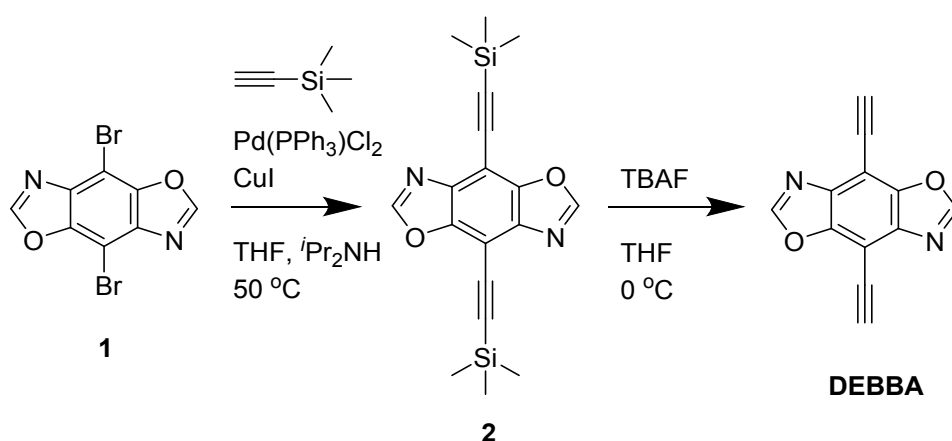


## Supporting Information

### Hydrogen Bond Guided Synthesis of Close-packed One-dimensional Graphdiyne on Ag(111) Surface

Zhi Chen, Tao Lin, Haohan Li, Fang Cheng, Chenliang Su,\* and Kian Ping Loh\*

#### Experimental



**Scheme S1.** The synthetic route of **DEBBA**.

#### 4,8-Bis(trimethylsilylethynyl)benzo[1,2-*d*:4,5-*d'*]bisoxazole (**2**)

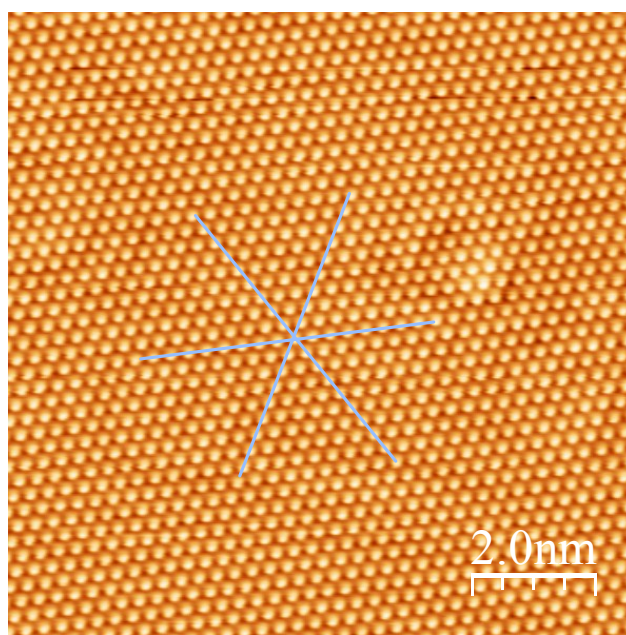
A dry three-neck, round-bottom flask equipped with a reflux condenser and addition funnel was placed under argon atmosphere and charged with 4,8-dibromobenzo[1,2-*d*:4,5-*d'*]bisoxazole (**1**) (2.510 g, 7.9 mmol) which was synthesized following literature,<sup>1</sup>  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.291 g, 0.4 mmol),  $\text{CuI}$  (0.160 g, 0.8 mmol), 50 mL dry/degassed diisopropylamine and 50 mL of dry/degassed THF. 2.8 mL trimethylsilylacetylene (1.960 g, 20 mmol) was added dropwise at room temperature and the mixture heated to  $50\text{ }^\circ\text{C}$  overnight. The mixture was allowed to cool to room temperature, and the volatile components were removed in vacuum. The crude product was purified by column chromatography on silica gel (hexane:  $\text{CH}_2\text{Cl}_2 = 2:1$ ) affording white needle product **2** (1.264 g, 45% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ , ppm 8.25 (2H, s), 0.36 (18H, s);

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ , ppm 154.4, 148.5, 139.6, 108.2, 100.1, 93.4, 0.0; MS (EI) calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{Si}_2$  352.1  $[\text{M}]^+$ , found 352.1.

