Supporting Information for

A Molecular Insight into the On-Surface Chemistry of an Organometallic Polymer

Yuxuan Lin, Mengxiao Diao, Jingxin Dai, Zhen Xu, Xinwei Zhao, Xiaojie Wen, Lingbo Xing, Xiong Zhou, Qiwei Chen,* Jing Liu,* and Kai Wu*

BNLMS, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

Emails: kaiwu@pku.edu.cn, jing.liu@pku.edu.cn, chenqw@pku.edu.cn



Figure S1. Statistic histograms of the proportions of the h-OM and b-OM segments as a function of the annealing temperature.



Figure S2. STM images of the samples at (a) low, (b) medium and (c) high molecular coverages after the thermal treatment at ~400 K, showing both the stepwise Cuelimination and cooperative reactivity of the OM segments within the same column at different molecular coverages and with (b,c) or without (a) the pre-covered Br adatoms. The purple and green arrows mark the orientations of the h- and b-OM segments, respectively. The preferential Cu-elimination at the h-OM segments in the isolated chains are exemplified by the white ellipses in (a). The cooperative reactivity of the OM segments on the samples at different molecular coverages is highlighted by light blue rectangles in (a-c). Imaging conditions: $V_{\text{bias}} = 100 \text{ mV}$, $I_t = 30 \text{ pA}$.



Figure S3. STM images of (a) the DCTP-Cu OM chains in coexistence with a separated island of Br adatoms and (b) two separated Br adatom islands. The superimposed white grids indicate the substrate lattices deducted from the lattice of the Br islands enclosed by the orange dashed rectangles. Two orientations of the OM segments in the zigzag chains are marked by the purple and green arrows in (a), respectively. Imaging conditions: $V_{\text{bias}} = 100 \text{ mV}$, $I_{\text{t}} = 30 \text{ pA}$.



Figure S4. STM image showing that the type of the OM segments, *i.e.*, either b- or h-OMs, retains the same before (as seen in the upper OM chain) and after (as seen in the lower partially Cu-eliminated chain) the formation of a QP segment. The Cu(111) lattice is superimposed with the white grid. The purple and green arrows mark the orientations of the h- and b-OM segments, respectively. The b-OM segment next to the QP segment is highlighted by the white circle. Imaging conditions: $V_{\text{bias}} = 100 \text{ mV}$, $I_t = 30 \text{ pA}$.