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Organometallic Dimers: Application to Work-Function Reduction of Conducting Oxides

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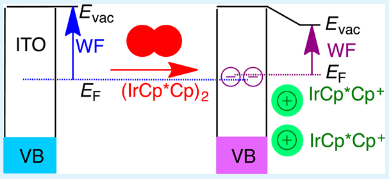
Supporting Information



ABSTRACT: The dimers of pentamethyliridocene and ruthenium pentamethylcyclopentadienyl mesitylene, $(IrCp^*Cp)_2$ and $(RuCp^*mes)_2$, respectively, are shown here to be effective solution-processable reagents for lowering the work functions of electrode materials; this approach is compared to the use of solution-deposited films of ethoxylated poly(ethylenimine) (PEIE). The work functions of indium tin oxide (ITO), zinc oxide, and gold electrodes can be reduced to 3.3−3.4 eV by immersion in a toluene solution of $(IrCp^*Cp)_2$; these values are similar to those that can be obtained by spin-coating a thin layer of PEIE onto the electrodes. The work-function reductions achieved using $(IrCp^*Cp)_2$ are primarily attributable to the interface dipoles associated with the formation of submonolayers of $IrCp^*Cp^+$ cations on negatively charged substrates, which in turn result from redox reactions between the dimer and the electrode. The electrical properties of C_{60} diodes with dimer-modified ITO cathodes are similar to those of analogous devices with PEIE-modified ITO cathodes.

KEYWORDS: *work function, dopant, electron injection, indium tin oxide, poly(ethylenimine), iridocene*

1. INTRODUCTION

Materials with low work functions (WFs) are required as electron-collecting or electron-injecting electrodes in devices such as organic photovoltaic cells, light-emitting diodes, and transistors. Although low-WF metals, such as those of groups 1 and 2, can be used as electrodes, they are highly unstable in air and, in some cases, may react with organics, for example, through abstraction of halide ions. Alternatively, surface modification can be used to lower the WF of materials that exhibit moderate or high WFs in their unmodified state; deposition of modifiers including molecules that can interact with the surface to form monolayers,[1−4] polyelectrolytes,[5−7] and nonconjugated neutral polymers such as poly(ethylene oxide)[8] and poly(ethylenimine)[9] can result in an appropriately oriented dipole layer, and consequent shift in vacuum level, at the surface of the material. Modification approaches also allow low WF to be combined with other desirable properties, for example, transparency in the case of tin-doped indium oxide (ITO) and other conducting oxide electrode materials. Strongly reducing molecules can also be used to lower electrode WFs; here electron transfer from the reductant molecules to the electrode results in a layer of the corresponding cations on the negatively charged surface and consequently in a surface dipole. For example, evaporation of tetrakis(dimethylamino)ethylene (TDAE),[10] neutral methyl viologen (MV(0)),[11] and acridine orange base (AOB)[12] (Figure 1) onto gold has been found to result in WF reductions of 1.3, 2.2, and 1.9 eV, respectively, which, in each case, have been attributed to electron transfer from the modifier to the gold. TDAE has also been found to reduce the WF of ITO by 0.9 eV.[13] Stronger reductants are expected to lead to a greater extent of electron transfer and, therefore, potentially larger WF modifications. The dimers of certain 19-electron sandwich compounds (effective redox potentials for the monomer cation/dimer couple, $E[M^+/$

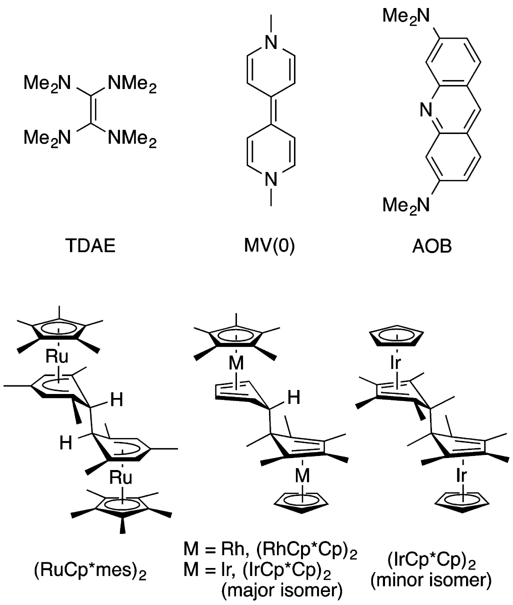


Figure 1. Chemical structures of reductants used in the literature and in this work to reduce the WF of various electrode materials.

