

Tuning the hole injection barrier height at organic/metal interfaces with (sub-) monolayers of electron acceptor molecules

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We demonstrate that the insertion of an electron acceptor molecular (sub-) monolayer at organic/metal interfaces enables systematic tuning of the hole injection barrier height (Δ_h). Ultraviolet photoemission spectroscopy results show that Δ_h for α -sexithiophene thin films deposited on Ag(111) can be reduced from 1.3 to 1.0 eV by introducing a chemisorbed monolayer of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) on the metal surface. Fine-tuning of Δ_h within the interval of 0.3 eV is achieved by using TCAQ coverages in the submonolayer range.

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As the field of organic electronics is growing, there is increasing need for fine-tuning the energy level alignment between conjugated organic materials (COM) and metal electrodes. In general, interface energetics are determined by the type of interaction between the COM and the metal. Approaches to tune charge carrier injection barriers include the use of molecules with dipoles attached to the electrode,¹⁻⁴ or “electrical doping” of a host COM (electron donor) with a strong molecular electron acceptor⁵⁻⁸ (i.e., formation of charge transfer complexes). However, little freedom exists for fine-tuning of injection barrier heights for a given material combination.

We present an alternative approach to the ones mentioned above, which consists of adsorbing a (sub-) monolayer of an electron acceptor molecule [11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ)] on a metal surface. Partial charge transfer from Ag to TCAQ results in a chemisorbed layer, which reduces the hole injection barrier (Δ_h) to subsequently deposited α -sexithiophene (6T). By choosing appropriate TCAQ pre-coverage, Δ_h can be varied systematically within an interval of 0.3 eV. It is anticipated that the chosen concept can also be applied for other material combinations. To some extent, the presented surface modification scheme is related to the use of alkali metals to control the work function and Schottky barrier height in inorganic III-V semiconductor materials, such as GaAs.⁹ However, the direction of charge transfer is reversed in the present study.

TCAQ was synthesized following a procedure from Ong *et al.*,¹⁰ and purified by train sublimation before use. Ultraviolet photoelectron spectroscopy (UPS) experiments were performed at the FLIPPER II endstation of HASYLAB

(Hamburg, Germany).¹¹ The interconnected sample preparation chamber (base pressure 2×10^{-9} mbar) and analysis chamber (base pressure 2×10^{-10} mbar) allowed sample transfer without breaking ultrahigh vacuum conditions. For Au surface preparation, the metal was evaporated *in situ* onto silicon (covered with native oxide), and Ar-ion sputtered. The Ag(111) single crystal was cleaned by repeated Ar-ion sputtering/annealing cycles until a clear low energy electron diffraction pattern was observed. TCAQ and 6T (Aldrich) were evaporated from resistively heated pinhole sources. Film mass-thickness was monitored with a quartz crystal microbalance. Photoelectron spectra were recorded with a double-pass cylindrical mirror analyzer (resolution: 150 meV) and a photon energy of 22 eV. The secondary electron cutoff (for determination of sample work function/ionization energy) was measured with -3 V sample bias.

First, the interaction between TCAQ and Au and Ag substrates was investigated. The deposition of 5 Å TCAQ (*ca.* one monolayer) onto the Au surface resulted in the observation of new photoemission features [Fig. 1(a)], and a decrease of the sample work function ϕ by 0.5 eV [inset of Fig. 1(a); ϕ of pristine Au: 5.1 eV]. Since the middle spectrum of Fig. 1(a) still contains contributions from the Au substrate, these were subtracted [after normalization to the intensity at E_F (Ref. 12)] to display the features of the organic adlayer only (bottom curve). The peak centered at 3.5 eV binding energy (BE) is tentatively assigned to be derived from the highest occupied molecular orbital (HOMO) of TCAQ. The low BE onset of this peak was found at 2.6 eV BE, which corresponds to the hole injection barrier (Δ_h) at this interface. Deposition of TCAQ onto Ag(111) also resulted in new photoemission features [Fig. 1(b)]. After the subtraction of spectral contributions from Ag (bottom curve) we observe that the overall spectral shape of TCAQ/Ag closely resembles that of TCAQ/Au. The only significant difference is a rigid shift of 0.2 eV towards higher BE. Noteworthy, the secondary electron cutoff energy position before and after

