Conjugated ionomers for photovoltaic applications: electric field driven charge separation in organic photovoltaics
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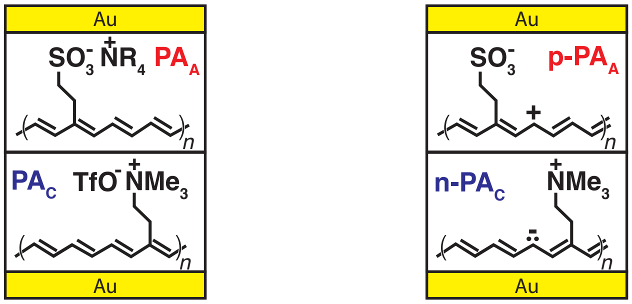


(a) (b)

Figure 1: Schematics of an (a) ionic junction based on undoped ionomers, and a (b) p-n junction based on doped ionomers.

1 Overview

The central goal of the work we completed was been to understand the photochemical and photovoltaic properties of ionically functionalized conjugated polymers (conjugated ionomers or polyelectrolytes)[1,2] and energy conversion systems based on them. We primarily studied two classes of conjugated polymer interfaces (see Figure 1) that we developed based either upon undoped conjugated polymers with an asymmetry in ionic composition (the ionic junction)[3] or doped conjugated polymers with an asymmetry in doping type (the p-n junction).[4,5] The materials used for these studies have primarily been the polyacetylene ionomers PA_A and PA_C shown in Figure 1. We completed a detailed study of p-n junctions with systematically varying dopant density,[4,5] photochemical creation of doped junctions,[3] and experimental and theoretical work on charge transport and injection in polyacetylene ionomers.[6,15] We have also completed related work on the use of conjugated ionomers as interlayers that improve the efficiency or organic photovoltaic systems[7] and studied several important aspects of the chemistry of ionically functionalized semiconductors, including mechanisms of so-called "anion-doping",[8] the formation of charge transfer complexes with oxygen,[9,10] and the synthesis of new polyfluorene polyelectrolytes.[11] We also worked worked with the Haley group at the University of Oregon on new indenofluorene-based organic acceptors.[12–14] These accomplishments are detailed in the sections that follow and resulted in the following publications.[2–15]

2 Publications acknolwedging DOE support

[1] Stay, D. P., Robinson, S. G., and Lonergan, M. C. Development and Application of Ion-functionalized Conjugated Polymers. In *Iontronics*; Leger, J., Berggren, M., and Carter, S., Eds.; CRC Press, Taylor and Francis Group, Boca Raton, Fl, 2010; pp 43–84.

[2] Robinson, S. G., and Lonergan, M. C. In *Conjugated Polyelectrolytes*; Liu, B., and Bazan, G. C., Eds.; Conjugated Polyelectrolytes: Fundamentals and Applications; Wiley-VCH Verlag GmbH & Co. KGaA, 2013; Chapter 3, pp 91–126.

[3] Lin, F., Walker, E. M., and Lonergan, M. C. Photochemical Doping of an Adaptive Mix-Conducting p-n Junction. *The Journal of Physical Chemistry Letters* **1**, 720–723, (2010).

[4] Robinson, S. G., and Lonergan, M. C. Polyacetylene p–n Junctions with Varying Dopant Density by Polyelectrolyte-Mediated Electrochemistry. *The Journal of Physical Chemistry C* **117**, 1600–1610, (2013).

[5] Robinson, S. G., Johnston, D. H., Weber, C. D., and Lonergan, M. C. Polyelectrolyte-Mediated Electrochemical Fabrication of a Polyacetylene p-n Junction. *Chemistry of Materials* **22**, 241–246, (2010).

[6] Mills, T. J., and Lonergan, M. C. Charge injection and transport in low-mobility mixed ionic/electronic conducting systems: Regimes of behavior and limiting cases. *Physical Review B* **85**, 035203, (2012).

[7] Weber, C. D., Bradley, C., Walker, E. M., Robinson, S. G., and Lonergan, M. C. Increased performance of inverted organic photovoltaic cells using a cationically functionalized fullerene interfacial layer. *Solar Energy Materials and Solar Cells* **129**, 90–94, (2014).

