Supporting Information

Synthesizing Highly Regular Single-Layer Alkynyl–Silver Networks at the Micrometer Scale via Gas-Mediated Surface Reaction

Yi-Qi Zhang,*†‡ Tobias Paintner,†‡ Raphael Hellwig,†‡ Felix Haag,† Francesco Allegretti,† Peter Feulner,† Svetlana Klyatskaya,‡ Mario Ruben,‡§ Ari P. Seitsonen,‡ Johannes V. Barth,† and Florian Klappenberger,*†

†Physics Department E20, Technical University of Munich, D-85748 Garching, Germany
‡Institute of Nanotechnology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany
§IPCMS-CNRS, Université de Strasbourg, 23 rue de Loess, 67034 Strasbourg, France
† Département de Chimie, École Normale Supérieure, 24 rue Lhomond, F-75005 Paris, France

*Email: yiqi.zhang@tum.de; florian.klappenberger@tum.de
†‡ These authors contributed equally.

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Methods

Sample preparation
All experiments were performed under ultrahigh vacuum (UHV) conditions (base pressure $p_{\text{base}} < 2.0 \times 10^{-10}$ mbar). After standard crystal cleaning cycles and molecular deposition at $T_{\text{sub}} = 200$ K, the as-prepared samples were kept at different substrate temperatures and exposed to molecular O$_2$ (or CO, H$_2$O) gas, which was introduced into the preparation chamber by backfilling via a leak valve or through a directional needle doser (XPS experiments). The synthesis of the 1,3,5-tris(4-ethynylphenyl)benzene (Ext-TEB) was reported earlier.

Scanning tunneling microscopy (STM)
STM measurements were carried out in a commercial Joule-Thomsom STM (base pressure $p_{\text{base}} < 2.0 \times 10^{-10}$ mbar). Data were recorded at an equilibrium temperature of 4.5 K.

X-ray photoelectron spectroscopy (XPS)
The XP spectra were recorded in a custom-built UHV chamber with a base pressure of about $4 \times 10^{-11}$ mbar using a SPECS Phoibos 100 CCD hemispherical analyzer in normal emission geometry and standard, non-monochromatized Mg Ka radiation ($h\nu = 1253.6$ eV). The pass energy of the analyzer was set to 15 eV in combination with a $7 \times 20$ mm$^2$ entrance slit and open exit slit, and the large area mode was used. The binding energy was calibrated against the Ag 3d$_{5/2}$ line of Ag(111) at 368.3 eV. For fitting of the XPS core-level spectra, a Shirley (C 1s) or linear (O 1s) background was subtracted from the raw data, and Voigt functions were used to reproduce the individual chemically shifted components.

Low-energy electron diffraction (LEED)
The LEED patterns were recorded using the BDL800IR-LMX-ISH spectrometer (by OCI Vacuum Microengineering Inc.) in the same chamber of the XPS experiments. The sample temperature was kept either at 90 K or 295 K. To avoid artifacts due to electron-induced damage, the LEED experiments were always performed after the XPS acquisition.

Temperature-programmed desorption (TPD)
The TPD measurements were performed with a quadrupole mass spectrometer mounted behind a copper-cap, with the distance between the aperture of the latter and the Ag(111) sample adjusted as close as possible (millimeter range). In order to minimize the pressure in the ionizer region, the inner surface of the copper-cap served to pump residual gases via deposition of a reactive titanium getter film and cryogenic trapping by liquid nitrogen cooling. In addition, during all experiments the combination of a cold trap, operated with liquid nitrogen flow, and a titanium sublimation pump reduced the chamber background pressure to the mid $10^{-11}$ mbar range.

Density functional theory (DFT)
The DFT calculations on the network were performed with the QuickStep module of the CP2K (https://www.CP2K.org/) software. We applied the rB86-vdW-DF2 approximation to the exchange-correlation energy in the Kohn-Sham equations. The Kohn-Sham orbitals were
expanded in the basis set DZVP-MOLOPT (DZVP-MOLOPT-SR on Ag)\textsuperscript{6} of Gaussian functions and the electron density with plane waves up to the cut-off energy of 700 Ry in the Gaussian-plane wave method\textsuperscript{7} together with Goedecker-Teter-Hutter type of pseudo potentials.\textsuperscript{8} Explicit diagonalization with Fermi-Dirac occupation numbers with a width of 300 K was applied. Due to the large size of the system we modeled the substrate with two rigid layers, and we relaxed only the adatoms and molecules. Only $\Gamma$-point sampling was used in the integration over the first Brillouin zone.

