Emission of a Single Conjugated Polymer Chain Isolated in Its Single Crystal Monomer Matrix

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The excitonic luminescence of a highly ordered single conjugated polymer chain is studied by microphotoluminescence. At $T \leq 10$ K it consists of a single Lorentzian line. The linewidth increases linearly with T between 6 and 60 K, from 350 μeV at 6 K, indicating a pure dephasing time of $\sim$2 ps. Above 10 K, other neighboring regions along the chain direction start to emit at a slightly higher (by $\sim$1 meV) energy. This indicates very small inhomogeneous broadening, very long chains ($\geq$10 μm), and a long range and very rapid exciton energy transfer ($>$10 μm in $<$100 ps).

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Polydiacetylene (PDA) chains in very low concentration in their single crystal diacetylene monomer matrix are highly ordered 1D noninteracting conjugated chains and thus provide a good experimental model for studying the electronic properties of conjugated polymers. They are a very good approximation of an organic semiconducting quantum wire.

Bulk PDAs are known to exist in either of two electronic structures, so-called "red" and "blue" phases, showing intense excitonic absorptions near 2.4 and 2.0 eV, respectively. It was found recently [1] that in one monomer crystal, 3BCMU [2] isolated chains of both types coexist. The majority population is of the blue type, with typical chain concentration of 10^{-5} to 10^{-4} in weight. Red chain concentration is smaller by a factor of about 10^{-3}. In these crystals, blue chains are over 2 μm long [3]. The length of red chains is not known and its determination by usual methods seems hopeless.

Both types of chains show exciton resonance fluorescence [1]. Thus, emission from defects or self-trapped states can be ruled out. Blue chain fluorescence is extremely weak; quantum yield is $\approx 10^{-4}$ [4]. On the contrary, red chains have a high fluorescence quantum yield of 0.30 at 15 K, with more than 90% of the emission concentrated in a narrow (1.5 to 2 meV at 15 K) zero phonon line at 543 nm, and the other 10% in a series of vibronic lines [4]. These differences indicate very different relaxation schemes for the two types of excitons, leaving thus a puzzling open question, since no conformational difference between the two types of chains could be detected yet from structural studies of bulk blue [5] and red [6] PDAs. In these 3BCMU monomer crystals, the blue and red polymer chains are almost unstrained, since the lattice parameter in the chains direction differs from the equilibrium repeat unit length of the polymer by less than 0.5% [7].

All the results mentioned above have been obtained on ensembles of isolated chains in a macroscopic crystal. The very high dilution of red chains in 3BCMU crystals and their high fluorescence quantum yield in the zero phonon line open the possibility of studying a *single* red chain in a microphotoluminescence (μPL) experiment. High spatial resolution spectroscopy at the micrometer scale and at low temperature has attracted considerable interest recently since it gives new insight into optical properties of individual nanostructures such as single molecules [8], and individual quantum wires or dots [9]. No such experiment has yet been performed on a highly ordered polymer chain. In this Letter, first results of such experiments are presented and discussed.

3BCMU monomer was synthesized [10] and carefully purified in the laboratory. Single crystals grown from such material contain 10 to 100 times less polymer chains than formerly studied crystals [1,3], and are thus almost colorless. In such crystals, red chain average concentration is less than 10^{-8} in weight. Absorption and emission are strongly polarized along the chain direction (measured linear dichroic ratio for blue chains is $\approx$600 [3]).

The excitation wavelength was chosen at 501.7 nm (argon line), approximately in resonance with a vibronic absorption line [1]. The majority blue chain population will not interfere except by acting as an internal filter absorbing part of the excitation and emission lines of the minority red chains. The optical density of the samples at these wavelengths is typically 0.1 to 1 of which more than 99% is due to inactive blue chains. The excitation power was kept below 100 nW and the results do not depend on excitation power, so the measurements are always in the low excitation regime: no nonlinear effect is observed.