[8] Weber, C. D., Bradley, C., and Lonergan, M. C. Solution phase n-doping of C60 and PCBM using tetrabutylammonium fluoride. *Journal of Materials Chemistry A* **2**, 303–307, (2014).

[9] Weber, C. D., Robinson, S. G., and Lonergan, M. C. Ionic Functionality and the Polyacetylene-Oxygen Charge-Transfer Complex. *Macromolecules* **44**, 4600–4604, (2011).

[10] Weber, C. D., Robinson, S. G., Stay, D. P., Vonnegut, C. L., and Lonergan, M. C. Ionic Stabilization of the Polythiophene-Oxygen Charge-Transfer Complex. *ACS Macro Letters* **1**, 499–503, (2012).

[11] Stay, D., and Lonergan, M. C. Varying Anionic Functional Group Density in Sulfonate-Functionalized Polyfluorenes by a One-Phase Suzuki Polycondensation. *Macromolecules* **46**, 4361–4369, (2013).

[12] Rose, B. D., Chase, D. T., Weber, C. D., Zakharov, L. N., Lonergan, M. C., and Haley, M. M. Synthesis, Crystal Structures, and Photophysical Properties of Electron-Accepting Diethynylindenofluorenediones. *Organic Letters* **13**, 2106–2109, (2011).

[13] Chase, D. T., Fix, A. G., Rose, B. D., Weber, C. D., Nobusue, S., Stockwell, C. E., Zakharov, L. N., Lonergan, M. C., and Haley, M. M. Electron-Accepting 6,12-Diethynylindeno[1,2-b]fluorenes: Synthesis, Crystal Structures, and Photophysical Properties. *Angewandte Chemie-International Edition* **50**, 11103–11106, (2011).

[14] Chase, D. T., Fix, A. G., Kang, S. J., Rose, B. D., Weber, C. D., Zhong, Y., Zakharov, L. N., Lonergan, M. C., Nuckolls, C., and Haley, M. M. 6,12-Diarylindeno[1,2-b]fluorenes: Syntheses, Photophysics, and Ambipolar OFETs. *Journal of The American Chemical Society* **134**, 10349–10352, (2012).

[15] Walker, E. M., and Lonergan, M. C. Characterizing Charge Injection, Transport, and Mobility in a Conjugated Polyelectrolyte by NIR Absorbance. *The Journal of Physical Chemistry C* **117**, 14929–14938, (2013).

3 Doped polymers: pn junctions

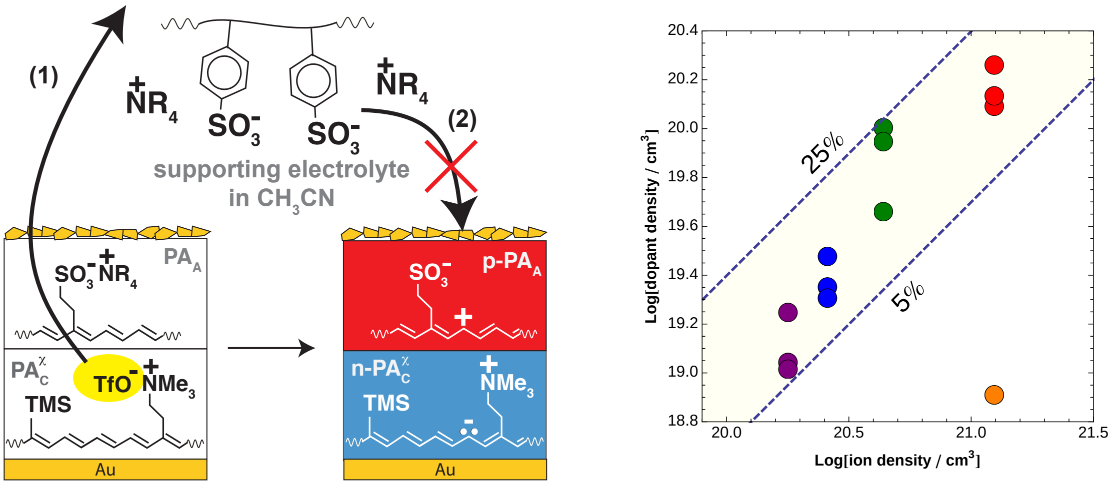
Dopant ion diffusion renders interfaces between differentially doped conjugated polymers and related materials unstable with respect to bulk redox reactions. We have demonstrated that conjugated ionomers, which can become internally compensated upon doping, can be used to overcome this problem. The charge injected into the polymer backbone is balanced by covalently bound, immobile ionic centers in internally compensated states. This has enabled us to fabricate conjugated polymer p-n junctions where the p- and n- refer to truly doped states rather than acceptor and donor, respectively. We have developed and studied this new class of junctions to better understand their properties, in particular as it relates to solar energy conversion. The studies are significant in part because of the central role inorganic p-n junctions play in photovoltaics. We made the following advances:

