Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Materials for

Direct On-surface Synthesis of Gold-phthalocyanine via Cyclization of Cyano-groups with Gold Adatoms

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Experiment and Methods

One-side polished Au(111) single crystal (MaTecK GmbH, Germany) was cleaned by sputtering with 2Kev Ar^+ ion for about 20 min, then post-annealed at 800 K for around 30 min (several cycles). After several hours of degassing, HTTN molecules (purity 98%) were vapor-deposited in vacuum from an effusion cell evaporator at 560 K onto clean Au(111) single crystal held at room temperature. STM images were acquired with a SPECS STM 150 Aarhus with SPECS 260 electronics at room temperature with a chemically etched W tip. All given voltages refer to the sample and the image were taken in constant-current mode. Photoemission spectroscopy experiments were performed at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The C_{1s} and N_{1s} core-level spectra were measured using a monochromatic Al K_α X-ray source. DFT calculations were performed using Vienna *Ab initio* Simulation Package with projector augmented wave and generalized gradient approximation.

Author contributions

Z.W., X.L., Y.L, S.W., W.L., L.W performed the experiment, Z.W., C.B., M.C., J.Z., H.J., F.R. M.D, L.W. performed the image analysis, all authors discussed the results and give the revision.

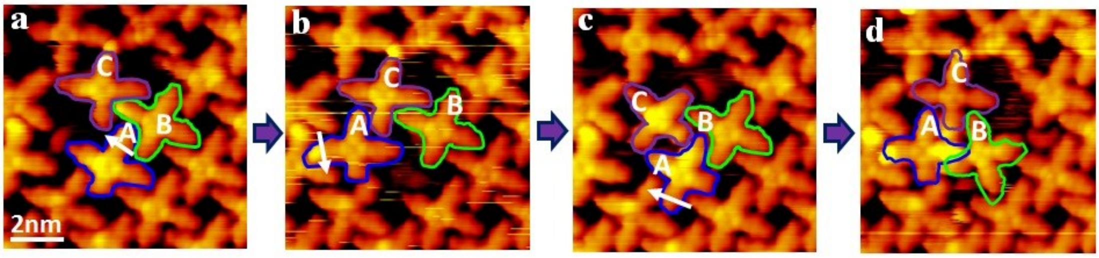

Figure S1: The cross-like supramolecular structure can be rotated and moved around on the surface as a whole by STM manipulation. Scanning parameters: V_s= 1.0V and I_s= 0.03nA.

The process to manipulate the cross-like structure on the gold surface following the way: The STM tip is positioned at the target location then suddenly lowering to an appropriate height so that the interaction between the tip and the molecule is strong enough to move or switch a molecule. In order to achieve a high success rate of operation, the STM tip is normally lowered to a certain height by reducing the voltage to V_m ~ 0.6 V and increasing the tunneling current to I_m ~ 2.5 nA. The predefined line in Supplementary Figure 1 decides the track of the STM tip during the manipulation process. The "A" cross-like structure marked by blue line is chosen as the target supramolecular structure manipulated by the STM tip. The interaction between these supramolecular structures drive the "B" and "C" cross-like structure to move and rotate when the rotation of "A" cross-like structure is induced by STM tip manipulation. These cross-like structures are very stable upon STM manipulation, it is suggested that the HTTN molecules, within the supramolecular structure, are chemically linked with each other.

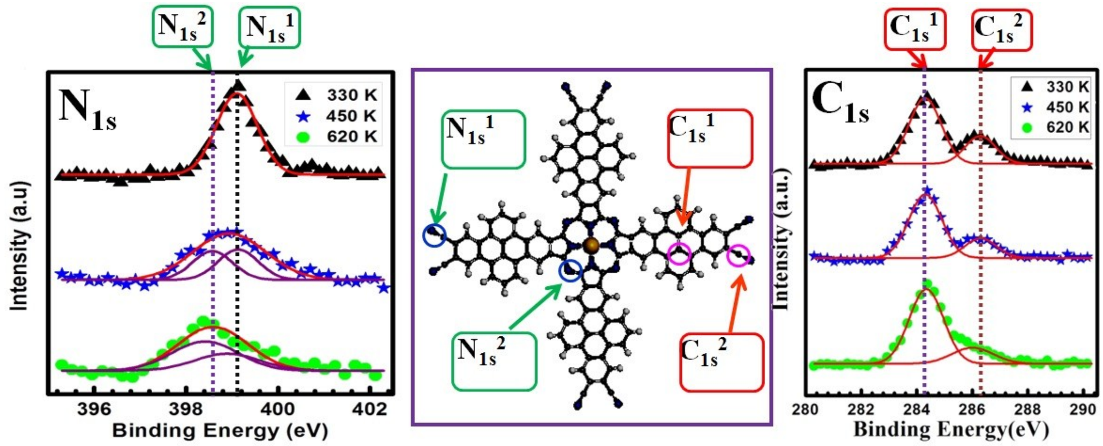

Figure S2: XPS core-level measurements of the C and N of HTTN/Au (111) experience a hierarchical on-surface reaction driven by thermal treatments.

