

Functionalizing Organic Semiconductors with Dipole Monolayers

Matthew C. Williams, Feifei Li, Jordan A. MacQueen, Demetra Z. Adrahtas, Jacob W. Ciszek*

Department of Chemistry and Biochemistry, Loyola University Chicago, 1032 West Sheridan Road, Chicago, Illinois 60660, USA.

This work seeks to improve OFETs performance via the addition of a chemisorbed monolayer on top of the organic material to address various issues such as contact resistance and charge trapping. The monolayer is made possible via site-specific Diels-Alder chemistry which only reacts with the semiconductor. By installing specific functional groups to the surface, the aforementioned issues can be eliminated, resulting in improved charge injection and/or charge transport in organic material.

We focused on the addition of monolayers which contain significant electronic charge separation (or molecular dipole) within their structure. This feature can act as a potential step, shift the mean energy in gaps, and/or align energy levels between materials. We first utilize the chemistry to selectively append dipole-containing molecules to trap states at grain boundaries for polycrystalline OFETs in order to shift the mean energy within the grain boundary and improve device performance. Grain boundaries are unavoidable flaws inherent to the materials, and the ability to address trap states would be a powerful way to address these flaws post-fabrication. This performance improvement is exemplified in conductance measurements with two orders of magnitude increases, improved threshold voltages, and doubling of mobility.

Additionally, we can optimize the surface potential of thin films by systematically varying similar dipole-containing monolayers. A linear relationship between dipole strength and surface potential shift is seen, as predicted by the Helmholtz equation. The achieved potential adjustments are attributed to the monolayer and result in a high degree of tunability of surface potential. With the capability to shift potential up to ~ 800 mV, reducing electron charge injection barriers is hypothetically feasible. The challenges arising in conductance measurements are discussed.

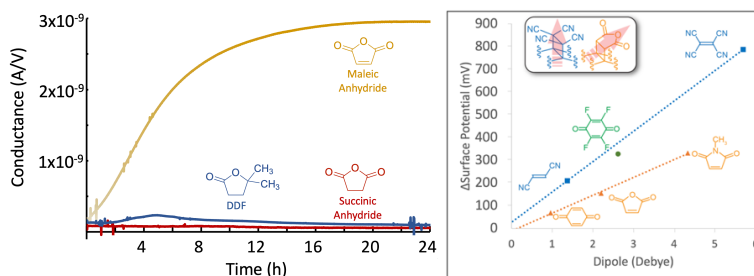


Figure 1. (Left) Conductance of pentacene reacted with maleic anhydride for 8 h as a function of time measured at 0.2 V. The controls are succinic anhydride (red) and DDF (blue). The relationship between dipole strength and the resulting surface potential is characterized by the bond dipole angle (right).

Supplemental Information

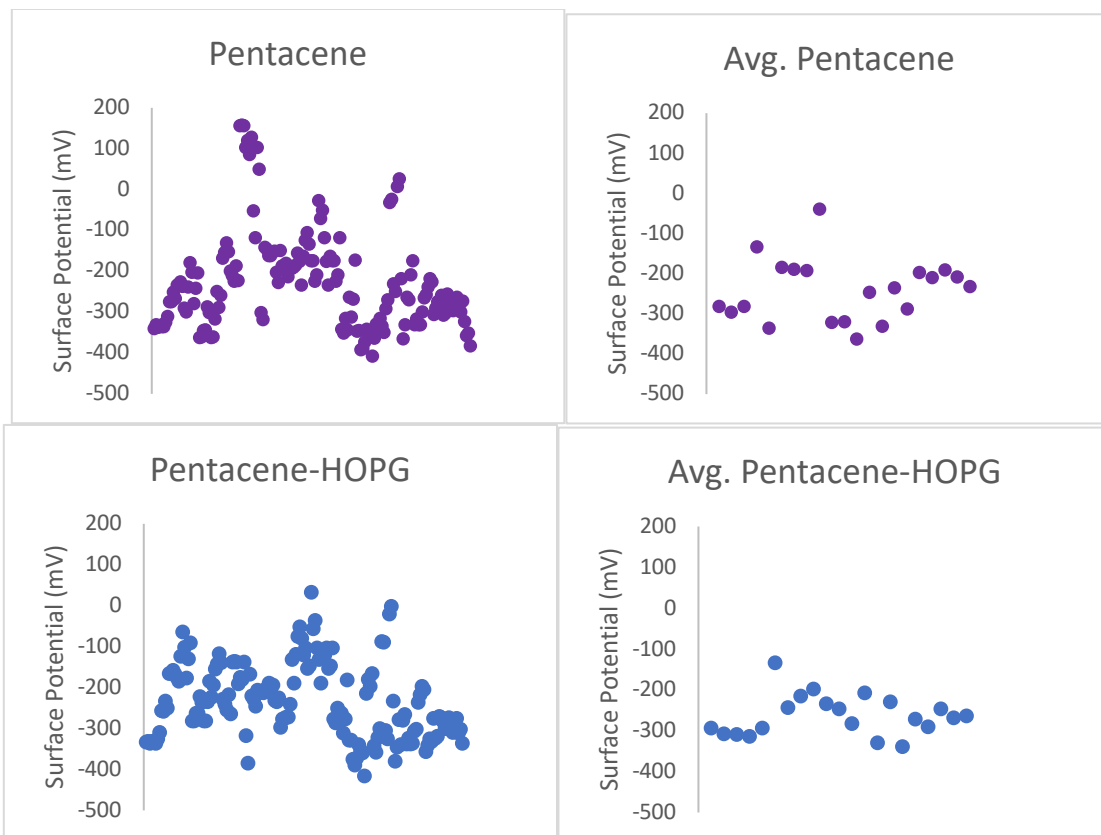


Figure S1. (a) Individual pentacene surface potential measurements and (b) surface potentials averaged by individual organic depositions. (c) Individual pentacene surface potential measurements once referenced to highly oriented pyrolytic graphite and (d) surface potentials averaged by individual organic depositions referenced to highly oriented pyrolytic graphite.