Supporting Information

Dynamics in Electronically Excited States of

Diketopyrrolopyrrole - Thiophene Conjugated Polymer Thin Films

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Data sets of the tr-2PPE measurements

Figures S1-S4 show the complete data of the time resolved photoemission measurements. For a better overview, a moving average over 20 points is applied along the energy axis. From these data cuts at certain energies representing the four states identified are shown in figures 4 and 5 in the main text. Only a smooth decrease of the photoemission intensities at all kinetic energies is observed. With increasing delay no increase from the previous decays can be seen. This implies that the states observed are not fed from each other. Photoemission intensity is observed before time zero. This intensity belongs either to a 2ppe signal from the UV pulse or states with a lifetime longer than the inverse pulse repetition rate of the laser, or longer than 250µs. For the present ultrafast dynamics this intensity represents a background and is subtracted from the data. To clarify the origin of this long-lived signal a new experimental set-up is required with an independent pumping laser, because the temporal delay between pump and probe has to be extended by more than 250 µs which is not possible with an optical delay.

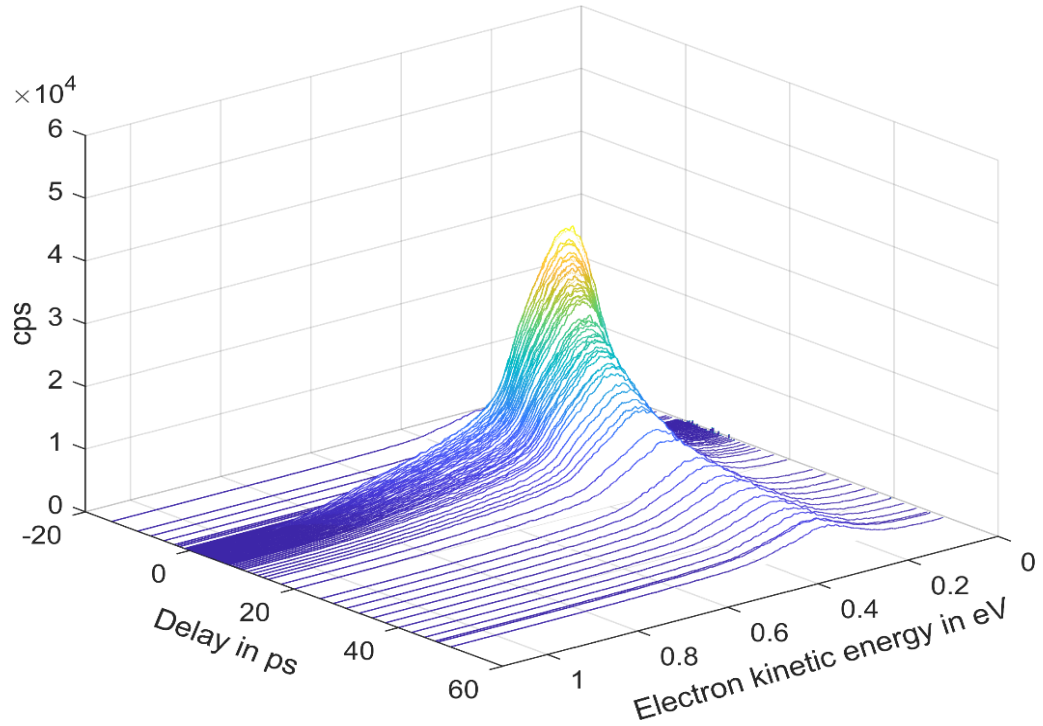

Figure S1 Data set of the time resolved two photon photoemission at PDPP4T in the as-prepared case

