

Supporting Information

Bromine Adatom Promoted C-H Bond Activation in Terminal Alkynes at Room Temperature on Ag(111)

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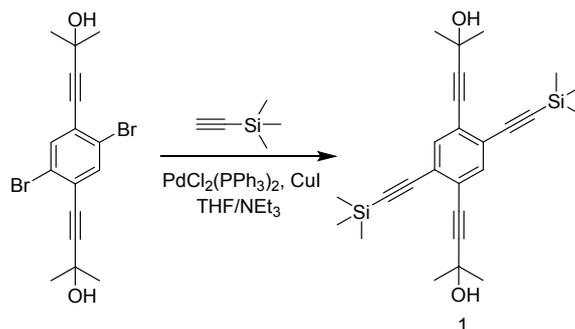
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1. Synthesis of 2Br-DEBPB

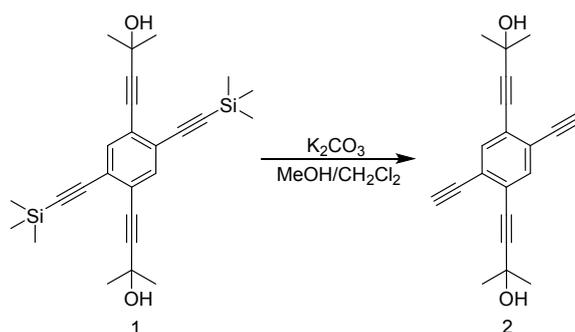
General methods:

¹H NMR spectra was obtained on BRUKER AVANCE III 400 spectrometers. Chemical shifts are reported in parts per million (ppm) with TMS (0 ppm) as the reference. Tetrahydrofuran, triethylamine and toluene were distilled over sodium, calcium hydride, and sodium under nitrogen atmosphere respectively. 4,4'-(2,5-Dibromo-1,4-phenylene)bis(2-methylbut-3-yn-2-ol) was synthesized according to previously reported procedures.¹



Preparation of 1:

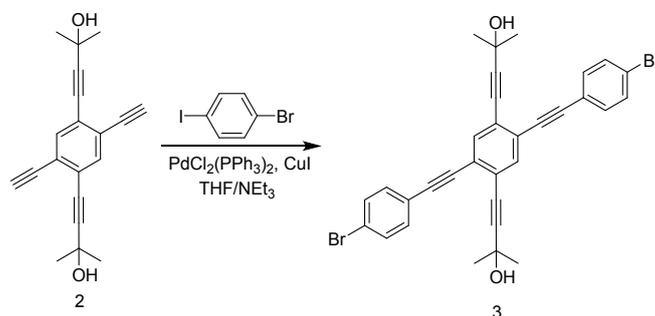
A solid mixture of 4,4'-(2,5-dibromo-1,4-phenylene)bis(2-methylbut-3-yn-2-ol) (400 mg, 1.00 mmol), CuI (19 mg, 0.10 mmol) and PdCl₂(PPh₃)₂ (23 mg, 0.033 mmol) was placed in a Schlenk flask and the flask was evacuated and filled with nitrogen for three times. Then, a solution of ethynyltrimethylsilane (2.450 g, 25 mmol) in tetrahydrofuran (6 mL) and trimethylamine (6 mL) was degassed with nitrogen for 5 min and added to the flask using a syringe under nitrogen atmosphere. The resulting solution was allowed to stir at 80 °C for 24 h. Upon cooling to room temperature, a saturated solution of ammonium chloride (20 mL) was added. The mixture was stirred at room temperature for a few minutes before it was extracted with dichloromethane (30 mL × 3). Organic layers were combined, dried with anhydrous sodium sulfate, and concentrated by rotatory evaporator. The residue was purified by column chromatography (silica gel, dichloromethane/ethyl acetate = 10:1) to give pure compound **1** (256 mg, 59% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (s, 2H), 1.99 (s, 2H), 1.62 (s, 12H), 0.26 (s, 18H).



