

Surface Modification of ITO with N-Heterocyclic Carbene Precursors Results in Electron Selective Contacts in Organic Photovoltaic Devices

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Surface modification of indium tin oxide (ITO) electrodes with organic molecules is known to tune their work function which results in higher charge carrier selectivity in corresponding organic electronic devices and hence influences the performance of organic solar cells. In recent years, N-heterocyclic carbenes (NHCs) have also been proven to be capable to modify the work function of metals and semimetals compared to the unfunctionalized surface via the formation of strong covalent bonds. In this report, we have designed and performed

the modification of the ITO surface with NHC by using the zwitterionic bench stable IPr-CO₂ as the NHC precursor, applied via spin coating. Upon modification, the work function of ITO electrodes was reduced significantly which resulted in electron selective contacts in corresponding organic photovoltaic devices. In addition, various characterization techniques and analytical methods are used to elucidate the nature of the bound species and the corresponding binding mechanism of the material to the ITO surface.

Introduction

Organic photovoltaics have shown a steady increase in their performance, reaching single junction efficiencies of 19% after the development and optimization of novel photoactive layer

materials processable from solution.^[1] For reaching the highest solar cell performance, the surface modification of the cells' electrodes to enable the highest possible charge carrier selectivity is mandatory as well. To this end, a wide range of materials has been assessed to modify the work function of commonly employed indium tin oxide (ITO) electrodes. Typically, these include inorganic salts or dipolar organic molecules, which can be processed from solution to form either thin bulk layers or self-assembled monolayers.^[2-12] It is worth to note that frequently employed hole or electron transport layer materials such as PEDOT:PSS or various metal oxides (e.g., ZnO, TiO₂, SnO₂, MoO₃, WO₃) are normally processed as bulk layers with thicknesses in the range of tens of nanometres and thus screen the ITO work function efficiently from adjacent organic functional layers. In this regard, they do not modify the work function of ITO directly, but mediate charge carrier selectivity via the alignment of their work function and/or their frontier orbital energies to the ones of the organic functional layer, for example, the photoabsorbers in organic photovoltaic devices.

Work function modification upon binding of dipolar materials is based on altering the electric potential distribution and creation of interface dipoles.^[13] These result from a vector addition of the molecular dipole of the material and the dipole induced by binding of the material to the surface.^[12] If the resulting dipole moment is pointing away from (to) the surface, the work function is reduced (increased). This effect has not only been described for ITO surfaces,^[3] but was also observed for the modification of Au or Ag surfaces.^[14] Within the last few years, N-heterocyclic carbenes (NHCs) have proven to be valuable ligands and found increasing popularity in a diverse range of applications such as material sciences, biosensor technology, and catalysis.^[15-30] Due to their synergistic strong σ -donating and weak π -accepting abilities of NHCs, they are

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capable to influence metal or semi-metal surfaces with their electronics. The tunability of the electronic as well as the steric properties of the NHCs, via the formation of stable covalent bonds to several metal centers, assist them to be superior activators for metal as well as semimetal surfaces.^[19,20,32] Glorius and Chi groups reported that the modification of gold electrodes with NHCs showed increased device performance by reducing the contact resistance in OFET transistors.^[31,32] NHCs have also been successfully employed on semimetal silicon surfaces, forming highly ordered self-assembled monolayers which leads to a significant reduction of work function compared to unfunctionalized surfaces.^[33] In addition, one of us has shown that also In complexes of NHCs (IPr, IMes) are accessible and stable.^[34] Due to the wide range of materials NHCs can bind to, surface modification of ITO with NHCs could present a viable option to tune the characteristics of the transparent conductive oxide (TCO) electrode in corresponding devices. However, the functionalization of metal oxide surfaces with NHCs is very rare in literature. Primarily transition metal NHC complexes have been utilized so far to functionalize metal oxide particles or surfaces.^[27–29] Recently, Crudden and co-workers reported the reduction of copper oxide surfaces in presence of NHCs allowing subsequent fabrication of NHC-modified clean metal surfaces.^[35] Keeping all this in perspective, in this report we have tried to functionalize the ITO surface with NHCs and utilize the NHC-modified surface in the fabrication of organic solar cells. To the best of our knowledge, this is the first report where NHCs have been employed as a thin layer to bind with ITO surface for application in photovoltaic devices.

