

The Influence of Alkyl Chain Substitution on Sexithienyl-Metal Interface Morphology and Energetics

S. Duhm, H. Glowatzki, J. P. Rabe, R. L. Johnson¹ and N. Koch

Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin, Germany

¹Institut für Experimentalphysik, Universität Hamburg, D-22761 Hamburg, Germany

The interface between Ag(111) and vacuum sublimated α,ω -dihexylsexithienyl (DH6T) was investigated using ultraviolet photoelectron spectroscopy (UPS). While the first monolayer of DH6T is lying flat on the metal surface, we found that already in the second molecular layer the molecules are significantly inclined. This abrupt change in molecular orientation lowered the hole injection barrier (Δ_h) of DH6T/Ag by 0.5 eV between monolayer and multilayer. Δ_h for DH6T multilayers was even lowered by 0.8 eV compared to unsubstituted sexithienyl multilayers. The reduction of Δ_h is attributed to different charge polarization abilities for lying and inclined DH6T on Ag(111).

UPS experiments were carried out at the FLIPPER II end-station at HASYLAB (Hamburg, Germany). The interconnected sample preparation chambers (base pressure 2×10^{-9} mbar) and analysis chamber (base pressure 2×10^{-10} mbar) allowed sample transfer without breaking ultrahigh vacuum (UHV) conditions. DH6T (H. C. Starck GmbH) and 6T (Aldrich) were evaporated using resistively heated pinhole sources. The film mass-thickness was monitored with a quartz crystal microbalance. Spectra were recorded with a double-pass cylindrical mirror analyzer with an energy resolution of 0.15 eV and a photon energy of 22 eV. The secondary electron cutoffs (CO) (for determination of the sample work function) were measured with the sample biased at -3.00 V.

The overall shape of the photoemission spectra of *ca.* a monolayer (nominal 4 Å) of 6T and DH6T on Ag(111) is expectedly very similar [see Fig. 1 (a)], since the conjugated moieties of both molecules are the same. However, the DH6T spectrum is rigidly shifted towards lower binding energy (BE). Close inspection reveals that Δ_h [defined as the energy difference between the low BE onset of the highest occupied molecular orbital (HOMO) and the metal Fermi-level] is 0.15 eV smaller for a monolayer of DH6T compared to a monolayer of 6T. The same energy difference is found for the ionization energies (IE) of the two thin film samples ($IE_{6T} = 5.0$ eV and $IE_{DH6T} = 4.85$ eV). The lower observed value for both Δ_h and IE of DH6T can be explained by increased intramolecular screening due to the additionally available electron density on the hexyl chains, which are absent for 6T. The similarity of 6T and DH6T photoemission spectra and electronic properties suggests that in a monolayer (ML) DH6T molecules are lying flat on Ag(111), as would be expected on general grounds for conjugated organic molecules on that metal surface.

In order to investigate the origin of the shift of DH6T multilayer spectra to *lower* BE compared with ML DH6T, we recorded coverage-dependent photoemission spectra of DH6T on Ag(111) [Figure 1(b)]. Notably, there is no gradual shift of DH6T features, but a new emission feature appears at the low BE side of the ML HOMO (centered at *ca.* 0.9 eV BE), and remains at constant BE for increasing coverage. The new HOMO-position for multilayer DH6T leads to a lowering of Δ_h by 0.5 eV compared to the ML. Noteworthy, we did not observe any further change in the sample work function (ϕ) after the initial ϕ -reduction due to ML formation [see inset of Fig. 1(b)].

We attribute the origin of the unexpected *lower* BE of a multilayer DH6T film compared to the ML to be related to the hexyl substitution, and an associated abrupt change in molecular orientation from lying molecules in the monolayer to inclined molecules in multilayer DH6T. A sketch of the proposed growth model is depicted in Fig. 1 (c), it has been proved with *in situ* atomic force microscopy (AFM) of DH6T/Ag(111) [1]. In fact, a change of the orientation (relative to the substrate surface) of rod-like conjugated organic molecules in thin

films as function of film thickness is a rather common observation, related to the release of stress existing in the ML or few multilayer systems. However, the changes in orientation are not well understood (in terms of a critical layer thickness that initiates these changes), and substantial changes in BE's derived from photoemission, such as those reported here, were not yet observed.

