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Living on the edge: A nanographene molecule adsorbed across gold step edges

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ABSTRACT

The unusual adsorption geometry of the large graphene-like polycyclic aromatic hydrocarbon hexa-*peri*-hexabenzocoronene (HBC) across kinks on the stepped vicinal Au(111212) surface has been studied by synchrotron radiation X-ray photoelectron diffraction (XPD) and scanning tunneling microscopy (STM). By a combination of the two techniques a complete characterisation of the adsorption behaviour is achieved, yielding information on preferential adsorption sites (STM) and molecular orientation (XPD). At low coverage (<0.15 ML) HBC adsorbs across kink sites in fcc-stacking regions with its axis rotated by 19° with respect to the step edge normal direction and the polyaromatic disc tilted by 12° relative to the (111) terraces of the substrate. Furthermore, a small fraction of HBCs adsorbs across straight step edges. The possible exploitation of the characteristic step- and kink-adsorption of molecular derivatives of HBC in supramolecular architectures is exemplified at the example of the adsorption of a HBC-derivative on the same substrate.

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Understanding the mechanisms that govern the adsorption, self-assembly and electronic properties of adsorbed organic molecules plays an important role towards a better insight into the organic–inorganic interface which is relevant to various fields of technology [1]. Since properties of organic nanostructures and thin films directly (and strongly) depend on the geometric order and conformation of the first layer(s), numerous studies have focussed on the determination of the adsorption behaviour of organic molecules on metallic substrates [2–6].

Scanning tunneling microscopy (STM) is among the most popular methods to characterise organic adsorbate systems in the (sub-) monolayer range. However, the information gained from STM by itself is often insufficient to allow for a complete characterisation of the adsorbate structure, geometry and possible adsorption-induced conformational changes. Combining the highly local STM with surface integrating probes such as low energy electron diffraction [7,8], normal incidence X-ray standing wavefield absorption [9] or near-edge X-ray absorption fine structure [10,11] allows for a more complete characterisation of organic adsorbate systems. Here, we show that the combination of the local and non-local probes STM and X-ray photoelectron diffraction (XPD) allows

for a complete determination of the adsorption behaviour and orientation of a large organic adsorbate at low coverage.

At low coverage many adsorbates preferentially decorate surface defect sites like steps or kinks [12–14]. Depending on the electronic structure of the adsorbate, the electron rich/deficient regions below/above the step edges are preferred. An unusual adsorption geometry with the molecular π -system lying across step edges has recently been suggested for hexa-*peri*-hexabenzocoronene (HBC; see Fig. 1a) on Au(111) [15]. The specific adsorption on kink sites and a well-defined orientation of the π -system make HBC-derived molecules a potential anchor in multicomponent supramolecular networks when extended with appropriate functional side groups. However, on Au(111) there are several types of differently oriented steps and the local step density will vary considerably between different sample areas. To study the usability of the on-kink adsorption for supramolecular assemblies we have chosen Au(111212), a naturally templated vicinal Au(111) crystal. Crystals of this (*nmm*) type exhibit highly regular arrays of steps in one direction and are – due to the quenching of the herringbone reconstruction – naturally patterned along the direction parallel to the steps [16]. Successive fcc- and hcp-stacking regions are separated by the so-called discommensuration lines. The resulting rectangular 5.8×7.2 nm superstructure has successfully been used to grow highly ordered metallic nanodots [17], molecular nanowires [18] and bi-component