To obtain DFT-XPS signatures, firstly, core-level shifts (CLSs) of all carbon atoms were obtained in the initial state approximation, i.e., using the C 1s Kohn-Sham all-electron eigenvalues weighted with the projection of those orbitals at each of the C atom sites, calculated via the Gaussian augmented plane wave method.\textsuperscript{9} Secondly, a simulated XPS spectrum was generated by summing up Voigt peaks centered at the energies of the CLSs and expressing shapes and widths adapted from the experimental fitting procedure. An offset energy was added to the theoretical CLSs to align the maximum intensity of the resulting theoretical spectrum with the experimental one. The energy deviation between calculated and experimental fitting components is due to the approximations in the exchange-correlation functional and the electronic structure not taking into account the presence of the core hole.

The DFT calculations of gas-phase structures used in Figures S1, S2, S3 and S6 have been performed using the ORCA quantum chemistry code.\textsuperscript{10}
Figure S1. (a) Large overview STM image of intact Ext-TEB molecules self-assembled on Ag(111). $I_t = 0.1$ nA, $U_b = 1$V. (b) High-resolution STM image of an intact Ext-TEB island. $I_t = 0.1$ nA, $U_b = 1$V. (c) Zoom-in image of an Ext-TEB island with superimposed molecular models and proposed registry. $I_t = 0.1$ nA, $U_b = 1$V. (d) Simulated LEED pattern using the parameters of the molecular unit cell shown in Figure S1c, (cf. also Figure S9a).

The elementary unit cell of the intact layer displayed in Figure S1c can be expressed in matrix representation as $egin{pmatrix}  \tilde{d} \\ \tilde{b} \end{pmatrix} = \begin{pmatrix} 5 & -3 \\ 3 & 8 \end{pmatrix} \begin{pmatrix} \tilde{\mu} \\ \tilde{\nu} \end{pmatrix}$. \cite{1,2} $|\tilde{\mu}| = |\tilde{\nu}| = 2.889 \text{ Å}$ and $|\tilde{d}| = |\tilde{b}| = 20.22 \text{ Å}$. The structural optimization of the intact monomer has been performed in gas phase and the B3LYP exchange-correlation functional\cite{11,12} and the def2-SVP basis set was used.
Figure S2. STM image of a domain comprising deprotonated Ext-TEB molecules on the Ag(111) surface ($I_t = 0.1$ nA, $U_b = -0.5$ V). The DFT molecular models as well as the Ag lattice are superimposed with proposed registries.

The elementary unit cell of the deprotonated layer can be expressed in matrix representation as $\begin{pmatrix} \vec{a} \\ \vec{b} \end{pmatrix} = \begin{pmatrix} 8 & -1 \\ 7 & 1 \end{pmatrix}$. $|\vec{a}| = |\vec{b}| = 2.889 \text{ Å}$ and $|\vec{a}| = |\vec{b}| = 21.8 \text{ Å}$. The structural optimization of the deprotonated monomer has been performed in gas phase and the B3LYP exchange-correlation functional$^{11,12}$ and the def2-SVP basis set was used.