1. Developed polyelectrolyte mediated electrochemistry (PMEC) to independently control the doping level on the n- and p-type sides of conjugated polymer p-n junctions fabricated from undoped $\mathrm{Au}|\mathrm{PA_A}|\mathrm{PA_C}|\mathrm{Au}$ bilayer precursors (see Figure 2).

2. Used PMEC to systematically control dopant density to tune the current-voltage characteristics of conjugated polymer pn junctions with equilibrium exchange current densities varying from 1×10^{-10} to 1×10^{-4} A cm^{-2}, and rectification ratios at 1.8V as high as 1600 (see Figure 3).

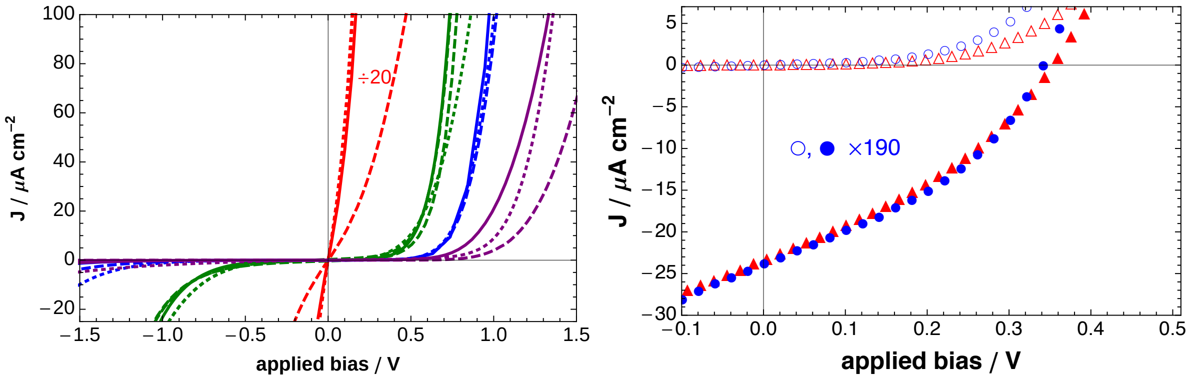
3. Measured the dopant density and voltage dependence of the capacitance and current to demonstrate that conjugated polymer pn junctions are very different from classic inorganic p-n junctions, for instance, not showing the classic voltage dependence of the capacitance nor agreement with Shockley diffusion theory governing inorganic p-n junctions.

4. Demonstrated that an asymmetry in dopant type (n- vs p-) can be used to generate a photovoltaic effect. This supports an initial hypothesis of the work that conjugated ionomer p-n junctions, without any nominal frontier orbital offset as in other organic energy conversion systems, can separate excitons and selectively collect the resulting carriers.



(a) (b)

Figure 2: (a) Polyelectrolyte mediated electrochemical fabrication of a conjugated ionomer p-n junction. Step (1) is a -1.5 V vs. SCE potential step to maximally n-dope the cationic layer and step (2) is a potential step to +0.6 V vs. SCE to *selectively* p-doped the anionomer layer. The cationomer layer is not p-doped during step (2) because the poly(styrenesulfonate) supporting electrolyte is too large to permeate the solid ionomer film. (b) Plot showing the range of dopant and ionic functional group densities in the cationic layer of the junctions that were prepared. The diagonal dashed lines represent 5 and 25% of the ionic functional group density as labelled.



