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Excited state dynamics in alternating polyfluorene copolymers

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Abstract

We present the excited state dynamics of the low band gap alternating polyfluorene copolymer, DiO-PFDTBT. The copolymer structure is an alternating sequence of donor and acceptor units consisting of 9,9-dioctyl-9H-fluorene and 4,7-di-thiophen-2-yl-benzo[1,2,5]thiadiazolyl units. Calculations have predicted that the first excited state has charge transfer character, while the second strongly allowed excited state is a delocalized π-conjugated state. We show that the excited state dynamics involves internal conversion (IC) from the second strongly allowed excited state to the first excited state. Furthermore, excitation energy transfer (EET) on the ∼1–10 ps time scale is observed as well as a subsequent formation of a stabilized long-lived emissive state, which has a decay time of 3.25 ns. The origin of this stabilized state is discussed in relation to the intrinsic charge transfer nature of the DiO-PFDTBT.

Keywords: Low band gap conjugated polymers; Photoinduced absorption spectroscopy

1. Introduction

The possibility of chemically tailoring the photonic and electronic properties makes conjugated polymers extremely attractive in a wide range of optoelectronic applications. A special type of designer molecules used in polymer LED’s, photodiodes, and solar cells are polyfluorene-based alternating copolymers [1–3]. The chemical structure consists of an alternating sequence of fluorene units and molecular moieties with electron accepting and/or donating properties. Two examples are DiO-PFDTBT, which consists of 9,9-dioctyl-9H-fluorene and 4,7-di-thiophen-2-yl-benzo[1,2,5]thiadiazolyl units in alternating sequence (see chemical structure in Fig. 1) and the related F8BT [4] whose chemical structure equals that of DiO-PFDTBT, but without thiophene units. The alternating donor–acceptor structure leads to a lowering of the optical band gap improving, e.g., the overlap with the solar irradiation spectrum in polymer-based solar cells.

Semiempirical quantum–chemical calculations by Cornil et al. [5] on F8BT have shown that the alternating donor–acceptor structure provides charge separation within the π-conjugated electron system. We have previously reported similar calculations based on the ZINDO method for both, F8BT and DiO-PFDTBT [6].

We showed that the first singlet excited state (S_1) is a charge transfer (CT) state with negative charge localized on the benzothiadiazolyl unit, while the transition to the second strongly allowed excited singlet (which we will refer to as the S_2 state throughout this paper) is a delocalized $\pi \rightarrow \pi^*$ transition corresponding to transitions observed in more conventional conjugated polymers such as polyfluorene. Furthermore, we found several intermediate states with low oscillator strength, so-called dark states, and which all had CT character similar to that of the S_1 state. The CT nature of the excited state makes the alternating copolymer an interesting object of study in ultrafast spectroscopy. Here we present our investigation of the excited state dynamics in the alternating DiO-PFDTBT polyfluorene copolymer in chloroform solution. Using fluorescence lifetime measurements, femtosecond transient absorption spectroscopy, and a global fitting procedure we are able to uncover the primary processes involving the CT state following optical excitation.

2. Experiment

The alternating polyfluorene-based copolymer, DiO-PFDTBT is dissolved in chloroform (2.4 mg per 10 ml) and subsequently sonicated to break-up residual aggregates. The solution is contained in a 1 mm quartz cuvette. The synthesis

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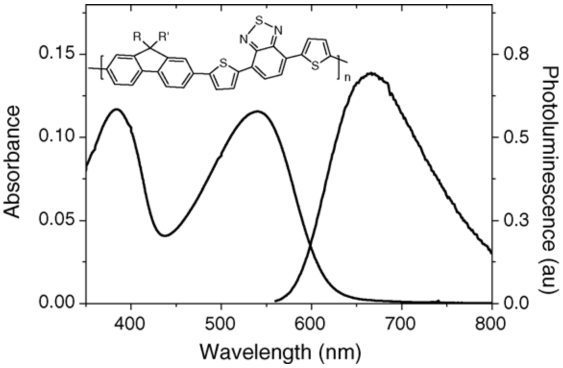

Fig. 1. Absorption and emission spectra of DiO-PFDTBT in chloroform solution. The inset shows the repeat unit of DiO-PFDTBT.

