

## Supplementary Information

### Controllable Synthesis of Graphene Using Novel Aromatic 1,3,5-Triethynylbenzene Molecules on Rh(111)

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**S1: The assessments of TEB fragments during the Thermogravimetry-Mass (TG-MS) measurement:**

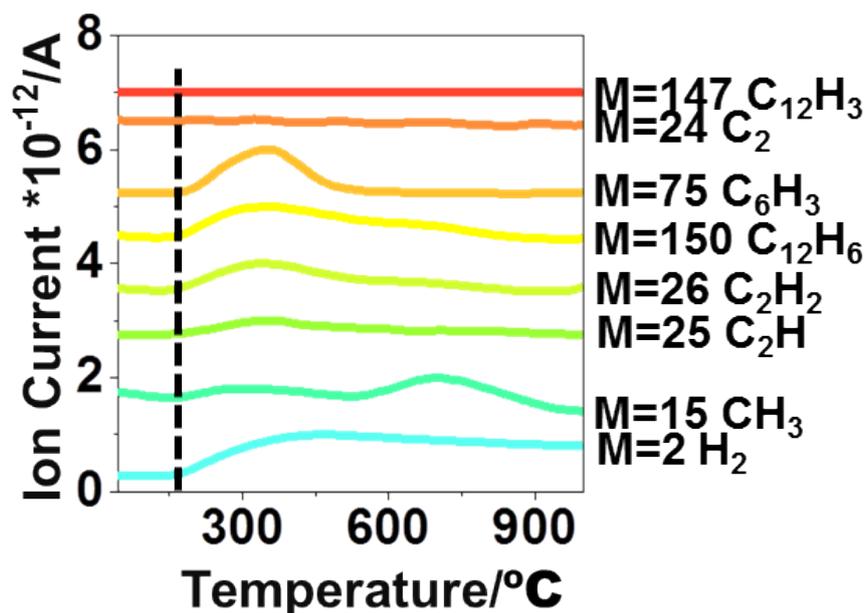


Fig. S1: Mass curves of TEB. The peaks of the mass spectroscopy (MS) spectrum arise from the fragments of TEB molecules at high temperature. The spectra are vertically displaced for clarity.

In the MS curve, the ion current becomes detectable at  $\sim 150$   $^{\circ}\text{C}$ , highly suggestive of the presence of pyrolysis fragments of TEB. The assessments of these fragments are marked in the MS curve. Peak 1 ( $m/z=150$ ) represents  $\text{C}_{12}\text{H}_6$  which is assigned to the volatilization of the intact TEB, and Peak 2 ( $m/z=75$ ) corresponds to  $\text{C}_6\text{H}_3$  arising from the cleavage of the terminal alkyne moieties ( $\text{CH}\equiv\text{C}$ ) from TEB. The peak of  $m/z=26$  is consistent with  $\text{C}_2\text{H}_2$ . It may come from the recombination of  $\text{CH}\equiv\text{C}$  ( $m/z=25$ ) and H detached from the TEB molecule. The peaks of  $m/z=24$  ( $\text{C}_2$ ) and  $m/z=2$  ( $\text{H}_2$ ) can also be found in this spectrum and they might be related to the decomposition and recombination of  $\text{CH}\equiv\text{C}$ . The  $m/z=15$  peak ( $\text{CH}_3$ ) at  $\sim 600$   $^{\circ}\text{C}$  is assigned to the collapse of the TEB carbon skeleton. Notably, in this analysis, only the peak in a single curve is concerned and the relative intensity of the peaks between different curves is meaningless.

**S2: STM images for TEB molecules evaporated at  $\sim 107^\circ\text{C}$  with Rh(111) hold at RT with larger coverage of TEB than the sample in Fig. 1c.**

