Supporting Information

Molecular Resonance Imaging and Manipulation

of Hexabenzocoronene on NaCl(001) and KBr(001) on Ag(111)

Thibault Ardhuin, Olivier Guillermet, André Gourdon and Sébastien Gauthier*

CEMES CNRS UPR 8011 and Université de Toulouse

29 rue Jeanne Marvig, 31055 Toulouse, France

1. HBC optimal adsorption configuration on NaCl(001) and KBr(001)

HBC is a flat, planar molecule. It stays planar when crystallized and in the form of thin films. We determined its adsorption geometry on NaCl(001) and KBr(001) by calculating the van der Waals and electrostatic interaction between the molecule and a slab without any structural optimization. We minimize for each (X,Y) position the total energy of the system with the molecule positioned parallel to the substrate surface, by varying the altitude Z and the angular position θ, without any structural optimization.

This approach, while crude, is nevertheless expected to give some useful indications. To evaluate the electrostatic interaction COMPASS attributes atomic partial charges as follows: Na(K)=+q, CL(Br)=-q, H=+0.1268q, C linked to H=-0.1268q, other C=0q, where q is the elementary charge.

The substrate slab was constituted of 8 (001) atomic planes of 5x5 surface unit cells for NaCl and 6 (001) atomic planes of 4x4 surface unit cells for KBr. The energy of the system was calculated on each point (X,Y) of a 20x20 grid mapping the unit cell, the molecule surface distance and the orientation of the molecule being varied by 0.01 nm and 5° steps. The minimum energy and the corresponding angle are displayed in Fig. S1 and S2 on 4 surface unit cell for better clarity. The configuration shown in Fig. S1(c) where the molecule is centered on a Cl ion corresponds to the origin (X, Y) = (0, 0) of the maps in Fig. S1(a) and (b) for an orientation angle of θ=0°.