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0.5M$_2$], estimated to be ca. −1.7 to −2.3 versus ferrocenium/ferrocene in tetrahydrofuran)[14,15] are considerably stronger reductants than TDAE ($E_{1/2}^{+/0}$ = −0.99 V in acetonitrile {MeCN}),[16−18] MV(0) ($E_{1/2}^{+/0}$ = −1.25 V in MeCN),[19] and AOB (+0.32 V in MeCN),[17,18,20] yet are relatively stable in air due to coupling of their redox chemistry to cleavage of the central C−C bond of the dimer. These dimers have been found to be useful n-dopants for organic semiconductors;[21] solutions of (RhCp*Cp)$_2$[22] {Cp* = pentamethylcyclopentadienyl; Cp = cyclopentadienyl} (E[M$^+$/0.5M$_2$] = −1.97 V)[14,15] have been used to modify the surface of graphene, achieving a WF reduction of 1.3 eV,[23] and evaporation of (RuCp*mes)$_2$ {mes = 1,3,5-trimethylbenzene}[24] onto ZnO single crystals has recently been found to give WF reductions of 1.5 eV.[25]

Here we show that the dimeric reductants (IrCp*Cp)$_2$[26] and (RuCp*mes)$_2$[24] can be used as solution-processable modifiers to lower the WF of ITO and other electrode materials. We compare the reduction in ITO WF obtained with that obtained using TDAE under similar conditions and with other work in the literature. We also compare the electrical behavior of C$_{60}$-based diodes in which the cathodes are unmodified, dimer modified, or modified with ethoxylated polyethylenimine (PEIE).

2. EXPERIMENTAL SECTION

2.1. Substrate Preparation for Surface Characterization. ITO on glass (purchased from Eagle-XG, Thin Film Devices, Anaheim, CA, surface roughness of 0.7−0.8 nm rms as measured with atomic force microscopy) was cut into 15 mm × 15 mm substrates. Samples denoted detergent-solvent cleaned (DSC) were scrubbed and subsequently sonicated for 20 min with a 5% solution of Micro-90 detergent in deionized (DI) water, sonicated in DI water for 20 min, sonicated in ethanol for 20 min, rinsed with ethanol, and dried under a flow of nitrogen to afford DSC ITO samples. Plasma-treating of some ITO (OP-ITO) surfaces was carried out using oxygen plasma with a Plasma-Preen II (100% Power, Plasmatic Systems, Inc., North Brunswick, NJ) for 5 min. For atomic layer deposition (ALD) of ZnO, 2.54 cm × 2.54 cm glass microscope slide substrates were cleaned in the same manner as reported for ITO, followed by oxygen plasma cleaning. Immediately after the plasma treatment, samples were loaded into an ALD system (Cambridge NanoTech, Savannah 100), and 30 nm of ZnO was deposited.[27,28] These larger surface samples were then cut into 15 mm × 15 mm squares prior to use, rinsed with ethanol, and dried under a flow of nitrogen. Commercially available glass/Ti/gold slides (EMF Corporation, Ithaca, NY) were cut into 15 mm × 15 mm samples. These smaller samples were sonicated for 10 min in ethanol, rinsed with ethanol, and dried under a flow of nitrogen. Samples were then cleaned by immersion in piranha solution (3:1 concentrated sulfuric acid/30% aqueous hydrogen peroxide) for 30 min, rinsing with DI water, followed by immersion in DI water for 20 min, washing with DI water, followed by ethanol, and drying under a flow of nitrogen. For all substrates, samples were immediately transferred to an X-ray photoelectron spectroscopy/ultraviolet photoelectron spectroscopy (XPS/UPS) for characterization of the unmodified materials (see below) upon completion of the cleaning.

2.2. Surface Modification. After characterization of the unmodified substrates using XPS and UPS, substrates were transferred to a nitrogen-filled glovebox (<0.1 ppm water and <0.5 ppm oxygen) under a positive pressure of nitrogen (using a Kratos air-sensitive transporter 39−322, which couples with the transfer chamber of the instrument). Samples were then treated in the glovebox with solutions of (IrCp*Cp)$_2$,[14,26] (RuCp*mes)$_2$,[14,24] or TDAE (distilled and deoxygenated with nitrogen), typically 2 mM, in toluene (dried by distillation from calcium hydride and subsequently freeze−pump−thaw deoxygenated). Samples were then rinsed three times with fresh toluene, dried with a flow of nitrogen, and transferred under inert atmosphere to the XPS/UPS for analysis or to a vacuum thermal evaporation system for device fabrication. A thick film of (IrCp*Cp)$_2$ for XPS comparison was obtained by drop-casting a concentrated solution in toluene onto DSC-ITO in the glovebox.