The excitation laser beam was focused using a microscope objective with a numerical aperture of 0.6, yielding a diffraction limited laser spot of $\approx$1 μm diameter. This spot could be focused anywhere within the total sample thickness of $\approx$100 μm.

The signal was analyzed through a TRIAX-550 Jobin-Yvon imaging spectrometer, coupled to a N_2-cooled 2D charge coupled device (CCD) camera. The spectral resolution of this setup is $\approx$100 μeV. The 1 μm^2 spot corresponds to one pixel of the CCD camera. When the polymer chain direction is aligned parallel to the spectrometer entrance slit, the 2D image shows the luminescence spectrum in the dispersion direction (perpendicular to the slits) and the spatial extension of the emission along the other direction, parallel to the slits.

The sample was mounted on the cold finger of a variable temperature cryostat (6 to 300 K) designed and built in the laboratory. Since the temperature dependence of the macroscopic emission line (position and width) is known [11], the position of the recorded line gives the actual temperature of the sample at the position of the chain under study. This is useful, due to the low thermal conductivity of monomer crystals at low temperature. In this cryostat, it is possible to keep the laser spot indefinitely at the same position within the crystal when the temperature is changed, so that the same single polymer chain can be studied.

Figure 1a shows the macroscopic photoluminescence spectrum of an ensemble of isolated red polymer chains at 10 K [1,11]. The line is centered at 2.282 eV (543 nm) and inhomogeneously broadened to 2 meV. Figure 1b shows a μPL spectrum obtained on a formerly prepared BCMU crystal. It consists of several resolved lines, all with similar widths of about 400 μeV, corresponding to several slightly different emitting sites. Figure 1c shows a typical μPL spectrum of a newly prepared crystal consisting now of a single Lorentzian line of width 350 μeV and peaking at 2.282 eV. Only the spectral region of the zero phonon line is presented here. Exploring different positions on such crystals typically yields similar single line spectra, with the same width but at slightly different wavelengths within the inhomogeneously broadened line of Fig. 1a. Such a spectrum can correspond only to emission of a single polymer chain. This will be confirmed in the discussion of Fig. 3.

Therefore, in this experiment at low temperature (Fig. 1c), a given chain emits a single homogeneously broadened line. This in turn suggests assigning the several lines of Fig. 1b to several different individual chains within the excited volume of the crystal.

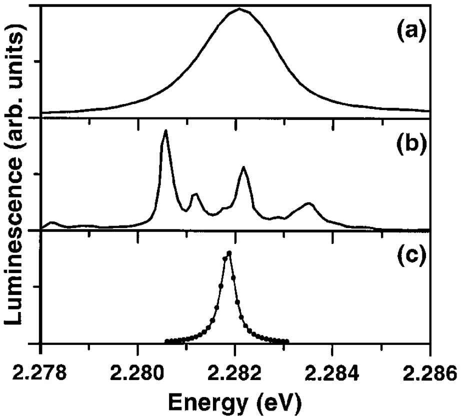

FIG. 1. (a) Macroscopic photoluminescence spectrum of red polymer chains. (b) μPL spectrum of red polymer chains in a dilute sample. (c) μPL spectrum of a very dilute sample. The dots represent the experimental curve and the solid line is the corresponding Lorentzian fit (width 350 μeV). All spectra given at 10 K.

Position and width of a line such as on Fig. 1c depend on temperature. The position shifts towards shorter wavelengths when the temperature is increased, and shows the same variation as the macroluminescence line [11]. Figure 2 shows the temperature dependence of the μPL linewidth Γ_μ compared to the macroluminescence width Γ_M. The line keeps Lorentzian and Γ_μ increases approximately linearly with T. Above 30 K, $\Gamma_\mu = \Gamma_M$. Below 30 K, Γ_M becomes constant (this inhomogeneous width is slightly sample dependent). Γ_μ shows no indication of leveling off even at 6 K, the lowest temperature presently accessible with our setup.

