

Electronic Supporting Information (ESI) for:

**Cooperativity and Coverage Dependent
Molecular Desorption in Self-Assembled
Monolayers: Computational Case Study with
Coronene on Au(111) and HOPG**

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S1. Preliminary calculations on the orientation of coronene molecules on Au(111) and HOPG.

Previous STM studies of coronene on Au(111)¹ and HOPG² have determined that coronene adsorbs with a head-to-head coronene hydrogens configuration with its nearest neighbor on Au(111), while a staggered configuration on HOPG. To verify this, we performed preliminary DFT calculations using B88-vdW DFT functionals (see computational methods section in the manuscript for other calculation details) on head-to-head and staggered configurations of coronene on Au(111) and HOPG (Figure S3). In these calculations just one coronene molecule per unitcell is considered with 4x4x1 slab of Au(111) and 5x5x1 slab of HOPG. The gold slab has 3 layers of gold and HOPG has 2 layers of carbon. Isolated coronene molecule and substrates (with bottom layer frozen) were optimized prior to creating an interface. Upon complete optimization to SCF convergence of ~ 0.001 eV, we found that head-to-head orientation is energetically favorable by 0.34 eV on Au(111) and staggered orientation is favored on HOPG by 0.28 eV. The respective 4x4 supercells of optimized coronene/Au(111) (Figure S3-B) and coronene/HOPG (Figure S3-C) were used to develop the models (Figure 2, 3 in manuscript) for coverage dependent desorption studies.

