LANGMUIR

Article

Cite This: *Langmuir* 2019, 35, 2997−3004

pubs.acs.org/Langmuir

ITO Work Function Tunability by Polarizable Chromophore Monolayers

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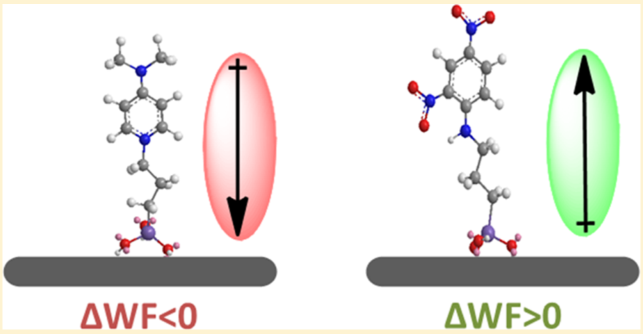
Supporting Information



ABSTRACT: The ability to tune the electronic properties of oxide-bearing semiconductors such as Si/SiO_2 or transparent metal oxides such as indium-tin oxide (ITO) is of great importance in both electronic and optoelectronic device applications. In this work, we describe a process that was conducted on n-type Si/SiO_2 and ITO to induce changes in the substrate work function (WF). The substrates were modified by a two-step synthesis comprising a covalent attachment of coupling agents' monolayer followed by in situ anchoring reactions of polarizable chromophores. The coupling agents and chromophores were chosen with opposite dipole orientations, which enabled the tunability of the substrates' WF. In the first step, two coupling agents with opposite molecular dipole were assembled. The coupling agent with a negative dipole induced a decrease in WF of modified substrates, while the coupling agent with a positive dipole produced an increase in WFs of both ITO and Si substrates. The second modification step consisted of in situ anchoring reaction of polarizable chromophores with opposite dipoles to the coupling layer. This modification led to an additional change in the WFs of both Si/SiO_2 and ITO substrates. The WF was measured by contact potential difference and modeled by density functional theory-based theoretical calculations of the WF for each of the assembly steps. A good fit was obtained between the calculated and experimental trends. This ability to design and tune the WF of ITO substrates was implemented in an organic electronic device with improved *I*−*V* characteristics in comparison to a bare ITO-based device.

INTRODUCTION

Self-assembled monolayers (SAMs) are widely used for controlling electronic properties, such as the work function (WF), the electron affinity (EA), and the band bending (BB) of various substrates.[1−4] These substrates include both metals or etched semiconductors as well as oxide-bearing surfaces, from semiconductors to metal oxides, both for organic electronic[5−8] and for optoelectronic[9,10] applications. Two main synthetic methods were used for the creation of those polar monolayers: the first one includes electrostatic anchoring of charged polymers,[11] whereas the other one is based on covalently attached polar molecules such as coupling agents and polarizable chromophores.[12,13] These coupling agents, comprising the immediate interface with the substrate, are carefully chosen in order to get a favorable interaction between the head group and the substrate, giving rise to an ordered and homogenous SAM. Traditionally, thiols and N-heterocyclic carbene[14] head groups are used for organic molecule assembly on noble metals.[15−18] Additionally, chloro- and alkoxy-silanes are used for assembly on hydroxyl-terminated substrates[9] and phosphonic acid groups for modification of indium-tin oxide (ITO).[3] For hydroxyl-terminated substrates, Si/SiO_2 substrates are widely used in microelectronics, whereas glass and quartz are used for optical applications. Due to the combination of transparency and conductivity, ITO and other metal oxides are widely used for optoelectronic devices such as organic light-emitting diodes and organic photovoltaics.[19] Considering the high WF of ITO (~4.8 eV),[20] these substrates are commonly used in devices as the anode or as a hole injection contact in organic electronic devices. A careful design of the junction between the electrode and the organic layer can improve the charge injection through the barrier, resulting in reduction of the operating voltage of the device. Therefore, a lot of effort is targeted on the possibility to tune

Received: November 26, 2018
Revised: January 30, 2019
Published: February 1, 2019

DOI: 10.1021/acs.langmuir.8b03943
Langmuir 2019, 35, 2997−3004

the electronic properties of the electrode, in this case, the ITO.[21] The WF of a substrate can be greatly influenced by monolayers of polar organic molecules as was shown both experimentally using the Kelvin probe technique by contact potential difference (CPD) measurements and theoretically in numerous studies.[8,22−24]