Herein, we deposited the model NHC molecule, 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-ide (IPr) on the ITO electrode by spin-coating. Most significantly, we have designed and performed the modification of the ITO surface with the NHC in such a way that we can utilize the advantage of the solution processability of the NHC precursors. The free carbene derived from the corresponding imidazolium salts is unstable even in presence of the slightest amount of moisture. Consequently, it is challenging to modify the ITO surface uniformly using the free carbene in solution. Keeping this in perspective, we have synthesized the zwitterionic bench stable, 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-carboxylate (IPr-CO₂) as the NHC precursor. The IPr-CO₂ adduct is stable in solution and in presence of the ITO surface, being able to generate free carbene *in situ* via releasing the CO₂. Conse-

quently, spin coating with the stable IPr-CO₂ in ethanol under a protective atmosphere and subsequent annealing of the modified surface leads to the uniform coating of the ITO surface with NHC (Figure 1). We present the work function reduction of ITO electrodes, resulting in electron selective contacts in corresponding organic photovoltaic (OPV) devices. Typically, ITO offers two chemically active sites for surface modifications: undercoordinated metal (cation) sites and surface hydroxyl groups.^[36] Due to the strong Lewis base properties of carbenes which are formed after thermal decomposition of IPr-CO₂, carbene molecules could bind to the undercoordinated metal sites.^[34] Alternatively, imidazolium cations could be formed by the interaction of carbene with surface-bound hydroxyl groups. Both binding mechanisms either through free carbene or imidazolium-based cations would result in surface dipoles with dipole moments pointing away from the ITO layer, reducing the effective work function of the electrode and thus rendering the contact more electron-selective.^[37,38] In the following sections, the effect of ITO electrode modification with IPr-CO₂ and subsequent annealing on the charge carrier selectivity in organic solar cells is investigated. The nature of the bound species is elucidated and a mechanism for binding the material to the ITO surface is suggested based on the applied characterization tools and techniques.

Results and Discussion

Kelvin probe

To determine the work function of unmodified and IPr-modified ITO electrodes, Kelvin probe measurements in ambient air were performed. Unmodified ITO had a work function of 4.77 eV. Upon UV/Ozone treatment, applied for surface activation and better wetting of spin-coated layers, an increased work function of 5.17 eV was measured, which we believe is due to the removal of carbon contaminants from the surface.^[39] It is worth to note that for non-uniform films, Kelvin probe measurements result in average work function values which are typically higher in comparison to values obtained from photoelectron spectroscopy measurements which reveal the lowest work function of the investigated surface area.^[40]

Both values for the unmodified ITO lie in between the HOMO and LUMO levels of the electron donor and acceptor

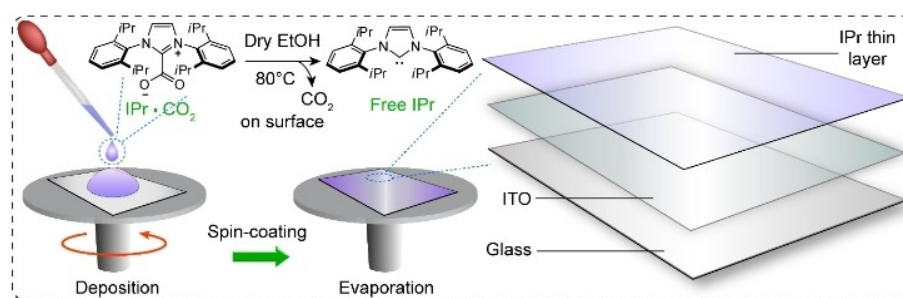


Figure 1. Deposition of IPr from IPr-CO₂ adduct in ethanol solution on ITO electrode by spin coating.

