Electronic Supplementary Information (ESI[†])

for

Two-dimensional delocalized states in organometallic *bis*-acetylide networks on Ag(111)

Zechao Yang,¹ Julian Gebhardt,^{2,†*} Tobias A. Schaub,^{3,§} Tim Sander,¹ Jörg Schönamsgruber,³ Himadri Soni,² Andreas Görling,² Milan Kivala,^{3,*} Sabine Maier^{1,*}

- ¹ Department of Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Erwin-Rommel-Straße 1, 91058 Erlangen, Germany
- ² Chair of Theoretical Chemistry, Department of Chemistry and Pharmacy, Friedrich-Alexander-University Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany
- ³ Chair of Organic Chemistry I, Department of Chemistry and Pharmacy, Friedrich-Alexander-University Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

Corresponding Author

*E-mail: <u>sabine.maier@fau.de</u>

*E-mail: milan.kivala@fau.de

*E-mail: julian.gebhardt@fau.de

[†] Present address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

[§] Present address: Department of Chemistry & Biochemistry, University of Oregon, Eugene, OR 97403-1253, USA

1. Supplementary STM Data



Source of Ag adatoms for the formation of organometallic Ag-bis-acetylide networks

Figure S1. (a) STM image upon deposition of **Br-TET** on the Ag(111) surface at room temperature. Pits with a measured depth of around 2.5 Å (b) are observed, which is comparable to the step height of a monatomic step on the Ag substrate. The pits have been assigned as monolayer-deep defects that provide a source of Ag adatoms for the formation of organometallic networks. STM parameters: U = 1 V, I = 50 pA.



Rotational domains of the organometallic Ag-bis-acetylide networks

Figure S2. STM images showing the two rotational domains of the networks on Ag(111). In (a) the **TET**-Ag-**TET** bridge is rotated 30° towards the $[1\overline{10}]$ direction of the substrate, while in (b) it is rotated by around 4°. STM parameters: (a) U = 0.3 V, I = 50 pA, (b) U = -0.3 V, I = 100 pA.

Confinement of surface electrons in the organometallic Ag-bis-acetylide networks



Figure S3. (a) STM topography image of the organometallic *bis*-acetylide network after depositing **Br-TET** on Ag(111) at RT. (b) The corresponding constant current dI/dV map shows the confinement of surface electrons within the pores of the organometallic network. The energy of the confined state depends on the geometry and size of the confining cavity. Therefore, the contrast within the pores in the measured dI/dV map in (b) varies. STM parameters: (a)-(b) U = 0.4 V, I = 180 pA.

2. Supplementary DFT Data



Figure S4. Calculation of free-standing dimer structures. Distances and binding energies of various dimer structures calculated by DFT. In comparison, we obtained an experimental value of $d=12.1\pm0.5$ Å on Ag(111) for the Br-TET network. The table shows that the experimentally proposed structure agrees well with the calculated distance *d* for the C-Ag-C bonding motif.



Figure S5. Fully relaxed network (a) and the relaxed polymer compressed to the lateral dimensions of the Ag(111) surface (b). The effect of this compression on the electronic structure is shown in (c-e). The band structure of the fully relaxed geometry (red) is compared with the one of the compressed structure (blue). Overall (c and d), the differences are negligible, despite there are some small changes in the band dispersion and relative energy shifts not larger than ~0.05 eV upon compression. This is with one exception: Due to the compression, the flat valence bands of the network show changes on a very small energy scale, leading to a fractional occupation of the HOMO state of the relaxed structure in the compressed case. Note, that this is due to the employed level broadening scheme and that both cases are likely to be small gap systems for T=0 K or metallic at elevated temperatures. More importantly, these small changes in the dispersion also shift the position of the smallest gap away from the M point in the relaxed system.