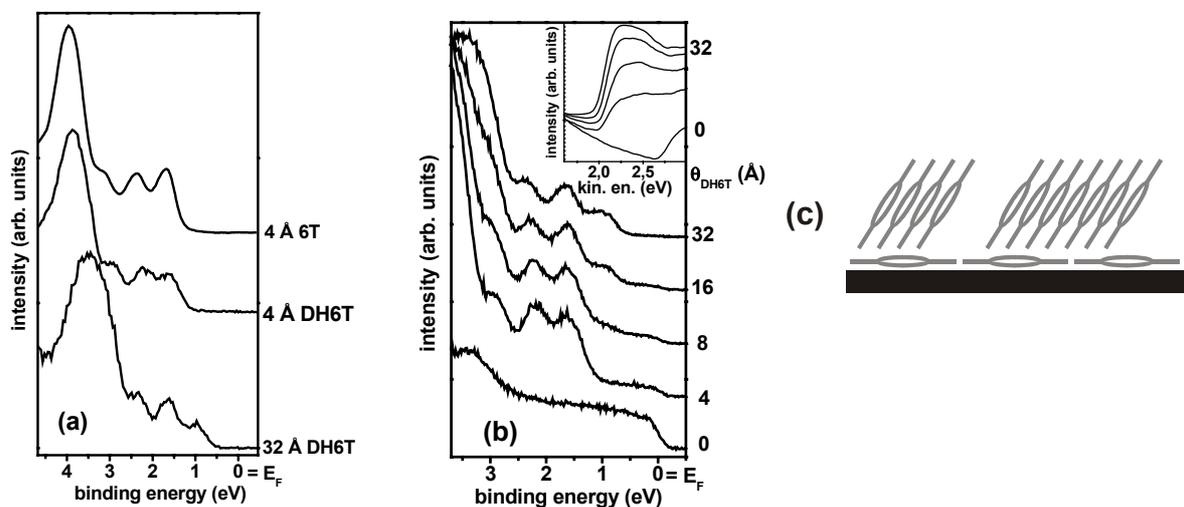


Figure 1 (a) UPS spectra of 4 Å 6T/Ag(111) (top), 4 Å DH6T/Ag(111) (middle), and 32 Å DH6T/Ag(111) (bottom). The contribution from the Ag substrate was subtracted from both 4 Å films. (b) Low BE range photoemission spectra for increasing DH6T coverage (θ_{DH6T}) on Ag(111). The inset shows the secondary electron cutoff, "kin. en." means kinetic energy. (c) Sketch of the proposed growth model of DH6T/Ag(111), with lying monolayer and almost standing multilayer.

The defined transition from lying to vertically inclined molecules observed for DH6T/Ag leads to fundamentally different electronic properties in comparison to unsubstituted 6T. Apparently, there is a transition from lying to almost standing 6T molecules on metal surfaces as a function of film thickness. However, aside from photohole-screening effects, no significant changes in Δ_h were observed. Since the ML of DH6T is lying flat on the metal surface (see above), the interface energetics are similar to 6T/Ag(111). However, already in the second layer of DH6T the molecules are vertically inclined on the surface. The shift of molecular levels may be induced by an increased polarization ability of inclined DH6T molecules compared to lying molecules.

In conclusion, combined UPS and AFM experiments showed that the growth of DH6T on Ag(111) exhibits a flat lying first monolayer, followed by a second layer, where the long molecular axis is inclined substantially relative to the surface. The consequence is a rigid shift of molecular levels in the second layer towards lower binding energy by 0.5 eV compared to the monolayer. The hole injection barrier for the DH6T multilayer on Ag(111) (0.60 eV) is significantly lower than for the unsubstituted 6T (1.4 eV).

Acknowledgements

The authors thank H. C. Starck GmbH for providing DH6T. NK acknowledges financial support by the Emmy Noether Program (DFG).

References

- [1] S. Duhm, H. Glowatzki, J. P. Rabe, N. Koch, R. L. Johnson, Appl. Phys. Lett. 88 (2006), 203109