(a) (b)

Figure 3: (a) Current density (J)-voltage traces for polyacetylene p-n junctions fabricated using PMEC and reducing (in the order red, green, blue, purple and corresponding to Figure 2b) ionic and doping density in the cationic layer. (b) Current density-voltage curve for one of the junctions in the light and in the dark.

4 Ionic Junctions

The undoped polyacetylene ionomer junction Au$|$PA$_\mathrm{A}|$PA$_\mathrm{C}|$Au that was the precursor to forming the p-n junction above stimulated our interest in ionic asymmetries in generating a photovoltaic effect. The vast majority of photovoltaics rely on an *electronic* asymmetry to generate a photovoltaic effect, such as an offset in relevant electronic energy levels or a discontinuity in electronic carrier density or type. We hypothesized that an asymmetry in ionic population in a mixed ionic/electronic conducting system can lead to a photovoltaic effect. In exploring this hypothesis we made the following advances:

1. Demonstrated a photovoltaic effect at the ionomer junction: Au$|$PA$_\mathrm{A}|$PA$_\mathrm{C}|$Au (see Figure 4). This junction nominally contains no asymmetry in the electronic subsystem with nominally no band edge offsets and only an asymmetry in the ionic subsystem. Ion motion in the system results in time dependent photovoltaic properties.

2. Developed a photochemical doping model to describe the photovoltaic effect observed at the ionic junction and involving the following steps

    (a) In the dark, the exchange of ions at the anionomer / cationomer interface leads to the generation of a built-in electric field of magnitude necessary to cancel the initial diffusive driving force due to gradients in free-ion concentration. It is possible that this exchange involves the precipitation of a salt at the interface given the low dielectric constant of the polymers.

    (b) Illumination results in photoexcitations, some portion of which are separated at the interface with holes traveling into the anionomer and electrons into the cationomer.

    (c) The space charge created by the photogenerated electrons and holes reduces the electric field at the interface resulting in further diffusion of ions. Equivalently, the motion of holes into the anionomer is coupled to the motion of an anion from the cationomer, and the motion of electrons into the cationomer is coupled to the motion of a cation from the anionomer leading to photochemically induced doping. The photochemical doping amounts to the formation of a p-n junction that responds adaptively to illumination.

3. Supported the photochemical doping model using transient absorption in the NIR (1300nm) to directly observed the formation of doped states during strong visible (532 nm) illumination. The NIR probe beam illustrates that the system becomes doped during illumination under open-circuit conditions and relaxes to a less doped state under short-circuit conditions (see Fig. 5).

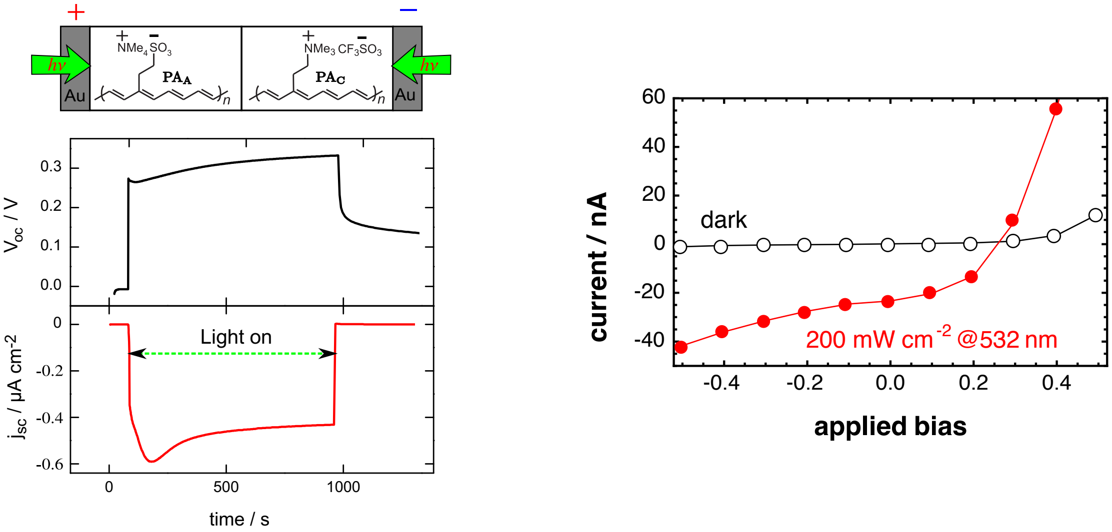


Figure 4: Photovoltaic properties of a Au|PA^4_A|PA^4_C|Au sample. (a): Time dependent open circuit potential V_{oc} and short circuit current density j_{sc} symmetric illumination of 200 mWcm^{-2} at 532 nm. (b) Steady-state J-V curve in the dark and under illumination.