Preparation of 2:

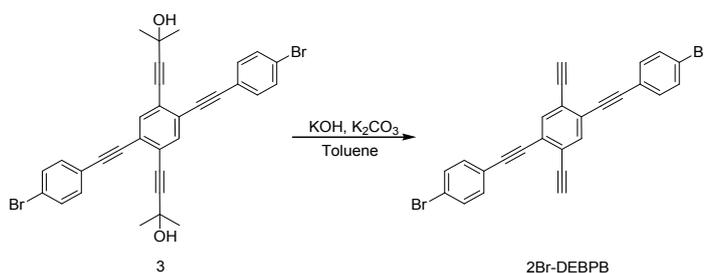
To a solid mixture of compound **1** (256 mg, 0.590 mmol) and potassium carbonate (651 mg, 4.72 mmol) in a round bottom flask, methanol (15 mL) and dichloromethane (15 mL) were added. The resulting solution was degassed with nitrogen for 5 min and stirred at room temperature for 1 h. Then, a saturated solution of ammonium chloride (20 mL) was added and the resulting mixture was extracted with dichloromethane (30 mL × 3). Organic layers were combined, dried with anhydrous sodium sulfate, and concentrated by rotatory evaporator. The

residue was purified by column chromatography (silica gel, dichloromethane/ethyl acetate = 10:1) to give pure compound **2** (142 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.54 (s, 2H), 3.37 (s, 2H), 2.03 (s, 2H), 1.63 (s, 12H).



Preparation of **3**:

A solid mixture of compound **2** (142 mg, 0.490 mmol), 1-bromo-4-iodobenzene (346 mg, 1.22 mmol), CuI (10 mg, 0.053 mmol) and PdCl₂(PPh₃)₂ (17 mg, 0.024 mmol) was placed in a Schlenk flask and the flask was evacuated and filled with nitrogen for three times. Then, tetrahydrofuran (5 mL) and triethylamine (5 mL) were added to the flask *via* syringe under nitrogen atmosphere. The resulting solution was allowed to stir at room temperature for 24 h. Then, a saturated solution of ammonium chloride (20 mL) was added. The mixture was stirred at room temperature for a few minutes before it was extracted with chloroform (30 mL × 3). Organic layers were combined, dried with anhydrous sodium sulfate and concentrated by rotatory evaporator. The residue was purified by column chromatography (silica gel, dichloromethane/ethyl acetate = 10:1) to give pure compound **3** (259 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.60 (s, 2H), 7.50 (d, J=8.4Hz, 4H), 7.41 (d, J=8.3Hz, 4H), 2.05 (s, 2H), 1.64 (s, 12H).



Preparation of **2Br-DEBPB**:

A solid mixture of compound **3** (160 mg, 0.268 mmol), potassium hydroxide (60 mg, 1.1 mmol) and potassium carbonate (74 mg, 0.54 mmol) was placed in a Schlenk flask and the flask was evacuated and filled with nitrogen for three times. Then, toluene (8 mL) was added to the flask *via* syringe under nitrogen atmosphere. The resulting solution was allowed to stir

at 80 °C for 4 h. Upon cooling to room temperature, a saturated solution of ammonium chloride (20 mL) was added. The mixture was stirred at room temperature for a few minutes before it was extracted with chloroform (30 mL \times 3). Organic layers were combined, dried with anhydrous sodium sulfate and concentrated by rotatory evaporator. The residue was purified by column chromatography (silica gel, petroleum ether/dichloromethane = 6:1) to give pure 2Br-DEBPB (63 mg, 49% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.69 (s, 2H), 7.50 (m, 4H), 7.41 (m, 4H), 3.46 (s, 2H).

2. Large-Scale STM Images of the Self-Assembled and Molecule-Br Co-Assembled Structures Formed by 2Br-DEBPB on Ag(111)

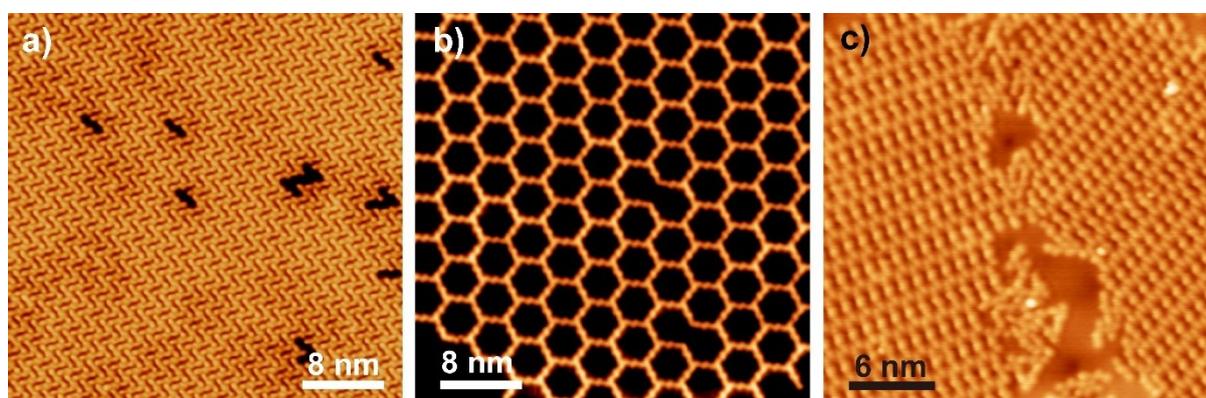


Fig. S1 STM images of (a) densely packed self-assembled chevron structure (120 mV, 100 pA, 4.2 K), (b) loosely packed self-assembled honey-comb structure (100 mV, 100 pA, 4.2 K), and (c) co-assembled structure of the molecule and detached Br adatoms (50 mV, 100 pA, 4.2 K).

