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Triplet-Exciton Generation Mechanism in a New Soluble (Red-Phase) Polydiacetylene

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The time scale of covalent state relaxation and singlet fission into triplet pairs is determined in a solution of isolated polydiacetylene chains showing a remarkably sharp excitonic transition by applying the transient transmission difference spectroscopy technique with sub-10 fs optical pulses. Photoexcitation into the band of ionic states is followed by a branching within the first 100 fs which populates the band of covalent states. The latter start to dissociate into triplet excitations, completing the process in about 300 fs.

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Triplet excited states play a major role in photophysical and photochemical molecular reactions [1]. The importance of these species is also recognized in the field of polymer optoelectronics, where they can represent an efficient nonradiative loss mechanism following charge coalescence or can be exploited in phosphorescence-based devices [2–4]. Triplet states are generated during energy relaxation following the population of an optically allowed state, because direct photoexcitation is forbidden by spin conservation. Energy relaxation in conjugated polymers involves two types of states, ionic or "charge-transfer" excitations and covalent or "spin-wave" excitations [5]; the energy ordering and interconversion dynamics of these states ultimately control the material properties [6]. Quantum mechanical models essentially describe the lowest lying covalent state in long conjugated chains as a pair of triplet excitations, which can eventually separate into single components [5,7]. This intriguing picture, which is common to the class of π-conjugated chains, could account for the fast photoproduction of triplet states during thermalization in many different systems of relevance for molecular optoelectronics, chemistry, and biology. Its relevance to natural photosynthesis, for instance, was recently pointed out [8]. The process can be investigated in greater detail in polydiacetylenes (PDAs), which appear as ideal candidates. In fact selected PDAs, known for their interesting potential in photonic applications [9,10], possess high intrachain order and remarkable optical properties, which offer a unique opportunity for investigating one-dimensional, strongly correlated π-electron systems. Ultrafast singlet fission in PDA is supported by magneto-optical experiments [11,12] as well as by recent pump and probe photoinduced absorption (PA) [13,14]. A still unknown key issue in the field, however, is the identification of the time scale and dynamics of the process.

In this Letter, we address this problem by reporting transient transmission difference measurements using sub-10 fs optical pulses on a novel soluble red-phase PDA, namely, poly[1,6-bis(3,6-dihexadecyl-N-carbazolyl)-2,4-hexadiyne] (polyDCHD-HS) [15]; see structure in Fig. 1(b). PolyDCHD-HS is soluble in common organic solvents and in benzene it displays an astonishing sharp and intense room temperature excitonic resonance [16], indicative of a highly ordered material. Moreover, polyDCHD-HS in benzene shows at room temperature a quite high (for PDAs) photoluminescence quantum efficiency (1%) with a well-resolved spectrum and a small Stokes shift (about 200 cm^{-1}). The extreme time resolution of our experiments, joined with the properties of polyDCHD-HS allows us to investigate fundamental processes till now reported with comparable time resolution only in blue-phase PDA films with reduced order with respect to our solutions [17]. The laser system [18] provides nearly transform-limited pulses of 7 fs duration and 500–700 nm bandwidth, as shown in Fig. 1(a). The pump beam is focused at energy density of about 0.2 $\mathrm{mJ/cm^2}$ (spot diameter 120 μm) on solutions of polyDCHD-HS in benzene ($c \approx 10^{-3}$ M), kept in a 0.2 mm cuvette at room temperature. Transient transmission changes ($\Delta T/T$) are measured both at the specific wavelengths and over the entire bandwidth of the probe pulse ($\Delta T/T$ spectra), following a standard procedure [14].

