SAM-Induced Modification of Electrode Workfunction and Energy-Level Alignment at the Interface between Organic Semiconductors

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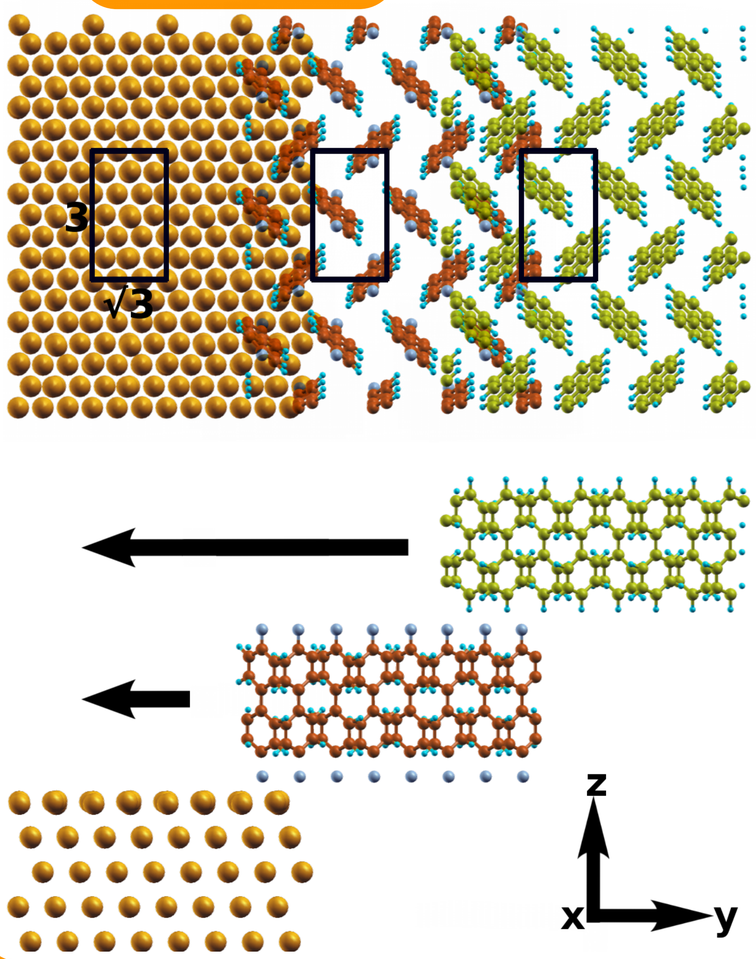
Motivation

Self-assembled monolayers (SAMs) of π-conjugated organic semiconductors (OSCs) provide a tool to modify the workfunction ϕ of metals over a range of several eV. A deep understanding of metal/SAM interfaces has already been reached. As a next step, we investigate the effect of $\Delta\phi$ on the level alignment at metal/SAM/OSC heterojunctions. In our calculations, eight SAMs - six of which were studied by Heimel et al.[1,2] - are used as interlayers between an Au(111) surface and a biphenyl (2P) monolayer representing the OSC.

Methodology

- Density Functional Theory based band structure calculations (VASP code)
- repeated slab approach with >20Å vacuum gap
- plane wave basis set and PW91 exchange-correlation functional
- plane wave energy cutoff: 20Ryd
- convergence criteria for
  - geometry relaxations: all forces F<0.01eV/Å
  - electronic relaxations: ΔE<0.1meV, Δμ<0.002eÅ

Unit cell



- bulk: 5 layers of Au (bottom 3 fixed)
- organic semiconductor: biphenyl monolayer
- unit cell: (3x√3)rect; (x*y) ≅ (8.86*5.11)Å²
- relative SAM/biphenyl positions according to experimental data and/or respective van der Waals radii
- 8 different SAMs analyzed:

(1) Pyr|2P|H	(5) S|2P|F
(2) CN|2P|H	(6) Pyr|2P|CN
(3) S|1P|H	(7) CN|2P|CN
(4) S|2P|H	(8) S|2P|CN

Level Alignment

The figures show the energy level schemes for a series of Au(111)/SAM/2P systems. The positions of the highest occupied [lowest unoccupied] π-states (HOPS [LUPS]) in the SAM [biphenyl] part of the density of states (Molecular DOS) can be seen. Further, each diagram shows the vacuum level of the gold surface (left third), the SAM-covered gold surface (middle third) and the complete system (right third).