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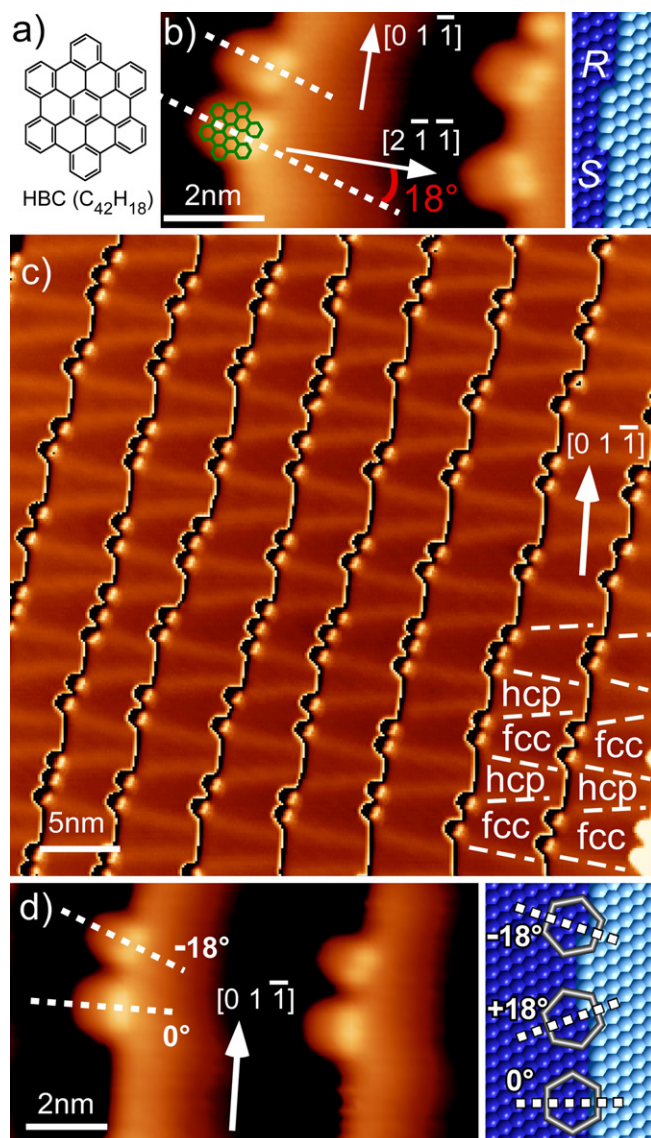


Fig. 1. Chemical structure and STM-images of ~ 0.12 ML HBC on Au(111212). (a) Chemical structure of HBC. (b) STM image of four kink-adsorbed HBC showing the two characteristic protrusions over the uppermost benzene rings and the rotation of the molecular axis (dashed white line) with respect to the $[2\bar{1}1]$ step normal direction. The molecules on the right are adsorbed across a *R*- resp. *S*-type kink. A model of an *R*- and *S*-type kink is given on the right (not to scale; -50 mV; 30 pA). (c) Overview STM image showing the confinement of HBC to fcc-stacking regions. Contrast has been applied to each terrace separately (2 V; 50 pA). (d) STM image showing molecules adsorbed across kinks (upper) and molecules adsorbed across straight step edges (lower). Model of the three adsorption sites observed on Au(111212) and the relative rotation of the molecular axis (dashed lines) in each case. From top to bottom: HBC adsorbed across *R*-kink, *S*-kink and straight step edge (-200 mV; 30 pA).

supramolecular structures [19]. The Au(111212) surface is nominally free of kinks but will always be imperfect in reality for entropic reasons. The intrinsic kink concentration of the employed crystal depended on the exact preparation procedure and allowed for a study of the kink-adsorption of HBC on this substrate. Typical local kink concentrations were on the order of 1–3 kinks per 5.8×7.2 nm² surface unit cell.

Angle-scanned X-ray photoelectron diffraction experiments were performed at the near node-endstation of the X11MA-SIM beamline at the Swiss Light Source. Low temperature STM (LT-STM) measurements were conducted using an Omicron LT-STM.

Both systems were operated at ultra high vacuum conditions with base pressure below 2×10^{-10} mbar. The Au(111212) substrate was cleaned by repeated cycles of Ar⁺ ion sputtering and subsequent annealing to 670 K. HBC was deposited at a deposition rate of approximately 3 ML/h from resistively heated stainless steel crucibles at 685 K onto the sample which was held at room temperature. Coverage was evaluated by comparison of the C1s signal to a reference sample of 1 ML which had been obtained by desorption of a multilayer upon heating. The synthesis of HBC is described elsewhere [20]. For the STM measurements, the sample was cooled down to 77 K after evaporation. XPD was performed with the sample held at room temperature and a photon energy of 920 eV. For XPD, the substrate orientation has been determined by the positions of the low index crystal directions in the Au4f-photoelectron diffraction pattern.