It is well known that the WF of a substrate includes the band bending (BB) and electron affinity (EA) components, which are related to surface states and surface dipoles of the layer, respectively. Since the difference between the Fermi level and the conduction band cannot be directly measured by CPD, it is easier to discuss relative parameters, namely, ΔWF, ΔBB, and ΔEA, that are related to p-type and n-type semiconductors as shown in eq 1

$$\Delta WF = \Delta EA \pm \Delta BB \tag{1}$$

To determine separately, by CPD analysis, the BB and EA components, the WF is measured in the dark and under illumination, which causes photosaturation. This photosaturation induces a flattening of the band banding, resulting in $\Delta BB_{\text{illuminated}} \approx 0$ and $\Delta WF_{\text{illuminated}} \approx \Delta EA$.[23,25−27] Moreover, it is important to notice that for highly doped Si and ITO, the ΔBB contribution to the ΔWF is negligible, and therefore ΔWF and ΔEA are nearly the same.[28]

The change of WF (ΔWF, $\Delta\Phi_s$), in this case, can be derived theoretically (in volts) by the Helmholtz equation in which both structural and dielectric parameters of the layer are expressed, as shown in eq 2

$$\Delta\Phi_s = \frac{N\mu}{\varepsilon\varepsilon_0}\cos\theta \tag{2}$$

where N is the dipole density (in molecule/m^2), μ is the dipole moment (in Debye, 1 D = 3.34×10^{-30} C·m), θ is the average tilt angle of dipole relative to the surface normal, ε is the effective dielectric constant of the molecular film, and ε_0 is the permittivity of vacuum.

For an n-type semiconductor, the convention is to define a positive molecular dipole when the negative pole points away from the surface, resulting in an increase of WF. On the other hand, negative pole pointing toward the surface decreases the WF.[29]

The WF tuning resulting from monolayer-derived modification can produce better band diagram adjustments, thus confirming the important influence of monolayer modification on the bulk characteristics and charge injection in electronic devices. Previous works in this field presented methods for WF tuning of semiconductors by molecular and ionic dipoles,[28,29] charged layers,[30] and anchored molecular polar monolayers.[12] WF modification of ITO is commonly achieved by various metrologies, such as molecular and ionic dipoles,[10,21,31−34] macromolecules including conducting polymers and ionic polymers,[35,36] and transition-metal complexes.[37,38]

In this work, we introduce a novel WF tuning of ITO substrates by covalent assembly of polarizable (D-π-A) chromophores and implement these findings in improving device performances. This strategy was based on a two-step consecutive assembly of coupling agents and chromophores. The coupling agents and chromophores were chosen with opposite dipole directions, which enabled the tunability and tailoring of ITO WF for specific purposes, as measured by CPD.

To rationalize the WF tunability of ITO, the modification steps and CPD measurements were conducted also on n-type Si/SiO_2 substrates and modeled by the density functional theory (DFT). A comparison of the calculated and experimental WF of the Si/SiO_2 substrate showed similar trends and gave insight on the correlation between the density of the chromophores and the changes of WF. As predicted, the same trend of WF tuning was obtained for both ITO and Si/SiO_2 modification. Moreover, as a proof of concept, the modified ITO substrates were used in organic electronic devices.[39−41] The ability to control the WF of ITO improved the $I-V$ performance of the modified ITO electrode-based device compared to the device built with bare ITO electrodes, thus proving the major role of monolayer modification on bulk and device features.

■ METHODS

Surface Characterization. CPD measurements were performed by Kelvin probe S (DeltaPhi Besocke, Jülich, Germany) with a vibrating gold electrode (work function 5.1 eV) in a home-built Faraday cage under Ar (argon) atmosphere. Variable-angle spectroscopic ellipsometry (VASE) measurements were carried out with ellipsometer VB-400, Woollam Co., at the Brewster angle of 75° for silicon. Contact angle (CA) measurements were carried out with triple-distilled water (TDW) using an Attension device goniometer (Theta Life, KSV Instrument, Biolin Scientific). X-ray photoelectron spectra (XPS) were collected at ultrahigh vacuum (2.5×10^{-10} Torr) on a 5600 Multi-Technique (atomic emission spectroscopy/XPS) system (PHI) using an X-ray source of Al Kα (1486.6 eV). Atomic force microscopy (AFM) measurements were carried out with Nanoscope IV (DI) in the tapping mode using a tapping etched silicon probe (DI) with a 30 N/m force constant.

