Dipolar ligands tune plasmonic properties of tin-doped indium oxide nanocrystals

Victor Segui Barragan,† Benjamin J. Roman,‡ Sofia A. Shubert-Zuleta,† Marina W. Berry,† Hugo Celio,¶ and Delia J. Milliron*,‡,#

†Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States
‡McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States
¶Texas Materials Institute, University of Texas at Austin, Austin, Texas, 78712, United States

E-mail: milliron@che.utexas.edu

Abstract

Surface functionalization with dipolar molecules is known to tune electronic band alignment in semiconductor films and colloidal quantum dots. Yet, the influence of surface modification on plasmonic nanocrystals and their properties remains little explored. Here, we functionalize tin-doped indium oxide nanocrystals (ITO NCs) via ligand exchange with a series of cinnamic acids with different electron withdrawing and donating dipolar characters. Consistent with previous reports on planar and nanocrystalline semiconductors, we find that withdrawing (donating) ligands increase (decrease) the work function, which we ascribe to an electrostatic potential shift across the molecular layer. Quantitative analyses of the plasmonic extinction spectra reveal that varying the ligand molecular dipole affects the near-surface depletion layer, with an anticorrelated trend between electron concentration and electronic volume fraction, factors that are positively correlated in as-synthesized NCs. Electronic structure engineering through surface modification provides access to distinctive combinations of plasmonic properties that could enable optoelectronic applications, sensing, and hot electron-driven processes.
The influence of surfaces on all material properties is amplified for nanomaterials, owing to their large specific surface areas. A powerful strategy for tuning the electronic properties of surfaces and interfaces is to introduce dipolar molecules that bind in an oriented manner to the surface of metals\textsuperscript{1} and semiconductors,\textsuperscript{2} modifying electronic properties such as the work function that is the energetic barrier to removing electrons from the material. Work function changes across a wide range of material compositions have been rationalized as due to the dipole of the molecules establishing a step in the potential energy of electrons as they cross the layer.\textsuperscript{3,4} Withdrawing (donating) molecules consistently result in an increase (decrease) of the work function.\textsuperscript{1,2,4–13} This approach has been used to engineer the band alignment at interfaces, raising or lowering the barriers to move electrons and holes between materials and strongly impacting optoelectronic properties in heterostructures ranging from metal/semiconductor contacts to films of colloidal quantum dots, leading to more efficient light emitting devices and solar cells.\textsuperscript{7,8,10,14,15} Varying the dipole in a surface molecular layer can modify the built-in potential, or the extent of band bending in the near-surface region,\textsuperscript{9,12} which controls the availability of photogenerated charge carriers for energy conversion or photocatalytic reactions.\textsuperscript{16–18}

Even though there has been considerable success in tuning the electronic properties of metal and semiconductors films, as well as colloidal nanomaterials, the influence of dipolar surface layers on plasmonic nanoparticles remains largely unexplored. In plasmonic nanoparticles, free charge carriers oscillate in response to light but are confined to the nanoparticles resulting in strong absorption or scattering at a specific frequency known as the localized surface plasmon resonance (LSPR). The LSPR frequency is sensitive to the nanoparticle environment, so changes in surface chemistry are expected to influence plasmonic properties.\textsuperscript{19} In a previous study, electron-donating and withdrawing ligands were bound post-synthetically to gold nanoparticles, impacting their optical and electronic properties, yet the electrostatic effects of the molecular dipoles were not considered in the analysis, leaving open the question of how surface dipolar ligands influence plasmonic nanomaterials.\textsuperscript{20} Furthermore, unlike conventional metals, plasmonic semiconductor nanocrystals (NCs) can be strongly influenced by a surface space charge layer\textsuperscript{19,21–23} and the interplay between surface dipole effects and band bending in governing their plasmonic properties is unknown. Therefore, we hypothesize that, since molecular layers are able to modify the electronic properties at the surface of materials, using surface modification with dipolar ligands on plasmonic doped metal oxide NCs can offer a new post-synthetic tunability handle and lead to changes in their plasmonic properties opening new routes to improving their performance for applications such as sensing, catalysis, or optoelectronic devices.\textsuperscript{19}