Figure 1(a) shows absorption and emission spectra of polyDCHD-HS in diluted benzene solution at room temperature. The purely electronic absorption peak at 534 nm is remarkably sharp (FWHM = 532 cm^{-1}). Vibronic replicas at 494 and 479.5 nm are assigned to C=C and C≡C bond stretchings. The large ratio of the intensity of the 0-0 transition relative to the vibronic bands indicates a rather small electron-phonon coupling, with a Huang-Rhys factor of about 0.28. The mode spacing corresponds well with the features observed in off-resonance Raman spectra [16]. Both results suggest a small geometrical relaxation in the excited state. The fluorescence spectrum, also well structured, only slightly deviates from the absorption mirror image and shows extremely small Stokes shift of about 2.5×10^{-2} eV. The emission quantum yield is estimated

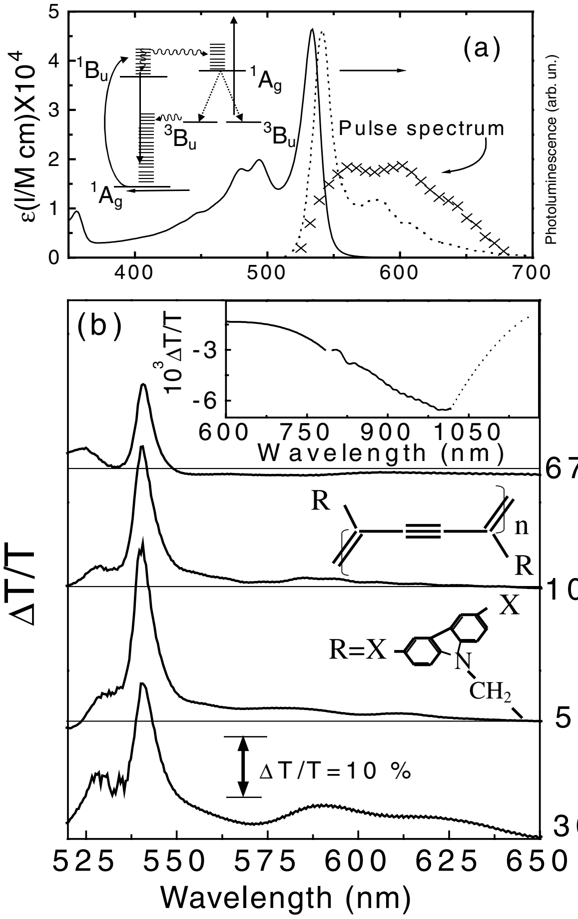

FIG. 1. (a) Ground-state absorption (solid line), photoluminescence (dotted line) and excitation pulse spectra (crosses) of polyDCHD-HS in C_6H_6 solution. Inset: Jablonski level diagram; see text for discussion. (b) $\Delta T/T$ spectra at several pump-probe delays (fs) for polyDCHD-HS after sub-10 fs optical excitation. Inset: PA in the longer wavelength region as measured with 200 fs pulses. The chemical structure of polyDCHD-HS is also shown. $X = (CH_2)_{15}CH_3$.

to be 10^{-2}[16]. The broad pulse spectrum is partially in resonance with the 0-0 absorption peak and allows probing the spectral region below the optical gap till about 650 nm.

Figure 1(b) presents transient $\Delta T/T$ spectra of poly-DCHD-HS/C_6H_6 solutions following photoexcitation with sub-10 fs pulses [19]. At 30 fs pump-probe delay, the spectrum clearly shows photobleaching (PB) of the optical transition peaked at 540 nm. The positive signals above 560 nm are assigned to stimulated emission (SE) on the basis of their correspondence with the vibronic fluorescence spectrum. At larger pump-probe delays, SE decays and ultimately disappears, being replaced by very weak photoinduced absorption with a rather flat band shape. This PA band was measured in the near-infrared (near-IR) region by using longer pulses (about 200 fs) and different excitation (at 390 nm), as shown in the inset of Fig. 1(b) for 500 fs pump-probe delay. The tail of this band appears, in our opinion, as the weak absorption observed in the visible for a time delay of 670 fs.