Sample Preparation. *Chemicals.* 3-Iodopropyl(trimethoxysilane) (IPTMS) was purchased from Gelest. 3-Aminopropyl(triethoxysilane) (APTES) 99%, 4-(dimethylamino)pyridine (DMAP) 99%, and anhydrous pyridine (Py) were purchased from Sigma Aldrich. Dinitrofluorobenzene (DNFB) 99% was purchased from TCI. Ethanol high-performance liquid chromatography graded, toluene, H_2SO_4, and H_2O_2 were purchased from Merck. Poly(4-vinylpyridine) (PVPy), $M_w \sim 50\,000$, was purchased from Polyscience, Inc. All materials were used without further purification except for the coupling agents IPTMS and APTES, which were vacuum distilled before use.

Substrate Cleaning and Activation (Substrate a). First, n-type Si ⟨100⟩ (Si-mat 0.003 Ω·cm) substrates were cleaned in aqueous detergent, washed with triple-distilled water (TDW), and dipped in piranha solution (H_2O_2/H_2SO_4 concentrated, 3:7 v/v, *Caution!* strong oxidizing solution) for 15 min. The substrates were then rinsed with TDW and sonicated in $NH_3/H_2O/H_2O_2$ (1:1:5 v/v/v) solution for 30 min at 60 °C.[27] Then, the substrates were washed three times with TDW and pure acetone and dried under a stream of nitrogen.

Substrate Cleaning and Activation (Figure 1, a). ITO substrates (Delta technology) were sonicated for 10 min at room temperature consecutively in TDW, ethanol, and acetone. The substrates were dried under a stream of nitrogen and activated by ultraviolet ozone cleaning system (UVOCS) activation and cleaning process for 20 min. Piranha solution cannot be used for ITO since the substrates are not stable in strong acidic solutions.

Si/SiO_2-$PrNH_2$ and ITO-$PrNH_2$ (Figure 1, b). A monolayer of freshly distilled APTES was assembled on Si/SiO_2 and ITO substrates.[11] Freshly cleaned and activated substrates of Si/SiO_2 were immersed in 0.2% (v/v) APTES/ethanol solution for 20 min. ITO-cleaned and UVOCS-activated substrates were immersed in 10% (v/v) APTES/ethanol solution for 20 h. After the proper immersion times, the substrates (Si/SiO_2 and ITO) were washed three times with ethanol and dried under a stream of nitrogen. All the substrates were cured in an oven at 100 °C for 30 min.

Si/SiO_2-DNPrA and ITO-DNPrA (Figure 1, c). A solution containing 0.005 g of KOH in 10 mL of ethanol was prepared. The amine-