2.3. Surface Characterization. All measurements were conducted in a combined XPS/UPS instrument (Kratos Axis Ultra) with an average base pressure of 10^{-9} Torr. For a given sample, UPS spectra were obtained prior to XPS with a 21.2 eV He I excitation, a pass energy of 5 eV using a 27 μm spot size, and a 8.96 eV sample bias. Each sample was examined in at least seven spots to ensure a representative sampling of the variation over the surface. The spectrometer was calibrated using a sputter-cleaned silver sample. The work function (WF) of samples were determined according to

$$\mathrm{WF} = \mathrm{BE}_{\mathrm{SEE}} - h\nu$$

where BE$_{\mathrm{SEE}}$ is the binding energy relative to the Fermi level of the calibrated spectrometer that corresponds to the secondary electron cutoff (see Figure S1 in the Supporting Information), and $h\nu$ is the He 1 photon energy (21.2 eV).

XPS data were collected with a monochromatic Al Kα source (300 W) using a 400 μm spot size and a pass energy of 160 eV for survey acquisition and 20 eV for high-resolution spectra. Exposure of the surfaces to X-rays was kept to a minimum (ca. 45 min), and spectra were acquired in three spots on each surface using a takeoff angle of 0°. XPS data for the drop-cast film of (IrCp*Cp)$_2$ required the use of charge neutralization. The binding energy values were then corrected by using the position of the In 3d peaks as a reference; more details are given in the Supporting Information. Data were analyzed using Vision Processing software (version 2.2.8).

The degrees of coverage were estimated from XPS data using the same approach previously used for phosphonic acid modifiers on ITO.[29] Specifically, Ir(4f)/In(3d) and Ru(3d)/In(3d) peak-intensity ratios, corrected for instrumental effects and differences in ionization cross sections, were compared to a model in which the ITO is modeled by replacing 1/8 of the In atoms in the crystal structure of In$_2$O$_3$ by Sn,[30] in which the cations IrCp*Cp$^+$ and RuCp*mes$^+$ are assumed to be oriented with their metal−ligand axes normal to the surface[31,32] and complete monoloayers are treated as close-packed arrays of disks with radii of 4.49 and 4.53 Å, respectively (based on Spartan modeling of the Cp* and mes ligands), which takes into account depth-dependent attenuation of photoelectrons.

2.4. Electrical Measurements. ITO-coated glass substrates (Colorado Concept Coatings LLC, Loveland, CO, average sheet resistance of 15 Ω/sq) were partially covered with Kapton tape and etched by exposure to a solution of aqua regia (3:1 concentrated hydrochloric acid/concentrated nitric acid) for 10 min at 80 °C. ITO on glass was cut into 2.54 cm × 2.54 cm substrates, which were cleaned in sequential ultrasonic baths of detergent water, DI water, acetone, and isopropanol. Each ultrasonic bath lasted for 20 min at 45 °C. PEIE solution (Sigma-Aldrich, 80% ethoxylated, M_w = 70 000 g mol^{-1}, 35−40 wt % in water) was diluted with 2-methoxyethanol to a concentration of 0.4 wt %. The solution was spin-coated on top of the ITO substrates at a speed of 5000 rpm for 60 s and an acceleration of 1000 rpm s^{-1}; the spin-coated samples then were annealed at 100 °C for 10 min in air (the effective thickness of these PEIE layers has previously been found to be ca. 10 nm using spectroscopic ellipsometry).[9] Dimer modifications were carried out in the glovebox as described above and transferred to a vacuum thermal evaporation system (SPECTROS, K. J. Lesker). C$_{60}$ (100−200 nm), MoO$_3$ (10 nm), and Ag (150 nm) were deposited sequentially through a shadow mask at a base pressure of 2 × 10^{-7} Torr on the unmodified, PEIE-modified, or dimer-modified ITO substrates. The effective area of the diodes was 11.2 mm^2. Current density−voltage (J−V) curves were measured in a nitrogen-filled glovebox by using a source meter (2400 SourceMeter, Keithley Instruments Cleveland, OH) controlled by a LabVIEW program.