of DiO-PFDTBT is described in Svensson et al. [7]. The molecular weight is 11,800 g/mol corresponding to ‘rod-like’ polymer chains of ∼20 repeat units. Fig. 1 shows the optical properties of DiO-PFDTBT including the molecular structure ($R = R' = C_8H_{17}$ indicates ‘octyl’ side-chains). The absorption spectrum consists of two broad peaks of approximately the same optical density centred at 384 nm and 540 nm. The photoluminescence spectrum shown in Fig. 1 corresponds to ‘red’ (540 nm) excitation. For ‘blue’ (388 nm) excitation, a similar spectral shape and peak position at 665 nm is observed. This suggests that the same emission channel is reached irrespective of the excitation wavelength.

Fluorescence lifetime measurements were conducted using standard streak camera detection and time correlated single photon counting (TCSPC) with a width of the response functions of 10 ps and 220 ps (FWHM), respectively. The excitation wavelength was 400 nm in both cases, generated by frequency doubling the output of a Millenia X pumped Tsunami oscillator from Spectra-Physics.

Time-resolved absorption experiments were performed using a transient absorption spectrometer with 120 fs pulses. The experimental setup was based on a commercial 1 kHz Clark MXR CPA-2001 femtosecond laser pumping two non-collinear optical parametric amplifiers (NOPA) for generation of single colour pump pulses and a broad probe continuum. The excitation wavelengths were 388 nm and 570 nm corresponding to the centre of the ‘blue’ absorption peak and the red tail of the ‘red’ absorption peak in DiO-PFDTBT. The probe continuum covered the spectral region from 490 nm to 750 nm (in some measurements 540 nm to 750 nm). In order to ensure linear optical excitation and thereby avoiding influence of bimolecular annihilation processes, we limited the pump intensity to $\sim 10^{13}$ photons/cm^2 using neutral density filters and a large pump beam diameter. Furthermore, the pump pulse was polarized at magic angle to the probe polarization and the photoinduced transient absorption spectra were recorded using a diode array. All measurements were conducted at room temperature.

3. Results and discussion

The spectral evolution following primary photoexcitation in DiO-PFDTBT in chloroform solution is measured using the transient absorption spectrometer from ∼0.1 ps to 450 ps. We consider the dynamics when exciting the S_1 and S_2 states, also referred to as the ‘red’ and ‘blue’ excitation channels. The dynamics is observed to be qualitatively the same after 0.5 ps for both excitation channels. In particular, this is in agreement with the observed steady state photoluminescence in Fig. 1. On very short time scales, the dynamics following blue excitation shows additional kinetic components corresponding to internal conversion (IC) and possibly faster excitation energy transfer (EET). First, however, we address the fluorescence lifetimes of DiO-PFDTBT.

3.1. Fluorescence lifetimes

The fluorescence lifetimes on intermediate and long timescale have been measured using streak camera detection and TCSPC, respectively. In TCSPC, we observe a single exponential decay with a time constant of 3.25 ns. The streak camera detected fluorescence lifetime shows a correspondingly slow decay together with additional fast decay components. Here the relative amplitudes are wavelength dependent. In order to ‘glue’ the two data sets, we curve-fit the streak camera data with a time constant locked at 3.25 ns and find the following fluorescence lifetimes: 8 ps, 230 ps, and 3.25 ns. The curve-fitting procedures all take the finite instrument response into account.

3.2. Transient absorption: red excitation

The transient absorption spectra after 0.5 ps and 466 ps are plotted in Fig. 2 for red excitation. The initial spectrum includes a photo bleach signal and stimulated emission. Above 750 nm, the differential absorption becomes positive indicating excited state absorption (data not shown). As time progresses, the stimulated emission is red shifted and a photoinduced absorption signal appears between 600 nm and 650 nm. In order to analyse the overlapping spectral features and relate them to dynamic processes, we resort to a global fitting approach using a linear combination of single exponential decay functions. This is a powerful approach for analysis, however, it should be noted that

