# A Conjugated Polymer pn Junction

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The discovery of the silicon pn junction is a landmark in the development of modern microelectronics. Consequently, the pn junction has been an important target in studies on conjugated polymers ever since the demonstration of high conductivity upon doping of polyacetylene in 1977.[1] Limitations in the doping chemistry of conjugated polymers, however, have made examples of pn junctions based on these materials elusive. In limited studies, press contacting,[2] photochemical doping,[3] and ion implantation[4] have been explored, but issues of dopant counterion diffusion remain a complicating factor.[5] The diffusion of dopant counterions through traditionally doped conjugated polymers renders a pn junction unstable with respect to a bulk chemical reaction between the two phases, e.g. with polyacetylene:

$$[M^+]_m[\sim\!\!\sim]_n{}^{m-} + [\sim\!\!\sim]_n{}^{m+}[X^-]_m \longrightarrow [\sim\!\!\sim]_n + m\,MX \quad (1)$$
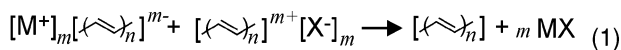
where X^- and M^+ are the charge compensating anion and cation for the oxidized (p-type) and reduced (n-type) forms, respectively, of polyacetylene. Dopant ion diffusion makes only the transient formation of pn junctions possible with traditionally doped conjugated polymers, as has been demonstrated in polymer light-emitting electrochemical cells.[6]

Herein, we report internal compensation as a route to prevent reaction 1 and realize a polyacetylene-based pn junction. Internal compensation refers to the situation where dopant counterions are covalently bound to the polymer backbone, and hence cannot diffuse to support a bulk redox reaction between dissimilarly doped regions. As precursors to internally compensated p- and n-type forms, respectively, anionically and cationically functionalized poly-acetylenes (P_A and P_C in Figure 1A) were previously synthesized.[7] As the doped forms of these materials are insoluble, direct solution casting to form a pn junction is not possible. Consequently, an electrochemical disproportionation and trapping method was developed.

The electrochemical disproportionation and trapping method is shown in Figure 1 and is described below using specifics pertaining to the representative sample for which all of the data herein are reported. First, a bilayer was fabricated consisting of sequentially deposited layers of undoped P_A (150 nm) and P_C (150 nm) sandwiched between gold electrodes (Figure 1A). The bilayer was then disproportionated by applying a bias (+2 V P_A vs P_C) to drive oxidation of P_A and reduction of P_C within the two-electrode geometry (Figure 1B). The reaction was conducted with the sample immersed in CH_2Cl_2 to dissolve away the liberated salt ($Me_4NCF_3SO_3$), thereby preventing the reverse reaction upon removal of the bias. After the bias was applied for sufficient time (1 min) to reach steady-state, the pn junction was trapped by removing first the wash solvent and then the applied bias. Figure 1C shows a schematic of the resulting trapped pn junction, idealized in that the density of injected charge is precisely balanced by the density of covalently bound ionic centers.
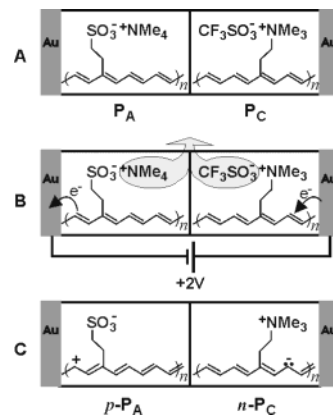

Figure 1. Conjugated ionomer bilayer (A) undergoing electrochemical disproportionation (B) with dissolution of salt ($NMe_4CF_3SO_3$) into a wetting solvent (e.g., CH_2Cl_2) to trap a pn junction (C).
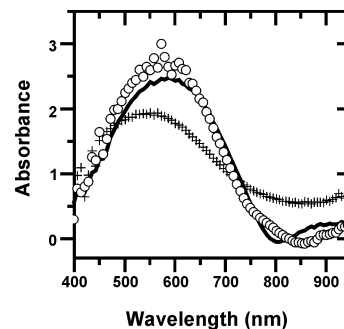

Figure 2. Electronic absorption spectra for a $P_A \mid P_C$ bilayer in its undoped form (line), following electrochemical disproportionation and trapping to form a pn junction (+), and after undoping by the addition of 0.1 M Bu$_4$-NBF$_4$/CH$_3$CN (○).

