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Photoinduced absorption spectra in polydiacetylenes for non linear optical applications

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Abstract

We report on the absorption, photoluminescence and photoinduced absorption of polydiacetylenes (PDAs) having in the side groups the photoconductive carbazolyl rings substituted by acyl $CO(CH_2)_nCH_3$ chains ($n = 10$, polyDLCHD; $n = 14$, polyDPCHD).

A novel feature in the absorption spectra is detected and assigned on the basis of theoretical calculation including the electron correlation. Different features are observed in the photoexcitations spectra of thin and thick samples and a preliminary interpretation is proposed.

Keywords: Polydiacetylene; Photoexcitation; Non linear optics; Photonics

1. Introduction

In recent years, we prepared several polydiacetylenes (PDAs) with interesting non linear optical properties which could be useful for photonic applications [1]. To exploit these materials in devices, a careful characterization of their electronic excited states is necessary. Furthermore, from these studies it is often possible to deduce interesting information on the photophysical properties of the materials, which may have a general validity for the whole class of conjugated polymers. For instance, the study of the photoinduced absorption of polycarbazolyldiacetylenes substituted with alkyl chains of different length allowed to evidenced the role played by interchain interactions in charged states generation [2]. Moreover, with highly ordered samples the role of singlet fission process in the ultrafast photogeneration of triplet excitons [3] as well as the solvent and state of aggregation dependent ordering of the forbidden and allowed states have been observed [4].

In this paper, we report on the absorption, emission and photoinduced absorption properties of a recently synthesized PDA [5] having in the side groups the photoconductive carbazolyl rings substituted by acyl $CO(CH_2)_nCH_3$ chains ($n = 10$, polyDLCHD; $n = 14$, polyDPCHD). The results are discussed on the basis of theoretical calculations including the electron correlation for long oligomers both isolated and in clusters.

2. Experimental

DPCHD and DLCHD monomers are synthesized according to [5]. Thin monomer films are spin cast from monomer solution on glass or fused silica substrates and then thermally polymerized at 115 °C for several hours. Thick films are obtained by multiple drop casting of the same monomer solution and then polymerized.

The absorption spectra are recorded with a doubly grating Varian mod. Cary 5E spectrophotometer. The long-lived photoinduced absorption spectra are recorded with a Bruker IFS 66/S Step-Scan FTIR spectrometer equipped with Silicon and InSb detectors and with an home-made cryostat. The photoexcitation is provided by the 532 nm line of a Suwtech DPGL-2200 Nd:YAG duplicated laser and its modulation is obtained by an AA Opto-Electronics acusto-optical modulator model AA.MTS.110/A3-Vis. Continuous scans with light on and off are alternatively recorded and co-added for several cycles to provide a suitable signal-to-noise ratio (usually about 10,000 total dark and light scans). The transmittance spectra with light on and off are then used to numerically obtain the $-\Delta T/T$ photoinduced absorption spectra. Time resolved photoinduced absorption spectra are recorded with the step-scan option of the spectrometer employing the

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internal 16 bit ADC for acquisition. Photoluminescence spectra are measured at room temperature by pumping the sample with the 514 nm line of a Coherent Innova 300 Ar^+ ion laser. The emitted light is dispersed with a doubly grating Jobin and Yvon model HG-25 spectrometer and then is recorded by a photomultiplier.

3. Results and discussion

The absorption and emission spectra of polyDPCHD and polyDLCHD at room temperature are reported in Fig. 1. Thick samples of polyDPCHD show an excitonic absorption at 2.29 eV followed by vibronic replicas at 2.47 and 2.55 eV. Below the main excitonic absorption a shoulder at 2.24 eV, typical of thick samples, is detected. In addition, at higher energies, weak features are observed at 2.74 and 2.82 eV. The spectra are affected by light scattering due to the sample thickness and dishomogeneity. The thinner films of both polyDPCHD and polyDLCHD show absorption spectra with negligible contribution from light scattering and with an intensity ratio between the purely excitonic transition and the first vibronic replica much higher than for thick samples. Their excitonic absorption at 2.30 eV is followed by vibronic progression at 2.49 and 2.57 eV. The additional high energy feature is now at 2.75 eV and does not seem to be split as in the case of thick polyDPCHD films. A similar feature was previously observed also in benzene solutions of a long alkyl chains substituted polycarbazolyldiacetylene (polyDCHD-HS) whose spectrum, astonishingly sharp at room temperature, is very similar to those here reported for the thinner films [4].

