

Supporting Information for

Spectroscopic evidence of new low-dimensional planar carbon allotropes based on biphenylene *via* on-surface Ullmann coupling

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Methods

The Cu(111) sample was cleaned by cycles of Ar⁺ sputtering and annealing. The cleanness of Cu(111) is checked by PES. Synthesis from the BBr₂ precursors and analysis of the 2D system were performed at the ANCHOR endstation of the ALOISA beamline of ELETTRA synchrotron facility. The molecule was deposited onto the Cu(111) surface through physical vapor deposition from a KentaxTM evaporator under Ultra High Vacuum (UHV). During deposition, the quartz crucible was heated to 43°C and the pressure is in 1×10^{-7} mbar range. Keeping the Cu(111) substrate at room temperature (RT), the growth of BBr₂ film is saturated at 1 monolayer (ML) coverage where the thickness was estimated by the attenuation method of Cu3p signal. The whole on-surface reaction is then monitored *in-situ* by Photoelectron Spectroscopy (PES). The NEXAFS spectra were acquired in Auger yield mode. The ARUPS scans were obtained with a He(II) non-monochromatized source (Omicron HIS 13), setting the pass energy of the electron analyzer to 10 eV.

Preliminary STM results

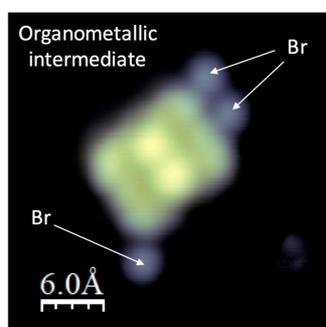


Figure S1: STM image of BBr₂/Cu(111) system prepared at RT. Scan parameters: Bias = -40 mV, It = 50 pA. Measuring temperature: 5 K. Scan area: 3 nm × 3 nm.

It is evident that the Br atoms have already detached from BBr₂ molecule but remained on the surface, supporting our spectroscopic results (Fig. 1 in the manuscript). The BBr₂ already forms organometallic intermediate (highlighted in yellow) as also shown in previous studies [1]. The bright spots in the middle of the organometallic intermediate prove its non-flat orientation of the benzene rings, in agreement with our NEXAFS dichroism results in the manuscript.

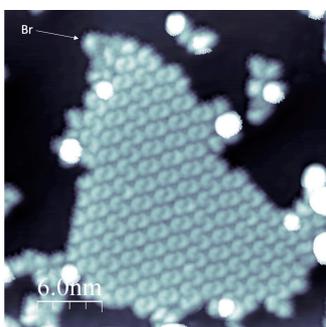


Figure S2: STM image of BBr₂/Cu(111) system after annealing to 200°C. Scan parameters: Bias = -1 V, It = 100 pA. Measuring temperature: 5 K. Scan area: 30 nm × 30 nm.

Fig. S2 shows the STM image of the BBr₂/Cu(111) system after annealing to 200°C. The morphology clearly shows that some polymerization process has happened and the product

is different from the RT sample. It is also evident that Br atoms are still on the Cu(111) surface (little dots around the polymerized products).

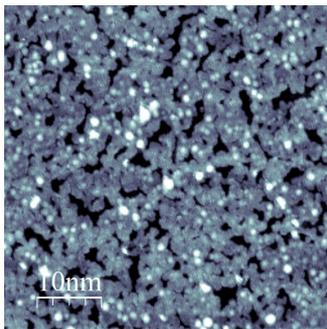
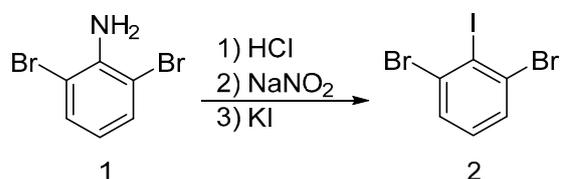


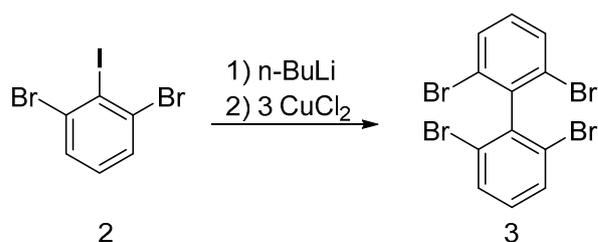
Figure S3: STM image of BPBr₂/Cu(111) system after annealing to 500°C. Scan parameters: Bias = -1 V, It = 100 pA. Measuring temperature: 5 K. Scan area: 50 nm × 50 nm.

Fig. S3 shows the STM image of the BPBr₂/Cu(111) system after annealing to 500°C. No Br is detected and an ultra-thin film (3 Å measured by STM height, ~1 monolayer) is formed. From the preliminary STM results so far, we believe the structure is more complicated than just BPC or BPN. We consider the possibility that there is a competition between the Ullmann type reaction and cyclobutadiene ring opening, which makes the reaction and the structure even more inspiring and interesting. More efforts are still needed to elucidate the reaction mechanism.