$\Delta T/T$ kinetics within the first 0.5 ps after photoexcitation are reported in Fig. 2 for a number of selected probe spectral regions. Treating the data with a low-pass filter suppresses oscillations in ΔT caused by the impulsive excitation of the nuclear motion [20]. The bleach of the ground-state transition, probed at 530–540 nm, shows a fast decay in the first 100 fs, with an approximate single exponential time constant $\tau_1 = 30$ fs, followed by a plateau. At all other wavelengths above the absorption edge the initial positive signal due to SE turns negative, indicating the buildup of absorption features. By using a single exponential fitting, an average time constant $\tau_2 = 70 \pm 10$ fs is obtained common to all wavelengths. Long time dynamics are reported in Fig. 3. Note that ΔT at 950 nm is measured in a different configuration, namely, with longer pulses (about 200 fs) and excitation at 390 nm, so it cannot be strictly compared with other data in the same figure although it is very similar to the decay at 650 nm. The induced absorption signal (650 nm) decays very slowly with nonexponential kinetics, clearly extending well beyond the present experimental time scale. The recovery of PB, also nonexponential, contains an initial decay, with a time constant of 10 ps.

At first glance, the experimental results suggest an interpretation based on the covalent model [21]: Energy

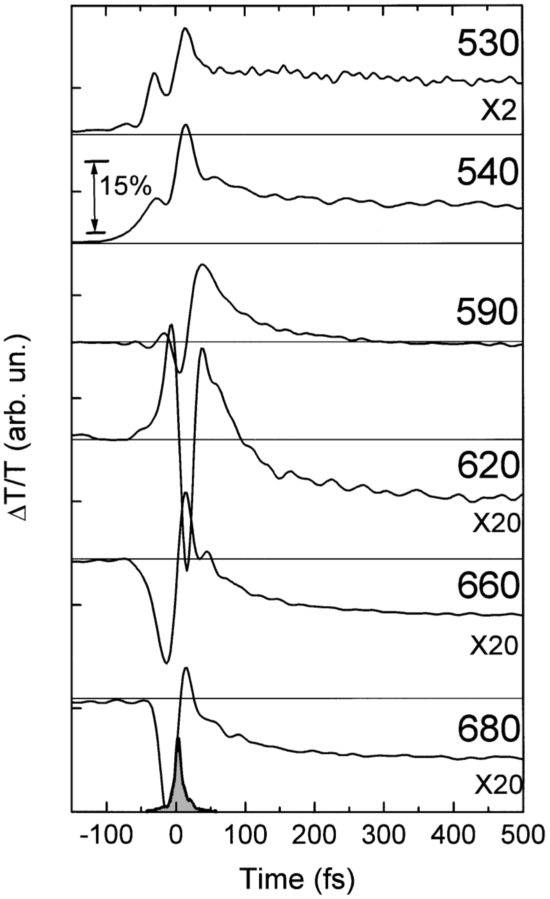

FIG. 2. $\Delta T(t)$ time traces measured after spectral filtering the transmitted probe at several wavelengths (nm). The pulse autocorrelation is also shown.

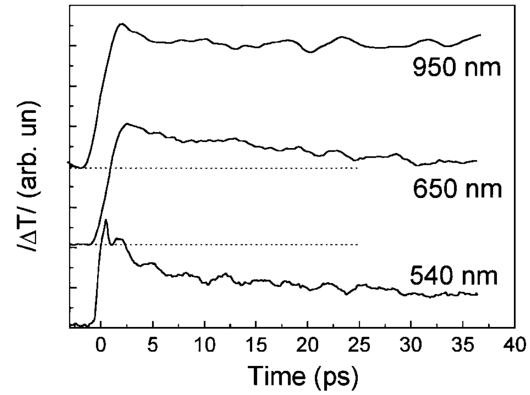

FIG. 3. Long time behavior of $\Delta T(t)$ in the PB region (540 nm) and PA (650 nm) after sub-10 fs optical excitation. Results at 950 nm using longer pulses are also plotted.

