

Ultrafast Charge Transfer in Solid-State Films of Pristine Cyanine Borate and Blends with Fullerene

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Electronic Supplementary Information (ESI)

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Analysis of transient absorption data

The recording of complete spectra as a function of time brings about tremendous advantages if the kinetic investigation includes the determination of the mechanism of a reaction together with the determination of the corresponding rate constants. Ultrafast transient absorption data were then collected in a pump-probe scheme using white-light continuum probe pulses covering the 420-720 nm wavelength domain. The excitation wavelength was set at 530 nm with an energy fluence of $45 \mu\text{J}/\text{cm}^2$. Taking into account light intensity losses due to reflection on the glass window of the sample chamber, the pump fluence at the sample was estimated as being at most of the order of $40 \mu\text{J}/\text{cm}^2$. This light intensity was chosen to ensure satisfying signal-to-noise ratios for measurements involving blends. No fluence effect was observed on the recorded kinetics (Figure S1). Time-resolved spectroscopy of pristine Cy3-B films, in particular, yielded identical dynamics for three different pump fluences applied onto the sample (Figure S1 a).

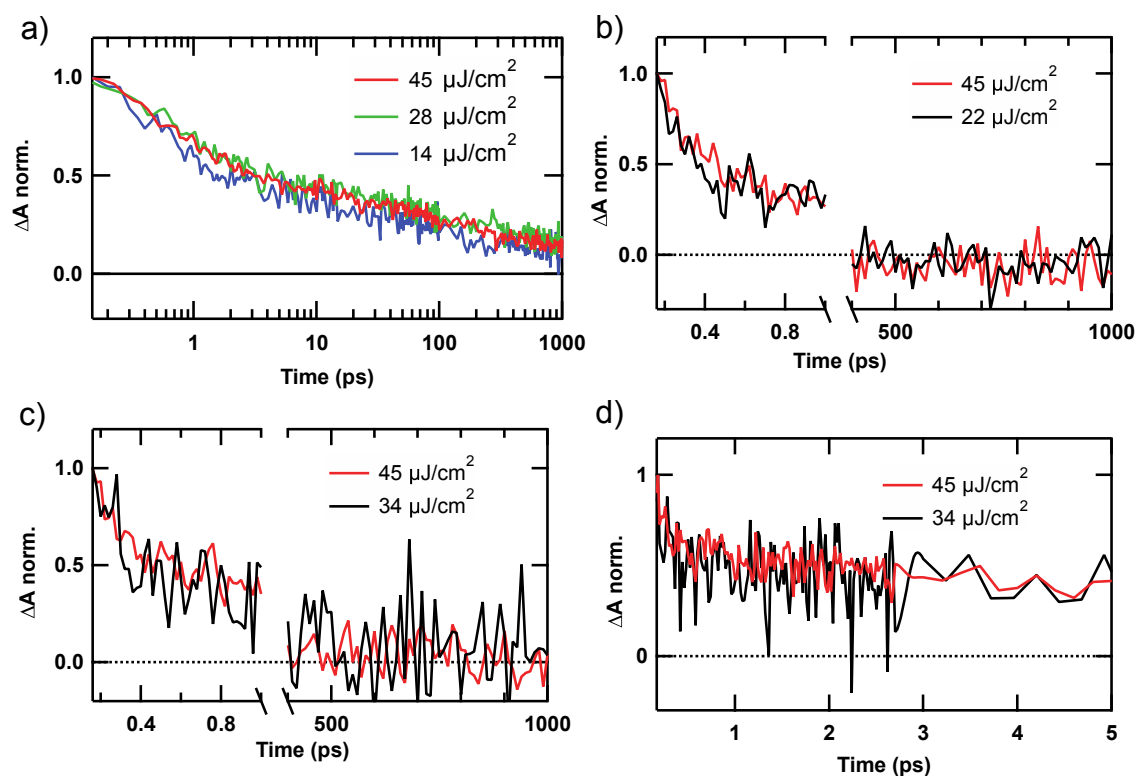


Figure S1. Transient absorption dynamics at 470 nm probe after 530 nm excitation for the various investigated samples at various fluences. a) Pristine Cy3-B, and PCBM: Cy3-B blends b) 0.44:1, c) 6.6:1 and d) 15.5:1.

Overlapping spectral features and multiphasic kinetic processes render the analysis of transient absorption dynamics quite difficult. Global analysis of multiwavelength kinetic data is a specialized technique to fit experimental measurements to one specified model.¹ There are several benefits in measuring and analyzing multiwavelength data. The more prominent include the fact that there is no need to determine a specific good wavelength to monitor the dynamics of a particular species. Moreover, the availability of resulting absorption spectra allows for the identification of intermediates and the determination of deconvoluted kinetic parameters.

The time-dependence of transient absorption at each probe wavelength between 420 nm and 720 nm was carefully corrected for spectral chirp (i.e. time zero) and background noise, yielding a time resolution ≤ 160 fs throughout the whole spectral range. The time-dependence of transient absorption recorded simultaneously for 60 different wavelengths between 420 and 720 nm (5 nm spacing) was submitted to a multivariate global analysis to disentangle the various photophysical processes. The global analysis procedure used a set of three exponentials:

$$\Delta A(t) = A_1 \cdot e^{-\frac{t}{\tau_1}} + A_2 \cdot e^{-\frac{t}{\tau_2}} + A_3 \cdot e^{-\frac{t}{\tau_3}}$$

where $\Delta A(t)$ is the time-dependent transient absorption, τ_n is the time constant and A_n the amplitude associated to the process n.

