Supporting Information

An on-surface Diels–Alder reaction

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1. In-solution synthesis

All reactions were carried out under argon using oven-dried glassware. TLC was performed on Merck silica gel 60 F254; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). 1H NMR were recorded at 500 MHz (Bruker DPX-500). APCI spectra were determined on a Bruker Microtof instrument. Commercial reagents were purchased from ABCR GmbH, Aldrich Chemical Co., and were used without further purification. THF was purified by a MBraun SPS-800 Solvent Purification System. Triyne 4 was prepared following a reported procedure (Figure S1).[1]

![Chemical diagram and synthesis steps]

Figure S1. Synthesis of triyne 4.[1]
**Cyclic triyne 1**

![Figure S2. Synthesis of triyne 1 by intramolecular Glaser coupling of compound 4.](image)

Cyclic triyne 1 was obtained by intramolecular Glaser coupling of triyne 4, following a modified procedure.[1] To a solution of Cu(OAc)$_2$ (1.03 g, 5.52 mmol) in 245 mL of a THF:pyridine mixture (48:1), a solution of compound 4 (380 mg, 1.00 mmol) in 165 mL of a THF:pyridine (32:1) mixture was added dropwise during 8 h at 50 °C under Ar. After the addition, the solution was stirred 30 min at 50 °C, and the reaction was quenched by the addition of H$_2$O (250 mL) and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 x 300 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The resulting mixture was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$:hexane, 2:8) to afford cyclic triyne 1 (186 mg, 49 %) as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ: 7.49 (dd, $J = 7.3$, 1.7 Hz, 2H), 7.46 – 7.35 (m, 8H), 7.32 – 7.27 (m, 4H), 7.23 – 7.20 (m, 2H) ppm.

MS (APCI (M+1)) for C$_{30}$H$_{16}$, found: 377.1327.
2. On-surface synthesis and computational calculations

STM and AFM experiments were carried out in a custom built combined STM-AFM equipped with a qPlus sensor,[2] and operated in frequency modulation mode.[3] The microscope is operated in UHV at a temperature of $T = 5$ K. The Cu(111) single crystal sample was partially covered with NaCl for CO pickup.[4] All images and data shown were recorded with CO functionalized tips. The oscillation amplitude $A$ was kept constant at $A = 0.5$ Å. The bias voltage $V$ was applied to the sample, and for AFM $V = 0$ V was applied. Precursors 1 where thermally sublimed onto the cold ($T \approx 10$ K) sample and imaged in areas of clean copper. The annealing steps of the sample to induce the chemical reaction of the adsorbed molecules were performed to the temperatures as indicated, and the final temperature of each annealing step was kept constant for two minutes.

Constant-height AFM images were obtained at tip heights $\Delta z$ with respect to the STM setpoint of $I = 1$ pA and $V = 0.1$ V on bare copper. A positive $\Delta z$ corresponds to an increased tip-sample spacing with respect to the setpoint. The $\Delta f(z)$ datasets were recorded with the feedback loop for the tip height being switched off.

Figure S3. Functionalizing the tip with CO molecule. (a) STM image of a CO molecule adsorbed on bilayer NaCl, recorded with a metallic tip at $I = 1$ pA, $V = 0.01$ V. (b) The same area was scanned again with increased tunneling current $I = 6$ pA, $V = 0.01$ V, that is, with reduced tip-sample distance, and the CO went from the sample to the tip while imaging (red arrow). The slow scan direction is top to bottom. (c) To verify a symmetric CO functionalized tip, another CO molecule on the surface was imaged and showed the characteristic contrast obtained by a CO functionalized tip ($I = 1$ pA, $V = 0.03$ V). All scale bars correspond to 5 Å.
DFT calculations and AFM image simulations.
Density functional theory (DFT) was employed using the FHI-AIMS code,[5] using the Perdew-Burke-Ernzerhof exchange correlation functional.[6] The geometry of the final flat product was calculated in gas phase. All other structures were simulated on a three-layer slab of copper of typically 8 by 8 atoms per layer. The atom positions in the lowest layer were constraint.

