

Exciton spectroscopy of red polydiacetylene chains in single crystals

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Abstract

The absorption and emission properties of excitons are investigated in a pure ‘red’ phase of luminescent polydiacetylene wires. The values of the binding energy ($E_b = 0.556$ eV) and Bohr radius ($r \sim 14$ Å) make the ‘red’ exciton similar to the one of the extensively studied ‘blue’ phase, so the conformational modifications which lead to a reordering of excited states and luminescent emission do not strongly affect the exciton structure. The opening of a thermally activated non radiative channel leads to an efficient quenching of the intense luminescence observed at low temperature.

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1. Introduction

Polydiacetylene (PDA) chains exist in the solid state as either of two electronic structures commonly called the blue and red phases. Single isolated chains of red-phase poly-3BCMU have remarkable electronic properties. A chain behaves like a quasi-perfect one-dimensional system [1] with the spatial coherence of the red exciton extending over macroscopic distances [2]. However, in these crystals, red chains coexist with a majority population of blue chains. The red chains can be discriminated from the weakly emitting blue ones only because of their strong luminescence. The coexistence of two populations of chains in the same crystal is a limiting factor since the absorption properties of the red polydiacetylenic structure cannot be selectively probed. For instance, photo-induced absorption experiments which have allowed the investigation of the relaxation dynamics of the blue phase exciton are impossible [3–5].

The differences in electronic properties of each phase are necessarily associated to modifications of the ground state structure. As the current data from X-ray diffraction experiments do not discriminate between red and blue geometries, the structural differences in the ground state must be quite small. The only results showing clear variations are from solid state ¹³C NMR spectroscopy [6,7]. Determination of the red chain conformation is thus a still unresolved issue which is related to the general question of the relationship between electronic configuration and structural parameters in conjugated polymers.

Given this situation, we have searched for a purely red system of PDA chains with the further requirement of being able to achieve sufficiently low polymer contents in a good crystallographic environment. The spectroscopic results presented in this Letter indicate that the polydiacetylene chain obtained from the polymerization of 1,6-bis(diphenylamino)-2,4-hexadiyne (THD) leads to the formation of a purely red phase, promising for comparative studies between the two conformational isomers of PDA. Up to now the structural and electronic properties of poly-THD have been addressed in a limited number of papers. The room temperature crystal structure has been

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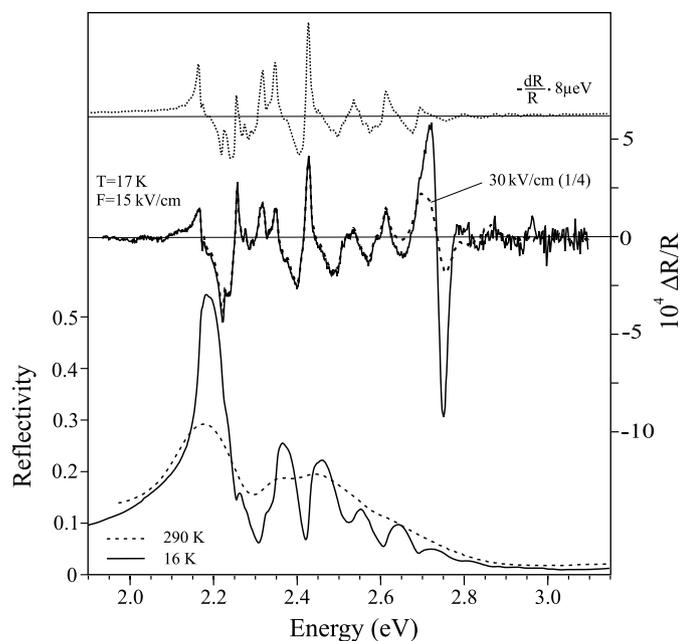


Fig. 1. Reflectance and electroreflectance spectra with light polarized parallel to the polymer chain. The ER spectrum obtained for 30 kV/cm is reduced in size by a factor 4. The dotted line shows the derivative of the reflectivity.

determined [8]. Room temperature reflectance and Raman scattering spectra have been measured by Morrow et al. [9]. The Kramers–Kronig transformation of the reflectance yields a zero phonon absorption band peaked at 568 nm and characteristic of a red PDA phase. The fluorescence spectra of thin films made of microcrystallites dispersed in a PMMA matrix have also been measured [10]. So far, all of the studies have dealt with fully or almost fully polymerized crystals.