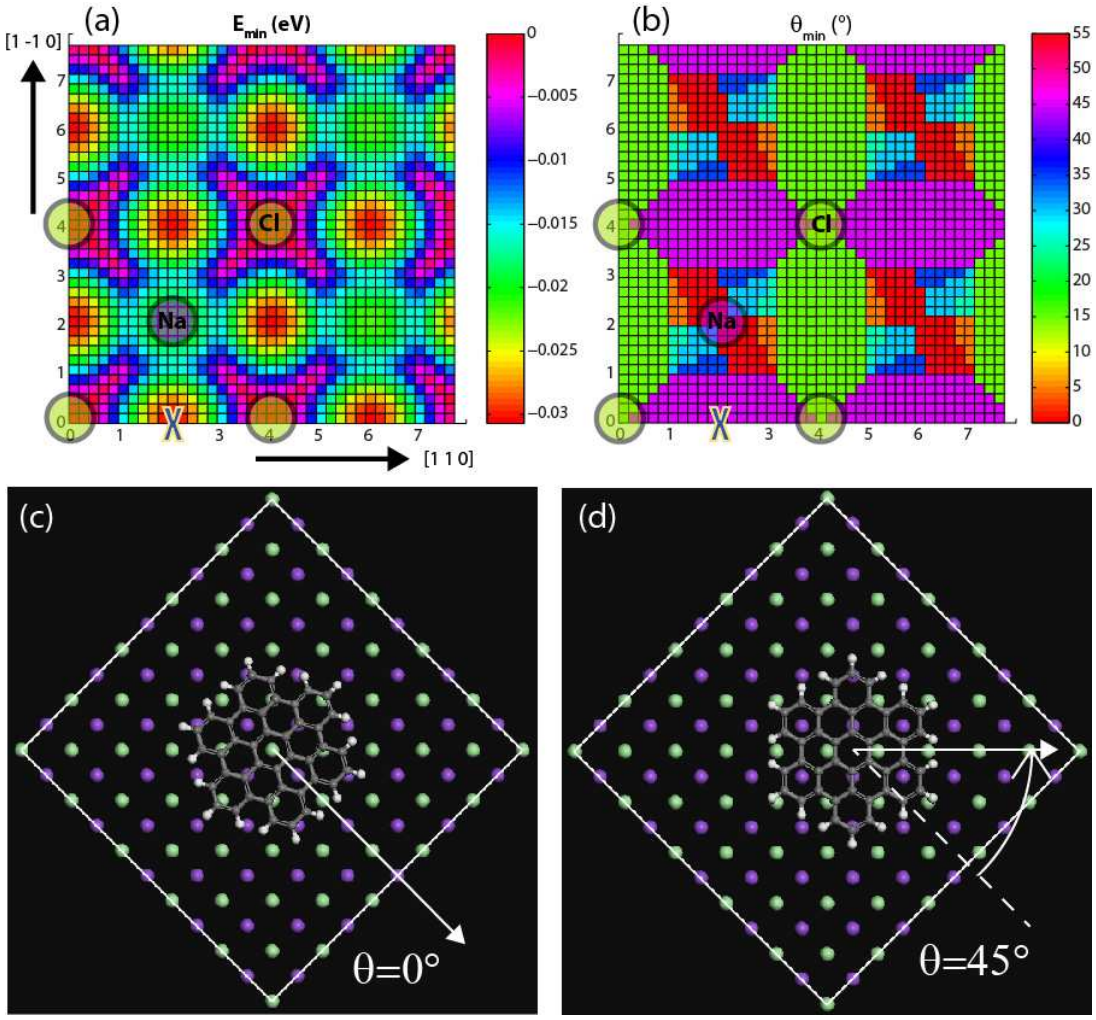

Figure S1: (a) Minimum energy and (b) corresponding angle for HBC/NaCl(001) as a function of (X,Y), the position of the center of the molecule. (c) shows the starting position X=0, Y=0 for the molecule when θ=0°. (d) shows the position of the molecule in its minimum energy configuration, indicated by '**X**' in (a) and (b). Green=Cl, pink=Na.

The altitude Z corresponding to the minimum energy is nearly constant at Z=0.39 nm. The minimum energy configuration [Fig. S1(d) and S2(d)] is similar for both substrates with an angle of 45° relative to the 0° situation of Fig. S1(c) and S2(c). With this angle, 8 H atoms are vertically aligned along a polar <001> [vertical in [Fig. S1(d) and S2(d)]. The adsorption energies deduced from the calculation are similar, with E_{NaCl}=0.85 eV and E_{KBr}=0.74 eV.

