

# Molecular Self-Assembly of DBBA on Au(111) at Room Temperature - Electronic Supplementary Information

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## Additional calculations - molecule on surface

The binding energy and the basis set superposition error (BSSE) corrected binding energies of the molecule at the gold surface are calculated as follows:

Table 1: Total energy results used for calculating the binding energies for the molecule at the surface. Structures are optimized with BP/D3BJ and the energies calculated for BP/D3BJ, BP/D2, and PBE/D2. The basis set superposition error was corrected. Total energies are given in Hartree

No	$E_{\text{Au-M}}^{\text{Au-M}}/\text{H}$	$E_{\text{M(ads)}}^{\text{Au-M}}/\text{H}$	$E_{\text{Au(Au)}}^{\text{Au-M}}/\text{H}$	$E_{\text{M(gas)}}^{\text{M}}/\text{H}$	$E_{\text{M(ads)}}^{\text{M}}/\text{H}$	$E_{\text{Au(Au)}}^{\text{Au}}/\text{H}$
BP/D3	-6290.66	-6224.24	-66.28	-6224.34	-6224.24	-65.99
BP/D2	-6291.18	-6224.18	-66.78	-6224.28	-6224.18	-66.49
PBE/D2	-6286.05	-6221.41	-64.51	-6221.51	-6221.41	-64.22

$$\begin{aligned}
E_0 &= - \left( E_{\text{Au-M}}^{\text{Au-M}} - E_{\text{Au(Au)}}^{\text{Au}} - E_{\text{M(gas)}}^{\text{M}} \right) \\
E_{\text{CP}} &= - \left( E_{\text{Au-M}}^{\text{Au-M}} - E_{\text{Au(Au)}}^{\text{Au-M}} - E_{\text{M(ads)}}^{\text{Au-M}} + E_{\text{M(ads)}}^{\text{M}} - E_{\text{M(gas)}}^{\text{M}} \right)
\end{aligned}$$

$E_{\text{Au-M}}^{\text{Au-M}}$  is the energy of one molecule adsorbed at the Au-surface.  $E_{\text{Au(Au)}}^{\text{Au-M}}$  and  $E_{\text{M(ads)}}^{\text{Au-M}}$  are the energies of the gold surface in its original structure and of the adsorbed molecule in the adsorbed structure, all calculated in the full basis set (superscript Au-M). For the molecule the energy necessary for deformation of the gas phase molecule  $E_{\text{M(gas)}}^{\text{M}}$  to the adsorbed structure  $E_{\text{M(ads)}}^{\text{M}}$  is calculated with the basis set of the molecule (superscript M).  $E_{\text{Au(Au)}}^{\text{Au}}$  is the energy of the gold surface with the basis of the gold atoms only. Positive sign of  $E_0$  and  $E_{\text{CP}}$  indicate binding.

Table 2: Binding energies for the molecule at the surface. Structures are optimized with BP/D3BJ and the energies calculated for BP/D3BJ, BP/D2, and PBE/D2. The basis set superposition error was corrected. Binding energies are given in eV

	BP/D3BJ	BP/D2	PBE/D2
$E_{\text{CP}}$ /eV	0.974	3.194	0.857
$E_0$ /eV	8.872	11.178	8.916

## Configurations used for *ab initio* calculations for a dimer composed of two DBBA molecules

All dimer configurations are stable and their calculated ground state adsorption energies are shown in table 2 in the main text. The model proposed for the structure observed in SFM images for very high coverage is derived from configuration number 7. In the configuration number 1, Br of both DBBA are pointing upwards, i.e. out of the paper plane. Due to thermal broadening, the Br atom could appear as an oval entity in SFM images. This configuration could also be at the basis of a possible model for the structure observed in SFM images although the distance