In this work, the exciton spectroscopy of highly ordered poly-THD chains dispersed in their monomer crystal is investigated at low temperature. As previous reports indicated a strong thermal reactivity of crystalline THD, particular attention has to be paid to avoid thermal reaction. In our work, the polymer content in weight, x_p , was kept around a few percent except for reflectance and electroreflectance experiments where x_p was $\sim 65\%$, as inferred by the absolute value of the reflectance and the sum rule of the oscillator strength (see Fig. 1).

2. Experimental

1,6-Bis(diphenylamino)-2,4-hexadiyne (THD) was prepared in two steps starting from commercial diphenylamine. In the first step, lithium diphenylamide was allowed to react with stoichiometric amounts of propargyl bromide, in THF, at -78°C . *N,N*-Diphenylpropargylamine was obtained as a white crystalline solid after purification by vacuum distillation and column chromatography (yield = 50%). THD was obtained in 65% yield by oxidative dimerization of *N,N*-diphenylpropargylamine [11–13].

^1H NMR, ^{13}C NMR and IR data fully agree with the expected molecular structure and previous literature reports [14]. Monomer crystals were grown from a 4:1 methylene chloride–diethyl ether mixture ($c \sim 15$ g/l), at 0°C , in the dark. The crystals are needle-shaped with a width of a fraction of millimetre, the chains being oriented along the main dimension.

Polarized reflectance spectra in the energy range between 1.5 and 5.8 eV were obtained from flat areas of about $0.5\text{ mm} \times 1\text{ mm}$ in size using a windowless vacuum spectrometer and calcite polarizers. For electroreflectance measurements, Cr/Mg contacts spaced by a 0.5 mm distance were evaporated to apply along the polymer backbone an external sinusoidal voltage at 1 kHz frequency. The field modulated light was collected by lock-in at twice the field frequency and evaluated as described in previous studies [15]. Absorption spectra were derived by Kramers–Kronig transformation for comparison with absorption for light polarized perpendicular to the chain. The latter spectra were measured in the double beam mode of a Cary 5000 double monochromator using freshly prepared samples with low polymer content and selecting 0.1 mm wide homogeneous areas. The spectral resolution was 4 \AA for reflectance and transmission measurements and 5 \AA for electroreflectance spectra.

Raman spectra were measured using a Jobin Yvon U1000 double monochromator and the excitation was the 647.1 nm line of a mixed Ar^+/Kr^+ laser. For both Raman and absorption measurements the samples were mounted on the cold finger of a He gas exchange cryostat that allows studies down to 10 K.

The emission was studied in a confocal-like configuration. Detailed description of the set-up can be found elsewhere [16].

3. Results

3.1. Reflectance and electroreflectance

The reflectivity of the samples in the visible region is very anisotropic. For light polarized perpendicular to the polymer chain, the reflectivity shows no structure and remains below 5% up to 3.8 eV where the absorption by the phenyl side-groups sets in. For parallel polarization of light, the room temperature spectrum in Fig. 1 shows a broad exciton peak of about 30% reflectance followed by a vibrational band as reported earlier [9]. Low temperature reflectance spectra show some narrowing of the main peak, and a manifold of vibronic exciton peaks appears as is typically observed in high-quality polydiacetylene single crystals [15,17].