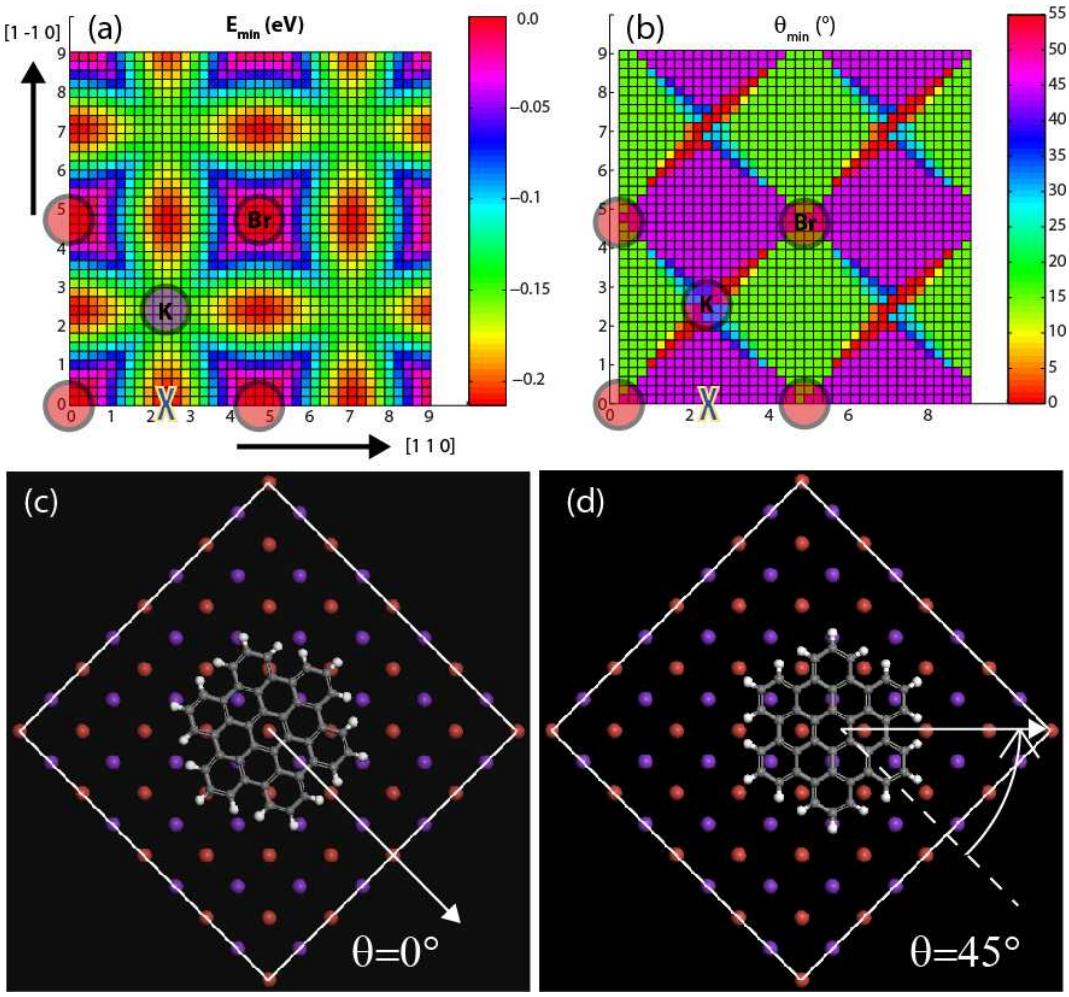

Figure S2: (a) Minimum energy and (b) corresponding angle for HBC/KBr(001) as a function of (X,Y), the position of the center of the molecule. (c) shows the starting position X=0, Y=0 for the molecule when θ=0°. (d) shows the position of the molecule in its minimum energy configuration, indicated by '**X**' in (a) and (b). Red=Br, pink=K.

Fig. S1(a) and S2(b).shows that molecular diffusion is favored along the polar rows of the substrate, as often observed for molecules on alkali halide substrates. An estimation of the diffusion barriers can be extracted from Fig. S3 where the plots of the minimum energy along a vertical line joining two sites of minimum energy in Fig. S1(a) and S2(b) have been plotted. One gets ΔE_{NaCl}=15 meV, ΔE_{KBr}=60meV, ie a 4-fold increase in the diffusion barrier.

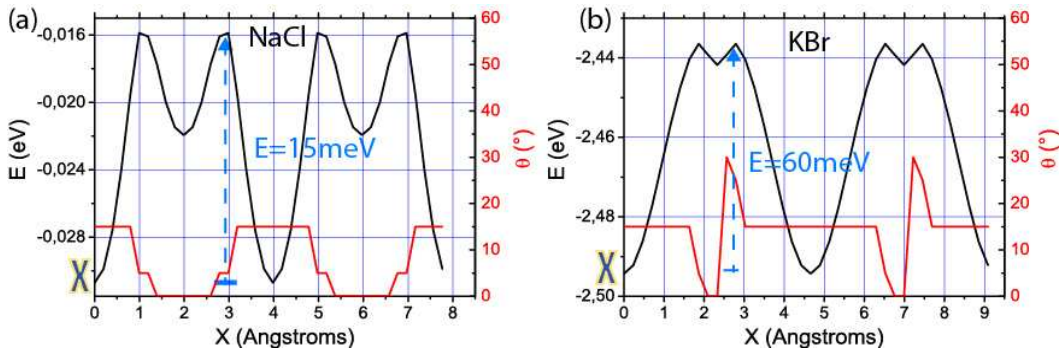

Figure S3: Minimum energy (black) and angle (red) along a polar direction between two minimum energy sites. (a) NaCl, (b) KBr. The "X" symbol corresponds to the position labeled in Fig. S2 and S3(a) and (b).

Observation of two molecular configuration on KBr/Ag(111)

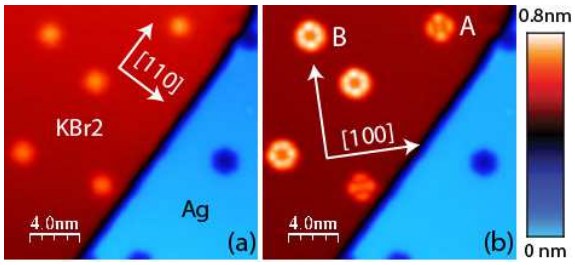

Figure S4: HBC on KBr bilayer on Ag(111): I=1pA, (a) V=1.4V, (b) V=1.5V.

