

Supplementary Information

On-surface synthesis of organocopper metallacycles through activation of inner diacetylene moieties

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SYNTHESIS

Reagents were purchased from Merck and used as supplied.

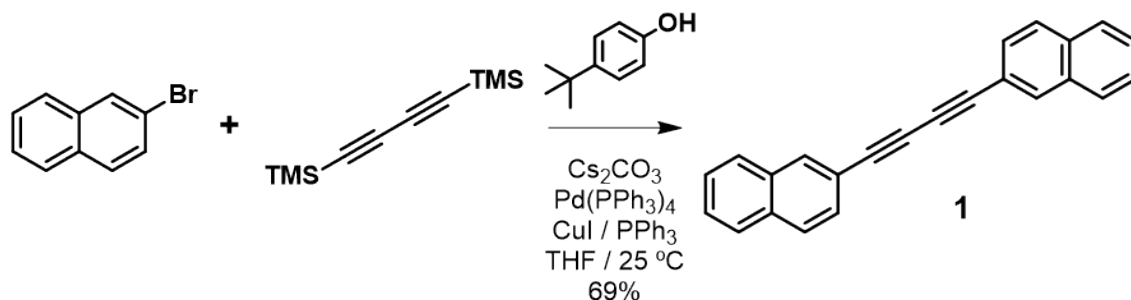


Figure S1. Synthesis of 1,4-di(naphthalen-2-yl)buta-1,3-diyne (**1**).

Following the recipe by M. Shigeta et al.¹, CuI (7 mg, 0.036 mmol) is added to a mixture of 2-bromonaphthalene (500 mg, 2.414 mmol), 1,4-bis(trimethylsilyl)buta-1,3-diyne (235 mg, 1.207 mmol), 4-*tert*-butylphenol (7.25 mg 4.828 mmol), Cs₂CO₃ (4.75 g, 12.07 mmol), Pd(PPh₃)₄ (42 mg, 0.036 mmol), and PPh₃ (9 mg, 0.036 mmol) in dry THF (50 mL), and stirred at 25 °C for 16 h. The reaction mixture is poured into aqueous HCl (2 M, 50 mL) and extracted with DCM (3 × 20 mL), dried over sodium sulfate, filtered and dried under vacuum. The resulting residue is then purified by column chromatography (silica gel, hexane) to yield a yellow solid (69%). ¹H-NMR (400 MHz, CDCl₃): δ = 8.10 (brs, 2H), 7.85-7.80 (m, 6 Hz), 7.57 (dd, *J*₁ = 8.5 Hz, *J*₂ = 1.6 Hz, 2H), 7.54-7.50 (m, 4H) ppm.

References

¹ M. Shigeta, J. Watanabe and G. Konishi, Preparation of arylbutadiyne derivatives by silyl migration inspired by the Mukaiyama protocol. *Asian J. Org. Chem.* 1, 43–46 (2012).