The packing geometry of the molecules is in close resemblance to that of the deprotonated Ext-TEB/Cu(111) system.$^{13}$ The stabilizing interaction can be classified as a trifurcated ionic C–H···π$^6$ hydrogen bond between the ionic alkynyl groups and the methane moieties of the adjacent benzene rings. Note that the DFT gas-phase optimization led to a flat geometry of the molecules, whereas in the case of the deprotonated Ext-TEB/Cu(111) both near-edge X-ray absorption fine structure (NEXAFS) measurements and DFT calculations with underlying surface revealed that the alkynyl groups are bent down toward the surface.$^{13}$ Slightly deviating from the packing geometry of deprotonated Ext-TEB/Cu(111), in Figure S2 the molecules with adsorption site B are slightly azimuthally rotated with respect to those on site A.
Figure S3. STM and XPS characterization of Ext-TEB/Ag(111) exposed to low O$_2$ dosage at a substrate temperature of 200 K. (a) STM image of sub-monolayer sample after exposing to 6 L O$_2$. $I_t = 0.1$ nA, $U_b = -1$ V. (b) DFT gas-phase modeling (RPBE-D3BJ/def2-SVP) of a three Ext-TEB molecule cluster (cf. yellow dashed squares in (a)) with one terminal alkyne deprotonated (highlighted by red). (c) STM image of the same sample after a total exposure of 66 L O$_2$. $I_t = 0.1$ nA, $U_b = -0.1$ V. (d) C 1s XPS spectra of a sub-monolayer Ext-TEB/Ag(111) before and after O$_2$ treatment at $T_{sub} = 200$ K.

It can be seen that after dosing $\approx$6 L O$_2$, a small amount of terminal alkynes has been deprotonated, which can be rationalized in terms of formation of small Ext-TEB clusters (cf. Figure S3b). With increasing O$_2$ dosage (≈66 L), small islands with close-pack geometry appear, Figure S3c. Via XPS characterization of a submonolayer sample under similar treatment, it can be estimated that $\approx$60% percent of the terminal alkynes have been deprotonated upon $\approx$60 L O$_2$ exposure. The formation of small islands (Figure S3c) could be interpreted in terms of the molecules at the island edge being not fully deprotonated, as corroborated by the XPS results, thus hindering further growth of the islands. After dosing $\approx$120 L O$_2$, the deprotonation ratio can be estimated as $\approx$80%. 

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Figure S4. DFT-XPS calculations. (a,b) DFT-optimized geometries for intact Ext-TEB and alkynyl-Ag network on Ag(111), respectively. (c,d) DFT simulated C 1s spectra for the two systems. The color coding for each component is consistent with that of the atoms in the molecules in (a) and (b). Black curves are the sum of all components. Their energy positions at maximum intensity have been aligned in accordance with the experimental values. Gray bars in (c,d) indicate the core-level shifts of the individual C atoms. The shape and width of each component are adapted from experimental fitting values. The DFT calculations employ periodic boundary conditions, thus molecules in (a,b) are fully supported by the substrate.

After geometry relaxation, the core-level shifts of all atoms have been calculated and are indicated in Figure S4c and S4d as gray bars. Atoms that have similar core-level shifts have been grouped and color-coded (red, purple, green and blue). For the adsorbed intact molecule, phenyl carbon atoms featuring C-H bonds contribute to the main component at around 285 eV (purple curves in Figure 1c and Figure S4c). Alkyne carbon atoms are responsible for the low binding energy component (red curve in Figure S4c), which is however indistinguishable in the experimental spectrum, thus contained in the purple curve (Figure 1c). The two remaining species (Figure S4c, blue and green) generate a higher binding energy shoulder at around 285.5 eV, again contained in one peak (blue) in Figure 1c due to the small relative shifts experimentally unresolvable.

In the case of the alkynyl-Ag network on Ag(111) (cf. Figure S4b and S4d), the core levels of the alkynyl atoms shift about 0.4 eV towards lower energies (red curve in Figure
S4d) and become experimentally resolvable as the emerging low binding energy shoulder (red) in Figure 1c. Thus, the performed DFT calculations corroborate our experimental assignment and demonstrate that both carbon atoms of an alkynyl group are involved in the organometallic bonding.

Ruling out desorption of HOO$^+$ and H$_2$O$_2$ as by-products

One possible mechanism of O$_2$-induced deprotonation can be rationalized by the formation of oxirene as a primary intermediate product, a 4π-annulene which subsequently undergoes pericyclic ring expansion to give alkynyl- and hydroperoxyl radicals (HOO$^+$). Oxirene intermediates have been postulated and verified in peracid oxidation of terminal alkynes.$^{14,15}$ The hydroperoxyl radical$^{16-18}$ can desorb directly from the Ag(111) surface or may combine with a surface hydrogen atom to generate H$_2$O$_2$ prior to desorption.