3. Extended OM Chains Achieved by Annealing the Sample at 310 K

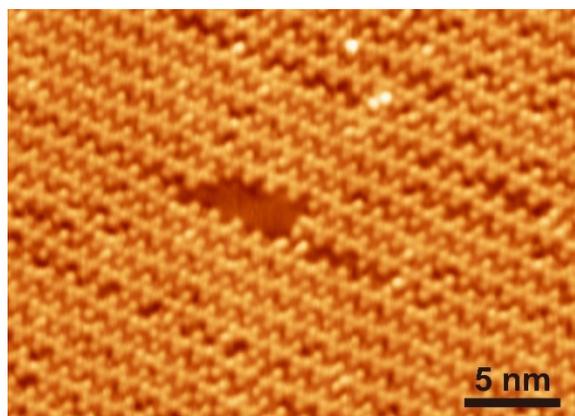


Fig. S2 STM image of the extended OM chains achieved by annealing of the sample at 310 K for 1 h (10 mV, 100 pA, 4.2 K).

4. Desorption of DEBPB on Ag(111) at Room Temperature

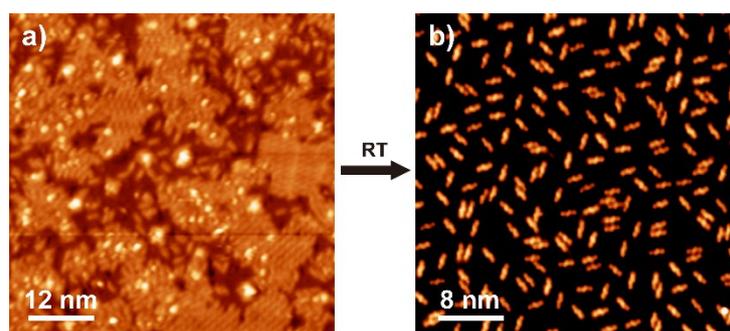


Fig. S3 Decrease in coverage of DEBPB monomers on Ag(111) induced by RT annealing. STM images of the Ag(111) surface (a) immediately after the deposition of DEBPB (210 mV, 100 pA, 4.2 K), and (b) after annealing of the sample at RT (10 mV, 100 pA, 4.2 K).

