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Ultrafast charge photogeneration dynamics in
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- *Supplementary Materials* -

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1. AFM microscopy characterization of samples

Characterization of the sample surfaces was performed by Tapping mode AFM microscopy. The AFM images were recorded by NanoScope MultiMode Atomic Force Microscope (Digital Instruments) with spatial resolution of 4 nm. Typical surface scans for the samples used in optical studies are presented Fig.A1.

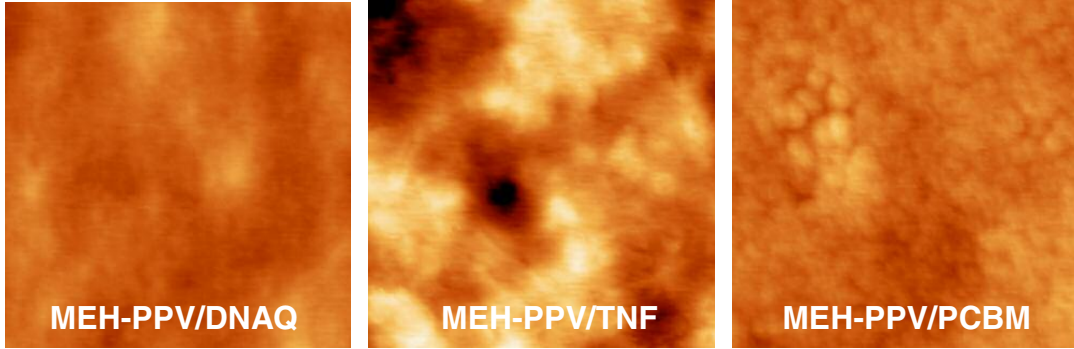


Figure A1. 500x500 nm AFM amplitude images of the studied films. Full color range corresponds to 12 nm in the Z-direction.

2. Data fitting and analysis

The data of the polarization-selective pump-probe experiments were fitted with the following generic model. The PIA signal amplitude was considered to be proportional to the overall concentration of charges N (which also accounts for possible variation in the IR absorption cross-section). The concentration was partitioned between two sub-ensembles N' and N''

$$N(t) = N'(t) + N''(t) \quad (\text{A1})$$

Time evolution of the first sub-ensemble was modeled as a sum of exponential decays to represent the charge concentration and anisotropy, respectively:

$$N'(t) = A_1 \cdot \exp\left(-\frac{t}{T_1}\right) + A_2 \cdot \exp\left(-\frac{t}{T_2}\right) + A_3 \cdot \exp\left(-\frac{t}{T_3}\right) \quad (\text{A2})$$

$$R'(t) = r_0 \left[a_1 \exp\left(-\frac{t}{\tau_1}\right) + (1 - a_1) \exp\left(-\frac{t}{\tau_2}\right) \right] \quad (\text{A3})$$

where T_i stands for the population relaxation time of the component with the amplitude A_i ($A_3 = 1 - A_1 - A_2$), τ_i is the anisotropy decay time weighted with the amplitude a_i , and r_0 is the initial anisotropy value.

The second ensemble was considered long-lived (at the time scale of our experiment) and possessing a constant anisotropy

$$N''(t) = A_0'' \quad (\text{A4})$$

$$R''(t) = r_0'' \quad (\text{A5})$$

The amplitudes of the parallel $\Delta T_{\parallel}(t)$ and perpendicular $\Delta T_{\perp}(t)$ polarization transients can now be expressed as:

$$\Delta T_{\parallel}(t) = A \cdot \left\{ N'(t) \cdot [1 + 2R'(t)] + N''(t) \cdot [1 + 2R''(t)] \right\} \quad (\text{A6})$$

$$\Delta T_{\perp}(t) = A \cdot \left\{ N'(t) \cdot [1 - R'(t)] + N''(t) \cdot [1 - R''(t)] \right\} \quad (\text{A7})$$

where A is a normalization coefficient. Making use of Eqs.2 and 3, one can derive the following expressions for the isotropic signal and transient anisotropy:

$$\Delta T_{Iso}(t) = \frac{\Delta T_{\parallel}(t) + 2 \cdot \Delta T_{\perp}(t)}{3} = A \cdot [N'(t) + N''(t)] \quad (\text{A8})$$

$$r(t) = \frac{\Delta T_{\parallel}(t) - \Delta T_{\perp}(t)}{3 \cdot \Delta T_{Iso}(t)} = \frac{N'(t) \cdot R'(t) + N''(t) \cdot R''(t)}{N'(t) + N''(t)} \quad (\text{A9})$$

As can be seen from Eq.A8, the isotropic transient is free of contamination by reorientational dynamics, i.e. directly proportional to the charge concentration. In contrast, the anisotropy calculated according to Eq.3, is presented by a mixture of purely reorientational and

concentration-related contributions. This reflects the fact that the anisotropy is not an additive quantity and therefore can not be analyzed as such. However, if one of the sub-ensembles dominates (for instance, $N'(t) \gg N''(t)$), the concentration contribution drops out:

$$r(t) = R'(t) \tag{A10}$$

Nevertheless, under the circumstances the anisotropy dynamics should be analyzed only together with the population kinetics.

Following this route, we fitted simultaneously the transients measured with parallel and perpendicular polarization, and the anisotropy transients. For that, the expressions given by Eqs.A6 and A7 were convoluted with the instrument response function (a Gaussian with a 100 fs FWHM). We found that inclusion of anisotropy into the fitting routine enhances greatly the accuracy at long times, i.e. where the PIA signals are relatively weak. The results of such a global fit procedure are depicted in Figs.A2 and A3 while the fit parameters are presented in Table 1. As can be concluded from these figures, the model reproduces all essential features of the experimental data. The anisotropy values at long times presented in Fig.5, are averaged over 5 adjacent points.

