Ultrafast broadband laser spectroscopy reveals energy and charge transfer in novel donor-acceptor triads for photovoltaic applications

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Abstract. Triggered by the quest for new organic materials and micro-structures for photovoltaic applications, a novel class of donor-acceptor-donor (DAD) triads extended with siloxane chains has been synthesized in our labs. Because of the siloxane chains, the molecules self-organize into a smectic liquid crystal phase, resulting in a stacking of the DAD cores. We report here a preliminary study of the ultrafast dynamics of energy and charge transfer studied by femtosecond broadband transient absorption experiments on isolated triads in chloroform.

1. Introduction
Solar cells made of organic broadband absorbing materials are coming of age, with the highest power conversion efficiency exceeding 7% [1]. Research is very active both with regard to the development of new electron donor D and acceptor A molecules featuring high absorption cross sections and improved frontier orbital properties [2] and with respect to the mesoscopic organization of D and A for optimized charge separation and collection.

Donor-acceptor dyads or triads exhibit very fast and efficient formation of intramolecular charge transfer (CT) states [3, 4], unlike polymer blends where excitons must be transported to the heterointerface before the CT is formed. Arranging the DA or DAD molecules in a liquid crystalline phase [5] is promising in view of improved charge mobility and collection efficiencies. In this context, a novel class of donor-acceptor-donor (DAD) molecules, made of thiophene-based donors and a perylenediimide (PID) acceptor, has been synthesized in our labs. Siloxane chain substitution at both ends of the DAD core are found to strongly stabilize the formation of a smectic liquid crystal phase (SmA type) in a wide temperature range, including room temperature. As a result, an intermolecular DAD core stacking is obtained with the formation of D and A sublayers. The present paper reports a first study of the ultrafast photo-induced energy and charge transfer processes in this DAD molecule in solution, performed by femtosecond broadband transient absorption (TA) laser spectroscopy. This approach not only identifies the nature of the photo-chemically generated species, but also measures the kinetics and the efficiencies of their generation and decay [6].

2. Experiment and methods
Figure 1: Absorption spectra of the donor (D, red) acceptor (A, blue) molecules and of the DAD triad (black). Absorbances per 1mm path length. The 400 nm pump pulses selectively excite the D moiety. The steady-state fluorescence of D (green) has large spectral overlap with the absorbance of A, facilitating resonance energy transfer in DAD.

Figure 1 shows the chemical structure of the DAD triad supplemented with terminal siloxane chains. Details regarding the synthesis and structural characterization will be published elsewhere. Optical excitation occurs on the conjugated parts, either in the thiophene-based donor (D) or the perylenediimide acceptor moiety (A). The absorption spectra of D and of DAD are given in figure 1. Note that the DAD absorption spectrum is in good approximation the sum of the D and A absorbances. Small deviations, as the broadening and peak shift in the low-energy part of DAD are indicative of excitonic interactions.

The CT state formation speed and efficiency has been studied for D and DAD in chloroform by femtosecond transient absorption (TA) spectroscopy. Details of the home-built experimental set-up can be found in [7]. Briefly, 400-nm, 50 fs pulses at 2.5 kHz repetition rate selectively excite the donor molecules. The absorption of A is almost zero at that wavelength (fig. 1). Molecules are pumped through a 0.5 mm quartz capillary so as to refresh the excited sample portion in between to laser shots. Care has been taken to work in a regime of linear dependence of TA signal versus excitation intensity. This means that typically less than 10% of the molecules are excited. Absorption changes are monitored in the range of 420-750 nm using a white-light supercontinuum generated in a 2-mm CaF₂ plate. The instrument response function is 80 fs, given by the FWHM of stimulated Raman scattering.
of the pump pulses in the solvent. After 1h data collection and averaging, the experiment has a sensitivity of $\Delta A_{\text{min}} \approx 5 \times 10^{-5}$.

3. Results and discussion
The present contribution focuses on the differences in excited state lifetime and photochemistry of D when isolated or bound in the DAD triad.

3.1. The donor molecule alone
Figure 2 shows the transient absorption changes of isolated thiophene-based molecules. The overall evolution can be divided in three time regimes: a) excited state equilibration in less than 1 ps, b) excited state decay due to intersystem crossing, on a 0.2-0.3 ns time scale, and c) quasi-stationary triplet-to-ground state difference absorbance spectrum. The latter is best seen in the 1 ns spectrum of fig. 2. With its maximum at 570 nm and relatively broad shape (FWHM > 100 nm) it is qualitatively in good agreement with the triplet-to-ground state difference spectrum determined for similar bi-thiophene compounds [8].

