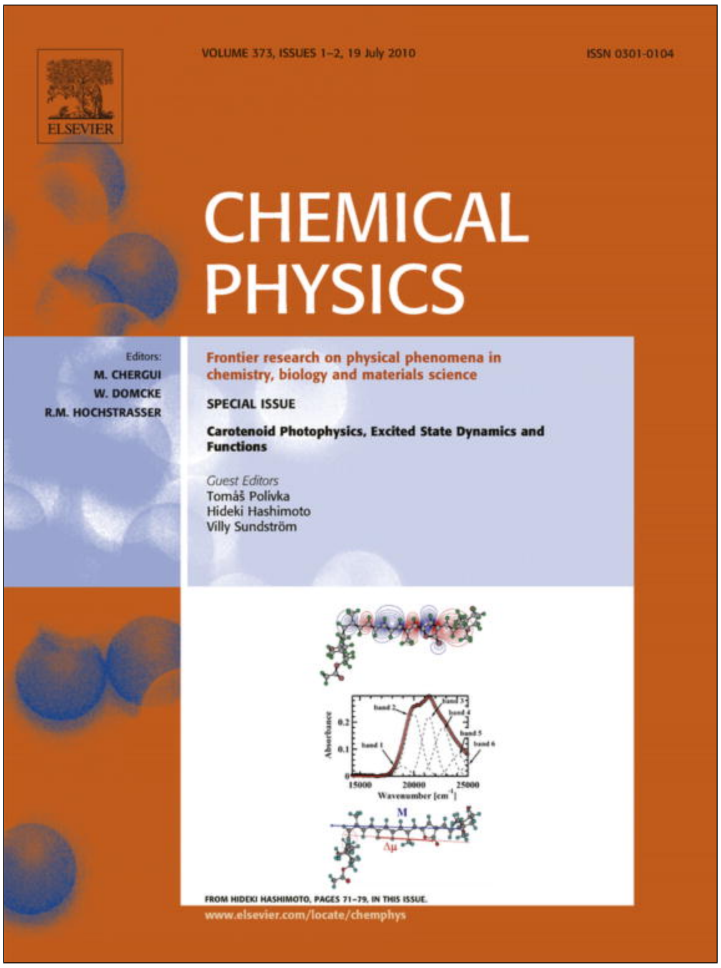

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Carotenoid Photophysics, Excited State Dynamics and
Functions

Guest Editors
Tomáš Polívka
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FROM HIDEKI HASHIMOTO, PAGES 71–79, IN THIS ISSUE.

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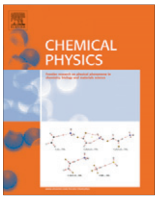

Ultrafast excited state relaxation in long-chain polyenes

Maria Rosa Antognazza [a,*], Larry Lüer [b,c], Dario Polli [b], Ronald L. Christensen [d], Richard R. Schrock [e], Guglielmo Lanzani [a,b], Giulio Cerullo [b]

[a] *Center for Nano Science and Technology of IIT@PoliMI, via Pascoli 70/3, 20133 Milano, Italy*
[b] *National Laboratory for Ultrafast and Ultraintense Optical Science, CNR-INFM, Dipartimento di Fisica, Politecnico di Milano, P.za L. da Vinci 32, 20133 Milano, Italy*
[c] *Madrid Institute of Advanced Studies, IMDEA Nanociencia, Faculdad de Ciencias, Av. Tomas y Valiente 7, 28049 Madrid, Spain*
[d] *Department of Chemistry, Bowdoin College, Brunswick, ME 04011, USA*
[e] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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ABSTRACT

We present a comprehensive study, by femtosecond pump–probe spectroscopy, of excited state dynamics in a polyene that approaches the infinite chain limit. By excitation with sub-10-fs pulses resonant with the 0–0 $S_0 \rightarrow S_2$ transition, we observe rapid loss of stimulated emission from the bright excited state S_2, followed by population of the hot S_1 state within 150 fs. Vibrational cooling of S_1 takes place within 500 fs and is followed by decay back to S_0 with 1 ps time constant. By excitation with excess vibrational energy we also observe the ultrafast formation of a long-living absorption, that is assigned to the triplet state generated by singlet fission.

1. Introduction

The electronic properties of polyenes, linear chains of π-conjugated carbon atoms, are under extensive investigation since the 1950s. There are several reasons for this interest:

(i) They are simple systems suitable for detailed experimental and theoretical characterization, so that they are considered as test banks for advanced quantum chemical methods [1];
(ii) They are model compounds for the class of conjugated polymers, which are the focus of intense fundamental research due to their important technological impact [2];
(iii) They are model compound for the class of carotenoids, sharing with them the backbone of alternating single and double carbon bonds [3]. Carotenoids perform a number of functions in photosynthetic systems [4], among which the most important are photoprotection and light harvesting. The molecular mechanisms of such processes are ultimately determined by the energies and lifetimes of their low-lying excited electronic states.