The AFM simulations were done using the DFT calculated atom positions using the probe particle model[7] with a tip charge of -0.05 elementary charges and a lateral spring constant of the CO molecule at the tip of 0.2 N/m.
Figure S4. Full set of precursor 1 adsorption conformations observed. Molecular models of compound 1 (first column), experimental constant-current STM images (second column), experimental constant-height AFM images recorded in far and close distance, with the respective tip height $\Delta z$ indicated (third and fourth column) and corresponding simulated AFM images (columns five and six). For far and close simulated images, the tip-sample spacing was changed by 0.4 Å, 1.3 Å and 1.2 Å for chemisorbed diyne, physisorbed monoyne and chemisorbed monoyne, respectively. All STM images were recorded at $V = 0.1$ V, $I = 1$ pA. The number of observed individual molecules in each conformation is indicated as white number in the top left of each STM image. All images are 20 Å by 20 Å.
Figure S5. Calculated adsorption geometries of the precursor 1. Models of DFT derived structures of precursor molecules adsorbed on the copper surface: Gray, white and orange balls correspond to carbon, hydrogen and copper atoms. For clarity only a part of the topmost copper layer is displayed. The first row shows top views onto the sample. Second and third row show side-views in the surface plane onto the diyne and the alkyne moiety of each molecule, respectively. The total energies of the calculations yield the lowest energy for the chemisorbed diyne, an energy that is 0.6 eV higher for the chemisorbed monoyne and a 1.1 eV increase of total energy for the physisorbed monoyne with respect to the chemisorbed diyne.
Figure S6. Force spectroscopy data and comparison to DFT for precursor 1. Vertical force spectroscopy $\Delta f(z)$ shows characteristic differences for the precursor adsorption geometries. Chemisorbed diyne: yellow; chemisorbed monoyne: blue; physisorbed monoyne: red. All spectra are background subtracted and recorded in the center of the molecule. A tip height of 0 Å corresponds to the setpoint height of $I = 1$ pA and $V = 0.1$ V on clean copper. Vertical black, dotted lines indicate the DFT derived height differences of the three structures of the highest carbon atom in the exposed monoyne/diyne group (the set of DFT derived heights with respect to the Cu surface are shifted to fit the experiment). The height $z^*$ of minimum in $\Delta f(z)$, indicated by a colored cross for each structure, has been shown to correspond to the differences in adsorption height. Here we observe that the adsorption height of the central molecular part is smallest for the chemisorbed diyne, about 0.4 Å larger for the chemisorbed monoyne and about 1.2 Å larger for the physisorbed diyne, by experiment and theory in excellent agreement.

Figure S7. Compound 1 (chemisorbed diyne) in an asymmetric conformation. One in three molecules of 1 with their alkyne on top, assigned as chemisorbed diyne, shows a slightly asymmetric contrast indicating a slightly tilted adsorption geometry. (a) STM image of such a molecule ($I = 1$ pA, $V = 0.1$ V). (b) Constant-height AFM image of the same molecule at $\Delta z = -0.2$ Å. A faint contrast asymmetry (between the left and the right side of the molecule) of this experimental image is also apparent in the DFT-derived AFM simulations (see Fig. S4, AFM simulations in far distance of chemisorbed diyne). Images are 20 Å by 20 Å.
Figure S8. Comparison of experimental and simulated images of 3'. (a) STM on compound 3’ (I = 1 pA, V = 0.1 V). (b, c) AFM with the tip-height offsets Δz indicated. (e, f) AFM simulation of the molecule adsorbed on copper at two different tip heights, the tip height in (f) is increased by 0.3 Å with respect to (e). All images are 20 Å by 20 Å.

Figure S9. Force spectroscopy data and comparison to DFT for 2 and 2’. Same method as for the precursors (see Fig. S6). Light blue corresponds to 2 and orange to 2’. Spectra were recorded at the most protruding position of each molecule. The minimum position is about 0.5 Å closer to the sample surface for 2’ with respect to the 2, indicating a lower height of the 2’ molecule. Vertical dotted lines indicate the DFT-derived height differences of the highest carbon atom within each molecule. For 2” no force spectroscopy data was obtained.
Figure S10. Calculated adsorption geometries and simulated AFM images of 2, 2', 2'' and other possible intermediates. Calculated adsorption geometries of potential intermediate structures are shown in top view (1st column) and side views (2nd and 3rd column), with only a part of the Cu atoms of the surface are shown for clarity. In column 4 – 7 simulated AFM images [7] at different tip heights are shown, with the differences in tip height for neighboring images indicated in Table S1. The 4th column is simulated for a tip height at the onset of repulsion, i.e., the appearance of bright features, above the respective molecule. Columns 5 – 7 are recorded at tip heights where atomic resolution is obtained on different parts of the molecule: In column 5 for atomic resolution on the parts that are most protruding from the surface and in column 7 for the parts that are closest to the surface, and in column 6 for a tip height in between.

