PCCP

SUPPLEMENTARY INFORMATION

Tuning of the gold work function by carborane films studied using Density Functional Theory

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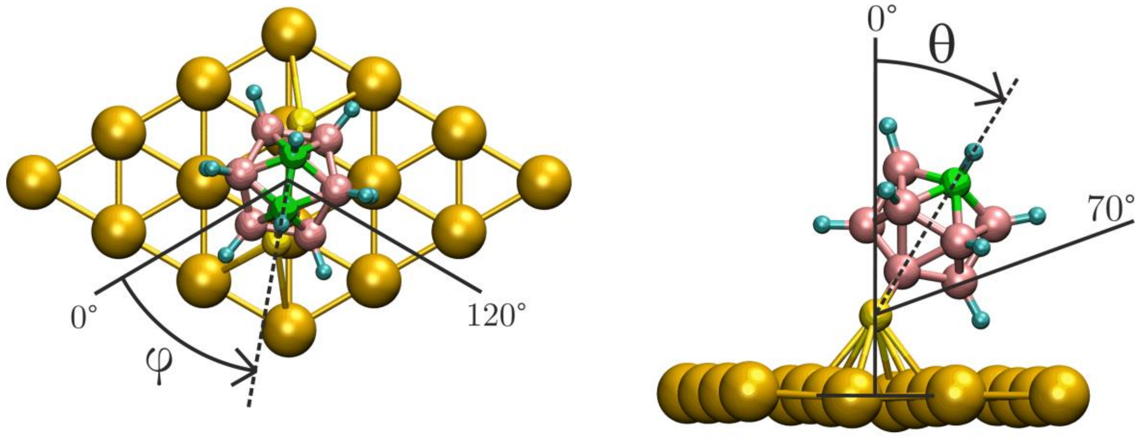
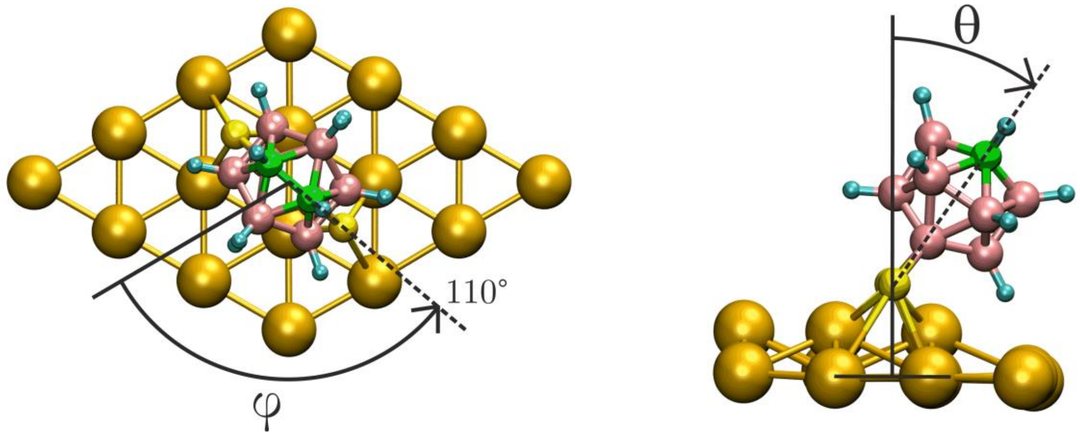
Contents

1. Metal-molecule structures for geometry optimization calculations



(a) (b)

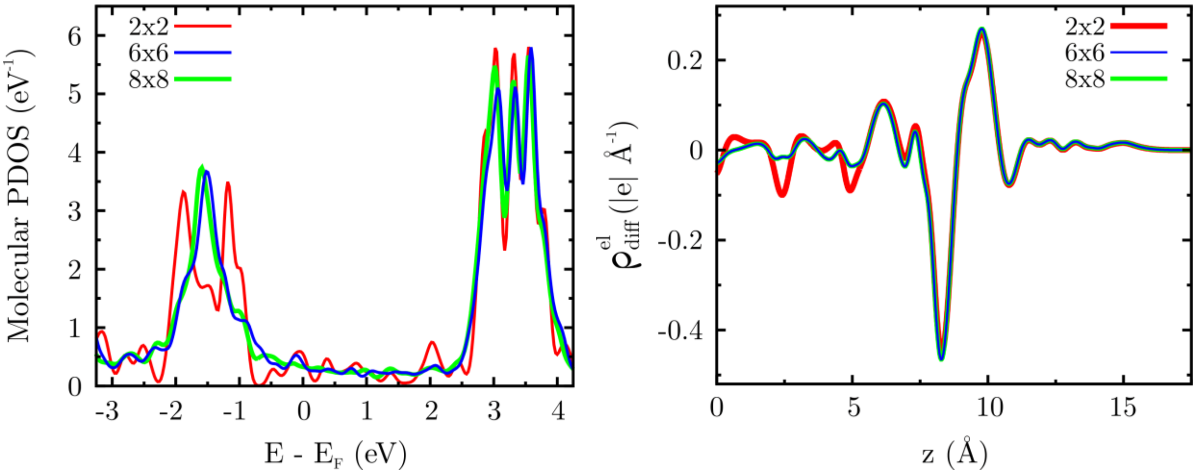
Fig. S1 *Generation of initial geometries for geometry optimization: (a) Azimuthal angle sampling: 0 to 120 degrees, in steps of 10 degrees. (b) Polar angle sampling: 0 to 70 degrees, in steps of 10 degrees.*



