

Effects of Controlled Backbone Planarity on Exciton Manifold and Polaron Generation in Polythiophene Crystalline Domains

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Conjugated polymers (CPs) are one of the most important classes of organic materials applicable to a wide range of optoelectronic devices, such as field-effect transistors (FETs), solar cells, and light-emitting diodes (LEDs).^[1] Their microstructures encompass various degrees of crystallinity, from amorphous to well-ordered crystalline domains, which pose energetic heterogeneity to the neutral and charged species generated upon photoexcitation. Based on the experimental consensus that polymers with large crystalline domains often transport excitons and polarons better than amorphous structures, persistent efforts have been put to engineer polycrystalline structures with a higher degree of crystallinity. However, a number of highly disordered amorphous polymer films with comparable or higher charge mobility recently

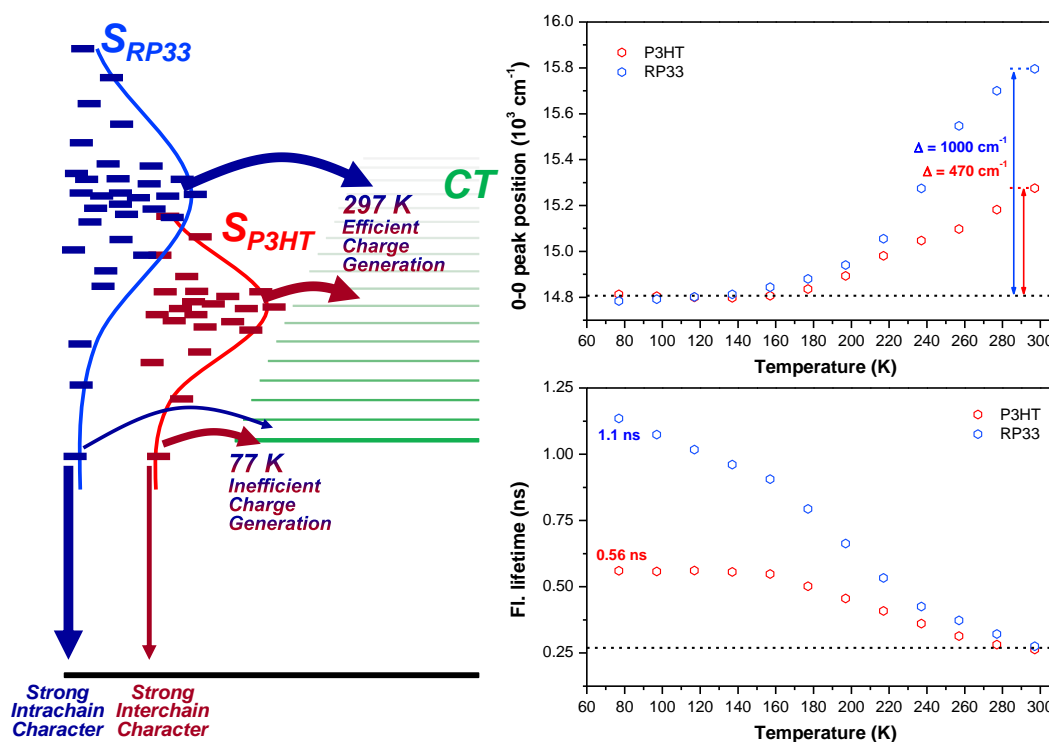


Figure 1. Temperature-dependent change in the 0-0 vibronic peak positions of photoluminescence spectra (top right) and corresponding change in the photoluminescence lifetimes (bottom right) of **P3HT** (red) and **RP33** (blue). Schematic representation of singlet exciton manifold of **P3HT** and **RP33** and their polaron generation dynamics at 297 and 77 K (left).

contradicted this view.^[2] It has been suggested that high charge carrier mobility is a consequence of interchain hopping aided by intrachain through-bond transfer process which permits connectivity between crystalline domains. This novel concept has motivated us to modify a prototype CP, poly(3-hexylthiophene) (**P3HT**), to include thiophene units without hexyl groups as comonomers. A random copolymer incorporating 33 mol% of thiophene units (**RP33**) was shown to have reduced crystallinity overall, but form smaller localized aggregates which enhance charge transport mobility to $1.37 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, far exceeding that of **P3HT**, $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[3]

Despite thorough characterization of charge transport phenomena by electrical measurements, the dynamics of neutral species, singlet exciton, which precedes the generation of polarons, has not been investigated in such structures. In this regard, we investigated the energetic breadth of exciton manifold in the **RP33** and the effect of crystalline ordering on the subsequent generation of polarons. By lowering temperature, distinction between photoluminescence (PL) peak positions at room temperature reduces and eventually coincide at 77 K, whereas PL lifetimes, which were essentially same at room temperature, diverge to produce two-fold difference at 77 K (Fig. 1). This implies that energetic breadth of **RP33** is large enough to cover the lowest energy states of **P3HT**, while charge separation, a major non-radiative deactivation channel, is less efficient. This is further supported by comparing the polaron generation yields of **RP33** and **P3HT** at different temperatures, which are demonstrated by femtosecond transient absorption spectroscopy. Further quantum calculation results will be present to compare inter-/intrachain characters of polythiophene aggregates with or without thiophene comonomers in conjunction with the polaron generation yields.

References:

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