Much more structure is resolved in low temperature electroreflectance (ER) spectra (Fig. 1). Two spectra scaled quadratically to the fields of 15 and 30 kV/cm (full and dashed lines, respectively) are almost identical. This proves that all features below ~ 2.6 eV increase quadratically with field strength and are reproduced in their spectral position

and shape by the first derivative of the reflectivity, displayed on top by the dotted line. The electroreflectance spectrum thus reveals a rigid redshift of the exciton and its vibronic satellites by a quadratic Stark effect. The shift in a field of 15 kV/cm is about 8 μeV , similar to that observed in other polydiacetylene crystals [15,18]. The derivative spectrum does not reproduce the large signal above 2.7 eV which increases sublinearly at high fields. This feature arises from the Franz–Keldysh (FK) effect of the exciton continuum [15,19]. The large signal at small fields indicates the excellent quality of the investigated area since it can be observed only if the scattering rate is small enough to allow a free electron hole pair to gain significant energy in an external field [15,20].

Kramers–Kronig transformation yields, with an accuracy better than 5 meV, the exciton transition energy, 2.171 eV and the free carrier gap, 2.727 eV, indicating an exciton binding energy $E_b \sim 556$ meV (see Table 1). This is about 10% larger than that obtained in bulk blue PDA crystals with exciton below 2 eV, but similar to that of red bulk crystals like TCDU [21]. The derivative lineshape of the ER spectrum is compatible with coupling of the exciton by the electric field F to its continuum of ionized states with the mean square displacement r of electron and hole representing the transition dipole [15]

$$\Delta E = \frac{|\mathbf{e}\vec{r} \cdot \vec{F}|^2}{E_{\text{exc}} - E_g} \quad (1)$$

Inserting the experimental values yields an exciton radius of 14 Å, slightly larger than that derived for the blue chains of DCHD [15]. The exciton ground state thus extends over 5 diacetylene repeat units and must be delocalized on the chain. ‘Blue’ and ‘red’ excitons are intrinsically similar states, with internal structure quasi-independent of the electronic structure of the chain. Note that presently, due to interfering contributions of band edges corresponding to vibronic exciton replica to the FK signal, a reliable determination of the coherence length of continuum states

Table 1
Transition energies of the exciton and its satellites, taken from spectra of $\text{Im}(\varepsilon)$ derived from the electroreflectance at low temperature

Assignment	E (eV)	ΔE (meV)	Raman (298 K)	Raman (15 K)
Exciton E	2.171	–	–	–
a	2.175	5 (0)	4.7	5.0
b	–	–	6.7	6.0
c	–	–	19.2	19.1
d	2.226	54 (7)	54.8	55.2
S	2.260	89 (2)	86.9	87.5, 87.0, 86.2
	2.276	105 (5)	106.1	106.3
D^*	2.327	156 (4)	153.2, 149.9	153.3, 149.8
D	2.356	185 (2)	184.1	183.8
T	2.439	267 (7)	261.7	261.5
Bandgap	2.727	556		

ΔE refers to the energy difference to the exciton and yields the vibrational energies in good agreement with Raman modes measured at room temperature [9] and low temperature (this work).

could not be deduced. Its amplitude is nevertheless of the same order than in bulk DCHD crystals [15], indicating highly ordered THD chains along which coherent motion occurs.

3.2. Absorption and luminescence

Thermal reactivity of the THD crystal is so high that the polymer content at the end of the sample growth precludes absorption in parallel polarization to be measured. We thus compare in Fig. 2 the experimental absorption for a polarization of the field perpendicular to the chain axis, α_{\perp} , to the calculated absorption obtained by Kramers–Kronig transformation of the reflectance shown in Fig. 1. α_{\perp} reaches only 100 cm^{-1} for a value of x_p estimated to be 2–3%, which confirms the strong anisotropy by more than 2 orders of magnitude of π – π^* absorptions. The larger linewidth of the exciton peak at high energy in parallel polarization is due to the rapid decrease of the refractive index n above the exciton resonance and is absent in spectra of the dielectric constant, $\text{Im}(\varepsilon) = n\alpha/\omega$. The arrow indicates the energy gap which, due to strong Coulomb coupling of electron and hole, does not have sufficient strength to be resolved in absorption under the excitonic progression.