Herein, we analyze the impact of dipolar surface ligands on the electronic structure and plasmonic properties of doped metal oxide NCs. A series of cinnamic acid ligands with differ-
ent electron withdrawing and donating dipolar characters are bound to colloidal tin-doped indium oxide (ITO) NCs via ligand exchange. The electronic properties are investigated by obtaining the work function \( (\Phi) \) of the modified ITO NCs via ultraviolet photoemission spectroscopy (UPS). Our results show that the functionalized ligands with a dipole moment pointing towards the surface (donating) lower the work function while withdrawing ligands raise the work function; this trend agrees with previous reports on a wide range of materials.\textsuperscript{1–4,11} The plasmonic properties are analyzed by optical spectroscopy of solvent-dispersed NCs, interpreted by fitting the spectra with the Heterogeneous Ensemble Drude Approximation (HEDA) model, which extracts quantitative parameters of interest including the free electron concentration \( (n_e) \) and depletion layer width \( (W_D) \). Our results demonstrate that by using post-synthetic surface modification, we access combinations of electronic properties not achievable by a direct synthetic approach. In particular, we observe when changing the ligand dipoles that \( n_e \) and the volume fraction of the plasmonic NC core \( (f_e) \) are anti-correlated, contrasting with the positive correlation between these parameters when tuning dopant concentration during synthesis.\textsuperscript{24,25} This new strategy for post-synthetically modifying \( W_D \), in particular, opens new opportunities to customize plasmonic metal oxide NCs for applications since the depletion layer governs the electronic and optical coupling of NCs to their environment and to adjacent molecules or other NCs.

**ITO NC Synthesis and Surface Modification**

ITO NCs 12.2 ± 1.1 nm in diameter and doped with 3 at.% Sn were synthesized by slow injection followed by mass action-driven ligand exchange to introduce variable surface functionalization. As detailed previously\textsuperscript{26} and based on methods developed by the Hutchison group\textsuperscript{27,28} a metal-oleate precursor solution containing both tin and indium was slowly added to a reaction flask containing oleyl alcohol. To functionalize the NC surface with dipolar molecules, oleate-capped ITO NCs (As Syn) are precipitated with ethanol and redispersed in their respective cinnamic acid ligand solutions; where 4H and OCH\textsubscript{3} were the electron-donating ligands, and CF\textsubscript{3} and 3,5F were the electron-withdrawing ligands. After stirring for 24-48 h, the NCs are precipitated by adding hexane, with the reversal of polarity indicative of a change in surface chemistry, then redispersed in suitable polar solvents selected for each ligand (further details in SI Text). The size and shape of the As Syn ITO NCs and the surface-modified ITO NCs are obtained via scanning transmission electron microscopy (STEM), with size distribution analysis (ImageJ) including at least 400 NCs (Figures 1a and S1). There is no apparent size or shape change following ligand exchange.

