

## Electronic Supplementary Information

# On-Surface Polymerization of 1,4-Diethynylbenzene on Cu(111)

Johanna Eichhorn,<sup>a,b</sup> Wolfgang M. Heckl,<sup>a,b,c</sup> and Markus Lackinger<sup>\*a,b,c</sup>

a) Department of Physics & TUM School of Education, Tech. Univ. Munich, Schellingstrasse 33, 80799 Munich, Germany

b) Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany

c) Center for NanoScience (CeNS), Schellingstrasse 4, 80799 Munich, Germany

\* Corresponding Author: E-mail: markus@lackinger.org, Tel: +49 89 2179 605

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## 1. Experimental Details

All experiments were conducted with a Scanning-Tunneling-Microscope (Omicron VT) at room temperature under ultra-high vacuum (UHV) conditions with a base pressure below  $2 \times 10^{-10}$  mbar. All STM images were recorded with a SPM-100 control electronics from RHK using the XPM Pro 2.0.1.3 software. Lattice parameters and intermolecular distances were derived from STM topographs with an accuracy of ~5% after calibration with atomically resolved topographs of highly oriented pyrolytic graphite(001).

Single crystal Cu(111) surfaces were prepared by cycles of Ar<sup>+</sup> ion-sputtering at 1 keV and annealing at 550 °C for 45 minutes. The cleanliness of the substrate was verified by STM imaging prior to deposition.

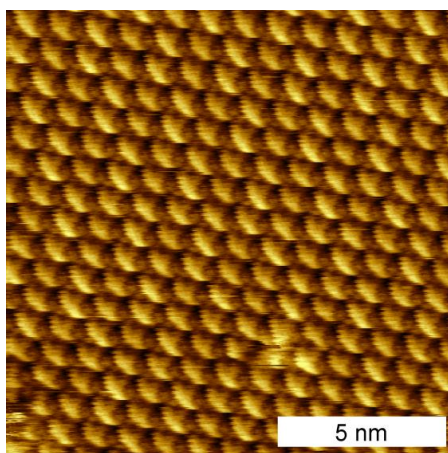
The monomer 1,4-diethynylbenzene (DEB) (CAS 935-14-8, purity  $\geq 95.5$  %) with the chemical formula C<sub>10</sub>H<sub>6</sub> and a molecular weight of 126.15 amu was obtained from Sigma Aldrich Germany. DEB was deposited through a precision leak valve with a metal capillary connected to the outlet to guide the molecules to the sample.

During deposition the Cu(111) substrate was either held at room temperature or heated to 300 °C.

## 2. Additional STM topographs

### 2.1. DEB deposited onto Cu(111) – without further thermal treatment

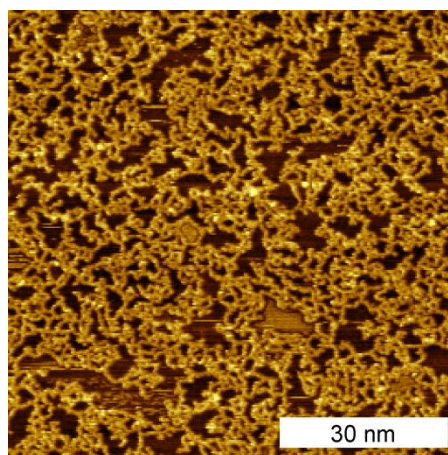
Deposition of DEB onto Cu(111) held at room temperature leads to self-assembled monolayers. The STM image depicted in Fig. S1 clearly confirms that all molecules have similar azimuthal orientation. The image is slightly distorted due to thermal drift.



**Fig. S1:** STM topographic image (11.6 mV, 0.9 pA) of a DEB monolayer prepared by deposition onto Cu(111) held at room temperature.

