Conjugated polymers find rapidly growing application in electroluminescent displays and are extensively studied for use in photovoltaics and laser diodes. For a wide range of conjugated materials ultrafast pump-probe experiments have revealed the excited state dynamics of singlet and triplet excitons as well as positively and negatively charged polarons. Charge carriers play a key role in all the above mentioned applications. However, there is yet no clear picture of the mechanisms which lead to their generation.

Photo-current excitation cross-correlation measurement on methyl-substituted ladder-type poly(para-phenyl (m-LPPP)), a prototypical conjugated polymer with very appealing properties for the above mentioned applications, have suggested that charge carrier generation occurs preferentially from higher lying states during energy migration.

Our approach to examining this mechanism consists of an innovative modification of the ultrafast time-resolved pump-probe technique, namely pump-push-probe (P3). In this technique the S1 state created by the pump pulse is re-excited by a second pulse ("push") to a higher lying state S3 and a third (probe) pulse measures the sample differential transmission. This method has previously been used with push and probe at the same wavelengths, so that only the dynamics of the S1-S3 absorption recovery could be observed. The broad band probe employed in the present work allows detection of the spectral signatures of the states created by the push carriers. The initial positive signal is again a signature of the depletion of the S1 population, but a significant portion of the S1 population recombines on a much longer time scale, suggesting the presence of a secondary process initiated by the push pulse.

Fig. 2 displays the 3P dynamics of the photoinduced absorption at 680 nm, containing contributions from the singlet exciton and the charge carriers. The initial positive signal is again a signature of the depletion of the S1 population. However the signal changes sign reaching a negative peak after 1 ps following push excitation, pointing out the formation of charged states. Both the magnitude of the absorption at 680 nm and that of the quenching at 490 nm are strongly dependent on the pump-push delays (see also inset of Fig. 3). This proves that the charge generation efficiency is significantly higher in the early stages after photoexcitation, which provides convincing evidence for dissociation of migrating singlet excitons at quenching centers. Experiments with 10-fs time resolution using push and probe pulses from a visible optical parametric amplifier are in progress.