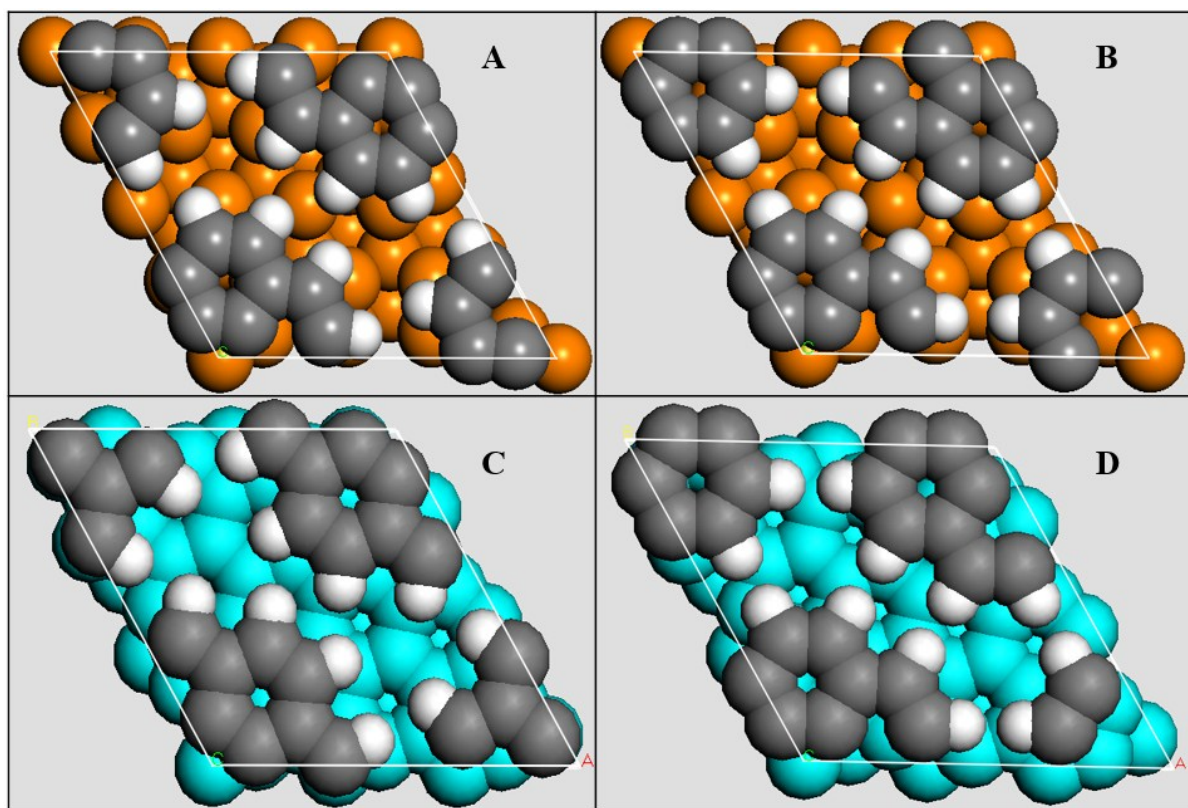


Fig. S1 Geometries of a) coronene/Au(111) in staggered configuration, b) coronene/Au(111) in head-to-head configuration, c) coronene/HOPG in staggered configuration, d) coronene/HOPG in head-to-head configuration. Colors: Au(111)-Orange, HOPG-cyan, grey-coronene and white line represents hexagonal lattice.

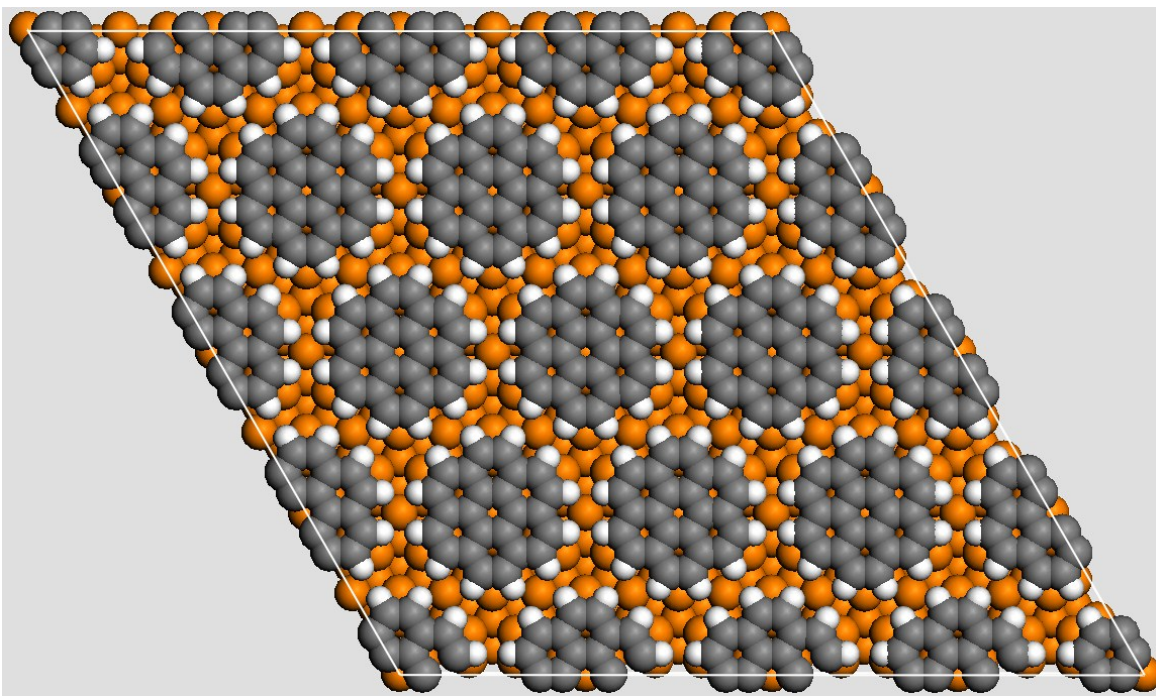


Fig. S2 Geometry of coronene/Au(111). Colors: Au(111)-orange, grey-coronene and white line represents hexagonal lattice. Note the head-to-head orientation of coronene molecules with its neighbor.