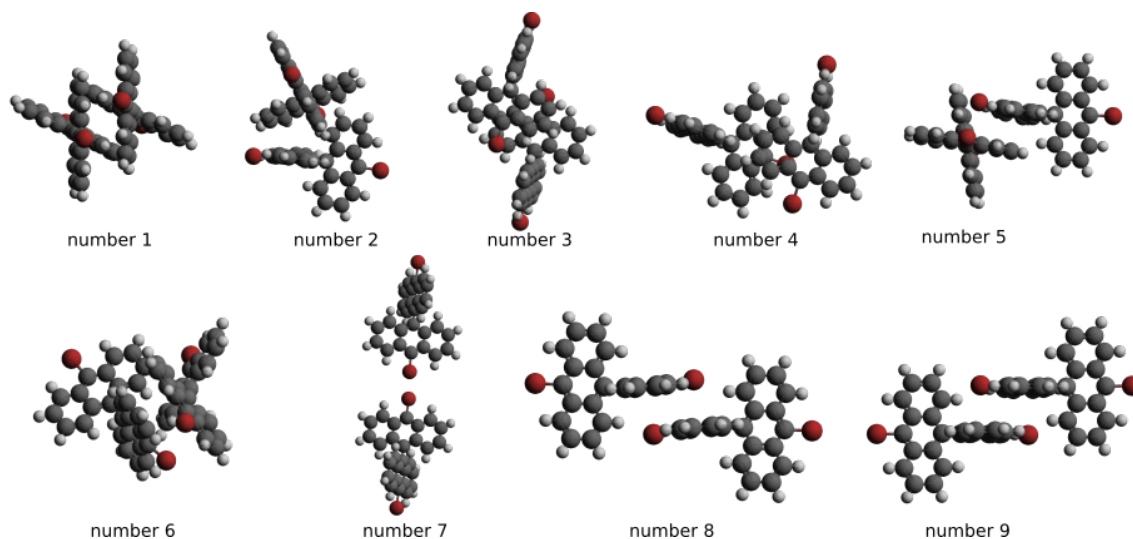


Figure 1: Configurations used for *ab initio* calculations for a dimer composed of two DBBA molecules. The numbering is as mentioned in Table 2 of the main text. The color code for the chemical elements is the same as in Figure 1 of the main text.

between two DBBA molecules in configuration 1 is small compared to the distance measured in SFM images. The other configurations lack the symmetry observed in the SFM images and could not form periodic linear chains due to this lack of symmetry. Note that configuration eight is obtained by restricting the calculations using  $C_{2h}$  symmetry and for configuration nine the top of the two anthracene units of the dimer are not located at the same height.

# Additional calculations - molecular dimers

Table 3: Analysis of the dimer energies. Structures are optimized with BP/B3BJ and the energies calculated for BP/D3BJ, BP/D2, and PBE/D2. For PBE/D2 the basis set superposition error was corrected.  $E_0$  is the binding energy,  $E_{\text{vdW}}$  the dispersion energy,  $E_{\text{CP}}$  the BSSE corrected binding energy. All energies are given in eV.

Dimer	BP/D3BJ			BP/D2			PBE/D2					
	$E_0$	$E_{\text{vdW}}$	$E_0 - E_{\text{vdW}}$	$E_0$	$E_{\text{vdW}}$	$E_0 - E_{\text{vdW}}$	$E_0$	$E_{\text{CP}}$	$E_{\text{vdW}}$	$E_0 - E_{\text{vdW}}$	$E_{\text{CP}} - E_{\text{vdW}}$	$E_{\text{CP}} - E_{\text{vdW}}$
1	1.348	2.264	-0.916	1.094	2.010	-0.916	0.869	0.529	1.426	-0.557	-0.897	-0.897
2	0.922	1.393	-0.471	0.744	1.215	-0.471	0.671	0.453	0.858	-0.187	-0.405	-0.405
3	0.946	1.501	-0.555	0.692	1.247	-0.555	0.584	0.353	0.881	-0.297	-0.528	-0.528
4	0.922	1.389	-0.467	0.730	1.197	-0.467	0.627	0.416	0.845	-0.218	-0.429	-0.429
5	0.916	1.407	-0.492	0.726	1.218	-0.492	0.618	0.409	0.861	-0.243	-0.452	-0.452
6	1.098	1.681	-0.583	0.913	1.495	-0.583	0.781	0.529	1.059	-0.278	-0.530	-0.530
7	0.108	0.114	-0.007	0.067	0.074	-0.007	0.086	0.059	0.044	0.042	0.015	0.015
8	0.807	1.160	-0.352	0.550	0.902	-0.352	0.497	0.310	0.635	-0.138	-0.325	-0.325
9	0.914	1.247	-0.333	0.670	1.003	-0.333	0.604	0.402	0.707	-0.103	-0.305	-0.305

