Hierarchical Construction of Cross-Junction of Molecular Wires with Covalent and Noncovalent Interactions at the Liquid/Solid Interface

Yanxia Yu,[ab] Ling Yang,[b]* Chunhua Liu,[b] Wei Quan Tian, [b] Yan Wang, [b] * Shengbin Lei[a]*

[a]Key Laboratory of Microsystems and Microstructures Manufacturing, Ministry of Education, Harbin Institute of Technology, Harbin, 150080, People's Republic of China; E-mail: leisb@hit.edu.cn

[b]School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150080, People's Republic of China; Email: yangling@hit.edu.cn, wangy_msn@hotmail.com

1. Experimental section

3, 3'-dihydroxybenzidine(**1**), benzidine(**2**), 2, 5-bis(octyloxy)terephthalaldehyde(**3**), terephthaldicarboxaldehyde(**4**), octanoic acid, and dimethylacetamide were purchased from J&K and used without further purification. Owing to the limited solubility of **1** in octanoic acid，**1** were first dissolved in dimethylacetamide with a mass concentration of 1 mg/g and then the solutions were dilute 2 or 10 times in octanoic acid. **2**, **3** and **4** were dissolved in octanoic acid with a mass concentration of 0.1mg/g, respectively. Then the solutions were diluted 2 times or 10 times in octanoic acid. Then the aromatic amine and aromatic aldehyde were mixed in a molar ratio of about 1:1. A~5μL amount of the mixing solution was drop-cast on the freshly cleaved surface of HOPG at room temperature, then characterized by scanning tunneling microscopy (STM). For sample preparation at the gas/HOPG interface, **1** were first dissolved in dimethylacetamide with a mass concentration of 1 mg/g and then the solution were dilute 10 times in octanoic acid. **3** was dissolved in octanoic acid with a mass concentration of 0.1mg/g, Then **1** and **3** were mixed in a mol ratio of about 1:1. A~5μL amount of the mixing solution was drop-cast on the freshly cleaved surface of HOPG. The drop-cast samples were positioned in a preheated vacuum oven or tube furnace equipped with a rotary-vane vacuum pump at 140°C for~30 min with a pressure of <133 Pa or 40 °C in ambient condition or 140 °C in low vacuum and oxygen free conditions. The samples were taken out of the oven or tube furnace and cooled to room temperature,

then characterized by STM.

STM measurements were performed by using an Agilent 5100 scanning probe microscope with mechanically formed Pt/Ir (80/20) tips under ambient conditions. All images were taken in the constant current mode. The calibration of STM images was carried out by using an atomic resolution HOPG lattice. The chemical structure models were built with HyperChem software.

2. Computational details

To have an insight into the mechanism of cross junction formation and clarify the interactions between the adjacent layers of the hierarchical architecture, three simulation models with different levels of complexity were built for the parallel and cross junction conformation of the 1DPs: simplified model contains only two 1DP chains, multilayer model with substrate, and multilayer model with substrate and coadsorbed solvents. The molecular mechanics calculations were performed firstly to get the most stable conformations.

For the simplified model, all calculations were performed using density functional theory (DFT) with functional PBE1PBE.[1,2] Geometry optimizations of the monolayer and the bilayer were carried out with the basis set 3-21G*. On the basis of these optimized geometries, more accurate energies were obtained by performing single-point calculations with the larger basis set 6-31G** for all elements. Thus the binding energies were obtained by $E_{BE} = E_{dilayers} - 2E_{monolayer}$ (without substrate). These calculations were performed by using the Gaussian 03 program packages.[3]

Taking into account the effect of the substrate, we designed larger models more close to the realistic structure. The models contain a single layer graphene (with 1100 atoms), a bottom layer contains three ($1DP_{1+3}$ or $1DP_{2+3}$) molecules, in which the n-octyloxy groups on one side of the edge chains was replaced by methoxyl groups. The top/second layer composed by only one ($1DP_{1+3}$ or $1DP_{2+3}$) molecule grown on top of the first layer, either parallel or cross the 1DP chain in the middle of the bottom layer. These larger models of $1DP_{1+3}$ and $1DP_{2+3}$ are composed of 1760 and 1780 atoms, respectively. In addition, the largest models were designed to consider the effects of both the substrate and the coadsorbed solvents. Eight n-octanoic acid molecules were coadsorbed in the bottom layer of the largest models. The largest models of $1DP_{1+3}$ and $1DP_{2+3}$ contain 1968 and 1988 atoms, respectively. The models of the multi-layers adsorbed on the graphene sheet were calculated using the density functional based tight binding (DFTB) method. All the geometry optimizations of the multilayer model on graphene were carried out using the DFTB+ program.[4-6] The binding energies of the larger model without and with the coadsorbed solvents were defined as

