



# Work function reduction by a redox-active organometallic sandwich complex



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## ABSTRACT

We have investigated, at the density functional theory level, the geometric and electronic structures of the pentamethyliridocene (IrCpCp\*) monomer and dimer adsorbed on the Au(111) and indium tin oxide (ITO) (222) surfaces, as well as their impact on the work functions. Our calculations show that the adsorption of a monomer lowers the work function of ITO(222) by 1.2 eV and Au(111) by 1.2–1.3 eV. The main origin for this reduction is the formation of an interface dipole between the monomer and the substrate via charge transfer. Dimer adsorption as well as adsorption of possible byproducts formed from dimer bond-cleavage in solution, show a lesser ability to lower the work function.

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## 1. Introduction

Organic optoelectronic devices, such as organic photovoltaic devices (OPVs), organic light-emitting diodes (OLEDs), or organic thin-film transistors (OTFTs), hold promise as they may be printed or processed at low cost over large areas and on flexible substrates [1–4]. One key part of the processing is the fabrication of a low work function ( $\Phi$ ) electrode for electron injection to (for OLEDs), or collection from (for OPVs) the electron transport levels of organic semiconductors. Traditional low- $\Phi$  metals, e.g. Ca or Mg, are highly reactive and have to be deposited on top of the organic semiconductor layer under inert atmosphere conditions [5,6]. Thus, alternative low- $\Phi$  electrodes are highly desirable.

Previous approaches include modifying an air-stable high work function transparent conducting electrode, such as indium tin oxide (ITO), by depositing a thin layer of a selected material to reduce its work function within an inverted device architecture. One of the most successful strategies is the deposition of a thin layer of a polymer containing simple aliphatic amine groups onto the conductor surfaces; for instance, Zhou et al. introduced a “universal” method for decreasing the  $\Phi$  of a number of conducting

electrodes based on commercially available polyethylenimine (ethoxylated) (PEI(E)) [5]. For conducting surfaces including metals, metal oxides, polymers, and graphene, it was found that the physisorption of PEI(E) could reduce the work function by as much as 1.8 eV. Such a large work function decrease has been analyzed by density functional theory (DFT) calculations and shown to come from a joined contribution of interface and molecular dipoles aligned in a cooperative fashion [5].

Another approach, based on a redox-active material, was taken by Osikowicz et al. Tetrakis-(dimethylamino)ethylene (TDAE) was deposited on ITO and led to a  $\Phi$  decrease of 0.9 eV, attributed to a double electron transfer to the ITO surface [7]. TDAE was also used to decrease the  $\Phi$  of gold by 1.3 eV, originating from a single electron transfer from TDAE to the gold surface [8]. Bröker et al. reported a reduction of the  $\Phi$  of gold by 2.2 eV by using an air stable molecular donor layer composed of neutral methyl viologen (MV0), which underwent electron transfer with the gold surface [9]. Hofmann et al. used viologen and tetrathiafulvalene (TTF) to reduce the  $\Phi$  of gold, silver, and copper by as much as 1.2 eV [10]. Bröker et al. reported reduction of the  $\Phi$  of Au(111), Ag(111), and Cu(111) by as much as 1.4 eV by using a molecular donor layer composed of 9,9'-ethane-1,2-diylidene-bis(N-methyl-9,10-dihydroacridine) (NMA) [11]. Li et al. used acridine orange base (AOB) as an n-type dopant to reduce the  $\Phi$  of gold by 1.9 eV [12]; this  $\Phi$  reduction is accredited to the formation of an interface dipole, caused by a single electron transfer from the AOB to the gold substrate.

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Redox-active, organometallic sandwich complexes have been investigated more recently and can be stronger reductants than TDAE, MV0, or AOB [13–20]. The major advantage of such compounds is that they can be applied as air- (and solution) stable dimers, and can be solution deposited. Upon reaction with an appropriate acceptor, two different mechanisms may occur: (i) either cleavage of the dimer followed by electron transfer from monomer to acceptor; or (ii) electron-transfer reaction between the dimer and the acceptor followed by dissociation of the dimer cation [13–15]. The products of this decomposition reaction are shown in Fig. 1. The redox activity of these compounds originates from the conversion of a ligand-centered radical with  $\eta^4\text{-Cp}$  ( $\eta^5\text{-Cp}^*$ )/ $\eta^5\text{-Cp}$  ( $\eta^4\text{-Cp}^*$ ) coordination to a metal-centered radical with  $\eta^5\text{-Cp}$  ( $\eta^5\text{-Cp}^*$ ) coordination. With a Group 8 central atom, the metallocene complex formally carries 19 electrons, and consequently has a low ionization potential. These sandwich compounds have been used to reduce the  $\Phi$  of ITO [17,18,20], ZnO [17,18], gold [17,20], and graphene [16] by as much as ca. 1.9 eV.

Here, we investigate these organometallic compounds at the density functional theory (DFT) level to understand: (i) the mechanism of work function modification ( $\Delta\Phi$ ); and (ii) the contributions from potential synthetic byproducts. We consider the interaction of a metal (Au) and a metal oxide (ITO) surface with pentamethyliridocene ( $\text{IrCpCp}^*$ ), a prototypical 19-electron sandwich complex, its dimer precursor, and potential byproducts. We have evaluated the electron donating ability of both the dimer and monomer, in terms of the  $\Phi$  reduction of Au(111) and ITO(222) surfaces.

