SUPPORTING INFORMATION

Charge Transfer and Orbital Level Alignment at Inorganic/Organic Interfaces: The Role of Dielectric Interlayers

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Theoretical estimation of the contribution of static substrate polarizability on HOMO-LUMO gap reduction.

In the main part of the paper, we have demonstrated how to disentangle the various contributions leading to the level alignment based on quantities accessible solely by measurements (compare Fig. 7). In particular, we could estimate the reduction of the HOMO-LUMO gap due to the polarizability of the substrate. Here, we present an alternative approach, which makes use of electronic structure calculations.[S1] However, as will be shown below, the two approaches lead to almost identical values within an accuracy of 0.1-0.2 eV.

For determining a theory-based estimate of the gap renormalization of the pentacene (5A) gap due to the substrate's polarizability, we proceed according to the following steps:

1) Calculate the EA and IP of gas-phase 5A at the same level of theory (semi-local PBE) as is done later for adsorbed 5A.
2) Calculate highly accurate values of EA and IP of gas-phase 5A using an optimally-tuned range-separated hybrid (OT-RSH) functional.
3) Determine the gas-phase self-energy correction Σ^0 by comparing the EA´s and IP´s of 1) and 2).
4) Calculate 5A adsorbed on the surface using the same semi-local PBE functional as in 1)
5) Correct the EA and IP of adsorbed 5A by Σ^0.
6) Compare the corrected EA and IP of surface 5A with the experimentally measured EA and IP and determine the difference Δ between these values, which are identified as polarizability effect due to the substrate.

The result of this procedure is summarized in Figs. S1 and S2 for 5A on Ag(001) and 5A on MgO(001)/Ag(001), respectively. Thus, we obtain a symmetric gap reduction for 5A/Ag(001) with polarization shifts of Δ=1.8 eV, both for the HOMO and LUMO. This value compares fairly well with our experimental estimate of 1.6 eV (see main text and Table S1). For 5A/MgO(001)/Ag(001) the computational procedure leads to a polarization shift of Δ=1.0 eV for the HOMO, which again compares very well with our experimental estimate of 0.9 eV. Since in our computational procedure we use a comparison with experiment in the final step 6) and since the LUMO splits into a SOMO and SUMO level, we do not unambiguously determine the corresponding polarization shift for the LUMO. Given the symmetric shift found for 5A/Ag(001), the assumption of a symmetric shift also for the 5A/MgO(001)/Ag(001) case seems reasonable, and has therefore been used for Fig. 7b.

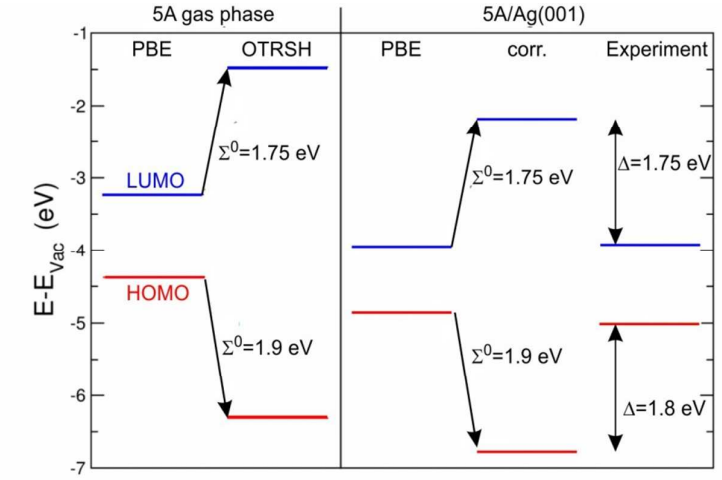

Figure S1. Level alignment for the HOMO (red) and LUMO (blue) for 5A/Ag(001) determined according to the procedure outlined in the text.

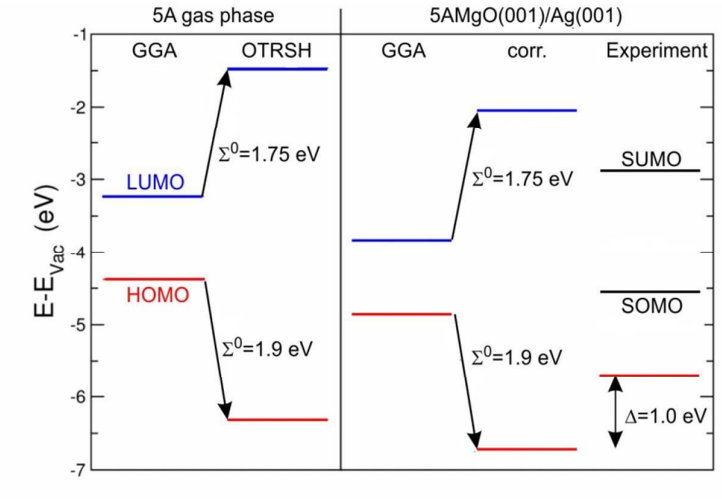

Figure S2. Level alignment for the HOMO (red) and LUMO (blue) for 5A/MgO(001)/Ag(001) determined according to the procedure outlined in the text.

Table S1. Polarization shifts for the HOMO and LUMO for 5A/Ag(001) and 5A/MgO(001)/Ag(001) determined from the experimental and computational procedures outlined in the text.

	5A/Ag(001)		5A/MgO(001)/Ag(001)	
	exp.	calc.	exp.	calc.
Δ_{HOMO}	1.6	1.8	0.9	1.0
Δ_{LUMO}	1.6	1.75	0.9	-

[S1] Khoo, K. H.; Chen, Y.; Li, S.; Quek, S. Y., Length Dependence of Electron Transport Through Molecular Wires – A First Principles Perspective. *Phys. Chem. Chem. Phys.* **2015**, *17*, 77-96.