The simplest approach to describe a linear conjugated chain, based on the observation that π-electrons have p orbitals overlapping along the backbone, is the free-electron model, that describes the electron as a one-dimensional "particle in a box". This model properly predicts that the optical (HOMO–LUMO) band-gap shifts to lower energies for increasing conjugation length n (number of conjugated double bonds in the chain). However, it also predicts that linear chains are emitting (since the lowest energy electronic excited state is "bright", i.e. optically allowed) and become metallic (i.e. with zero gap) for infinite chain length. Both assertions turn out to be wrong, particularly the second one which contrasts with the Peierls theorem [5]. An efficient correction is provided by the model suggested by Kuhn [6], which phenomenologically introduced a modulation of the potential in order to describe alternation in the bond lengths along the chain, leading to a chain-length dependence of the energy levels of the type $= A + B/n$. The predicted saturation of band-gap for the infinite chain limit is indeed observed experimentally. Yet the model again fails in predicting the correct ordering of the excited states, and consequently their ability to reemit light. It turns out that simple one-electron models cannot account for the photophysics of linear chains, but both electron correlation and electron–phonon coupling must be included. A well-known model, proposed in 1979 and including only electron–phonon interaction, predicted the existence of exotic excited states in long chains, named solitons (for a review see [7]). While the latter have never been definitively confirmed experimentally, this prediction certainly fostered a huge research activity. Inclusion of electron correlation not only allows to correctly predict the chain-length dependence of the energy levels, but also explains the lack of emission in many polyenes and carotenoids.

According to the C_{2h} point group symmetry, the first allowed optical transition in polyenes occurs from an $1^1A_g^-$ state (the

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[*] Corresponding author. Tel.: +39 02 23993783; fax: +39 02 23996126.
E-mail address: mariarosa.antognazza@polimi.it (M.R. Antognazza).

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ground state S_0) to a B_u^+ state. However, for all polyenes with $n > 3$, there is an additional "covalent" excited state of A_g^- symmetry with energy lower than the B_u^+ state [8,9]. For this reason, the bright $1^1B_u^+$ state is called S_2, while the lower energy dark $2^1A_g^-$ state is known as S_1. The dark state acts as a sink for the excitation energy, so that the excited state dynamics of polyenes is characterized by very rapid energy relaxation processes. Following photoexcitation, deactivation of S_2 to S_1 occurs via an Internal Conversion (IC) process on the timescale of a few hundreds of femtoseconds [10–12]; S_1 then decays back to the ground state S_0 through another, slower, IC process, on the picosecond timescale [13].

An open issue of the photophysics of linear conjugated chains is understanding the chain-length dependence of the IC rates. The energy gap law for radiationless transitions in large molecules [14] predicts a transition rate $k \div \exp(-\beta\Delta E)$, where ΔE is the energy gap between the levels. According to this law, the IC rate should decrease with increasing energy gap between the converting levels. The gap law describes quite well the $S_1 \rightarrow S_0$ relaxation, since the S_0–S_1 gap shrinks for increasing conjugation length, leading to an increase of the IC rate, as experimentally observed [13]. Such simple description, however, fails for the $S_2 \rightarrow S_1$ relaxation process. Both theoretical and experimental results indicate that the S_1–S_2 gap increases with n, so that the IC rate, according to the gap law, is expected to decrease for increasing conjugation length. However, experiments using both fluorescence up-conversion [15] and transient absorption [16] showed a different behaviour. The S_2 lifetime was found to increase with n for short carotenoids ($5 \leqslant n \leqslant 9$), in accordance with the energy gap law; for $n > 9$, on the other hand, it was found to decrease with conjugation length. To explain this peculiar chain-length dependence the presence of additional excited singlet states besides the $1^1B_u^+$ has been invoked; such states (more specifically the $1^1B_u^-$ and $3^1A_g^-$ states) have been predicted theoretically [17,1]. It has been proposed that, for carotenoids with conjugation length $n > 9$, their energy lies within the S_1–S_2 gap and thus they become active, as intermediate states, in the $S_2 \rightarrow S_1$ IC process. However, their direct experimental observation is still controversial [18].

In addition to IC, another possible deactivation pathway for S_2 and S_1 is intersystem crossing (ISC) to the triplet manifold. In naturally occurring polyenes excited triplet states play a key role in vital photoprotection processes, by scavenging triplet excited states in (bacterio)chlorophylls and singlet oxygen. Only limited experimental data are available on the energy of triplet states in polyenes [19], due to an extremely low phosphorescence quantum yield, of the order of 10^{-4}–10^{-5}. ISC through the usual spin-flip mechanism is expected to display a very low quantum yield, since the singlet excited state lifetime of carotenoids is very short. An alternative ISC pathway is singlet fission, i.e. spontaneous breaking of a singlet into two triplet states. Such process has been recently observed in carotenoids bound to BChls in antenna complexes [20,21] and in long polydyacetylene chains [22].