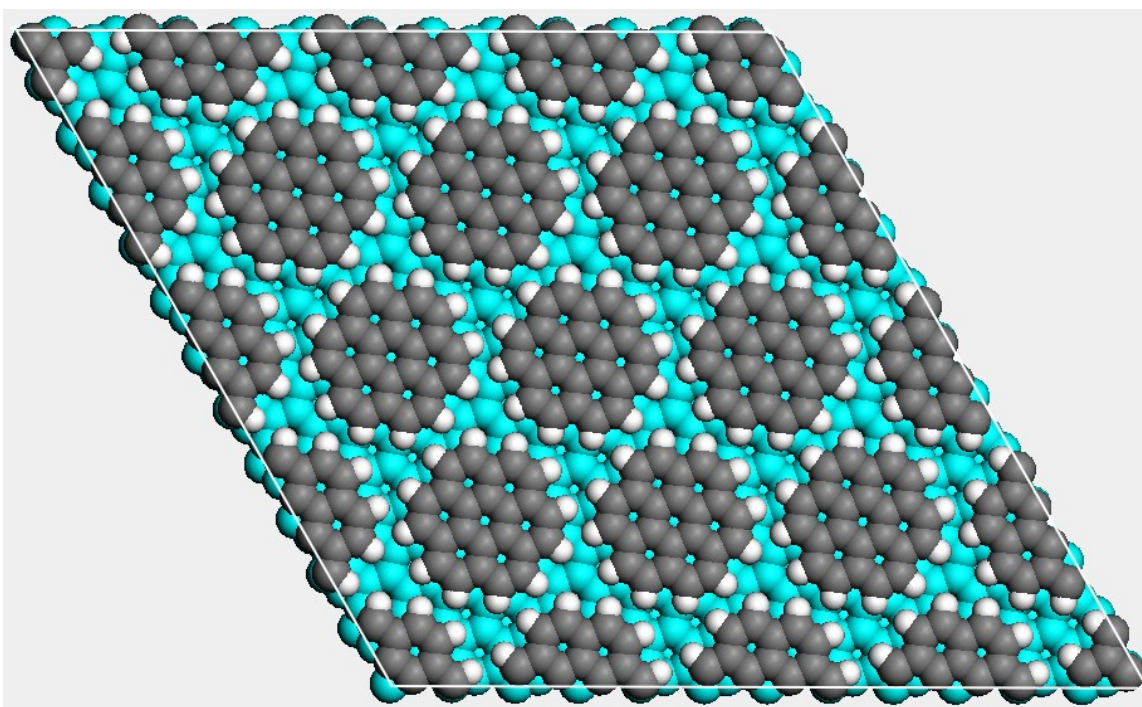


Fig. S3 Geometry of coronene/HOPG. Colors: HOPG-cyan, grey-coronene and white line represents hexagonal lattice. Note the staggered orientation of coronene molecules with its neighbor.

S2. Determination of desorption energy (E_d) of single coronene molecule on Au(111) and HOPG substrates

The adsorption energy of molecules adsorbed on surfaces are traditionally obtained by using isolated single molecule adsorbed on substrates. In periodic DFT calculations, involving molecule-substrate binding energy in ultrahigh vacuum (i.e., no solvent or air) three unique calculations are performed.

- Energy of optimized single isolated molecule (E_{mol}) with no intermolecular interactions
- Energy of clean optimized periodic substrate (E_{sub}) much larger than the size of the molecule.
- Energy of optimized periodic molecule-substrate interface (E_{int}) in which the substrate dimensions are much larger for the molecule to avoid any periodic interactions with its image.

The adsorption energy (E_a) is obtained by the following equation

$$E_a = E_{\text{int}} - E_{\text{sub}} - E_{\text{mol}} \quad (\text{eq-S1})$$

The desorption energy (E_d) is the negative of adsorption energy (E_a) term

$$E_d = - E_a \quad (\text{eq-S2})$$

S3. $F(a)_i$ and $F(a)_i/c_i$ for coronene/Au(111) and corresponding “coronene ML only” systems with vdW-DF PBE functional