material employed in the photoactive layer of organic solar cells investigated in this study, PM6^[42] and DTY6^[41] (Figure 2). This renders the contact unselective for both electrons and holes^[43] and would lead to a high surface recombination resulting in a low open circuit voltage (V_{OC}) of corresponding devices. Upon coating with IPr-CO₂ and subsequent annealing, a significant decrease of work function ~ 1.3 – 1.4 eV was observed, comparable to the modification of ITO electrodes with other dipole materials.^[3] In an earlier study, we could show that in principle, the V_{OC} of organic solar cells scales with work function (Wf) of the electron contact upon modification with dipolar materials, as long as Wf lies within the bandgap ($Wf > |E_{LUMO}|$).^[3] With work function values lower than the LUMO energy level of the electron acceptor DTY6, the modified ITO electrodes are rendered contacts with potentially high electron selectivity in organic solar cells.

Organic Solar Cells

Organic solar cells have been fabricated in an n-i-p architecture, in which the photoabsorber is sandwiched between an electron transport layer (ETL) deposited on the ITO glass and a hole transport layer (HTL) on top. The layer stack of the solar cells was Glass/ITO/ETL/PM6:DTY6/MoO₃/Silver (Figure 3a), in which

the ETL was either aluminium doped zinc oxide (AZO) or IPr. UV/Ozone treated ITO-glass was selected as the substrate on purpose, as the high work function of the electrode should not result in a charge carrier selective contact. Corresponding devices consequently feature a low V_{OC} of only 420 mV. Additionally, reference devices with untreated ITO glass were fabricated in parallel, resulting in solar cells with relatively high V_{OC} of 630 mV but otherwise still mediocre performance, indicating a non-optimized contact (Supporting Information Figure S3). Devices in which AZO was employed as ETL revealed increased V_{OC} of 820 mV and device performance up to $\sim 8\%$, independent of UV/Ozone pre-treatment. Thus, the AZO thin film screened the high work function of both UV/Ozone treated and untreated ITO electrodes whose nominal work function is 3.9 eV.

Solar cells in which ITO electrodes were coated with IPr-CO₂ and subsequently annealed had high V_{OC} , surpassing the performance of devices based on the AZO ETL and matching optimized literature results of V_{OC} up to 860 mV (Figures 3b and 4),^[41,44] which to the best of our knowledge has not been demonstrated for a device using PM6:DTY6 in n-i-p (inverted) architecture before. Best performing devices reached a power conversion efficiency of 11.8% ($V_{OC} = 0.858$ V, $J_{SC} = 19.0$ mA/cm², FF = 0.72). It is worth to note that in comparison to published values^[41] the short circuit current density (J_{SC}) is reduced, but

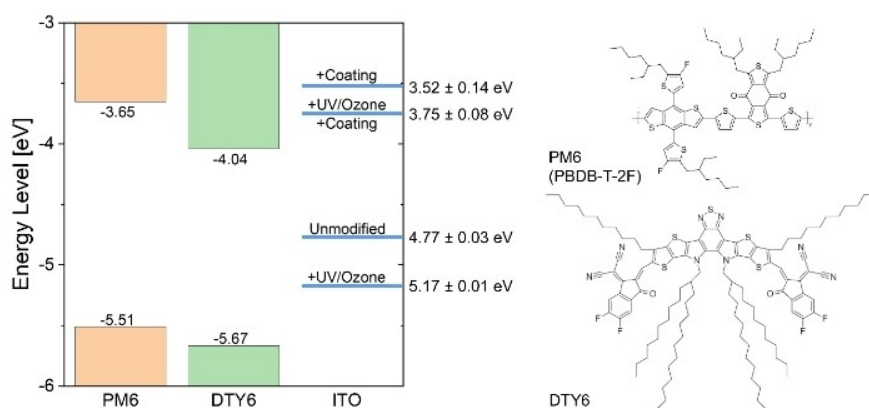


Figure 2. Energy level diagram displaying highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of PM6 and DTY6^[42] and work function values of unmodified and modified (+ Coating) ITO before and after (+ UV/Ozone) UV/Ozone treatment as determined by Kelvin Probe measurements. The chemical structure of PM6 and DTY6 are shown on the right.