## Additional calculations - periodic lattice

For the periodic DFT calculations the vienna ab initio simulation package (VASP) (*Kresse and Furthmüller(1996), Kresse and Furthmüller(1996)*) was used. The core electrons were described by the projector augmented wave (PAW) method (*Blöchl(1994)*). For the plane wave expansion, a kinetic energy cutoff of 400 eV and an energy convergence threshold of  $10^{-6}$  were used. Throughout the calculations the PBE functional with the D2 dispersion correction of Grimme was employed. The structures dimer1 and dimer8 were relaxed with the conjugate gradient method until the change in the total energy between two ionic relaxations was smaller than  $10^{-5}$ . Moreover the initial unit cells were constructed in such a way that they represent the models shown in Fig. 6 d) and e) (in the paper). There the  $x$ -axis is perpendicular to the surface. In the case of dimer8 the cell was optimized, while the bromine atoms were fixed in  $x$ -plane, since otherwise the dimers would overlap strongly and this would not represent the model of the dimer molecular chains on the surface (Fig. 6 e)). For both cases the angles between the lattice vectors are close to  $90^\circ$ . Afterwards the lattice vector in  $x$ -direction was enlarged by 20 Å to model the situation on the surface, since there is no interaction between dimers in that direction. Additionally the vectors in  $y$ - and  $z$ -direction were also enlarged by 20 Å together with the  $x$ -direction to estimate the stabilisation arising due to the dispersion interaction between the dimers in  $y$ - and  $z$ -direction. The Brillouin zone was sampled by a  $4 \times 4 \times 2$  Monkhorst-Pack  $k$ -point mesh for the cell optimizations. If the vector was increased, the number of  $k$ -points in that direction was divided by two. In table 4 the binding energies of the dimers are shown. The structures, where only the  $x$ -direction is enlarged, are shown in Fig. 2 and 3.

In the case of dimer1 the highest binding energy (1.07 eV) is observed when  $x$ - and  $z$ -direction are enlarged, indicating that the dispersion interaction in the  $y$ -direction, mainly the interaction between anthracene rings, is very attractive. Additionally decreasing the distance

Table 4: The binding energy is calculated as:  $E_B = 2E_M - E_D$  where  $E_M$  is the energy of the monomer and  $E_D$  the energy of the dimer where the unit cell was enlarged either only in  $x$ -direction or additionally in  $y$ - or  $z$ -direction.

	dimer1	dimer8
$E_B$ [eV]( $x$ -direction)	0.84	1.50
$E_B$ [eV]( $x$ and $y$ -direction)	0.96	0.53
$E_B$ [eV]( $x$ and $z$ -direction)	1.07	1.30

in  $z$ -direction lowers the binding energy. This points out that the interaction in  $z$ -direction is slightly repulsive. However on the surface the molecules should be as closely packed as possible, and the positive binding energy for this case (0.84 eV) shows that this arrangement should be feasible. For dimer8 also an attractive interaction in  $y$ -direction between the anthracene rings is observed, indicated by the high binding energy (1.30 eV) for the case where the  $x$ - and  $z$ -direction are enlarged. Moreover we also observe attractive dispersion interactions when decreasing the distance in  $z$ -direction, which is lower than in  $y$ -direction. This is expected, since there are mainly bromine atoms interacting with anthracene. Comparing both dimers directly the binding energy of dimer8 is almost twice as large as the one of dimer1 (1.50 eV vs. 0.84 eV) for the case where only the  $x$ -direction was enlarged. This could be a hint that dimer8 is the preferred structure on the surface where the dimers are closely packed in  $y$ - and  $z$ -direction.

