Supplementary Materials for

Dehalogenative Homocoupling of Terminal Alkynyl Bromides on Au(111): Incorporation of Acetylenic Scaffolding into Surface Nanostructures

Qiang Sun, Liangliang Cai, Honghong Ma, Chunxue Yuan*, Wei Xu*

Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Caoan Road 4800, Shanghai 201804, P.R. China

*To whom correspondence should be addressed. E-mail: xuwei@tongji.edu.cn, cxyuan@tongji.edu.cn

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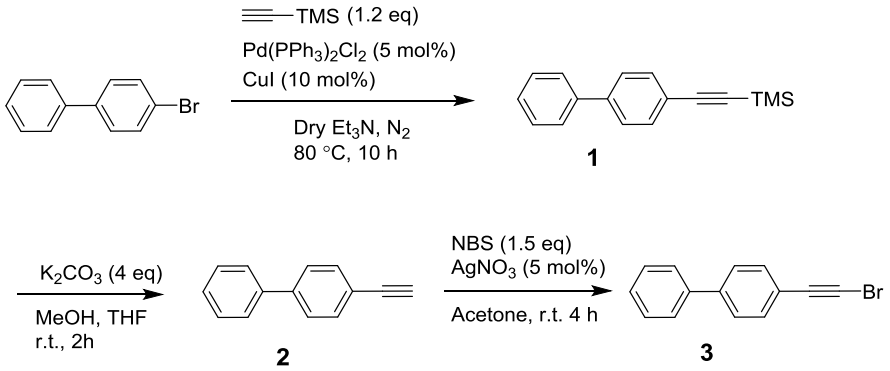
A. Synthesis of the BEBP molecules.

Materials and Methods. All commercially available chemicals were purchased from Adamas, Aldrich and TCI, and used as received without further purification except triethylamine which was distilled over CaH_2. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The chemical shifts are reported in δ ppm with reference to residual protons and carbons of $CDCl_3$ (7.26 ppm in ^1H NMR and 77.16 ppm in ^{13}C NMR). Thin layer chromatography (TLC) was performed on glass plates coated with 0.20 mm thickness of silica gel. Column chromatography was performed using neutral silica gel PSQ100B.

Synthesis.



4-[2-(Trimethylsilyl)ethynyl]-1,1'-biphenyl (**1**):To a mixture of 4-Bromobiphenyl (2.33 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.50 mmol) and CuI (0.18 g, 1.00 mmol) in dry Et_3N (40 mL) was added trimethylsilylacetylene (1.18 g, 12 mmol, 1.7 mL). The reaction mixture was stirred at 80 ℃ for 10 h under N_2 and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.32) to afford **1** (2.10 g, 8.39 mmol, 84% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 – 7.58 (m, 2H), 7.54 (s, 4H), 7.46 – 7.42 (m, 2H), 7.37 – 7.34 (m, 1H), 0.31 – 0.25 (m, 9H).

4-ethynyl-1,1'-biphenyl (**2**): **1** (1.80 g, 7.20 mmol) and K_2CO_3 (3.98 g, 28.80 mmol) were suspended in THF (36 mL) and methanol (16 mL), and stirred for 2 h at r.t.. After the reaction completed (monitored by TLC), the reaction mixture was neutralized with a 1 M HCl solution and was extracted in CH_2Cl_2 and washed with water three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The mixture was purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.35) to afford **2** (1.0953 g, 6.15 mmol, 85% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 – 7.57 (m, 6H), 7.47 – 7.43(m, 2H), 7.39 – 7.35 (m, 1H), 3.13 (s, 1H)

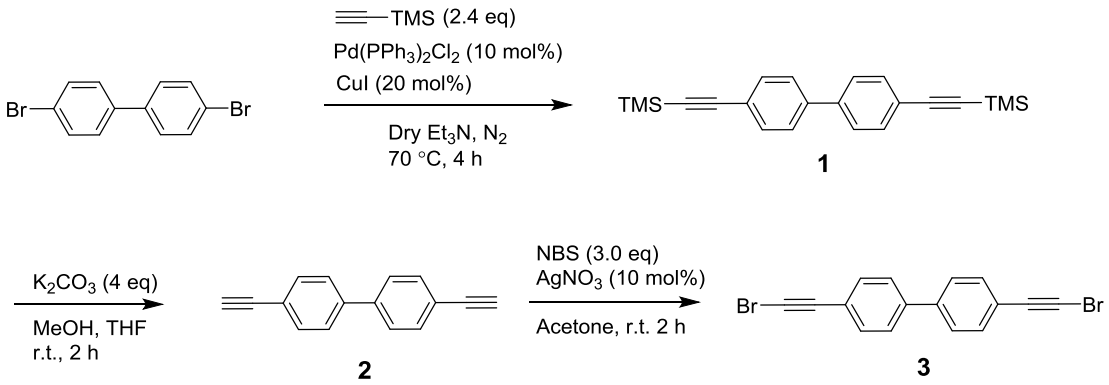
4-(bromoethynyl)-1,1'-biphenyl (**3**): To a solution of **2** (1.08g, 6.04 mmol) in acetone (36 mL)

was added NBS (1.61 g, 9.06 mmol) and $AgNO_3$ (0.05 g, 0.302 mmol) at r.t.. After 4 h (monitored by TLC), the reaction mixture was diluted with hexane (100 mL) and filtered off the crystals formed. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.47) to afford **3** (1.09 g, 4.23 mmol, 70% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 – 7.51 (m, 6H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 140.3, 132.6, 129.0, 127.9, 127.2, 121.7, 80.1, 50.5.

