A single polymer chain as an organic quantum wire: optical evidence of a purely 1D density of states

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The excitonic luminescence of an isolated polydiacetylene polymer chain in its monomer matrix is studied by micro-photoluminescence. These chains behave as perfect 1D semiconducting wires with the expected \( \frac{1}{\sqrt{E}} \) density of states between 5 and 50 K. The temperature dependence of the homogeneous width is explained by interaction with longitudinal acoustic phonons of the crystal in the range of temperature explored. The optical phonons of the chain which are involved in the vibronic transitions are found to have coherence times ranging from 300 to 600 fs.

Excitons are the dominant optically accessible states in conjugated polymers. They are usually discussed in terms of single discrete states, as in an isolated molecule. The exciton band structure and density of states (DOS) are usually not considered, unlike in inorganic semiconductors for which the exciton energy dispersion and DOS are important properties. For the past decade, an important effort has been made in order to obtain a 1D semiconducting system exhibiting a \( \frac{1}{\sqrt{E}} \) DOS. Such a DOS has neither been observed in the quantum wires which have been realized [1], nor in organic "1D" J-aggregates [2]. In the present letter, we report micro-photoluminescence (µ-PL) experiments on a single isolated poly-3BCMU red chain and show that to properly describe excitons in this system the actual band structure must be considered. We show as well that the DOS is the one of perfect 1D systems with the expected \( \frac{1}{\sqrt{E}} \) singular variation. The temperature dependence of the homogeneous width is explained by interaction with acoustic phonons [4], and the values found for the chain optical phonon coherence times are also presented.

PDA chains diluted in 3BCMU crystal monomer matrix exist in two electronic structures so called "red" and "blue" phases. Both types of chains exhibit an excitonic resonance fluorescence [5]. Blue chain fluorescence is very weak with a quantum yield of \( 10^{-4} \) whereas red chains have a high fluorescence quantum yield of 0.3 at 15 K [5]. The emitting species of such chains are excitons with a large binding energy of 0.5 eV [6]. The luminescence spectrum of red chains exhibits an intense zero phonon line and several much weaker vibronic replicas. The zero phonon line is centered at 2.28 eV at low temperature. The two main vibronic peaks correspond to the stretching of the C=C and C≡C bounds and will now be denoted by D and T respectively. These two lines are centered at 2.09 and 2.01 eV and are due to radiative recombination with emission of a chain optical phonon with the appropriate momentum [5]. The very high dilution of red chains and their high fluorescence yield allow the study of a single red chain by µ-PL experiments. The zero phonon line was studied giving access to the homogeneous linewidth \( \Gamma_0 \) and its temperature dependence. It also brought evidence on long range energy transfer along the chain [5]. In the present paper this study is extended to the vibronic emission lines.

Macro-PL experiments on an ensemble of red chains show that up to 50 K the exciton lifetime increases with temperature while the fluorescence rate decreases. This suggests that non-radiant states are populated by thermal excitation of radiant ones, a known process in exciton bands of semiconductor quantum wires. Nevertheless, in organic materials the exciton is usually considered as a single excited state. The analysis of the vibronic peaks line-shapes remove this ambiguity since they reflect the DOS in a band description.

The 3BCMU single crystals analyzed here were identical to the ones described in [8]. The average concentration of red chains is smaller than \( 10^{-8} \) in weight, allowing the study of a single chain. The µ-PL experimental setup is the same as in [5]. The excitation wavelength of the
$Ar^+$ laser was chosen at 497 nm, nearly resonant to the D (Double bound stretch) absorption line. The excitation power was of the order of one $\mu$W to keep the measurement in the low excitation regime, i.e. with at most one exciton per chain.

The D emission line at $T=43$ K is shown in Figure 1a. The line-shape is clearly non lorentzian, this emission can then not be that of a single state. In Fig.1a, a fit barely distinguishable from the experimental data is presented as well, and the corresponding error is given in Fig.1b. This fit is based on 3 assumptions:

- The excitons in the chain are at thermodynamic equilibrium with the surrounding medium. Their energy distribution then follows a Maxwell-Boltzmann distribution characterized by the crystal’s overall temperature.