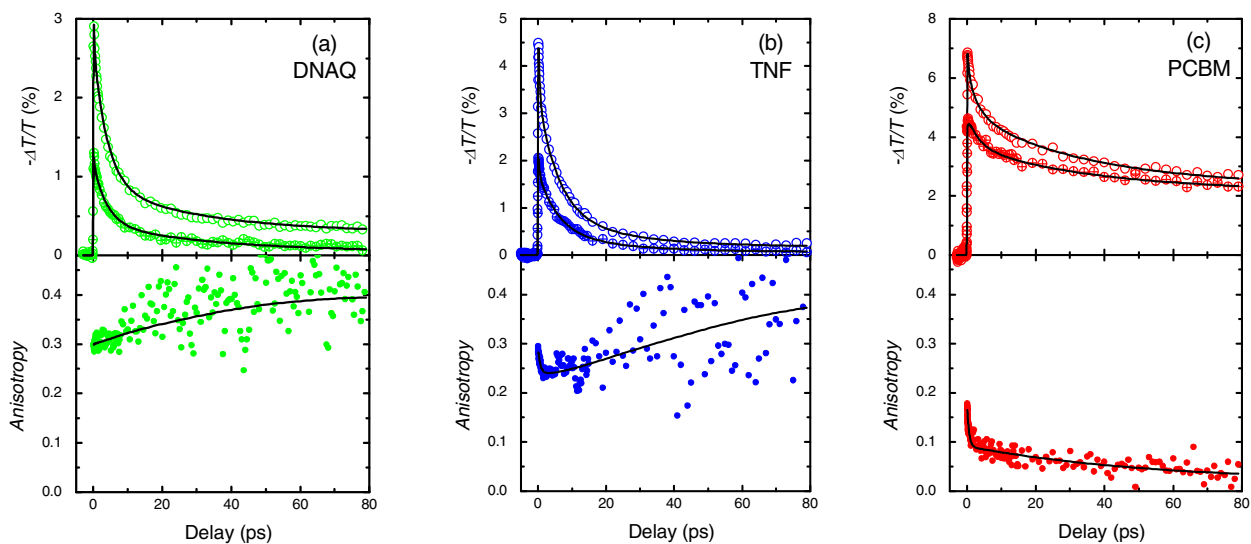


Figure A2. Top panels: absorption transients measured in parallel (open circles) and perpendicular (crossed circles) polarizations between the pump and probe beams in MEH-PPV/DNAQ (a) and MEH-PPV/TNF (b) CTCs excited at 650 nm, and in MEH-PPV/PCBM (c) excited at 540 nm. Bottom panels: corresponding transient anisotropies. Symbols and solid curves show experimental data points and best fits, respectively.

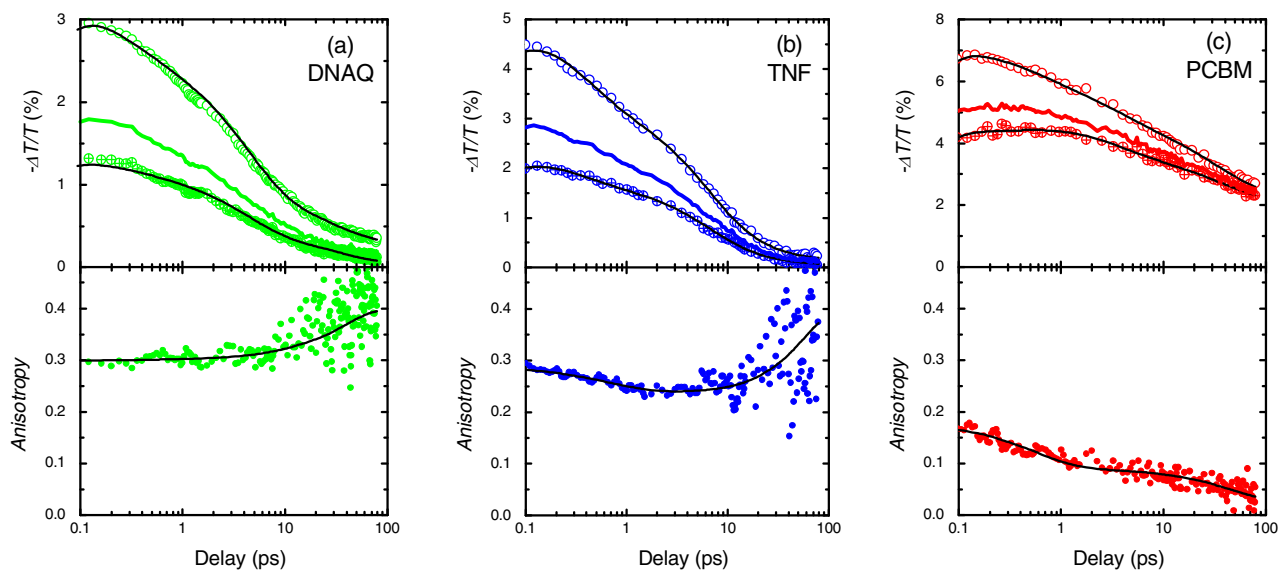


Figure A3. The same as Fig.A2 but presented at the logarithmic time scale. Thick solid curves on the top plots show the isotropic data.