Proton nuclear magnetic resonance (\(^{1}\text{H} \) NMR) spectroscopy was used to characterize the molecular layers resulting from the cinnamate ligand exchange process. NMR is commonly used to analyze ligands on NC surfaces because bound molecules have distinctly broadened spectral features that easily distinguish them from freely diffusing molecules.\textsuperscript{29–31} In our case, the presence of bound cinnamate molecules after ligand exchange is evident based on the line broadening compared to the free cinnamic acids (Figures 1b and S2). A weak signal from the alkene protons of the native oleate ligands (5.3 ppm) remains, indicating that a small amount of oleic acid persists on the surface after ligand exchange. The incomplete exchange is expected since molecules with the same anchoring group (here, carboxylate) have a similar surface binding energy.\textsuperscript{32–34} Nevertheless, the presence of remaining native oleates
is beneficial in promoting the colloidal stability of the cinnamate-functionalized ITO NCs. In comparison, it has been shown that phosphonic acid-terminated ligands have a stronger binding affinity to metal oxides and quantum dots, which leads to a full displacement of the native oleates.\textsuperscript{32,35–37} In a trial experiment, functionalizing ITO NCs with an aryl phosphonic acid ligand (phenylphosphonic acid) produced a poorly dispersed colloid, so we selected cinnamate ligands for this study. Ligand quantification by thermogravimetric analysis gave consistent results across the dipolar series studied; after ligand exchange, the ITO NCs all have a similar cinnamate surface coverage of 4.8 ± 0.4 cinnamates/nm\textsuperscript{2} (see SI text and Table S1).

![Figure 1](image)

**Figure 1:** **ITO NCs surface functionalization** (a) STEM images and size histograms of 3 at.% Sn 12 nm ITO NCs before and after ligand exchange. Scale bars are 30 nm. (b) \textsuperscript{1}H-NMR spectra in CDCl\textsubscript{3} of oleic acid, as synthesized ITO NCs, 3,5F-cinnamic acid, and 3,5F-capped ITO NCs (from top to bottom), in which line broadening indicates ligand binding on the surface. The resonance peak at 7.26 ppm corresponds to residual CDCl\textsubscript{3}. (c) Cinnamic acid ligands used in this study: 4-methoxycinnamic acid (OCH\textsubscript{3}), cinnamic acid (4H), 3,5-difluorocinnamic acid (3,5F), and 4-trifluoromethylcinnamic acid (CF\textsubscript{3}). From left to right, the ligand’s dipole goes from more donating to more withdrawing towards the NC surface, with the oleate dipole lying in middle of the series. The computed dipole moments of the cinnamic acid ligands in vacuum are as reported in Ref. 11.

**Electronic Properties**

Dipolar ligands bound to a surface generate a potential energy step that changes electronic properties of the material, notably the work function (\(\Phi\)).\textsuperscript{4} Dipoles commonly arise from polarization across heterointerfaces and deliberately introducing dipoles by molecular engineering has been used to reduce onset potentials in light-emitting devices, enhance photovoltages in solar cells, and more.\textsuperscript{1,3,7–9,36,38} The electrostatic effects of molecular dipole layers
also influence electronic properties of nanomaterials and they have been shown to systematically modify $\Phi$ of colloidal quantum dots. Regardless of material composition or dimensions, donating ligands produce a downwards potential energy step for electrons escaping the material that lowers $\Phi$. Conversely, withdrawing ligands create an upward step that increases $\Phi$. These results have been understood based on simple electrostatics using the Helmholtz equation as an approximation, $\Delta E = -\mu_z/(A\varepsilon_r\varepsilon_0)$, where the change in potential energy ($\Delta E$) is related to the molecular dipole moment normal to the surface ($\mu_z$) and the surface area per ligand molecule ($A$). In our case, the surface density of cinnamate ligands and the dipole arising from their bonding to the NC surface are considered to be approximately constant throughout, so the dipole moment is the main variable responsible for trends in electronic and optical properties.

The impact of the molecular surface dipole on the electronic properties of ITO NCs was determined using UPS on films of functionalized NCs. The secondary electron cutoff is used to obtain $\Phi$ (Figure 2a), while the low binding energy region (Figure 2b) allows the determination of the ionization energy and the valence band maximum (VBM) relative to the Fermi energy ($E_F$) (SI Text and Table S2). A correlation is observed between $\Phi$ and the ligand dipole (Figure 2c). Increasing the strength of the donating ligand decreases $\Phi$ compared to the As Syn ITO NCs, while withdrawing ligands result in higher $\Phi$. Between the most withdrawing ($\text{CF}_3$) and most donating ($\text{OCH}_3$) ligands studied $\Phi$ varies by 1.2 eV. Similar trends and magnitudes of $\Delta\Phi$ have been found for planar ITO films, other bulk semiconductors, and films of quantum dots. Based on the Helmholtz equation, even greater changes could be anticipated for molecules with larger magnitude dipole moments or higher surface density.