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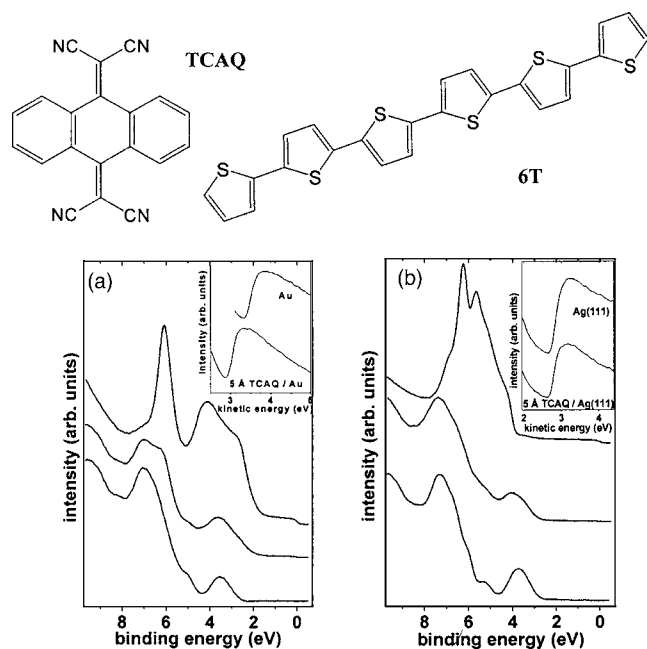


FIG. 1. (Top) Chemical structures of TCAQ and 6T. (a) UPS spectra of pristine polycrystalline Au (top), 5 Å TCAQ on Au (middle), and the Au-contribution subtracted (bottom). Inset: secondary electron cutoff spectra. (b) UPS spectra of pristine Ag(111) (top), 5 Å TCAQ on Ag(111) (middle), and the Ag-contribution subtracted (bottom). Inset: secondary electron cutoff spectra.

adsorption of TCAQ on Ag did not change [inset Fig. 1(b)], i.e., sample ϕ was constant at 4.45 eV. The ionization energy (IE) for both TCAQ/Au and TCAQ/Ag is measured as 7.25 eV.

We propose a rather weak interaction between TCAQ and Au, since no interaction-induced occupied states in the empty energy gap could be observed^{13–15} [cf. bottom curve Fig. 1(a)]. The reduction in sample ϕ [often labeled interface dipole (ID) in the literature] after adsorbing molecules is then explained by a decrease of the pristine metal surface dipole due to the electron “pushback” effect.^{16,17} The same effect (i.e., sample ϕ decrease upon adsorption) is observed for weakly interacting molecules on Ag surfaces.¹⁸ Therefore, the absence of changes in ϕ for the deposition of TCAQ on Ag points towards a stronger type of interaction. The fact of constant ϕ instead of a decrease suggests an electron transfer from the metal towards the molecular layer. Furthermore, close inspection of the TCAQ/Ag spectrum reveals that a new photoemission feature appears close to E_F (at 0.7 eV BE in Fig. 2). This peak is absent for the pristine

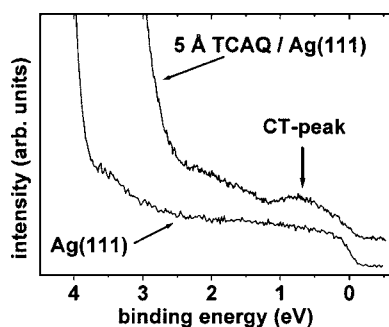


FIG. 2. Near- E_F UPS spectra of pristine Ag(111) (bottom) and 5 Å TCAQ on Ag(111) (top), displaying the additional photoemission feature (CT-peak) centered at 0.7 eV BE.

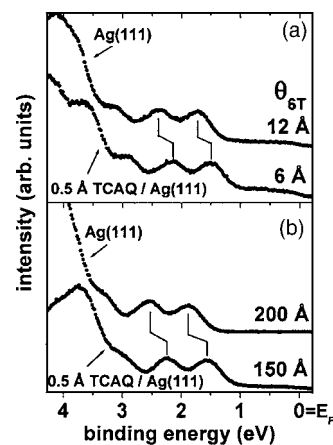


FIG. 3. Comparison of UPS spectra for (a) low and (b) high 6T coverage (θ_{6T}) on Ag(111) with and without 0.5 Å TCAQ preadsorbed (as indicated).

Ag surface, as well as for TCAQ/Au. (Partial) occupation of the lowest unoccupied molecular orbital (LUMO) of conjugated molecules due to electron transfer from metals is known to result in new photoemission features close to E_F .^{13–15} Consequently, we propose that a TCAQ monolayer adsorbed on Ag undergoes such a charge transfer (CT). However, the photoemission intensity of the CT-peak is surprisingly weak: the intensity ratio of HOMO:CT-peak is $\approx 20:1$. In many other CT systems (e.g., conjugated molecules and alkali metals) the intensity derived from the (partially) occupied LUMO can reach that of the pristine HOMO.^{13–19} The reason for the low intensity for TCAQ/Ag could be a very small CT at room temperature (only fractions of an electron per molecule). This would also explain why the overall spectral features for TCAQ/Au and TCAQ/Ag look very similar (substrate contributions subtracted), despite the different type of interaction. Alternatively, the photoelectron cross section for the new emission may be small. A thorough theoretical description of TCAQ adsorbed on Ag should help to understand details of the interaction, and will be the subject of future work. To summarize the first part, the interaction of TCAQ with Au is very weak, while it involves CT with Ag, which results in a different energy level alignment.