Due to discrepancy in calculated average coronene-coronene contact energies ($\langle a \rangle$) for coronene/Au(111) systems with B88 and B86 functionals (Table 2), we performed additional set of calculations on all the geometries (Fig. 2, 3) of coronene/Au(111) with vdW-DF PBE functionals with VASP. With PBE functional, the average coronene-coronene contact energies ($\langle a \rangle$) is determined to be 78 meV analogous with B88 functional (Table 2). The respective E_0 is 2.06 eV and the total errors, $F(a)_i$, errors per contact, $F(a)_i/c_i$, are shown in Fig. S4 and S5 respectively. The total errors ($F(a)_i$) fluctuate with the range of ~650 meV (Fig. S1). This range is rather high than that obtained with both B88 and B86 functionals (Fig. 4). The error values ($F(a)_i$) come down significantly if you distribute the error per contact instead of the total error. Note that the number of contacts vary from geometry to geometry (Table 1). The corresponding errors per contact, $F(a)_i/c_i$, plot (Fig. S5), indicate that the errors now range within ~60 meV instead of 650 meV. These results agree with the error trend observed for coronene/Au(111) system (Fig. 4, 5) with B88 and B86 functionals. Hence the additional calculations with PBE functional on coronene/Au(111) system justify the findings from B88 calculations while addressing the anomaly of negative $\langle a \rangle$ value for B86 functional.

To determine the role of substrate we performed PBE calculations “coronene ML only” systems like our B88 and B86 calculations (see manuscript and Fig. 6, 7). Fig. S6 and S7 shows the $F(a)_i$ and $F(a)_i/c_i$ plots obtained with PBE functional for “coronene ML only” system. The corresponding E_0 is 0.00 eV and $\langle a \rangle$ value for “coronene ML only” system was determined to be 64 meV which is slightly higher than for B88 and B86 functionals which is expected for PBE functional.³ The E_d of coronene on Au(111) is found to be 2.09 eV with PBE functional.

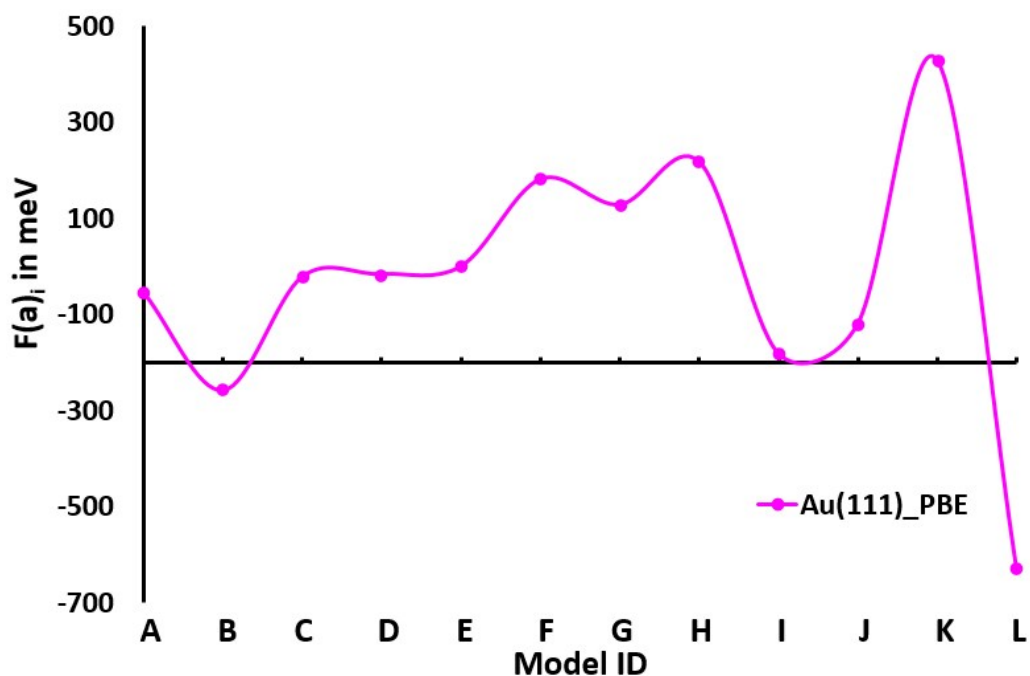


Fig. S4 Errors ($F(a)_i$) in contact energy for each model (see Fig. 3) of coronene/Au(111) with PBE functional. The error fluctuation (y-axis) in the plot is relative to energy (E_0) of single isolated coronene molecule on substrate. The line connecting points is solely meant to guide the eye.