Generally, changes in $\Phi$ are caused by changes in the electron affinity or changes in the band bending, i.e., the energy difference between bulk and surface, also known as built-in potential. Both effects have been previously reported in different semiconductor films modified by dipolar molecular layers and they can occur simultaneously. Although UPS cannot directly differentiate these two electronic effects, the data suggest changes in band bending are occurring for the different dipolar ligands. Specifically, if band bending remained fixed while changing $\Phi$, the VBM would shift identically to the secondary electron cut-off. While we do observe changes in the VBM (Figure 2b) the shifts are modest compared to changes in $\Phi$ and they do not correlate with dipole. Thus, besides the shifts in electron affinity and ionization energy that follow the electrostatic step in the potential energy, the band bending must also be changing. Considering the importance of surface band bending for plasmonic properties of ITO NCs, we hypothesized that functionalization with dipolar ligands should impact the spatial distribution of free electrons and the associated optical properties.
Figure 2: Electronic characterization of surface modified ITO NCs via UPS (a) Secondary electron cutoff region of UPS spectra. (b) Valence band maxima region of UPS spectra. (c) Change in work function with the dipole moment of cinnamic acid derivatives shown in Figure 1c.

Plasmonic Properties

The electronic band structure of doped metal oxide NCs has a considerable impact on their plasmonic properties.\cite{22,39,40} For example, increasing the Sn dopant concentration during ITO NC synthesis causes a downward shift of the conduction band minimum ($E_{CBM}$) while filling conduction band states, leading to a larger optical band gap energy (Moss-Burstein effect).\cite{25,26} However, the free electrons are not distributed uniformly throughout the NC volume since surface states pin the $E_F$ at the surface and induce band bending, resulting in a near-surface depletion layer. The NC volume fraction accessible to the conduction band electrons, $f_e$, and their concentration within that volume, $n_e$, both substantially influence plasmonic properties including the LSPR frequency, the extinction coefficient, and the near-field enhancement of resonant light.\cite{21} As the dopant concentration is increased, the conduction band is filled with more free electrons causing an increase in $n_e$ as well as $f_e$, making these plasmonic properties positively correlated for synthetically accessible variations of doped metal oxide NCs.\cite{22} In this study, the UPS data suggest changes in the band bending of the ITO NCs when functionalizing their surfaces with dipolar molecules, which implies an impact on their plasmonic properties.

The LSPR frequency is significantly influenced by changes in $n_e$, per Eqs. 1 and 2

$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{\varepsilon_\infty + 2\varepsilon_m} - \gamma^2}$$

$$\omega_p = \sqrt{\frac{n_e e^2}{m^* \varepsilon_0}}$$

where $\omega_{LSPR}$ and $\omega_p$ are the LSPR frequency and bulk plasma frequency respectively, $\varepsilon_\infty$ is the constant background polarizability of the material, $\varepsilon_m$ is the dielectric constant of the surrounding solvent, $\gamma$ is the damping constant, and $m^*$ and $e$ are the effective mass and charge of the electrons.\cite{21}

Contrary to our initial expectations, comparing the extinction spectra of dispersed ITO
NCs capped with the different cinnamic acid ligands revealed little change (Figure 3a). Each sample is dispersed in a different solvent, so variations in $\varepsilon_m$ may disguise any peak shifts due to changes in $n_e$. Although the actual peak is obscured by solvent vibrational bands, the LSPR peak maxima could be extracted by fitting and the shifts were minimal and uncorrelated with molecular dipole (Figure S4 and Table S3). So, even though UPS suggests changes in band bending which would impact the plasmonic properties of the NCs, changes that may be occurring in $n_e$ or $f_e$ are not apparent by qualitatively examining the optical spectra (Figure 3a).

