Understanding Degradation Pathways in Organic Photovoltaics

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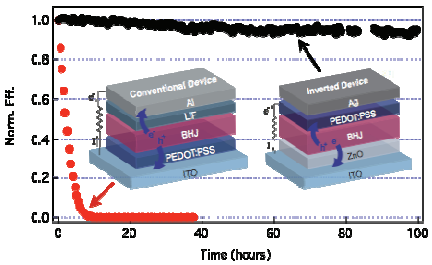
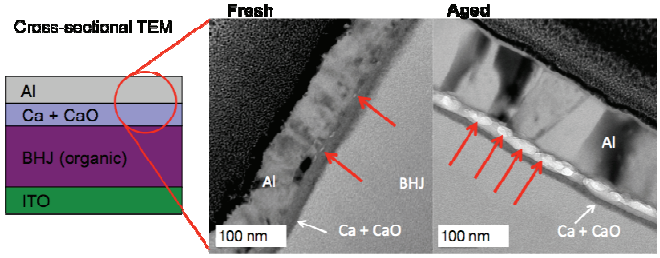
Enhanced Environmental Stability via Contact Selection

Organic photovoltaics (OPVs) require an offset in the work function of the anode and cathode in order to efficiently extract charge from the active layer. Conventional devices rely on low work function contacts, such as LiF/Al or Ca/Al, the chemical reactivity of which precludes fabrication or operation outside of an inert atmosphere glovebox. By employing ZnO as the electron accepting contact and using PEDOT:PSS to collect holes, the relative stability of these materials enables extended operation in air without an encapsulation layer.



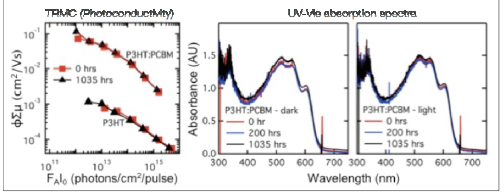


Lloyd et al., J. Mater. Chem., 19, 7638 (2009).

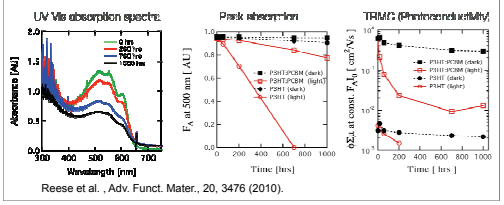
Impact of Oxygen and Moisture on the Active Layer

Contrary to conventional wisdom, in an inert atmosphere the electronic and optical properties of the polymer-fullerene blend prove to be inherently stable. After 1000 hrs illumination in an inert atmosphere there is is no change in the photoconductivity or the UV-Vis absorption spectrum for bare films of P3HT:PCBM on glass (i.e. not functional devices). Outside of the glovebox, however, there is an appreciable loss in light-absorbing chromophores in pristine P3HT. When blended with PCBM, photobleaching of the active layer system can be mitigated significantly.

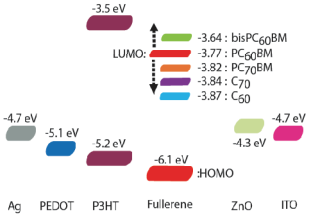
Inert atmosphere



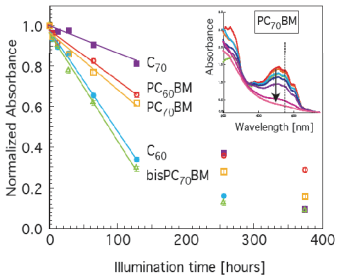
Ambient atmosphere

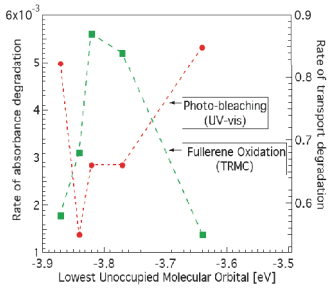


Reese et al. , Adv. Funct. Mater., 20, 3476 (2010).



The degree of stabilization imparted to P3HT by the electron acceptor is intimately related to the D/A morphology, exciton lifetime, and the energy levels that drive charge transfer. Preliminary data indicate that a smaller the LUMO-LUMO offset results in a higher rate of photobleaching in P3HT. We have also observed this trend in D/A systems where the LUMO level of the acceptor can be systematically tuned via molecular functionalization.



