MAR14-2013-020196

Abstract for an Invited Paper
for the MAR14 Meeting of
the American Physical Society

Direct observation of ultrafast long-range charge separation at polymer:fullerene heterojunctions

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In polymeric semiconductors, charge carriers are polarons, which means that the excess charge deforms the molecular structure of the polymer chain that hosts it. This effect results in distinctive signatures in the vibrational modes of the polymer. We probe polaron photogeneration dynamics at polymer:fullerene heterojunctions by monitoring its time-resolved resonance-Raman spectrum following ultrafast photoexcitation. We conclude that polarons emerge within 200 fs, which is nearly two orders of magnitude faster than exciton localisation in the neat polymer film. Surprisingly, further vibrational evolution on $\lesssim$ 50-ps timescales is modest, indicating that the polymer conformation hosting nascent polarons is not significantly different from that in equilibrium. This suggests that charges are free from their mutual Coulomb potential, under which vibrational dynamics would report charge-pair relaxation. Our work addresses current debates on the photocarrier generation mechanism at organic semiconductor heterojunctions, and is, to our knowledge, the first direct probe of molecular conformation dynamics during this fundamentally important process in these materials.