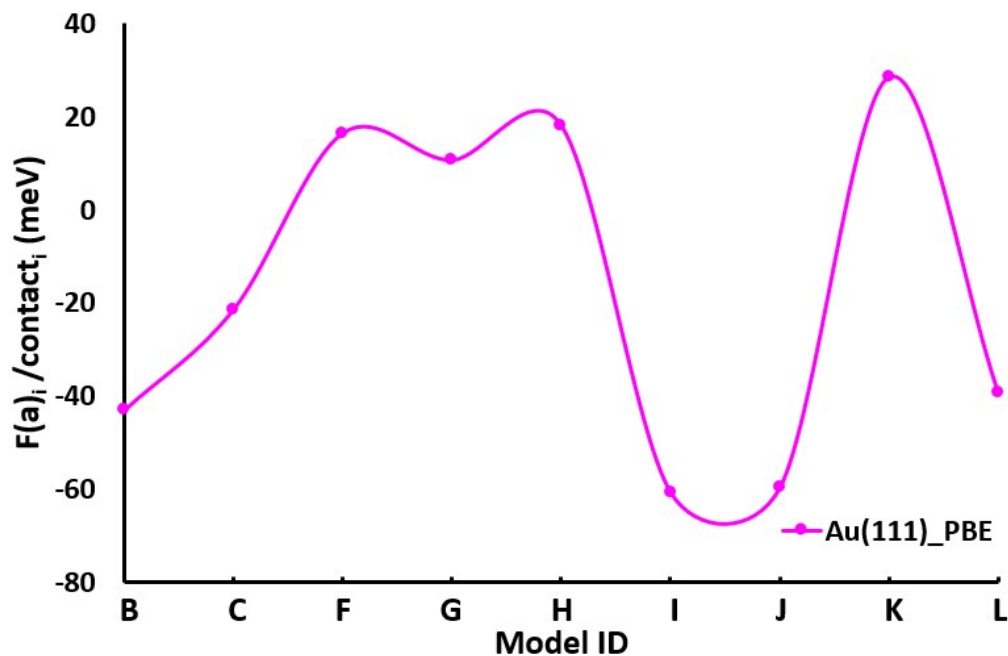


Fig. S5 Errors per contact ($F(a)_i/c_i$) for models with contacts (see Fig. 3) of coronene/Au(111) with PBE functional. The error fluctuation (y-axis) in each plot is relative to energy (E_0) of single isolated coronene molecule on substrate. The line connecting points is solely meant to guide the eye.