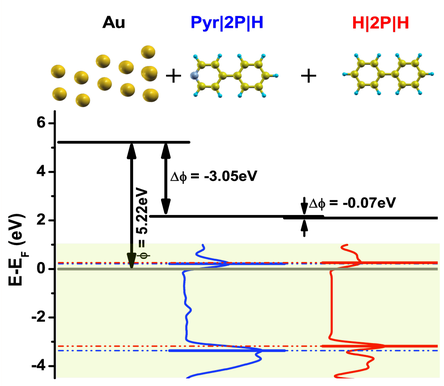


Fig. 1

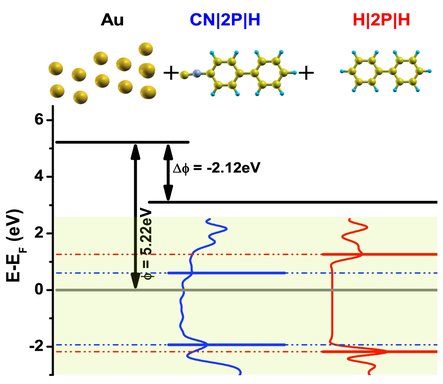


Fig. 2

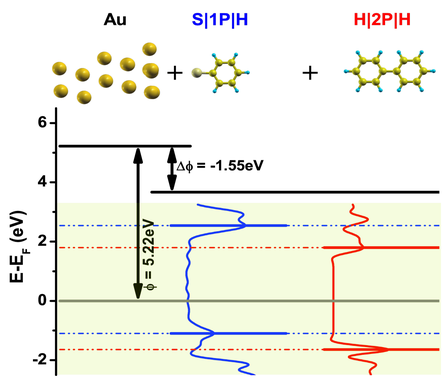


Fig. 3

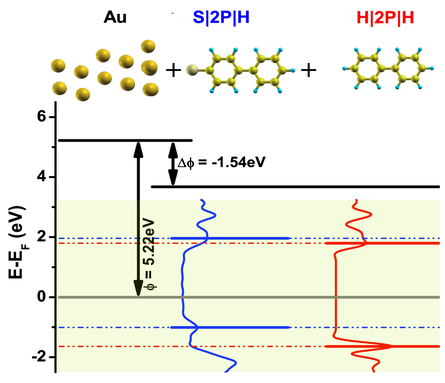


Fig. 4

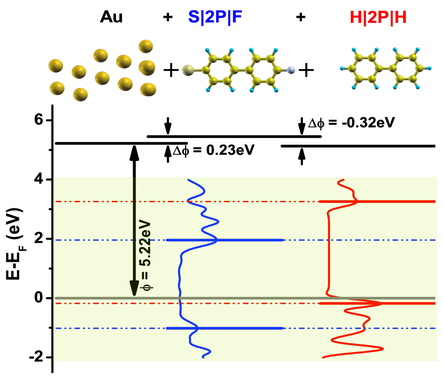


Fig. 5

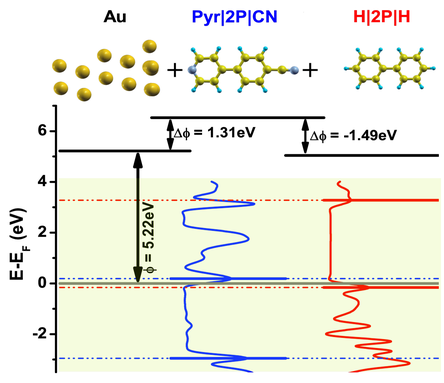


Fig. 6

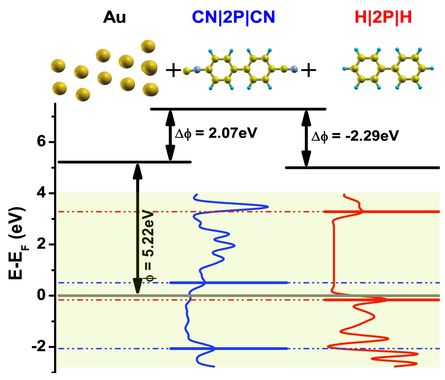


Fig. 7

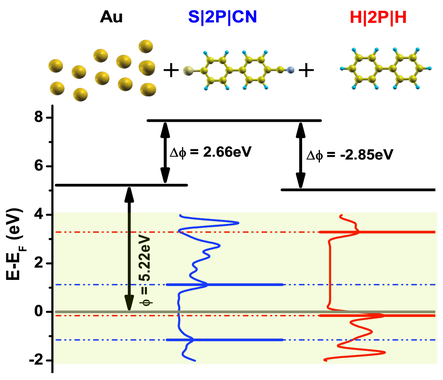
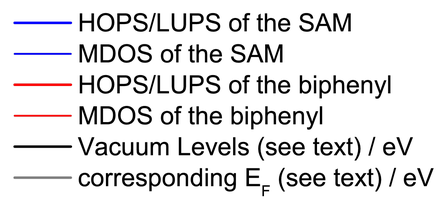


Fig. 8



The level alignment at the SAM/2P interface is directly controlled by the workfunction modification due to the SAM in Figs. 2-4 (vacuum level alignment). A small interface dipole (Δϕ=-0.07eV) at the organic/organic interface is seen when using phenylpyridine as SAM (Fig. 1). In Figs. 5-8 Fermi level pinning of the biphenyl HOPS is observed.

Alignment Regimes

