Below bandgap excitation of polaron pairs in P3HT

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To further improve organic photovoltaics, it is crucial to understand the generation and decay of photoexcited charge species. In P3HT-based organic photovoltaics, the formation of polaron pairs and their eventual decay significantly impacts the overall efficiency of photovoltaic devices, such as solar cells [1]. We have conducted time-resolved femtosecond pump-probe spectroscopy on neat P3HT samples and P3HT-based diode-like devices. The schematic in figure 1 shows our experimental design. Different experiments were performed with varying pump and probe wavelengths. In this study, we have observed that photoexcitation with below-bandgap wavelengths provides a direct and efficient pathway for generating polaron pairs. This effect was observed in both neat P3HT thin films and P3HT-based diode configurations. Alongside the rapid polaron pair (PP) dynamics, we have also observed a longer-lived species, which we tentatively attribute to delocalized PP states. To investigate this further, we have analyzed PP dynamics under a static external electric field with reverse and forward bias at varying excitation fluences [2]. Our results indicate that the bimolecular annihilation of delocalized PPs competes with a recombination process. Additionally, when the annihilation process saturates at high fluences, the external electric field accelerates the recombination rate. We present these results both in a talk and as a poster.



Figure 1: Schematic representation of pump-probe experiments in (a) neat P3HT Film and (b) P3HT diode

- (1) Debkumar Rana, Patrice Donfack, Vladislav Jovanov, Veit Wagner, Arnulf Materny, *Phys. Chem. Chem. Phys.*, 2019, *21*, 21236-21248
- (2) Debkumar Rana, Ayush Kant Ranga, Arnulf Materny, *Phys. Chem. Chem. Phys.*, 2025, 27, 4475-4486