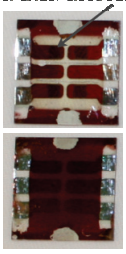


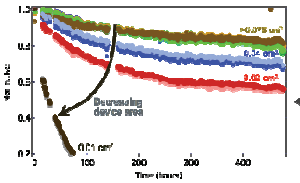
Routes of Ingress for Devices Under Operation

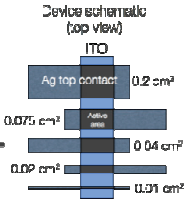
Using a combinatorial degradation system we are able to compare the relative performance of 360 diodes subjected to constant illumination. By varying the aspect ratio of the device active area we are able to observe an increase in device lifetime as the relative fraction for "unprotected edge" is decreased. For these small pixels, edge-in diffusion represents a significant route for degradation of the active layer. Generally, we find that the top contact acts as barrier to prevent oxygen and water vapor transport through the contact. Hence, most aged devices are photobleached around the active areas, but there is little color loss under the electrode.

Combinatorial degradation system designed and fabricated by Matthew Reese.

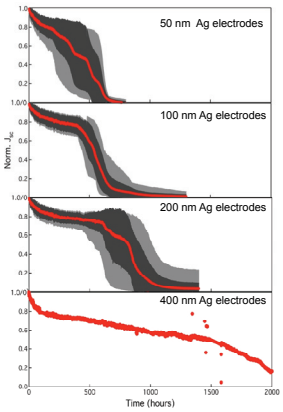
Unbleached active layer under electrodes



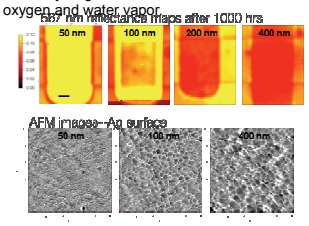




Device Lifetime Primarily Determined by Top Contact

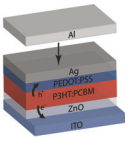


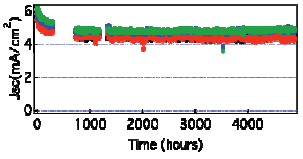
We find that the thickness of the top contact is the first-order, rate limiting factor in determining device lifetime. The average (red), standard deviation (dark grey), and max/min (light grey) behavior are shown (left) for devices with 50, 100, 200, and 400 nm electrodes. Reflectance maps indicate that the thinner electrode eventually become susceptible to oxygen or water vapor transport, indicated by loss of chromophores within the active layer. Tapping mode AFM images suggest that in addition to offering shorter diffusion lengths, thinner top contacts also display a greater density of grain boundaries that assist in the transport of oxygen and water vapor.

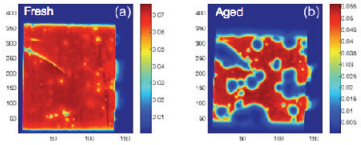


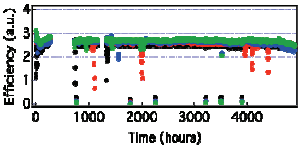
Nucleation and Island Growth Suggests Pinhole Ingress

Photocurrent mapping measurements display regions of zero photocurrent, which nucleate and grow radially as the device ages. This is strongly indicative of point source ingress followed by lateral diffusion into the active layer. This mechanism is also consistent with the dramatic increase in device lifetime when thicker contacts are used. If pinhole ingress can be arrested by filling or creating a tortuous path for diffusion, one should be able to see additional gains in device lifetime. We show that Ag/Al composite electrodes, although only 200 nm in combined thickness, extend the lifetime of these devices to ~5000 hrs.









Lloyd, et al., Sol. Energy Mater. Sol. Cells (2011), doi:10.1016/j.solmat.2010.12.036

Conclusions

- Degradation in conventional devices stems from the reactivity of low work function metals, not the active organic layers
- In larger area devices, electrode thickness dependence studies indicate gas permeability in thin metal electrodes. Photocurrent mapping measurements show nucleation and growth of dark spots in the photocurrent, indicating pinhole ingress of oxygen and water vapor.
- Multilayer electrodes yield surprisingly high stability demonstrating unencapsulated lifetimes of 5000 hours.

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