Gold work function reduction by 2.2 eV with an air-stable molecular donor layer

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Ultraviolet photoelectron spectroscopy was used to investigate neutral methyl viologen (1,1’-dimethyl-1H,1’H-[4,4’]bipyridinylidene, MV0) deposited on Au(111). As a result of molecule-to-metal electron transfer, the work function of Au(111) was decreased from 5.50 to 3.30 eV. The energy levels of electron transport layers deposited on top of modified Au surfaces were shifted to higher binding energies compared to layers on pristine Au, and the electron injection barrier was reduced by 0.80 eV for tris(8-hydroxyquinoline)aluminum (Alq3) and by 0.65 eV for C60. The air-stable donor MV0 can thus be used to facilitate electron injection into organic semiconductors even from high work function metals. © 2008 American Institute of Physics. [DOI: 10.1063/1.3049616]

In the present study, we demonstrate the applicability of neutral 1,1’-dimethyl-[4,4’]bipyridinylidene, commonly termed (di-)methyl viologen (MV0, see inset in Fig. 1), for the reduction of EIBs at the interface between gold electrodes and organic electron transport materials. MV0 was deposited onto Au(111), and the interfacial electronic structure was characterized using ultraviolet photoelectron spectroscopy (UPS). In spite of being a strong reducing agent, MV0 is known to be temporarily stable in air in its crystalline form, thus rendering it useful for practical applications. Our results show that the work function (φ) of Au(111) after MV0 adsorption is even lower than that of pristine magnesium. Accordingly, EIBs into subsequently deposited tris(8-hydroxyquinoline)aluminum (Alq3) and C60 layers are strongly reduced compared to clean Au(111). The lowering of φ is explained by electron transfer from MV0 to Au, as inferred from theoretical modeling using density functional theory (DFT).

UPS experiments were performed at the endstation SurICat (beamline PM4) at the synchrotron light source BESSY II (Berlin, Germany). Spectra were collected with a hemispherical electron energy analyzer (Scienta SES 100) using an excitation photon energy of 35 eV. Additional UPS experiments were conducted at Humboldt-Universität Berlin.© 2008 American Institute of Physics

FIG. 1. Secondary electron cutoff (SECO) spectra for (a) pristine Au(111), (b) 0.5 Å MV0 on Au(111), (c) 30 Å Alq3 on Au(111), (d) 30 Å Alq3 on MV0 precovered Au(111), and (e) 45 Å C60 on MV0 precovered Au(111). The sample was biased at −10 V during measurement. The inset shows the chemical structure of MV0.
using He I radiation and a Specs Phoibos 100 hemispherical energy analyzer. The secondary electron cutoff was exposed to air for a few minutes during source mount-
ing. No color change to blue was observed for the MV0 powder.16

DFT calculations were performed using the repeated slab approach applying the VASP code,18,19 employing the methodology outlined in Ref. 20. The band structure was sampled on a $3 \times 3 \times 1$ Monkhorst-Pack grid of $k$ points and states were occupied following a Methfessel-Paxton scheme (broadening: 0.2 eV). A single lying MV0 molecule was considered in a $5 \times 3 \sqrt{3}$ unit cell on an Au(111) surface modeled by a five-layer Au slab. This corresponds to a loosely packed monolayer, which is chosen to avoid spurious interactions between molecules (no experimentally determined structure for a densely packed layer is available). All atoms of the molecule as well as the top two Au layers were allowed to fully relax until the remaining forces were smaller then 0.01 e Å$^{-1}$.

The SECO spectra in Figs. 1(a) and 1(b) evidence that upon MV0 deposition, $\phi$ of Au (111) decreases from 5.50 eV [Fig. 1(a)] to 3.30 eV [0.5 Å MV0 covered Au, Fig. 1(b)]. Similarly, low $\phi$ values were obtained for MV0 deposited on Ag(111) and Cu(111) (spectra not shown). Valence band (VB) spectra for pristine and 0.5 Å MV0 covered Au(111) are plotted in Figs. 2(a) and 2(b). The overall attenuation of Au(111) photoemission features is accompanied by the emergence of three features attributed to molecular levels between 2 and 12 eV binding energy (BE), denoted by arrows in Fig. 2. The Au(111) surface state at about 0.3 eV BE, which evidences a clean surface, disappears after MV0 depo-

![FIG. 2. UPS valence band spectra for (a) pristine Au(111), (b) 0.5 Å MV0 on Au(111), (c) 30 Å Alq3 on pristine Au(111), (d) 30 Å Alq3 on MV0 precovered Au(111), and (e) 45 Å C60 on MV0 precovered Au(111). The arrows denote weak features of MV0 on Au(111), and $E_F$ the Fermi energy.](image-url)

The modeling enables us to rationalize the origin of the $\phi$ lowering by MV0 deposition: For the MV0 covered Au surface, the Fermi level of the system cuts through the high-
est occupied molecular orbital (HOMO) derived peak of the density of states (data not shown), indicative of a significant electron transfer from the molecular HOMO derived band to Au. From integration over the plane averaged charge rearrangements (for methodological details, see Ref. 24), a transfer of $\sim$0.8 electron from the molecule to the metal can be inferred, which results in the formation of an interface dipole. This dipole leads to a calculated reduction of the system $\phi$ by 1.40 eV. The smaller value compared to the experimental observation is most likely a consequence of the low coverage of the monolayer used in the calculations.25 For example, for a more tightly packed layer with one MV0 molecule in a $3 \times 3 \sqrt{3}$ unit cell the $\Phi$ modification is $\sim$1.9 eV.

As the work function of the MV0 precovered Au(111) surface is similar to Mg or Mg:Ag,26,27 the prototypical electron transport materials Alq3 and C60 were deposited on MV0 precovered Au(111) in order to assess whether a reduction of the EIB compared to pristine Au can be achieved. The measured VB spectra for 30 Å Alq3 (approximately three layers) on pristine [Fig. 2(c)] and 0.5 Å MV0 precovered [Fig. 2(d)] Au reveal that the Alq3 HOMO onset (low BE side) shifts from 1.60 eV BE (for Alq3/Au) to 2.40 eV BE (for Alq3/0.5 Å MV0/Au). Using the suggested transport gap for Alq3 of $E_T$ = 4.60 ± 0.40 eV,28 the EIB can be estimated to be 3.00 ± 0.40 eV (for Alq3/Au) and 2.20 ± 0.40 eV (for Alq3/0.5 Å MV0/Au). The resulting energy level diagrams are shown in Figs. 3(a) and 3(b), and the corresponding SECO spectra are plotted in Fig. 1(e) [for 30 Å Alq3/Au(111)] and Fig. 1(d) [for 30 Å Alq3/0.5 Å MV0/Au(111)]. No shift in the vacuum level is observed for the deposition of Alq3 on MV0 precovered Au(111), as expected for physisorptive interfacial interaction. In contrast, the deposition of 30 Å Alq3 on pristine Au(111) results in a vacuum level shift of $\sim$1.30 eV relative to Au(111), which is related to the “push back effect.”29-31

The VB spectra for 45 Å C60 (approximately four layers) on MV0/Au(111) in Fig. 2(e) show clear C60 molecular features with the HOMO onset at 2.25 eV BE. The reported transport gap values for C60 range from 2.3 ± 0.10 eV Ref. 32 to 2.6 ± 0.10 eV,33 where both values are obtained by leading edge extrapolation of UPS and inverse photoemission spectroscopy data. This results in an EIB in the range of (0.05–0.35) eV ± 0.10 eV for C60 on our modified Au, compared to an EIB range of (0.70–1.00) eV ± 0.10 eV for C60.

![FIG. 3. Energy level diagrams for (a) pristine Au(111) and (b) 30 Å Alq3/Au(111).](image-url)
on pristine Au(111). The SECO for $C_{60}/0.5 \, \text{Å} \, \text{MV0}/\text{Au}(111)$ [Fig. 1(e)] shows that the vacuum level moves up again due to the $C_{60}$ deposition to yield a $\phi$ value of 4.10 eV. This observation is reminiscent of the $C_{60}$ lowest unoccupied molecular orbital (LUMO) being pinned at the Fermi level. The schematic energy level diagrams for $\text{Alq}_3$ and $C_{60}$ on pristine and MV0 precorroded Au(111) are summarized in Fig. 3.

We have shown that MV0 acts as a strong electron donor on Au(111). The experimentally observed decrease of the work function by 2.2 eV was rationalized by DFT calculations, which point to a significant electron transfer from the molecule to the metal. The low work function surface can thus be used to realize low electron injection barriers into subsequently deposited organic electron transport materials. The EIB was decreased by 0.80 eV for $\text{Alq}_3$ and by 0.65 eV for $C_{60}$-MV0 and analogs thus represent promising candidates for fabricating alternative electron injection contacts in electronic devices.

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23Note that the sticking coefficient for MV0 may differ for Au(111) and the quartz microlactance surface; therefore, coverage values given for MV0 may not represent the actual molecular mass deposit.