### 2.2. DEB deposited onto Cu(111) – after thermal treatment

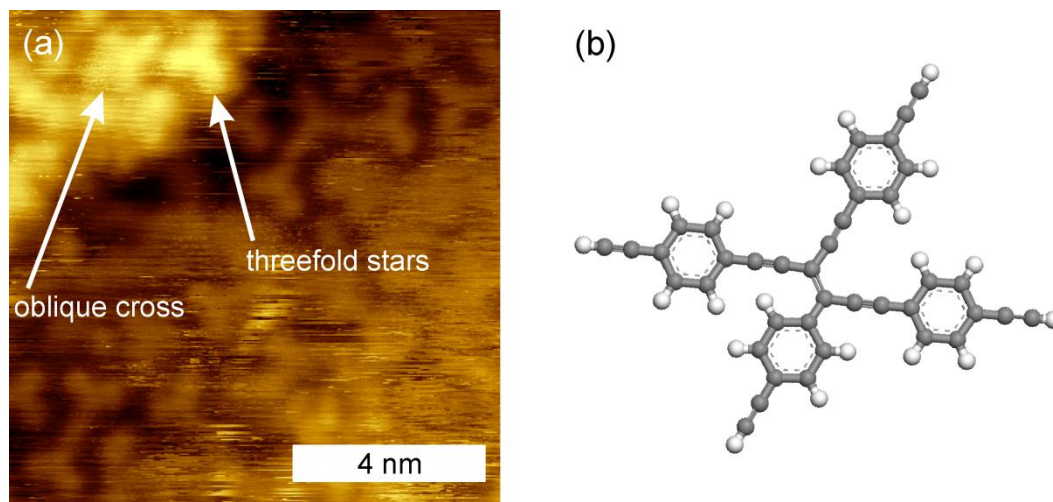
Annealing self-assembled DEB structures to 300 °C results in drastic structural changes. An overview STM image obtained at room temperature after cooling down is depicted in Fig. S2



**Fig. S2:** Overview STM image (-0.72 V, 2.3 pA) of an annealed DEB monolayer on Cu(111) obtained at room temperature after the sample was cooled down. Thermally activated reactions yield covalent networks

The high-resolution STM image presented in Fig. S3 shows different structural motifs resulting from self-reactions of DEB on Cu(111). In the upper left corner, a threefold star adjacent to an oblique cross can be recognized. The threefold star is also threefold symmetric, i.e. all lobes have similar length, whereas the oblique

cross features three similar lobes and one shorter lobe, in good agreement with the DFT simulation shown in Fig. S2(b).