The study of conjugation length dependence of the photophysics of polyenes has been both a tool and an object for research. Changing the conjugation length provides a set of data for better matching with theory, and it also shows how the system evolves from a molecular-like behaviour to the limit of a one-dimensional quantum confined solid. So far, however, spectroscopic studies on polyenes have been limited to molecules with no more than fifteen double bonds, essentially because of the lack of suitable synthesis methods. Some extrapolations from short-chain models have been used to predict properties and behaviour of the longest polyene compounds, but they have not been matched by a corresponding amount of experimental work.

In this work, we aim at filling this gap by studying a polyene that approaches the infinite chain limit, poly-diethyldipropargylmalonate, poly(DEDPM) [23]. Previous investigations showed that a poly(DEDPM) solution contains a distribution of conjugation lengths, mainly dominated by the longer segments with a number of conjugated double bonds greater than 100. This system is ideal for studying the excited state dynamics of polyenes for the limiting case of infinite chain length. First this allows us to study the IC process in very long chains, and second it allows us to explore what happens in long chains when excess energy is provided to the excited states, possibly highlighting quasi-particles dynamics. In particular we want to verify the possibility that, for high n values, bound covalent states can undergo fission into triplet pairs, as predicted by theory [1].

2. Materials and methods

Poly(DEDPM) (molecular mass $\sim 4 \times 10^5$) was obtained by living cyclopolymerization of the monomer DEDPM, as described in detail in [23]; the number of conjugated carbon double bonds is in our case greater than 100, justifying the approximation of an infinitely-long chain. The absorption spectrum of poly(DEDPM) is shown in Fig. 1 together with the chemical structure of the molecule. It is broader and red-shifted with respect to naturally occurring carotenoids with shorter conjugation lengths (usually absorbing in the 400–500 nm region of the visible spectrum) and does not present any clear vibronic structure, due to conformational disorder of the chains. Previous work by Christensen et al. [24] demonstrated that these features are due to a distribution of polyene conjugation lengths, whose spectra are linearly superimposed: the shortest segments give rise to the tail at the highest energies, but the longest ones approach the infinite polyene limit. Poly(DEDPM) samples were dissolved in tetrahydrofuran (concentration of ~20 g/l); experiments were performed at room temperature and under atmospheric pressure.

We carried out pump–probe experiments using two different setups, both based on a regeneratively-amplified mode-locked Ti:sapphire laser, delivering pulses at 1.6-eV with 1-kHz repetition rate, 150-fs duration and 500-μJ energy. The first setup provides sub-10-fs time resolution with 10-ps scan range, while the second setup has a lower resolution (200 fs) but a longer scan range (up to 400 ps).

The first setup is based on a Non-collinear Optical Parametric Amplifier (NOPA) pumped by the Second Harmonic (SH) of Ti:sapphire and seeded by the White-Light Continuum (WLC) generated in a 1-mm-thick sapphire plate [25]. The NOPA produces ultrabroadband visible pulses with spectrum extending over the 1.8–

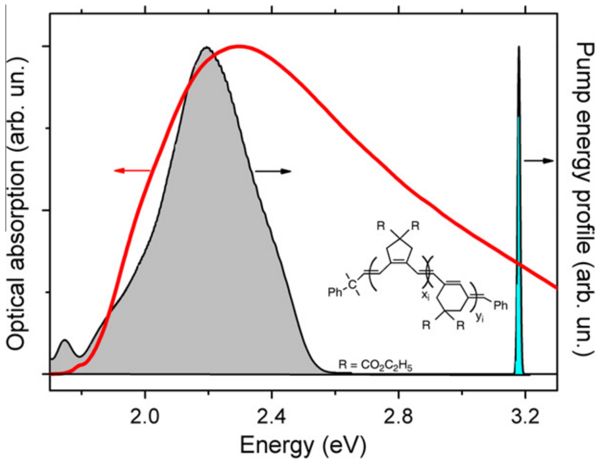

Fig. 1. Absorption spectrum of polymer of poly(DEDPM) in Tetrahydrofuran solution. The chemical structure of the polymer is also shown. The shaded lines correspond to the two different pump pulses used.

2.5 eV range, with energy up to 1 μJ, compressed by multiple bounces on dielectric chirped mirrors to nearly transform-limited ≈7-fs duration. As can be seen from Fig. 1, the NOPA spectrum is well matched to the low energy tail of the $S_0 \rightarrow S_2$ transition of the polyene. The NOPA pulses are sent to a degenerate pump–probe setup, based on a balanced Michelson interferometer and using a spherical mirror ($f = 100$ mm) to focus non-collinearly pump and probe pulses. After the sample, kept in a home-made cuvette with 200-μm fused silica windows and 200-μm path-length, the probe pulses, spatially selected by an iris, are focused on the entrance slit of a spectrometer equipped with a fast photodiode array, allowing recording the probe spectrum at the full 1 kHz laser repetition rate [26]. The pump beam is modulated at 500 Hz by a mechanical chopper with the frequency locked to the laser pulse train, to allow collection of probe spectra with and without excitation and to obtain 2D differential transmission ($\Delta T/T$) maps as

$$\Delta T/T(\lambda,\tau) = [T_{\mathrm{on}}(\lambda,\tau) - T_{\mathrm{off}}(\lambda)]/T_{\mathrm{off}}(\lambda),$$

where λ is the probe wavelength and τ the pump–probe delay. By averaging over 1000 consecutive laser shots, $\Delta T/T$ sensitivity better than 10^{-4} over the whole probe wavelength region can be reached.