The central part of the present work is to demonstrate that the different type of interaction between TCAQ and the two metals also leads to a difference in the energy level alignment of subsequently deposited organic layers. When depositing 6T on top of a monolayer of TCAQ preadsorbed on Au, we observed by UPS no differences in the energy level alignment compared to 6T directly deposited onto Au. For both cases, we measured Δ_h between 6T and Au of 0.75 eV (spectra not shown), consistent with previous reports on 6T/Au.²⁰ In contrast, we found a significantly lower Δ_h for 6T on Ag(111) when TCAQ was preadsorbed on the metal surface, even in the submonolayer range. Δ_h for low 6T coverage [Fig. 3(a), top curve] on pristine Ag was 1.3 eV, and only 1.05 eV on Ag with only 0.5 Å TCAQ adsorbed before 6T deposition [Fig. 3(a), bottom curve]. Similarly, Δ_h for high 6T coverage [Fig. 3(b), top curve] on pristine Ag was 1.4 eV, and 1.1 eV on Ag with 0.5 Å TCAQ preadsorbed [Fig. 3(b), bottom curve]. In all cases, the spectra resemble pristine 6T.²⁰ The rigid shift of spectra towards higher BE when comparing low and high 6T coverage (0.1–0.2 eV for peak maxima) is due to a decreased screen-

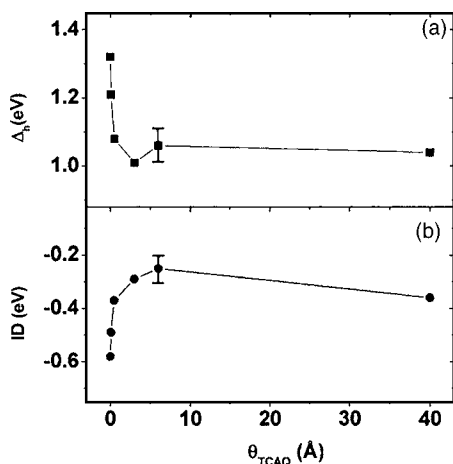


FIG. 4. (a) Hole injection barrier (Δ_h) and (b) interface dipole (ID) relative to pristine Ag(111) (ID) for ≈ 25 Å thick 6T films on Ag(111) as function of TCAQ preadsorbate coverage (θ_{TCAQ}).

ing efficiency of the photohole farther away from the metal substrate.¹²

Increasing TCAQ precoverage did not lead to a significant further decrease of Δ_h for 6T on Ag. However, if only 0.1 Å TCAQ were adsorbed onto Ag before 6T deposition, Δ_h was reduced by only 0.1 eV relative to 6T on pristine Ag. The values of Δ_h for varying TCAQ coverage (θ_{TCAQ}) are summarized in Fig. 4(a). Interestingly, as Δ_h decreases for increasing θ_{TCAQ} , so does the measured ID value [Fig. 4(b)].

We propose the following mechanism for our observations: First, we can rule out appreciable charge transfer between the electron acceptor TCAQ and the donor 6T. The ionization energy of 6T (measured in the present experiments at 5.2 eV) is much larger than the estimated electron affinity of TCAQ [upper limit: ionization energy (7.25 eV) – optical gap (3.1 eV, Ref. 21) = 4.15 eV]. Furthermore, if charge transfer were the cause for the lowering of Δ_h (in analogy to the reports on “doping” with fluorinated tetracyanoquinodimethane),^{5–8} we would observe this effect also for Au as substrate; this was not the case. The molecular levels of a TCAQ layer are pinned relative to the Ag substrate by a CT-type interaction. However, for submonolayer coverage, the surface potential felt by subsequently deposited (physisorbed) 6T molecules is an average of local ϕ 's of covered and uncovered substrate patches.^{22,23} The levels of 6T are then aligned relative to the (coverage dependent) area-averaged surface potential established by the TCAQ layer (which is discontinuous for submonolayer coverage).²³ A detailed study of implications of the observed energetic effects on molecular order is subject of future work.

In conclusion, we have demonstrated that the hole injection barrier height at the interface between 6T and Ag(111) could be reduced by 0.3 eV by insertion of a monolayer of TCAQ. This was possible due to the charge transfer type

interaction between the electron acceptor TCAQ and Ag. A barrier lowering effect was also observed for submonolayer coverage, however, to a smaller extent. These results show that by choosing appropriate material combinations it seems possible to fine-tune Δ_h at organic/metal interfaces by the insertion of an electron acceptor with defined (sub-)monolayer coverage.

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