Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Adsorption properties of a paracyclophane molecule on NaCl/Au surfaces: A first-principles study

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1. Comparison between PBE/DFT-D3(BJ) and optB86b-vdW

Table S1 shows the calculated adsorption energy of the PCP molecule on bare Au surface and 3ML-NaCl/Au surface with PBE + D3 (BJ) and optB86b-vdW. It can be found that the general trend as predicted by these two calculation schemes is quite similar. Both methods predicted the same adsorption sites (the fcc site on Au and the Na-top site on 3ML-NaCl/Au) as the most stable sites. The most significant discrepancy is that PBE+D3(BJ) seems to overestimate the adsorption energy when the molecule was adsorbed on Au while underestimates the adsorption for the case of PCP/3ML-NaCl/Au when compared to the results of optB86b-vdW. Other than that, these two methods generally agree with each other which indicates that the PBE+D3(BJ) method is sufficient to describe the current system.

Adsorption energy (eV)					
PCP/Au			PCP/3ML-NaCl/Au		
Site	PBE+D3(BJ)	optB86b-vdW	Site	PBE+D3(BJ)	optB86b-vdW
fcc	-1.40	-1.35	Cl_{top}	-0.67	-0.71
hcp	-1.39	-1.34	Na_{top}	-0.72	-0.78
bridge	-1.38	-1.33	Na-Cl_{bri}	-0.69	-0.75
top	-1.27	-1.21	Na-Na_{hol}	-0.68	-0.72

Table S1. Adsorption energies of the PCP molecule on bare Au and 3ML-NaCl/Au surfaces as computed with different methods.

2. Test calculations for the applied supercell

In order to test if the applied supercell is sufficient to avoid the interactions between the PCP molecule and its periodic images, we performed the following test calculations.

Firstly, we tested the influence of neighboring periodic images of the PCP molecule on its total energy by using a set of calculations with increasing supercells

without the Au and NaCl substrate. In this set of calculations, we set the distance between the molecule and its neighboring periodic images to be 20 Å in the x (a) and y (b) directions and kept the z (c) direction as a changing variable. The molecules are aligned shoulder-to-shoulder with their periodic images in the z-direction, while maintaining a large distance in the x, y-direction, as shown in Fig. S1.

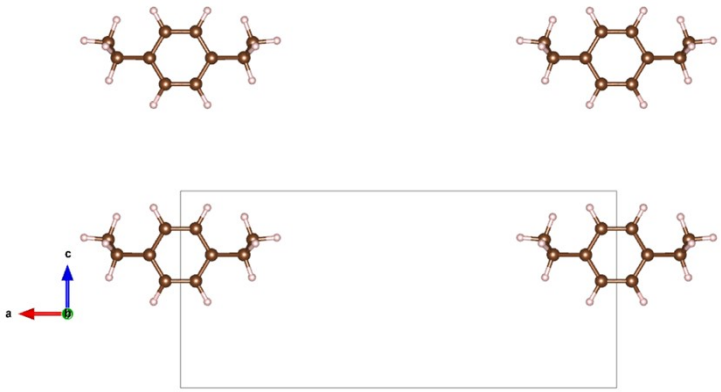

Fig. S1. Top view of the PCP molecule and its periodic images.

The total energies of the molecule as a function of the molecular distance can be found in Table S2. It can be found that, the total energies become converged at distances larger than 6.61 Å, which suggests that the direct interaction between the PCP molecule and its periodic images should not play a significant role for distances larger than 6.61 Å.

Supercell (Å)	Molecule distance (Å)	Total energy (eV)
20 × 20 × 6	3.61	-236.0556495
20 × 20 × 9	6.61	-237.5254555
20 × 20 × 12	9.61	-237.5255538
20 × 20 × 20	17.61	-237.5258521

Table S2. Total energy of the PCP molecule as calculated with different super cells. The nearest distance between the PCP molecule and its neighboring periodic images were also shown.