3. RESULTS AND DISCUSSION

Detergent/solvent-cleaned (DSC) ITO surfaces were modified under inert atmosphere by dipping in 2 mM toluene solutions

Table 1. Summary of UPS-Determined Values of Work Function and Energies of Valence Band Maxima for Various Substrates (eV) before and after Treatment with Toluene Solutions of Reductants

		unmodified substrate		modified substrate				
substrate	reductant[a]	WF	E_{VBM}[b]	WF	ΔWF[c]	E_{VBM}[b]	ΔE_{VBM}[d]	ΔE_{vac}[e]
DSC-ITO	$(IrCp^*Cp)_2$	4.63 ± 0.04	−2.98 ± 0.03	3.29 ± 0.08	−1.34	−3.22 ± 0.04	−0.24	−1.10
DSC-ITO	$(RuCp^*mes)_2$	4.53 ± 0.04	−3.02 ± 0.02	3.46 ± 0.07	−1.07	−3.17 ± 0.05	−0.15	−0.92
DSC-ITO	TDAE	4.57 ± 0.06	−3.00 ± 0.04	3.87 ± 0.06	−0.70	−3.21 ± 0.03	−0.21	−0.49
OP-ITO	$(IrCp^*Cp)_2$	5.29 ± 0.06	−2.85 ± 0.05	3.69 ± 0.03	−1.60	−2.98 ± 0.05	−0.13	−1.47
ALD-ZnO	$(IrCp^*Cp)_2$	3.90 ± 0.02	−3.56 ± 0.06	3.40 ± 0.03	−0.50	−3.72 ± 0.03	−0.16	−0.34
Au	$(IrCp^*Cp)_2$	5.22 ± 0.03	0	3.35 ± 0.03	−1.87	0	0	−1.87

[a] All 1 min in 2 mM toluene solution, followed by rinsing. [b] Energy relative to the Fermi level corresponding to the onset of ionization from the valence band (equal to $-BE_{VBM}$, as defined in Figure S1 in the Supporting Information). [c] $\Delta WF = WF_{modified} - WF_{unmodified}$. [d] Change in the position relative of the onset of valence-band ionization relative to the Fermi level, $\Delta E_{VBM} = E_{VBM(modified)} - E_{VBM(unmodified)}$. [e] Change in the vacuum level associated with the interface dipole; inferred from $\Delta WF = \Delta E_{VBM} + \Delta E_{vac}$.

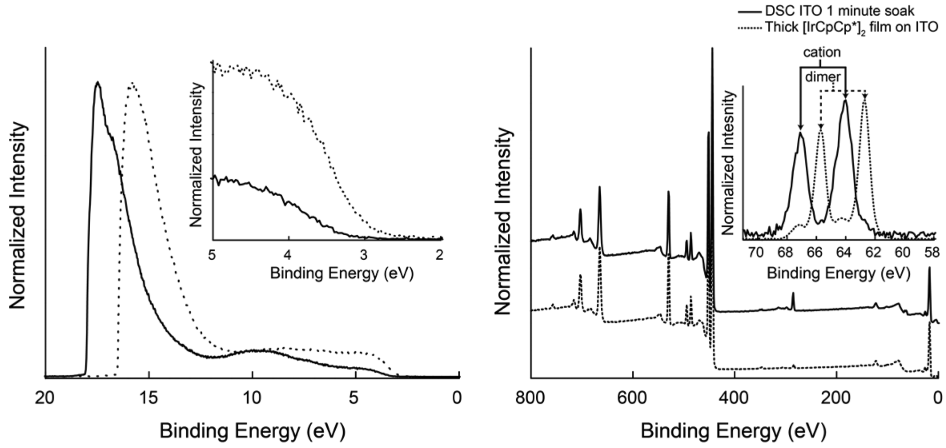

Figure 2. (left) Representative UPS spectra of DSC-ITO before (dotted line) and after (solid line) modification with $(IrCp^*Cp)_2$ (1 min, 2 mM in toluene) showing the large shift in the low-energy cutoff. (inset) The slight shift in the onset of ionization from the valence band. (right) XPS spectra of ITO before (dotted line) and after (solid line) modification with $(IrCp^*Cp)_2$ (1 min, 2 mM in toluene). (inset) High-resolution 4f Ir XPS spectra after modification with $(IrCp^*Cp)_2$ (1 min, 2 mM in toluene) and with a thicker film of $(IrCp^*Cp)_2$ (drop cast from a more concentrated toluene solution).