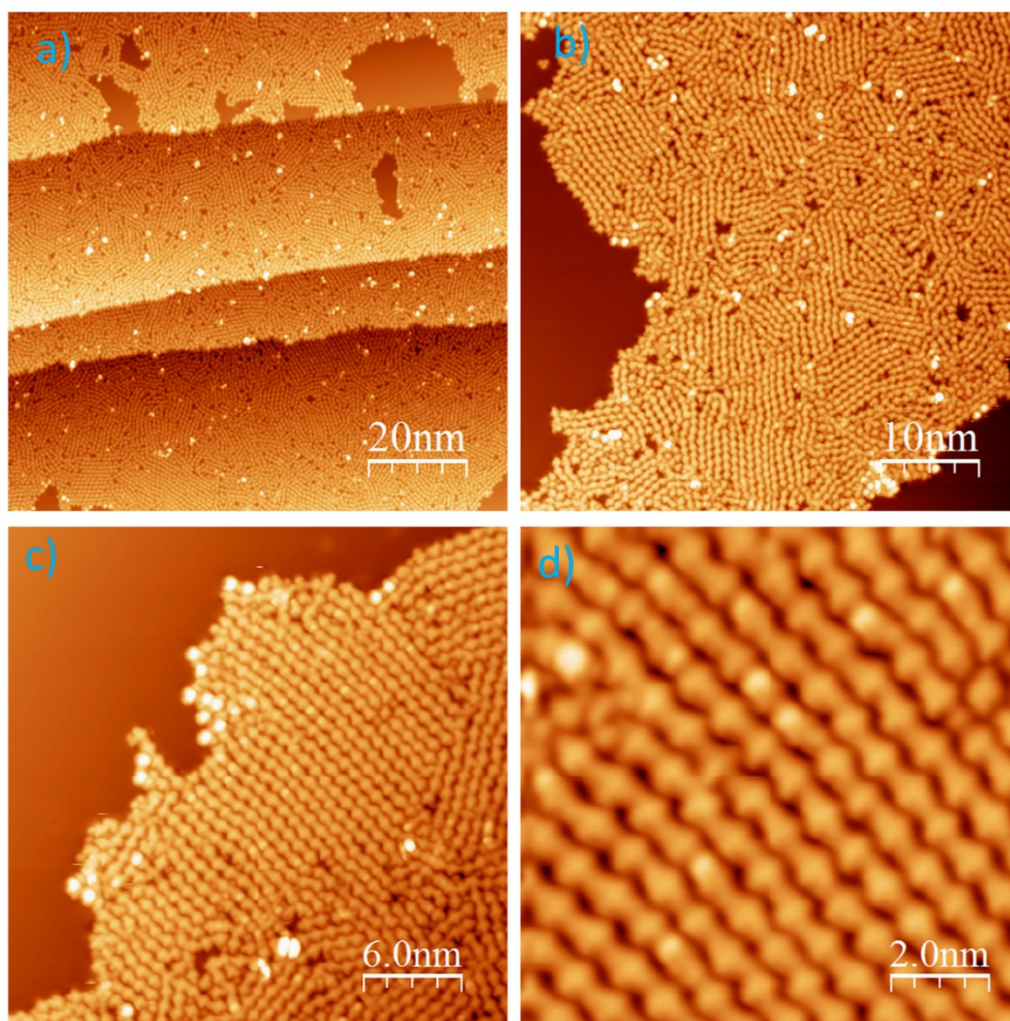
#### 4,8-Diethynylbenzo[1,2-*d*-4,5-*d'*]bisoxazole (DEBBA)

Compound **2** (0.176 g, 0.5 mmol) was dissolved in THF (20 mL) under an argon atmosphere at 0 °C. Then tetrabutylammonium fluoride (0.630 g, 2 mmol) was added. After 30 min, the reaction was poured into 100 mL deionized water. The precipitate was filtered and washed by methanol and hexane. The product was collected to yield a little yellow solid **DEBBA** (0.095 g, yield 92 %).

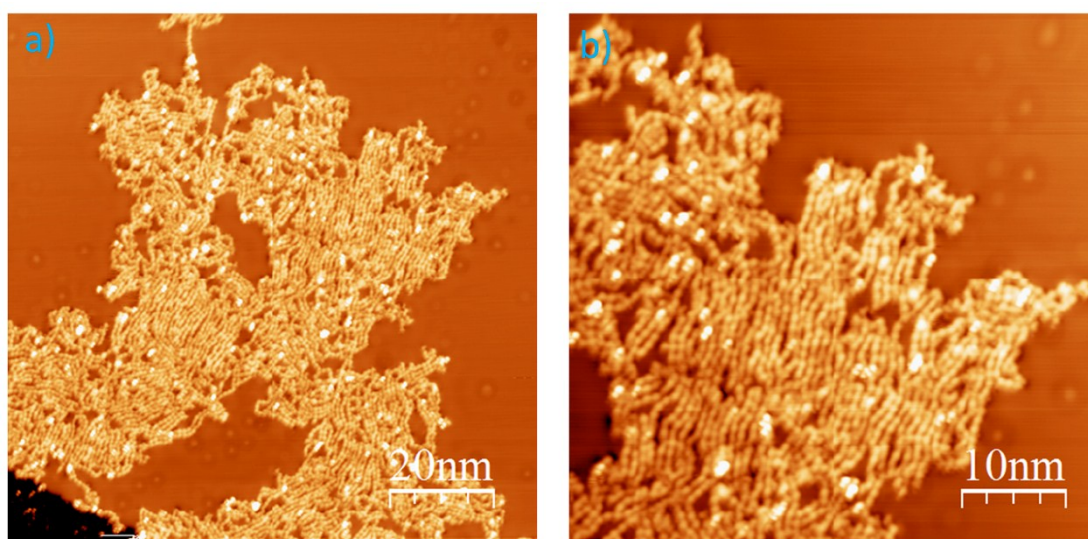
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.27 (2H, s), 3.86 (2H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_6$ -DMSO)  $\delta$  ppm 156.9, 148.3, 139.9, 98.6, 92.7, 73.9; MS (EI) calcd for  $\text{C}_{12}\text{H}_4\text{N}_2\text{O}_2$  208.0  $[\text{M}]^+$ , found 208.0.