The alignment regimes are characterized by the values of the slope parameter S. It is defined as

$$S = d(E_{\mathrm{F}} - E_{\mathrm{HOPS}})/d(\Delta\Phi_{\mathrm{SAM}})$$

E_F and E_{HOPS} denote the energies of the Fermi level and the HOPS of 2P (peak maximum). Vacuum level alignment applies where S=-1, systems (1) to (4). Systems (5) to (8) are governed by Fermi level pinning, S=0.

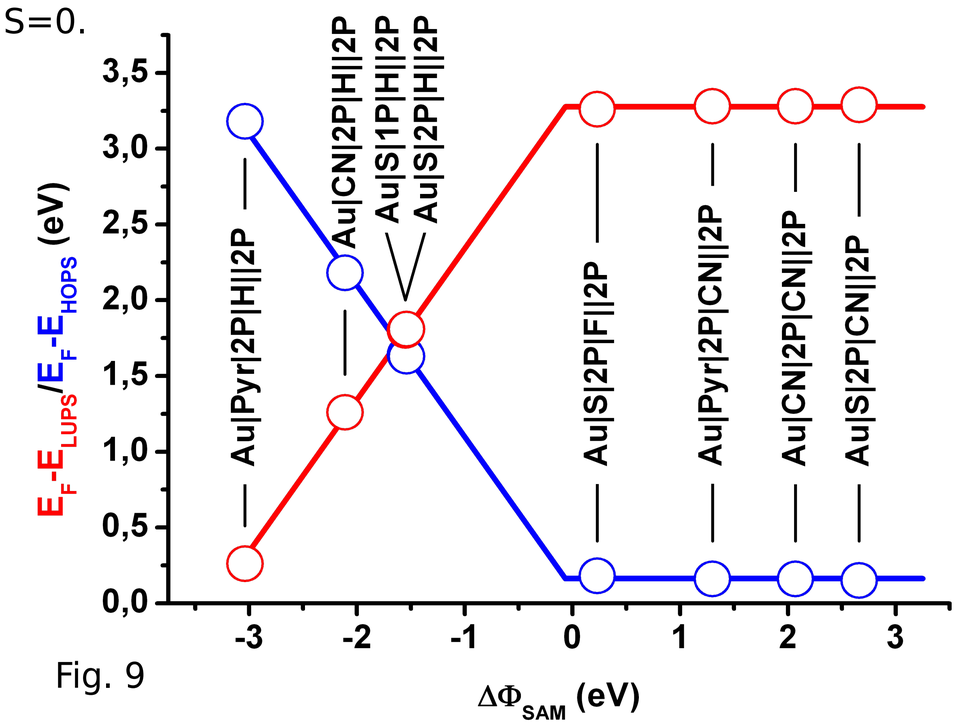


Fig. 9

Fig. 9 shows the values (E_F -E_{HOPS}) for the investigated systems (blue circles) as a function of the SAM-induced workfunction modification and the slope parameter S (blue line). The corresponding information for the LUPS of 2P is depicted as red circles and red line.

REFERENCES:
[1] Heimel et al. Nano Lett. 2007; 7: 932-940
[2] Heimel et al. Proc. SPIE, Vol. 6999, 699919

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