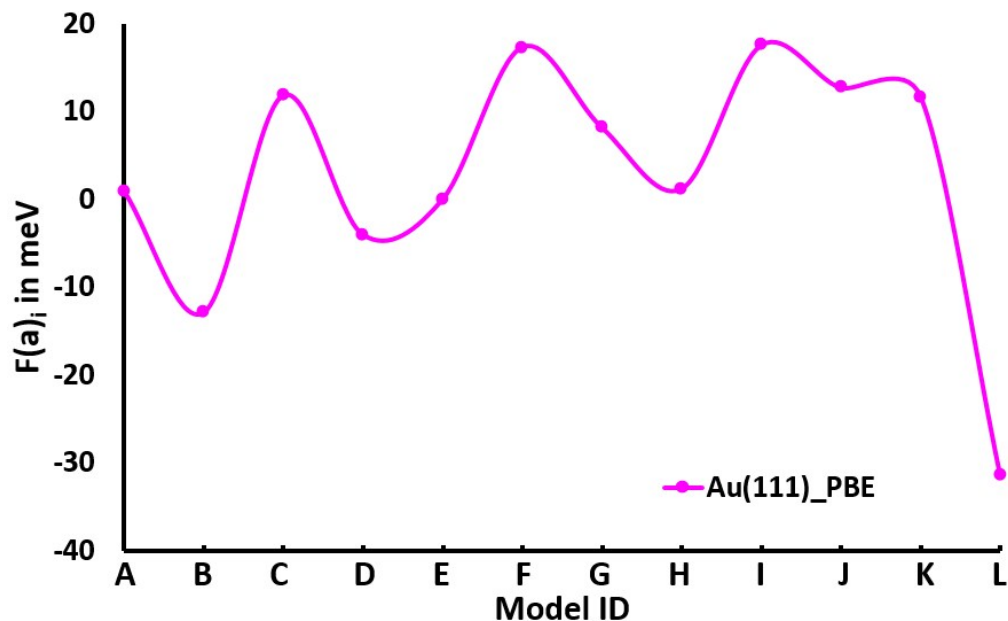


Fig. S6 Errors ($F(a)_i$) in contact energy (in meV) for each model (see Fig. 3) of coronene only layer (where, substrate removed = Au(111)) with PBE functional. The error fluctuation (y-axis) in each plot is relative to energy (E_0) of single isolated coronene molecule without the substrate. The line connecting points is solely meant to guide the eye.

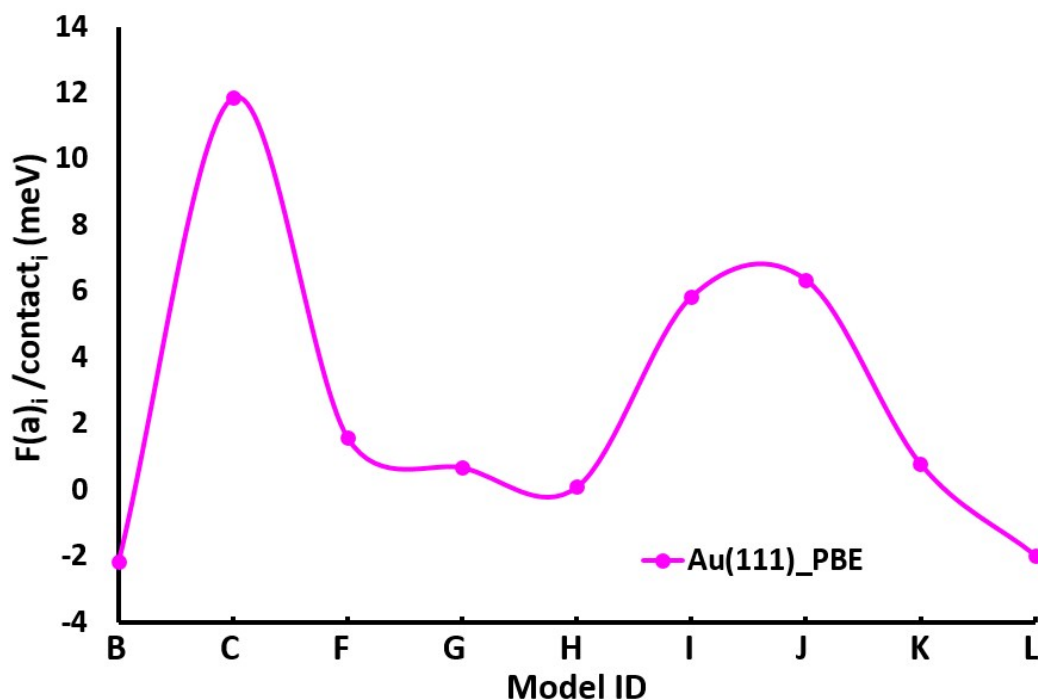


Fig. S7 Errors per contact ($F(a)_i/c$) for models with contacts (see Fig. 3) of coronene only layer (where, substrate removed Au(111)) with PBE functional. The error fluctuation (y-axis) in each plot is relative to energy (E_0) of single isolated coronene molecule without the substrate. The line connecting points is solely meant to guide the eye.