The luminescence spectrum is well resolved and is nearly a mirror image of the absorption. The inhomogeneous broadening of the zero phonon line is ~ 40 meV at 10 K, comparable to the absorption linewidth. It is affected by re-absorption and cannot be considered as an origin for the emission. This origin is recovered by adding the energy of ground states normal modes measured by Raman spectroscopy to the corresponding vibronic lines in the emission. Using the C=C and C=C stretching modes values

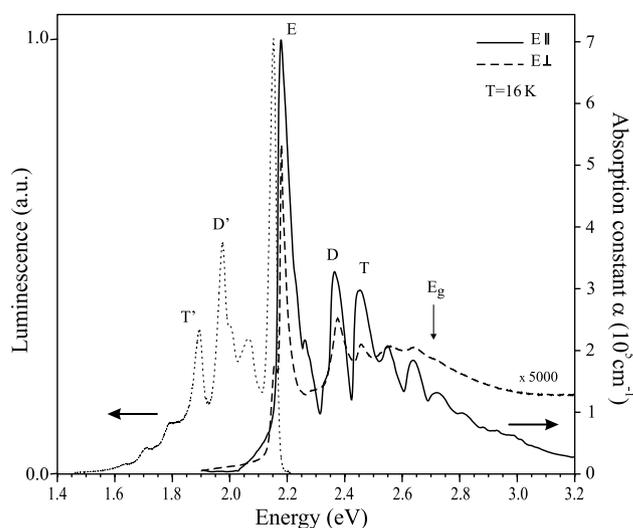


Fig. 2. Absorption spectra with polarization parallel (Kramers–Kronig transform) and perpendicular (experimental) to the polymer chain, derived from the reflectance and transmission spectra, respectively. The luminescence at 10 K (dots) is for a 488.0 nm continuous wave excitation and a sub-microwatt pump fluence.

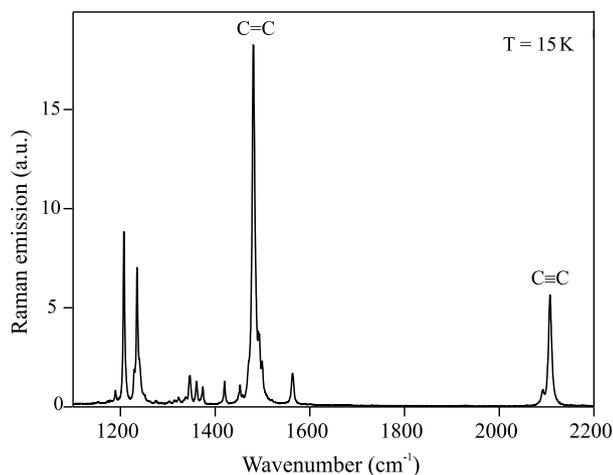


Fig. 3. Typical low temperature Raman spectrum of a THD crystal having low polymer content ($x_p \leq 3\%$). The excitation power is 10 mW at 647.1 nm. The frequency of the double bond and triple bond stretching modes are, respectively, $1481 \pm 2 \text{ cm}^{-1}$ and $2107 \pm 2 \text{ cm}^{-1}$. For a detailed discussion of the attribution of the other lines, see [9].

(Fig. 3) places the origin at 2.153 eV, that is $\sim 18 \text{ meV}$ below the exciton energy deduced from electroreflectance. This Stokes shift cannot be associated to diffusion of excitons to low energy sites since ER data imply a highly regular chain similar to poly-3BCMU red chains. The presence of such sites would indeed suggest a disordered state of the chains, which is inconsistent with the observation of the FK effect in the field modulated signals. It thus corresponds to a real shift between the emission and absorption origins. No such Stokes shift is observed in the red phase of highly diluted poly-3BCMU chains [22] and its origin in poly-THD is under study.