of $(IrCp^*Cp)_2$[26] (estimated $E[M^+/0.5M_2]$ = −2.01 to −2.14 V)[14,15] for periods of 1 min and 1 h; the WF of the samples was then measured using UPS. Both $(IrCp^*Cp)_2$-treated surfaces exhibited similarly reduced WF,[33] and, thus, subsequent experiments involved immersion for 1 min. As shown in Table 1, final WF values of 3.3 eV (ΔWF = −1.3 eV) were obtained for the 1 min samples; a final WF value of 3.3 eV was also previously obtained for DSC ITO treated with ethoxylated poly(ethylenimine).[9]

The XPS results indicate the presence of Ir on the surface (Figure 2). The inset of Figure 2 compares the Ir 4f spectrum of a sample modified for 1 min with that of a thicker film obtained by drop casting a solution of the dopant onto ITO. In the drop-cast film the major doublet in the Ir 4f spectrum is assigned to unreacted dimer. The doublet for the sample modified by dipping is seen at higher binding energy. This is consistent with the redox chemistry of dimers of this type, which are usually oxidized to the corresponding monomeric cation;[34] in this case the expected product is the $IrCp^*Cp^+$ cation,[35] for which both the net positive charge and higher formal oxidation state (Ir^{III}) are expected to lead to higher binding energy than for the Ir^{I} dimer. Moreover, very similar binding energies are seen for a film of an n-doped organic semiconductor containing the same monomeric cation (see Supporting Information).[36] A doublet with similar binding energies is also present alongside the doublet assigned to the dimer in the spectrum of the drop-cast film and is assigned to $IrCp^*Cp^+$ cations formed as a result of the same redox reaction occurring at the immediate dopant/ITO interface (the film is sufficiently thin that In 3d signals from the substrate are observable). Analysis of the XPS Ir/In ratio is consistent with the cations forming 73 ± 9% of a close-packed monolayer (treating the cations as disks with diameters equal to that of Cp* ligand).

Under the same conditions $(RuCp^*mes)_2$[24] (estimated $E[M^+/0.5M_2]$ = −2.04 V)[14,15] afforded a slightly higher final WF of 3.5 eV (ΔWF = −1.1 eV) (see Figure S5 in the Supporting Information). Although overlap of Ru $3d_{3/2}$ and C 1s ionizations limits the precision with which the coverage can be estimated using the XPS Ru/In ratio, the coverage is clearly lower (ca. 30%) than in the case of the Ir dimer.[37] While the lower coverage is consistent with the smaller magnitude of ΔWF, this is unexpected based on the thermodynamics and kinetics associated with the solution redox reactions of the two dimers,[14] and may reflect differences in the details of the cation−cation and cation−surface electrostatic interactions for the different dopants. DSC ITO was also treated for 1 min with a 2 mM toluene solution of the TDAE for comparison; consistent with the less cathodic redox potential of this dopant, the resultant WF change (WF = 3.9 eV; ΔWF = −0.7 eV)[38] is substantially less than that obtained using the dimer dopants. As shown in Table 1, solutions of $(IrCp^*Cp)_2$ (2 mM toluene,