High resolution LT-STM images [21] show that HBC adsorbs across the regularly spaced steps of the Au(111212) surface (Fig. 1b). The characteristic feature of this adsorption geometry are two protrusions centred above the uppermost benzene rings and a rotation of the molecular axis by $18^\circ \pm 2^\circ$ with respect to the $[2\bar{1}1]$ axis of the substrate. As shown in Fig. 1c, at low coverage (<0.15 ML) only the step edges within the fcc-stacking regions are decorated, with some of the molecules lying on the discommensuration lines. Selective decoration of fcc-stacking regions on Au has been reported for various organic adsorbates in the literature [13,22]. However, a universal understanding of this stacking-selective adsorption is still missing. Up to three HBC molecules can be found within a single fcc-stacking region (including the discommensuration lines) while the step edges within the hcp-stacking regions are free from adsorbates. It should be noted that the adsorption across kinks is also found at room temperature by STM [15].

A confinement of kinks to fcc-stacking regions – as reported for Au(677) [23] – prior to deposition of HBC has been observed, implying that the kinks are already present within the fcc-regions when HBC is being deposited and are not moved to these sites by the adsorbate. The energy difference – computed by DFT [15] – between adsorption across a kink and across a straight step edge is 0.16 eV. Computed kink formation energies on vicinal Au(111) [24,25] are between 0.24 and 0.26 eV and hence substantially larger than the energy gain per molecule for adsorption across a kink as compared to adsorption across a straight step edge. Therefore, it can be concluded that HBC does not reconstruct the step edges to create a kink site but rather decorates kinks that are naturally present on this substrate with our employed substrate preparation conditions. This is confirmed by the observation of a second stable adsorption geometry where the molecule adsorbs across straight step edges in a way similar to the adsorption across kinks (see Fig. 1d). As for the on-kink adsorption, there is an apparent elevation of two of the peripheral benzene rings which is seen as an elongated protrusion in the STM images. Unlike in the kink-adsorption, the mirror axis of the molecule is perpendicular to the step edge in this adsorption geometry. Removing molecules from this site by the STM-tip – by lowering the tip-surface distance while scanning in the vicinity of the adsorbates – shows that the underlying portion of the step edge is completely straight. Since kinks are not created by the HBC molecules, the local density of molecules adsorbed across a straight step edge can vary considerably depending on the local substrate quality.

Since XPD does not require long range order of the adsorbate, it is ideally suited to study the kink-adsorption of HBC on Au(111212). The C1s photoelectron diffraction pattern from a submonolayer of HBC on Au(111212) is shown in Fig. 2a. The pattern corresponds to the sum of five different samples with coverages between 0.1 and 0.2 ML with a total integration time of 45 s per emission direction. All diffraction features seen in Fig. 2a are also