In order to trace the putative oxygen-involved reaction by-products species, i.e., HOO$^+$ or H$_2$O$_2$, we carried out TPD measurements employing a home-built mass spectrometer (cf. Methods). The time-dependent TPD data zooming into a m/z range from 32 to 34 have been recorded during exposure of the intact Ext-TEB/Ag(111) sample held at 200 K to O$_2$ gas (total O$_2$ amount $\approx$ 600 L). Notably, XPS studies show that 120 L O$_2$ would trigger deprotonation reaction among $\approx$ 80% of terminal alkyne groups (cf. Figure S3d).

Since the natural distribution of oxygen isotopes is $^{16}$O : $^{17}$O : $^{18}$O = 99.76% : 0.04% : 0.2%,$^{19}$ we tried to monitor the variation of the peak area ratios as a function of time, given that the reaction produced HOO$^+$ (amu = 33) or H$_2$O$_2$ (amu = 34), which would change the peak area ratios between the three masses in the reaction time window. However, as displayed in Figure S5d, there is no clear time dependence in the plots of the relative peak area ratios. Three ratios presented in Figure S5d are close to ideal values of 0.0008, 0.004 and 0.2 corresponding to the relative abundance between $^{16}$O$^{16}$O, $^{16}$O$^{17}$O and $^{16}$O$^{18}$O.$^{19}$ Therefore, within the sensitivity of the measurements, we conclude that HOO$^+$ or H$_2$O$_2$ are not likely to be possible reaction by-products, thus pointing to a more sophisticated reaction pathway taking place at the interface.
Figure S5. Time-dependent TPD data zooming in $m/z$ between 30.5–35.5 upon dosing O$_2$ onto intact Ext-TEB/Ag(111) at $T_{\text{sub}} = 200$ K. (a) Time evolution of the TPD spectra. Note that two different color scales are applied to two areas separated by the grey line. (b) Selected single-profile display of intensity versus time at $m/z = 32$, corresponding to the horizontal dashed red line in (a). (c) Selected single-profile display of intensity versus $m/z$ at time = 500 s, corresponding to the vertical dashed orange line in (a). (d) The evolution of peak area ratios between the three masses as a function of time. amu denotes unified atomic mass unit.
Figure S6. High-resolution STM image of a domain comprising Ag-*bis*-acetylide motifs on the Ag(111) surface ($I_t = 0.1$ nA, $U_b = -0.2$ V). The high-symmetry directions of the Ag(111) surface are indicated. The models of Ext-TEB alkynyl-silver dimers and hexamers are obtained via gas-phase DFT calculations (B3LYP/def2-SVP).
Figure S7. Impurities in the Alkynyl-Ag network. (a) STM zoom-in image in a subregion of Figure 2a in the text. $I_t = 0.1$ nA, $U_b = -0.1$ V. (b) High-resolution STM image of the area highlighted by the dashed rectangle in (a). $I_t = 0.1$ nA, $U_b = -0.1$ V. Bright protrusions in the network correspond to the adsorbed impurities. Trapped molecules with a triangular shape are also present and imaged with lower brightness.
Figure S8. Large-scale STM overview image of a sample prepared by dosing O\textsubscript{2} (≈6000 L) onto Ext-TEB/Ag(111) held at 300 K (\(I_t = 0.1\) nA, \(U_b = -1.0\) V).

Mild annealing a submonolayer Ext-TEB/Ag(111) sample at \(T_{\text{sub}} = 300\) K under UHV condition free from O\textsubscript{2} gas yields covalent dimers together with remaining intact monomers.\textsuperscript{20} In contrast, exposing the submonolayer Ext-TEB/Ag(111) at \(T_{\text{sub}} = 300\) K to O\textsubscript{2} yields two types of domains: the alkynyl-Ag network (phase I) and organometallic macrocycles (phase II, cf. also Figure S6).