initially stored in an optically allowed S_2 state (ionic) is quickly transferred to a lower lying S_1 dark state (covalent), which gives rise to induced absorption. Emission originates from the $S_2 \rightarrow S_1$ transition. The fluorescence yield is then limited by the radiationless decay $S_2 \rightarrow S_1$, similar to the case of long chain polyenes [22]. By using the Strickler-Berg relation valid for resonant emission,

$$\frac{1}{\tau_{\mathrm{rad}}} = 2.88 \times 10^{-9} n^2 \langle \tilde{\nu}^{-3} \rangle^{-1} \int \frac{\varepsilon(\nu)}{\nu}\, d\nu\,, \quad (1)$$

we can work out the radiative time τ_{rad} of the $1^1B_u \rightarrow 1^1A_g$ ($S_2 \rightarrow S_0$) transition, $\tau_{\mathrm{rad}} = 4.5$ ns. If we assign $\tau_2 = 70$ fs to 1^1B_u lifetime, however, we obtain an estimated emission quantum yield [1] of $\Phi = \tau_2/\tau_{\mathrm{rad}} \approx 10^{-5}$, which is 3 orders of magnitude lower than the experimental value. Alternatively, it is possible that the lower lying covalent state (2^1A_g), optically activated by vibronic coupling, is the origin of photoluminescence. To get a rough estimate of the location of the latter with respect to the 1^1B_u, the energy separation $|\Delta E|$ can be estimated by using a simplified version [22] of the gap law [23]

$$\tfrac{1}{\tau} = A e^{-|\Delta E|/B}, \quad (2)$$

where τ is the lifetime of the S_2 state, A is a preexponential factor, and B is related to the relaxation energy of the transition [23]. Since the values of A and B for PDAs are not known, we used the corresponding values which have been proposed for polyenes and carotenoids ($A = 3.90 \times 10^{15}$ s^{-1}) and ($B = 1353$ cm^{-1}) [22]. The validity of this procedure is then limited to a qualitative level. Since the lifetime increases with increasing $|\Delta E|$, using in the formula the lowest decay, we observed ($\tau_1 = 30$ fs), a lower bound for $|\Delta E|$ is obtained which is 6455 cm^{-1} = 0.8 eV. This value indicates that the state reached by internal conversion should be located well below the optical gap and thus it cannot be the origin of the quasiresonant emission shown in Fig. 1. The covalent "polyenelike" picture is then unsuitable for describing the observed phenomena.

According to the ionic picture, emission originates from the 1^1B_u state, which remains optically allowed during the whole relaxation process [24]. The extremely small Stokes shift and the quasimirror image between absorption and fluorescence spectra indicate, however, that the conformational relaxation of 1^1B_u is quite small, which implies that the 2^1A_g state is higher in energy than the 1^1B_u state. The energy gap between the two states cannot be too large, otherwise the fluorescence efficiency would be much larger than 1% [16]. The relative position of the 1^1B_u and 2^1A_g states, recently corroborated by two-photon absorption spectra of the same solutions [25], implies that the 2^1A_g state cannot be responsible for the long-lived photoinduced absorption growing within 300 fs. In order to explain the experimental results we propose a picture, summarized in the Jablonski diagram in the inset of Fig. 1, in which both the singlet and triplet manifolds are considered.

Photoexcitation creates a wave packet in the singlet ionic manifold, which contains optically allowed states. Vibrational energy redistribution opens up a branching of the subsequent energy relaxation route. Thermalization populates the bottom of the 1^1B_u state in competition with internal conversion to the covalent 2^1A_g state, within 100 fs ($\tau_1 = 30$ fs). The hot 2^1A_g state, which is initially localized on a segment of the long conjugated chain, can separate into its components, giving rise to a pair of triplet excitations located below the 1^1B_u state and responsible for the induced absorption buildup within the 300 fs time domain. Advanced quantum chemical methods for correlated systems describe the 2^1A_g state as a superposition of the triplet pair with other less relevant configurations [7]. The optical spectrum of the triplet pairs is essentially that of isolated triplets [14], i.e., it shows a sharp feature in the near-IR with a flat tail extending to the visible [26], consistent with the photoinduced spectrum reported in the inset of Fig. 1. These triplets then decay and trap with dynamics in the hundreds of ps domain, which was previously studied by us in a polyethylene-blended PDA [14]. We can roughly evaluate the order of magnitude of the time scale for hot singlet fission into triplet pairs by adopting the localized wave packet picture possibly caused by coupling with lattice distortions. The propagation speed of phonon-dressed excitations is ultimately controlled by the speed of acoustic waves [27]. By assuming an average phonon wave number of 1500 cm^{-1}, the sound speed along the chain is $\nu_s = \frac{1}{2}\omega_0 a \approx 21$ nm/ps, where $a = 1.5$ Å is the average carbon-carbon distance in the backbone [28]. Figure 4 reports the bond length changes between the 1^3B_u and the 1^1A_g states in a seven-unit oligomer, as computed at the AM1 level [7], showing that the full extension of the triplet state is about 2.5 repeating units. We can then safely argue that a triplet pair can be considered separated if their distance is five repeating units. Under these conditions, the time for fission is 125 fs, which is shorter than the time scale for internal conversion. The covalent state dissociation would thus behave as