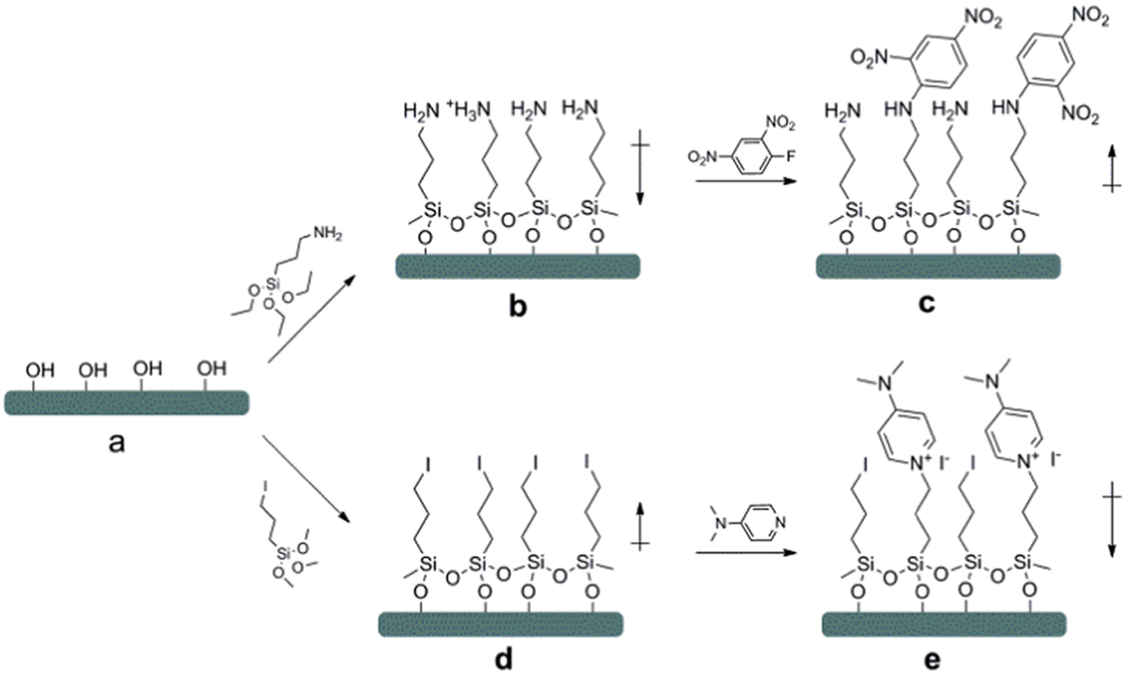


Figure 1. Scheme of substrate modification: (**a**) bare surface of silicone or ITO with exposed hydroxyl groups; (**b**) condensation and hydrolysis reactions between the APTES coupling agent and hydroxyl groups of the surface; (**c**) in situ condensation reaction between the coupling-agent APTES layer and the DNFB chromophore; (**d**) condensation and hydrolysis reactions between the IPTMS layer coupling agent and hydroxyl groups of the surface; and (**e**) in situ S_N2 substitution between the IPTMS coupling agent and the DMAP chromophore. The orientation of the layers' dipoles is shown schematically.

terminated modified substrates (Si/ITO-$PrNH_2$) were immersed in 1% (v/v) dinitrofluorobenzene (DNFB) solution in ethanol with KOH for 10 min at room temperature. After completion of the reaction, the substrates were washed three times with toluene and dried under a stream of nitrogen.

*Si/SiO_2-PrI and ITO-PrI (Figure 1, **d**).* Freshly cleaned and activated substrates (Si/SiO_2 or ITO) were immersed in 1% (v/v) IPTMS/toluene solution with 0.002% acetic acid for 90 min at 80 °C under inert N_2 atmosphere. After reaction completion, the substrates were washed three times with toluene, dried under a stream of nitrogen, and finally cured at 100 °C for 30 min.

*Si/SiO_2-DMAPrP and ITO-DMAPrP (Figure 1, **e**).* A solution containing 0.18 g of dimethylaminopyridine (DMAP) in 50 mL of acetonitrile was prepared. The modified Si/ITO-PrI substrates were immersed in this solution for 20 h at 80 °C under nitrogen. These substrates were washed three times with isopropylalcohol and dried under a stream of nitrogen.

Smart Gel Preparation and Organic Electronic Device Fabrication. Poly(4-vinylpyridine)−pyridine (PVPy−Py) gel was prepared.[39,41] A powder mix of PVPy was swollen in equal total weight of Py and kept at dark overnight for spontaneous gelation. This gel was sandwiched between ITO electrodes.

Computational Methods. The experimental WF measurements were complemented with density functional theory (DFT)-based calculations. For this purpose, a 15.36 Å × 7.68 Å reconstructed Si⟨100⟩-(2 × 1) surface was used with six interconnected molecules coupled via propyl-siloxane. These siloxanes were terminated by either amino/iodide or chromophore functional groups. The remaining two silicon surface sites were then passivated by hydrogen atoms. All calculations were done using the Quantum Espresso software package[42] with projector augmented-wave pseudopotentials and the Perdew−Burke−Ernzerhof exchange−correlation potential[43,25] with nonlocal dispersion corrections (vdW-DF).[44−46] The kinetic energy cutoff was set to 40 Ry, whereas the charge density cutoff was chosen to be 10 times higher. The integration over the Brillouin zone was performed employing a 3 × 6 × 1 Monkhorst−Pack mesh.[47] The distance between adjacent slabs was set to 20 Å, and the dipole correction of Bengtsson[48] was used. The atomic positions were relaxed until all force components on every atom were less than 10^{-3} Ry/a_0 and the changes in total energy less than 10^{-4} Ry.