**Figure S1.** Atomic resolution STM image of Ag(111). The blue star shows the three directions of close-packing of Ag atoms. Scanning parameter:  $U = -0.26$  V,  $I = 0.5$  nA.

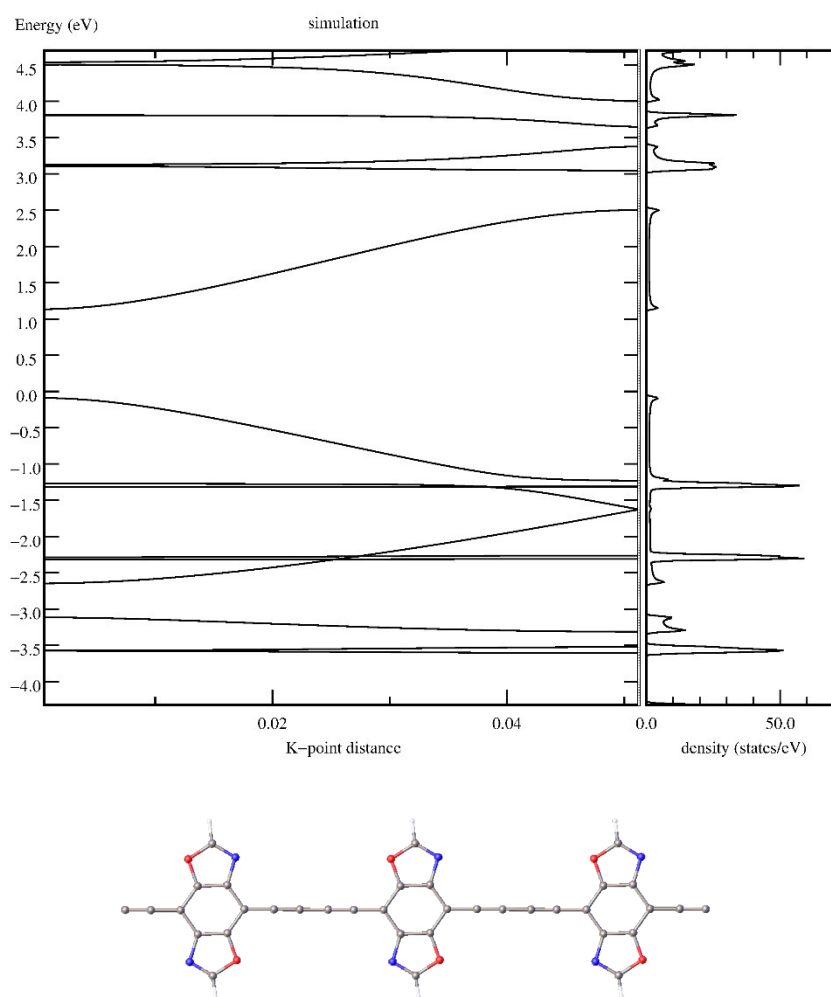


**Figure S2.** STM images of 1D Graphdiyne after annealing **DEBBA** self-assembly at 100 °C for 1 hour. Scanning parameter for (a-d):  $U = -1.5$  V,  $I = 0.1$  nA. At some edges of these self-assembled wire domains, there are some white contrast protrusions, which may originate from vertically oriented DEBBA molecules.



**Figure S3.** STM images of 1D graphdiyne which was formed by annealing **DEBBA**

self-assembly at 250 °C 10 min. Scanning parameter:  $U = -1.5$  V,  $I = 0.1$  nA.



**Figure S4.** Electronic band structure and DOS (up) obtained from DFT calculations of an infinite 1D graphdiyne (down).

- 1 B. C. Tlach, A. L. Tomlinson, A. Bhuwalka and M. Jeffries-El, *J. Org. Chem.*, 2011, **76**, 8670.