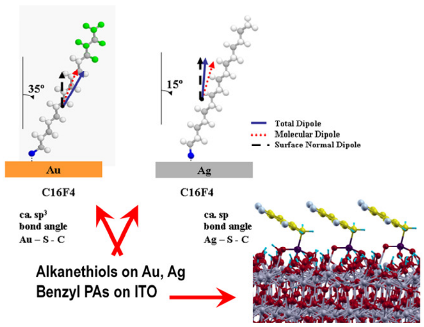
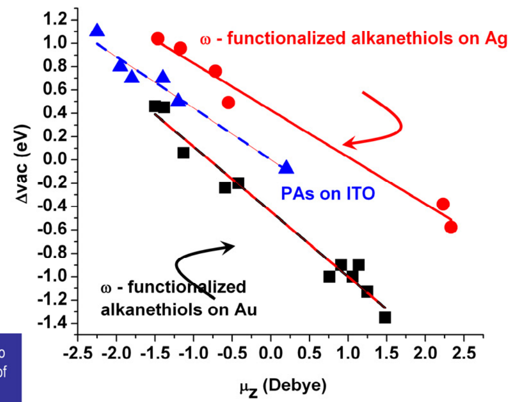
Control of Effective Work Function for Metal and Oxide Contact Materials

ACHIEVEMENT: We have demonstrated control of the effective work function of a variety of OLED, OPV and OFET contact materials, using both ω-functionalized alkanethiols (for metals such as Au, Ag) and both alkane- and aryl-phosphonic acids (PAs) for metals oxides such as ITO. Work function (ϕ) can be tuned over a range of ca. 1.5 eV. Control of ϕ is achieved either by choice of terminal functional group, or dilution of one modifier in another in the monolayer film.





Impact: Nanometer-scale control of effective work function can be used to tune the charge injection properties of metals and metal oxides in a variety of emerging molecular electronic technologies, including OLEDs, OPVs and OFETs

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IMPACT: The effective work function, polarity (wettability) and “contact selectivity” are now tunable over an extremely wide range for both metals and metal oxides, using simple, readily accessible interface chemistries. It is noteworthy that widely differing modifiers, on both metals and metal oxides, appear to give nearly the same slope (Δϕ/ΔD), suggesting that work function tunability is governed most by the type of terminal functional group on the modifying layer.

DISCUSSION:
Tuning of the effective work function of metal and semiconductor surfaces using molecular adsorbates is an area that has seen increased emphasis owing to the importance of metal/organic and semiconductor/organic interfaces in emerging molecular electronic technologies. The impact of these adsorbates on the current/voltage properties of simple diodes and transistors is significant. Single monolayers of certain molecules can alter the onset voltages, leakage currents, rectification ratios and quality factors of simple diodes, and greatly alter the sub-threshold slopes, saturation currents, and drive frequencies of organic field-effect transistors. Our recent studies have focused on the use of semi-fluorinated alkanethiols, and mixtures of these thiols, on Au and Ag surfaces, and various alkane and aryl phosphonic acids on ITO, using primarily UV-photoelectron spectroscopy (UPS) to estimate effective surface work functions and changes in these work functions as a function of functional groups in the modifying layer, and their relative concentrations in mixed monolayers. We have shown fine tunability of work function over a range of ca. 1.5 eV, with similar Δϕ/ΔD slopes, suggesting that the outermost functional group in the modifying layer plays the most significant role in determining work function. Kelvin probe and device characterization using these PAs on ITO substrates (BK) appears to bear out the conclusions reached using UPS estimates of work function.

Relevant publications:

“Tuning the Effective Work Function of Gold and Silver Using ω-Functionalized Alkanethiols: Varying Surface Composition through Dilution and Choice of Terminal Groups,” Dana M. Alloway, Amy L. Graham, Xi Yang, Anoma Mudalige, Ramon Colorado, Jr., Vicki H. Wysocki , Jeanne E. Pemberton, T. Randall Lee, Ronald J. Wysocki, Neal R. Armstrong, Journal of Physical Chemistry C, 113, 20328-20334, (**2009**).

“Oxide Contacts in Organic Photovoltaics: Characterization and Control of Near-Surface

Composition in Indium-Tin Oxide (ITO) Electrodes,” Neal R. Armstrong, P. Alex Veneman, Diogenes Placencia, Erin Ratcliff, Michael Brumbach, Accounts Chemical Research (**Invited**), 42, 1748-1757, (**2009**).

"Modification of the Surface Properties of Indium Tin Oxide with Benzylphosphonic Acids: A Joint Experimental and Theoretical Study" by Peter J. Hotchkiss, Hong Li, Pavel B. Paramonov, Sergio A. Paniagua, Simon C. Jones, Neal R. Armstrong, Jean-Luc Brédas, Seth R. Marder Advanced Materials, 21, 1-6 (**2009**).

“Theoretical characterization of the indium tin oxide surface and of its binding sites for adsorption of phosphonic acid monolayers,” Pavel B. Paramonov, Sergio A. Paniagua, Peter J. Hotchkiss, Simon C. Jones, Neal R. Armstrong, Seth R. Marder, and Jean-Luc Brédas, Chemistry of Materials, 20, 5131-5133 (**2008**).

“Phosphonic Acid Modification of Indium-Tin Oxide Electrodes: Combined XPS/UPS/Contact Angle Studies,” Sergio A. Paniagua, Peter J. Hotchkiss, Simon C. Jones, Seth R. Marder, Anoma Mudalige, F. Fathima Saneeha Marrikar, Jeanne E. Pemberton, Neal R. Armstrong, J. Phys. Chem. C. (invited paper, Larry Dalton Festschrift) J. Phys. Chem. C 112, 7809–7817 (**2008**).

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