Supplementary Material to Coverage-Driven Dissociation of Azobenzene on Cu(111): A Route Towards Defined Surface Functionalization

M. Willenbockel,^{†,‡} R. J. Maurer,^{¶,§} C. Bronner,^{||,⊥,#} M. Schulze,^{||,⊥} B. Stadtmüller,^{†,‡,@} S. Soubatch,^{*,†,‡} P. Tegeder,^{||} K. Reuter,[¶] and F. S. Tautz^{†,‡}

†Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany ‡Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany
¶Chair of Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching, Germany
§Department of Chemistry, Yale University, 225 Prospect Street, 06520 New Haven, USA
∥Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany
⊥Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany
#Present address: University of California at Berkeley, Department of Physics, 375 Birge Hall, Berkeley, CA 94720, USA
@Present address: Department of Physics and Research Center OPTIMAS, Universität

^(Q)Present address: Department of Physics and Research Center OPTIMAS, Universitat Kaiserslautern, Erwin-Schrödinger-Straße 46, 67663 Kaiserslautern, Germany

E-mail: s.subach@fz-juelich.de

Experimental Details

Sample preparation

The Cu(111) sample was prepared in the conventional way by a series of sputtering (1 keV Ar^+ ions, 20 minutes) and annealing (800 K, 20 minutes) cycles. The cleanness of surface was checked by XPS and LEED.

To deposit azobenzene, the Cu(111) sample was placed in front of an effusion cell filled with azobenzene. The evaporator was kept at 300 K during exposure. The dosage of azobenzene was controlled by the exposure time.

Four samples were prepared: (1) The submonolayer azobenzene film refered to as subML was prepared by exposing clean Cu(111) at 300 K to an azobenzene pressure of 2×10^{-9} mbar for 15 s. (2) The monolayer azobenzene film refered to as ML was prepared by exposing clean Cu(111) at 300 K to an azobenzene pressure of 2×10^{-9} mbar for 40 s. (3) The multilayer sample refered to as MultiL was prepared by exposing clean Cu(111) at 220 K to an azobenzene pressure of 4×10^{-8} mbar for 600 s. (4) The fourth sample was prepared as a coverage reference, corresponding to a saturated monolayer of dissociated azobenzene (phenyl nitrene), by short term flashing the MultiL film at 315 K.

Photoemission spectroscopy and coverage estimation

All photoemission experiments – off-Bragg XPS and NIXSW – were conducted at 60 K in order to prevent a possible thermal or irradiationinduced desorption of molecules. To rule out beam damage (molecular desorption, structural modifications of the layer, *trans-cis* isomerisation of azobenzene, or molecular decomposition), the non-destructive radiation dose was established in preparatory experiments for each sample, by monitoring the XPS binding energies and the peak shapes of N1s and C1s core levels. The measurement times for the ensuing XPS and NIXSW experiments were selected accordingly. Furthermore, every second XPS and/or NIXSW measurement was conducted at a fresh spot on the sample that had not yet been exposed to the x-ray beam before. In particular, for the subML sample the XPS-based chemical and NIXSW-based structural analyses reveal the presence of only one chemical species on the surface, namely the intact azobenzene molecule in its *trans* configuration, which is also fully confirmed by DFT calculations.

For off-Bragg XPS, an excitation energy of 2960 eV was used in order to avoid any influence of the standing wave effect at the Cu(111) Bragg energy of 2975 eV. Off-Bragg XPS data were used for estimating the coverage and for developing fitting models for C1s and N1s core levels that were then applied to the NIXSW analysis.

The quantification of the coverage for the various samples has to take into account different molecular species as well as different adsorption configurations: intact transazobenzene molecules in contact to the substrate (cf. Fig. 1, black curve), a mixture of intact trans-azobenzene and phenyl nitrene (cf. Fig. 1, green curve), a saturated monolayer of phenyl nitrene (reference sample), and second and higher layers of azobenzene molecules on top of a saturated monolayer of phenyl nitrene (cf. Fig. 1, blue curve). All quoted coverages are related to the XPS N1s core level intensity of the saturated phenyl nitrene film, defined as 100 % coverage. Against this reference, the coverage of the subML sample (Fig. 1, black curve) is 40% and the total coverage of the ML sample (Fig. 1, green curve) is 90 %, the ratio between phenyl nitrene and trans-azobenzene being 1.3. In calculating the total coverage of the MultiL sample, the photoelectron damping in the organic film has been accounted for. This

yields a coverage of approximately 4 monolayers. This relatively low coverage indicates a much lower sticking coefficient of azobenzene on the molecular layer than on Cu(111).