5. Optimization and Natural Bond Orbital (NBO) Analysis of the Organometallic Dimer in Gas Phase

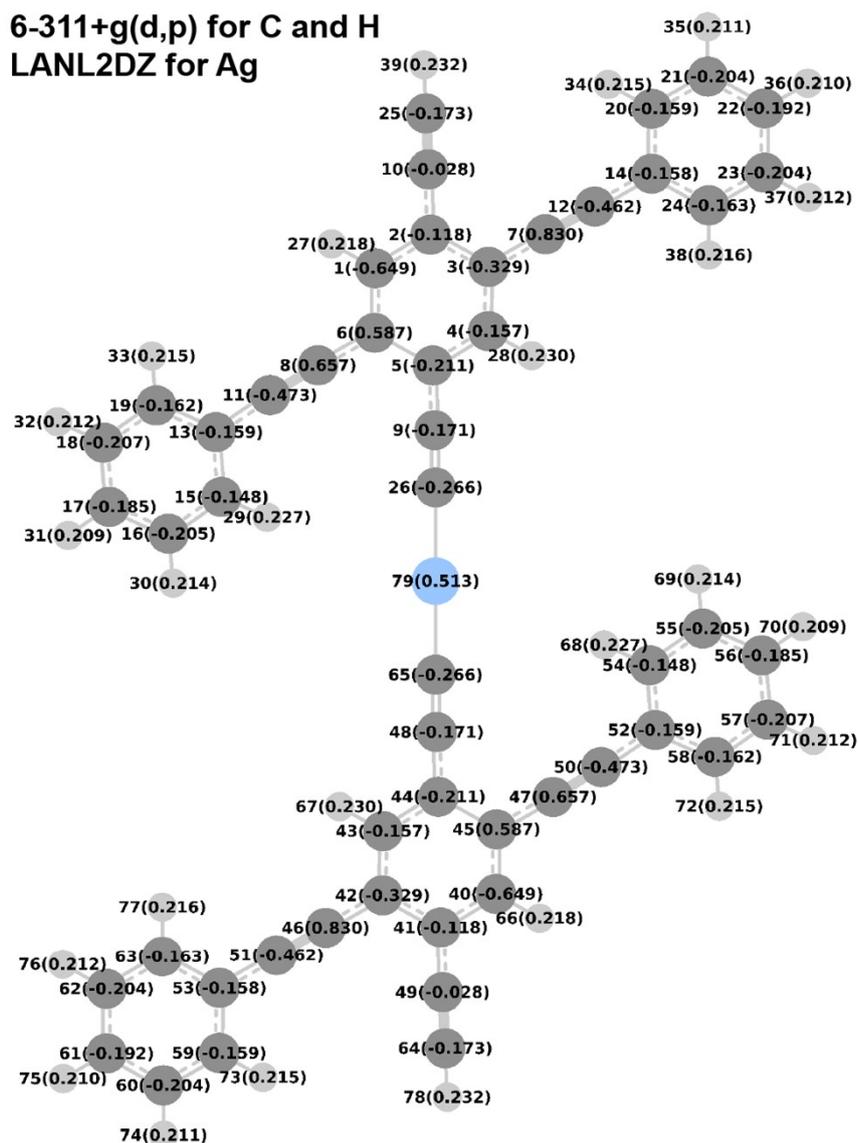


Fig. S4 Optimized model of an organometallic dimer obtained by using 6-311g(d,p) for the C and H atoms, and LANL2DZ basis set with the corresponding ECP⁷⁻¹⁰ for the Ag atom. The values of natural charge are marked by numbers in parentheses on the corresponding atoms.

6. Calculation Details for the Model of 2Br-DEBPB Monomer with an Approaching Br Atom

The geometry of a 2Br-DEBPB monomer was first optimized. Following that, a Br atom was located beside one of the terminal alkynyl groups of the optimized model of 2Br-DEBPB. Then, optimization and NBO analysis of the “2Br-DEBPB monomer + Br atom” model were conducted. In order to mimic the influence of the substrate to the molecular geometry, the molecule was constrained to a planar conformation, and the movement of the atoms in the model was restricted to the plane. Since only the interaction between the Br atom and the

terminal alkynyl group is concerned, apart from the atoms in the two terminal alkynyl groups (C9, C26, H40, C10, C25 and H39) and the atomic Br41, the coordinates of other atoms in the model were frozen. Furthermore, one negative charge was set in the input model to simulate the negative charge state of the Br atom absorbed on Ag surfaces due to the charge transfer with the substrate.^{2,3} All the DFT calculations as described above were performed with the Gaussain09 software⁴ by using B3LYP functional^{5,6} with tight convergence criteria. 6-311+g(d,p) basis set was applied for the C and H atoms in the model, and LANL2DZ basis set with the corresponding effective core potential (ECP)⁷⁻¹⁰ was used for the Br atoms.