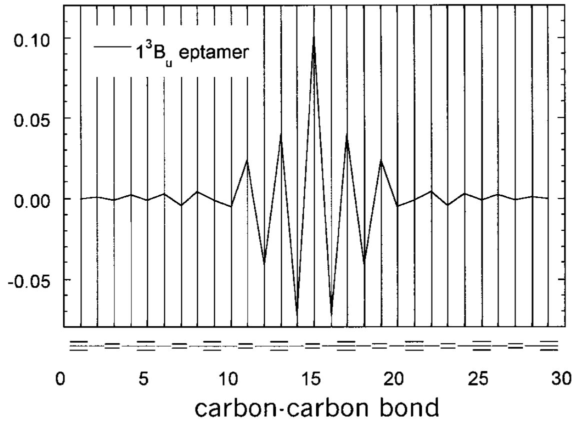

FIG. 4. Bond length differences (ΔL) between 1^3B_u and 1^1A_g states in a PDA eptamer as computed at the AM1 level.

an efficient funnel driving the excitation energy out of the singlet manifold to the lowest configuration in the triplet manifold, which has energy much deeper in the optical gap. Accordingly, we propose to assign the buildup of induced absorption to internal conversion and singlet fission into triplet pairs [29]. Emission is assigned to the thermalized singlet state, which is quite reasonably a superposition of the close-lying B_u and A_g states, with a small oscillator strength as indicated by the disappearing SE. The tiny Stokes shift and the minor deviation from the mirror image in the fluorescence spectrum could be due to minimum geometrical relaxation or solvent cage readjustment.

In conclusion we report on the early events following photoexcitation in polyDCHD-HS in a solution with sub-10 fs optical pulses. We demonstrate that, following photoexcitation into the band of ionic states, competition between thermalization and internal conversion generates a relaxed ionic excitation, responsible for stimulated emission, and a covalent, nonequilibrium excitation. Dissociation of the latter into two separate triplets is time resolved for the first time, revealing a time constant of 70 fs. Its efficiency may change, depending on the energy position of the covalent state undergoing fission. This process, ubiquitous in conjugated chains, is the dominant triplet generation mechanism when the spin-orbit coupling does not play a major role. The understanding of these fundamental photophysical processes provides useful suggestions for the chemical engineering of polymers with suitable radiative quantum efficiency.

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[28] This process, involving hot excitations, is then about 10 times faster than the intersite triplet hopping taking place during their recombination in the picosecond time domain [14].

[29] This would explain why in PDAs the triplet excitons are generated in a few hundred fs after photoexcitation, and not during singlet decay, as observed in polythiophene and assigned to intersystem crossing mediated by spin-orbit coupling [see, for instance, B. Kraabel, D. Moses, and A. J. Heeger, J. Chem. Phys. **103**, 5102 (1995)]. Singlet fission, which is a general feature of conjugated chains, could be singled out because of the peculiar properties of polyDCHD-HS, namely, the ordering and energy position of the states involved $\{2E(2^1A_g) = E(1^3B_u)\}$ and their suitable spectral signatures.