

Ullmann coupling reaction of aryl chlorides on Au(111) using dosed Cu as catalyst and the programmed growth of 2D covalent organic frameworks

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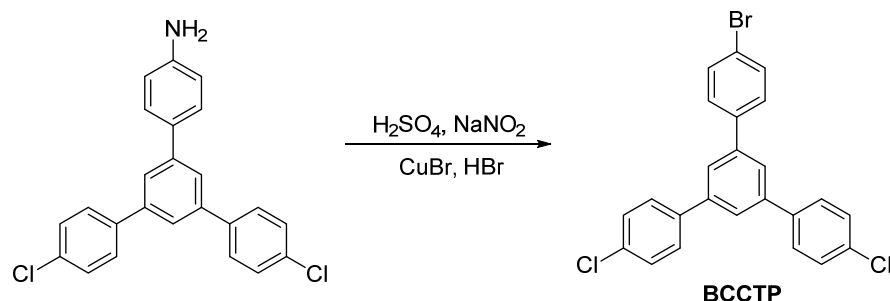
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Supporting Information

- 1. Synthesis of organic molecules**
- 2. Supplemental STM image**
- 3. References**

1. Synthesis of organic molecules

Synthesis of 4,4''-dichloro-1,1':4',1''-terphenyl (DCTP) followed known procedures.¹



4-Bromo-4''-chloro-5'-(4-chlorophenyl)-1,1':3',1''-terphenyl (BCCTP). In a three-necked round-bottom flask, 4''-chloro-5'-(4-chlorophenyl)-[1,1':3',1''-terphenyl]-4-amine² (1.5 g, 3.84 mmol) was added to glacial acetic acid (21.17 mL) at room temperature. Sulfuric acid (98%, 5.24 mL) was added to the reaction mixture, and then saturated sodium nitrite (0.636 g, 9.22 mmol) solution was added. The reaction mixture was stirred at 60 °C and cooled to room temperature after 1 h. The mixture of CuBr (0.595 g, 4.15 mmol) and HBr·H₂O (2.61 mL) was added to the reaction mixture, then the reaction mixture was warmed to 100 °C. After 1 h, the reaction mixture was cooled to 0 °C and extracted by Et₂O, then washed with saturated sodium bicarbonate and dried with Mg₂SO₄. Flash chromatography on silica gel gave the product (0.123 g, 0.271 mmol) as a white solid. Mp:226.1-228.5 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.45 (4H, d, *J* = 8.4 Hz), 7.53 (2H, d, *J* = 8.4 Hz), 7.58-7.61 (6H, m), 7.68 (2H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 122.2, 125.1, 125.2, 128.7, 129.0, 129.2, 129.3, 132.2, 134.1, 139.3, 139.8, 141.6; HRMS (EI, TOF) calcd for C₂₄H₁₅BrCl₂⁺ [M]⁺: 451.9734, found: 451.9736.

2. Supplemental STM image

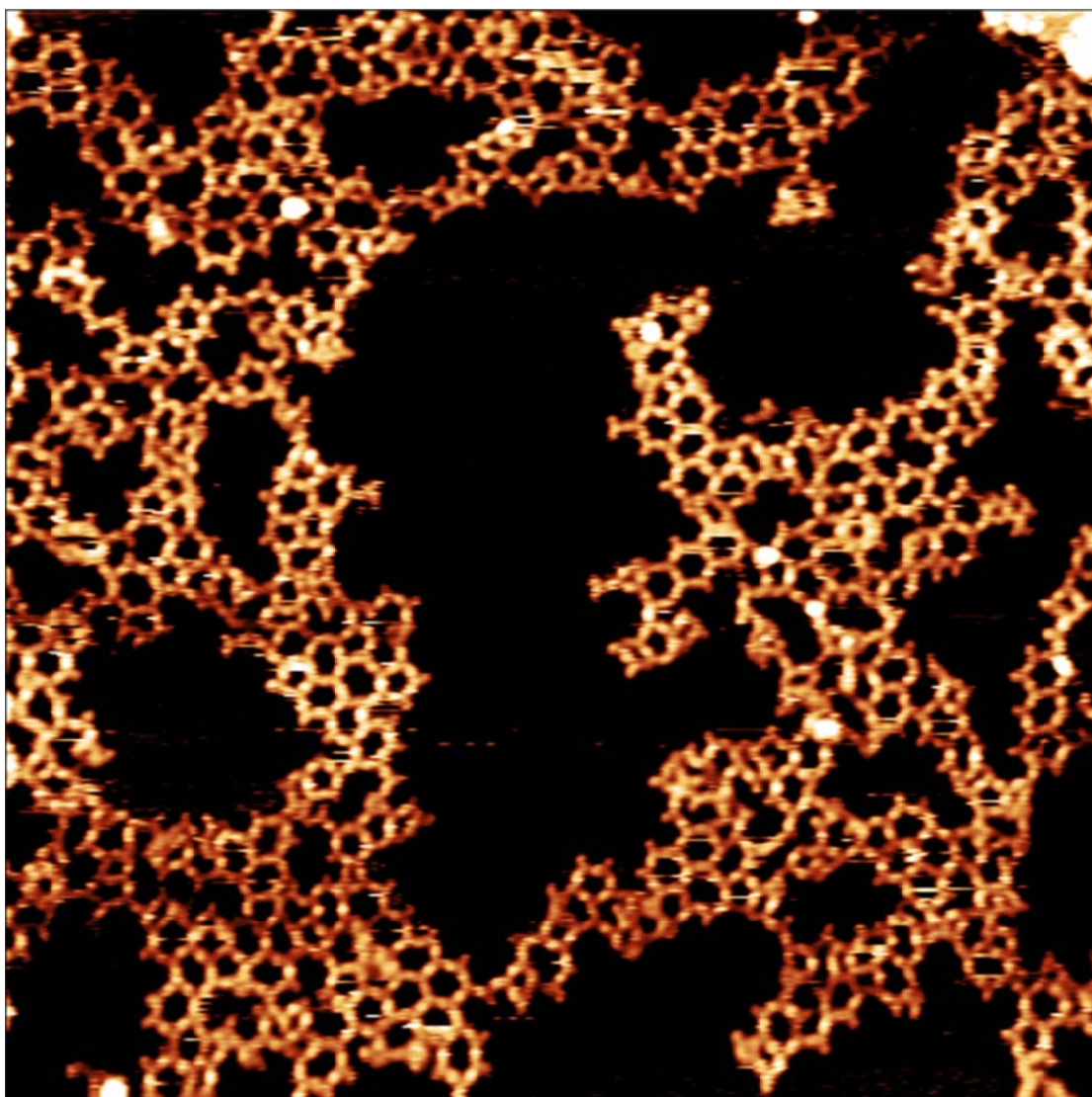


Figure S1. BCCTP deposited on Cu(111) held at room temperature and annealing to 280 °C for 30 mins. (65 nm × 65 nm, -2.5 V, -0.09 nA)

3. References

- [1] K. J. Shi, D. W. Yuan, C. X. Wang, C. H. Shu, D. Y. Li, Z. L. Shi, X. Y. Wu, P. N. Liu, *Org. Lett.* **2016**, *18*, 1282–1285.
- [2] J. Eichhorn, T. Strunskus, A. Rastgoo-Lahrood, D. Samanta, M. Schmittel, M. Lackinger, *Chem. Comm.*, **2014**, *50*, 7680-7682.