At times earlier than 0.3 ns, the molecule is in excited singlet state $S_1$ (phases a) and b)). This is readily deduced from the negative $\Delta A$ signal at shorter wavelengths with a maximum in the 460-475 nm range. Due to its similarity with the steady-state fluorescence spectrum of D (not shown), it is unambiguously attributed to stimulated emission along the $S_1 \rightarrow S_0$ transition. Bleach of the $S_0 \rightarrow S_1$ ground state absorption transition gives rise to a similar negative signal, but is located at wavelengths shorter than 400 nm (not shown). The positive $\Delta A$ at $\lambda > 520$ nm is then due to excited state absorption (ESA, $S_1 \rightarrow S_n$). During the first picosecond (phase a)), important changes in the spectral shape of ESA are occurring, together with a decay of the peak-like feature at 585 nm. Note that the SE also decays by almost 50% on that time scale. We attribute these changes to intra- and inter-molecular vibrational energy relaxation. Ultrafast planarization of the bi-thiophene rings, as invoked by other authors [8], cannot be excluded. The subsequent $S_1$ decay during phase b) leads to the formation of the triplet-to-ground state difference spectrum. A global multi-exponential fitting procedure yields two excited state decay times of $2.0 \pm 0.5$ ps and $220$ ps, for $S_1$ equilibration and decay respectively. The photochemical reactions of D can thus be summarized as follows

$$S_0 \xrightarrow{hv} S_1^* \xrightarrow{\sim 2 \text{ps}} S_1^{eq} \xrightarrow{220 \text{ps}} T_1$$
Figure 2: Time-resolved transient absorption spectra of the isolated D molecules, displaying intersystem crossing on a 220 ps time scale. The initial sub-ps spectral relaxation is due to excited state structural equilibration of the molecule and the solvent.

3.2. Energy and charge transfer dynamics in the DAD triad

Figure 3A shows the primary dynamics in the first 400 fs after optical excitation of the D moiety in the triads. The initial excited state species is D*AD. The negative signals at λ< 570 nm displays the characteristic modulations of the perylene-diimide (A) absorbance (cf. fig. 1) and is therefore due to bleach of the ground state of A. As the 400 nm pump beam is absorbed by the D but not by A, this indicates that A is excited indirectly through Förster resonant fluorescence energy transfer from D to A, forming the excited state species DA*D. The evolution of ΔA at longer wavelengths is consistent with this process. Indeed, the early 67 fs spectrum bears a lot of similarity of the ESA signal observed for the isolated D (cf. 50-fs spectrum in fig. 2). Spectra at later times indicate additional signals due to stim. emission along the S1→S0 transition in A, most obvious by the negative dips at 576 and 620 nm, and the build-up of A's excited state absorption at 705 nm (cf. fig. 3 b with the steady state fluorescence spectrum of A). These observations are consistent with those reported for a DAD triad with the same A and a different but similar thiophene-based donor \[3\].

The subsequent events related to the DA*D decay are revealed by the evolution of ΔA at longer delay times (fig. 3 B). The ground state bleach and stim. emission signals decay on a 5-10 ps time scale, and new absorption features at 633 and 712 nm are observed. Comparison with literature data \[9, 10\] allows to identify these as the absorption due to the cationic forms of D and the anions of A, meaning that charge transfer (CT) has occurred and the D+A-D species is formed. Additional experiments extending the present probe wavelength range into the near-IR and comparison with electro-absorption spectroscopy confirm these assignments (to be published). The D+A-D species is not stable however. Rather we observe the system returning to its DAD ground state after 200-300 ps. Clearly, the molecular orbital properties and the proximity of D and A make the charge transfer state
unstable, and very fast recombination occurs. This issue will be a major concern for functional materials and thin films when photovoltaic applications are targeted. A detailed quantitative analysis using "global analysis strategies" with multi-exponential fitting of the reaction kinetics yields the following reaction scenario and lifetimes.

\[ \text{DAD} \xrightarrow{hv} D^* \rightarrow DA^* \rightarrow D^+ A^- \xrightarrow{46\,ps} \text{DAD} \]

The charge transfer process DA* \rightarrow D+A-D seems to involve two different reaction times (1.2 and 4.4 ps) possibly related to structural heterogeneity of the triads. In addition, the decay of A's SE is complete, indicating that the charge transfer build-up occurs with close to 100% quantum efficiency. This is not the case for the initial energy transfer process. As a matter of fact, recent time-resolved fluorescence experiments indicate that \( \approx 10\% \) of the triads are non-reactive, as they display the characteristic fluorescence of isolated donor molecules.

**Figure 3.** Time-resolved transient absorption spectra of the DAD triad. **Left:** The first 300 fs are characterized by excitation of the A via resonant energy transfer from D*. Spectra show the progressive build-up of A's ground state bleach and stim. emission (<600 nm) and the crossover from excited state absorption due to D* (160 fs) to the one of A* (410 fs) at longer wavelengths. **Right:** Decay of A's SE and formation of D+ and A- with the absorption bands at 633 and 712 nm (at 10 ps).

4. **Conclusions**

Femtosecond transient absorption has been used to reveal the ultrafast photochemistry at work in the molecular building blocks of novel photosensitive materials. When combined with ultrafast fluorescence techniques both the reaction kinetics and the quantum efficiencies of each reaction step can be determined. For the present DAD triad, we show that the large majority of the thiophene-based donor transfers its charge within less than 5 ps to the PDI acceptor. The data show that the non-radiative energy occurring on a 120 fs time scale is not detrimental to the charge transfer in this particular system, indicating that the electron transfer occurs between the HOMO levels of D and A.

Further studies will address the challenge of stabilizing the CT state, which in the isolated triads has only a very short lifetime (46 ps). Preliminary experiments on thin films of DAD indeed show a prolonged CT lifetime, most probably due to interchain delocalization. The application of an external bias should further contribute to reduction of CT recombination. The results of the photovoltaic property investigation of these novel DAD triads in their smectic phase will be reported in a subsequent paper.
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