B. Synthesis of the bBEBP molecules.

Materials and Methods. All commercially available chemicals were purchased from Adamas-beta, Aldrich and TCI, and used as received without further purification except triethylamine which was distilled over CaH_2. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The chemical shifts are reported in δ ppm with reference to residual protons and carbons of $CDCl_3$ (7.26 ppm in ^{1}H NMR and 77.16 ppm in ^{13}C NMR). Thin layer chromatography (TLC) was performed on glass plates coated with 0.20 mm thickness of silica gel. Column chromatography was performed using neutral silica gel PSQ100B.

Synthesis.



4,4'-di[(trimethylsilyl)ethynyl]-1,1'-biphenyl (**1**): To a mixture of 4,4'-dibromo-1,1'-biphenyl (1.56 g, 5 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.50 mmol) and CuI (0.18 g, 1.00 mmol) in dry Et_3N (30 mL) was added trimethylsilylacetylene (1.18 g, 12 mmol, 1.7 mL). The reaction mixture was stirred at 70 ℃ for 4 h under N_2 and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/CH_2Cl_2 = 20/1, R_f = 0.32) to afford **1** (1.40 g, 4.03mmol, 81% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 8H), 0.26 (s, 18H).

4,4'-diethynyl-1,1'-biphenyl (**2**): **1** (1.25 g, 3.60 mmol) and K_2CO_3 (3.98 g, 14.40 mmol) were suspended in THF (18 mL) and methanol (8 mL), and stirred for 2 h at r.t.. After the reaction completed (monitored by TLC), the reaction mixture was neutralized with a 1 M HCl solution and was extracted in CH_2Cl_2 and washed with

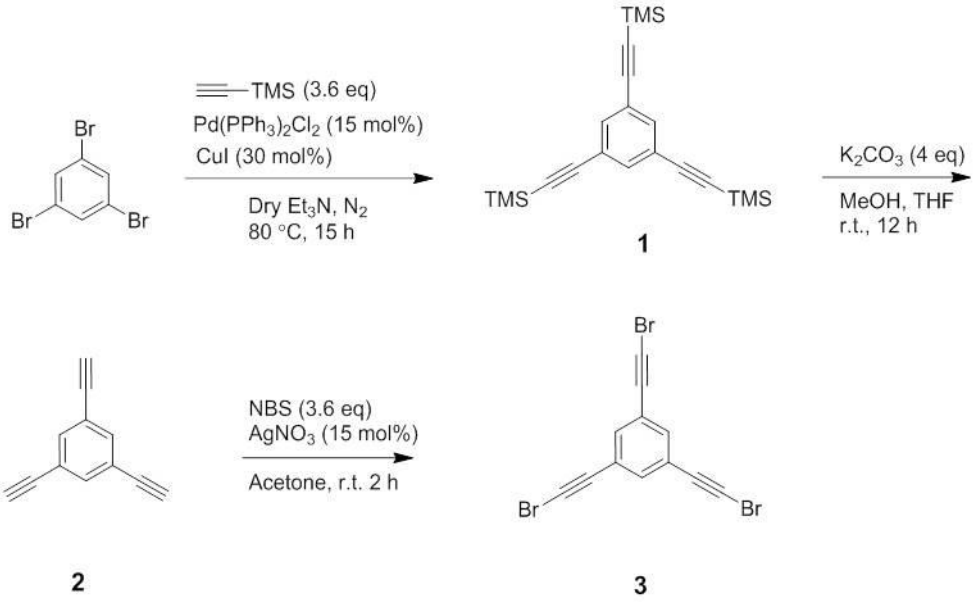
water three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The mixture was purified by column chromatography on silica gel (eluent: petroleum ether/CH_2Cl_2 = 5/1, R_f = 0.61) to afford **2** (0.62 g, 3.07 mmol, 85% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 8H), 3.15 (s, 2H).

4,4'-di(bromoethynyl)-1,1'-biphenyl (**3**): To a solution of **2** (0.06 g, 0.30 mmol) in acetone (4 mL) was added NBS (0.16 g, 0.90 mmol) and $AgNO_3$ (0.005 g, 0.03 mmol, 5 mol %) at r.t.. After 2 h (monitored by TLC), the reaction mixture was diluted with hexane (6 mL) and filtered off the crystals formed. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.47) to afford **3** (0.052 g, 0.14 mmol, 48% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 132.7, 127.0, 122.2, 79.9, 50.9.

