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SUPPLEMENTARY INFORMATION

Steering alkyne homocoupling with on-surface synthesized metal-organic complexes

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METHODS

The experiments in this work were run on a commercial Scienta-Omicron low-temperature scanning probe system operating at 4.3 K under ultra-high vacuum. The surface of Au(111) single crystal of was cleaned by Ar^+ sputtering and subsequent annealing cycles. The crystal was then let to cool down to room temperature in the preparation chamber before the molecules were sublimed from home-built Knudsen-cell evaporators. The sublimation temperatures of BMB and 1-ethynyl pyrene molecules are 380 K and 300 K respectively.

STM measurements were performed with a Pt/Ir tip sharpened by poking into the bare metal surface. For CO-functionalization of the STM tip, NaCl was deposited on the surface by sublimed at 780 K. The sample is then moved to the STM, cooled down to 4.3 K and exposed to a CO partial pressure of 5E-9 mBar in the STM chamber with open LT-

STM shields. The gas is introduced through a leak valve in the preparation chamber, for which the gate valve between the chambers is opened. The maximum sample temperature reached during this CO deposition process is 7 K. The only reason for NaCl deposition in this work is to facilitate the visualization of carbon monoxide molecules for the subsequent tip functionalization, which results in a notable resolution enhancement and allows for bond-resolving imaging of the molecular structures. The bias values indicated refer to sample bias with respect to the STM tip. dI/dV spectroscopy and mapping were performed with a lock-in amplifier with oscillation frequency set to 731 Hz. STM images were analyzed using WSxM software.[1]

Theoretical AFM images were calculated using the probe particle model.[2] The parameters of the tip were selected to mimic a CO-tip, using a quadrupole with a stiffness of 0.24 Nm-1 and a charge factor of -0.2 e. The electrostatic force was included in the AFM calculations using the hartree potential calculated by DFT.

DFT calculations were performed using the Fritz Haber Institute ab initio molecular simulations package (FHI-AIMS).[2] We used the general gradient approximation PBE potential and Van der Waals corrections were described by Tkatchenko−Scheffler method.[3,4] The structure was relaxed in a 1 layer gold slab with a energy convergence criteria of 10^{-5} eV.

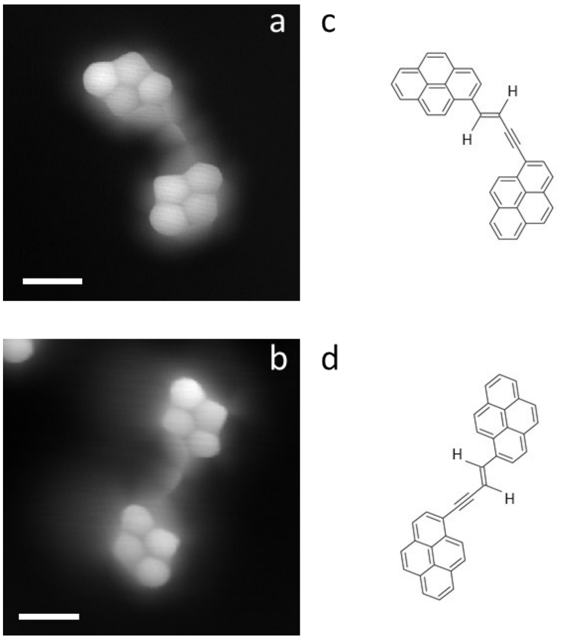

Figure S1. a-b) High-resolution STM images with CO-functionalized probes depicting the cis and trans dimer structures c-d) sharing the same coupling motif. For both a and b: U= 2 mV and Scalebars = 5 Å.