■ RESULTS AND DISCUSSION

Two synthetic routes were used to tune the WFs of Si and ITO (Figure 1, **a**). Both routes consisted of covalently attached polar molecular layers produced by a two-step synthetic method. The first step of coupling layer formation (Figure 1, **b**, **d**) was followed by in situ chromophore anchoring via either condensation (Figure 1, **c**) or substitution (Figure 1, **e**) reactions. The first WF tuning was produced by the APTES coupling-agent layer yielding a propyl-amine active interface, which in a protonated state has a negative calculated dipole of −1.77 D (Figure 1, **b**), thus causing a decrease in WF.[49] The ratio of amine/ammonium groups is controlled by the pH as was previously demonstrated,[28] that is, at lower pH, more ammonium groups are formed. The assembly of APTES results in a layer containing both alkylammonium (pK_a ∼ 10) and alkylamine functionalities.[28] This amine/ammonium moiety with the dipole pointing toward the surface was coupled with DNFB to produce a 2,4-dinitro-*N*-propylaniline (DNPrA) moiety with a positive molecular dipole (Figure 1, **c**) that increases the WF. The second surface was fabricated by the IPTMS coupling agent with a calculated surface dipole of 2.08 D, which increases the WF (Figure 1, **d**). The propyl-iodide (PrI) modified surface reacted with DMAP to form a layer with 4-dimethylamino-1-propyl pyridinium (DMAPrP) moiety with a negative molecular dipole (Figure 1, **e**).

To verify the layer formation on the surface, contact angle (CA), variable-angle spectroscopic ellipsometry (VASE), and atomic force microscopy (AFM) were performed on the activated Si substrate (Figure 1, **a**). The hydrophilic Si wafer

DOI: 10.1021/acs.langmuir.8b03943
Langmuir 2019, 35, 2997−3004

with CA of 8° reacted with APTES and IPTMS, which resulted in CAs of 55 and 73° and thicknesses of 6.7 and 7.3 Å, respectively. The increase in hydrophobicity and layer thickness confirmed the first modification step. It was expected that the IPTMS would produce a more hydrophobic layer in comparison with APTES since it lacks the ability to form hydrogen bonds that exist in the amine-terminated APTES. Reaction between DNFB and an APTES functionalized surface resulted in increase of surface thickness by 4.8 Å and the CA to 67°. This suggests that the DNFB chromophore assembly (Figure 1, **c**) modified surface is formed. In parallel, the IPTMS modified surface reacted with DMAP (Figure 1, **e**). This modification increased the layer thickness by 4.6 Å. However, the CA did not change after this modification since both layers are fairly hydrophobic with iodide (**d**) or dimethyl (**e**) terminal groups. The smoothness of the layer as measured by AFM confirmed that the layers are homogeneous (see SI-1).

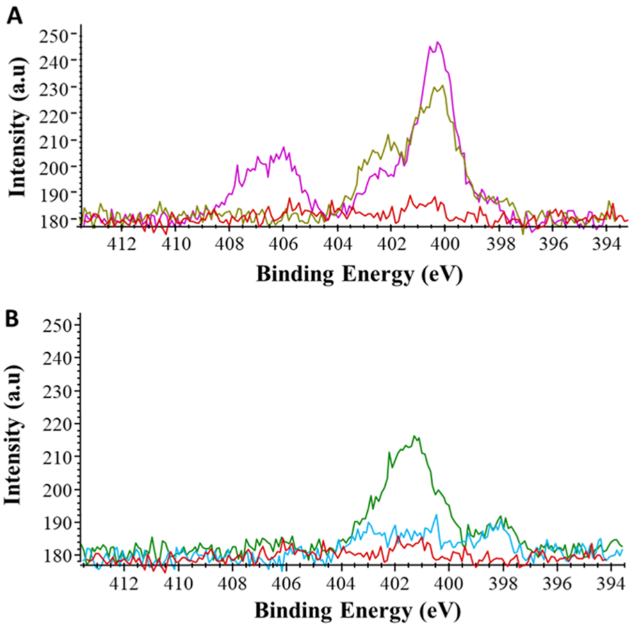


Figure 2. XPS analysis of N [1s] binding energy regions for Si substrate **a** (red) modifications: (A) with coupling agent **b** (olive) and chromophore **c** (magenta) and (B) coupling agent **d** (blue) and chromophore **e** (green).