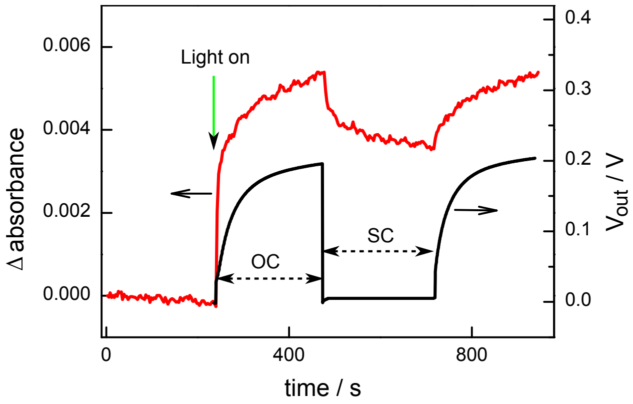


Figure 5: The change in NIR (λ =1305 nm) absorbance as the Au|PA^4_A|PA^4_C|Au junction undergoes transition from dark to illuminated, and from open circuit (OC) to short circuit (SC) under constant illumination.

5 Numerical Simulation of Charge injection and transport in conjugated ionomers

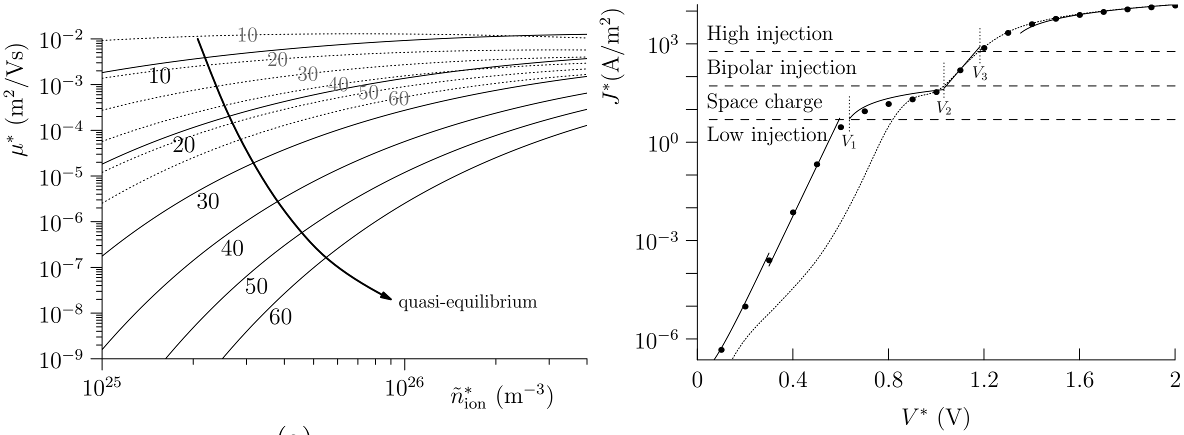
In an effort to better understand the properties of the junctions described above, we completed numerical simulations and theoretical work to mechanistically study charge injection into conjugated ionomers. The numerical simulation were based on an ionic model characterized by a drift-diffusion transport equation that explicitly accounts for volume constraints of the ions, a standard drift/diffusion model for electronic transport through the bulk, and a model for the electrode interfaces that includes a spatially dependent tunneling process, accounts for both forward and backward fluxes, as well as the state of quasi-equilibrium that occurs in low-mobility materials. Our studies helped resolve substantial controversy over the precise mechanisms by which ionic redistribution in ion-containing conjugated polymers impact charge carrier injection and transport. More specifically, we contributed in the following ways:

1. Delineated the major regimes of behavior for transport through conjugated ionomer layers, and demonstrated how previously proposed models can be viewed as limiting cases. This included developing analytical expressions for the current-voltage behavior in each regime (see Fig. 6b).