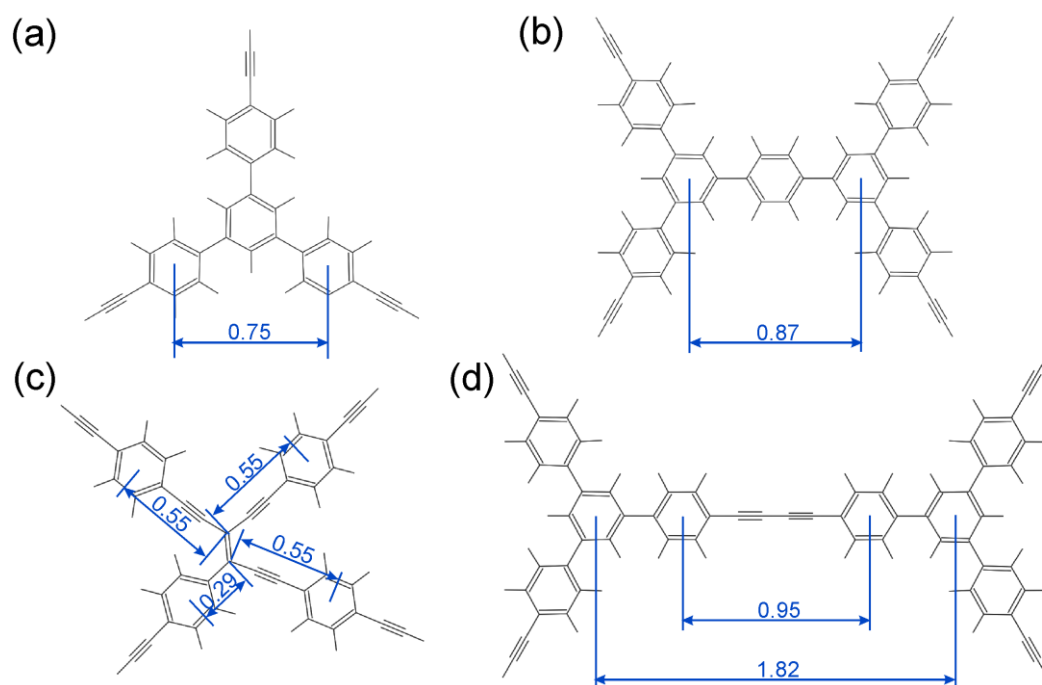


**Fig. S3:** (a) STM topograph (0.4 V, 1.7 pA) of reacted DEB on Cu(111). The sample was annealed to 300 °C for 60 min.  
(b) DFT optimized geometry of an oblique cross.

### 3. DFT details and results

#### Covalent aggregates

Intramolecular distances derived from density functional theory calculations of threefold star, small and large dumbbell, and oblique cross are summarized in Fig. S3. Optimized geometries were used for a precise structural comparison with the STM data. DFT calculations were conducted for isolated molecules using the Gaussian03 package with a B3LYP functional and a 6-31G\* basis set applying standard convergence criteria.<sup>1</sup> The surface influence was mimicked by fixing the z-coordinates of all atoms.

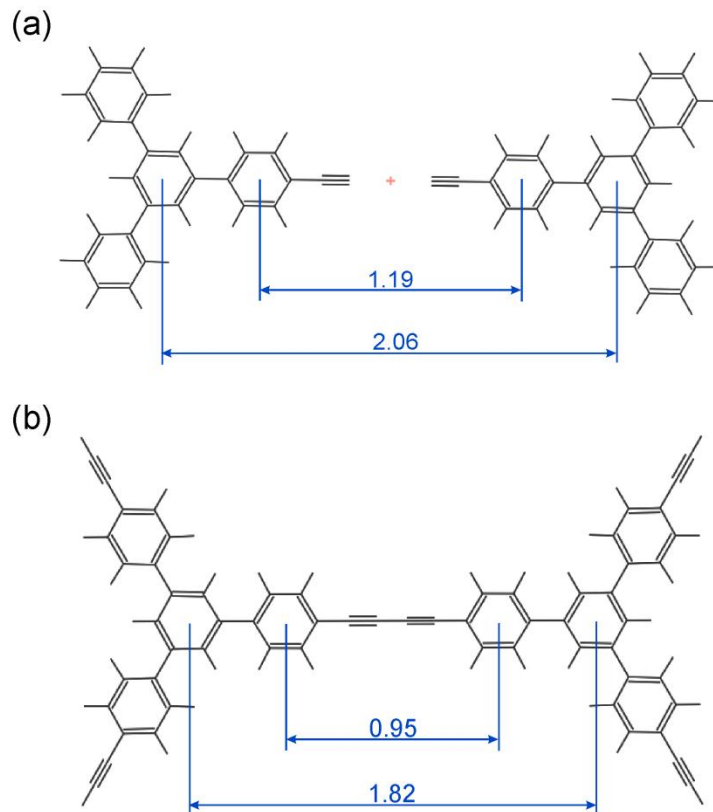


**Fig. S4:** Intramolecular distances from DFT geometry optimized structure of experimentally observed reaction products of DEB (a) trimerization (b) sequential double trimerization (c) cross-coupling and (d) combined trimerization and homo-coupling. All distances are given in nm. Based on these calculations, we anticipate that size differences between (b) and (d) are clearly distinguishable in STM measurements.