The three experimentally observed structures of intermediates we assigned to structures 2, 2' and 2'', for which AFM simulations and measurements fit well. In addition, the differences in the
height of the most protruding carbon atom for these \(2\) and \(2'\) (see Table S1), fits well with force distance spectroscopy (see Fig. S9, not measured for \(2''\)).

From the other potential intermediates for which adsorption geometries and AFM images have been calculated we can with high confidence rule out structures \(20, 21, 22, 23,\) and \(25\) which do not fit to the experimental AFM data. In the simulated AFM images of structures \(20-23,\) at the onset of repulsive interaction (4th column), the entire outline of the molecule appears with dark contrast, in contrast to the experiment. In addition, the range of tip-sample distances to simulate AFM images from the onset of repulsive/bright contrast at the highest part to repulsion on the lower laying parts of the molecule is smaller than in the experiment. The simulated contrast of structure \(25\) is significantly different to any of the measured molecules.

The simulated images of structure \(24,\) however, are similar to those of \(2.\) Also, the height of the most protruding carbon atom above the copper surface differs by less than 0.1 Å for these two structures. The main difference is the amount of out of plane orientation of the six-membered ring in the lower right, best observed in the simulations at second to closest tip-sample distance (column 6). While this carbon ring shows faint contrast variation in case of \(2,\) the contrast variation is more pronounced for \(24,\) due to the larger out of plane tilt. Since the experimental image (see Fig. 4d of the main text) shows barely any contrast variation in this carbon ring, we tentatively exclude structure \(24.\)

| Structure | Distance of most protruding C atom from Cu surface | Tip-height difference of simulated AFM images in Fig. S10, between columns 4 to 5 | 5 to 6 | 6 to 7 |
|-----------|-----------------------------------------------|-----------------------------------------------|--------|--------|
| 2         | 5.31                                          | 2.8                                           | 0.4    | 0.4    |
| 20        | 4.19                                          | 1.2                                           | 0.3    | 0.5    |
| 21        | 3.01                                          | 0.5                                           | 0.2    | 0.4    |
| 22        | 3.72                                          | 0.6                                           | 0.3    | 0.5    |
| 23        | 3.89                                          | 0.8                                           | 0.2    | 0.5    |
| 2'        | 4.71                                          | 1.9                                           | 0.4    | 0.4    |
| 24        | 5.39                                          | 2.8                                           | 0.4    | 0.3    |
| 2''       | 4.64                                          | 1.5                                           | 0.3    | 0.4    |
| 25        | 5.51                                          | 1.6                                           | 1.0    | 0.5    |

**Table S1:** Additional parameters of DFT calculations and AFM simulations on possible reaction intermediates shown in Fig. S10, in Å.
3. References

[1] S. Nobusue, H. Yamane, H. Miyoshi, Y. Tobe, Org. Lett., 2014, 16, 1940
[2] F. J. Giessibl, Appl. Phys. Lett. 1998, 73, 3956–3958.
[3] T. R. Albrecht, P. Grütter, D. Horne, D. Rugar, J. Appl. Phys. 1991, 69, 668–673.
[4] L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, Science 2009, 325, 1110–1114.
[5] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, Comput. Phys. Commun. 2009, 180, 2175–2196.
[6] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
[7] P. Hapala, G. Kichin, C. Wagner, F. S. Tautz, R. Temirov, P. Jelinek, Phys. Rev. B 2014, 90, 085421.
[8] B. Schuler, W. Liu, A. Tkatchenko, N. Moll, G. Meyer, A. Mistry, D. Fox, L. Gross, Phys. Rev. Lett. 2013, 111, 106103.