X-ray photoelectron spectroscopy (XPS) measurements were performed to verify the coupling layers' formation and composition (Figure 1, **b**, **d**). The peak at 621 eV (SI-2) obtained for **d** corresponds to iodide [3d] binding energy and confirmed propyl-iodide layer formation. The formation of the Si/SiO_2-$PrNH_2$ monolayer (Figure 1, **b**) was supported by binding energies of 399.8 and 402.2 eV (Figure 2A), corresponding to N [1s] propyl-amine ($PrNH_2$) and propyl-ammonium (PrN^+H_3), respectively. By analyzing the N [1s] binding energy, an estimation of the ratio between the amine and ammonium groups can be evaluated as 3:1, respectively. This indicates that about 30% of the N derivatives present on the surface are quarternized. XPS analysis confirmed the layer modifications with both chromophores by the appropriate appearances of relevant peaks. For DMAP chromophore assembly (Figure 1, **e**), a peak of N [1s] at 401 eV appeared, thus indicating amine derivative groups on the surface (Figure 2B). In the case of DNFB chromophore (Figure 1, **c**), appearance of the oxidized nitrogen peak was observed, thus confirming the presence of nitro group with N [1s] 406 eV on the surface (Figure 2A). By comparing areas of the peaks, it can be estimated that a third of the amine groups were condensed with the DNFB chromophore.

DFT calculations were conducted for Si substrate modified by**c** and **e** with various chromophores' densities and resulted in a range of possible WF values (SI-3) for coupling-agent/chromophore ratios from 6:4 to 6:2. Based on XPS analysis for chromophore coverage, we chose to compare the calculated WF of 6:2 coupling-agent/chromophore ratios, that is, two chromophores on six coupling-agent groups (Figure 3). The corresponding calculated results are presented in Table 1 and Figure 4. Whereas we find a surface dipole of −0.75 D for the DMAP chromophore (**e**) and a value of 6.96 D for the DNFB chromophore (**c**), the dipoles of their corresponding coupling agents point in the opposite direction. Notice that the dipoles of the plain chromophore layers were calculated by substituting the trialkoxysilane functional groups of the coupling agents by hydrogen atoms. Therefore, the work function is tailored especially by the ratio of the chromophore molecules to their corresponding coupling agents. Best agreement with experimental results for both chromophores was found at a packaging ratio of 2:4, which is also in agreement with the above-mentioned XPS results, which correspond to a chromophore density of 0.017 $Å^{-2}$ resulting in the molecular footprint of about 58 $Å^2$.

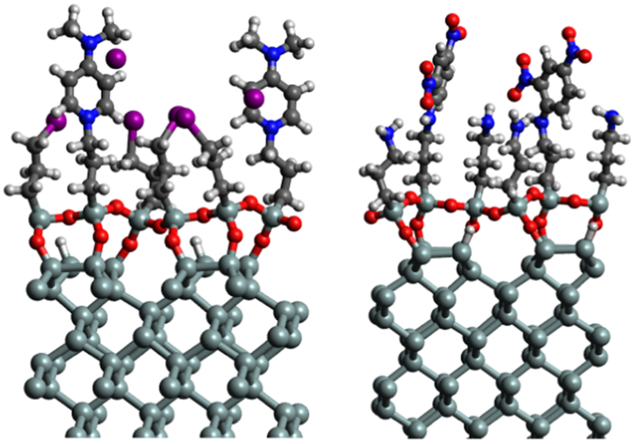


Figure 3. Sketch of the supercell of the chromophore layer: **e** (left) and **c** (right) assembled on their corresponding coupling agents.

Table 1. CA, VASE, and CPD Measurements and DFT Simulations of Deposited Molecules on Si/SiO_2 Substrate

	CA (deg)	VASE (Å)	exp. WF (eV)	calc. WF (eV)
a	8 ± 1	14.6 ± 0.9	4.86 ± 0.06	4.45
b	55 ± 2	6.6 ± 0.3	4.29 ± 0.04	3.88
c	67 ± 2	4.8 ± 0.5	4.60 ± 0.04	5.97
d	73 ± 2	7.3 ± 0.2	4.88 ± 0.07	5.10
e	71 ± 1	4.6 ± 0.4	4.24 ± 0.02	4.04

CPD measurements on the Si-modified substrate showed a difference of 0.6 eV between the highest work function for **d** (4.88 eV) and the lowest one for **b** (4.29 eV). As was expected, the positive dipole of the C−I terminal group of the PrI (**d**)