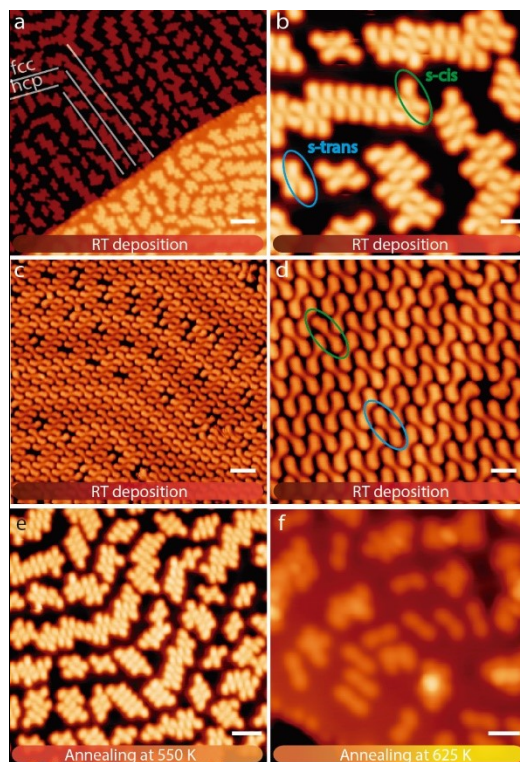


Figure S2. Adsorption, self-assembly and evolution with substrate temperature of **DNBD** on Au(111). a-b) Long-range and zoom-in STM images of the self-assembly observed for 0.4 ML, showing the preferential adsorption of intact species avoiding domain walls of the herringbone reconstruction of the underlying Au(111) substrate. a) Scale bar = 5 nm, $I_t = 50$ pA, $V_b = -1$ V; b) scale bar = 1 nm, $I_t = 200$ pA, $V_b = -1$ V). c) Large-scale and d) zoomed-in STM topography of a close to a monolayer coverage of **DNBD** on Au(111). c) Scale bar = 2 nm, $I_t = 100$ pA, $V_b = -0.25$ V. d) Scale bar = 1 nm, $I_t = 100$ pA, $V_b = -0.25$ V). In b) and d) s-cis and s-trans isomers are encircled in green and blue, respectively. e) STM image after annealing at 550 K for 20 minutes a submonolayer coverage of **DNBD** on Au(111), illustrating that molecular species and their self-assembly are still intact upon thermal annealing (scale bar = 3 nm, $I_t = 100$ pA, $V_b = -1$ V). f) STM topograph of a submonolayer coverage of **DNBD** on Au(111) after annealing at 625 K for 20 minutes, revealing uncontrolled intermolecular reactions (scale bar = 2 nm, $I_t = 50$ pA, $V_b = -1.0$ V).

Component	Binding Energy (eV)	Full width at half maximum (eV)	Relative amount (%)
C-H	284.11	0.61	58.3
C-C sp ²	284.55	0.40	25.0
C-C sp	285.06	0.60	8.3
C-Cu	283.47	0.70	8.3

Table S1. Fitting parameters of the fit of the C 1s signal reported in Figure 2m in the main text.