The formation of the pn junction was monitored in situ using electronic absorption spectroscopy. As a pristine sample, the bilayer exhibited a broad $\pi-\pi*$ absorbance peaking at 600 nm, as shown in Figure 2. The electrochemical driving discussed above resulted in a decrease in the 600 nm absorbance and an increase in the absorbance above 750 nm. The steady-state spectrum after 1 min of driving was nearly identical to that measured after trapping by removal of the CH_2Cl_2 and applied bias (Figure 2). The differences between the trapped pn junction spectrum and the pristine undoped bilayer are characteristic of either the n- or p-type doping of polyacetylene and consistent with the formation of a pn junction. The absorbance spectrum for the sample of Figure 1 varied little over the 22 h it was observed (see Supporting Information), as was the case for samples observed over as long as 150 h. The dopant density of the fabricated pn junction is estimated to be of the order 1 e$^-$/100 double bonds (10^{20} cm^{-3}) based on the magnitude of change in the absorbance spectrum and comparison to separate three-electrode experiments. This dopant density is much less than
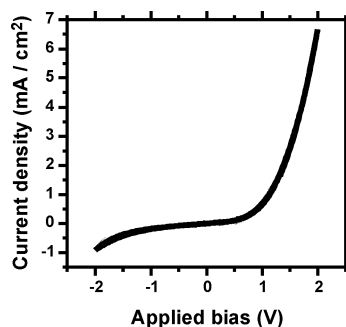
Figure 3. Current density as a function of applied bias for a $P_A \mid P_C$ pn junction after drying under vacuum for 20 h.

the density of the ionic functionality, indicating that a relatively large density of mobile ions remains. It is also much greater than typically found in nondegenerate and rectifying silicon-based pn junctions.

Electrical characterization also supports pn junction formation. The overall conductance of the $P_A \mid P_C$ bilayer greatly increased following doping with, for example, the current at +2 V increasing more than 3 orders of magnitude (see Supporting Information). The functional form of the current density-applied bias ($J-V_{app}$) behavior evolved (see Supporting Information) as the sample dried under vacuum. Immediately after being trapped, the $J-V_{app}$ behavior was nonlinear but symmetric. After 8 h under vacuum to drive off residual solvent, this gave way to relatively stable and asymmetric diode behavior with the rectification ratio of the current at +2 V to that at −2 V being ~7 (see Figure 3). Varying the voltage scan rate had little effect on the $J-V_{app}$ behavior over the range studied (0.1−1000 V/s) implicating a purely electronic, rather than ionic, current. After leveling off, the rectification ratio remained roughly constant over a period of many hours, but the overall current decreased gradually (see Supporting Information). Single-layer films of either n-type P_C or p-type P_A doped to similar levels as in the bilayer showed linear and symmetric $J-V_{app}$ behavior. It is also noted that the undoped bilayer of Figure 1A exhibits rectification, but only at slow scan rates, owing to the mixed ionic/electronic character of the effect.[10]

It is expected that the $P_A \mid P_C$ pn junction could be released from its trapped state by reintroducing salt to reverse the disproportionation reaction. To test this, the pn junction described above was swollen with 0.1 M Bu$_4$NBF$_4$/CH$_3$CN 22 h after it was initially formed, and indeed the absorption spectrum (Figure 2) and overall conductance reverted back to that of the undoped bilayer. Subsequent rinsing to remove residual salt then allowed the pn junction to be reformed by repeating the procedure of Figure 1. As expected, the pn junction could not be successfully trapped if the wash solvent was replaced with a salt solution (e.g., 0.1 M Bu$_4$NBF$_4$/CH$_3$CN).

The $J-V_{app}$ behavior of Figure 3 is reminiscent of a silicon pn junction. In both cases, diode behavior is observed with the same sign of applied bias, corresponding to the forward direction. It is premature, however, to attribute the behavior of the $P_A \mid P_C$ pn junction to the same mechanisms that operate in a silicon pn junction. In fact, significant differences between these systems make anything more than a casual correspondence unlikely. The most notable difference arises from the presence of mobile counterions that are present because the doping level is lower than the density of ionic functional groups in P_A and P_C. As these counterions are not directly compensating for electronic charges injected during

the doping process, they cannot destroy the pn junction, but they will help shape any electric potential gradient between the n- and p-type regions. Studies are underway to better understand the $J-V_{app}$ behavior and why, for instance, residual solvent appears to have such a large effect.

The practical impact of this pn junction is tempered by its low rectification ratio and the poor environmental stability of the doped forms of polyacetylene.[9] Nevertheless, the demonstrated fabrication of a pn junction shows the promise of internal compensation for polymer electronics. On the simplest level, these types of polymers enable the fabrication of important interfaces between dissimilarly doped regions. Consequently, internal compensation opens the door to a wide range of device architectures not possible with conventionally doped polymers. Indeed, polymeric dopant ions, leading to a situation similar to internal compensation, have been exploited in the fabrication of interfaces between doped and undoped conjugated polymers toward applications in light-emitting diodes and photovoltaics.[11] At a more sophisticated level, internally compensated forms where the density of charge injected into the polymer backbone is *precisely* balanced by the density of bound ionic charges are expected to be pure electronic conductors. The development of pure electronic conducting doped conjugated polymers is an exciting and largely unexplored area of basic and applied research.

Supporting Information Available: Experimental details and additional time-dependent data. This material is available free of charge via the Internet at http://pubs.acs.org.

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