Structural and Electrical Properties of Molecularly-Doped Semiconducting Polymers Fabricated by Sequential Doping

Semiconducting polymers represent a versatile class of materials used in many electronic device applications. However, due to their low intrinsic conductivity, doping is often necessary to achieve the desired electrical properties for specific applications. Adding large amounts of dopant molecules by traditional methods often leads to detrimental effects that hinder film quality and ultimately electrical properties. Our group has developed a new method (Sequential Doping) to overcome these issues, which are largely present in the high doping regime, and to gain new insights general to molecular doping of polymers afforded by this method. We demonstrate that this new method produces highly doped samples with superior film quality allowing for accurate optical and electrical measurements over large length scales, including Hall effect measurements, which had previously been unrealized. Sequential doping also offers the unique advantages of being able to tune the undoped polymer film morphology prior to doping, and to maintain that same morphology after doping allowing for a detailed study of how polymer crystallinity affects the optical and electrical properties of the doped state. Using sequential doping we discovered that for the commonly studied polymer:dopant system poly(3-hexylthiophene): 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (P3HT:F4TCNQ), that the dopant anions reside in the side chain regions of the polymer crystallites as opposed to in the π-stacks as commonly believed. This larger distance between the dopant anion and the polymer hole allows for greater charge delocalization resulting in more mobile charges which can be tracked spectroscopically. We can also decouple the interplay between polymer crystallinity and the energy level offset between the polymer and the dopant by the use of statistical copolymers with independently tunable crystallinity and energy levels. We find that the crystallinity of the polymer after being doped has a more drastic effect on the resulting electrical properties than the energy level offset, emphasizing the importance of structural compatibility between a dopant and polymer host. Overall, sequential doping is an effective way to produce highly doped semiconducting polymer films and allows for novel studies on how physical properties of materials influence their doped counterparts.

Presented by:

Tyler Scholes
Professor Ben Schwartz’s Group
Department of Chemistry & Biochemistry
University of California, Los Angeles