



## Ultrafast electronic relaxation and vibrational dynamics in a polyacetylene derivative

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### ABSTRACT

Real-time vibrational spectra in a polyacetylene derivative, poly[*o*-TFMPA([*o*-(trifluoromethyl)phenyl]acetylene)] in a broad electronic spectral region were observed using a sub-7-fs laser. Using the frequencies and initial phases of vibrational modes obtained by the spectroscopy, the assignment of the wavepackets was made. From the first moment, Huang–Rhys parameters were determined for six most prominent modes, which characterize the potential hypersurface composed of multi-dimensional vibrational mode spaces.

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### 1. Introduction

One-dimensional conjugated polymers have been of interest for the last two decades because of their characteristic properties including the tailorability by chemical synthetic processes to change the side groups and physical or physico-chemical modification processes of morphological, mechanical, electrical, and optical properties. The capability is useful for the preparation of materials with various electrooptical, optoelectrical, and photonic properties, which are of vital importance for varieties of applications, such as electroluminescent devices, nonlinear optical devices, and field-effect transistors [1–5]. Among them large ultrafast optical nonlinear property is based on the dimensionality and conjugation of the polymer [1,6]. Conjugation of  $\pi$ -electrons along the main chain of the polymer supports the correlated electrons to induce enhanced transition probability with a large transition dipole. This results in the large third-order nonlinearity because of the existence of the deviation from the bosonic properties of exciton due to the Pauli Exclusion Principle. Ultrafast relaxation is expected in such a one-dimensional system due to a barrierless potential between the free exciton and self-trapped exciton [7].

The combination of the large third-order nonlinearities due to the electronic correlation and the ultrafast response is quite attractive for basic techniques such as the optoelectro-switching and

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optical information processing. Many experimental and theoretical studies have been made to clarify the mechanism which is responsible for the macroscopic nonlinear properties characteristic of this class of materials [8]. The optical nonlinearities of the one-dimensional conjugated polymers are closely related to geometrically relaxed excitations such as a pair of solitons, and polarons, and a self-trapped exciton (STE). STE is equivalent to an exciton polaron and a neutral bipolaron, and is formed via strong coupling between electronic excitations and lattice vibrations [9]. A free exciton formed in such a one-dimensional system spontaneously relaxes within  $\sim 100$  fs because of the absence of barrier between free exciton minimum and STE minimum of the potential curves [10] and change optical properties of the conjugated polymers, inducing the absorption coefficients and refractive indices [10,11]. Relaxation dynamics of photoexcitations in polydiacetylenes and polythiophene are thus related to the ultrafast nonlinear response dynamics. Their formation and relaxation processes are, therefore, quite essential and one of the most fundamental subjects to be investigated. The change is induced not only by the localized electronic excitation but also by vibrational excitation coupled to the electronic excitation through vibronic coupling start to modulate the molecular structure [12–15]. The structural modulation changes the energy-level scheme and the transition probability. The former changes the electronic spectrum and hence the intensity at some specific wavelength. The latter modulates the intensity in the way in the relevant homogeneous spectral range.

In the present Letter, the delay time dependence of difference absorbance and time-resolved spectrum is shown in Section 3.1, and the effect of the electronic transition spectrum by molecular vibration is discussed in Section 3.2. Initial phases of the

vibrational modes coupled to the electronic transition via impulsive excitation are used to identify the mode observed either to the ground state or to the excited state in Section 3.3. From the analysis of dynamics of the mean distribution energy of the vibrational energy, the rate of the descending process of the vibrational ladder is calculated for several modes. Vibrational phase relaxation rate is also calculated from the FWHM of the Fourier spectrum in Section 3.4. Section 3.5 discusses the electronic phase relaxation is obtained from the data in the negative time range when the probe pulse proceeds the pump pulse.

## 2. Experimental

### 2.1. Sample

The sample polymer studied is poly[*o*-TFMPA(*o*-(trifluoromethyl)phenyl)acetylene)] (hereafter abbreviated as PTPA), whose molecular structure is shown in the inset of Figure 1. It was synthesized in the following way: The monomer, *o*-TFMPA (*o*-(trifluoromethyl)phenyl)acetylene) was prepared according to the procedure by Okuhura [16]. Polymerization of the monomer was carried out under dry nitrogen. It was initiated by 1:1 mixtures of WCl<sub>6</sub> or MoCl<sub>5</sub> with various organometallic cocatalyst (mixture of WCl<sub>6</sub> with Ph<sub>4</sub>Sn) and achieved molecular weights as high as 160 kDa (this is unit for molecular weight). Metal carbonyl based catalysts were prepared by irradiation of carbon tetrachloride solution of a metal carbonyl with UV light (200-W high-pressure Hg lamp, distance 5 cm) at 30 °C for 1 h. A mechanically strong film could be obtained by solution casting. The polymer was thermally fairly stable in air. The high molecular weight, film formation, and fair thermal stability of the present polymer are notable characteristics, which are not seen in poly(phenylacetylene).