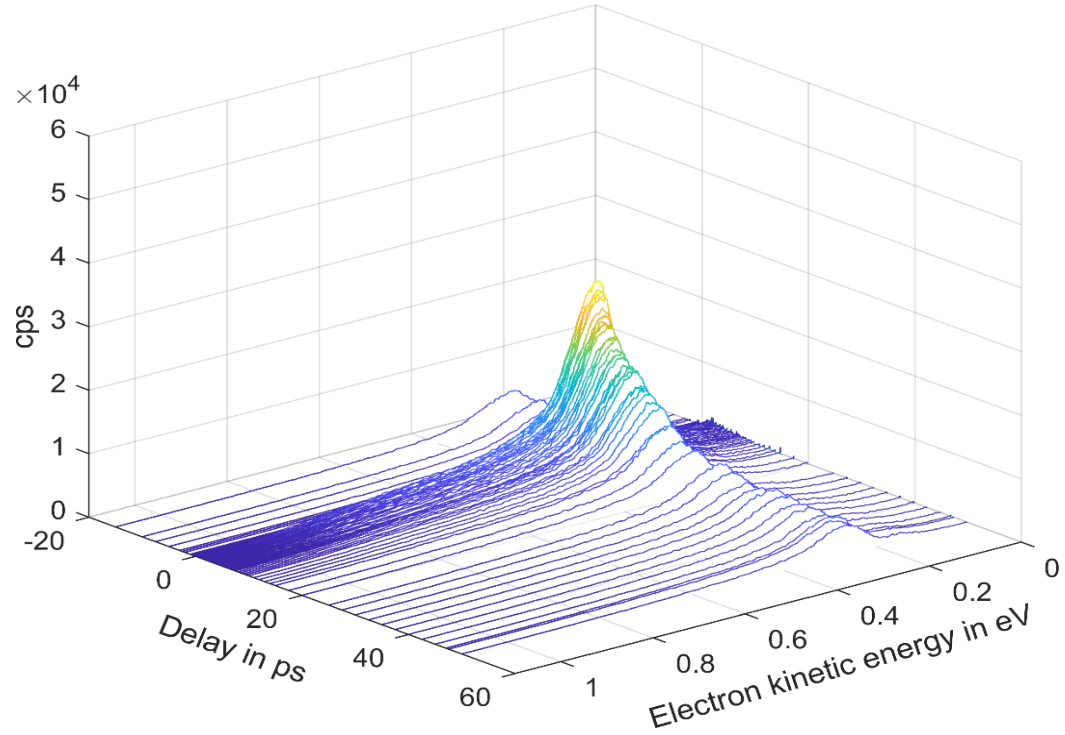

Figure S2 Data set of the time resolved two photon photoemission at PDPP4T in the annealed case

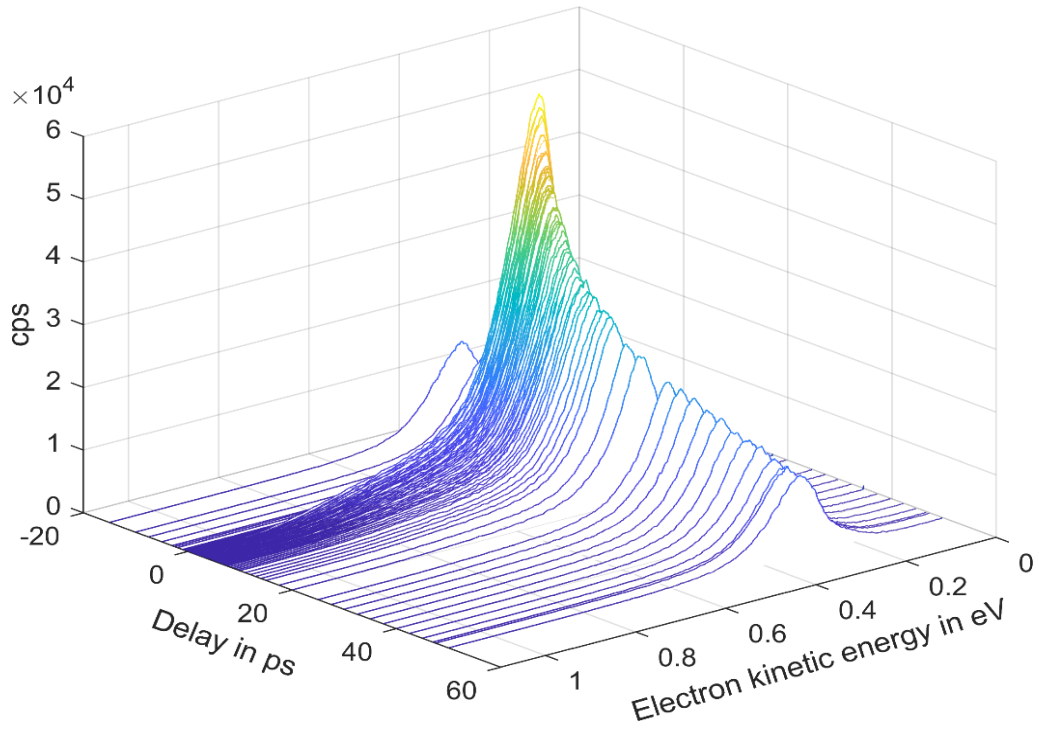

Figure S3 Data set of the time resolved two photon photoemission at PDPPTTT in the as-prepared case