Different features between thin and thick samples are also observed in the photoluminescence spectra. The electron–phonon coupling for thick polyDPCHD films seems to be stronger with respect to those observed for thinner films, though the high energy band of the thick sample is partially affected by re-absorption due to the small Stokes shift and to the high absorbance of the film (Fig. 1b). The peak positions detected are 2.26, 2.09 and 2.02 eV for thick polyDPCHD; 2.27, 2.10 and ∼2.01 eV for thin polyDPCHD; 2.29, 2.11 and 2.06 eV for polyDLCHD. The fluorescence emission spectra are characterized by quite small Stokes shift with an almost vanishing value (10 meV) for the thin film of polyDLCHD thus showing that relaxation of chain conformations is quite limited. We would like to notice that even though the difference in the spectra can be due to different electron–phonon coupling, we cannot at present exclude a role of interchain interactions play a role in the emission properties like that recently observed in [6].

The steady state photoinduced absorption spectra of our samples are reported in Fig. 2. Thick polyDPCHD films show an intense and sharp photoinduced transition at about 1.4 eV, i.e. in the spectral region where triplet excitons are usually detected in PDAs [2]. In addition, a well-defined band at ∼1.2 eV is also observed. In the thin samples of polyDPCHD and polyDLCHD very similar characteristics occur, but the intensity of the satellite band is reduced to a weak shoulder. The pumping power dependence of both these photoinduced bands follows the I^{α} law with $\alpha = 0.3$–0.4 indicating the saturation of the signal.

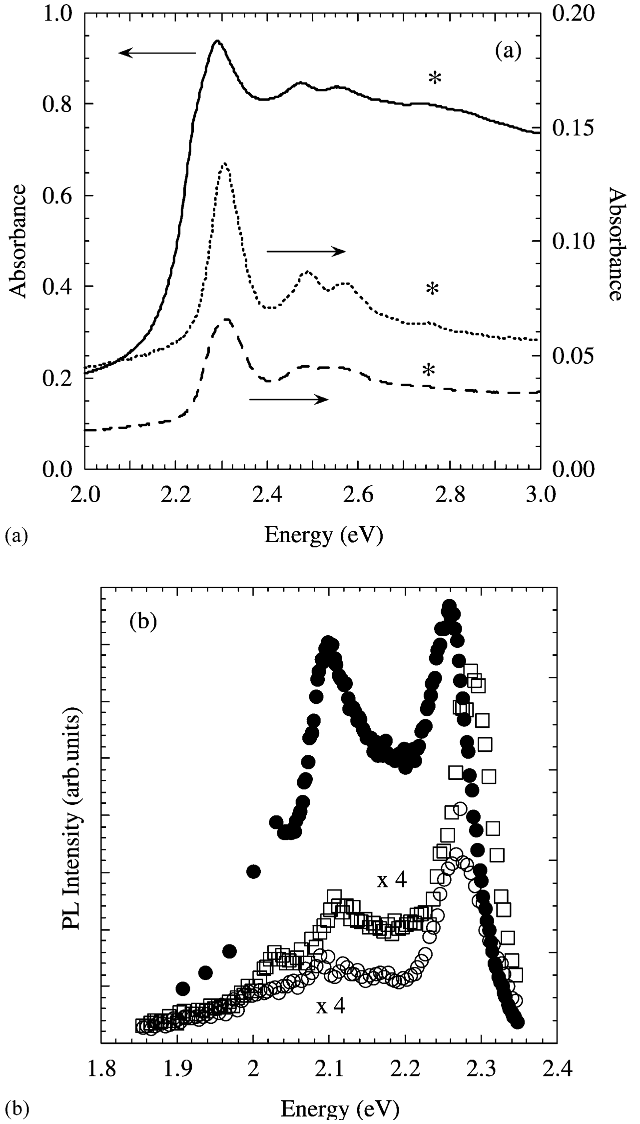

Fig. 1. Room temperature absorption (a) and photoluminescence spectra (b) of polyDPCHD (thick, full line/filled circles; thin, dashed line/open circles) and polyDLCHD (dotted line/open squares). Asterisks indicate the high energy weak feature.