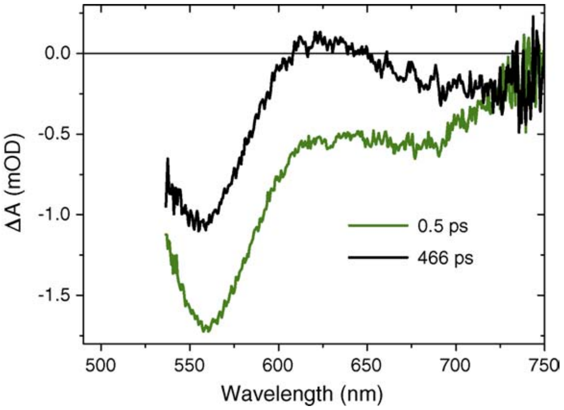

Fig. 2. Transient absorption spectra for the red excitation (570 nm). Gray is at 0.5 ps and black is at 466 ps delay.

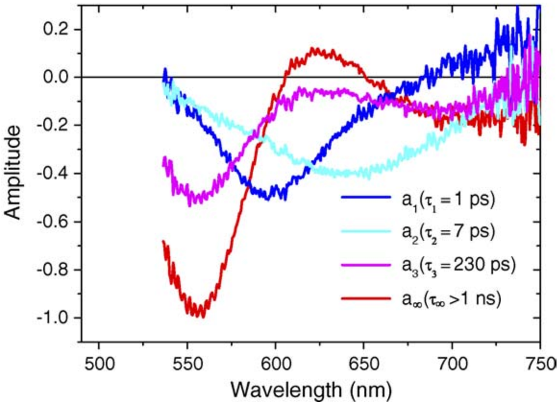

Fig. 3. Decay-associated spectrum for red excitation (570 nm).

the use of single exponential decay functions will only lead to approximate results in the case of, e.g., excitation energy transfer and other inherently nonlinear dynamical processes.

The global fitting of the spectral evolution is performed according to the expression

$$\Delta A(\lambda, t) = R(\lambda, t) \otimes \left[\sum_i a_i(\lambda) \mathrm{e}^{-t/\tau_i} + a_\infty(\lambda) \right],$$

for the differential absorption, ΔA [8]. Here $a_i(\lambda)$ is the decay-associated amplitude, τ_i is the decay time, and $a_\infty(\lambda)$ is the 'infinite time' amplitude connected to a very long lifetime (>1 ns), which is not accounted for by the i processes. The decay functions are convolved with the response function $R_{(\lambda, t)}$. The global fitting is restricted by fixing one time constant to 230 ps decay, i.e., the intermediate fluorescence lifetime obtained using streak camera detection.

In Fig. 3, the decay-associated spectra for red band excitation are plotted. They reveal at least four dynamical processes with distinct decay constants. Initially, we see a process with 1 ps decay time that has negative amplitude.

This process is only slightly coupled to the ground state recovery because the amplitude is low in the spectral region of the photo bleach. On the other hand, the negative sign at short wavelengths and the positive sign at long wavelengths suggest that the 1 ps process is the sum of a decay of stimulated emission from the primary photoexcited state and a formation of stimulated emission from a more red-shifted state. We believe this is evidence for EET on the 1 ps timescale.

The following process with 7 ps decay time has similar but further red-shifted characteristics in the decay-associated spectrum, i.e., only weak recovery of the ground state but rather a formation or transition to a new state, which is lower in energy. The nature of this process, we believe, is also exciton hopping. Hence, using the global fitting approach, we observe two energy transfer time constants. This result is corroborated by anisotropy decay measurements of the excited state (data not shown). As mentioned previously, the result is influenced by the use of single exponential decay functions in the global fit, and we must therefore anticipate that the observed bi-exponential EET is in fact a distributed process with a distribution of hopping times in the 1–10 ps time range. We note that the exciton hopping process is also observed in the streak camera detected fluorescence as a spectral shift towards red. Here, an 8 ps lifetime component was found.

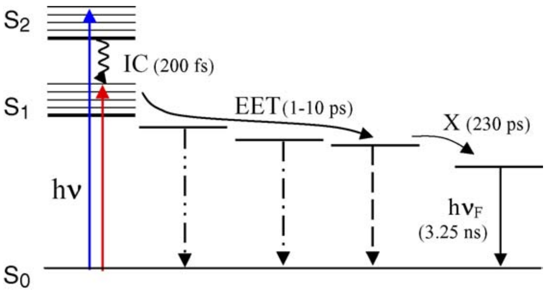

Fig. 4. Schematic energy diagram for DiO-PFDTBT. IC is internal conversion, EET is excitation energy transfer, and X indicates a stabilization process or conformational relaxation.