## References

- Kresse and Furthmüller(1996). G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15.
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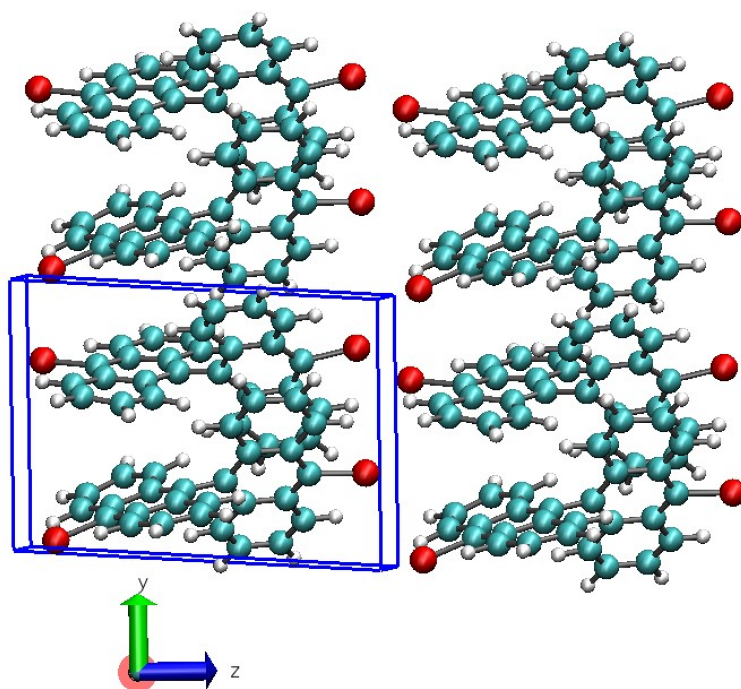


Figure 2: Structure of dimer1, where the  $x$ -direction was enlarged. The unit cell is shown with blue lines. In  $y$ - and  $z$ -direction the dimers of the neighbouring cell are shown.

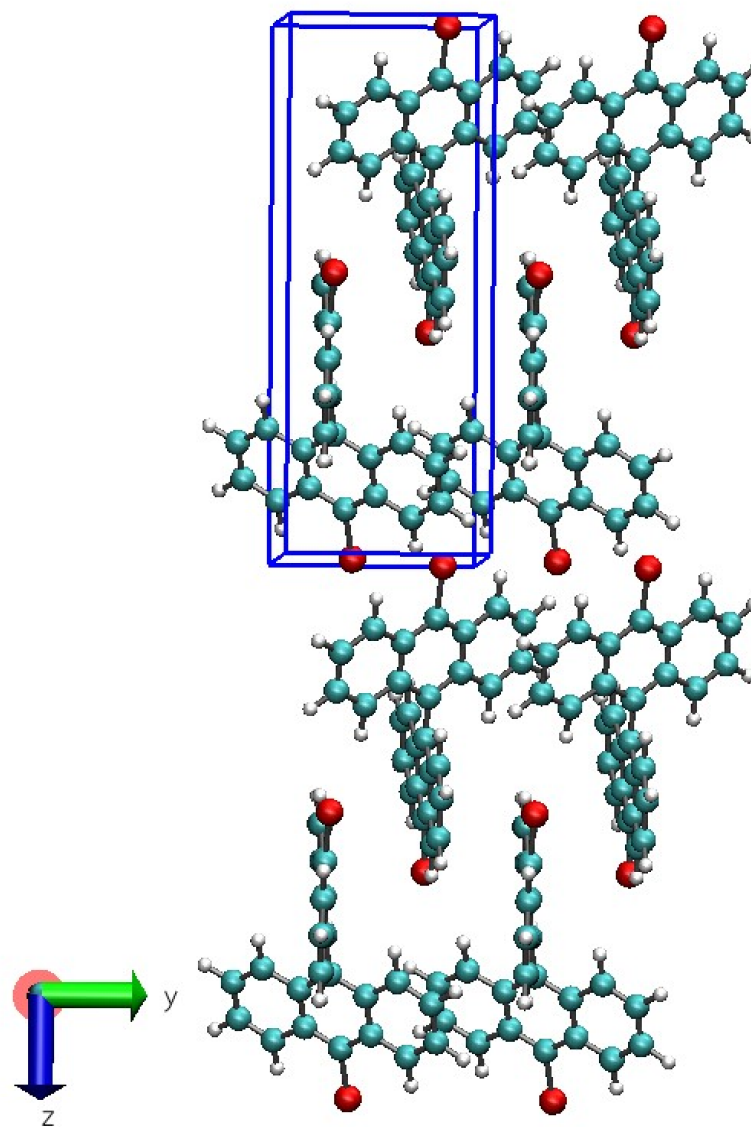


Figure 3: Structure of dimer8, where the  $x$ -direction was enlarged. The unit cell is shown with blue lines. In  $y$ - and  $z$ -direction the dimers of the neighbouring cell are shown.