## 2. Computational methodology

To describe the ITO(222) surface, we use the repeated-slab approach and a surface structural model proposed in our previous work [21], which consists of 84 indium, 12 tin, 144 oxygen, and 24 hydrogen atoms in an orthogonal  $24.79 \times 14.32 \text{ \AA}^2$  surface unit cell, where all of the oxygen atoms above the top layer of metal atoms are fully saturated by hydrogen atoms. The ITO slab consists of three In(Sn)–O layers. When a monomer is added to the ITO surface unit cell, the resulting molecular coverage is  $2.82 \times 10^{13}$  molecules  $\text{cm}^{-2}$ . This coverage is close to the experimentally evaluated coverage based on the Ir/In ratio obtained from XPS experiments [17]. The atomic positions of the top layer, surface hydroxyls, and molecular adsorbate are allowed to relax over the course of geometry relaxations while the bottom two layers of the slab remain fixed.

The same repeated-slab approach is applied to the Au(111) surface. As the molecular coverage on gold is difficult to ascertain from experiments [17], we used three coverages, realized by orthogonal unit cells with different sizes, to explore the effects of variations in molecular coverage. The lateral dimensions of the unit cells along the [11–2] and [1–10] directions are  $8.63 \times 9.97 \text{ \AA}^2$ ,

$17.27 \times 9.97 \text{ \AA}^2$ , and  $17.27 \times 19.94 \text{ \AA}^2$ , and are taken from the experimental bulk lattice parameters [5,22]. We note here that the lattice parameters optimized at the PBE-D2 level for bulk gold have been shown to be very close to the experimental values [23]. When one monomer or dimer is present in the unit cell, the molecular coverages are  $1.16 \times 10^{14}$  molecules  $\text{cm}^{-2}$ ,  $5.81 \times 10^{13}$  molecules  $\text{cm}^{-2}$ , and  $2.90 \times 10^{13}$  molecules  $\text{cm}^{-2}$  for the smallest, second largest, and largest gold unit cells, respectively. When the monomer is in the smallest unit cell and when the dimer is in the second largest unit cell, the iridium to gold ratios are the same, and these cases will be denoted as high coverage (HC). If the monomer is in the second largest unit cell or the dimer is in the largest unit cell, the iridium to gold ratio is again the same, and these will be denoted as medium coverage (MC). The monomer in the largest unit cell will be denoted as low coverage (LC). The largest gold unit cell has approximately the same surface area as the ITO model. Each gold slab consists of five atomic layers with the bottom three layers frozen at the optimized crystal structure while the top two layers, and any molecular adsorbate, are allowed to relax over the course of geometry relaxations. In both the gold and ITO cases, the slabs are separated by a vacuum space larger than 20 Å.

All calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) [24,25]. The calculations were performed with plane-wave basis sets with an energy cut off of 400 eV and 300 eV for the gold and ITO calculations, respectively; the projector augmented wave (PAW) method [26] was used to describe the valence-core electron interactions. We chose the generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) [27,28], augmented by the empirical D2 dispersion correction of Grimme [29] in order to describe the non-specific interactions of pentamethyliridocene [17] with the metal or metal oxide surfaces. While PBE-D2 has deficiencies in the binding energies and geometries [30], it gives a qualitative description, compared to more expensive methods. As the monomer has an odd number of electrons, spin-polarized calculations were performed for both the isolated monomer and the monomer on the surface. The spin-polarized results for the monomer-on-surface complex show little change in the Fermi energy, magnetization, and density of states compared to those in the absence of spin-polarization (therefore, the results presented below are essentially from calculations without spin-polarization, with a detailed comparison given in the Supporting Information). Despite the limitations of PBE, it has been used to describe charge transfer systems, such as perylene-3,4,9,10-tetracarboxylicdiimide (PTCDI) [31], perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) [32] and  $\text{C}_{60}$  [33] on ZnO, as well as a donor-acceptor complex of tetrafluorotetracyanoquinodimethane ( $\text{F}_4\text{-TCNQ}$ ) with *t*-butyl carbazole-phosphonic acid modified ITO [34]. In these earlier works, the work function changes and charge-transfer characters have been calculated at the PBE level and good agreement with

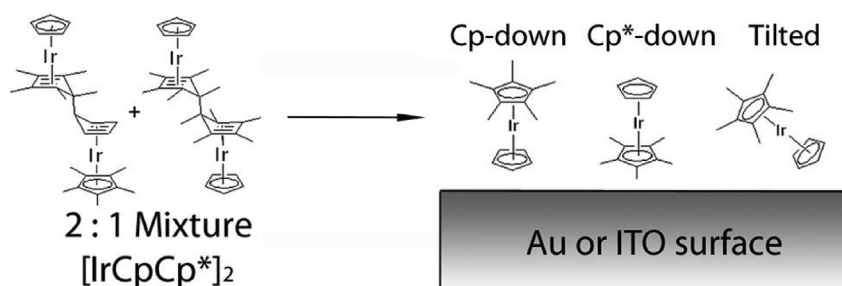


Fig. 1. The  $\text{IrCpCp}^*$  dimer and the possible orientations of the monomers and their abbreviations used throughout this work.

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