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Controlling the Work Function of Indium Tin Oxide: Differentiating Dipolar from Local Surface Effects

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Because of the ubiquitous use of indium tin oxide (ITO) as an anode material for optoelectronic devices, considerable effort has gone into the development and testing of models aimed at enhancing hole injection from ITO into an organic overlayer. Among these models[1] is an elegant one based on simple concepts of electrostatics:[2] organization of a dipole layer at the surface of an ITO electrode is predicted to affect its work function (ϕ) linearly, and ultimately its carrier injection ability.[1] This model predicts that organizing a dipolar layer on an electrode surface with its negative end furthest from that surface should increase ϕ of that electrode.[2,3] Impressive tests of the dipole model have been conducted with use of self-assembled monolayers of para-substituted arylthiols on gold[3] or copper[4] and para-substituted benzoic acids on CdTe,[5] CdSe,[6] GaAs,[7] TiO_2,[8] and ITO.[9] However, such tests suffer from a degree of ambiguity in that para-substitution in these surface modification reagents affects not just their molecular dipole moments, but the electronegativity of their ligating groups (thiolate or carboxylate) analogously. Thus, attempts to understand, and ultimately exploit, para-substituted aryl reagents for control of ϕ are compromised: Local electronegativity effects, including proton transfer from the reagent to the electrode surface, cannot be excluded as causative for any changes in ϕ observed. (Also problematic is that any proton transfer from an acid to an electrode surface could have a deleterious effect on device performance.[10,11]) We describe herein surface modification of ITO using organotin complexes which enables systematic control of the ITO electrode work function and which obviates the problem of net proton transfer to the ITO surface.[12,13] Furthermore, our system enables clear differentiation between the effects of group dipole and electronegativity of our surface modification reagents on the measured change in ϕ for ITO.

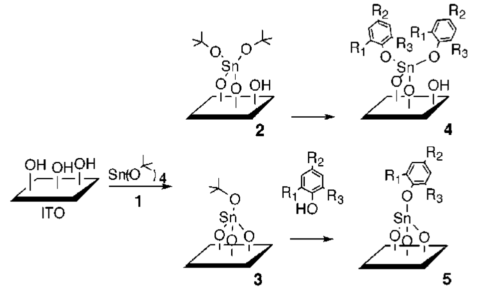
We have described[12] the reaction between surface OH groups of ITO and tetra(*tert*-butoxy)tin (**1**), which gives surface tin alkoxides. Tin alkoxide **1** (Strem; 90L exposure) was deposited on the hydroxylated ITO, which was held at 150 K; the sample was then warmed to 293 K to give $[ITO]\text{-}[O]_2\text{-}Sn(OBu^t)_2/[ITO]\text{-}[O]_3\text{-}Sn(OBu^t)$ (**2/3**), as determined by X-ray photoelectron spectroscopy (XPS) from surface C:Sn ratios (see Table 1).[12,13] Next, a series of substituted phenols was vapor deposited onto **2/3** (approximately 90 L, with the substrate held at 150 K). Substrates were then heated to 290 K (except for *p*-nitrophenol, which was heated to 390 K) to enable ligand metathesis and to desorb multilayer phenol.[13] Stoichiometries of the tin phenoxide surface complexes formed, $[ITO]\text{-}[O]_2\text{-}Sn(OC_6H_4\text{-}X)_2/[ITO]\text{-}[O]_3\text{-}Sn(OC_6H_4\text{-}X)$ (**4/5**; **a**, $R_1 = R_2 = R_3 = H$; **b**, $R_1 = R_3 = H$, $R_2 = OCH_3$; **c**, $R_1 = R_3 = H$, $R_2 = F$; **d**, $R_1 = R_3 = H$, $R_2 = CF_3$; **e**, $R_1 = R_3 = H$, $R_2 = NO_2$; **f**, $R_1 = R_3 = F$, $R_2 = H$; **g**, $R_1 = OCH_3$, $R_2 = R_3 = H$; **h**, $R_1 = F$, $R_2 = R_3 = H$), were determined by XPS (Table 1; Scheme 1); no appreciable change in ratios of starting materials **2**:**3** to products **4**:**5** was measured, except for **4e/5e**, because of heating.[12,13] XPS analysis of F, N, organic O, or fluorinated alkyl C provided a complementary determinant of surface complex stoichiometries. Using the In($3d_{5/2}$) peak as an internal standard allowed relative changes in surface tin complex loading to be quantified. Measurement of the In:Sn ratio for each sequence of deposition of **1** and ligand exchange determined that these complex loadings were consistent among experiments within 25%.