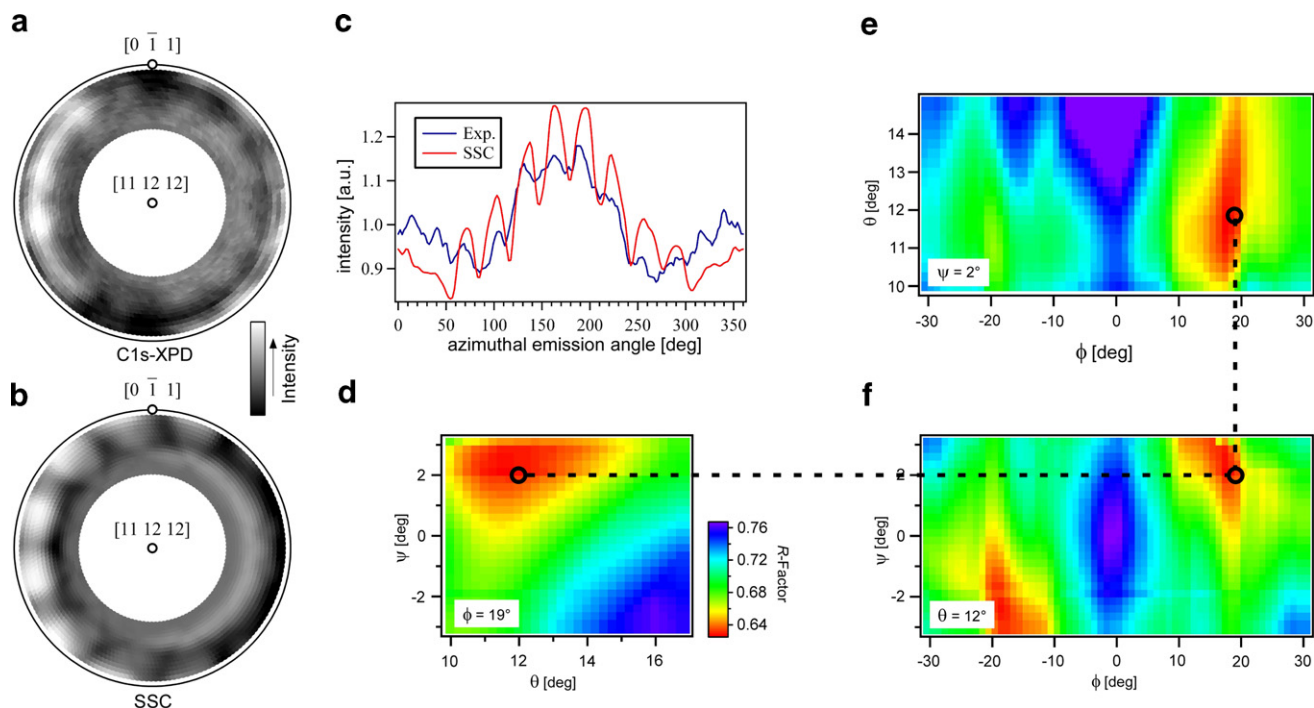


Fig. 2. (a) Experimental and (b) simulated C 1s XPD patterns of ~ 0.15 ML of HBC on Au(111212) for polar emission angles between 86° and 56° . (c) C 1s intensity at a polar emission angle of 80° . (d)–(f) R-factor plots for the three angles ϕ , θ and ψ defining the orientation of the molecular disc with respect to the Au(111212) surface (see Fig. 3).

present in the individual patterns from each sample showing that all measured coverages correspond to the same adsorption regime. The samples did not show any sign of degradation during measurements. The central part of the diffraction pattern (not shown) does not show diffraction features due to the adsorbate. The diffraction maxima on the left hand side of the pattern are overlapping forward-focussing features which directly show that the molecules must be adsorbed in a tilted configuration. The asymmetry of the pattern with respect to the $(0\bar{1}1)$ plane stems from the inequivalent abundance of molecules adsorbed across *R*- and *S*-type kinks [26], thus directly reflecting the deviation of the used crystal from the nominal $(11\bar{1}212)$ orientation. Single scattering cluster (SSC) simulations [27] have been used to find the molecular orientation yielding the best agreement with the experiment and hence the lowest reliability factor (*R*-factor) [28]. Scattering by hydrogen atoms was neglected since the elastic scattering cross-section is negligible compared to the one of carbon. Backscattering from substrate atoms has not been included in the calculations since the backscattering yield is very low within the kinetic energy range used for this work (>600 eV). Furthermore, because of the unusual adsorption geometry the number of inequivalent carbon–substrate atom orientations and distances is very large so that backscattering from the substrate is expected to be almost isotropic. Partial wave phase shifts have been computed within a muffin-tin formalism [29]. The orientational angles of the adsorbate with respect to the substrate which were left as free parameters in the simulations are defined in Fig. 3a. The abundance of molecules adsorbed across *R*- and *S*-type kinks has equally been left as a free parameter. The simulated diffraction pattern corresponding to the minimized *R*-factor is shown in Fig. 2b. The lowest *R*-factor is obtained for $\theta = 12.0 \pm 3^\circ$, $\phi = 19.0^\circ \pm 2^\circ$, $\psi = 2.0^\circ \pm 2^\circ$ (see Fig. 2d–f) and a ratio of *R*- to *S*-type kinks of 4:5. Diffraction signal due to molecules adsorbed straight across steps has also been included in the simulation. It was found that less than 10% of all adsorbates are adsorbed across straight step edges, which is in line with the much lower abundance of step-adsorbed HBC compared to kink-adsorbed mol-