(a) (b)

Fig. S2 *Top and side view of a converged (final) geometry.*

2. Convergence of geometry and electronic structure with k-point sampling



(a) (b)

Fig. S3 *Comparison of a B-bonded carborane electronic properties at the junction calculated with different reciprocal-space Monkhorst-Pack grids: (a) molecular PDOS at the junction; (b) electron density difference upon adsorption.*

Table S1 *Reciprocal space grid in the direction parallel to the surface, binding energies (including corrections to basis-set superposition errors), and change in the junction dipole with respect to that of the clean Au slab, of the B-bonded carborane.*

k-point mesh	*E_b (eV)*	*Δμ (D)*
2x2	-3.41	4.30
6x6	-3.52	4.16
8x8	-3.58	4.18

3. STM images

STM topographical images were calculated using the Tersoff-Hamann approximation[1,2]. In this model, the electronic structure of the tip is neglected and the STM amplitude is proportional to the substrate Local Density Of States (LDOS). The images were calculated 1 Å above the top H atoms or 8.4 Å above the Au surface at the LUMO energy of each isomer.

The character of the LUMO for each isomer (Fig. S4) results in changes in the calculated STM images. The LUMO of the B-bonded molecule involves B as well as C contributions, and is strongly delocalized over the whole carborane cage. On the other hand, the LUMO of the C-functionalized isomer has strong C contributions, but for this isomer the B character is much smaller. Consequently, the isocontour at the LUMO energy is localized mostly around the C atoms, close to the interface. Thus the STM images (at almost identical height) show much more prominent features for the B-bonded than for the C-bonded isomer.

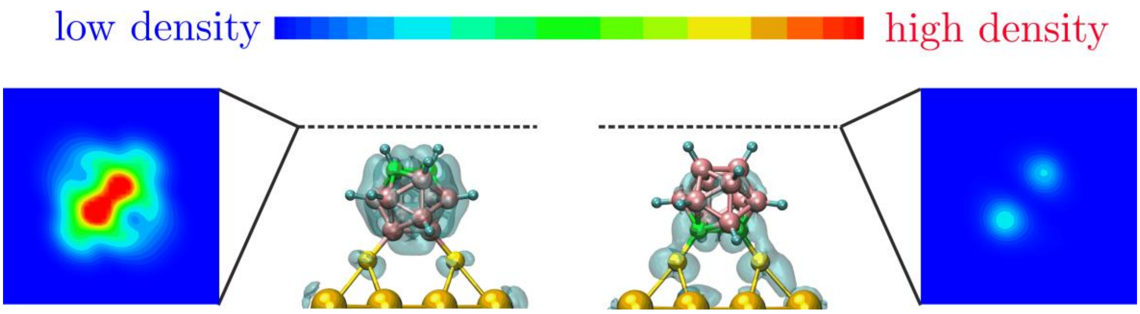
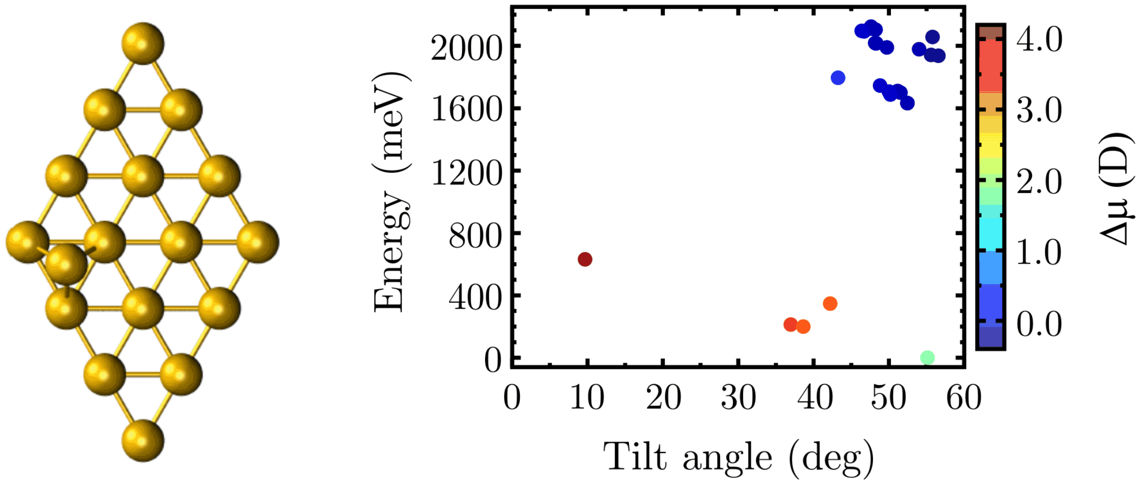