The polymerization using a WCl<sub>6</sub> or MoCl<sub>5</sub> catalyst was made to achieve a high (80–100%) yield. The polymers have molecular weights significantly larger than 10<sup>6</sup>, and therefore, contain 10<sup>4</sup> repeat units in a chain. The synthesis and various chemical properties of the conjugated polymers are described and discussed in detail elsewhere [16,17].

### 2.2. Ultrafast spectroscopy

Using the 6.8 fs pulse, the pump induced absorbance change ( $\Delta A$ ) in PTPA film sample was measured at 128 different wavelengths from 529 to 726 nm (2.34–1.71 eV) [18,19]. The pump and probe beams were both from the non-collinear parametric amplifier (NOPA), which is reported in detail in Refs. [18,19]. In brief description, the pump source of the NOPA system is a

commercially supplied regenerative amplifier (Spectra Physics, Spitfire). The central wavelength, pulse duration, power of the output, and repetition rate of this amplifier were 800 nm, 50 fs, 740 mW, and 5 kHz, respectively. The output pulse from the NOPA was compressed with a compressor composed of a pair of prisms and a set of two chirp mirrors. The polarizations of the pump and probe beams were parallel to each other.

The pump–probe experiment setup was described in detail in our Refs. [20–23]. The pump–probe signal was spectrally dispersed with a polychromator (JASCO, M25-TP) over 128 photon energies (wavelengths) from 1.65 to 2.23 eV (753–555 nm). It was detected by 128 sets of avalanche photodiodes and lock-in amplifiers with a reference from an optical chopper intersecting the pump pulse at the repetition rate of 2.5 kHz.

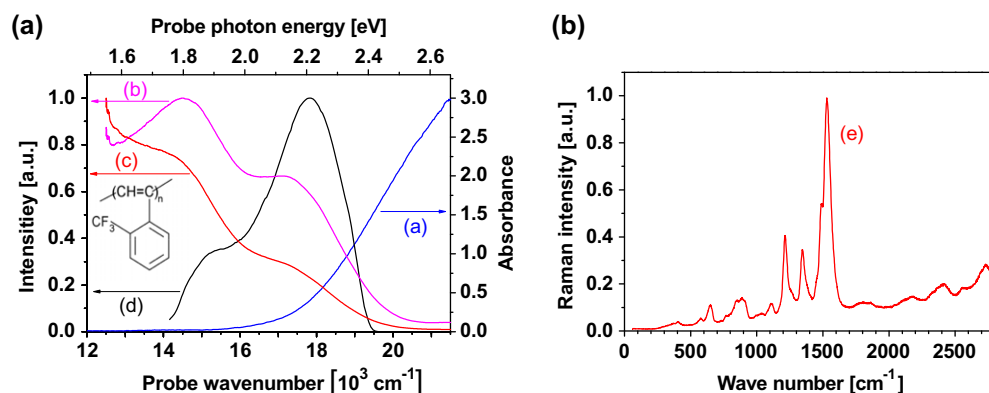
## 3. Results and discussion

### 3.1. Delay time dependence of difference absorbance and time-resolved spectrum

Figure 1 shows the absorption, spontaneous fluorescence, and stimulated emission spectra. The last one is calculated from the spontaneous emission spectrum of the polymer sample. The laser spectrum also shown in the figure is overlapping with the tail of the absorption. Figure 2a shows the traces of difference absorbance  $\Delta A(t)$  at 10 different probe photon energies. In the absorbance traces shown on the left hand side of Figure 2a, the electronic and vibrational effects are both apparent. The former appears as slow changes, which decay slowly due to the electronic relaxation. The latter effect appears as rapid modulation of the transition due to molecular vibration.

The time trace signals depicted in red color lines in Figure 2a are the multiplied traces by appropriate factors to show the modulation due to molecular vibration in the traces more clearly. Figure 2b shows the Fourier power spectra of  $\Delta A(t)$  traces at the 10 different probe photon energies corresponding to the real-time traces in Figure 2a.

To investigate the mechanism of electronic relaxation, we first analyze the change of spectral shape during relaxation and then decay dynamics using analytic functions. Figure 3a shows the time-resolved spectrum integrated for 100 fs delay time duration with the center delay times between 100 and 1700 fs with a 100-fs step. For example, the spectrum at the center delay time of 400 fs is the time-resolved spectrum integrated over the 351–450 fs range. To see the change in the spectrum better, the time-resolved spectra normalized to the peak intensity are shown in Figure 3b. The spectral shift is to be discussed later in this Letter



**Figure 1.** (a) Absorption, (b) spontaneous fluorescence, and (c) stimulated emission spectra of the PTPA film sample and (d) the 6.8-fs laser spectrum. Inset is the molecular structure of PTPA. Raman spectrum of PTPA excited at 442 nm is depicted in (e).

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