Continuing the analysis, we see a 230 ps process, which couples negative amplitude in the region of stimulated emission to recovery of the ground state. We conjecture that this process is a quenching process linked to stabilization or conformational relaxation (indicated by an X in Fig. 4) due to the charge transfer, which is intrinsic to the S_1 state. Such a conformational relaxation could be influenced by the choice of solvent, however, further investigations varying the solvent polarity are needed to determine the coupling between solvatization and the conformational relaxation. An alternative explanation for the 230 ps process could be a slow EET, which has a hopping time in the very long tail of the hopping time distribution. However, we believe this to be less likely since if the hopping time distribution is very broad we expect several time constants in the global fit lying between 10 ps and 300 ps. This is not the case. The 'infinite time' amplitude a_∞ in Fig. 3 can be considered a process that couples decay of the excited state absorption and decay of stimulated emission in the final stabilized state. A good estimate for the lifetime of this process is 3.25 ns, which is the single exponential fluorescence lifetime obtained using TCSPC.

A general scheme for the dynamics is summarized in the energy diagram in Fig. 4. We emphasise that the presented model is consistent with independent fluorescence lifetime measurements.

3.3. Transient absorption: blue excitation

When exciting the blue $\pi \rightarrow \pi^*$ transition, qualitatively similar dynamics compared to the red band excitation is obtained for 0.5–450 ps. A significant difference is observed only at the very early times following excitation (<0.5 ps). The decay-associated spectra are shown in Fig. 5. Here we have fixed a 7 ps and a 230 ps time constant in the global fitting corresponding to the EET time constant observed under red excitation and the intermediate fluorescence lifetime observed with streak camera. We obtain an additional fast process with decay time of 200 fs. The amplitude is positive at long and negative at short wavelengths. We associate the positive part to the decay of excited state absorption

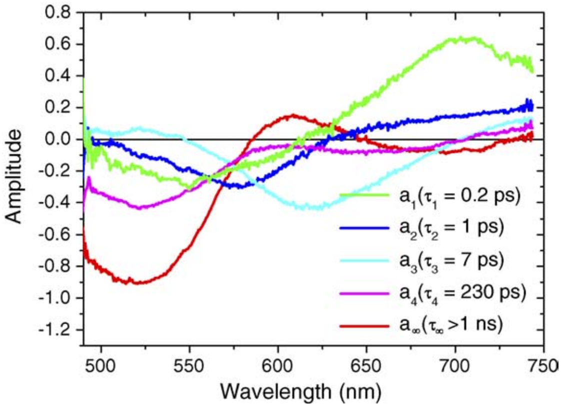

Fig. 5. Decay-associated spectrum for blue excitation (388 nm).

in the S_2 state, while the negative part is the sum of correlated formation of excited state absorption and stimulated emission in the S_1 state.

Hence, this is an IC process from S_2 to S_1. This process is also resolved in the kinetics (data not shown). Moreover, we believe that a very fast EET process is included in the same decay-associated spectrum. We expect this since higher excited excitons have more degrees of freedom to transfer its energy. The fact that we have a limited sensitivity and we use a limited number of fitting parameters makes it likely that we observe IC and EET in a single time component.

The remaining features of the decay-associated spectra are in very good agreement with those obtained for the red excitation channel.

4. Summary

We have measured the excited state dynamics in DiO-PFDTBT dissolved in chloroform. The spectral analysis is based on decay-associated spectra obtained by global fitting of transient absorption spectra. The initial dynamics following optical excitation is seen to be dependent on the excitation wavelength, while the long timescale dynamics is qualitatively the same. Exciting the S_1 charge transfer state results in excitation energy transfer, followed by the formation of a stabilized lowest excited state, having a long radiative lifetime. Exciting the π-conjugated S_2 state leads to ultrafast internal conversion down to the S_1 charge transfer state, followed by dynamics corresponding to that observed when exciting the charge transfer state directly.

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