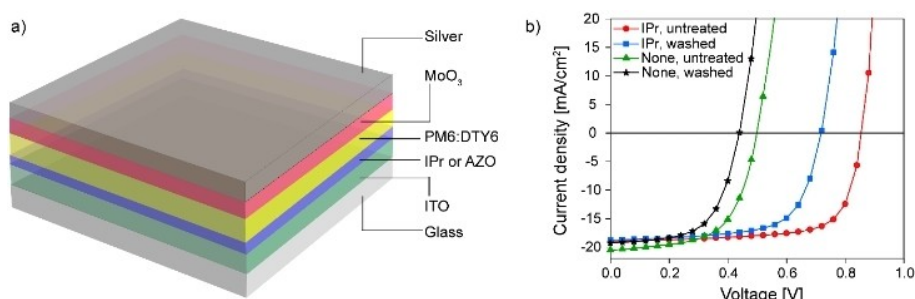


Figure 3. a) Architecture of organic solar cells investigated in this study. IPr or aluminium-doped zinc oxide (AZO) were employed as the electron selective layer, and molybdenum oxide (MoO₃) as the hole selective layer. b) Current density-Voltage curves of organic solar cells with PM6:DTY6 absorber layers and with (IPr) and without (none) IPr employed as ETL. Before deposition of the absorber layer, substrates were either washed by spin coating with EtOH or used without further treatment.

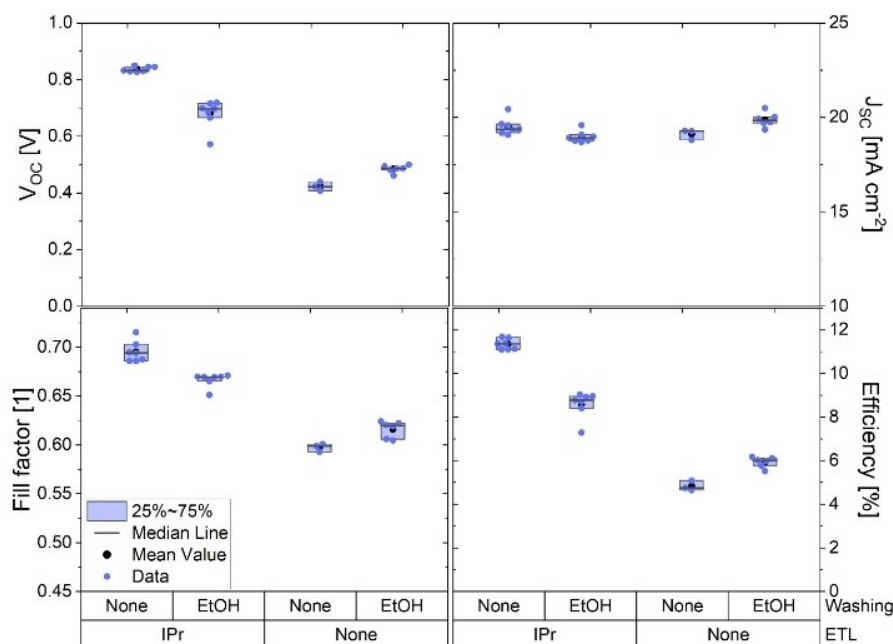


Figure 4. Figures of merit for organic solar cells with PM6:DTY6 absorber layers and with (IPr) and without (None) IPr employed as ETL. Before deposition of the absorber layer, substrates were either washed by spin coating with EtOH or used without further treatment.

reproducible across all fabricated solar cells and thus independent of the presence of the ETL. A higher J_{SC} can be expected after optimization of the absorber layer thickness and light incoupling into the absorber layer by for example using ITO glass with higher transparency and antireflective coating. This, however, was beyond the scope of this study. Upon washing the IPr-coated substrates with ethanol, the V_{OC} of the resulting cells was reduced, indicating that the coated material is not covalently bound to the ITO and does not form a self-assembled monolayer, as could be expected from an NHC. To identify the nature of the deposited material, a more detailed characterization of coated ITO substrates was performed as outlined below.