2. Revealed several important differences between mixed ionic/electronic systems where only one sign of ion is mobile ("one-ion systems" as in a conjugated ionomer) relative to where both signs are mobile ("two-ion systems" as in a conjugated polymer / solid electrolyte blend). For example, the relative values of the double-layer potential drops in the one- and two-ion systems are different because of the different amounts of charge that can build up in the ionic double layers. This leads to differing dependencies of the electronic current on bias, especially at small voltages where there is a relatively low level of electronic charge injection.

3. Precisely demonstrate the mechanism by which ion polarization leads to an increase in electronic current. It is often stated that this is due to increased tunneling injection through the narrowing of the potential profiles near the electrodes. Instead, it is due to the fact that these narrowed profiles can allow the electrodes to reach quasi-equilibrium with the electronic carriers at the inner edges of the double layers. The high rate of tunneling transfer, while responsible for the large exchange current that leads to quasi-equilibrium, does not determine the overall current. This may seem like somewhat of a subtle distinction in mechanism, but it does lead to a very different functional form for the current; indeed, it shows that in a low-mobility system, applying the Nernst equation across the double layers is much more appropriate than applying a model such as Fowler-Nordheim near the electrode.

4. Delineated the conditions of mobility, ion concentration, and applied bias that lead to quasi equilibrium (see Figure 6a), and concluded that conjugated ionomers generally satisfy the conditions of low mobility and high ion concentration that establish quasi-equilibrium at the electrodes.



(a)

(b)

Figure 6: (a) Phase diagram showing the conditions of mobility μ, ion concentration n_{ion} and applied bias leading to quasi-equilibrium for two-ion (dashed lines) and one-ion systems (solid lines). The numbers label the applied bias in units of kT/q. (b) Current-density-voltage behavior simulated (solid circles) for a conjugated ionomer between metal electrodes. The solid lines are analytical approximations to each region of behavior.

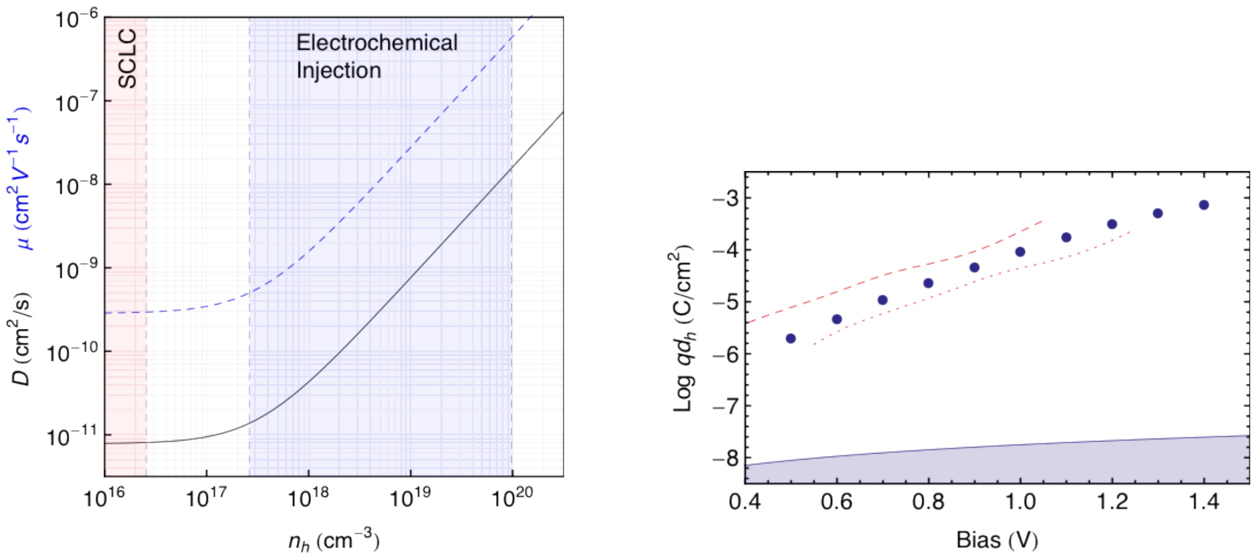
6 Experimental measurement of charge injection and mobility