The imaging spectrometer allows one to study spatial extension of the emission zone. Figure 3a shows a 2D image taken at 10 K. The dispersion direction gives a spectrum similar to the one of Fig. 1c. The spatial extension in the other direction is ≈ 3 μm, which is comparable to our present experimental spatial resolution, so the length of the emitting region is shorter than that. The image on Fig. 3b was obtained at 30 K at the same position in the crystal. Two emission regions are now seen. The lower one at 540.7 nm corresponds to the excitation region and also to the emission region at 10 K, and does not show any spatial broadening beyond the instrumental resolution. The other emission is a line at slightly higher energy ($\delta E \approx 1.4$ meV or about $kT/2$, about half the common Γ_μ of both lines) coming from a different spatially resolved region outside the excitation region. Experimental values of δE are typically between 0.5 and 1.5 meV. The distance between the two sites is ≈ 10 μm along the chain direction. However, since the sample displacement is at present done by micrometer screws, a controlled translation from one site to the other is not yet possible. The necessary instrumental improvement is presently being made.

The emission lines are always Lorentzian and their width Γ_μ at a given T is the same whatever their emission energy,

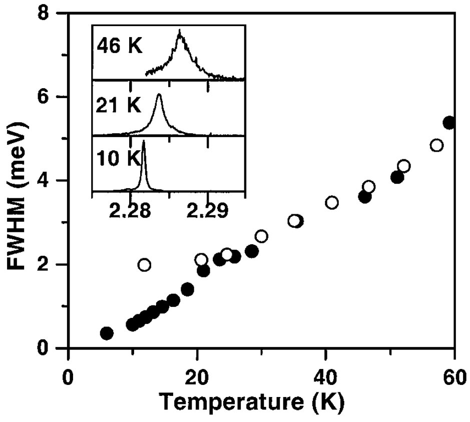

FIG. 2. PL linewidth (FWHM) versus temperature. The open circles correspond to the macroPL widths (Γ_M), and the filled circles to the μPL widths (Γ_μ). Three μPL spectra at three temperatures are shown in the inset.

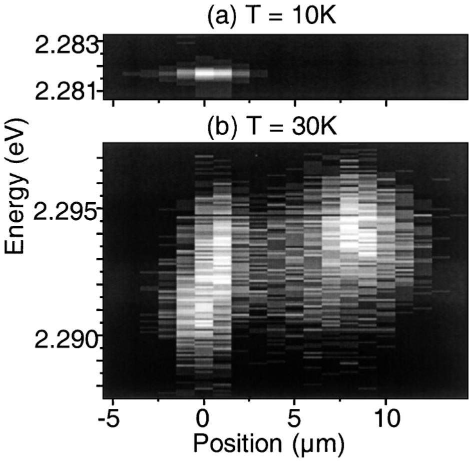

FIG. 3. Images of a single red polymer chain emission at 10 K (a) and 30 K (b). Horizontal axis: position in the sample along the chain direction (zero is the laser spot position); vertical axis: energy of the emission.

indicating homogeneous broadening. The corresponding time is ≈2 ps at 6 K, much shorter than the measured effective lifetime of ≈80 ps at the same temperature [11]. Thus, a pure dephasing time is measured here, and is a common property of excitons on all chains. This suggests that the linear increase of Γ_μ with T shown in Fig. 3 is due to intrinsic dephasing processes, probably related to phonons. This will not be further discussed here, since many types of phonons may play a role: a polymer chain has phonons of its own, distinct from those of the surrounding crystalline matrix. Very low energy optical phonons (2 to 10 meV) are observed in the resonance Raman scattering spectra of blue chains [12] and a similar situation may be expected in red ones. In the case of blue chains, it has been shown that the absorption lines are Lorentzian and their width increases linearly with T above 80 K [13]. At 60 K, the width is about 2–3 of that in red chain emission, supporting a common broadening mechanism in both types of chains.