Assessment of the bound species

In order to gain insight into the electronic coupling between IPr and the ITO electrode, we performed X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to examine the modified samples.

In particular, the N 1s binding energy can be used to determine the NHC binding to the ITO electrode (Figure 5).^[45–48] The major signal is found at 401.6 eV which can be assigned to species that were protonated (IPr-H⁺) during the modification due to the interaction of the present surface-bound free hydroxyl group on ITO electrodes. Therefore, electrostatic interaction between IPr-H⁺ and the hydroxide anion could be

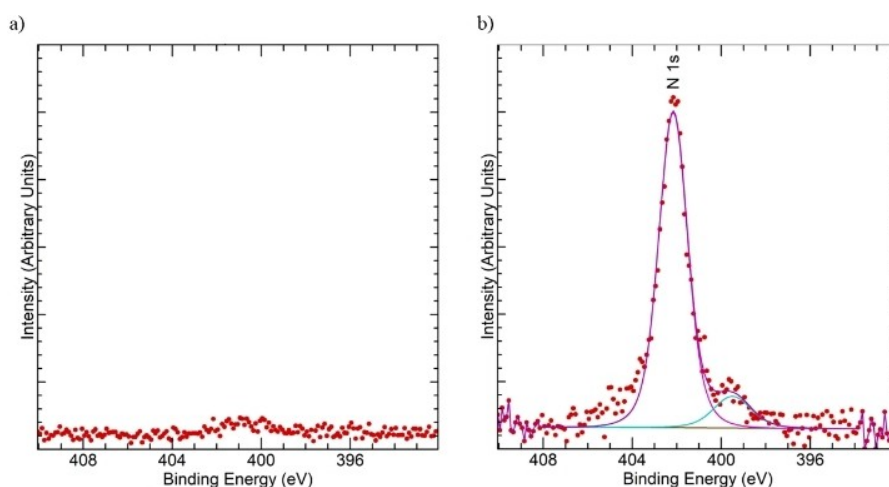


Figure 5. N 1s signal of XPS for, a) ITO surfaces after modification with IPr-CO₂ adduct, b) ITO surfaces before modification.

present on the electrode after successful modification (Figure 7). Furthermore, an intense ToF-SIMS signal of the protonated IPr carbene species is also indicative of the presence of imidazolium ion on the modified ITO electrode. Therefore, both XPS and ToF-SIMS analysis confirmed the successful immobilization of IPr-H⁺ species on planar ITO surface. However, the possibility of forming IPr-O species on ITO electrodes cannot be ruled out.^[49,50]

To gain further insight into the conditions on the surface, ATR-IR spectroscopy was used. With a penetration depth in the μm range, ATR-IR spectroscopy can be considered as a bulk analysis of the modified ITO. The ATR-IR spectrum of the ITO glass coated with the IPr-CO₂ adduct (Figure 6) exhibits an intensive band at 1677 cm⁻¹ before annealing, characteristic of the asymmetric stretching vibration $\nu(\text{C}=\text{O})$ of the IPr-CO₂ adduct. Additional bands are visible between 1200 and 1500 cm⁻¹, which can be assigned to the vibrations of the NHC backbone. The bands between 2869 cm⁻¹ and 2960 cm⁻¹ are characteristic of aliphatic C-H stretching modes, this pattern could be caused by the diisopropyl substituents. Furthermore, the spectrum exhibits additional C-H bending vibrations and bands from the aromatic part of both nitrogen substituents.

The ATR-IR spectrum (Figure 6; Supporting Information Figure S2) of the sample after heat treatment shows the absence of the very intense band at 1677 cm⁻¹, indicating the decomposition of the IPr-CO₂ adduct on the ITO surface under CO₂ release. Furthermore, the rest of the spectrum seems to be almost unchanged and the band positions are almost the same.