Low energy electron diffraction measurement

Figure S1 shows the LEED patterns of the subML, ML and annealed MultiL samples. The diffuse image of the subML (Fig. S1 a) reveals the absence of any order at low coverage. In contrast, the ML sample (Fig. S1 b) is ordered. The observed diffraction pattern can be described by the superstructure matrix

$$\left(\begin{array}{cc} 2.9 & 0\\ 0.7 & 5 \end{array}\right).$$

It corresponds to a point-on-line coincidence between the lattices of the molecular film and the substrate.

MultiL and annealed MultiL samples exhibit identical diffraction patterns (Fig. S1 c) which can be described by a (4×4) superstructure with a glide plane symmetry. Since according to XPS the annealing of the multilayer at 315 K completely removes the excess of azobenzene from the sample, leaving behind only a monolayer of phenyl nitrene, the identical LEED images before and after annealing indicate Stranski-Krastanov growth of thick azobenzene films on Cu(111).

Normal incidence x-ray standing wave measurement

NIXSW was carried out at 60 K using the Cu(111) Bragg reflection ($E_{\gamma}=2975 \text{ eV}$) in grazing emission. Hence, the hemispherical electron analyzer (SPECS Phoibos 225) was directed perpendicular to the x-ray beam. This experimental geometry has two benefits. Firstly, the grazing emission enhances the surface sensitivity of the photoemission experiment, thus suppressing the background signal from bulk photoemission, which is especially desirable due to low photoemission cross-sections of N1s and C1s at the relevant excitation energy. Secondly,



Fig. S1 LEED patterns of *trans*-azobenzene adsorbed to Cu(111):. (a) subML coverage, (b) ML coverage, (c) MultiL annealed at 315 K.

in this geometry non-dipolar effects in the angular distribution of the photoelectrons can be neglected 1,2 .

In our experiments we nevertheless find that disregarding non-dipolar effects results in an artificial increase of the coherent fraction of fitted electron yield curves. Most likely, this is a result of the finite acceptance angle of the electron analyser. For instance, for the subML azobenzene sample the heights of atomic species provided in Tab. 1 of the paper correspond to the coherent fractions

$$d_{\rm Cu-N} = 2.02(2) \text{ Å/ } F_c({\rm Cu-N}) = 0.97(1)$$

$$d_{\rm Cu-CN} = 2.23(6) \text{ Å/ } F_c({\rm Cu-CN}) = 0.80(2)$$

$$d_{\rm Cu-CC} = 2.36(2) \text{ Å/ } F_c({\rm Cu-CC}) = 0.70(8).$$

For phenyl nitrene the coherent fractions are

$$d_{\rm Cu-N} = 1.17(4)$$
 Å/ F_c(Cu-N)=1.21(7)
 $d_{\rm Cu-CC} = 4.25(4)$ Å/ F_c(Cu-CC)=0.61(6).

In particular, in few cases F_c approaches and even exceeds unity. This is inconsistent with the mathematical definition of the coherent fraction as such, which may only vary between 1 (all photoemitters are at the same height) and 0 (photoemitters are homogeneously distributed along the x-ray standing wave pattern). We have observed this effect of artificial increase of coherent fraction on several molecular systems at two different photoemission endstations with grazing emission.³⁻⁵ We have validated that the high coherent fractions do not influence the coherent positions, i.e. the adsorption heights.

Although for the reasons given above our coherent fractions must be interpret with care, the very high $F_c(Cu-N)$ of the phenyl nitrene monolayer (1.21(7)) points toward a very good vertical alignment of all N atoms and, accordingly, to a well-defined and rather strong *chem*ical bond between N and Cu atoms. The coherent fraction for intact *trans*-azobenzene at subML coverage (0.97(1)) is noticeably smaller, indicating more vertical disorder and thus a weaker molecule-metal interaction. In contrast, the $F_c(Cu-CC)$ of the subML azobenzene layer is higher than that of phenyl nitrene (0.70(8))vs. 0.61(6)). This indicates a stronger tilt of the phenyl rings in the saturated phenyl nitrene monolayer.