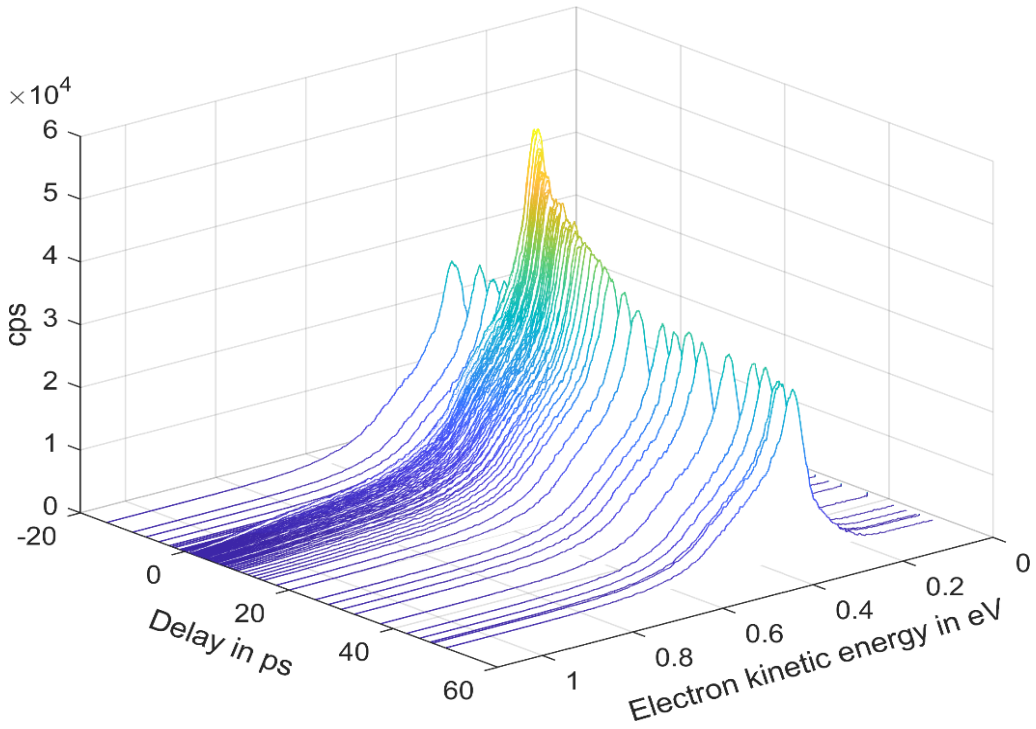

Figure S4 Data set of the time resolved two photon photoemission at PDPPTTT in the annealed case

Pulse characterization with the cross-correlation:

The cross correlation between the Ti:sapphire fundamental (800 nm) and its third harmonic (266 nm) was measured in a BBO crystal at the sample equivalence image outside the vacuum, see Fig. S5. The FWHM of a Gaussian fit yields a correlation width of 141fs. With the pulse duration of the fundamental of 30fs a pulse duration of 137fs is derived for the third harmonic. This comparatively long pulse duration is caused by the dispersion in the doubling and tripling crystals which has not been compensated by re-compressing the pulses after each step.

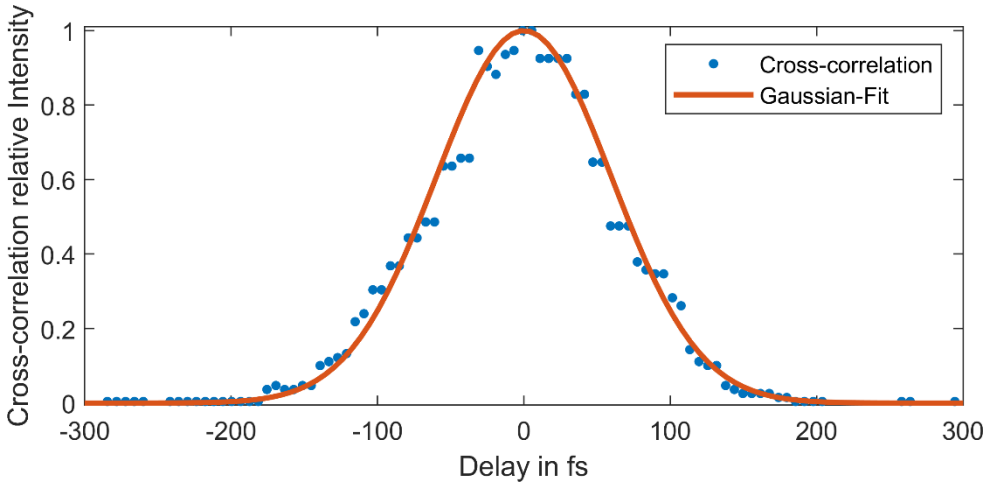

Figure S5 Cross-correlation of the fundamental and third harmonic, the correlation width is 141fs.

A longer-range cross-correlation (fig. S6) exposes a pre-pulse with an intensity of $I_p = I_0 /12.5$ at about -1860fs before the maximum of the main pulse. The cause of the pre-pulse could not be finally clarified, we assume a back reflection of an optic (thin film polarizer) or a mismatch of the third order dispersion in the chirped pulse amplifier.