C. Synthesis of the tBEP molecules.

Materials and Methods. All commercially available chemicals were purchased from Adamas-beta, Aldrich and TCI, and used as received without further purification except triethylamine which was distilled over CaH_2. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The chemical shifts are reported in δ ppm with reference to residual protons of $CDCl_3$ (7.26 ppm in ^{1}H NMR). Thin layer chromatography (TLC) was performed on glass plates coated with 0.20 mm thickness of silica gel. Column chromatography was performed using neutral silica gel PSQ100B.

Synthesis.



1,3,5-tris((trimethylsilyl)ethynyl)benzene (**1**): To a mixture of 1,3,5-tribromobenzene (0.63 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (0.21 g, 0.30 mmol) and CuI (0.11 g, 0.60 mmol)

in dry Et_3N (30 mL) was added trimethylsilylacetylene (1.0 mL, 7.2 mmol). The reaction mixture was stirred at 80 ℃ for 15 h under N_2 and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.4) to afford **1** (0.4162 g, 1.14 mmol, 57% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 3H), 0.22 (s, 27H).

1,3,5-triethynylbenzene (**2**): **1** (0.36 g, 0.98 mmol) and K_2CO_3 (0.54 g, 3.9 mmol) were suspended in THF (4.5 mL) and methanol (2.2 mL), and stirred for 12 h at r.t.. After the reaction completed (monitored by TLC), the reaction mixture was neutralized with a 1 M HCl solution and was extracted in CH_2Cl_2 and washed with water three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The mixture was purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.26) to afford **2** (0.13 g, 0.95 mmol, 97% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 3H), 3.11 (s, 3H).

1,3,5-tris(bromoethynyl)benzene (**3**): To a solution of **2** (0.103 g, 0.68 mmol) in acetone (12 mL) was added NBS (0.436 g, 2.45 mmol) and $AgNO_3$ (0.017 g, 0.102 mmol, 15 mol %) at r.t.. After 2 h (monitored by TLC), the reaction mixture was diluted with hexane and filtered off the crystals formed. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: petroleum ether, R_f = 0.68) to afford **3** (0.18 g, 0.14 mmol, 68% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 3H).

II. Supplementary STM images.

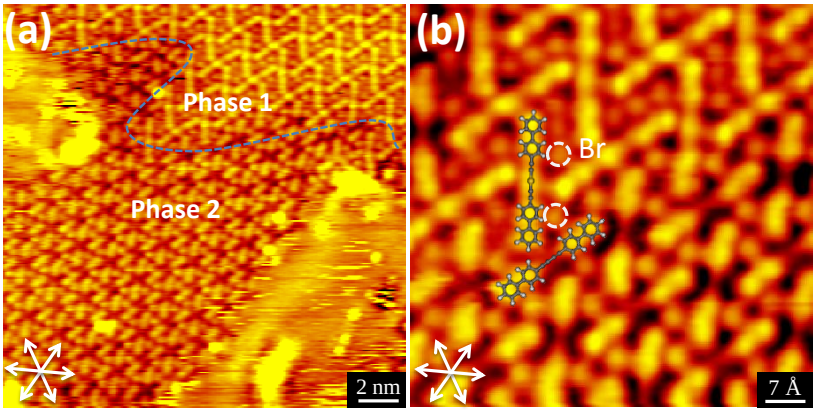


Fig. S1. (a) Large-scale and (b) close-up STM images showing the coexistence of two phases which are composed of C-Au-C organometallic intermediate and C-C diyne compound, respectively. The phase boundary is indicated by blue dashed line in (a). The equally scaled models of two different compounds are superimposed on their corresponding STM features in (b).

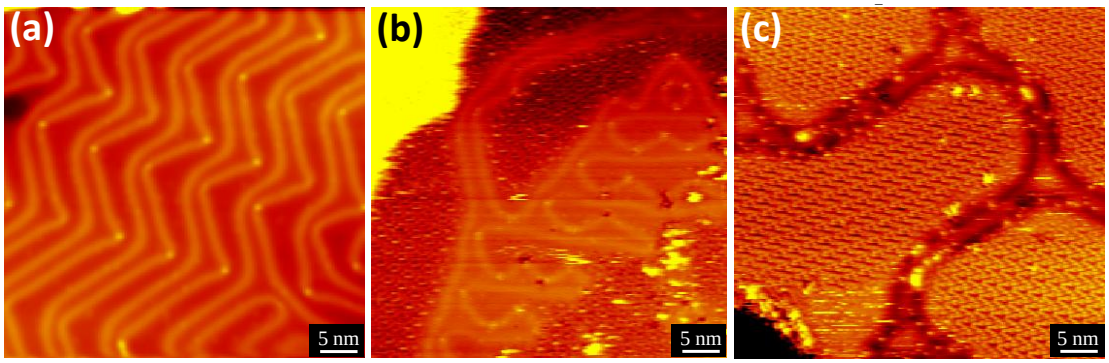


Fig. S2. (a) STM image showing the herringbone reconstruction of a clean Au(111) surface. (b) STM image showing the herringbone reconstruction is lifted after deposition of BEBP molecules on the surface at RT. (c) STM image showing the herringbone reconstruction is not restored after the demetalation from C-Au-C organometallic intermediates to C-C coupled products.