Theoretical Calculations

Computational details

All density functional theory calculations have been performed including a pair-wise dispersion correction that also effectively accounts for many-body screening within the substrate $(DFT+vdW^{surf})$.⁶⁻⁸ We employ a setup very similar to what we have used in previous studies.⁹⁻¹¹ In short, we construct (111)-oriented slabs of Cu metal surfaces with 4 layers. Hereby the first two layers have been relaxed in geometry optimizations, the others are frozen. Different surface unit-cells have been used to model the different experimentally observed structures, including (4×4), (5×3), (6×4), and (5×5) cells. All optimizations and energy evaluations have been performed with the ultrasoft-pseudopotential plane-wave code CASTEP V8^{12,13} using standard-library pseudopotentials¹⁴ and the exchange-correlation functional as proposed by Perdew, Burke, and Enzerhof.¹⁵ Geometries have been converged up to a maximal force component of 0.025 eV/Å. Electronic convergence and Brillouin-zone sampling have been tested to yield converged results in the envisioned accuracy regime (± 25 meV).

Adsorbate structure

To model the experimentally observed lowcoverage situation (subML), we have optimized the geometry of *trans*-azobenzene in a flatlying adsorption configuration in a (6x4) surface unit cell. The optimal adsorption site (diazobridge in bridge position on Cu(111)) was already known from previous work.⁶ The resulting adsorption structure is depicted in Fig. S2 and structural parameters are given in Table S1. The calculated adsorption energy in this structure is 2.39 eV. The calculated adsorption structure is close to the experimentally observed one and the most stable geometry in a previous simulation study.⁶

For the monolayer (ML) phase, two models have been tested. In the first model, we assume a high density packing of intact trans/azobenzene molecules, in analogy to azobenzene adsorbed on Ag(111).¹¹ This is modelled by (5×3) (containing one molecule) and (5×5) (containing two molecules) surface unit cells. The corresponding optimized geometries can be found in Table S1, the structures are shown in Fig. S3. Both these phases exhibit structural parameters that do not explain the experimentally found Cu-N and Cu-C distances.

We therefore calculated a second model, namely the dissociation of azobenzene at the diazo-bridge into two phenyl nitrene (Ph-N) fragments. We simulated this dissociation by elongating the diazo-bond to 2.9 Å and using this deformed structure as a starting point for a local structure optimization. In this optimization the molecule dissociates (barrierless) and transforms into two phenyl nitrene fragments that adsorb in fully upright positions at hollow sites (see Fig. S4).

Table S1. Structural parameters for simulated phases of azobenzene (Ab) on Cu(111): (6×4) and (5×3) containing one molecule in the unit cell and (5×5) containing two molecules.

trans-Ab@Cu(111)	$d_{\rm Cu-N}$	$d_{\rm Cu-(CN)}$	$d_{\rm Cu-(CC)}$
$PBE+vdw^{surf}$		in Å	
1 trans-Ab in (6x4)	2.03	2.15	2.28
1 trans-Ab in (5x3)	2.06	2.18	2.38
2 trans-Ab in (5x5)	1.99	2.78	2.76

LEED measurements reveal a commensurate (4×4) superstructure of these fragments. We simulated this structure with 3 phenyl nitrene units adsorbed vertically on the Cu(111) surface (see Fig. S5). The adsorption structure is in very good agreement with the geometry parameters extracted from the NIXSW analysis (the calculated d_{Cu-N} is 1.18 Å, compared to the measured 1.17 Å.) Note, however, that spot extinctions in LEED images prove the existence of a glide mirror plane in the commensurate (4×4) superstructure. The calculated structure in Fig. S5 would exhibit this glide symmetry if all molecules were *precisely* oriented along the atomic rows of the Cu(111) surface. This requires only minor corrections of their calculated orientations. This dissociated structure has a higher adsorption energy per surface area (2.77)eV) than the intact *trans*-azobenzene molecule, therefore suggesting a thermodynamic driving force for the dissociation process.