To test the predictions of our numerical simulations and advance understanding of charge injection in conjugated ionomers, we conducted studies of charge injection into polyacetylene ionomers. A distinguishing feature of this work is the use of NIR absorbance to directly probe the density of injected carriers. We made the following advances in this area:

1. Used NIR absorbance as a method to measure the concentration-dependent carrier mobility in undoped conjugated ionomers as a function of the carrier injection level (see Fig. 7a). The presence of mobile ions in these materials renders most standard approaches to determining mobility invalid. The NIR absorbance provides an independent measure of charge injection.

2. Demonstrated the validity of the electrochemical charge injection model in the quasi-equilibrium limit by comparing the density of injected charge with cyclic voltammetry studies (see Fig. 7b). This work also showed that the density of injected charge is far too great to be treated by the space-charge-limited model normally used to describe organic semiconductors.

3. Showed the limitations of short-circuit discharge measurements in determining the density of injected charge in conjugated ionomers. At low bias, it overestimates because of contributions from the charge stored in the ionic double layers. At high bias, it underestimates because of internal recombination.



(a) (b)

Figure 7: (a) Mobility (dashed line) and diffusion coefficient (solid line) calculated for holes in a cationic polyacetylene ionomer as a function of concentration, and (b) comparison of the injected charge density (circles) to the space-charge-limited model (bottom blue area) and that determined from cyclic voltammetry. The red dashed lines are the electrochemical data and reflect a range due to uncertainty in the initial Fermi level of the polymer.

7 Unusual chemistry and photochemistry of ionically functionalized semiconductors

During the course of our study of conjugated ionomers and related materials, we provided new insight into how ions affect the chemical and photochemical oxidation/reduction of organic semiconductors. Our contributions in this area include:

1. Demonstrated that ionically functionalized polyacetlyenes and polythiophenes react very quickly with oxygen, but to initially form a charge-transfer complex that is much more stable than in non-ionically functionalized conjugated polymers. This charge-transfer complex is greatly stabilized by, in particular, anionic functional groups associated with alkali metal cations. Fig. 8 illustrates the central observation. The two images stacked on the right of Fig. 8 show the results of long-term exposure of a sulfonate functionalized polyacetylene ionomer to air and constant illumination. The top panel shows an image immediately after ion exchanging a portion of the film. The polymer is a Na^+ salt except in the O-shaped region, and it is a tetramethylammonium (NMe_4^+) salt in the remainder of the film. The change in color of the Na^+ region is due to the rapid formation of the polymer-oxygen charge transfer complex, as is clearly evident in the NIR spectrum of the polymer shown on the left side of Figure 8. Despite this initial reaction with oxygen, the overall photobleaching of the Na^+ salt is much slower than the NMe_4^+ salt. The image on the bottom panel shows the same film after 15 days under photooxidative conditions. As can be seen, the NMe_4^+ region is completely bleached, whereas the Na^+ region remains highly colored. The sulfonate func-

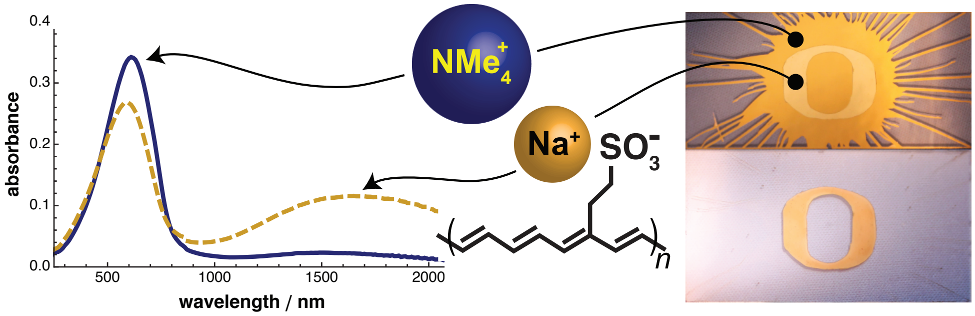


Figure 8: Photochemical oxidation of a sulfonate functionalized monomer schematically shown center. Left: absorbance spectrum of a the polymer with NMe_4^+ counterion and immediately after ion exchange in air for Na^+. Right: image of a solid film of the ionomer with NMe_4^+ (O-shaped region) and Na^+ counter ion immediately after ion exchange (top) and after 15 days under photo-oxidative conditions (bottom).