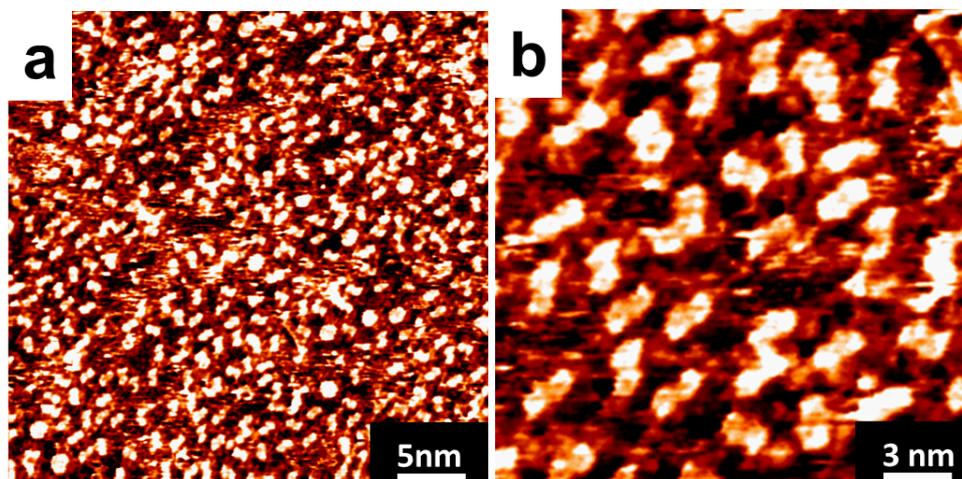


Fig. S2. STM images for TEB molecules evaporated at  $107^\circ\text{C}$  with Rh(111) hold at RT with larger coverage (a nominal coverage of 0.6 ML) than the sample in Fig. 1c (a nominal coverage of 0.1ML). (Scanning conditions: (a)  $V_T = -0.03\text{ V}$ ,  $I_T = 0.93\text{ nA}$ ; (b)  $-0.03\text{ V}$ ,  $0.93\text{ nA}$ .)

In the STM images, many dimeric products can be noticed to show a lateral size of 2 nm along the long axis of the dimeric products.

**S3: STM images of TEB layers adsorbed at room temperature and of the intermediates evolved after annealing treatments:**

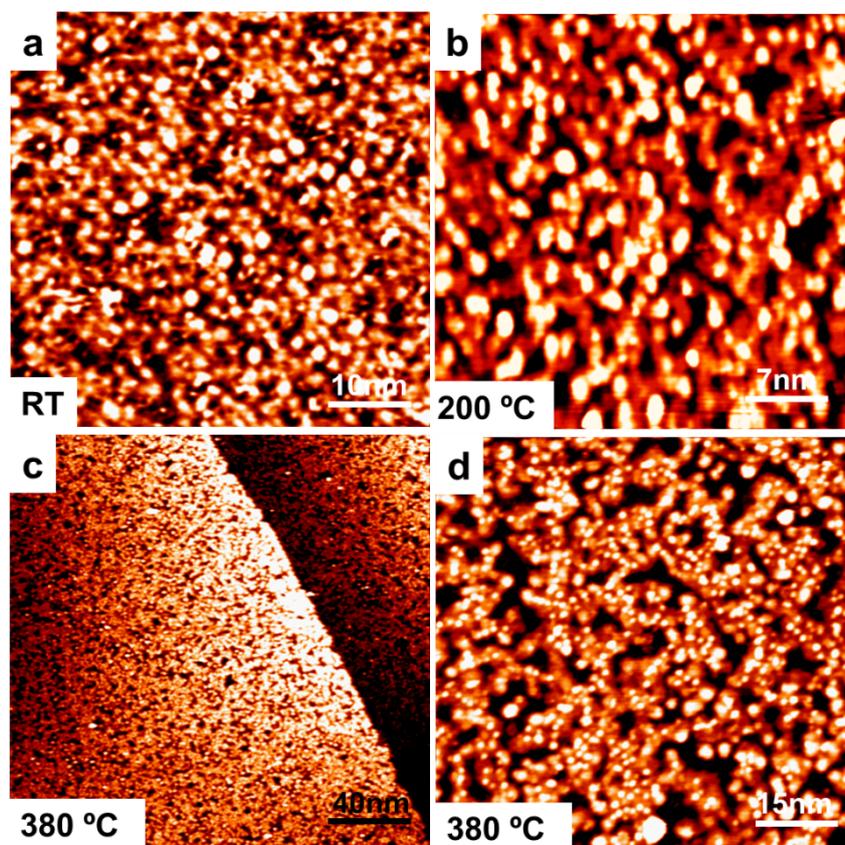


Fig. S3: STM images of a nominal 1.2 ML TEB layer adsorbed at room temperature and of the intermediates evolved after annealing treatments. (a) TEB layers adsorbed on Rh(111) at room temperature. (b) Covalent polymer formed after annealing at 200 °C for 10 min. (c, d) After annealing at 380 °C for 10 min, dendritic polymer formed with a nominal coverage at 0.9 ML. (Scanning conditions: (a)  $V_T = -0.66$  V,  $I_T = 1.20$  nA; (b)  $-0.86$  V,  $0.60$  nA; (c)  $-0.18$  V,  $1.33$  nA; (d)  $-0.18$  V,  $1.33$  nA.)

