

Ultrafast energy and charge transfer processes in a flexible molecular triad designed for organic photovoltaics

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Abstract: A detailed spectro-temporal analysis of the ultrafast transient absorption and fluorescence signals allows deciphering multiple energy and charge transfer processes in a light-harvesting molecular triad designed as photo-sensitizing unit featuring a novel BODIPY compound.

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1. Introduction

Replacing the standard electron-donating P3HT polymer in organic solar cells made of blends with the acceptor PCBM is a very active field in organic material chemistry, with the specific aim to harvest photons in the red or near-IR part of the spectrum. BODIPY (boron-dipyrromethene) is a widely studied dye with extinction coefficients larger than $\epsilon=100'000 \text{ M}^{-1}\text{cm}^{-1}$, which offers a versatile chemical platform for tuning of the optical properties. A solar cell based on a thienyl-BODIPY/PCBM blend was recently reported with a remarkable 4.7 % power conversion efficiency[1]. Here, we study a BODIPY dye conjugated with styryl and ethyleneoxide groups that shift the absorption spectrum into the 600-680 nm range (fig.1, BOD). Together with a diketopyrrolopyrrole (DPP) and a triphenylamine (TPA) unit a molecular triad is formed whose extinction coefficient fully spans the 300 to 700 nm range with ϵ peak values well above $120'000 \text{ M}^{-1}\text{cm}^{-1}$. Both DPP and TPA were expected to act as ancillary light-harvesting components enabling energy transfer towards BOD. The aim of our combined fluorescence and transient absorption (TA) studies is to pinpoint the ultrafast light-induced processes in terms of time scales and efficiency.

2. Results

Fig. 1 shows the ground state absorption spectra and extinction coefficients of the triad (black line) and two isolated reference compounds BOD-TPA (red line) and TPA-DPP-TPA (blue line) in THF. 1. The DPP di-substituted with TPA groups mimics best the molecular orbitals of the DPP moiety in the triad. TPA has only negligible absorption at wavelengths longer than 380 nm (not shown). The triad spectrum matches well the algebraic sum of both DPP and BOD (pink line), indicating small electronic coupling between DPP and BOD.

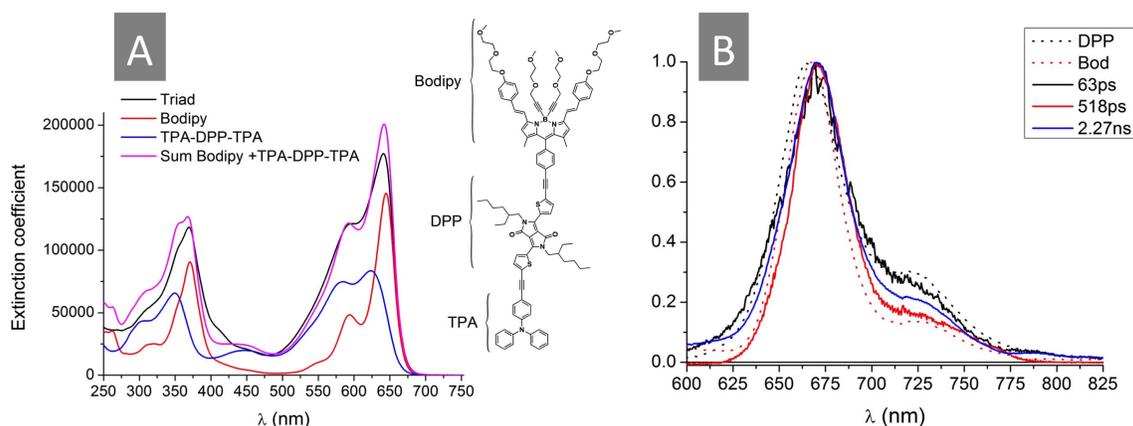


Fig. 1 (A) Extinction coefficients of the isolated reference compounds BOD-TPA, TPA-DPP-TPA, and of the triad in THF. The sum of the isolated compound spectra almost exactly matches the triad absorbance, indicating negligible electronic coupling. TPA absorbs at $\lambda < 380 \text{ nm}$. (B) Time-integrated fluorescence of the BOD-TPA and TPA-DPP-TPA in THF (dotted lines), and the DAS of the three-exponential emission decay of the triad. See text for the assignment of the quenching mechanisms. The spectral signature of radical anions and cations were characterised by spectrovoltametry on the isolated BOD-TPA, TPA-DPP-TPA and TPA compounds and on the full triad. Since TPA is known to have a smaller redox

potential than both DPP and BOD, we expect to observe the DPP and BOD anions and TPA cations in the photo-reaction of the triad. The TPA cation has a broad peak centered at 730 nm, the BOD anion shows a main peak centered at 595 nm and a smaller peak at 455 nm, the DPP anion peak is centered at 753 nm (data not shown).