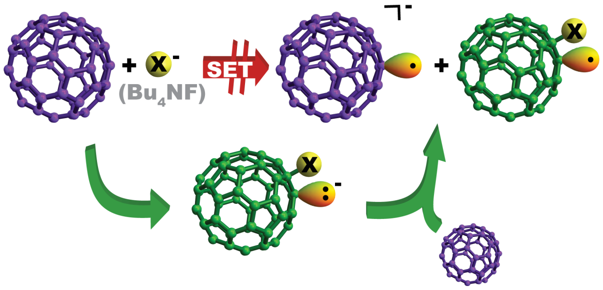


Figure 9: Schematic showing nucleophilic attack by anions and subsequent electron transfer to yield an n-doped C_{60} as an alternate mechanism to single electron transfer (SET).

tional groups and Na^+ counter-ions are believed to participate in the formation of an oxygen charge-transfer complex that results in substantial stabilization.

2. Developed mechanistic insight into the n-doping of C_{60} by anions. There has been controversy in the literature regarding the mechanism by which certain anions can enhance the conductivity of fullerenes. It has been proposed that anions, such as fluoride, act as direct single-electron reductants of C_{60} resulting in a highly conductive, so-called "n-doped" state. This is surprising because available thermodynamic data would suggest such a reaction highly unlikely. We demonstrated in C_{60} and related derivatives that fluoride ion (or the unavoidable accompanying hydroxide ion) leads to n-doping through a very different mechanism: initial nucleophilic attack followed by subsequent electron transfer (see Fig 9).

3. Used the anion-induced doping of a cationic fullerene derivative to improve the efficiency of an organic bulk heterojunction by improving contact properties.

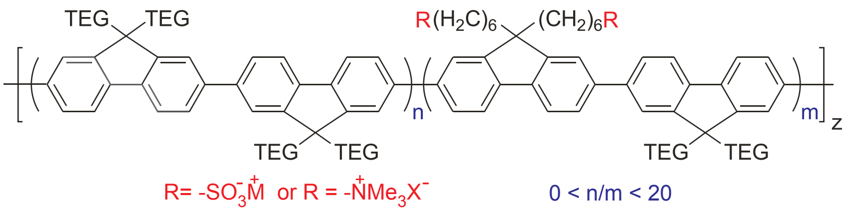


Figure 10: Family of polyfluorene ionomers synthesized.

8 Controlling ionic density in polyfluorene ionomers

Ionic functional group density is a key parameter in determining the properties of conjugated ionomers. It is a valuable handle in understanding the origin of various phenomena in these materials, as our work on p-n junctions illustrates. We developed a synthetic approach to anionic and cationic polyfluorenes with controlled densities of ionic functional groups (see Fig. 10). Polyfluorenes are typically synthesized using Suzuki polycondensation. The two-phase nature of this polymerization, however, created problems in that the ionic and nonionic monomers segregated into different phases. This resulted in the preferential polymerization of the nonionic monomers, and hence, to a mixture of polymers rather than a single polymer with a controlled density of ionic functional groups. The two-phase problem was overcome by redesigning the ancillary functionality on the monomers to introduce oligoether chains (TEG). This functionality made it possible to identify a one phase solvent system. Using this method, we were able to successfully synthesize anionic and cationic polyfluorenes with varying ionic functional group density.

9 New organic acceptors

Fullerenes are by far the dominate acceptor material in organic semiconductors, and the variety of relatively easily reduced (n-type) materials that are available for our studies is limited. To address this, we have been collaborated with the group of M. Haley at the University of Oregon to explore the electrochemistry of some indenofluorene-based molecules that may be good candidates for n-type conduction. Our specific role in this collaboration was to characterize the thermodynamics of n-type doping. We have found that many of the indenofluorenes have similar first reduction potentials to that of the standard n-type organic semiconductor PCBM.