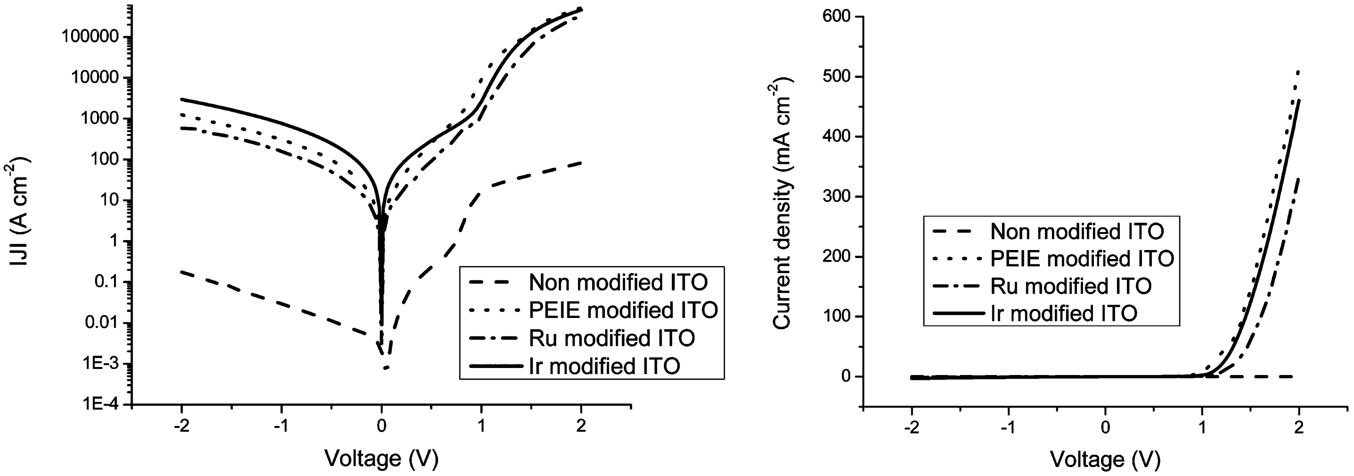

Figure 3. Semilogarithmic (left) and (right) linear plots of J−V characteristics for devices with structure DSC-cleaned ITO(with or without modification)/C_{60}(100 nm)/MoO_x(10 nm)/Ag(150 nm). The ITO acts as the cathode under forward bias.

1 min) also reduce the WF of other materials including ITO cleaned by an oxygen plasma (OP) prior to modification, gold, and ZnO films produced by ALD (see Figures S6 and S7 in the Supporting Information for examples of UPS and XPS spectra).[27,28] As in the case of DSC ITO, the final WF values are similar to those previously reported using PEIE as a surface modifier (3.3, 3.4, and 3.6 eV for plasma-ITO, Au, and ALD-ZnO, respectively).[9] The WF obtained for gold modified with $(IrCp^*Cp)_2$ solution is similar to WFs previously reported for gold modified by evaporation of MV(0) or AOB in UHV (both down to 3.3 eV),[11,12] and lower than that for gold modified by evaporation of TDAE (3.9 eV).[10] The Ir 4f binding energies for both $(IrCp^*Cp)_2$-treated Au and ZnO are very similar to those seen for ITO treated with the same dimer, which strongly suggests that the iridium species is also the expected Ir^{III} cation, $IrCp^*Cp^+$ (see Figure S7, Supporting Information).

UPS indicates that for both ITO and ZnO, the modification results in a change in the position of the valence band relative to the Fermi level (ΔE_{VBM}, Table 1) that is fairly small compared to the overall WF modification; the major contributor to ΔWF is, therefore, the effect on the vacuum level (ΔE_{vac}, Table 1) of the surface dipole formed between the submonolayer of organometallic cations and the electrons transferred to the oxides, which is consistent with the previous study of ITO modified by an evaporated submonolayer of TDAE.[13] This situation may be contrasted with the interfacial doping of single-layer graphene by $(RhCp^*Cp)_2$; here, the shift of Fermi level relative to the Dirac point, at which valence and conduction bands touch, accounts for over half of ΔWF at high doping levels and for an even greater proportion at lower doping levels.[23,39,40] The differences presumably reflect a much higher density of states accessible to the donated electrons in the oxides than in the monolayer of graphene. While the ΔWF and ΔE_{VBM} values are clearly indicative of formation of an interface dipole and, therefore, suggest that the electrons originating from the dimers are transferred to the oxide, the fate of the transferred electrons is unclear. It has previously been suggested that TDAE may lead to localized reduction of In^{III} ions,[13] but presumably other localized or delocalized states tailing below the oxide conduction-band edge could be important.[41] Another possibility is that acidic surface hydroxyl groups are reduced with concomitant generation of H_2; however, no significant change is seen in the O 1s XPS spectra (including angle-resolved spectra in which surface effects are accentuated), and the WF modifications are larger than those induced by treatment with bases such as NaOH (+0.05 eV in our work where the substrate was immersed in a 10 M aqueous overnight and then rinsed with water; −0.2 eV in a previous study[42]) or NBu_4OH (−0.9 eV[42]), the effects of which have, in any case, been attributed to coordination of hydroxide ions to vacant surface metal coordination sites, rather than to deprotonation of acidic surface groups.[42]