Secondly, we performed calculations on the PCP/Au system by using a supercell

that was doubled in size in the y-direction, as shown in Fig. S2. In this system, the distance between the PCP molecule and its neighboring periodic images was increased to 23.24 Å in the y-direction. The calculated adsorption energy for this larger supercell is -1.473 eV, which is almost the same as the adsorption energy of -1.472 eV obtained with the original supercell. This suggests that both the possible interactions between the PCP molecule and its periodic images should have been sufficiently suppressed with the applied surface supercell.

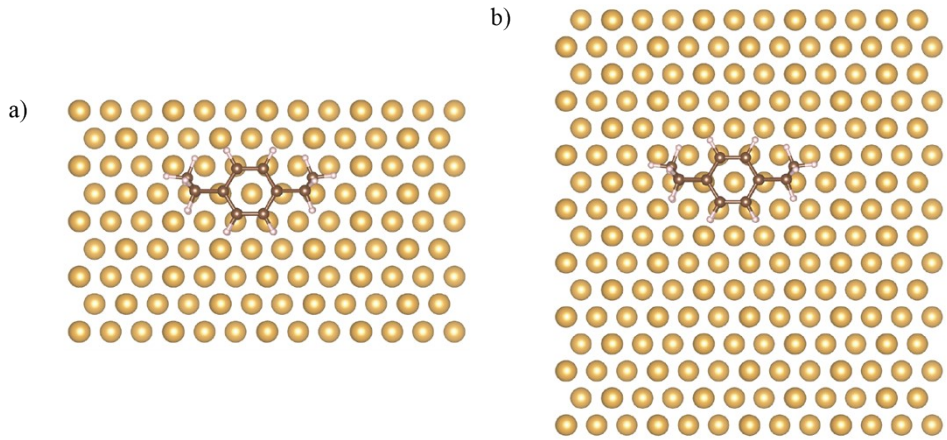

Fig. S2. Top views of the original super cell used in the manuscript (a) and the enlarged super cell (b).

3. Test calculations for the adsorption configurations

We also tested the effect of different adsorption configurations on the adsorption energy. Fig. S3 (a) shows the adsorption configuration where the PCP molecule adsorbs on Au with the molecule lying on its side (Model 1). In this configuration, the branched chain linking the two benzene rings was on the bottom side. The adsorption energies of this model, together with the original model (Fig. S3 (b), termed Model 2 here), at different adsorption sites were listed in Table S3.

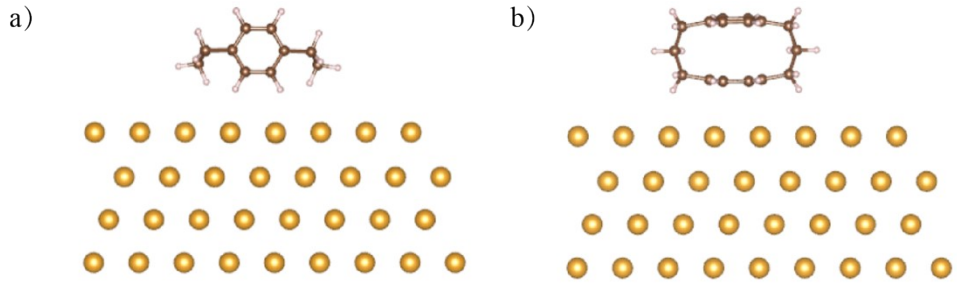

Fig. S3. (a) Side view of Model 1 where the PCP molecule is lying sideways on the surface. (b) Side view of the original model used in the manuscript (termed Model 2 here for convenience).

It can be found that Model 2 is more stable in all four adsorption sites that were considered here. The difference between the adsorption energies of the two most stable configurations is 0.16 eV. These results suggest that the configuration with one deck facing the surface should be more stable than Model 1.

	Model 1 (eV)	Model 2 (eV)
bri	-1.238	-1.379
fcc	-1.227	-1.396
hcp	-1.214	-1.394
top	-1.217	-1.270

Table S3. Adsorption energy of the PCP molecule as obtained with the two models shown in Fig. S3.