In the second setup, the pump is provided by the SH of Ti:sapphire at 3.2 eV, with ≈200-fs duration, and the probe is the WLC generated in a sapphire plate. The visible portion of the WLC, spectrally selected by a short-pass filter and covering the 1.6–2.7 eV range, is focused on the sample, spatially overlapped with the pump pulse, using only reflective optics, to minimize pulse chirping effects. The transmitted probe beam is selected by an iris and focused on the entrance slit of a spectrograph. The dispersed light is imaged on a sensitive CCD detector equipped with fast low-noise electronics, enabling single-shot recording of the WLC spectrum at the full 1-kHz repetition rate. 2D $\Delta T/T(\lambda,\tau)$ maps are generated as described above, with sensitivity down to $\Delta T/T \sim 10^{-5}$.

We also performed Continuous-Wave Photoinduced Absorption (CW-PA) experiments, which are sensitive to long-lived photoexcitations (triplets and charged states), having lifetimes in the order of $1/f$, where f is the pump-beam modulation. Transmission (T) spectra are recorded using the light beam of a tungsten halogen lamp; the probe beam is focused onto the sample by spherical mirrors, in order to avoid chromatic aberrations; the transmitted light is dispersed with a monochromator and detected by a photodiode. Photoexcitation of the sample is provided by a cw green laser, with emission wavelength $\lambda = 532$ nm, modulated by a mechanical chopper; the photoinduced variation in the sample transmission ΔT is measured by a lock-in amplifier using as reference the pump chopper frequency (80 Hz).

3. Results and discussion

3.1. Energy relaxation dynamics

The 2D $\Delta T/T(\lambda,\tau)$ map of poly(DEDPM), following excitation by a 7-fs visible pulse resonant with the $S_0 \rightarrow S_2$ 0–0 transition is displayed in Fig. 2. In particular, Fig. 2a zooms in on the early time dynamics. The features observed at negative times are a characteristic coherent artifact of pump–probe experiments with broadband pulses, and can be explained by pump-perturbed free induction decay [27]. At positive times, one can observe the prompt rise of a positive $\Delta T/T$ signal (blue[1] in Fig. 2), due to the population of the S_2 state by the pump pulse. This signal is a superposition of PhotoBleaching (PB) of the ground state absorption and Stimulated Emission (SE) from S_2. The PB/SE signal displays an initial ultrafast decay which is completed within ~50 fs. Such fast dynamics is also clearly visible in the time traces at selected probe wavelengths, shown in Fig. 3a.

Following this initial process, we can time-resolve the formation, within ≈150 fs, of a photoinduced absorption (PA) band ($\Delta T/T < 0$, red in Fig. 2), extending from 1.8 to 2 eV. This band, which we call PA_1 in the following, is assigned to the transition from S_1 to an higher lying state S_n. PA_1 is a common feature of polyenes and carotenoids and usually peaks in the visible, shifting progressively to the red for longer chains [3]. Interestingly, we also observe the build-up of an additional PA band (PA_2) peaking at 2.5 eV. Due to the similarity in the formation and decay dynamics of PA_1 and PA_2 (see red and green traces in Fig. 3), this new band is also assigned to a transition from S_1, to an higher lying state S_m.

Following its formation, the PA_1 band displays a pronounced blue shift within the first ≈500 fs. This shift is highlighted in Fig. 2c, presenting a zoom of the $\Delta T/T$ map around the isosbestic point, which moves from 1.9 to 2 eV. This is a typical feature of carotenoids [28–30] and has been attributed to vibrational relaxation of the hot S_1 state. Finally, Fig. 2e shows the $\Delta T/T$ map on a longer timescale (4 ps); here we observe the decay of the PA_1, PA_2 and PB bands, which is indicative of a relaxation of S_1 back to S_0. The observed time constant for this process is ≈1 ps (see also Fig. 3).

The time traces shown in Fig. 3a are clearly modulated by well-resolved oscillations. These correspond to vibrational wavepackets with ≈1195 cm^{-1} and 1520 cm^{-1} frequencies, due to single- and double-bond stretching of the carbon atoms, respectively. Such oscillations are ascribed to impulsive stimulated resonant Raman scattering in the ground electronic state and have been discussed in detail in Ref. [31].