We would like to discuss all these data and try to find out the physical mechanism responsible for the different features observed in thick and thin samples. In a recent theoretical study on the electronic properties of long (15 repeat units) oligodiacetylenes isolated molecules and clusters it was shown that, above the excitonic transition and in addition to the vibronic replicas, other allowed modes are present and can be described with sufficient accuracy in analogy with the vibration of a string [7]. The main excitonic transition is due to an excitation delocalized along the whole

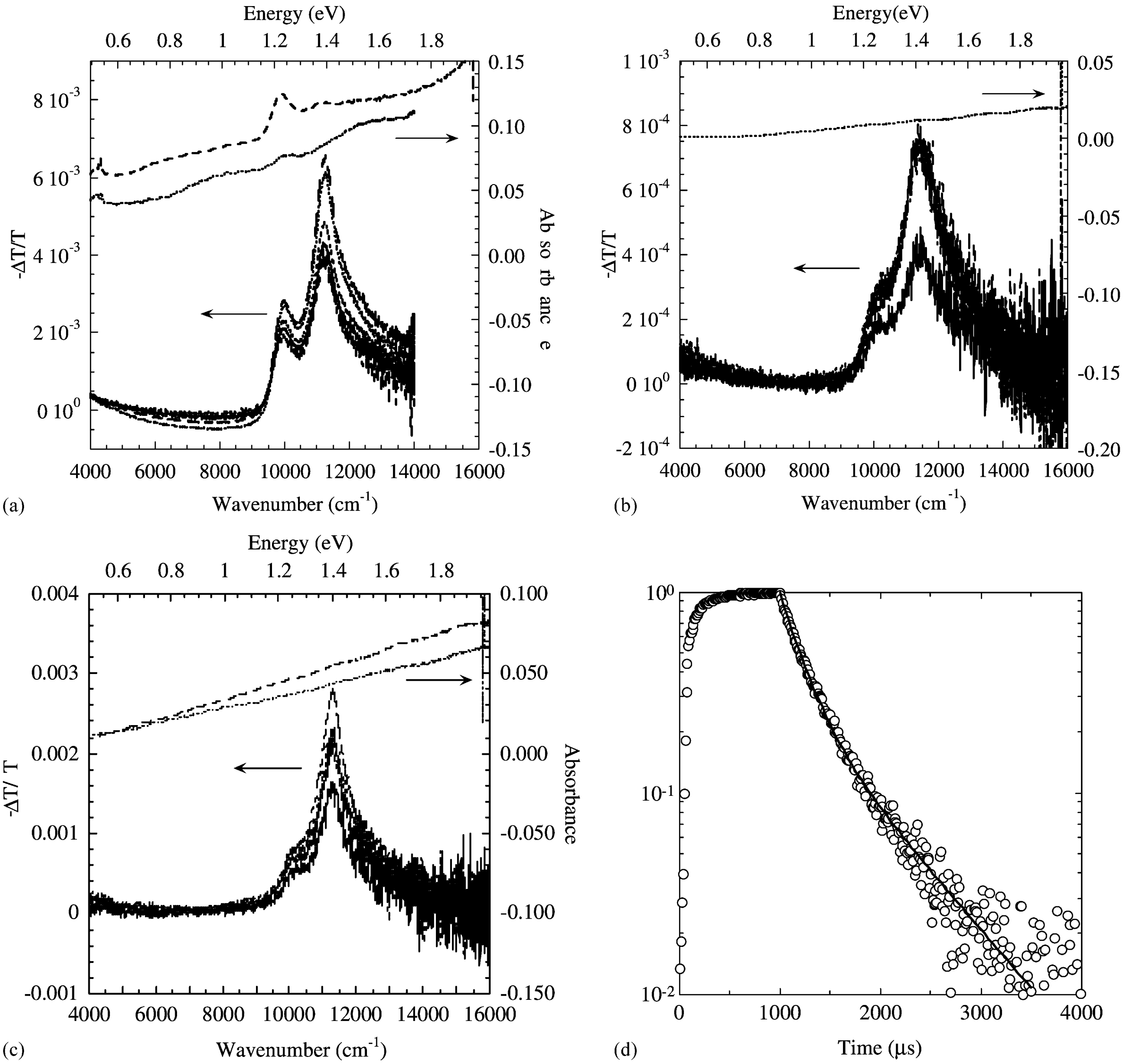

Fig. 2. Intensity dependence of the photoinduced absorption spectra and absorbance of thick polyDPCHD (a), thin polyDPCHD (b), and polyDLCHD (c); $T = 80$ K. The laser power ranges from 5 to 60 MW. The absorbance spectra are recorded at room temperature (full line) and 80 K (dashed line). (d) Decay of the photoinduced peak fitted with a doubly exponential function.