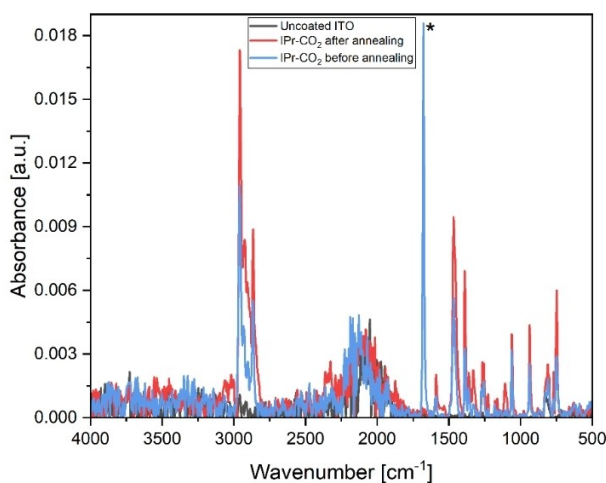


Figure 6. Baseline-corrected ATR-IR spectra of uncoated ITO glass (black curve) and ITO glass coated with IPr-CO₂ before (blue curve) and after (red curve) annealing.

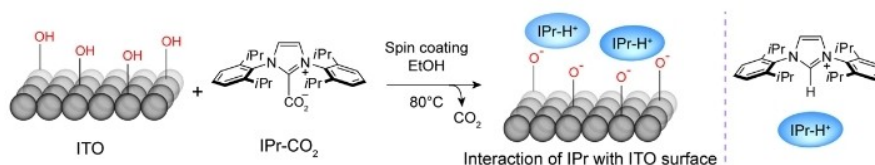


Figure 7. Plausible interactions of bound IPr with ITO electrodes after successful modification of ITO.

The ATR spectra indicate that the NHC backbone and the nitrogen-substituents remain intact during annealing. Spectra for both unannealed and annealed samples correspond well with spectra for IPr-CO₂ and IPr, respectively, which were obtained from quantum chemical calculations (cf. Supporting Information and Figure S5). ATR-IR spectroscopy supports the proposed modification pathway (Figure 7) of ITO with IPr-CO₂ but does not reveal information about the binding mode of the converted material. Also, the steric requirements of the bulky IPr-ligand appear in better agreement with the distal H-bonding coordination than the closer metal coordination. In addition, the bridging O-H-IPr hydrogen bonding interaction would typically lead to a very broad and poorly visible IR band of the latter, in agreement with the observation. Moreover, imidazolium cations like IPr-H⁺ are known to be very good hydrogen bonding entities.^[51]

Conclusions

In this study, the bench stable NHC precursor IPr-CO₂ – a CO₂ adduct of the NHC – has been successfully employed for the modification of ITO electrodes in organic solar cells, leading to a significant reduction of the electrodes' work function. Consequently, the IPr-modified ITO electrodes with work function (3.75 eV) lower than the LUMO energy (4.04 eV) of the electron acceptor DTY6, manifests a potentially high electron selectivity contact in corresponding OPV devices. Furthermore, organic solar cells with modified ITO electrodes have shown high V_{OC} of up to 860 mV, which is one of the highest values for devices using PM6:DTY6 in n-i-p (inverted) architecture, and a power conversion efficiency of 11.8%. XPS and ToF-SIMS analysis indicated the formation of imidazolium ions on the surface which could potentially interact with the surface-bound hydroxide ion. Nevertheless, free IPr-NHC binding on ITO surfaces can also not be completely excluded and further work on optimization of binding of NHCs as modifiers on ITO electrodes and their effect on organic solar cells performance are required. To the best of our knowledge, this report is the first example of the use of NHC-precursors for the modification of ITO electrodes, which lays the groundwork for the future application of NHCs in organic photovoltaic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Additional references cited within the Supporting Information.^[52–65]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: N-heterocyclic carbene · ITO electrode · organic photovoltaics · solar cells · work function

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