X-ray photoelectron spectra

We assume negligible effects of intermolecular interactions on the XPS signal of the multilayer and approximate it by modelling an isolated gas-phase azobenzene molecule. We do this by simulating the N1s XPS signal of an optimized isolated azobenzene molecule using the Δ SCF approach. In the case of Δ SCF the XPS energy is calculated by taking the difference between the total energy $E_{\rm GS}$ of the electronic ground state and an electronically excited state E^* in



Fig. S2 trans-azobenzene adsorbed to Cu(111) in a (6×4) unit cell. The system is depicted from the side (left) and from a top view (right).



Fig. S3 *trans*-azobenzene adsorbed to Cu(111) in a (5×3) unit cell (left) and two molecules adsorbed in a (5×5) unit cell (right).



Fig. S4 Azobenzene on Cu(111)-(6×4): Optimization starting structure with elongated diazo-bridge (left). Optimized structure of dissociated phenyl nitrene fragments from side (center) and top (right) view.



Fig. S5 Three Ph-N fragments adsorbed to Cu(111) in a (4×4) commensurate superstructure.

which one electron is removed from the 1s orbital of the N atom:

$$E_{\rm XPS}^{\Delta \rm SCF} = E^* - E_{\rm GS} \tag{1}$$

In this and all following calculations this is done individually for all N atoms, and the resulting XPS shifts are averaged over all nitrogen species. Calculations are performed with tight, converged basis settings using the FHI-Aims package.¹⁶

In addition, we have modelled the N1s XPS excitation spectrum of the monolayer and submonolayer. The submonolayer is modelled as a single azobenzene molecule adsorbed in a (6×4) surface unit cell. The monolayer is modelled as a (4×4) surface unit cell containing three upright-standing phenyl nitrene molecules. The corresponding XPS excitations have been calculated using CASTEP $V8^{12}$ and excited corehole pseudopotentials.^{17,18} Hereby a pseudopotential for a single nitrogen species is generated by selecting an excited atomic electron configuration $(1s^1, 2s^2, 2p^4)$. As a result, an additional electron is placed into the valence shell, which leads to an increase of the Fermi level. This is expected to have little effect on the overall excitation energy, due to the large number of electrons in the system, the metallic character and the thereby resulting small variation of the density of states at and around the Fermi level for coinage metals. The excitation energy is calculated as the energy difference between

the core-hole excited state and the electronic ground state. The final shifts reported in Table S2 are averages over all N species in the system.

Table S2. Calculated N1s XPS binding energies for isolated azobenzene (modelling the multilayer), azobenzene/Cu(111) and phenyl nitrene/Cu(111) (first line). Binding energy shifts relative to phenyl nitrene/Cu(111) are given in the second line. The same relative shifts, but corrected for the work function to allow direct comparison between the free and adsorbed molecules, are given in the third line. Experimental binding energy shifts from Fig. 1 in the paper are listed in the fourth line.

\mathbf{E}_{XPS}^{N1s}	Ab isol.	Ab/Cu(111)	Ph-N/Cu(111)
abs.	412.7	405.5	404.1
rel.	8.6	1.3	0.0
rel. corr.	3.8	1.3	0.0
rel. exp.	3.9	1.5	0.0

In order to compare the XPS shift obtained for the isolated molecule (azobenzene) with the ones for the adsorbed molecules (azobenzene/Cu(111) and phenyl nitrene/Cu(111)), the former value has to be corrected by the work function. Work functions of phenyl nitrene and azobenzene on Cu(111) are almost identical with 4.82 and 4.83 eV. Relative shifts reported in the third row of Table S2 have been corrected in this way and are in excellent agreement with experiment. Regarding the absolute values of the calculated XPS binding energies, we note that, because of the periodic boundary conditions, the asymptotic electrostatic potential in the calculation does not decay to zero, but rather to a constant positive value. Therefore, all binding energies are shifted towards higher values compared to what an external 'detector' at zero potential would measure. All calculations have been performed using the latest version of CASTEP containing a self-consistent dipole correction for which the work function of the system can be evaluated as the difference between the negative Fermi energy and the asymptotic value of the surface electrostatic potential furthest away from the surface slab.

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