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### Supplementary information for

## **On-Surface Polymerization Reactions of Dibrominated Hexaphenylbenzene**

# Influenced by Densely Packed Self-assembly

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Figure S1. Substrate temperature dependence of the self-assembled structure of HPB polymer chains on Au(111).

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Figure S1. Substrate temperature dependence of the self-assembled structure of HPB polymer chains. (a,b) STM image (30 nm × 30 nm,  $V_s = -3.0$  V, and  $I_t = 20$  pA) taken after deposition of Br<sub>2</sub>-HPB onto hot Au(111) held at around 200 °C. The HPB polymer chains form small domains, and the orientation of HPB polymer chains are randomly distributed for the different domains. (c,d) STM image (30 nm × 30 nm,  $V_s = -3.0$  V, and  $I_t = 20$  pA) taken after deposition of Br<sub>2</sub>-HPB onto room-temperature Au(111) and subsequent annealing at 200°C for 20 h. The HPB polymer chains are self-assembled into the long-range ordered straight rows. The orientations of each HPB polymer chain and the domain boundaries between straight rows are indicated by black and red lines, respectively. For (a-d), intact Br<sub>2</sub>-HPB precursors has no longer been observed.



Figure S2. Length distributions of HPB polymer chains in (a) the mixture phase after 200 °C 1 h annealing and (b) the self-assembled straight rows after 200 °C 20 h annealing. Although the ratio of longer chains (more than 5 HPB cores) increased slightly by further annealing, the most observed length (3-4 HPB cores) is identical, indicating minimal influence of annealing time on chain length.