- The energy dispersion of the optical phonons generated in the vibronic emissions is very small compared to the one of the excitons and is neglected. Since the effective mass of the exciton is found to be $\approx 0.3 \ m_0$ ($m_0$ is the bare mass of an electron), this hypothesis seems very reasonable.

- The transition matrix elements between all the initial $k$ exciton states and the final state (emission of one photon and one chain optical phonon) are equal (including the $k=0$ state). The contribution of the initial $k$ state to the overall homogeneous width is the same for all $k$.

The fitting function $f(E)$ is the convolution of the homogeneous lorentzian profile and the population of emitting states ($\Gamma_D$). This population is the product of the DOS by the occupation probability. In $f(E)$, $E_0$ is the lorentzian’s center position and $\Gamma_{vib}$ its half width. $A$ is a constant including the amplitude of the lorentzian and the constant parameters of the DOS. The only relevant parameter in the fitting routine is $\Gamma_{vib}$ (e.g. $\Gamma_D$ for the D line) which dependence with temperature will be discussed.

$$f(E) = \frac{A}{(E - E_0)^2 + \Gamma_{vib}^2} \exp\left(-\frac{E - E_0}{\kappa_B T}\right) \times DOS$$

A quantitative 1D fit, i.e. with a $(E - E_0)^{-1/2}$ DOS, is obtained for all vibronic lines at all temperature studied (5-50 K). Fitting with a 2D DOS is always worse. The 2D DOS corresponds to the lowest dimensionality non singular density of states, and has been found to fit data on J aggregates [2]. The fitting error for the 1D and 2D model are presented in Fig.2, and show the very good accuracy of our model when a 1D DOS is used.

$\Gamma_D(T)$ and $\Gamma_0(T)$ are presented in Fig.2. The present data on $\Gamma_0(T)$ confirm previous measurements presented in [8]: $\Gamma_0$ is 250 $\mu$eV at 5 K, then increases linearly up to 35 K. The model used to account for the variation with temperature of $\Gamma_0$ assumes that the dominant process is the absorption of a single acoustic phonon (LA phonon) of the crystal [8]. It is an adaptation of the deformation potential theory to a 1D system such as poly-3BCMU (see for instance Oh and Singh [10]). Due to the energy and momentum conservation rules, LA phonons confined on the polymer chain can only make exciton transitions between $k=0$ and $k=k_{2 \text{min}}$ (see Fig.3). This does not agree with the experimental observation that all $k$ states emit within an energy range $\kappa_B T$. On the contrary, exciton scattering by crystal LA phonons connect $k=0$ and a continuum of $k$ states with $k > k_{1 \text{min}}$. The $k_{1 \text{min}}$ is defined in Fig.3 since only the component parallel to the chain of the total momentum must be conserved. Further scattering can populate the rest of the band. Therefore, we have considered interactions with LA phonons of the crystal. This process quantitatively explains the variation of $\Gamma_0(T)$ in the range of temperature explored (see Fig.4). The sound velocity is assumed isotropic in the crystal and is taken as $2.5 \times 10^3 \ m.s^{-1}$ as in another diacetylene [11]. This is a typical value for molecular crystal.

Besides the chosen sound velocity, the calculation involves three parameters: the exciton Bohr radius, its effective mass, and $(D_\epsilon + D_\delta)$ the sum of the deformation potential for the conduction and valence band respectively. Experiments and theory indicate that the Bohr radius of the exciton on PDA chains is between 10 and 20 Å [8] [12]. The chosen value for this parameter is not critical as shown in Figure 1c. From the temperature dependence of radiative lifetime, an exciton effective mass ($m_\chi^*$) of approximately 0.3 $m_0$ is deduced with a large uncertainty [8]. To $m_\chi^* = 0.3 \pm 0.1 \ m_0$ correspond $(D_\epsilon + D_\delta)$ values equal to 6.1 $\pm 0.8 \ eV$, which are typical deformation potentials. Since the scattering rate of