ecules observed by STM. The overall agreement between the experimental and simulated diffraction patterns is very good, with the positions – in both the azimuthal and polar direction – of the most prominent diffraction features being well reproduced by the simulations (see cut-views in Fig. 2c). The larger anisotropy in the simulated diffraction signal stems from the well-known overestimation of the forward-focussing peaks by SSC [27]. The orientational angles of the molecule suggest, that the adsorbate not only adopts a position that aligns its π -system with the smoothed out electron density over the step edge, but – because of the non-zero value of ψ – also adjusts its orientation along the step due to the smoothing of the electron density contours around the kink. These results from XPD experimentally prove that the most stable adsorption geometry (see Fig. 3b) is a tilted one as predicted by DFT. The azimuthal orientation $\phi = 19^\circ \pm 2^\circ$ is in excellent agreement with both results from STM ($18^\circ \pm 2^\circ$) and DFT (17°). The experimentally determined tilt angle $\theta = 12^\circ \pm 3^\circ$ with respect to the terraces is somewhat larger than the corresponding value suggested by DFT (9°) but clearly confirms the unusual tilted adsorption geometry.

In the gas phase, the polyaromatic disc of HBC is perfectly planar. However, there are several almost isoenergetic conformations [30]. A slightly nonplanar conformation has been suggested by DFT [15] for kink-adsorbed HBC with some of the outer benzene rings tilted by up to 2° with respect to the coronene core. Because of the multitude of isoenergetic conformations in the gas phase, a small adsorption-induced conformational change is likely to accompany the adsorption process as the energetic cost to change the conformation is low. It was not possible to evidence or exclude such small conformational changes from the SSC calculations since the variation in *R*-factor is too low to yield unambiguous information.

The unusual adsorption of HBC across straight and kinked step edges may be used in supramolecular assemblies by anchoring a properly functionalized HBC-derivate within the fcc-stacking regions of a Au(*nmm*) crystal surface. A subsequently deposited molecular species with matching functionalization can then be