The time constants were linked for each analyzed sample, without any additional constraint. No fixed parameter was imposed on the amplitudes. The fitting procedure was iterated until the standard deviation (2σ) of the two fastest time constants was $\leq 10\%$ with 20'000 fit points. The uncertainties are reported in Table 1. The largest time constant resulting from the global analysis yielded a value > 1 ns, exceeding the longest time delay experimentally accessible with our femtosecond instrument. As this extrapolated time constant could be vitiated by a large uncertainty, it is reported only as being > 1 ns, without further accuracy. Associated spectra, such as the one presented in Figure 3b, are obtained by plotting the fitted amplitudes (or pre-exponential factors) as a function of probe wavelength.

Blend morphology

AFM pictures shown in Figure S2 were obtained with a Mobile S NanoSurf instrument.

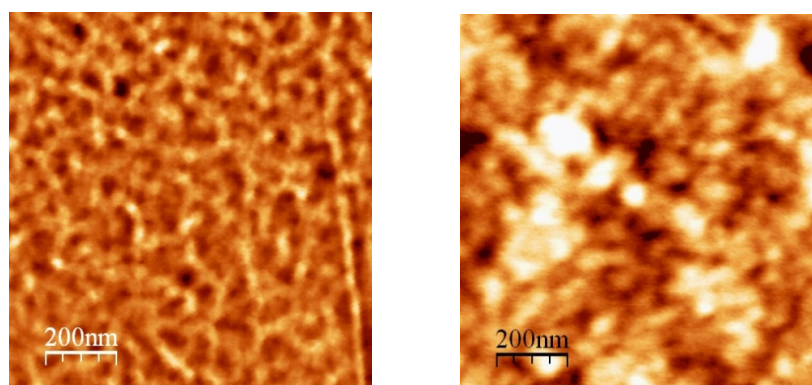


Figure S2. AFM image of a PCBM:cy3-B blend film (1:1 molecular weight percent). Left: AFM phase contrast image of the sample. Right: AFM topography image obtained after dissolving the dye surface domains.

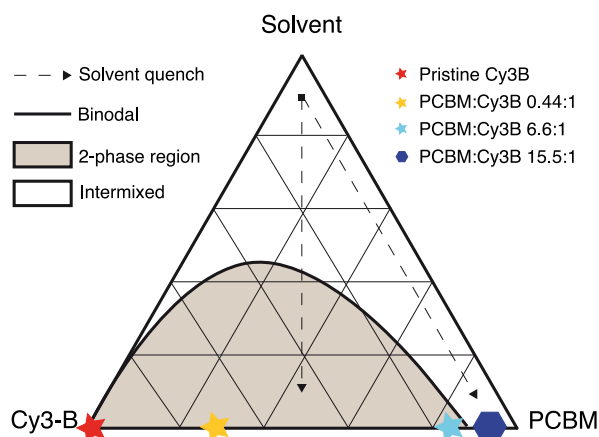


Figure S3. Schematic phase diagram of PCBM: Cy3B blends. Upon solvent evaporation, the blend is either fully intermixed (high PCBM concentrations) or segregates into two phases (low dye concentrations).

Transient absorption data

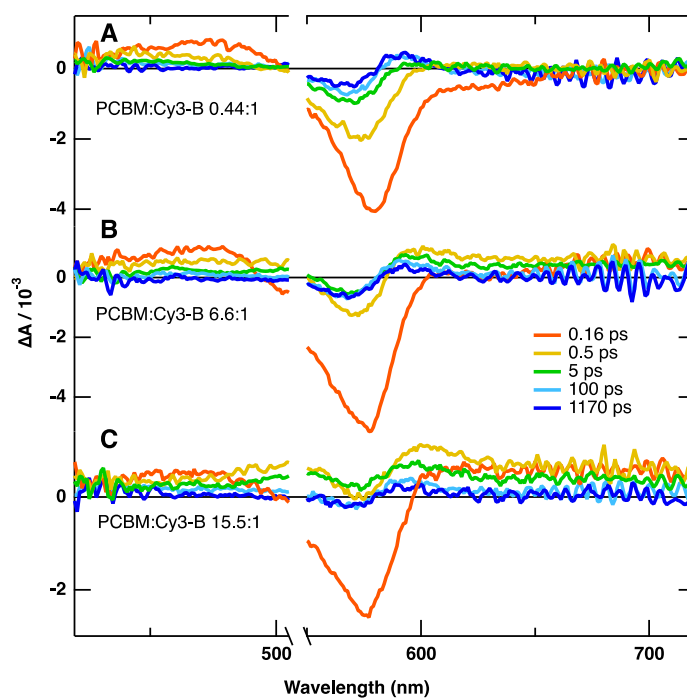


Figure S4. Transient absorption spectra at various time delays after 530 nm excitation for the various PCBM: Cy3B blends.

Reference

1. I. H. M. van Stokkum, D. S. Larsen, and R. van Grondelle, Global and target analysis of time resolved spectra. *Biochimica et Biophysica Acta (BBA) - Bioenergetics*, **2004**, 1657, 82–104.