to PDTT1, calculated using Eq. (5). Thus, based on the excitation dependence of the RRS in the series of PDTTs, we expect PDTT3 to have the lowest $2A_g$ level among these three π -conjugated polymers.

The relatively large values of D for the PDTTs strongly indicate that the LEP state, $2A_g$, is considerably lower than that in PT, possibly as low as the PDTTs energy gap. A semi-quantitative estimate of the LEP state may be obtained realizing that the LEP scales as $D^{-1/2}$ (Eq. (5)). Assuming then that the PDTTs have a scaled down electronic structure similar to that of PT, we write: $E_{2A_g}(\text{PDTT}) \approx [D(\text{PT})/D(\text{PDTT})]^{1/2} E_{2A_g}(\text{PT})$. Taking $E_{2A_g}(\text{PT}) \approx 2.2\text{--}2.5$ eV [19], we obtain E_{2A_g} for PDTTs, as shown in Table 1 (row 3). These values of the LEP level are clearly in the vicinity of the optical gap, and indicate that the PDTTs should be either non-luminescent if ($E_{2A_g} < E_g^0$) or weakly luminescent if ($E_{2A_g} \geq E_g^0$) π -conjugated polymers, making them potentially preferred active media in photovoltaic cells.

4. Summary

We have shown that in low band gap π -conjugated polymers, for which two photon absorption measurements 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 fre-

quencies, in the series of π -conjugated polymers PDTTs ($s=1, 2, 3$), is found to increase linearly, with a relatively high rate of change, D , as the photon excitation energy increases. The relatively large values of D indicate a very low even parity $2A_g$ state.

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