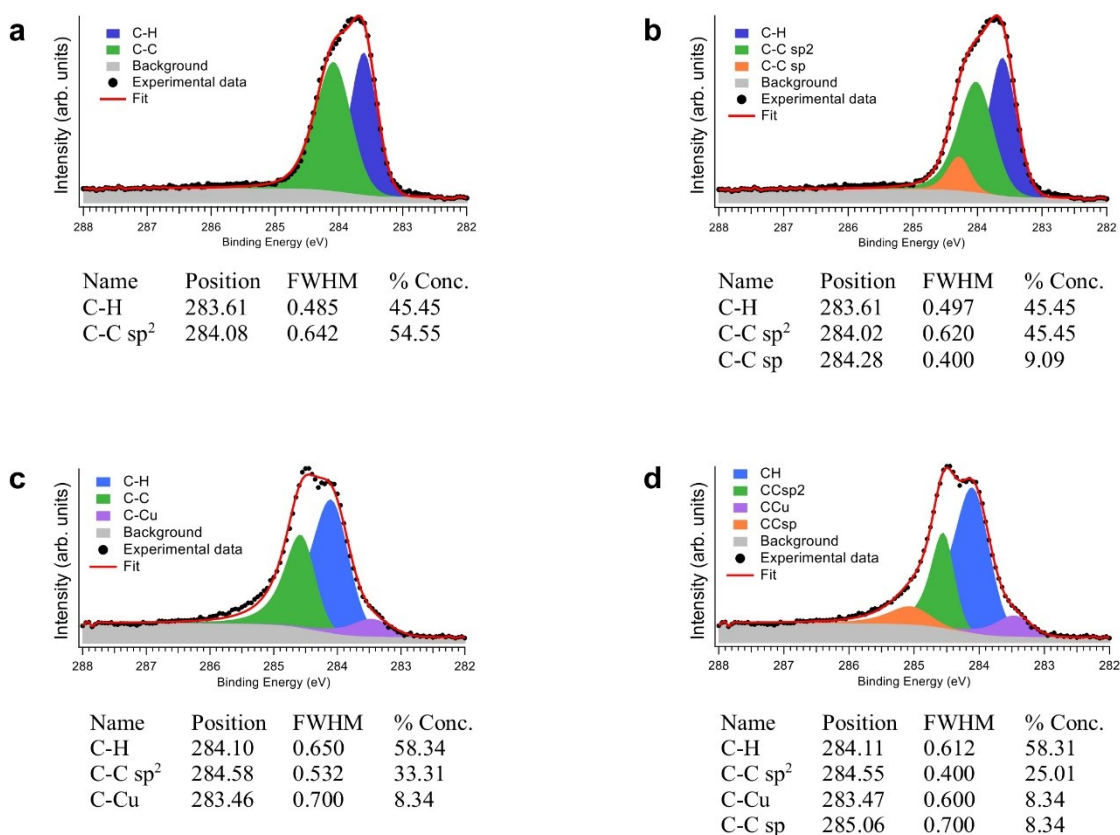


Figure S3. Comparison between deconvolution of the C 1s XPS signal of cumulene polymers reported in *Angew. Chem. Int. Ed.* 2020, 59, 13281–13287 (a,b) and the organocopper metallacycles reported in the present work (c,d). a,c): Fits without the cumulene (sp) component, where the carbon atoms in the cumulene bridge are considered as being the same as those in the sp² hybridization. b,d): Fits where the atoms in the cumulene bridges are considered as being different from those in the sp² hybridization. The lack of a separate cumulene component still produces a good fit of the experimental data in the case of cumulene polymers (a), whereas it leads to a very poor fit for the dimers of the present work (c).

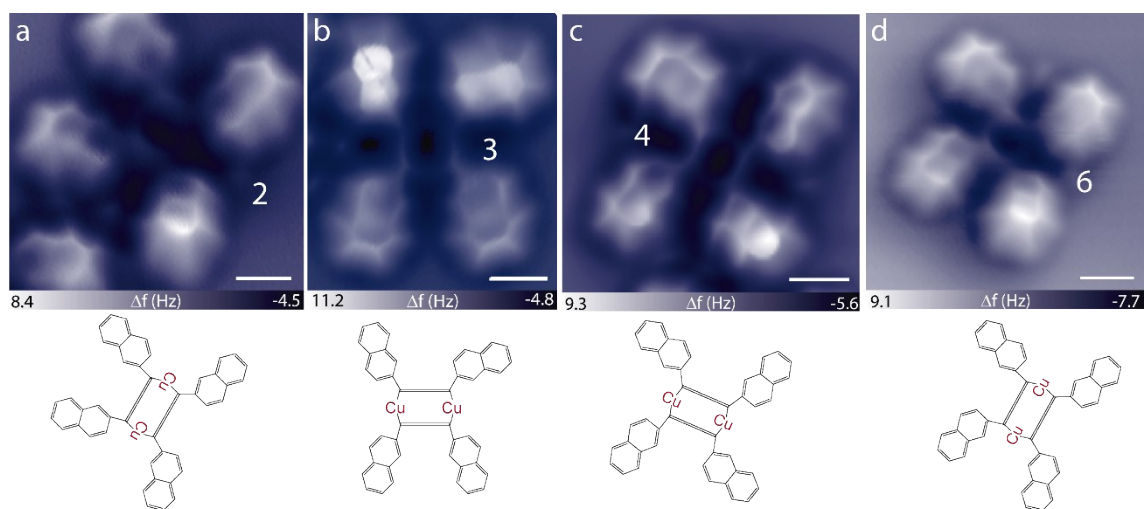


Figure S4. Non-contact AFM images with the corresponding molecular structure of distinct conformations of organocopper metallacycles, as discussed in the main text. Scale bars: 5 Å. The numbers in the nc-AFM images correspond to the numbers in the STM images and molecular structures of Figure 2 in the main text.

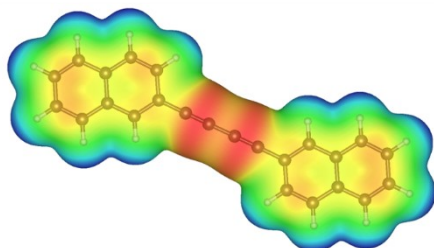


Figure S5. Calculated electrostatic potential surface of a gas-phase **DNBD** precursor. The isosurface level is $0.01e/\text{Å}^3$. Blue and red color scale means positive (electron repulsion) and negative (electron attraction) electrostatic potential, respectively. The plot shows enhanced electron density near the triple C-C bonds.