Table 1. Gas-Phase Dipole Moments and Measured Changes in ϕ for **4/5**

phenol	$\mu_{z\ phe}{}^{a}$	$\Delta\phi^{b}$	phenol	$\mu_{z\ phe}{}^{a}$	$\Delta\phi^{b}$
a	−0.44	0.47	**e**	5.14	1.11; 1.08
b	−0.55	0.48	**f**	−1.85	0.29
c	1.20	0.67	**g**	−1.47	0.30
d	3.06	0.92; 0.87	**h**	−1.18	0.29

[a] Dipole moments[15] are reported along the *z*-axis, defined as the C−O bond of the phenol. [b] Work function changes are between measured values of ϕ for the tin phenoxides (**4/5**) versus the alkoxides (**2/3**) for each sample.

Scheme 1. Synthesis of ITO Surface Bound Tin Phenoxides



a: $R_1 = R_2 = R_3 = H$; **b**: $R_1 = R_3 = H$, $R_2 = OCH_3$; **c**: $R_1 = R_3 = H$, $R_2 = F$;
d: $R_1 = R_3 = H$, $R_2 = CF_3$; **e**: $R_1 = R_3 = H$, $R_2 = NO_2$; **f**: $R_1 = R_3 = F$, $R_2 = H$;
g: $R_1 = OCH_3$; $R_2 = R_3 = H$; **h**: $R_1 = F$; $R_2 = R_3 = H$

Changes in ϕ for ITO on substitution were also measured by XPS. Secondary electrons in photoemission are produced by inelastic scattering of primary electrons within the sample. Electrons with a kinetic energy equal to or larger than the vacuum level of the sample can be detected. A negative bias was applied to the sample, ensuring that all low kinetic energy electrons (including those possessing “zero” kinetic energy) could be detected. The work function is obtained from eq 1, in which the incident photon energy ($h\nu$), the kinetic energy of electrons emitted from occupied states at the Fermi energy (E_{EF}), and the low kinetic energy onset of the secondary electron distribution (E_{onset}) are related.[1] E_{EF} is constant when the photon energy is fixed and the sample and spectrometer are in thermodynamic equilibrium, in electrical contact; therefore, a change in the sample ϕ can be determined by measuring the corresponding shift in the low kinetic energy onset of the secondary electrons. Resolution in this experiment is determined by the pass

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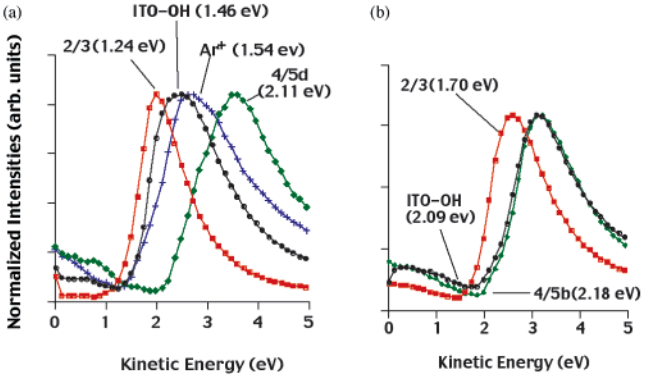

Figure 1. Onset energies (eV) for secondary electron emission for (a) *p*-CF_3 and (b) *p*-OCH_3 substituted **4/5** complexes. Values for hydroxylated ITO (ITO-OH), dehydroxylated ITO (Ar^+), and **2/3** are also given.