Fortunately, more information can be gleaned by analyzing the LSPR spectra quantitatively, using the known NC size and measured NC concentration to constrain the fitting. In the Heterogeneous Ensemble Drude Approximation (HEDA), LSPR spectra are fit to a model that approximates the NC electron distribution as a metallic core surrounded by a depleted space charge layer in a core-shell structure where the plasmonic core occupies a volume fraction $f_e$ and contains a radially invariant electron concentration $n_e$. To extract these electronic characteristics with confidence, the number of free parameters is limited by independently measuring input values including NC concentration, size, and size distribution. To fit the measured extinction spectra to the HEDA model (Figure S4), NC sizes and size distributions obtained by STEM and concentrations of NCs in solution, determined by inductively coupled plasma-mass spectrometry, were used (further details in SI Text).

By fitting LSPR spectra with the HEDA model we found that the electron-withdrawing (donating) ligands induce a decrease (increase) of $n_e$ and a larger (smaller) $f_e$, which indicates a reduction (increment) of $W_D$ (Figure 3b). These changes in $W_D$ are consistent with the influence of the ligand dipoles on band bending implicit in the UPS results. Overall, we obtain a tunability of 17% in $n_e$, of 39% for the number of free electrons per NC ($N_e$), and of 66% for $f_e$ (Table S3). Thus, the ligand dipole-induced changes in band bending are indeed evident in the NC plasmonic properties, though a cursory look at normalized LSPR spectra obscured the trends.

Together, these results indicate an anticorrelation between $n_e$ and $f_e$ as the ligand dipole is varied (Figure 3b and Scheme 1). Since raising $n_e$ by synthetically boosting the Sn concentration or growing larger NCs also increases $f_e$, this anticorrelation is uniquely accessible by post-synthetic ligand exchange. Such a combination of properties suggests new opportunities to design NCs for specific applications. For example, electron-withdrawing ligands enable access to NCs with a low $n_e$, which can facilitate the generation of hot electrons, while reducing $W_D$ to allow rapid extraction of those excited electrons.
Figure 3: **LSPR characteristics of surface-modified ITO NCs** (a) Normalized extinction spectra obtained from HEDA model fits for each sample of the series. The inset shows a zoom of the LSPR maximum region. (b) Electron concentration (red) and electron-accessible volume fraction (blue) for different surface ligands, in order of their dipoles from most withdrawing to most donating. Error bars represent the standard deviation in the fit results when analyzing four independently prepared dispersions with different NC concentrations.

Scheme 1: **Summarized results relating surface modification impacts to the plasmonic properties of ITO NCs**

There are two possible mechanisms by which a molecular layer on a semiconductor surface modifies band bending and both are related to the surface states: state mixing, which is based on surface state hybridization, and static fields, which is based on electrostatics. First, in the state mixing case, the change in band bending is driven by the interaction between the material’s surface states with the molecular LUMO level of the ligand, producing hybridized...
Hybridization shifts the filled surface states to lower energy, causing a change in the band bending. If this mechanism was governing the influence of dipolar molecules on ITO NCs, we would expect to see that for electron-withdrawing ligands, as the LUMO level of the ligand is lower in energy,$^{43,44}$ the band bending will become more significant due to better energetic alignment with the surface states. However, this is the opposite of the observed trend since our experiments revealed diminished band bending for more withdrawing ligands. Therefore, the state mixing mechanism is inconsistent with our results. In the static fields mechanism, the change in band bending results from the molecular dipole-derived step in the potential energy. If this mechanism was governing our observations, we would expect that the downward electrostatic potential step induced by donating ligands would increase band bending, while the upwards step associated with withdrawing ligands would decrease band bending (Figure 4). In the experimental data, we see this exact trend in which withdrawing (donating) ligands result in a decrease (increase) of the band bending of the material, producing the observed effects on plasmonic properties. Furthermore, an increase (decrease) in optical band gap occurs for NCs functionalized with withdrawing (donating) ligands (Figure S5), in agreement with the expected change in energy difference from $E_{VB}$ to $E_F$ (Figure 4). All these observed trends are consistent with those expected based on the static fields mechanism, indicating that field effects dominate in determining the influence of dipolar ligand functionalization on the electronic and plasmonic properties of ITO NCs.