Fig. S4 *Calculated STM images of adsorbed B-bonded (left) and C-bonded (right) carboranedithiols at the LUMO energies, 1 Å above the topmost H atoms, and electron density isocontours.*

4. Effect of Au surface asperity: adatom and trimer structures

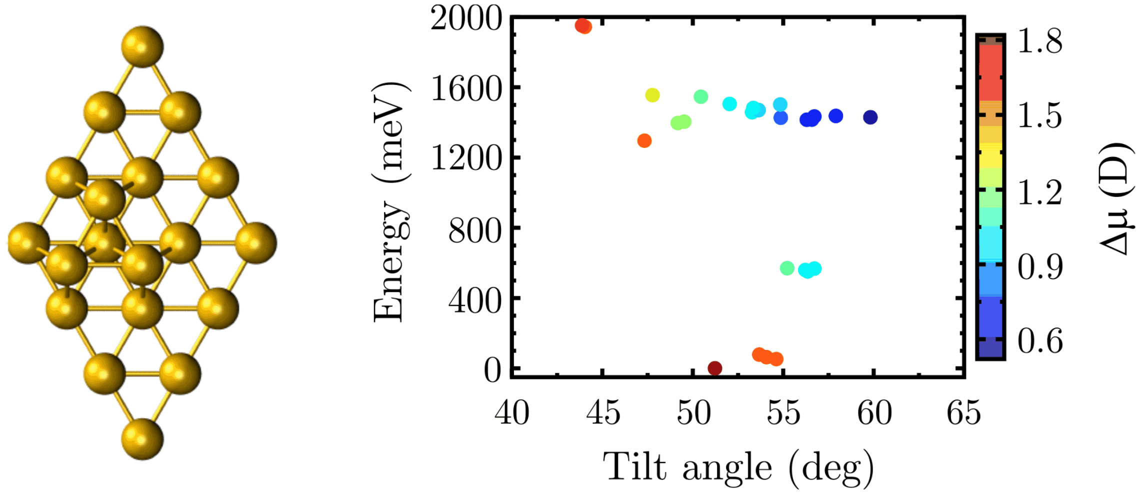
We investigated the adsorption and electronic properties of boron-functionalized carboranes on Au(111) slabs which had surface asperities in the form of adsorbed adatom(s). We considered junctions which had either one or three Au atoms adsorbed on hollow sites (see insets of Figs. S5 and S6). Initial geometries were prepared by placing the carborane molecules partially above the Au adatoms. In these initial geometries, one S atom was placed above the Au adatom(s), while the other one was close to the (111) surface. Structures where the azimuthal angle spanned the range 0-120 degrees were generated as input for geometry optimizations by rotating the carborane around the center of the Au adatom(s).

Figs. S5 and S6 summarize the calculated properties when the carborane molecule was adsorbed over an Au adatom (Fig. S5) or above an Au trimer (Fig. S6). The geometry of the S closest to the surface was similar to the results on the clean (111) surface. However, the final (optimized) geometry of the S atom bonded to the Au adstructures was strongly influenced by the coordination of this S atom. Relaxed structures where the S atom was bonded to two Au atoms in a bridge-like configuration led to the lowest total energy and are shown at the bottom of Figs. S5 and S6. Final geometries where the S atom was bonded to a single Au adatom had significantly higher energy. Geometry relaxations showed substantial atomic rearrangement, including distortion of the trimer structure and extraction of metal atoms from the Au surface layer. No differences were found between adsorption of the Au structures on hcp or fcc sites.



(a) (b)

Fig. S5 *(a) Structure of the surface layer with an Au adatom adsorbed on a hollow site, used in the simulations. (b) Total energy (relative to the most stable structure) and change in the calculated dipole with respect to the clean Au(111) surface plus adatom (color bar).*



(a) (b)

Fig. S6 *Same as Fig. S5 for Au trimer structures.*

5. References

1 J. Tersoff and D. R. Hamann, Theory and Application for the Scanning Tunneling Microscope, *Phys. Rev. Lett.*, 1983, **50**, 1998–2001.

2 J. Tersoff and D. R. Hamann, Theory of the scanning tunneling microscope, *Phys. Rev. B*, 1985, **31**, 805–813.