DOI: 10.1021/acs.langmuir.8b03943
Langmuir 2019, 35, 2997−3004

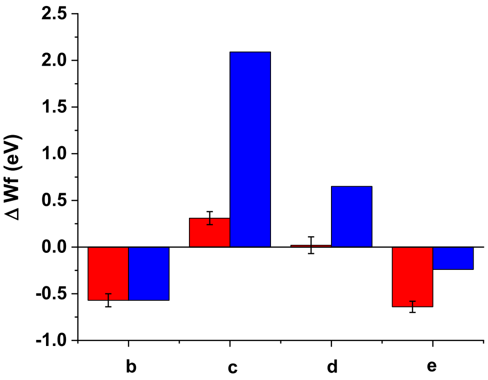


Figure 4. Change in WF of modified Si surfaces: theoretical (blue) and experimental (red), differences were calculated relative to the previous modification step.

induced an increase in the WF of Si, while the amine/ammonium monolayer **b** induced a decrease in the WF (Figure 4).

It is noteworthy that the difference in the WF between those modified substrates is about half of the band gap of the Si substrate. These findings were also confirmed by our calculations.

By comparing the last two columns in Table 1, one can see that DFT-based results are in agreement with the experimental findings. The large differences in the absolute WF values of the chromophores are mainly explained by a disparity in density between the experimental and simulation results. Theoretically and experimentally obtained ΔWF values were calculated by subtraction of the previous layer from the current one (Figure 4). In this way, the ΔWF values of the coupling agents' layers (**b** and **d**) were calculated by subtracting the Si substrates' (**a**) WF from the coupling agents' modified Si' WF. For the chromophore assemblies of (**c** and **e**), the ΔWF was calculated by subtracting the WF of the relevant coupling layer (**b** or **d**) modified Si from the chromophore modified Si' WF. It is clear that the propyl-amine functionalization decreased the WF in comparison to the bare substrate, while the propyl-iodide modification increased the WF in comparison to the bare substrate. As projected, for the DNFB chromophore assembly (**c**), an increase in the WF compared to the previous modification was obtained, but for the DMAP chromophore layer (**e**), a decrease is observed versus the previous modification. A good fit is obtained for both calculated and experimental values of ΔWF although the quantitative agreement is not fully achieved (Figure 4); a similar trend is obtained for the ΔWF of the various steps as compared with the previous modification step.

After verifying the adsorption of the molecules on the silicon substrates, the same synthetic steps were conducted on ITO (Figure 1) since ITO substrates have analog hydroxyl-terminated functionality[50] with an advantage of being transparent and a candidate for further possible applications in optoelectronic devices. The results of the CA and WF measurements for all the steps are summarized in Table 2.

The results of CA present almost similar behavior as on silicon substrates, confirming the formation of the desired layer and its homogeneity. However, the substrate hydrophobicity after both chromophore assemblies was lower than the same step on the silicon substrate.

Table 2. CA and CPD Measurements of Deposited Molecules on ITO Substrate

	CA (deg)	WF (eV)
a	9 ± 1	5.54 ± 0.06
b	48 ± 3	4.78 ± 0.02
c	42 ± 3	5.19 ± 0.01
d	72 ± 3	5.39 ± 0.06
e	49 ± 8	4.84 ± 0.02

Chemical analysis of the layer was measured by XPS (SI-2, SI-4, SI-5). These results showed exactly the same peaks for (**d**) ITO-PrI at I [3d] 620.7 eV and for (**b**) ITO-PrNH$_2$ at N [1s] 400 and 402.1 eV as had been observed on the Si substrate (SI-5). CPD measurements that were conducted on ITO substrates had shown the same trends that were observed for Si (Figure 5). It was verified that the ΔBB component is negligible compared to ΔEA, resulting in similarity between the ΔEA and the ΔWF of the modified substrate (SI-6, SI-7). Namely, PrI coupling (**d**) gave the highest work function (5.39 eV), and PrNH$_2$ coupling (**b**) gave the lowest WF (4.78 eV). The difference in hydrophobicity can be explained by the different morphologies and acidities of the substrates.[51,52] However, the change in WF for both substrates remains with the same trend.