**S4: STM images of graphene synthesized through temperature-programmed annealing growth pathway and direct annealing growth pathway.**

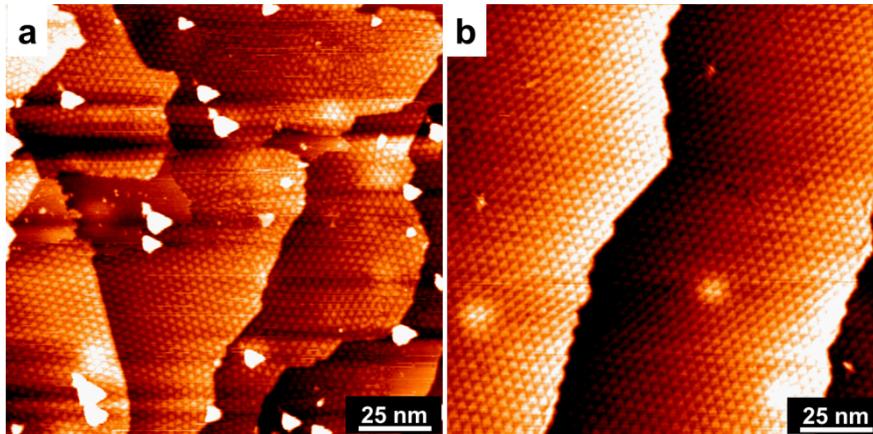


Fig. S4. STM images of graphene synthesized through two different growth pathways. (a) STM image of the graphene synthesized through temperature-programmed annealing growth pathway. (b) STM image of the graphene synthesized through direct annealing growth pathway. (Scanning conditions: (a)  $V_T = -1.07$  V,  $I_T = 0.96$  nA; (b)  $-0.02$  V,  $8.36$  nA.)

The two STM images show the effects of the different annealing pathways on the quality of graphene. Obviously, the latter sample possesses higher quality than that of the former one

**S5: SEM image of graphene synthesized by the direct annealing growth pathway and Raman spectrum of the same sample performed on Rh foil.**

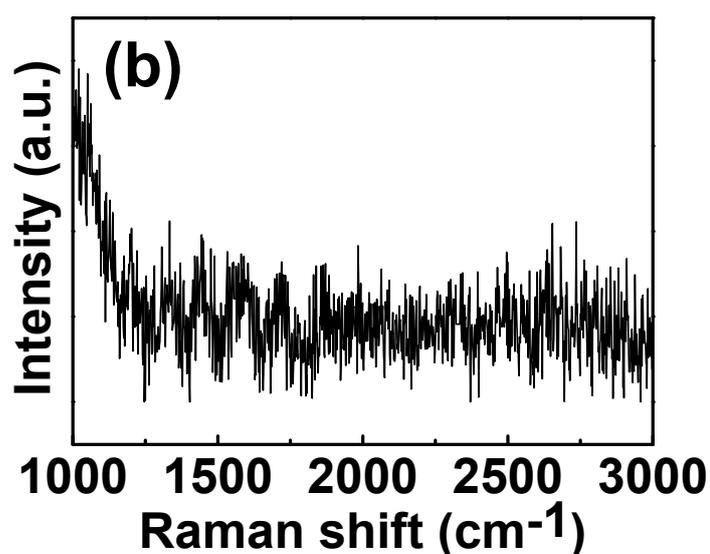
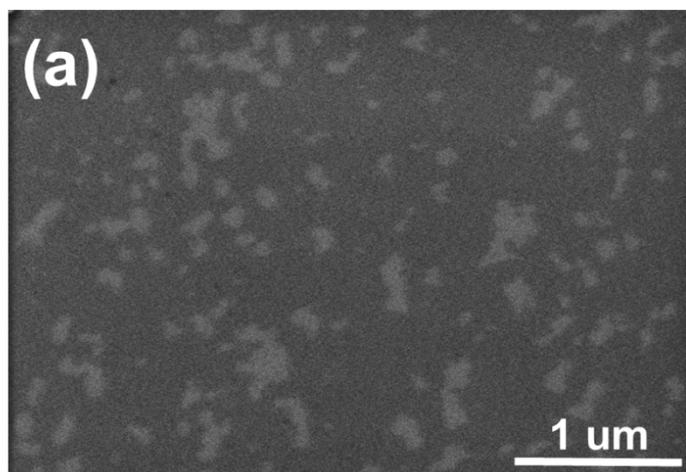


Fig. S5. (a) SEM image of graphene synthesized by the direct annealing growth pathway with coverage at  $\sim 70\%$ . (b) Raman spectrum of the same sample performed on Rh foil.

As we know that, the graphene synthesized on metals usually experience very strong electronic doping effects from the metal substrates, especially for some strongly coupled system of graphene/Rh(111). The Raman signal of graphene is usually suppressed by this substrate effect, and the typical bands of graphene (2D band at  $\sim 2680\text{ cm}^{-1}$  and G band at  $\sim 1584\text{ cm}^{-1}$ ) are absent on Rh.