The stability of the WF of $(IrCp^*Cp)_2$-modified ITO and ZnO in air was examined; even after 5 min of exposure the WFs of the two materials were found to increase by 0.5 and 0.3 eV, respectively. This is qualitatively similar to what was previously observed for ITO modified with vacuum-deposited TDAE, where the WF was found to increase by ca. 0.2 eV after a few minutes in air.[13] After several days exposure to air the WFs of both ITO and ZnO reach values of ca. 4 eV, which are significantly lower than that of unmodified ITO and similar to that of unmodified ZnO. XPS reveals little change in the Ir 4f spectra (ca. 0.2 eV decrease in binding energy; see Figure S8, Supporting Information), consistent with the expected air stability of the $IrCp^*Cp^+$ ion. Presumably the increase of WF results from reduction of O_2 and/or H_2O by some of the electrons initially transferred to the oxide by the dopant, resulting in a decrease of the surface dipole.[43]

To examine whether dimer-modified ITO still behaves as a low-WF material when coated by an organic semiconductor, simple sandwich devices with the structures DSC-ITO(with or without modification)/C_{60}(100−200 nm)/MoO_x(10 nm)/Ag-(150 nm) were fabricated. Reference devices in which the ITO was modified by the spin-coating of PEIE from water/ethoxyethanol solution were also fabricated for comparison, since this treatment has previously been shown to result in an ITO WF of ca. 3.3 eV as determined by UPS *and* to act as a low-WF electrode in a variety of device architectures.[9] As shown in Figure 3, the electrical characteristics of the sandwich structures incorporating dimer-modified ITO strongly resemble those of reference devices with PEIE modification: the devices act as diodes and their behavior is consistent with more facile electron injection from the dimer- or PEIE-modified ITO than from unmodified ITO.[44] Thus, in terms of WF reduction *and* facilitating electron injection, the current approach has fairly similar effects to the use of PEIE.

Good sample-to-sample reproducibility is found for the portions of the *J*−*V* plots for both dimer- and PEIE-modified devices in which the injected diode current is dominant, with some variation in the leakage currents seen at lower voltages and at reverse bias (see Supporting Information, Figure S9), and devices are reasonably stable to repeated cycling over a range of ±2 V (Figure S10). Annealing the devices with $(IrCp^*Cp)_2$-modified ITO cathodes at temperatures of up to 150 °C has little effect on the *J*−*V* characteristics, the main effect being an increase of the leakage current (Supporting Information, Figure S11). Consistent with these findings, the WF of $(IrCp^*Cp)_2$-modified ITO (as determined by Kelvin probe in inert atmosphere, Supporting Information, Figure S12) is also found to exhibit little variation following analogous annealing conditions. However, while $(RuCp^*mes)_2$- and PEIE-modified ITO samples also exhibit thermally stable WF values, the electrical properties of the corresponding C_{60} diodes are less stable. Diodes containing $(RuCp^*mes)_2$ electrodes cease operation after heating to ca. 50−75 °C; the reason for this is unclear. PEIE-containing diodes show a shift of the turn-on voltage to increasingly low voltage with increased annealing temperature. Given the stability of the WF of PEIE-modified ITO, this change may be attributable to a change in the fullerene/PEIE interaction, perhaps as a result of thermally induced n-doping of the fullerene; although PEIE has a high ionization energy (6.5 eV),[9] simple amines such as triethylamine can still act as reductants due to coupling of the electron transfer reaction to irreversible chemistry,[18] especially in the presence of light,[45] and indeed PEIE has been observed to n-dope the conduction channels of PCBM- and naphthalene diimide polymer-based field-effect transistors.[9]

4. CONCLUSIONS

Organometallic dimers such as $(IrCp^*Cp)_2$ can be used for solution-based electrode WF modification. This approach can be applied to a variety of electrode materials and can be used to lower the WF of ITO by ca. 1.5 eV. The reduced WF values obtained by this approach are lower than that obtained using TDAE under comparable conditions.[46] As well as being more powerful reductants and inducing greater WF changes, the dimers are moderately air-stable solids that are more easily handled than TDAE, which is an oxygen-sensitive liquid, although surface modifications should still be carried out in inert atmosphere owing to the sensitivity of the reduced-WF surfaces.

The WF values obtained by treating various electrode materials with $(IrCp^*Cp)_2$ are comparable to those previously obtained by spin-coating a thin layer of PEIE from water/ethoxyethanol. Furthermore, similar behavior is found for diodes with dimer- and PEIE-treated ITO cathodes, both of which act as effective *electron*-injecting electrodes. The PEIE approach has the advantages that the modified electrode surfaces are air stable and that the modification can be carried out in air. On the other hand, the necessity of processing PEIE from solution in polar solvents may be a limitation for some applications, whereas the dimeric dopants may be processed either from solution in low-polarity solvents, as in the current work and some previous work on n-doping organic semiconductors,[21] or by vacuum deposition, as has also been demonstrated for the doping of organic semiconductors[21] and for modifying the WF of single-crystal ZnO.[25] Thus, the dimer dopant approach is, to some extent, complementary to the PEIE approach and provides a viable alternative for modifying the WF of a variety of materials.