The case of an isolated polymer chain differs from that of a single molecule in that the questions of localization of the excitation and its transport along the chain arise. Also, the inhomogeneous broadening can be due to intrachain disorder, in addition to the usual fluctuations from a molecule to another (corresponding here to interchain differences). Imaging spectrometry will bring information about these questions.

It is seen in Fig. 3a that, at 10 K, emission comes only from the excited region. Figure 3b shows that, when the same region of space is excited at 30 K, light is also emitted at a slightly different energy from a region located ≈10 μm farther along the chain direction. The most likely explanation is that the excited chain extends over at least ≈10 μm, and that the excitation is mobile along that chain via thermally activated processes. One cannot exclude, however, that energy is transferred from one chain to another one along the chain direction; this requires the exciton interchain transfer to be much faster than its decay, which is impossible if the chain ends are not in the closest possible contact. In both cases, the length of red chains is larger than 5 μm.

These observations confirm our assumption that only one polymer chain is studied in Fig. 1c. Observation of a single Lorentzian line would require that, if several chains are present in the excited volume, all exciton energies are the same within a small fraction of the homogeneous linewidth (i.e., $\ll 100$ μeV). But when two or more emission lines are observed, as in Fig. 1b, corresponding to at least as many chains in the excited volume, their energy differences are in fact of the order of 1 meV, i.e., comparable to the macroscopic inhomogeneous linewidth. An intermediate situation of a single broader (inhomogeneously broadened) line is never observed.

Red chains are thus very long. Figure 3 shows that the extension of emitting regions is limited by our present instrumental spatial resolution. Therefore, the excitation becomes localized over a length small compared to the total polymer chain length in a time short compared to the exciton effective lifetime, and the energy differences are smaller than kT at 30 K.

Energy must be transferred over ≈10 μm in a time shorter than the exciton lifetime (≈110 ps at 30 K [10]). μPL experiments open the possibility to study exciton transport *within* a single chain (time-resolved experiments are planned). The present results indicate that energy transfer is very rapid: in the case of ballistic transport, it would correspond to a velocity of at least 10^7 cm/sec, and for diffusive transport the diffusion coefficient would have to be about 10^4 cm^2/sec. Whatever the transport mechanism, these are large numbers. This is the first experimental information about singlet exciton transport in ordered conjugated chains.

The present system is quite analogous to J aggregates, which are also 1D ordered (though noncovalently bound) chains showing highly delocalized excitons. As in J aggregates, the red chains show only weak vibronic emission compared to the zero phonon line, as well as short radiative lifetimes, of the order of 100 ps [4,11].

Our results are also relevant to recent work in which single disordered conjugated polymer chains have been studied by confocal microscopy; it was found there that such macromolecules show intermittency [14–16] or ultrafast energy transfer [17].

Figure 3 also yields information about inhomogeneous broadening in red chain populations: the two emission line energies differ by ≈1.4 meV, which is approximately the inhomogeneous broadening at low temperature (Fig. 1a). If Fig. 3b shows indeed the response of a single chain, then intrachain exciton energy fluctuations account for a significant fraction of the total inhomogeneous broadening. We propose that this broadening is mainly due to small static, long range deformation fluctuations in the monomer lattice surrounding the red chains, corresponding to elastic strain due to the stresses generated in the crystal by the presence of the blue and red chains which are much stiffer than the monomer crystal [18].

In conclusion, we have presented microfluorescence experiments performed on a single conjugated polymer chain isolated in its crystalline monomer matrix. Such a chain is a highly ordered 1D system embedded in a periodic potential. The emission lines are homogeneously broadened (Lorentzian). The low temperature (6 K) linewidth corresponds to a dephasing time of 2 ps. Evidence is given that these chains are very long (of the order of 10 μm) and that exciton transport along the chain is extremely rapid at low T.

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