The observed excited state relaxation dynamics is in agreement with the trend observed on shorter chain carotenoids [16]. The very fast decay of the positive $\Delta T/T$ signal observed within the first 50 fs is consistent with a very rapid depopulation of the photoexcited S_2 state; in this way the SE from S_2 is rapidly quenched, while the PB of the $S_0 \rightarrow S_2$ transition remains. Such a fast decay is not matched by the rise of S_1 population; in fact, the PA_1 and PA_2 bands are formed over a significantly longer timescale of ≈150 fs. Similar observations on shorter chain carotenoids were previously explained by invoking an intermediate excited state (S_x) mediating the $S_2 \rightarrow S_1$ IC process [16]. Here, we can make a similar conjecture, although a definitive assignment would require extending the probing window to the near-IR region, where the S_2 state presents a PA band. The build-up and decay dynamics of PA_1 are in agreement with measurements on long-chain carotenoids ($n = 15$) which gave time constants of 42 ± 5 fs for the $S_2 \rightarrow S_1$ IC process and of 1.1 ps for the $S_1 \rightarrow S_0$ IC process [16]. This is consistent with the scaling laws for energy levels in polyenes, $E = A + B/n$ [6], indicating a saturation for increasing conjugation length.

The observed photoinduced dynamics in poly(DEDPM) were reproduced by a numerical model, performing a global analysis based on a rate equation description of excited state dynamics [32], which completely reproduces time-dependent spectroscopic data with a strongly reduced set of parameters. The different states s_i are connected via a sequential model according to the processes $s_i \xrightarrow{k_i} s_{i+1}$, where k_i is the transition rate. The number of states, and thus the resulting photophysical model, are selected by critically considering the obtained basis spectra. We found that a minimum of four states was needed to correctly describe the observed $\Delta T/T$ spectra. The obtained fits are shown in Fig. 2b, d, f and Fig. 3b, and display an excellent agreement with the experimental data.

In Fig. 4a, we give the species associated difference spectra (SADS) for the four excited states introduced in the model. The first SADS is strongly different from the others, in that it is dominated

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[1] For interpretation of color in Figs. 1, 2, 3 and 6 the reader is referred to the web version of this article.

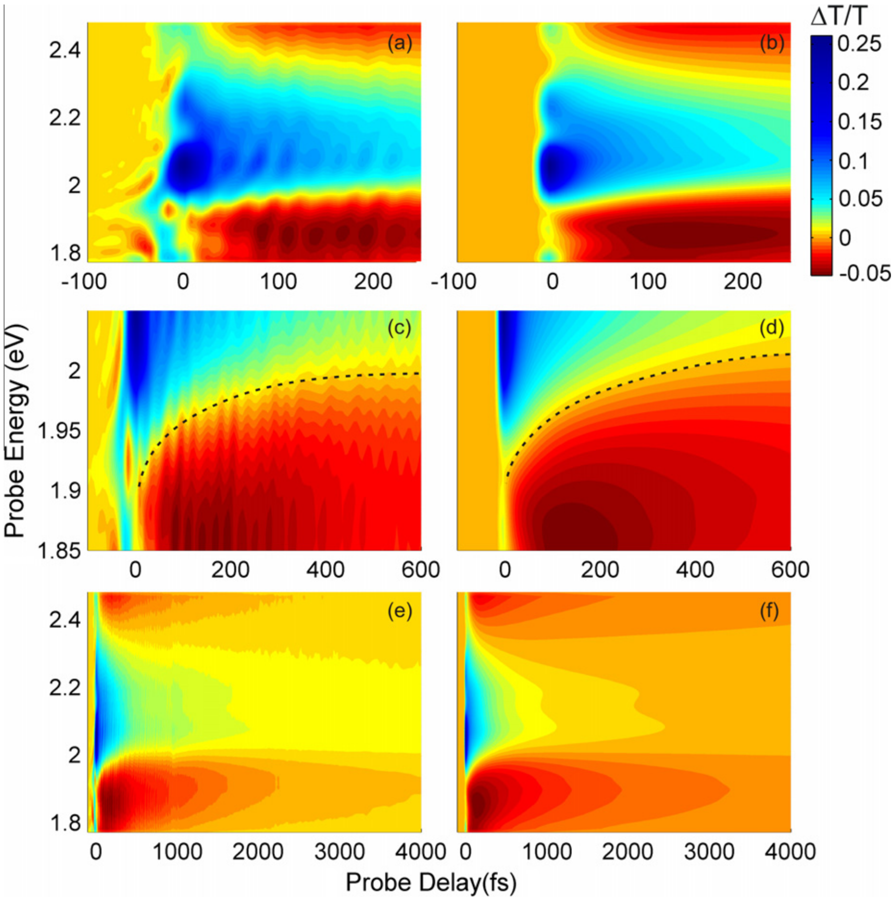

Fig. 2. 2D map of the $\Delta T/T$ signal, as a function of probe energy and time delay, during the first 250 fs after photoexcitation (a) and on an extended timescale, up to 4 ps (e), as obtained by resonant pumping. Panel (c) shows in greater detail the blue shift of the isosbestic point, from 1.9 to 2 eV. Global fitting results are also correspondingly reported, in the right panels (b), (d), (f).

by a negative cross-section feature around 2.0 eV with relatively narrow bandwidth. Since the pump spectrum is centred at higher energy (around 2.2 eV), and ground state absorption is weak at 2.0 eV, this negative cross-section should be associated with the (optically allowed) SE from the S_2 state to the ground state. We thus associate the s_1 state with the bright singlet state S_2. The second SADS s_2 still displays a negative cross-section, which is assigned to the PB of the $S_0 \rightarrow S_2$ transition; we tentatively assign this to the elusive intermediate state S_x. Finally, the last two SADS are characterized by a PB of the S_0 absorption, surrounded by two PA bands at lower (1.9 eV) and higher (2.5 eV) probe energies. They are assigned to the hot (s_3) and vibrationally relaxed (s_4) S_1 state. The relaxation rates extracted from the numerical model are reported in Table 1.