■ ASSOCIATED CONTENT

Supporting Information

Determination of work function from UPS spectra; details of XPS measurements for the drop-cast film of $(IrCp^*Cp)_2$ on ITO; XPS spectra for $IrCp^*Cp^+$ derivatives (including NMR evidence for the presence of $IrCp^*Cp^+$); additional UPS and XPS spectra of modified electrode materials; additional plots of *J*−*V* data (showing sample-to-sample variation and effects of voltage cycling and thermal annealing; Kelvin probe data showing effect of temperature on WF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(33) For a sample immersed for 1 h the initial WF was 4.78 ± 0.04 eV and the final WF was 3.45 ± 0.06 eV, giving a ΔWF value of −1.33 eV, identical within experimental uncertainties with that found for 1 min. The coverage for this sample was estimated as ca. 92 ± 9% of a monolayer.

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(35) The open-shell dimer monocation $(IrCp^*Cp)_2^+$ is highly unstable according to solution electrochemical measurements. Based on solution and computational work (references 14 and 34), the dimer likely reacts with ITO through an electron transfer to the substrate, followed by cleavage of the central C—C bond to form the stable $IrCp^*Cp^+$ and the highly reducing (−2.62 V vs $FeCp_2^{+/0}$) monomer, which then transfers a second electron.

(36) The pattern of Ir 4f binding energies here is very similar to that in the Rh 3d binding energies seen for $(RhCp^*Cp)_2$-doped graphene, in which the Rh 3d binding energies for doped samples were higher than those for the dimer by ca. 1.5 eV and essentially the same as seen for $RhCp^*Cp^+PF_6^-$ (reference 23).

(37) Smaller differences in core-level binding energies between the neutral dimer and monomer cation are found in the RuCp*mes system (reference 25) than for IrCp*Cp (this work) or RhCp*Cp (reference 23), since, although differing in overall charge, both species are formally Ru^{II}. However, the $3d_{5/2}$ binding energy for $(RuCp^*mes)_2$-modified ITO (Supporting Information, Figure S5) is consistent with the species assigned to $RuCp^*mes^+$ on single-crystal ZnO modified by $(RuCp^*mes)_2$ (reference 25).

(38) These results are fairly similar to previous results for TDAE-modified ITO, but are not directly comparable in that the previous study started with O_3-plasma-cleaned ITO with WF = 4.7 eV and was carried out by evaporation of the dopant, rather than in solution.

(39) A relatively large contribution to ΔWF from ΔE_{VBM} is also found in another 2D system: trilayer MoS_2 n-doped using a benzoimidazoline dimer (reference 40).

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(41) In principle, XPS could help distinguish these possibilities; however, the large number of In atoms per dopant molecule within the information depth probed by the technique mean that this was not possible in practice.

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(43) In a nitrogen-filled glovebox (ca. 1 ppm O_2) the WF modifications were considerably more stable; the WF of an $(IrCp^*Cp)_2$-treated ITO sample increased from 3.3 to only 3.8 eV over 30 d.

(44) The semilogarithmic plot shows that the currents in reverse bias also increase by many orders of magnitude in the diodes with PEIE- or dimer-modified ITO electrodes. As shown in the Supporting Information (Figure S9), there is considerable device-to-device variation in these currents, whereas the magnitudes of the currents that dominate the *J*−*V* plots at forward biases of >1.0−1.5 V are much more consistent. Since the overall electrical characteristics can be considered as a superposition of diode and resistor characteristics, with the latter originating from leakage currents and typically represented as a shunt resistance, it is these leakage currents, rather than the reverse saturated current of the diode, that dominate the *J*−*V* characteristics in reverse bias. The origin of the large difference in currents between devices with unmodified and modified ITO elecrodes is unclear; however, the morphology of the C_{60} close to the interface may be affected by the modification.

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(46) Treatment of ITO cleaned using an O_2 plasma with $(IrCp^*Cp)_2$ in solution results in a WF value similar to that obtained in a previous study of the effect of a reductant on the WF of ITO in which TDAE was *evaporated* onto ITO treated with an O_3 plasma (3.7 eV) (reference 13).