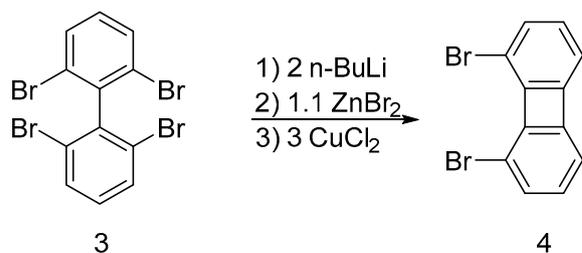
Synthesis route for BPBr₂ [2]



2,6-Dibromo-iodobenzene (2). A solution of NaNO₂ (7.97 g, 115 mmol) in H₂O (60 mL) was added dropwise to a suspension of 2,6-dibromoaniline (26.3 g, 105 mmol) in aqueous HCl (100 mL, 12 M) at 0 °C. The mixture turned orange. The mixture was stirred at 0 °C for 90 min to afford an opaque red mixture. Additional NaNO₂ (2.11 g, 30.5 mmol) was added. The mixture was stirred for an additional 45 min at 0 °C and then filtered through a plug of glass wool into an ice-cooled jacketed addition funnel. The resulting red solution was added dropwise to a stirred solution of KI (173 g, 1.02 mol) in H₂O (260 mL) at 20 °C to form a foamy black mixture. The mixture was stirred at 20 °C for 2 h. Aqueous Na₂SO₃ (114 mL, 1.00 M, 114 mmol) was added and the mixture turned clear yellow. Methylene chloride (200 mL) was added and the mixture was stirred for 7 h. The mixture was separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 250 mL). The organic fractions were combined and washed with aqueous KOH (100 mL, 1 M), and dried over MgSO₄. The solvent was removed under vacuum. The resulting red solid was recrystallized from hot ethanol to afford 2,6-dibromoiodobenzene as off-white needles in two crops (total yield 32 g, 84%). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, J= 8.0 Hz, 2H, H3 and H5), 7.07 (t, J=8.0 Hz, 1H, H4).



2,2',6,6'-Tetrabromo-biphenyl (3). A solution of n-BuLi (2.66 M in hexane, 16.2 mL, 43.2 mmol) was added dropwise to a solution of 2,6-dibromoiodobenzene (15.6 g, 43.4 mmol) in Et₂O (300 mL) at -78 °C. The mixture was stirred at -78 °C for 2 h. Anhydrous CuCl₂ (17.4 g, 129 mmol) was added. The mixture was stirred at -78 °C for 2 h and allowed to warm to room temperature. Cold water (300 mL) was added and the mixture was stirred until no brown residue was left. The ether layer was separated. The aqueous layer was extracted with Et₂O (3 x 300 mL) and benzene (100 mL). The organic fractions were combined and dried over MgSO₄. The solvent was removed under vacuum. The resulting off-white solid was recrystallized from boiling cyclohexane to afford 2,2',6,6'-tetrabromobiphenyl as colorless crystals (7.24 g, 71%). This yield is improved from the literature yield (33%). ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J= 8.0 Hz, 2H, H3 and H5), 7.17 (t, J= 8.0 Hz, 1H, H4).



1,8-Dibromobiphenylene (4). 3 A solution of n-BuLi (2.5 M in hexane, 3.5 mL, 8.8 mmol) was added dropwise to a solution of 2,2',6,6'-tetrabromobiphenyl (1.49 g, 3.17 mmol) in THF (60 mL) at -78 °C. The mixture was stirred at -78 °C for 2 h and a fine white solid gradually precipitated. A solution of ZnBr₂ (0.783 g, 3.47 mmol) in THF (10 mL) was added dropwise via cannula. The flask was transferred to a cold bath maintained at -50 °C. The mixture was stirred for 2 h during which time the white solid slowly dissolved and the solution turned a bright yellow. The solution was cooled to -78 °C and cannula-transferred to a flask containing a suspension of anhydrous CuCl₂ (1.32 g, 9.82 mmol) in THF (80 mL) at -78 °C. The suspension was stirred for 1 h at -78 °C and allowed to warm to room temperature. HCl (3 M aqueous solution, 100 mL) was added and the resulting green solution was stirred for 10 min. The solution was extracted with benzene (3 x 200 mL), the extracts were combined and dried over MgSO₄, and the solvent was removed under vacuum. The crude product was dissolved in benzene (10 mL), evaporated onto silica and purified by column chromatography with hexanes to yield a bright yellow microcrystalline solid (0.49 g, 50%). Attempts to scale up this procedure gave lower yields, probably due to inadequate temperature control. ¹H NMR (400 MHz, CDCl₃): δ 6.84 (d, J = 8.0 Hz, 2H, H2 and H7), 6.55 (dd, J = 8.0 Hz, 2H, H3 and H6), 6.58 (d, J = 8.0 Hz, 2H, H4 and H5).

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- [2] S. M. Kilyanek, X. Fang, R. F. Jordan, *Organometallics* **2009**, 28, 300-305.