conjugated segment while the others allowed (forbidden) transitions are due to excitations, having an odd (even) number of nodes, delocalized into shorter conjugated segments responsible for the absorption at higher energies. The oscillator strengths of these modes are roughly proportional to the inverse square number of nodes. According to the calculations, the spectral position and the relative intensity of the high-energy transitions observed in all our samples, as well as in polyDCHD-HS benzene solutions [4], strongly suggest that their origin could be related to the second mode of the string vibration. Usually, these transitions cannot be detected in PDAs probably due to their low oscillator strength that, in the presence of intense vibronic progression, are buried in the absorption spectra.

The theoretical results, which also consider the interchain interactions, stimulate further comparisons with the experimental data, in particular for the broadening of the excitonic transition and the presence of a satellite band in the triplet-to-triplet transition. These features are in fact predicted in case of strongly interacting chains where the excitonic transition is split and shifted and several symmetry forbidden transitions bear in the HOMO–LUMO gap of the isolated molecule. These dark states, whose fission was shown to be related to the triplet exciton generation [3], could be involved in the origin of the triplet satellite band. Although fascinating, this interpretation must be compared with the real interchain distance. When PDAs carry bulky substituents, their interbackbone separation distance in microcrystal powders samples is very large and it excludes interactions between the backbones [2]. However, in the films where the microcrystal ordering is destroyed by the solubilization process, we cannot exclude the presence of side groups interactions which can affect the backbone conformation and therefore the electronic properties.

The role of polar side groups is not fully elucidated in this context. The only well established case, i.e. that of polydiacetylene toluene-sulphonate single crystal, indicates that modification of side group alignment in different chains gives rise to phase transitions involving interchain interactions [8] as well as to the presence of multiple two-photon resonances below the excitonic absorption [9]. We would like to notice that the Raman spectra of thick and thin polyDPCHD films (not reported here) show a modification in the frequency of the stretching modes relative to the bonds carrying the side groups, thus suggesting a possible role of the substituents. Since this topic is not fully understood, further theoretical and experimental work is still in progress.

Let us now turn back to the photoinduced absorption spectra where for the thick films a transition with not negligible intensity, spectrally overlapped to the satellite band, is observed in the low temperature absorption spectra (Fig. 2a). This band is not detected at room temperature as well as in the thinner samples even at 80 K (Fig. 2b and c). Preliminary data (not reported here) seem to indicate that in the near infrared a broad absorption band gains intensity upon laser irradiation accompanied by a bleaching of the UV-Vis spectrum. Although good stability upon UV irradiation was shown for the excitonic transition of polyDPCHD [10] no data are available for possible modification and/or damaging affecting the near infrared spectral region. At present, the origin and nature of the satellite band is not well understood. Instead, the band at 1.4 eV can be assigned on the basis of our previous works [2], to a triplet-to-triplet transition. The triplet band of acyl-substituted polycarbazolyldiacetylenes is very sharp if compared to that of other polydiacetylenes in the red form [2] indicating a very small distribution of conjugation lengths even for PDA films cast from monomer solution. The possibility to observe triplet excitons in polyDPCHD and polyDLCHD with the steady state photoinduced absorption technique used here, which can only detect long-living species in a time domain where trapping effects play an important role, suggests that they might have a complicate dynamics. In fact, Fig. 2d shows that the decay of the 1.4 eV-photoinduced band can be fitted with a double exponential whose time constants are 237 and 851 μs. The first lifetime value is very similar to those previously observed in other PDAs [2] while the second, very long and never detected before, could be related to the trapping phenomena. Trapping can be responsible for the sublinear dependence ($I^{0.3–0.4}$) of the photoinduced signal that unambiguously indicates the presence of saturation effects as previously observed for charged states in blue PDAs [11].

In conclusion, we have shown that different photophysical features are observed in thin and thick polyDPCHD and polyDLCHD films. A preliminary interpretation of these data is proposed. Further theoretical and experimental investigations are in progress to clarify this matter in detail.

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