It can be seen that the alkynyl-Ag networks terminate mostly with zigzag edges and do not continue when crossing steps. This reparation also infers that excessive O\textsubscript{2} gas treatment (cf. also Figure S3d) will not trigger further chemical transformations in the alkynyl-Ag networks.
Figure S9. (a) LEED pattern of intact Ext-TEB molecules at submonolayer coverage on Ag(111) taken at 90 K. (b) LEED pattern of the alkynyl-Ag network formed at a submonolayer coverage upon O₂ exposure at $T_{\text{sub}} = 200$ K ($T_{\text{meas}} = 90$ K). (c) LEED pattern of the alkynyl-Ag network taken at $T_{\text{meas}} = 295$ K. Red circles mark the first-order diffraction spots of Ag(111). The yellow and blue circles in (a) highlight the first-order diffractions spots of supramolecular Ext-TEB domains with two different orientations, consistent with the reported STM results (cf. Figure S1d). The yellow circles in (b,c) highlight the first-order diffraction spots of the alkynyl-Ag network, in agreement with the STM measured parameters.
Figure S10. (a) Overview STM image of alkynyl-Ag network after annealing at 450 K ($I_t = 0.1$ nA, $U_b = -1.0$ V). (b) Zoomed-in image of an area in (a), featuring irregular structures, broken connections as well as distorted pores ($I_t = 0.1$ nA, $U_b = -0.2$ V).
Reactions among coadsorbed oxygen species and Ext-TEB molecules on Ag(111)

In an alternative preparation procedure, the Ext-TEB/Ag(111) was exposed to O$_2$ gas ($\approx$6000 L) at $T_{\text{sub}} = 90$–100 K, leading to coadsorption of oxygen species as well as Ext-TEB molecules (cf. Figure S11a). XPS characterization of this sample shows that both molecular as well as atomic oxygen were present on the surface (Figure S12b), being consistent with earlier studies.$^{21,22}$ The main peak in the C 1s spectrum shifts significantly ($\approx$0.6 eV) to the lower energies with a developed component at 283.6 eV, similar to the O$_2$-induced changes at $T_{\text{sub}} = 200$ K (Figure 1c). Annealing this sample to 200 K yielded reaction products other than purely deprotonated Ext-TEB. There are additional species coexisting with Ext-TEB silver-acetylides (Figure S11b,d). Firstly, the surface was covered with depressions, which have been recently identified as vacancies surrounded by oxygen atoms.$^{23}$ Secondly, the wriggling stripes as well as sombrero-shaped protrusions (Figure S11d) also indicate the presence of O atoms, which is in a close resemblance to the O/Ag(110) system.$^{24}$ The presence of atomic oxygen species was confirmed by the O 1s spectra, in which a peak at around 530 eV remained after annealing at 200 K (Figure S12b). Further annealing this sample to 300–400 K resulted in irregular molecular structures and small silver islands (Figure S11e,f), whereby the latter were very likely formed by the extracted Ag atoms upon O$_2$ dissociation. Notably, in this temperature range the atomic oxygen species (dark holes in Figure S11e,f) remain on the surface (cf. also XPS data in Figure S12b).
Figure S11. (a) STM overview image of a sample with coadsorbed Ext-TEB and oxygen species on Ag(111) prepared at $T_{\text{sub}} = 100$ K. $I_t = 0.1$ nA, $U_b = 1.0$ V. (b) STM overview image of the same sample annealed at 200 K. $I_t = 0.1$ nA, $U_b = -0.1$ V. (c) Zoomed-in image of the area outline by a rectangle in (a). $I_t = 0.1$ nA, $U_b = 1.0$ V. (d) Zoomed-in image of the area outlined in (b). $I_t = 0.1$ nA, $U_b = -0.1$ V. (e) STM overview image of the same sample after annealing at 300 K. $I_t = 0.1$ nA, $U_b = -0.1$ V. (f) STM overview image of the same sample after annealing at 400 K. $I_t = 0.1$ nA, $U_b = -1.0$ V.
Figure S12. C 1s and O 1s XPS spectra of Ext-TEB/Ag(111) exposed to O\textsubscript{2} gas (∼6000 L) at $T_{\text{sub}} = 90$ K. A series of annealing steps were performed in sequence.
References:


