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Use of a High Electron-Affinity Molybdenum Dithiolene Complex to p-Dope Hole-Transport Layers

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The doping of organic molecular semiconductors and the conduction mechanisms in these doped materials have become very active research topics.[1−4] One significant challenge is to identify n- and p-type dopants for a range of technologically relevant hosts. Candidate p-dopants include both inorganic[5−7] and organic molecules.[2,3,8,9] 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ) is so far the most commonly used p-type dopant. Its electron affinity (EA), 5.2 eV, is sufficient to p-dope many hole-transport materials (HTM). However, instability vs diffusion has led to a search for alternatives.[10−12]

Here we show that molybdenum tris[1,2-bis(trifluoromethyl-)ethane-1,2-dithiolene] [$Mo(tfd)_3$][13−16] (Figure 1a) is a promising alternative p-dopant and demonstrate its use to p-dope the widely used HTM *N*,*N*′-di[(1-naphthyl)-*N*,*N*′-diphenyl]-1,1′-biphenyl-4,4′-diamine (α-NPD, Figure 1b).

$Mo(tfd)_3$ was synthesized and purified as previously described;[14] films 6 nm thick were deposited for electronic structure determination. To assist the interpretation of experimental spectra, the $Mo(tfd)_3$ geometry and electronic structure were calculated at the density functional theory (DFT) level using the B3LYP exchange-correlation functionals and LANL2DZ basis set[17] (d polarization functions added for C, F, and S). A similar computational approach has been shown to describe molybdenum dithiolene complexes well.[18] A standard procedure,[19] which effectively allows solid-state polarization effects to be taken into account, was used to simulate ultraviolet/inverse photoelectron spectroscopy (UPS/IPES) spectra; the calculated density of states was convolved with a Gaussian function of full width at half-maximum set at 0.8 eV for the empty states and 0.55 eV for the filled states; then, a rigid shift along the energy axis was applied to the entire spectra of the filled and the empty states, independently, to match against experimental peaks.

The He I UPS and IPES spectra (the energy resolutions are 0.15 and 0.45 eV, respectively) of the $Mo(tfd)_3$ film (red in Figure 2a) are referenced to the vacuum level (E_{vac}), which is determined from the secondary electron cutoff of the UPS spectrum. The thickness of the film, 6 nm, is sufficient to eliminate the contribution from the substrate. The ionization energy (IE) of the condensed film, defined as the difference between E_{vac} and the linear extrapolation of the leading edge of the highest occupied molecular orbital (HOMO), is 7.84 eV. The EA, defined as the difference between E_{vac} and the linear extrapolation of the leading edge of the lowest unoccupied molecular orbital (LUMO), is 5.59 eV, ~0.4 eV higher than that of F_4-TCNQ.[3] The high EA is consistent with expectations based on previous electrochemical data[15] as well as our cyclic voltammetry measurements, included in the Supporting Information, which show $Mo(tfd)_3$ to be strongly oxidizing in solution.

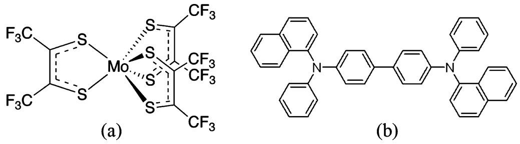

Figure 1. Chemical structures of (a) $Mo(tfd)_3$ and (b) α-NPD.

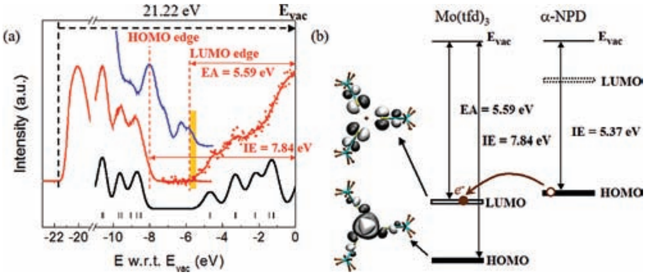

Figure 2. (a) (Red) Combined filled (UPS) and empty (IPES) states spectra measured on a 6 nm $Mo(tfd)_3$ film on Au; (black) simulated spectra based on DFT calculations (vertical tick marks denote the DFT orbital energy levels); (blue) α-NPD filled states spectrum. (b) Energy level diagram of $Mo(tfd)_3$ (with corresponding DFT wave functions) and α-NPD.

The experimentally determined molecular levels are confirmed by excellent agreement with the theoretical spectra (black in Figure 2a). The agreement is particularly important for the empty states, as (i) they define the characteristics of $Mo(tfd)_3$ as a p-dopant and (ii) the experimental resolution in IPES often makes the LUMO energy assignment difficult. The singly occupied MO (SOMO) level of the geometry-optimized anion, $[Mo(tfd)_3]^-$, is calculated to be delocalized over the ligands (Figure 2b). The *total* extra charge is found (from a Mulliken population analysis) mostly on the S (−0.49) and F atoms (−0.35). It is important to note that the IE and EA deduced from Figure 2a are strictly valid for a $Mo(tfd)_3$ film. The polarization energies that result from the formation of a hole (via UPS) or an electron (via IPES) on the molecule depend on the molecular environment and are, thus, likely to differ slightly from those resulting from embedding $Mo(tfd)_3$ in an HTM film for doping purposes. However, past experience shows that these polarization energies are quite close and that the EA obtained above should prove to be an accurate indication of the efficiency of $Mo(tfd)_3$ as a p-dopant.[3]

The UPS spectrum of a 5 nm film of α-NPD (Aldrich) on Au (blue in Figure 2a) gives an IE of 5.37 eV, in good agreement with the literature.[3] The overlap between the $Mo(tfd)_3$ low-energy empty states and the α-NPD high-energy filled states (yellow rectangular area) points to an energetically favorable electron transfer from the host to the dopant in the doped film (Figure 2b).