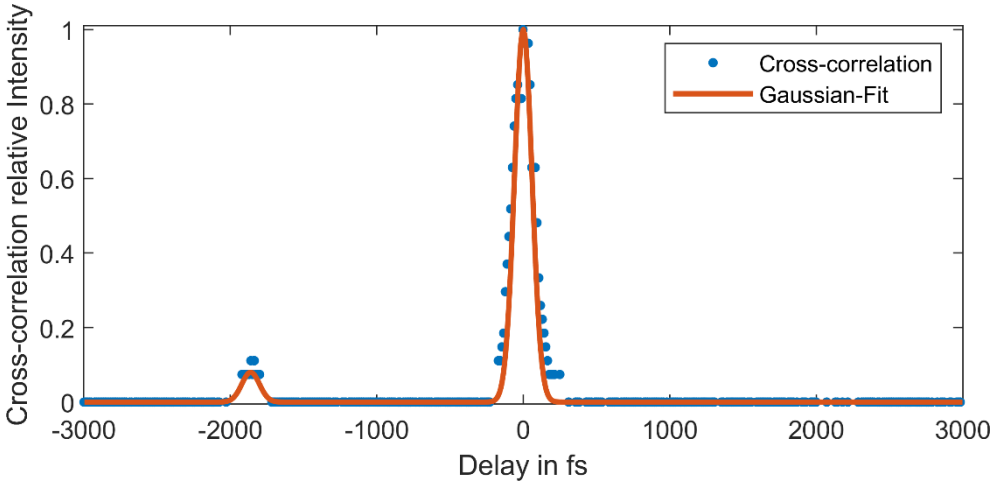

Figure S6 Cross-correlation of the fundamental and third harmonic on a longer timescale.

Detailed representation around the temporal zero

Figure S7 shows an enlarged version around time zero between pump and probe pulse. The rise of the 2PPE signal is well described by the cross-correlation between pump and probe pulses. Between -2 and 0ps the pre-pulse mentioned in the text and its action on the signal can be seen. The blue line is a fit to the data including this cross correlation signal.

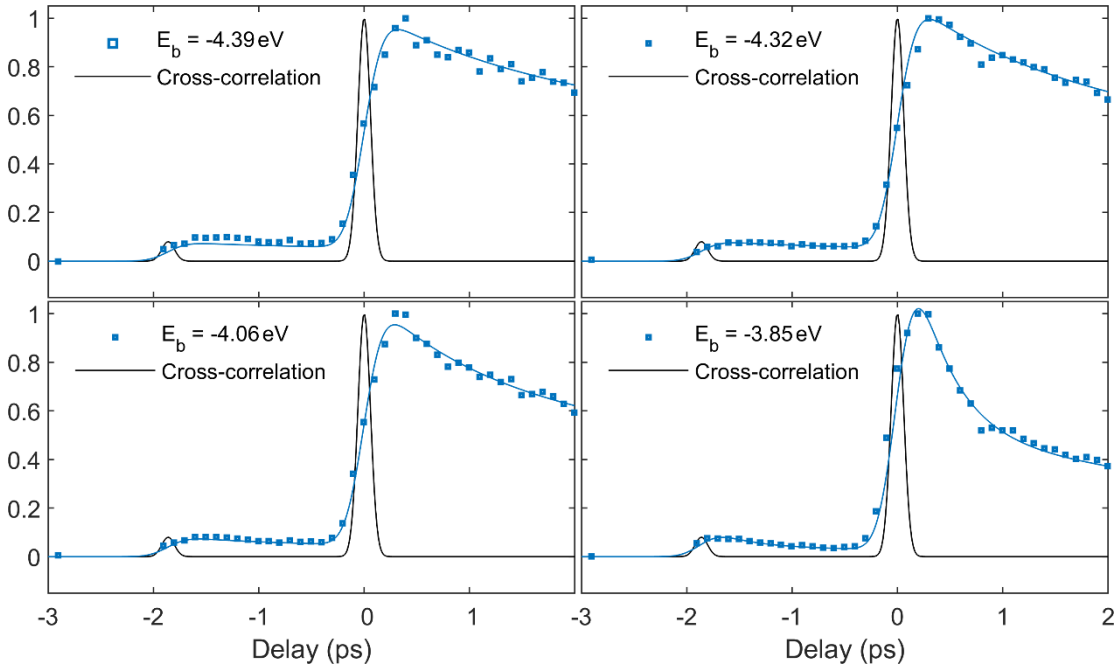

Figure S7 An exemplary representation of the data around the time origin (blue dots and line) between -3 and 2ps at PDPPTTT as-prepared including the cross correlation (black line) of the laser pulses.