When imaged on KBr at bias voltages between 1.5 and 1.7 V, HBC appears under two different aspects. At V=1.5 V, HBC appears under two different aspects labelled A and B in Figure S4(b). They differ mainly by the position of the LUMO peak in the dI/dV spectrum, which appears at 1.67 V form HBC-A (Figure 7) and 0.1V lower for HBC-B. At 1.5V, the LUMO is fully developed for HBC-A but only beginning to appear for HBC-B, as observed in Figure S4(b).

We were not able to experimentally determine the difference between A and B. It was possible to change from one state to the other by molecular manipulation. This change is associated with a lateral displacement suggesting that A and B sit on different sites of the

KBr surface but our measurements are not precise enough to determine it. We also checked by lateral manipulation that neither species was adsorbed on a defect.

Furthermore, our calculations are not realistic enough to understand why HBC is observed in states A or B. They point to only one adsorption site. No extra –metastable- site that could explain our observations is revealed. This is not surprising since the relaxation of the substrate and the molecule have not been taken into account as well as the presence of the Ag(111) surface under the KBr bilayer. Further studies and more realistic calculations are needed to clarify this point.

HBC assemblies

A. **Profiles on an assembly of 2 HBC**

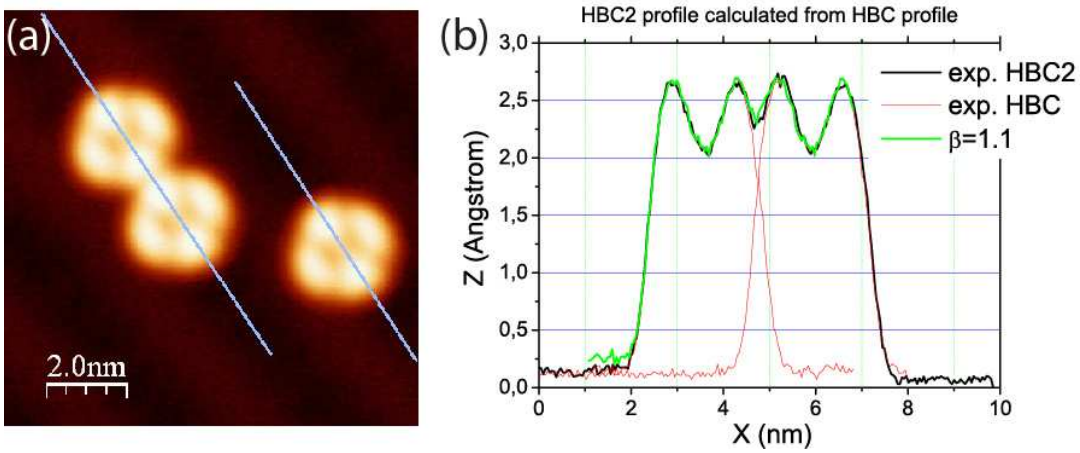

Figure S5: (a) STM image of 3 HBC molecules on KBr(2ML)/Ag(111). V=1.5 V, I=1pA. (b) Profiles along the lines drawn in (a) on HBC2 (black), on HBC (green) and calculated profile on HBC2 (red).

Figure S5 shows another example illustrating our method for predicting the profile on an assembly of two HBC from the experimental profile on a single HBC. It differs from the case presented in the main paper by the HBC-HBC distance, which is larger here (d=2.3 nm instead of 1.83 nm) and the orientation of the molecules, which are now rotated by 90°. A very good agreement between the

calculated (green) and experimental (black) profiles is reached with the same value of β=1.1. In particular, the minimum in the profile above the junction between the two molecules, which is visible in the image as a dark line, is well reproduced.

B. **Images of a linear assembly of 4 HBC**

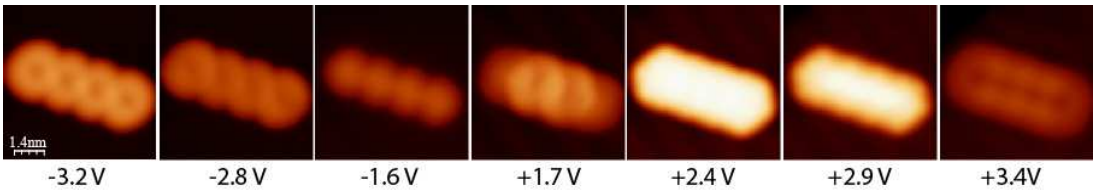

Figure S6: Images measured on an assembly of 4 HBC on NaCl. I= 1pA. The bias voltages are the same as in Figure 4 for comparison.