S4. Cooperativity in coronene/Au(111) geometry with a cavity (Fig. 3B)

Coronene-Au(111) adsorption distances vary with surface coverage (Fig. 6). Also, within the same geometry, variable adsorption distances can be seen for coronene on Au(111). To illustrate this, we have chosen geometry 3B (Fig. 3), which has a single cavity in the middle of the monolayer. We measured distance from various carbon atoms of coronene adsorbate to the Au(111) substrate. Fig. S8 shows an enlarged image of geometry 3B, with multiple colored carbon atoms from coronene adsorbate chosen around the cavity to measure the adsorption distances. The colored atoms represent variable distances from the center of the cavity. Fig. S9 shows the averaged measured distances from each colored atom depicted in Fig. S8 to the underlying Au(111) substrate. Additionally, the average measured distance from complete monolayer (Fig. 2) to Au(111) is also shown Fig. S9 for reference. The measurements were obtained from optimized DFT geometries from three different vdW-DF functionals.

One can notice from Fig. S9 that the red atoms are attracted closer to the substrate, followed by cyan, orange/pink (nearly similar) and green (farthest from the cavity). It looks like the carbon-gold distance oscillates as you move from the center on to out of the cavity. The carbon-gold distance is shorter when close to the cavity but increases slightly as you go away from the cavity. The adsorption distance should oscillate back down and a stable value like a full monolayer (colored grey in Fig. S9) as you move farther away from the cavity. But the optimized geometry only allows us to measure only up to two hexagons (of coronene molecules) from the center of the cavity. Hence, these distances provide us evidence of cooperativity in the adsorption of coronene on Au(111) as function of surface coverage.