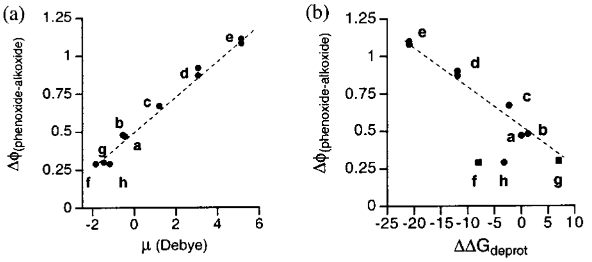

Figure 2. (a) A good correlation exists between calculated gas-phase dipole moments for both para- and ortho-substituted phenols and measured changes in ϕ for ITO electrodes.[17] (b) A good correlation exists between deprotonation free energies vs phenol for para-substituted phenols and measured changes in ϕ for ITO electrodes. Note the deviations measured (●)[16] for ortho-substituted **h** and calculated (■)[15] for **f** and **g**.

energy of the electron spectrometer (Perkin-Elmer Precision Electron Energy Analyzer Model 15-255 GAR; pass energy = 5 eV), with onset measurement being accurate to ±0.1 eV. Data were analyzed by extrapolating the slope of the measured secondary electron distribution for each case to the baseline intercept (Figure 1). Measured values of ϕ (Table 1) for a series of substituted surface tin compounds **4/5** were independent of X-ray photon flux and applied voltage bias; they were standardized against work functions measured for corresponding samples of **2/3** to obviate effects of experimental variation in ITO surface complex loading, Ar^+ ion bombardment, or hydroxylation.

$$\phi = h\nu - (E_{\mathrm{EF}} - E_{\mathrm{onset}}) \qquad (1)$$

According to a simple structural model, *relative* dipole moments normal to an idealized surface ($\mu_{z\ \mathrm{avg}}$) of a series of bound tin phenoxides **4** and **5** can be related to (gas phase) calculated normal dipole moments for the individual phenols ($\mu_{z\ \mathrm{phe}}$), assuming any surface dipole induced by Sn coordination, surface complex loadings, stoichiometries and geometries for all series members, and ITO surface roughness are, on average, similar. Examination of an idealized structure for a tetrahedrally substituted surface tin complex shows that rotation about the Sn−O−C linkage in a surface phenoxide generates a family of rotamers; each member of this family contributes to $\mu_{z\ \mathrm{avg}}$ according to its particular conformation. For example, consider **4d** ($\mu_{z\ \mathrm{phe}} = 3.06$ D). For a Sn−O−C angle of 118°,[14] the maximum, relative contribution to $\mu_{z\ \mathrm{avg}}$ is ≈ 6.1 D (where both ligands are oriented about 7° from the surface normal), and the minimum is 0 D (with both ligands lying parallel to the surface). For **5d**, the contribution to $\mu_{z\ \mathrm{avg}}$ is ≈ 1.4 D. Should our model hold, a linear relationship[2] should exist between calculated phenol dipole moments[15] and changes in ϕ for ITO. In fact, measured data for ϕ for a series of complexes **4/5**, reported relative to ϕ for **2/3** (Table 1), do vary linearly with gas-phase dipole moment calculations (Figure 2a). However, these data also correlate with relative free energies (vs phenol) for deprotonation[16] of the para-substituted phenols (Figure 2b). Most significant, though, are data for ortho-substituted phenols, in which dipole moment and deprotonation free energy trends are opposed. Note the good adherence to the qualitative "fit" between measured work functions for **4f**−**h**/**5f**−**h**-substituted ITO with calculated phenol dipole moments (Figure 2a); the small deviation from this "fit" measured for the ortho-substituted phenoxide complexes might be due to interactions of their substituents with the Sn, which could change average ligand conformational arrangements from those for para-substituted phenoxides. Contrast this relationship with the pronounced deviation from "fit" between the measured work function for **4h**/**5h**-substituted ITO with deprotonation free energy data (Figure 2b).[16] This dichotomy unambiguously demonstrates that it is in fact dipolar properties of the surface bound species, and not local electronegativity effects, that control the work function of the modified ITO electrode. The efficacy of tin complex-based surface modification procedures to affect carrier injection in simple diode devices is now being tested.

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Supporting Information Available: Work function measurements for ITO with surface bound phenoxytin complexes **4a/5a**, **4c/5c**, **4e/5e**, **4f/5f**, **4g/5g**, and **4h/5h**, from onset energies for secondary electron emission (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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