Establishing the Optoelectronic Interactions between Conjugated Polymers and Organic Radicals

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Design rules and application spaces for closed-shell conjugated polymers have been well established in the field of organic electronics, and this has allowed for significant breakthroughs to occur in myriad device platforms [e.g., organic field-effect transistors (OFETs) and organic light-emitting devices (OLEDs)]. Conversely, organic electronic materials that are based on the emerging design motif that includes open-shell stable radicals have not been evaluated in such detail, despite the promise these materials show for charge transfer, light-emission, and spin manipulation platforms. Moreover, recent results have demonstrated that the materials performance of hybrid systems will allow for future applications to harness both of these platform design archetypes to generate composites that combine the performance of current state-of-the-art conjugated polymer systems with the novel functions provided by open-shell species. Thus, establishing the underlying physical phenomena associated with the interactions between both classes of materials is imperative for the effective utilization of these soft materials.

In the first part of this work, Förster resonance energy transfer (FRET) is demonstrated to be the dominant mechanism by which energy transfer occurs from a common conjugated polymer to various radical species using a combination of experimental and computational approaches. Specifically, this is determined by monitoring the fluorescence quenching of poly(3-hexylthiophene) (P3HT) in the presence of three radical species: (1) the galvinoxyl; (2) the 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO); and (3) the 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals. Both in solution and in the solid-state, the galvinoxyl and PTIO radicals show quenching on par with that of a common fullerene electron-accepting derivative. Conversely, the TEMPO radical shows minimal quenching at similar concentrations. Using both ultrafast transient absorption spectroscopy and computational studies, FRET is shown to occur at a significantly faster rate than other competing processes. These findings suggest that long-range energy transfer can be accomplished in applications when radicals that can act as FRET acceptors are utilized, forming a new design paradigm for future applications involving both closed- and open-shell soft materials.

Following this, addition of the galvinoxyl radical to P3HT is shown to alter the thin film transistor response from semiconducting to conducting. This is accompanied by a modest enhancement in electrical conductivity. This interaction is not seen with either the TEMPO or PTIO radicals. While an increase in charge carrier concentration is observed, the interaction is not otherwise consistent with a simple charge-transfer doping mechanism, due to the mismatched reduction and oxidation potentials of the two species. Additionally, no freeze-out of charge carriers is observed at reduced temperatures. It is also not due to parallel conduction through the radical fraction of the bulk composite, as the radical species is non-conductive. Hole mobility is enhanced at lower concentrations of the radical, but it decreases at higher concentrations due to the reduced fraction of conductive material in the polymer bulk. Despite the increase in mobility at lower concentrations, the activation energy for charge transport is increased by the presence of the radical. This suggests that the radical is not improving the charge transport through filling of deep trap states or by reducing the activation energy for the charge transport reaction; however, the galvinoxyl radical is likely filling shallow trap states within the P3HT for the composite thin film.

Finally, a novel analysis technique for polymer relaxation is investigated through dielectric spectroscopy of model polyalcohols. An understanding of relaxation phenomena and the physics of amorphous solids in general remains one of the grand open challenges in the field of condensed matter physics. This problem is particularly relevant to organic electronics as many organic electronic materials are found in the amorphous state, and their physical relaxation can lead to undesirable effects such as hysteresis and instability. Current procedures describe relaxation phenomena in terms of empirical functions, but the physical insights provided by this representation are limited. The new approach instead represents the dielectric response as a spectrum of Debye processes. Rather than varying the spectral strength at fixed time points as traditional spectral analysis implicitly does, this approach instead varies the characteristic time of each spectral element while the strength remains fixed. This allows the temperature dependence on relaxation time of each spectral element to be determined, and the α- and β-relaxation are interpreted in light of this analysis.