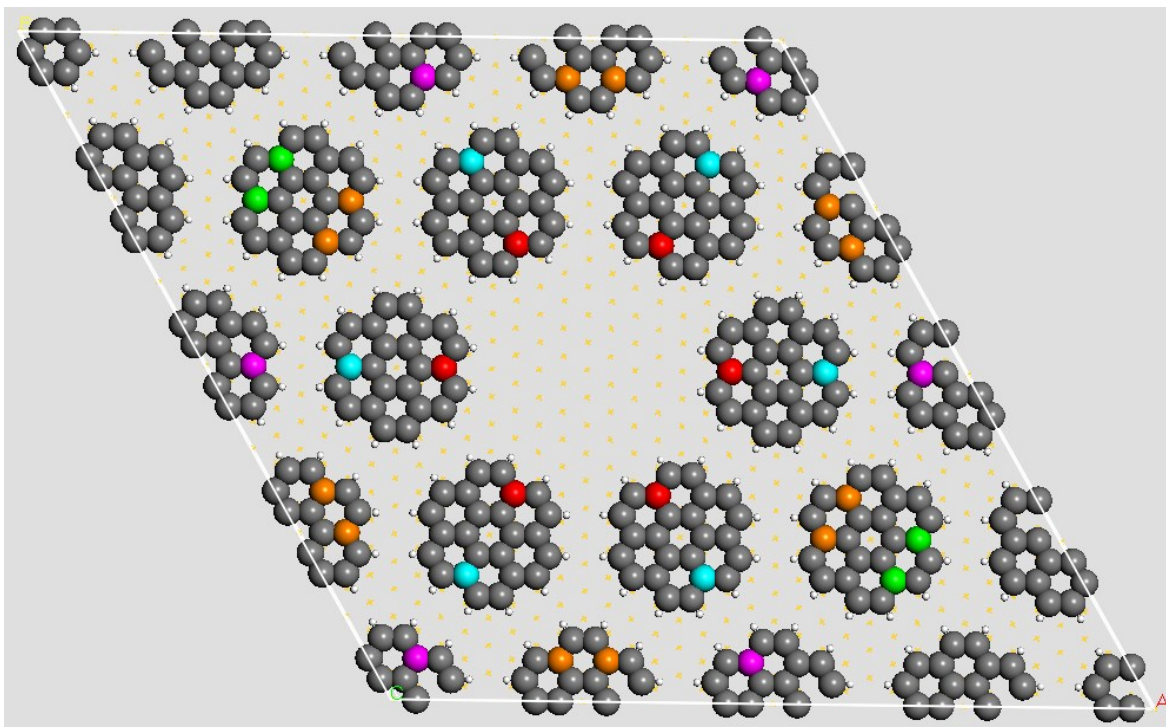


Fig. S8 Coronene monolayer on Au(111) with a single cavity based on geometry 3B from Fig. 3. The coronene molecules are colored grey (carbons) and white (hydrogens), while the Au(111) substrate is masked for clarity. The cavity is at the center of the hexagonal unit cell. Red, Cyan, Orange, Pink and Green colored carbon atoms represent equidistant (in each color) atoms from the center of the cavity.

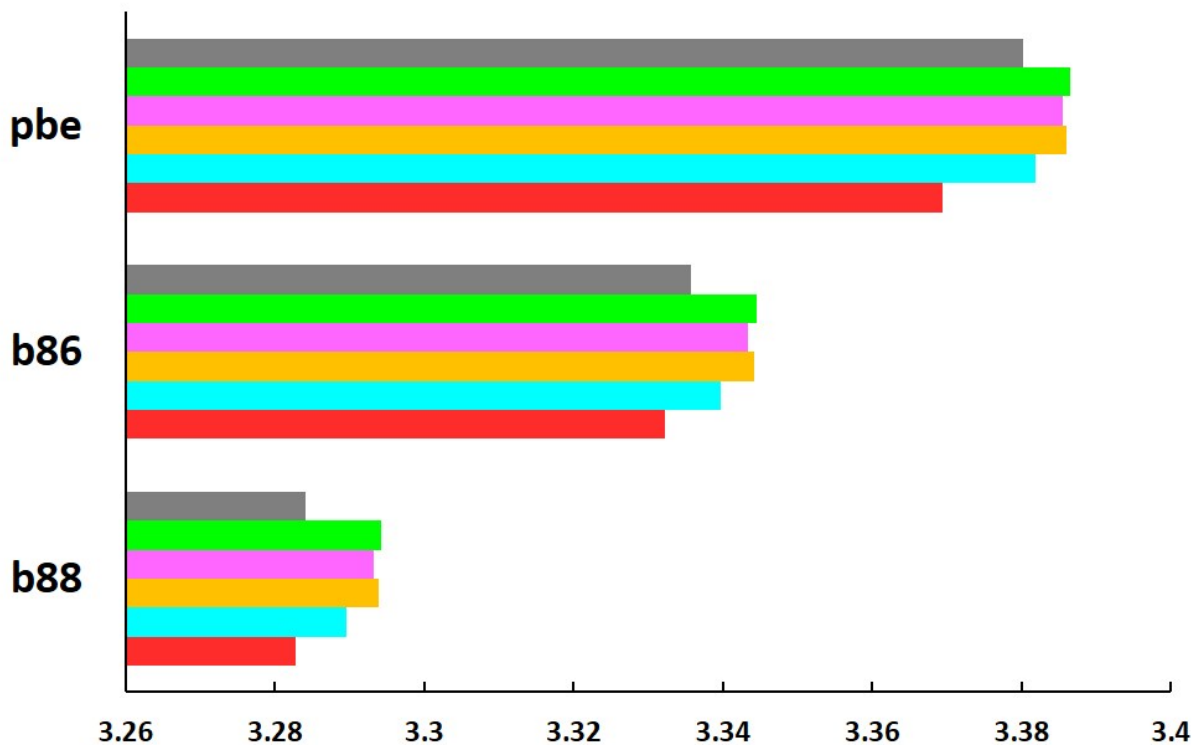


Fig. S9 Average distance between selected (see Fig. S5) atoms in coronene adsorbate and Au(111) from DFT optimized structures with different functionals. The colored bars represent distances in Å for 2 geometries. Red, Cyan, Orange, Pink and Green bars represent distances from selected atoms of the same colors in Fig. S5 to Au(111) in geometry 3B (monolayer with one cavity). The grey bar represents average measured distance from complete monolayer to Au(111) substrate in each DFT calculation.

ESI References

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