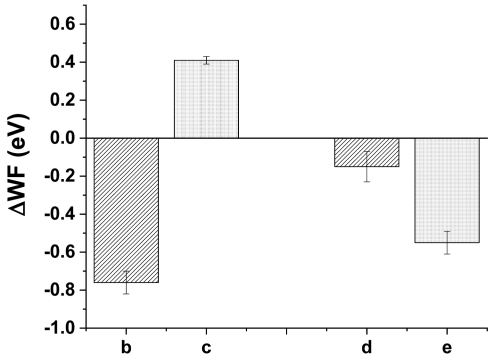


Figure 5. Experimental WF differences of the ITO surface modification process of coupling agents **b** and **d** (diagonal pattern) and chromophores **c** and **e** (dotted pattern) vs the previous step for both assembly steps.

The characteristic peaks of N [1s] were observed as a function of the chemical environment by XPS analysis. Namely, for DMAP chromophore assembly (**e**), N [1s] peak was observed at 400.1 eV. For DNFB chromophore (**c**), a second peak of N [1s] at 406.7 eV was observed, corresponding to the binding energy of the nitro group (SI-4).

The fact that the WF of ITO could be easily altered with chosen monolayer formation encourages us to verify whether these modifications can improve the electrical properties of an organic electronic device. To demonstrate that the performance of a device can be improved by WF tuning, the modified ITO substrates were used as electrodes in the organic electronic device. We demonstrate this concept on poly(4-vinylpyridine) (PVPy)−pyridine (Py) smart gel optoelectronic devices.[41] This material proved to be useful in optoelectronics[53] and memory devices.[54] A PVPy−Py-derived device was fabricated from the smart gel as a photoactive material and assembled with modified ITO substrates. The ITO-modified electrodes with high ΔWF were integrated in the PVPy optoelectronic component. Namely, the device structures are ITO/PVPy/ITO and ITO-DMAPrP/PVPy/PrI-ITO. The latter has both electron and hole transport layers, which should improve the device performance. *I*−*V* measurements were conducted on the two devices, and the results are shown in Figure 6.

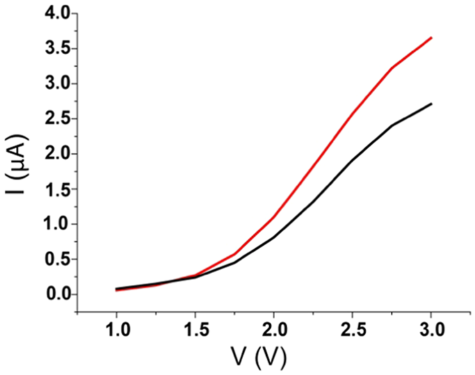


Figure 6. Device *I*−*V* characteristics with modified ITO electrodes (red: ITO-DMAPrP/PVPy/PrI-ITO) and bare ITO electrodes (black: ITO/PVPy/ITO) as a reference.

From the *I*−*V* curves, it is clear that the highest current was obtained for the anode ITO modified with PrI coupling layer (**d**), that is, the electrode with the highest work function, and chromophore DMAP assembly (**e**), that is, cathode ITO electrodes with the lowest work function (SI-9). The lowest current was observed in the device built with bare ITO electrodes as was predicted. This demonstrates that the molecular tuning of ITO electrodes improves the performance of the device.

CONCLUSIONS

In this work, we demonstrate an easy method for tuning the WF of Si and ITO substrates via two-step assembly of polarizable chromophores. The density of the layers was estimated by XPS analysis. Moreover, DFT calculations of the WF showed the same trend as experimental WF. ITO work function tuning range between the lowest (ITO-PrNH$_2$, **b**) and the highest work function (ITO-PrI, **d**) electrodes was found to be 0.61 eV. Using this WF tuning, enhanced *I*−*V* characteristics of organic electronic devices were achieved. This improvement in charge injection can be used in new molecular tuning of Si and ITO electrodes for various electronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b03943.

> AFM measurements of bare and modified silicon, XPS measurements on Si/SiO$_2$ substrates, calculated chromophore **c** surface number density correlation plot, XPS measurements on ITO and Si/SiO$_2$ surfaces, WF measurements of modified ITO, electron affinity and ΔBB of modified Si and ITO substrates (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the RECORD-IT project. This project received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 664786. S.Y. is the Binjamin H. Birstein Chair in Chemistry. TU Dresden gratefully acknowledges computing time by the Center for Information Services and High Performance Computing (ZIH). R.S. is grateful for the support by Azrieli College of Engineering—Jerusalem Research Fund. The authors would like to thank Dr. Vitaly Gutkin for XPS analysis.

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