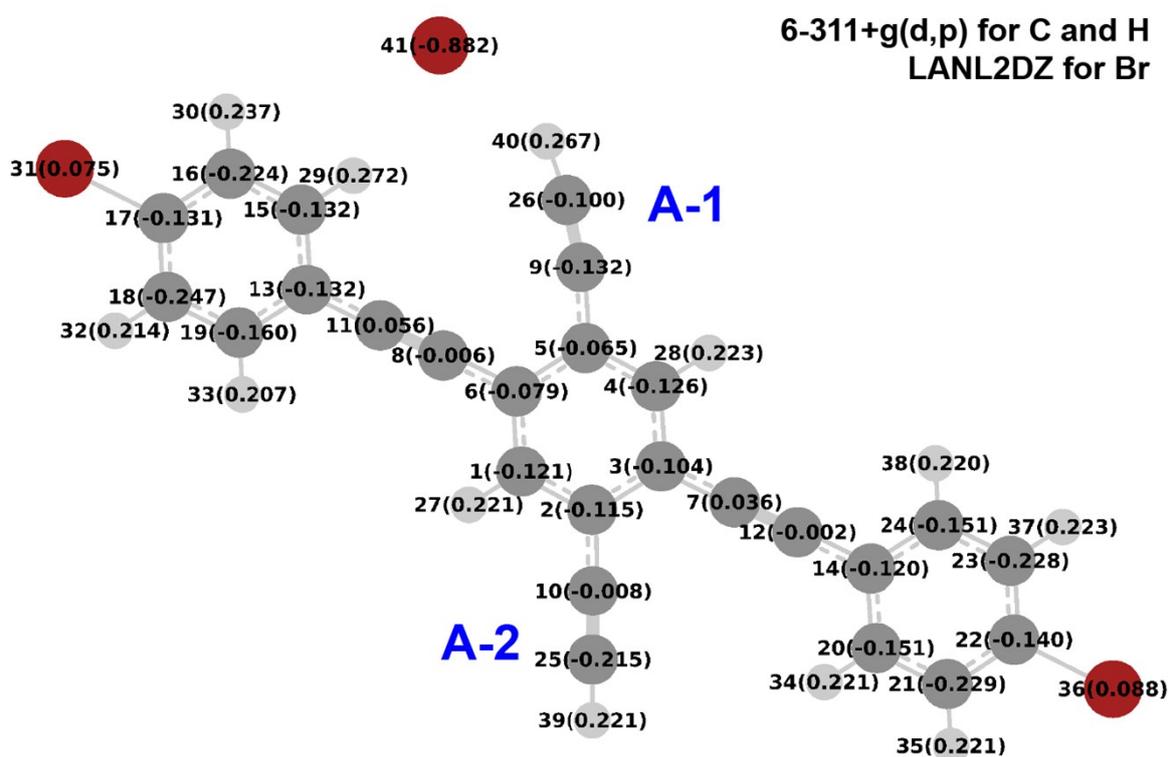


Fig. S5 Optimized model of a 2Br-DEBPPB monomer with a Br atom approaching to one of its terminal alkynyl groups.

7. Proposed C-H Bond Activation Process Promoted by the Br Adatoms on Ag(111)

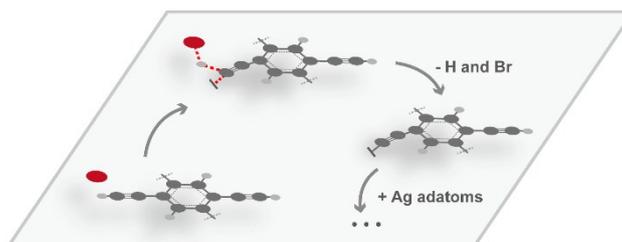


Fig. S6 Schematic illustration of a proposed C-H bond activation process promoted by the Br adatoms on Ag(111).

8. Formation of Alkynyl-Ag Dimers after Annealing of the Sample at RT for 2.5 h

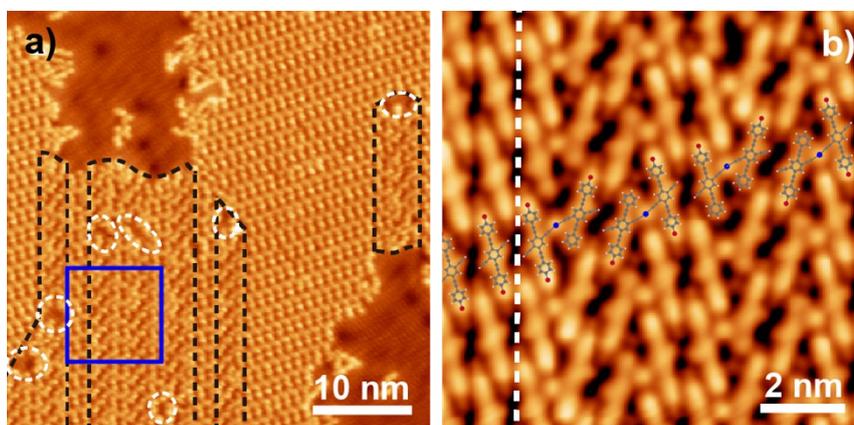


Fig. S7 (a) Large area STM image of the sample after being annealed at RT for 2.5 h (10 mV, 100 pA, 4.2 K). In addition to the molecule-Br co-assembly, a new structure appeared inside the co-assembled domains, as highlighted by the black dashed lines. (b) High-resolution STM image of the area marked by the blue square in (a) (10 mV, 100 pA, 4.2 K). The co-existing molecule-Br co-assembled structure (left part) and the newly formed structure (right part) are separated by a white dashed line. The new structure was formed by packed alkynyl-Ag dimers, as shown by the superimposed molecular models. The defects in the domains of alkynyl-Ag dimers, as highlighted by the white dashed circles in (a), were originated from the reduction in intermolecular distance and the molecular rotation due to the formation of the organometallic dimers, implying that the organometallic dimers were formed by in-situ reaction of the molecules in the molecule-Br co-assembly. This observation also suggests direct conversion of the molecular monomers to the alkynyl-Ag species. Except for the alkynyl-Ag structures, no other organometallic species such as phenyl-Ag-phenyl or phenyl-Ag-alkynyl species were observed on this sample.

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