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-diyn (1).

Following the recipe by M. Shigeta et al.\textsuperscript{1}, CuI (7 mg, 0.036 mmol) is added to a mixture of 2-bromonaphtalene (500 mg, 2.414 mmol), 1,4-bis(trimethylsilyl)buta-1,3-diyn (235 mg, 1.207 mmol), 4-tert-butylphenol (7.25 mg, 4.828 mmol), Cs\textsubscript{2}CO\textsubscript{3} (4.75 g, 12.07 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (42 mg, 0.036 mmol), and PPh\textsubscript{3} (9 mg, 0.036 mmol) in dry THF (50 mL), and stirred at 25 ºC 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%). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.10\) (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

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

| 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                 |

**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\(^2\)) component, where the carbon atoms in the cumulene bridge are considered as being the same as those in the sp\(^2\) hybridization. b,d): Fits where the atoms in the cumulene bridges are considered as being different from those in the sp\(^2\) 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/Å³. 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.