The C_{1s} spectrum of the HTTN self-assembly structure at 330K has been decomposed with two Gaussian peaks at about 284.3 and 286.3 eV, related, respectively, to carbons of the aromatic rings ($C_{1s}{}^1$) and carbons bonded with nitrogen atoms ($C_{1s}{}^2$). As the annealing temperature elevated to 450K, the cross-like structure not result in any shift of the $C_{1s}{}^1$ but lead to $C_{1s}{}^2$ peak intensity decreases and broaden. This is in good agreement with the transformation of half of carbonitrile carbons into pyrrole carbons. As the reaction further progresses to form polymeric grid, the $C_{1s}{}^2$ peak intensity gradually decreases and the width is broadened. The N_{1s} spectrum of the self-assembled HTTN network exhibits only one Gaussian peak at about 399.1 eV related to the nitrogens of cyanogroup, marked N_{1s}^1 in Supplementary Figure 2. As the annealing temperature gradually increased, the structure leads to a slight shift towards lower binding energy and the width of the peak is gradually broadened. The new peak lies at 398.6 eV related to the binding energy of the pyrrolic nitrogens, marked N_{1s}^2 in Supplementary Figure 2. As the annealing temperature elevated to 620K, the N_{1s}^2 peak intensity gradually increases following the N_{1s}^1 peak intensity gradually decreases. These change of the N_{1s} peak can then be explained by the carbonitrile nitrogens are gradually translated into pyrrole nitrogens with the increase of annealing temperature.

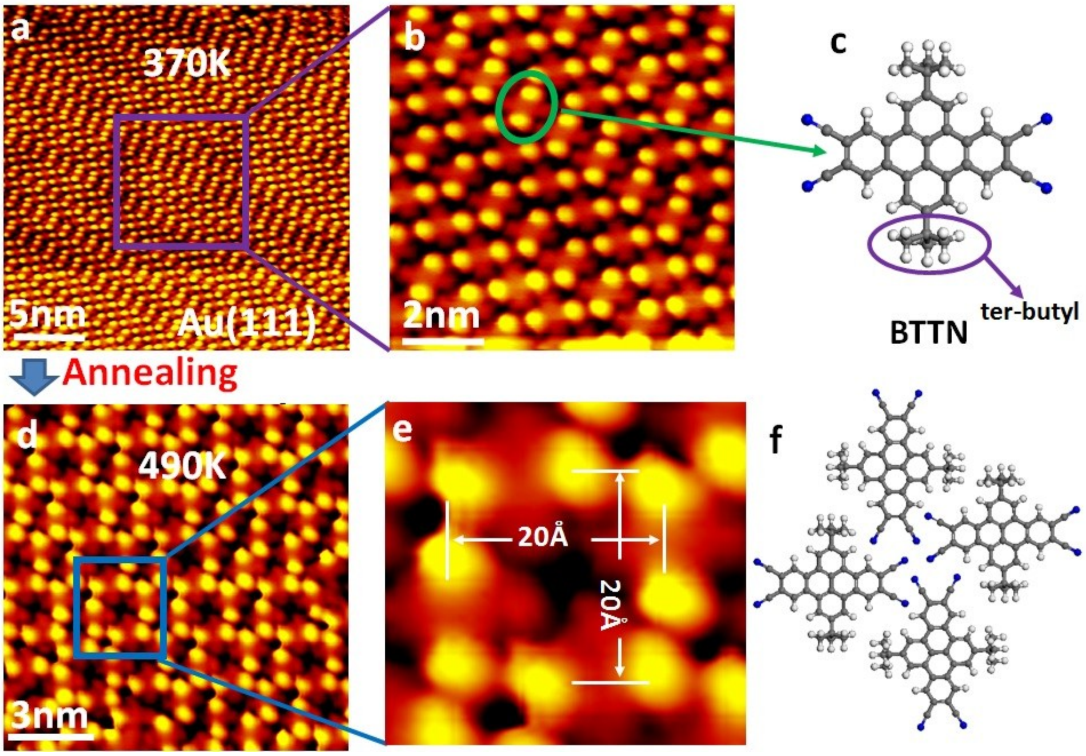

Figure S3: BTTN molecules are deposited and adsorbed on a Au (111) substrate. (a) STM image for order structure of BTTN/Au(111) by annealing treatments at 370K for 5min (acquired at V_s= -1.58V and I_s= -0.03nA). (b) High-resolution STM image for the region surrounded by purple rectangle in (a); (c) Structural model for single BTTN molecule. (d) STM image for order structure of BTTN molecules by annealing treatments at 490K for 5min (acquired at V_s= -1.49V and I_s= -0.06nA). (e) High-resolution STM image for the region surrounded by blue rectangle in (d). (f) Structural model for order formation in (e).

When the H atoms in the position 2 and 9 of HTTN are substituted by ter-butyl to synthesize 2,9-diter-butyldibenzo [fg, op] tetracene-5,6,12,13-tetracarbonirile (BTTN) molecules. The cyano-group of BTTN leaving the metal surface for the steric-hinerance of the tertiary butyl leads to the failure coordination between the cyano-group and gold adatoms, which effectively hindering the cyanogroup polymerization reaction of BTTN on Au(111) surface.