3.2. Ultrafast triplet formation

The previous paragraph shows that, upon resonant excitation of the long chains of the polyene, the $\Delta T/T$ signal goes to zero at delays longer than 5 ps, indicating complete ground state recovery. It has been previously reported [33] that excitation of carotenoids with excess energy leads to triplet states photogeneration. To test this mechanism in our polyene, we recorded transient absorption spectra using 200-fs pump pulses at 3.2 eV and WLC probing. As can be seen from Fig. 1, this pump frequency falls on the high-energy tail of the absorption spectrum. Therefore, in addition to providing excess vibrational energy to the longer chains, it also efficiently excites the shorter polyene chains, which have blue-shifted $S_0 \rightarrow S_2$ transition.

The 2D $\Delta T/T(\lambda,\tau)$ map of poly(DEDPM), following excitation by a pulse at 3.2 eV, is shown in Fig. 5. With this experimental setup, the time resolution is too low to enable observation of the $S_2 \rightarrow S_1$ IC process, so that we immediately observe the PA_1 band arising from the $S_1 \rightarrow S_n$ transition. With respect to the experiments with resonant pumping of the long chains, we can make the following observations: (i) the PA_1 band extends to higher energies, up to 2.5 eV; (ii) the band displays a considerably longer lifetime, with transient signals observed up to 300 ps delay; (iii) the peak of the PA_1 band shows a pronounced blue shift with time over the timescale of several tens of picoseconds (see Fig. 6a). All of these observations are consistent with the fact that the higher frequency pump predominantly excites the shorter chain polyenes. In fact, it is well-known that in polyenes, for decreasing conjugation length, the PA_1 band shifts to the blue and the S_1 lifetime becomes progressively longer [3,13]. The pronounced blue shift of the PA_1 band with time cannot be explained by vibrational relaxation of the hot S_1, because the observed timescale is too long. Instead we attribute it to simultaneous excitation of a mixture of polyenes with different chain length. For increasing time delays, the fraction of photoexcited long chains becomes progressively lower and the resulting PA band, being predominantly due to the short chains, shifts to the blue.

Interestingly, we also observe in Fig. 6 an absorption peak at 1.85 eV (PA_3 band) that does not shift with time, but remains at a fixed position over the considered timescale. The PA_3 band seems to be present immediately after photoexcitation (red line in Fig. 6a) but it can be observed more clearly only at longer delays, after the PA_1 band has shifted to the blue. The PA_3 band cannot be assigned

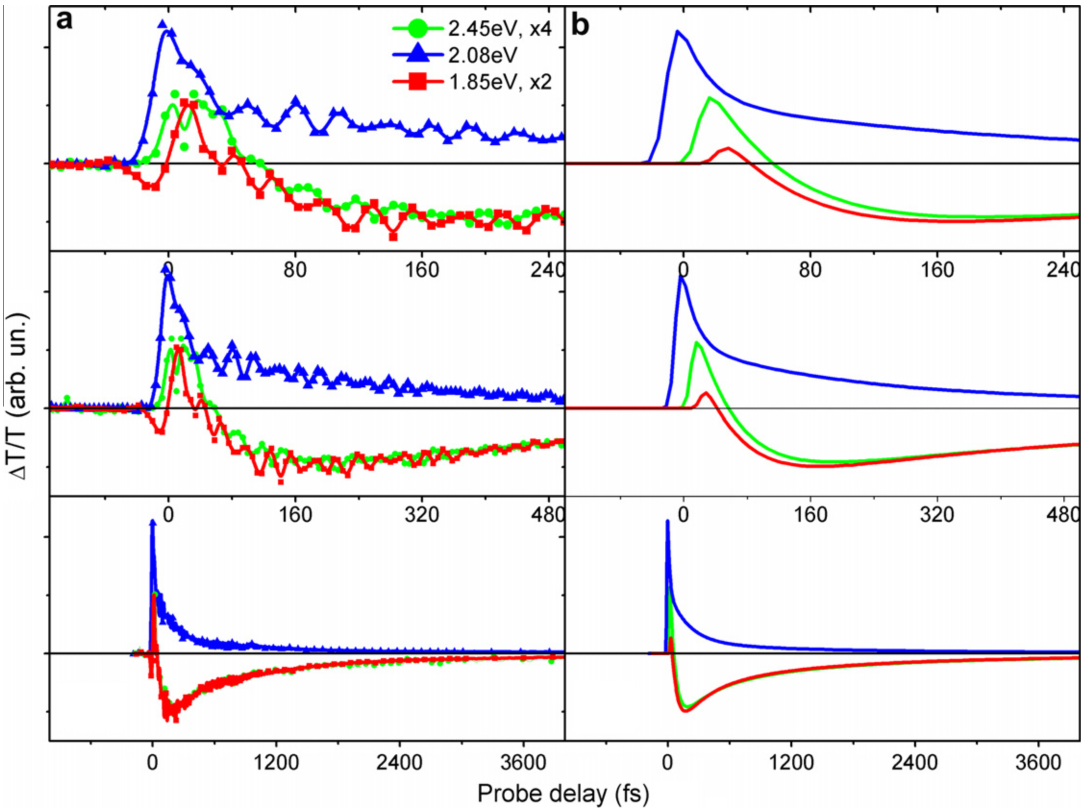

Fig. 3. (a) Pump–probe dynamics at selected probe energies and (b) calculated dynamics according to the model described in the text.

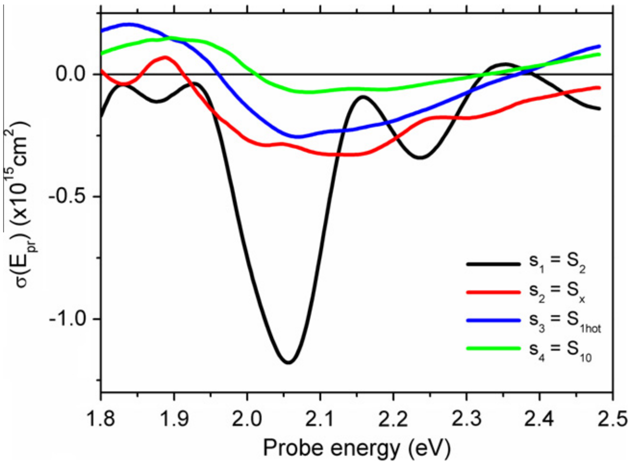

Fig. 4. Species associated difference spectra obtained from the global fitting procedure.

Table 1
Transition rates values, as obtained from the global fitting procedure.

Rate constant (fs)	
k_1 ($S_2 \rightarrow S_x$)	17
k_2 ($S_x \rightarrow S_{1hot}$)	51
k_3 ($S_{1hot} \rightarrow S_{10}$)	175
k_4 ($S_{10} \rightarrow S_0$)	1200

to a singlet state, since the $S_1 \rightarrow S_n$ transition at 1.85 eV corresponds to the longer chain polyenes, which have lifetime of the order of 1 ps. Charged states are also unlikely, since their photogeneration efficiency in solution is expected to be low and their PA bands fall in the near-IR spectral range [7]. For these reasons, we tentatively assign the PA_3 band to a triplet state, more specifically to the $T_1 \rightarrow T_n$ absorption. In short polyenes, it has been found that the T_1–T_n transition is red-shifted by about 0.09 eV against the ground state absorption [19]. Since the longest chains in our sample absorb at about 1.95 eV, it is reasonable to attribute this band to triplet–triplet absorption.

To corroborate our assignment, the presence of a long-lived triplet state in this spectral region has been verified by measuring CW-PA spectra in the ms time domain. In these measurements, the sample is in the solid state, at liquid nitrogen temperature and in vacuum. The obtained spectrum is shown in Fig. 6a as a dashed line. We find a long-lived PA band, peaking at ≈1.87 eV, in the same energy region as the PA_3 band. While the experimental conditions of the CW-PA measurement are quite different from those of the pump–probe experiments, this result is helpful in confirming our assignment.

To investigate the triplet formation dynamics, we fitted the experimental data. We did not adopt the previously described global fitting procedure due to the distribution of lifetimes of the S_1 state in the different chain lengths and the ensuing spectral evolution of the PA_1 band. We rather used a simplified model in which the transient spectra are reproduced by the superposition of two Voight profiles, corresponding to the singlet (PA_1) and triplet (PA_3) bands, respectively. The widths of both bands and the central position of PA_3 (1.87 eV) were kept constant, while the central position of PA_1 was allowed to shift in time. The results of the fit are reported in Fig. 6b and are in good agreement with the experiments. The PA_3 profile is reported as a shaded line in Fig. 6b. According to this model, the PA_3 band is generated within the pump pulse duration; this excludes spin-flip as a possible mechanism, since it would occur on a much longer timescale. The most

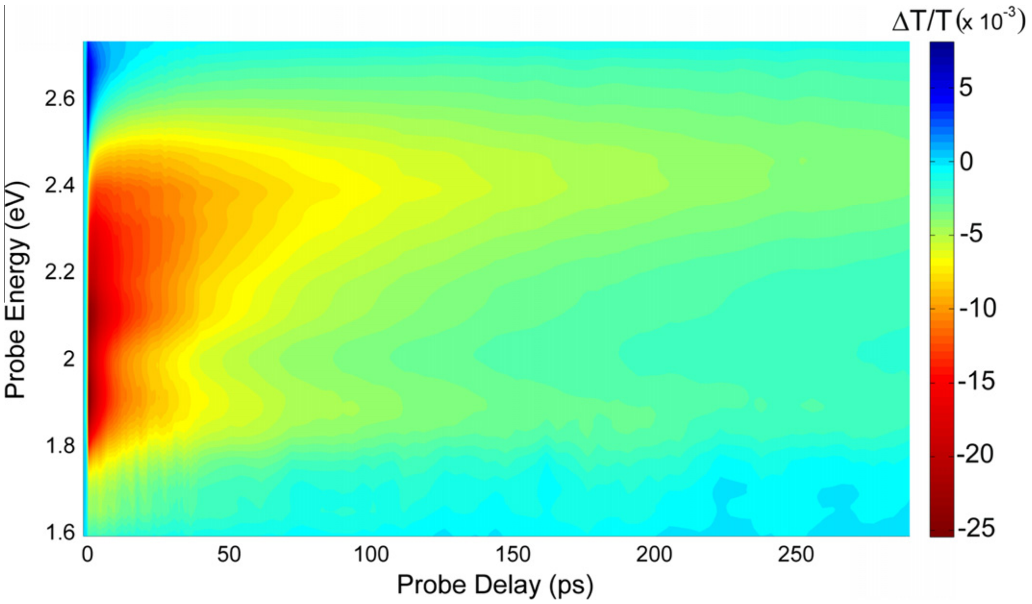

Fig. 5. 2D map of the $\Delta T/T$ signal following excitation by 200-fs pulses at 3.2 eV.

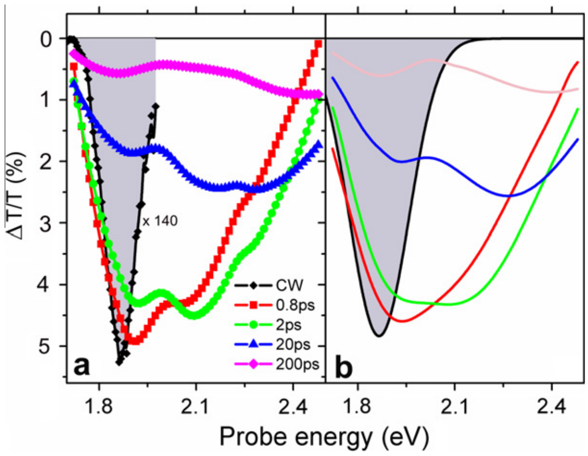

Fig. 6. (a) $\Delta T/T$ spectra at selected time delays; the CW-PA spectrum is reported as shaded line. (b) Fits according to the model described in the text; the PA_3 band is reported as shaded line.

likely mechanism thus appears to be singlet fission, starting from the covalent S_1 state, according to the description of $2^1A_g^-$ as a doubly excited, spin-correlated triplet state $1^3B_u \otimes 1^3B_u$ [1].

4. Conclusions

In this paper, we have presented a comprehensive study, by femtosecond pump–probe spectroscopy, of excited state dynamics of a polyene that approaches the infinite chain limit. By excitation with sub-10-fs pulses resonant with the 0-0 $S_0 \rightarrow S_2$ transition, we observed rapid loss of stimulated emission from the S_2 state, followed by delayed formation of the hot S_1 state within 150 fs. Vibrational cooling of S_1 takes place within 500 fs and is followed by decay back to S_0 with 1 ps time constant. We find that the ultrafast dynamics (timescale < 50 fs) of the optical states in long (infinite) chain polyenes presents the same anomaly found in shorter chain carotenoids [28]: SE from S_2 displays a much faster decay than the build-up of the PA from S_1. At this stage we cannot further speculate on the interpretation and the consequences of this phenomenon, yet its presence suggests it is a rather general behaviour for small gap polyenes and carotenoids.

Upon photoexcitation with excess vibrational energy, in the blue wing of the broad inhomogeneous absorption band, we show that a long-lived PA appears in the transient spectra, which we assign to triplet–triplet absorption. The photogeneration of triplets in polyenes remains an elusive and rather inefficient process (quantum yield lower than 10^{-2}). Here we point out the role of the chain length and suggest, because of the ultrafast formation, that ISC is due to singlet fission. This supports theoretical models on infinite chains for non-degenerate ground state systems, predicting the fissioning of covalent states into triplet states. We speculate that long conjugation segments are required in order to support the separation of the nascent triple pair, i.e. the limiting size is the volume (in 1D a length) occupied by two separated triplet wavefunctions. Assuming that a typical triplet state fills about 10 double bonds, a length of about 20 double bonds would be the minimum requirement. Once separated, triplets pairs will recombine back, or possibly get trapped at chain segments to become long-lived. The latter process would explain detection of long-lived triplets that we demonstrate by using steady state techniques. This work confirms that linear conjugated chains are valuable test banks for molecular dynamics, with many open issues still to be addressed.

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