Upon excitation at 320 nm, the time-resolved fluorescence, measured by a streak camera with 10 ps resolution, displays a monoexponential decay for the separated components TPA, TPA-DPP-TPA and BOD-TPA, of 1.5, 2.2 and 4.5 ns, respectively. In contrast, the triad shows a three-exponential decay in the red part of the spectrum, where the fluorescence of DPP and BOD almost perfectly overlay, apart from a low-energy shoulder that allows to discriminate the two (fig. 1B). A detailed analysis of the decay-associated spectra (DAS) shows that approximately 70% of excited DPP* quenches in 63 ps, 80% of BOD* in 0.5 ns and the remainder of both species fluoresce with a lifetime close to the isolated unquenched reference molecules. This multi-exponential decay is a clear indication for structural heterogeneity of the triads, leading to these quenched and unquenched sub-populations.

A global fit with five lifetimes allows to cast the femtosecond TA data (fig. 2A) into a small set of DAS (not shown). These can be reconstituted by linear combinations of the excited state and radical ion-associated difference spectra of all three molecular components (e.g. fig. 2B). This approach reveals up to three DPP* and BOD* subpopulations, assigned to distinct molecular configurations, and reacting on separate time scales. TPA* exhibits sub-200fs energy transfer onto DPP* (not shown). A 6.3 ps energy transfer process from DPP* to BOD* is revealed (fig. 2B), a DPP* quenching process that remained unresolved in the streak camera experiments. Most importantly, the 60 ps quenching of DPP* is due to the formation of a (TPA+/DPP-) intramolecular charge transfer state that recombines within 0.5 ns (broad band at 710-800 nm in the 106ps spectrum, fig. 2 A). The 0.5 ns BOD* quenching does not lead to a detectable photoproduct and is thus assigned to internal conversion or intersystem crossing [2, 3].

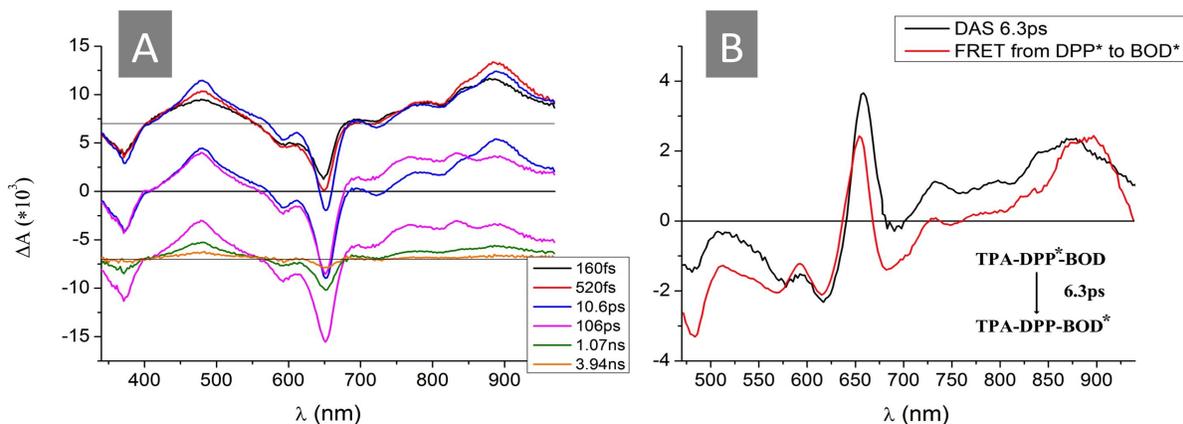


Fig. 2 (A) Time-resolved TA spectra of the TPA-DPP-BOD triad in THF display BOD bleach (375 and 645 nm), BOD* ESA at 483 nm and SE at 670 and 725 nm. DPP's bleach overlays with the one of BOD in the 500-620 nm range. The ESA at > 850 nm is dominated by DPP* plus a small BOD* contribution. The top panel displays vibrational relaxation in S_1 of DPP* and BOD* in < 500 fs. The TPA*/DPP* absorption and a mixture of BOD* SE are responsible for the modulated spectral feature in the 700-850 nm at 106 ps (middle panel). The CT state and the remaining non-reactive DPP* and BOD* decay on a ns time scale (bottom panel). (B) The 6.3 ps DAS spectrum (black) is well reproduced by the difference $\Delta A(\text{DPP}^*) - \Delta A(\text{BOD}^*)$, separately determined on the reference compounds. Most prominent is the rise of BOD bleach at 655 nm and BOD* ESA at 483 nm (neg. amplitude), and the ESA decay of DPP*. This is clear evidence for DPP* > BOD* resonance energy transfer.

Conclusions

Despite multiple conformations and reactions pathways the flexible TPA-DPP-BOD triad shows very efficient photo-sensitizing properties featuring sub-10ps energy transfer to BOD and ≈ 60 ps formation of a CT state. When blended with PCBM, efficient charge transfer from BOD and DPP is expected to occur on a sub-100 ps time scale, as observed for other BOD [2] and DPP [4] derivatives. CT formation would then also quench the species involved in the longer-lived non-reactive pathways (≥ 0.5 ns) reported here for the isolated triad. Further work is in progress.

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