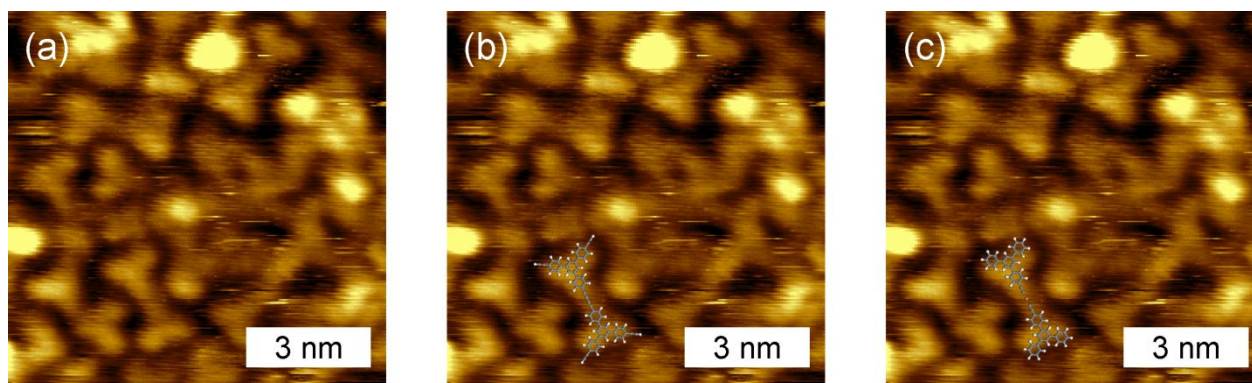
#### Metal-coordinated complexes

Additional DFT calculations were conducted for a direct size-comparison of the large covalent dumbbell with a copper coordinated 1,3,5-tris(4'-ethynylphenyl)benzene dimer, the closest matching metal-coordinated complex. The latter is a hypothetical aggregate that might form on the surface between deprotonated ethynyl groups and copper adatoms. As before, DFT calculations were conducted for isolated structures using the Gaussian03 package with a B3LYP functional and a 6-31G\* basis for hydrogen and carbon, whereas a LanL2DZ basis set is used for copper applying

standard convergence criteria.<sup>1</sup> Results are shown in Fig. S5. Straight metal-coordination bonds are ~0.24 nm longer than the direct covalent carbon-carbon bond. This bond length difference is large enough to safely exclude formation of coordination complexes with copper adatoms based on distance measurements in STM data.



<sup>5</sup> **Fig. S5:** Intramolecular distances from DFT geometry optimized structure of (a) copper coordinated (peripheral ethynyl groups discarded) and (b) homo-coupled trimerized DEB. All distances are given in nm.



<sup>10</sup> **Fig. S6:** (a) STM topograph (0.8 V, 1.2 pA) of reacted DEB on Cu(111) after annealing at 300°C for 60 min. Overlays with the DFT optimized structures of (b) the larger covalent dumbbell and (c) the copper coordinated 1,3,5-tris(4'-ethynylphenyl)benzene dimer. Due to the obvious mismatch the metal-coordination complex can be ruled out.

## References

1. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, J. R. C. M. A. Robb, G. Scalmani, V. Barone, B. Mennucci, H. N. G. A. Petersson, M. Caricato, X. Li, H. P. Hratchian, J. B. A. F. Izmaylov, G. Zheng, J. L. Sonnenberg, M. Hada, K. T. M. Ehara, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, O. K. Y. Honda, H. Nakai, T. Vreven, J. A. Montgomery, Jr., F. O. J. E. Peralta, M. Bearpark, J. J. Heyd, E. Brothers, V. N. S. K. N. Kudin, T. Keith, R. Kobayashi, J. Normand, A. R. K. Raghavachari, J. C. Burant, S. S. Iyengar, J. Tomasi, N. R. M. Cossi, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, C. A. V. Bakken, J. Jaramillo, R. Gomperts, R. E. Stratmann, A. J. A. O. Yazyev, R. Cammi, C. Pomelli, J. W. Ochterski, K. M. R. L. Martin, V. G. Zakrzewski, G. A. Voth, J. J. D. P. Salvador, S. Dapprich, A. D. Daniels, J. B. F. O. Farkas, J. V. Ortiz, J. Cioslowski, and a. D. J. Fox, *Gaussian, Inc., Wallingford CT, 2010*.