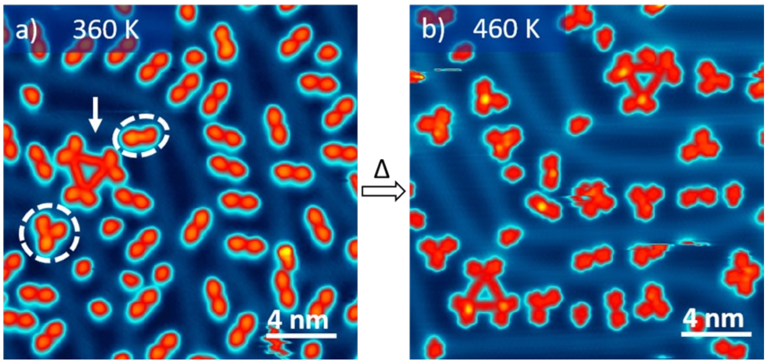

Figure S2. Larger scale STM images of sample with Au_3BMB_3 complexes and **m1** reactants after annealing to 360 K (a) and 460 K (b). It can be seen from the images that, at 360 K, all **m1** molecules remain unreacted, except the dimers directly at the metal-organic complex (marked with an arrow), as well as a nearby dimer and a trimer marked with the white ovals. At 460 K, as occurred in the absence of the metal-organic complexes, most reactants appear covalently bonded into dimers and trimers (occasionally even some tetramers).

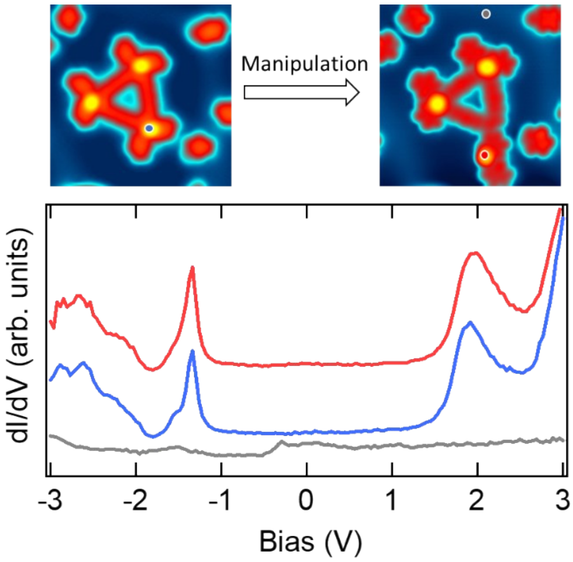

Figure S3. STM images of a **d2**-decorated Au_3BMB_3 complex before and after manipulation. The graph below shows the associated STS spectra of the **d2** dimer before (blue) and after (red) manipulation taken at the same position marked by blue and red dots on the images. The reference spectrum on the bare Au(111) surface is shown in grey.

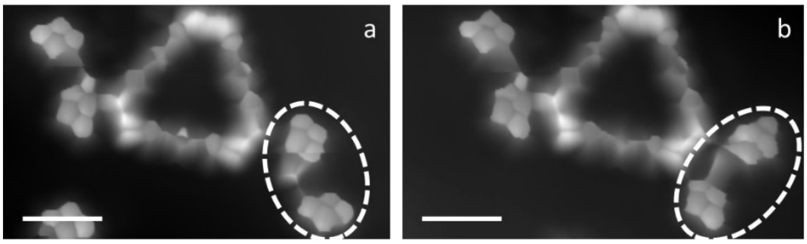

Figure S4. High-resolution imaging of **d2** dimer after manipulation (a) helps for better seeing the chemical structure which cannot be nicely resolved at the vertex due to the nonplanarity of the BMB triangles. By normal constant-height scanning as well as constant-current at low bias voltages we notice the tendency of the manipulated dimer to jump back to their initial position at the vertex (b) although STS data with the associated dI/dV maps show no strong bonding of the dimers at the vertices. Scalebar: 1nm for a and b. U = 2 mV.

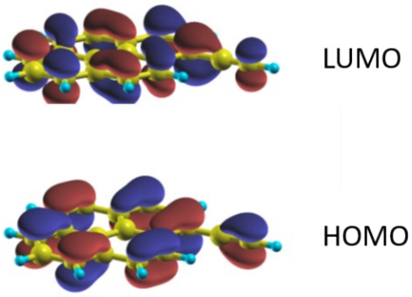

Figure S5. Calculated wavefunctions for the HOMO and LUMO orbitals of the reactant, revealing the HOMO's bonding character and the LUMO's antibonding character on the alkyne.

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