Figure 4: **Schematic representation of the changes in the band bending of ITO NCs depending on the dipolar character of the surface ligands.** The modified band bending in the depletion layer is highlighted with colored lines extending the conduction ($E_{CB}$) and valence band edges ($E_{VB}$) radially out from the center of the NC and the potential steps in the molecular layers are shown by the change in vacuum level ($E_{vac}$).

In conclusion, we demonstrated that post-synthetically modifying ITO NCs with dipolar ligands changes their electronic band structure and tunes the electron concentration and radial distribution. Dipolar ligands systematically increase or decrease band bending, causing the electron concentration and plasmonic volume fraction to vary in an anticorrelated manner. Post-synthetic surface modification can provide access to combinations of plasmonic properties that cannot be achieved by direct synthetic routes like changing size and doping density.$^{25}$ Considering the two known mechanisms that can explain how a molecular layer
influences band bending, our data suggest that the static fields mechanism based on  
electrostatics is dominant in this case. In future studies, direct observations of the surface state  
energies, e.g. with energy-resolved electrochemical impedance spectroscopy,\textsuperscript{45,46} and direct  
analysis of the band bending, e.g. with angle-resolved photoemission spectroscopy,\textsuperscript{18} may  
be used to further analyze the influence of dipolar ligands, ligands with different binding  
groups,\textsuperscript{47,48} and other surface chemical modifications.

**Acknowledgement**

The authors acknowledge support from the National Science Foundation (NSF) (CHE-  
1905263), the Welch Foundation (F-1848), and the NSF Graduate Research Fellowship Pro-  
gram (DGE-2137420). Partial support was also provided by the Center for Dynamics and  
Control of Materials, an NSF Materials Research Science and Engineering Center under  
Cooperative Agreement DMR-1720595.

**Supporting Information Available**

Details of ITO NC synthesis, surface modification procedure, and characterization techniques  
used (STEM, NMR, TGA, UPS, optical spectroscopy, ICP-MS, and HEDA model) for all  
samples, plus supporting characterization data.

**References**

(1) Zehner, R. W.; Parsons, B. F.; Hsung, R. P.; Sita, L. R. Tuning the Work Function of  
Gold with Self-Assembled Monolayers Derived from $X$-$[C_6H_4-C|C-]_nC_6H_4-SH$ ($n = 0,  
1, 2; X = H, F, CH\textsubscript{3}, CF\textsubscript{3}, and OCH\textsubscript{3}$). *Langmuir* 1999, **15**, 1121–1127.

(2) Brown, P. R.; Kim, D.; Lunt, R. R.; Zhao, N.; Bawendi, M. G.; Grossman, J. C.;  
Bulović, V. Energy Level Modification in Lead Sulfide Quantum Dot Thin Films  

(3) Vilan, A.; Ghabboun, J.; Cahen, D. Molecule - Metal Polarization at Rectifying GaAs  

(4) Cahen, D.; Kahn, A. Electron Energetics at Surfaces and Interfaces: Concepts and  

(5) Bruening, M.; Moons, E.; Cahen, D.; Shanzer, A. Controlling the Work Function of  
CdSe by Chemisorption of Benzoic Acid Derivatives and Chemical Etching. *J. Phys.  

(6) Krüger, J.; Bach, U.; Grätzel, M. Modification of TiO\textsubscript{2} Heterojunctions with Benzoic  
451.


TOC Graphic
TOC Graphic