**FIG. 2: $\Gamma_D$ (filled circles) and $\Gamma_0$ (open circles) versus temperature. The crosses represent the difference between $\Gamma_D$ and $\Gamma_0$.**
FIG. 3: Dispersion relations of the excitons and LA phonons. (1) and (2) are the dispersion curves of LA phonons of the crystal and LA phonons confined on the chain respectively. In the first case the sound velocity is assumed isotropic and is $2.5 \times 10^3 \text{ m.s}^{-1}$. In the latter case the sound velocity is $5.5 \times 10^3 \text{ m.s}^{-1}$. $k_{1,2}^{\text{min}}$ denotes the scattering thresholds in each case.

FIG. 4: Experimental data (open circles) and model of the broadening of $\Gamma_0$ with temperature for an exciton Bohr radius of 10 and 20 Å((a) and (b) respectively) and an effective mass of 0.3 $m_0$. In both cases, the sum of the deformation potential for the valence and conduction band is 6 eV.

excitons by LA phonons goes to zero at 0 K, a constant value corresponding to the residual linewidth at 0 K has been added. Its fitted value is 150 $\mu$eV, much larger than the contribution of the effective lifetime of the exciton at 1 K (approximately 6 $\mu$eV). This remains an open question and will be the subject of further analysis.

The inelastic processes thermalizing the excitons in their band are thus either the emission or absorption of LA phonons in the temperature range studied. The absorption is the slowest process and has a characteristic time of 2 ps or less (see the widths in Fig.2). The excitons are then at thermodynamic equilibrium since their effective lifetime is over 100 ps in the range of temperatures studied.

In Fig.4 one notes that $\Gamma_D$ is 3 times larger than $\Gamma_0$ at low temperature. Let us assume that the width of a vibronic line is the sum of the terms resulting from the initial and final state. The contribution of the initial state is $\Gamma_0$. The one from the final state represents the coherence time of the optical phonon emitted in the recombination which is slowly decreasing with temperature (see for instance the Fig.2 for the D line). One would expect that the coherence time so obtained is not the same for all vibronic peaks. This is indeed observed: a coherence time of approximately 300 fs is found for the D and T lines while in another vibronic line centered at 2.15 eV, distinctly narrower, a coherence time of 600 fs is found. These different values are in agreement with previous measurements made in another PDA by Chen et al. using a completely different method (CARS).

Fitting the line-shape of the vibronic peaks has enabled us to deduce that our system exhibits a $1/\sqrt{E}$ DOS. Let us associate this conclusion with the analysis of the exciton decay time presented in [9]. Indeed, the radiative lifetime of excitons increases as $\sqrt{T}$ for $T$ up to 80 K at least, as it is expected for an ideal 1D wire. Therefore, localization effects do not seem to affect the exciton lifetime and DOS, contrary to the case of inorganic semiconductor quantum wires. Time resolved $\mu$-PL experiments are then planned to further study exciton transport and localization on a single chain.

To summarize, we have presented microfluorescence experiments performed on a single conjugated polymer chain in its crystalline matrix. The zero phonon emission line is lorentzian while the vibronic ones are asymmetric. Fitting the line-shape of these vibronic peaks shows that the chain is a one dimensional system which has to be described by an excitonic band with a $1/\sqrt{E}$ DOS. Furthermore, the variation of $\Gamma_0$ in temperature is explained by interactions with longitudinal acoustic phonons of the crystal in the range of temperature studied. The chain optical phonons involved in the vibronic emissions are found to have coherence times ranging from 300 to 600 fs at low temperature.

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The general formula of PDA is $(= CR - C \equiv C - CR')_n$. In 3BCMU, the side groups $R$ and $R'$ are identical, with the following molecular formula: $(CH_2)_3OCONHCH_2COOC_4H_9$

F. Dubin et al., to be published

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