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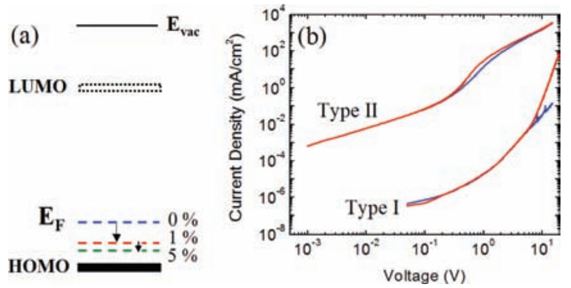

Figure 3. (a) E$_F$ shift toward the HOMO as a function of Mo(tfd)$_3$ concentration. (b) *I*−*V* characteristics of type I and type II Au/α-NPD/Au devices (see text), with bias polarity corresponding to holes injected from the bottom contact (red curves) and from the top contact (blue curves).

α-NPD films (7−8 nm) doped with various amounts of Mo(tfd)$_3$ were grown at room temperature by coevaporation and studied by UPS. The measured position of the Fermi level (E$_F$) in the gap of α-NPD on Au is shown in Figure 3a. The limits of the gap are the HOMO and LUMO edges of α-NPD. As the doping concentration increases from 0 to 1 and 5 mol %, E$_F$ shifts toward the HOMO, a clear indication of p-doping. The dopant concentrations used here were small enough that no line shape change or new gap states were observed. The total shift between the undoped α-NPD and 5 mol %-doped α-NPD is 0.57 eV, at which point E$_F$ is pinned at 0.42 eV above the HOMO edge. This position is in good agreement with the position obtained for α-NPD:F$_4$-TCNQ, which has been attributed to the relaxation energy of the ionized molecules.[3] The films considered in Figure 3a are thicker than the expected doping-induced depletion region,[3] and the E$_F$ positions can therefore be assumed to represent the bulk values of the Fermi level in the doped material.

I−*V* characteristics measured *in situ* on two hole-only devices made by sequential metal/organic/metal evaporation in ultrahigh vacuum (UHV) are shown in Figure 3b. The device structure is (30 nm) Au/(170 nm) α-NPD/(30 nm) Au, where α-NPD is either undoped (type I) or homogeneously doped with 1 mol % Mo(tfd)$_3$ (type II). The bias polarity corresponds to holes injected from the bottom contact (red curves) or the top contact (blue). The current density in the type I device is plotted down to 4×10^{-7} mA/cm^2, below which noise dominates in our experimental setup. The *I*−*V* curve is nearly linear with a slope equal to unity on a log−log scale for $V \leq 0.5$ V, consistent with an ohmic conduction regime. The applied bias is insufficient to provide substantial injected charge carriers. Current in this device is injection-limited and can be modeled with the Richardson−Schottky thermionic emission equation,[3,20] as will be discussed in detail elsewhere. Note that the *I*−*V* curves for injection from top and bottom electrodes overlap nearly perfectly, emphasizing the equivalence of α-NPD/Au and Au/α-NPD contacts made under UHV.[21]

The current density in the type II device is orders of magnitude higher over the whole bias voltage range. The linear part of the logarithmic *I*−*V* with slope ~1 at low *V* indicates ohmic conduction, yet with a much higher carrier density than that in the type I device. The ratio of "free" carriers is difficult to estimate at this point, as the carrier mobility is expected to be affected by doping. The more rapid increase in current density at ~0.5 V signals the onset of injection and/or additional trap filling. At voltages of 5−10 V, the current density in the type II device is nearly $10^4\times$ higher than the type I device. Beyond this point, the difference decreases, suggesting that bulk transport (i.e., space charge-limited current) limits the current density.[3] Here again, *I*−*V* curves for injection from the bottom and top electrodes nearly overlap.

Finally, we briefly mention Rutherford backscattering (RBS) measurements performed on two types of samples: (i) α-NPD (100 nm)/α-NPD:2 mol % Mo(tfd)$_3$ (55 nm)/Si; and (ii) α-NPD (150 nm)/α-NPD:2 mol % Mo(tfd)$_3$ (40 nm)/α-NPD (150 nm)/Si. The latter samples were annealed for 15 min in dry nitrogen at 70, 90, or 110 °C, and RBS was used to investigate the distribution of Mo within the samples. None of these samples exhibited any evidence of dopant diffusion, which bodes well for the structural immobility of Mo(tfd)$_3$ in the host matrix. This behavior is presumably due to the bulky three-dimensional structure of Mo(tfd)$_3$, in contrast to the planar structure of F$_4$-TCNQ. Further details on this study will be reported elsewhere, with additional electrical characterization and X-ray photoelectron spectroscopy studies of Mo(tfd)$_3$ and its use as a dopant.

In summary, we have shown that Mo(tfd)$_3$ has a larger electron affinity than F$_4$-TCNQ, a commonly used p-dopant in organic electronics. With an EA of 5.6 eV, Mo(tfd)$_3$ can efficiently p-dope a number of important molecular hole-transport materials. The LUMO level of Mo(tfd)$_3$ is calculated to be delocalized over the whole molecule, which is expected to lead to low pinning potential. Evidence of p-doping on α-NPD includes a shift of the Fermi level toward the semiconductor HOMO and orders of magnitude increase in the conductivity of the doped material. The stability of Mo(tfd)$_3$ vs diffusion in α-NPD is confirmed by RBS.

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Supporting Information Available: Solution reaction between Mo(tfd)$_3$ and α-NPD, electrochemical measurements, and complete ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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