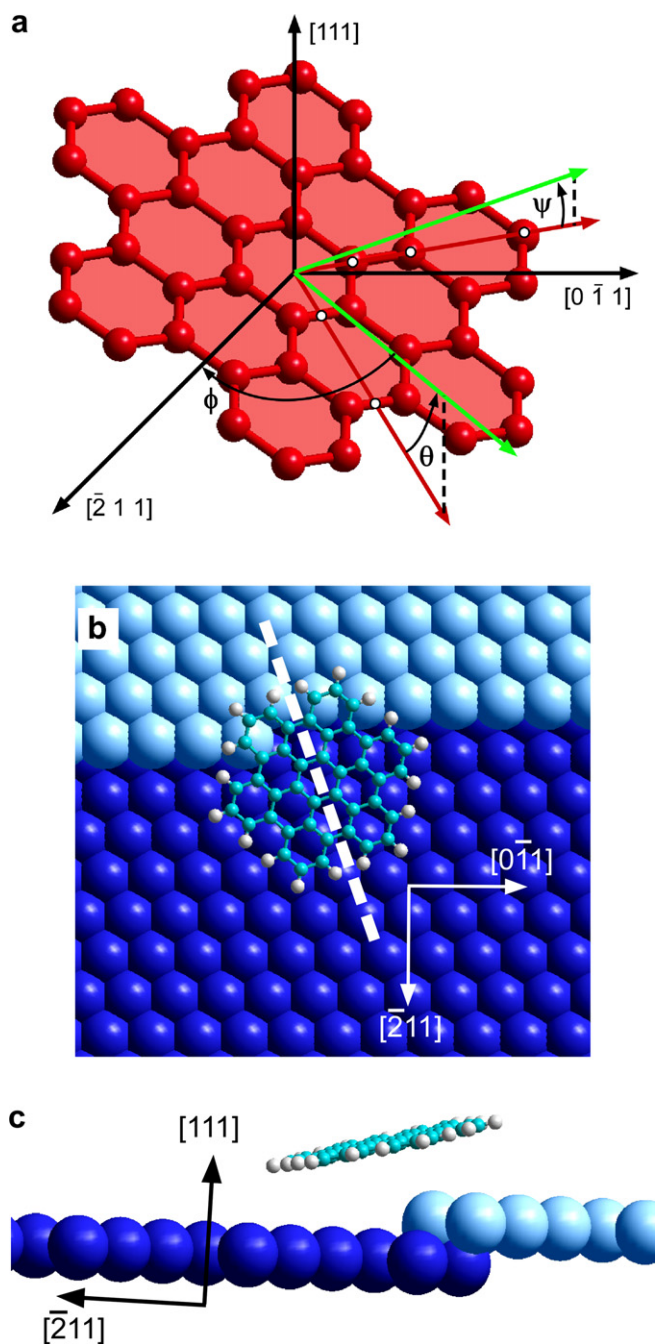


Fig. 3. (a) Definition of orientational angles for across-kink adsorption of HBC on Au(111212). The red axes are lying in the plane of the molecular disc. Green arrows correspond to projections of the red axes onto (111) along $[111]$. (b) Visualization of the tilted adsorption geometry of HBC across a S-type kink. The dashed line visualizes the molecular axis (see also Fig. 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

used to form template-mediated supramolecular assemblies. In Fig. 4 we show that dodecamethyl-HBC (ddmHBC) adsorbs in a way similar to HBC across steps and kinks within fcc-stacking regions on Au(111212). Simulated STM-images based on extended Hückel calculations of ddmHBC show that molecules adsorbed in a planar way on the flat terrace should be imaged as three identical elongated protrusions centred over two neighbouring upwards-facing methyl-groups. Three protrusions can be discerned on the molecules shown in Fig. 4. These protrusions have significantly different apparent heights with the two protrusions lying on the upper terraces appearing 1.5–2.5 Å higher than their counterpart

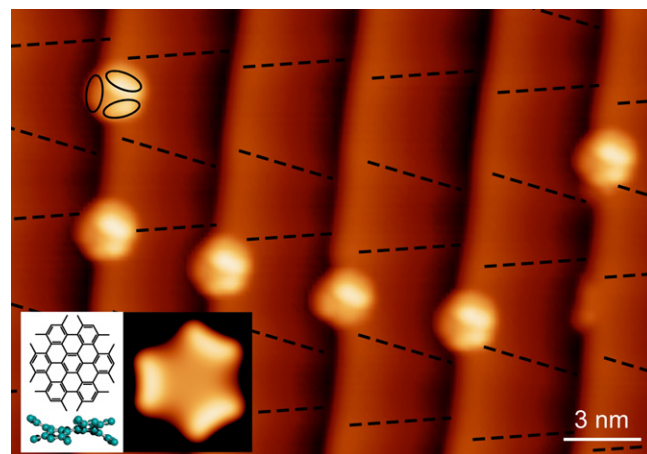


Fig. 4. STM image showing kink- and step-decoration of ddmHBC. Molecules are imaged as three elongated protrusions (visualized on a molecule on the upper left side) of which two appear higher than the third one. Dashed lines indicate the position of the discommensuration lines (tunneling parameters: -1.9 V; 20 pA). The insets show the chemical structure and nonplanarity of ddmHBC and a simulated STM image for a molecule adsorbed on a planar terrace based on extended Hückel calculations.

on the lower terrace. Based on the tilted adsorption geometry determined for HBC we conclude that ddmHBC also adsorbs in a tilted way across steps and kinks. Even though the π -system of ddmHBC is distorted (inset Fig. 4) and lifted above the surface because of the methyl groups, the adsorption behaviour is very similar to HBC. Due to their tilted adsorption geometry across kinks and step edges, functionalized HBCs may thus be used as anchoring molecules on Au(nmm) template surfaces and act as specific linkers between supramolecular assemblies on adjacent terraces.

In conclusion, we have shown that synchrotron-based XPD can be used for the determination of the orientation of large organic adsorbates at coverages as low as 0.15 ML if the number of coexisting adsorption configurations is small. The adsorption geometry of HBC on Au(111212) determined by XPD experimentally confirms the tilted adsorption of HBC across gold kinks suggested by DFT. Furthermore, we have shown how the tilted adsorption across step edges of functionalized HBC-derivates may be exploited in supramolecular assemblies on naturally templated vicinal Au surfaces.

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