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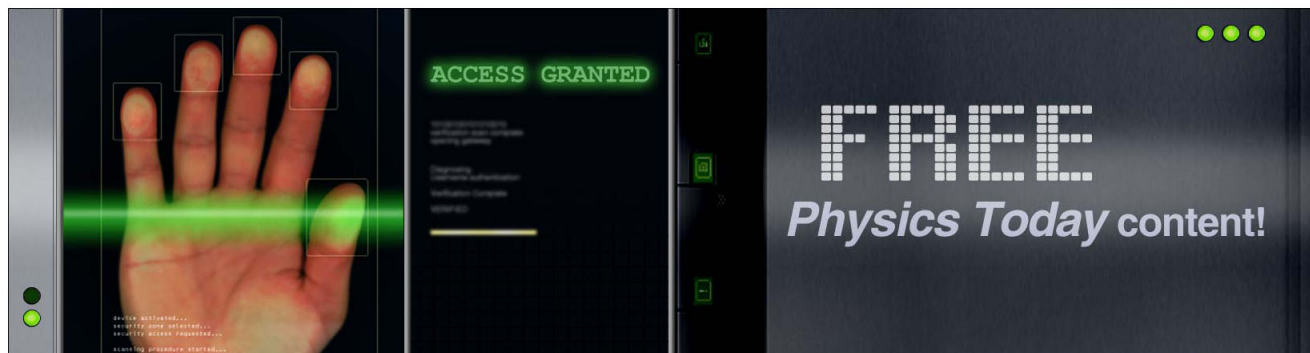
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Gold work function reduction by 2.2 eV with an air-stable molecular donor layer

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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 past years, the field of organic electronics, including devices such as light emitting diodes, field effect transistors, and photovoltaic cells, has made tremendous progress.¹ Organic semiconducting materials have been improved in terms of structure, functionality, and processability, which led to significant increase in device performance. Nevertheless, interfaces between organic materials and electrodes still offer room for improvement, as they are often the limiting factor for charge carrier injection due to large energy barriers.^{2,3} A possibility for reducing the injection barriers at these interfaces comprises the adsorption of molecules that undergo a charge-transfer-type reaction with the electrode materials.⁴⁻⁶ In the case of anodes, it was shown that the insertion of a thin layer of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) can lower the hole injection barrier into *p*-sexiphenyl by as much as 1.2 eV.⁷ At the cathode side, the electron injection barriers (EIBs) can be reduced by employing thin layers of alkali halides^{8,9} or using alkali/alkaline-earth metals^{10,11} or small molecular donors¹²⁻¹⁴ as dopant for the electron transport layer. The drawback of using alkali/alkaline-earth metal atoms is their tendency to diffuse throughout organic layers, thus rendering devices unstable.¹⁵ To circumvent this problem, a molecular donor layer at the cathode side may be used instead of alkali/alkaline-earth metal layers. For instance, it was shown that the exposure of indium tin oxide electrodes to the vapor of tetrakis(dimethylamino)ethylene can yield electron injection barriers similar to those achieved with Al due to a strong interfacial chemical reaction.⁵

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 spec-

troscopy (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.¹⁶ 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).¹⁷ 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

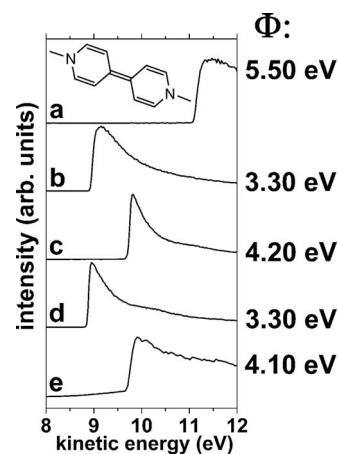


FIG. 1. Secondary electron cutoff (SECO) spectra for (a) pristine Au(111), (b) 0.5 Å MV0 on Au(111), (c) 30 Å Alq₃ on Au(111), (d) 30 Å Alq₃ on MV0 precovered Au(111), and (e) 45 Å C₆₀ on MV0 precovered Au(111). The sample was biased at -10 V during measurement. The inset shows the chemical structure of MV0.