The emission of crystals with low polymer content is surprisingly strong. Given that the geometry of the collecting optics does not differ from one experiment to the other, it is possible to compare the emission intensities of poly-THD and poly-3BCMU isolated chains, the yield of which is known [23]. A rough estimate of the quantum yield, η_F , leads to $\eta_F(\text{THD}) > 0.6$ at 10 K. An extremely fast drop in the luminescence intensity with increasing temperature is also observed; this phenomenon follows an Arrhenius-type law with a thermal activation energy $E_{\text{act}} \sim 4.3 \text{ meV}$ (Fig. 4). This corresponds to the opening of a non radiative channel. The origin of this process is not known yet but it seems to be a generic property of the red structure. Isolated poly-3BCMU chains indeed show a similar behaviour above 50 K, with a much higher activation energy, $E_{\text{act}} \sim 38 \text{ meV}$ [24].

4. Discussion and conclusions

The present results can be compared to those obtained on red and blue poly-3BCMU chains. At the lowest temperature, poly-THD is more fluorescent than these red chains, and much more than any other PDA red phase.

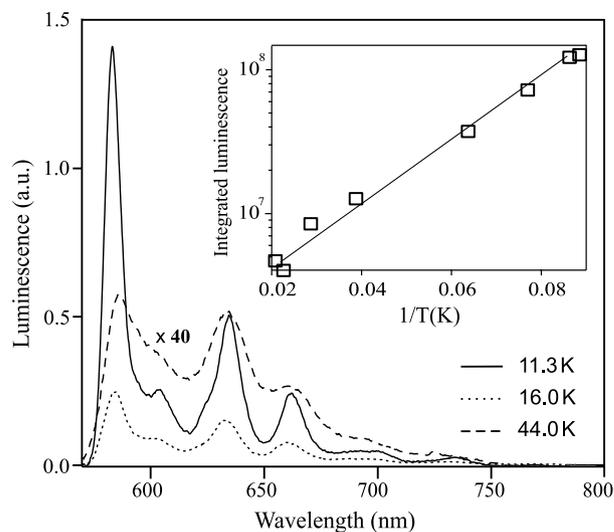


Fig. 4. Luminescence spectra at 11.3 K (solid line), 16.0 K (dots) and 44.0 K (dashes) excited at 488.0 nm for a polarization parallel to the chains. Inset: Arrhenius plot of the luminescence integrated over the 566–800 nm range (squares) and the associated linear fit.

However, the poly-THD exciton energy is lower by $\sim 150 \text{ meV}$ than that of red poly-3BCMU, and its Raman frequencies are also intermediate between those of red and blue poly-3BCMU.

The blue chain is planar and the red one cannot be so [25]. A model in which successive repeat units are alternatively tilted out of the average plane by $+\theta$ and $-\theta$ angles is reasonable, and furthermore agrees well with NMR results [6,7]. The unit cell of the red chain thus contains two non-translationally equivalent monomer units. In poly-3BCMU, side-groups are linked by hydrogen bonds which certainly influence the value of θ . In poly-THD there are not such bonds and successive repeat units differ in the packing ($\text{C-H} \cdots \pi$ interactions) of phenyl groups. This may lead to a different θ value.

Simple considerations show that increasing θ decreases conjugation, hence increases the energy of the excited states. The value of θ in poly-THD would then be smaller than in poly-3BCMU. Different excited states shift differently, and the occurrence of fluorescence may correspond to a much faster shift of the ‘dark’ A_g states which are present in the optical gap of blue chains [3], so that in red ones they lay above the optical gap.

The activated decay of fluorescence yields may thus be associated with an activated transfer of the excitonic population to this A_g state. However, the quenching mechanism can also imply a virtual state positioned slightly above the gap and corresponding to the dissociation threshold of a singlet exciton in two triplets, as observed in blue chains [26]. In the latter case, delayed luminescence should result associated to the long lifetime of the triplets. Time resolved luminescence experiments will give an insight into the nature of the process.

Poly-THD chains thus form quantum wires, the excitonic properties of which, on the whole, compare well with

those of isolated poly-3BCMU red chains. The observation of an intense Franz-Keldysh effect in the electroreflectance spectra is the signature of a mixed monomer–polymer crystalline phase of ‘red’ nature possessing a high degree of order. The latter appears as a promising model system of 1D crystals, in particular for the investigation, through time-resolved non-linear optical spectroscopy, of how the electronic structure is affected by the conformations in the frame of strongly interacting electrons.

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