Figure S6. ELF for exemplary metalorganyls, namely a classical organyl HgMe₂ (a), a silver organyl AgMe (b), and a hypothetical silver organyl bound to two carbon moieties $AgMe_2(c)$ as present in our acetylide bonded networks for ELF values of 0.74, 0.75, and 0.78, respectively. This demonstrates the ionic character of such typical metal organic bonds, with no electron pair localized between the C and the metal atom, in contrast to truly covalent bonds, e.g. as shown for the C-H bonds.



Figure S7. Effective masses determined for the free-standing relaxed (a and b) and compressed (c) network, using VB and CB along MK before (a) and after (b) the VB maximum and in the vicinity of M along Γ M (c). Effective masses are obtained by fitting the bands quadratically, in order to determine $\frac{\partial^2 E}{\partial k^2}$ analytically, from which the effective mass is determined via $m^* = \frac{\hbar^2}{2\frac{\partial^2 E}{\partial k^2}}$. For electrons (CB) and holes (VB) we obtain effective masses of $m_h^*(a) = 1.96m_e$, $m_e^*(b) = 1.41m_e$, $m_h^*(b) = 2.23m_e$, $m_e^*(c) = 0.53m_e$, and $m_h^*(c) = 0.82m_e$ (note that $m_e^*(a)$ was not determined since a quadratic approximation is clearly not applicable in this direction).

3. Synthesis of the precursors

General. Starting materials were purchased reagent grade from Acros and Sigma-Aldrich and used without further purification. Acetone was dried over K_2CO_3 and subsequently distilled over $CaCl_2$. 2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-triazine¹ was prepared according to a procedure from the literature. Reactions were carried out in flame-dried glassware and under an inert atmosphere of purified N₂ using Schlenk techniques. Thin-layer chromatography (TLC) was performed on the aluminum plates coated with 0.20 mm thickness of Silica Gel 60 F-254 (Macherey-Nagel). Column chromatography was performed on silica gel (230–400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.1 MHz for ¹H and 100.6 MHz for ¹³C) in CD₂Cl₂ at RT. Chemical shifts (δ) are reported in ppm and were referenced to the residual solvent signal as an internal reference (CD₂Cl₂, 5.32 ppm for ¹H and 53.8 for ¹³C). Coupling constants (*J*) are given in Hz and the apparent resonance multiplicity is reported as s (singlet). Mass spectra were obtained from a MicrOTOF II (Bruker, HR ESI and APPI) mass spectrometer. The signal of the molecular ion [M]⁺ is reported in *m/z* units. Infrared spectra (IR) spectra were recorded on a 660-IR (Varian, ATR mode) spectrometer. Characteristic IR absorptions are reported in cm⁻¹ and denoted as strong (s) and medium (m).

Synthesis



2,4,6-tris(2-bromoethynyl)-1,3,5-triazine (Br-TET). Under N₂ atmosphere and in the absence of light 2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine (100 mg, 0.27 mmol) was dissolved in dry, deoxygenated acetone (14 mL). *N*-Bromosuccinimide (217 mg, 1.22 mmol, 4.5 equiv.) and silver nitrate (69.0 mg, 0.41 mmol, 1.5 equiv.) were added and the reaction mixture was stirred for 16 h at RT. The solvent was removed under reduced pressure and the residues were dissolved in CH₂Cl₂ and filtered through a plug of Celite (CH₂Cl₂). The residue was purified by column chromatography (SiO₂, CH₂Cl₂/hexanes 2:1) to give product **Br-TET** as a white solid (45.3 mg, 43%) that was stable for several weeks at -20 °C. $R_f = 0.69$ (SiO₂, CH₂Cl₂/hexanes 2:1); IR (ATR): \tilde{v} 2195 (s), 1478 (s), 1344 (m) 817 (m), 657 (m) cm⁻¹¹; HR-ESIMS (MeOH, positive mode): calculated for C₉HBr₃N₃ ([M + H]⁺) 387.7715, found 387.7713; Owing to decomposition in solution ¹³C NMR spectra could not be obtained.

4. References

1. Kouvetakis, J.; Grotjahn, D.; Becker, P.; Moore, S.; Dupon, R. Chem. Mater. 1994, 6, 636-639.