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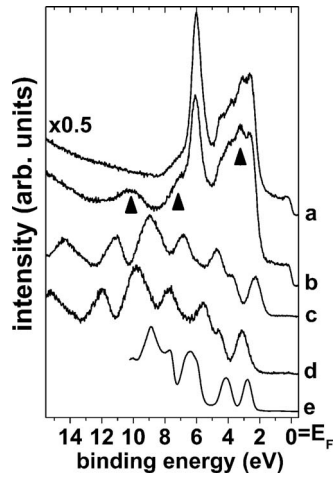


FIG. 2. UPS valence band spectra for (a) pristine Au(111), (b) 0.5 Å MV0 on Au(111), (c) 30 Å Alq₃ on pristine Au(111), (d) 30 Å Alq₃ on MV0 precovered Au(111), and (e) 45 Å C₆₀ on MV0 precovered Au(111). The arrows denote weak features of MV0 on Au(111), and E_F the Fermi energy.

using He I radiation and a Specs Phoibos 100 hemispherical energy analyzer. The secondary electron cutoff (SECO) spectra were obtained with the samples biased at -10 V in order to clear the analyzer work function. The error of energy values reported below is estimated to be ± 0.05 eV. Both experimental setups consist of interconnected sample preparation (base pressure $< 5 \times 10^{-8}$ mbar) and analysis (base pressure 1×10^{-10} mbar) chambers, which enable sample transfer without breaking vacuum. Metal single crystals were cleaned by repeated cycles of annealing (up to 550 °C) and Ar-ion sputtering. Organic materials were sublimed from resistively heated Al₂O₃ crucibles. The mass thickness of the organic layers was monitored with a quartz crystal microbalance. All experiments were carried out at room temperature. Alq₃ and C₆₀ were used as received (Aldrich). MV0 was synthesized and stored under Ar atmosphere prior to use, and was exposed to air for a few minutes during source mounting. No color change to blue (indicative of the formation of the cation MV⁺) or transparent (indicative of the dication MV²⁺) 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-Pack²¹ grid of k points and states were occupied following a Methfessel-Paxton²² 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 than 0.01 e Å⁻¹.

The SECO spectra in Figs. 1(a) and 1(b) evidence that upon MV0 deposition, ϕ 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 ϕ 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 deposition. Further deposition of MV0 does not change the photoemission spectra (VB and SECO, up to 100 Å MV0). This suggests that the Au(111) surface is “saturated” with MV0 molecules already at a nominal coverage of 0.5 Å MV0 at room temperature.²³ Two scenarios can explain this observation: after completion of a saturated monolayer additional MV0 molecules (i) aggregate to three-dimensional islands with a very low surface area coverage, thus hardly contributing to the photoemission signal, or (ii) do not form stable multilayers.

The modeling enables us to rationalize the origin of the ϕ lowering by MV0 deposition: For the MV0 covered Au surface, the Fermi level of the system cuts through the highest 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 ~ 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 ϕ 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 Φ modification is -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 $E_t = 4.60 \pm 0.40$ 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(c) [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 -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

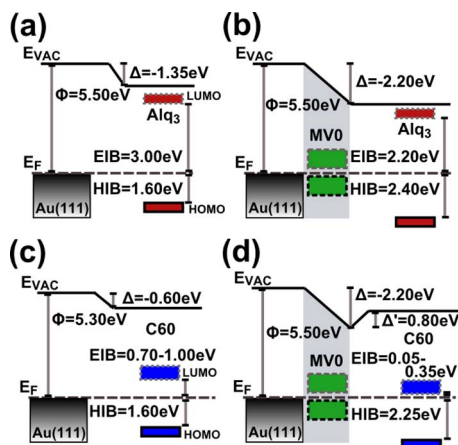


FIG. 3. (Color online) Energy level diagram for the interfaces of Alq₃ and C₆₀ on pristine [(a) and (c)] and MV0 precovered Au(111) [(b) and (d)]. The HOMO-LUMO transport gaps are taken from Refs. 28, 32, and 33 and the values of diagram (c) are taken from Ref. 34. MV0 HOMO and LUMO positions are not directly accessible in experiments, and are therefore sketched schematically following DFT modeling results.

on pristine Au(111).³⁴ The SECO for C₆₀/0.5 Å MV0/Au(111) [Fig. 1(e)] shows that the vacuum level moves up again due to the C₆₀ deposition to yield a ϕ value of 4.10 eV. This observation is reminiscent of the C₆₀ lowest unoccupied molecular orbital (LUMO) being pinned at the Fermi level.³⁵ The schematic energy level diagrams for Alq₃ and C₆₀ on pristine and MV0 precovered 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 Alq₃ and by 0.65 eV for C₆₀. MV0 and analogs thus represent promising candidates for fabricating alternative electron injection contacts in electronic devices.

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