

## Ultrafast excited state relaxation in long-chain polyenes

Maria Rosa Antognazza<sup>a,\*</sup>, Larry Lüer<sup>b,c</sup>, Dario Polli<sup>b</sup>, Ronald L. Christensen<sup>d</sup>, Richard R. Schrock<sup>e</sup>,  
Giulio Lanzani<sup>a,b</sup>, Giulio Cerullo<sup>b</sup>

<sup>a</sup> Center for Nano Science and Technology of IIT@PoliMI, via Pascoli 70/3, 20133 Milano, Italy

<sup>b</sup> National Laboratory for Ultrafast and Ultraintense Optical Science, CNR-INFN, Dipartimento di Fisica, Politecnico di Milano, P.za L. da Vinci 32, 20133 Milano, Italy

<sup>c</sup> Madrid Institute of Advanced Studies, IMDEA Nanociencia, Facultad de Ciencias, Av. Tomas y Valiente 7, 28049 Madrid, Spain

<sup>d</sup> Department of Chemistry, Bowdoin College, Brunswick, ME 04011, USA

<sup>e</sup> Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

### ARTICLE INFO

#### Article history:

Received 20 October 2009

In final form 2 March 2010

Available online 7 March 2010

#### Keywords:

Polyenes

Carotenoids

Ultrafast spectroscopy

Triplet states

### 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.

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### 1. Introduction

The electronic properties of polyenes, linear chains of  $\pi$ -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  $\pi$ -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

\* Corresponding author. Tel.: +39 02 23993783; fax: +39 02 23996126.

E-mail address: [mariorosa.antognazza@polimi.it](mailto:mariorosa.antognazza@polimi.it) (M.R. Antognazza).

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  $\Delta E$  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 ( $5 \leq n \leq 9$ ), 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 polydiacetylene 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  $\sim 20$  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- $\mu$ J 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 ultra-broadband visible pulses with spectrum extending over the 1.8–

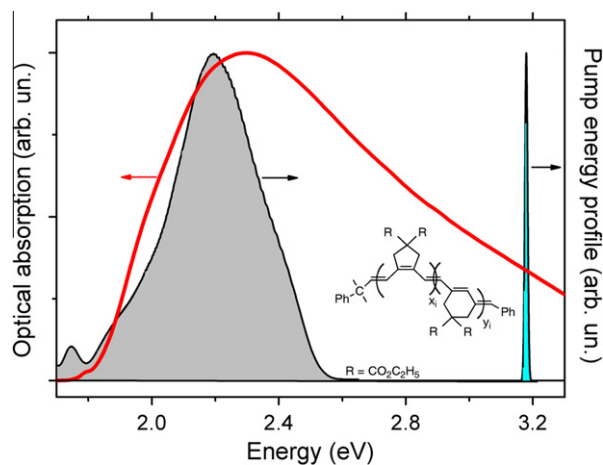


Fig. 1. Absorption spectrum of polymer of poly(DEDPM) in Tetrahydrofuran solution. The chemical structure of the polymer is also shown. The shaded lines correspond to the two different pump pulses used.

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