

Engineering Transport in Confined Environments of Stable Radical Polymers

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Primary CNF Tools Used: GCA 5X stepper, wet stations, CVC evaporators, Heidelberg mask writer DWL 2000, DISCO dicing saw

Abstract:

We study properties of a doped radical polymer with a conjugated backbone, which is a promising potential material for an organic radical battery electrode. To compensate the exponential decay of conductivity caused by steric hindrance from covalently attached stable radical, we dope the conjugated backbone using either iodine or 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). We characterize the electrical properties as we vary the pendent radical concentration. Transport measurements confirm that doping increases the conductivity by a few to several orders of magnitude, depending on the dopant. Additionally, we use electron paramagnetic resonance (EPR) to investigate the interplay between polarons and stable radical electrons.

Summary of Research:

For enhanced performance of radical polymer based energy storage materials, a high conductivity and a large volume density of electroactive radical electrons are required for efficient current collection and increased capacity, respectively. Our first study in this line of works was to confirm the intrinsic conductivity of poly(2,2,6,6-tetramethyl- piperidinyloxy-4-yl methacrylate (PTMA), which is one of the model polymers suggested for energy storage [1].

In this work we found that without alternative conduction channels, such as swelling of the polymers with an ionic liquid, the conductivity of non-conjugated radical polymers are closer to that of an insulator than to organic semiconductors. Next, we tried including alternative conductive channels by attaching pendent radical (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) to the conductive conjugated backbone poly(3-hexylthiophene-2,5-diyl) (P3HT) [2].

In this study we were able to achieve increased conductivity, however, we discovered that there is an exponential decrease in conductivity as we increase the number of pendant radicals due to the disorder they create in stacking. In other words, we found a tradeoff between conductivity and the volume density of radical electrons.

As a natural extension to these works, we've focused on doping of the conjugated backbone to increase the conductivity relative to what we found in the intrinsic polymers. In our experiment we chose two dopants: iodine and F4-TCNQ.

The low sublimation point and volatility of iodine allows an easy doping process at room temperature. We were able to see more than five orders of magnitude increase of conductivity for the P3HT control sample that did not have pendent radicals. This trend continued for the polymers with different fractions of pendent radicals showing that the entire curve is shifted upward in conductivity with doping. (Figure 1.) However, iodine also imposes some technical challenges such as dedoping at ambient condition and chemical reaction with metal that composes crucial parts of experimental setup. Thus, while iodine as a dopant for P3HT-TEMPO is very effective at increasing conductivity, at the same time it has limited technical applications due to its volatility and reactivity.

One alternative dopant, which does not suffer from this problem, is F4-TCNQ. When mixed with conjugated backbone polymer in solution state, it is known to form a rigid and semicrystalline charge transfer complex that creates polarons. Due to the rigid formation of a charge transfer complex, it also makes it easier to trace polarons using solution-state EPR.

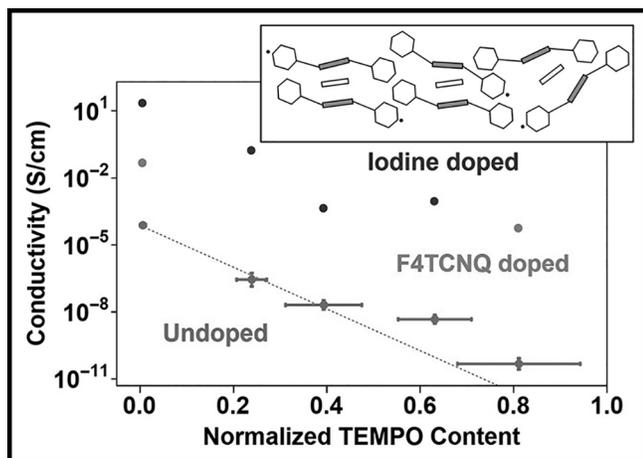


Figure 1: Trend of conductivity as a function of normalized TEMPO content. Blue dots and magenta dots correspond to iodine and F4-TCNQ doped P3HT-TEMPO. Inset shows a schematic of steric hindrance in system of conjugated backbone (orange) with pendent radical (hexagon) in presence of dopants (yellow). (Find full color on pages xiv-xv.)

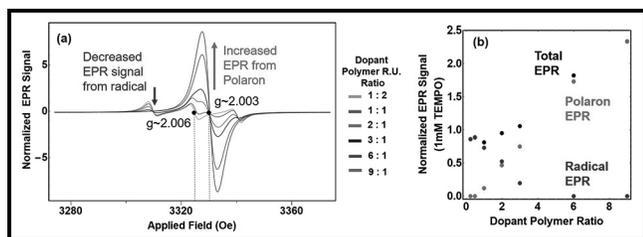


Figure 2: (a) EPR curve of doped conjugated polymer with pendent radical obtained from varying ratio of dopant molecule to polymer repeating unit. (b) Relative contribution of polaron and radical electron to total EPR signal size as a function of dopant polymer ratio. (Find full color on pages xiv-xv.)

In our experiment we've used in-solution doping where we simply mix conjugated polymer and F4-TCNQ in a vial for EPR results. We then cast the dopant on a conjugated polymer film for electrical transport measurement.

The effect of doping of conjugated radical polymer in EPR is clearly visible in Figure 2 (a). In this system, the first source of EPR signal is pendent radicals. Due to hyperfine coupling in the nitroxide radical, we observe a triplet signal when the radicals are isolated from each

other. When two or more radical molecules are brought in close distance, exchange coupling become dominant and singlet signal with broader linewidth is observed. Thus, when we vary the percentage of stable radicals that are pendent to the backbone, we get a statistical combination of triplet and singlet. The additional source of EPR signal we introduce from doping of the backbone is polarons. Since polarons are mobile radicals unaffected by hyperfine coupling, they show a singlet lineshape.

These two signals can be distinguished from each other because they have different g-factors and therefore different resonant fields at the same frequency. By fitting the data with known EPR curves for radical electron and polaron, we can quantitatively extract the contribution each component. In Figure 2 (b) we see that the polaron contribution increases linearly with increasing dopant concentration while the radical electron signal decreases. This shows that there is electron transfer between pendent radicals and polarons formed in the backbone.

Finally, with F4-TCNQ doped P3HT-TEMPO we get around 2~3 orders of magnitude increase in conductivity (Figure 1, magenta points, see page XX for full color). While conductivity increase is not as large as iodine doped case, F4-TCNQ is more stable doping technique, which have negligible dedoping at ambient air and no reaction problem with metal. The consistent trend of decreasing conductivity for higher ratio of pendent stable radical shows that steric hindrance still plays a role in conductivity of thin film doped conjugated polymers (Figure 1, Inset).

References:

- [1] Y. Zhang, et al., "Impact of the Synthesis Method on the Solid-State Charge Transport of Radical Polymers." *J. Mater. Chem. C* 6 (1), 111-118 (2017).
- [2] Y. Zhang, et al., "Charge Transport in Conjugated Polymers with Pendent Stable Radical Groups." *Chem. Mater.* 30 (14), 4799-4807 (2018).