$E_{BE} = E_{trilayers} - 2E_{monolayer} - E_{graphene}$ (with substrate). All the binding energies were listed in Table 1. All the structures were plotted with Gaussview (Shown in Fig. 4 and Figure S6&S7).[7]
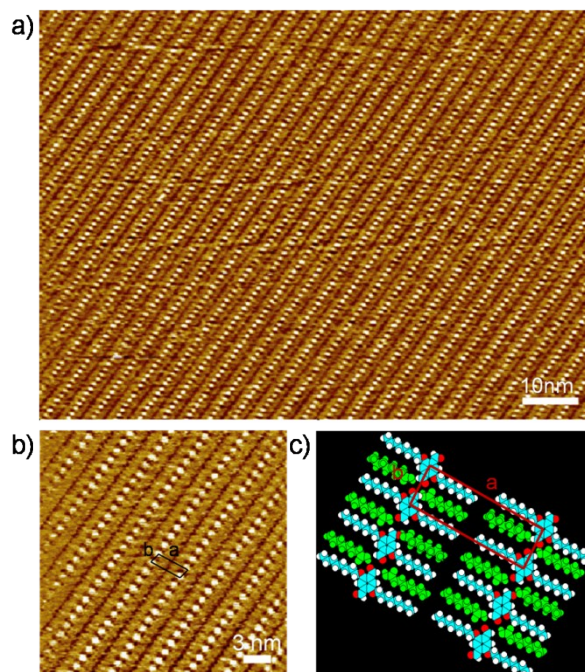
3. Additional STM data and simulated models

Figure S1. a) large-scale and b) high resolution STM images of **3** (2.3×10^{-3} mol/L) at the octanoic acid/HOPG and c) molecular model of molecule **3** adlayer on HOPG. Imaging conditions: (a) I_{set} = 22 pA, V_{bias} = 0.68 V; (b) I_{set} = 22 pA, V_{bias} = 0.68 V.
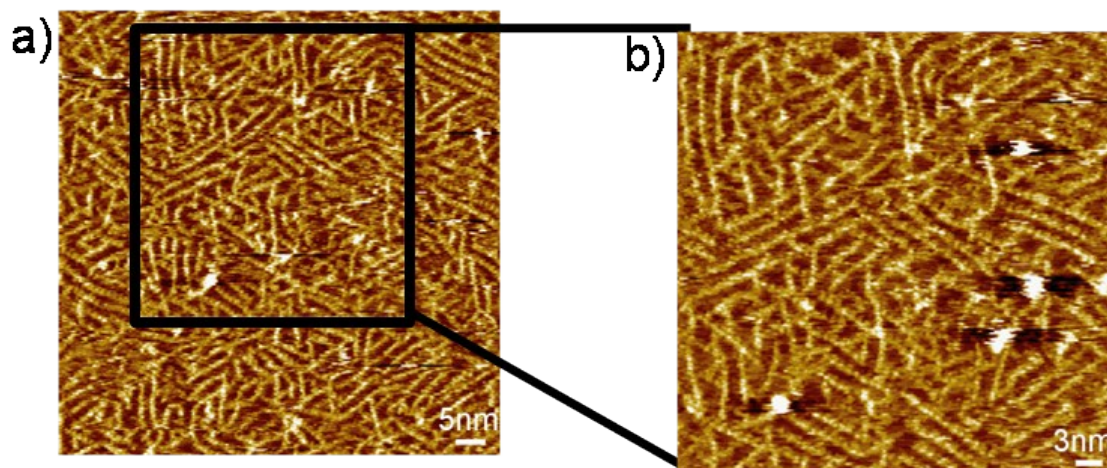

Figure S2. a) large-scale and b) high resolution STM representative images of the addition of **1** (4.2×10^{-3} mol/L) in solution on top of the existing **3** (2.3×10^{-3} mol/L) monolayer. Imaging conditions: (a) I_{set} = 19 pA, V_{bias} = 0.52 V; (b) I_{set} = 16 pA, V_{bias} = 0.52 V.
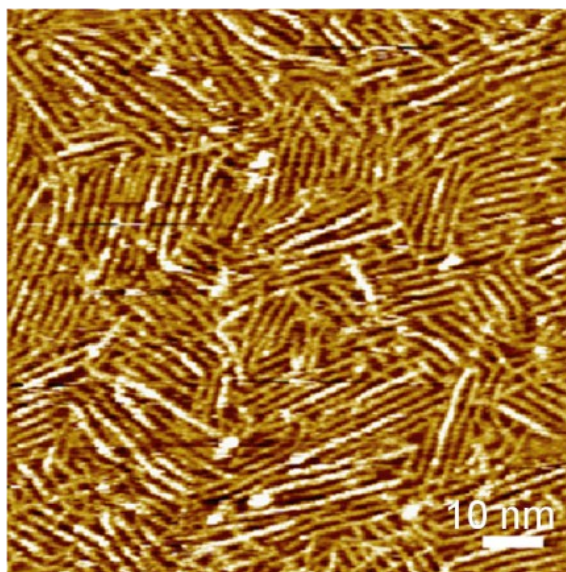
Figure S3. STM images of polymer from Schiff-base coupling of **1** with **3** with concentration of 1.5×10^{-4} mol/L at the octanoic acid/HOPG interface. Imaging conditions: $I_{set} = 14$ pA, $V_{bias} = 0.52$ V.
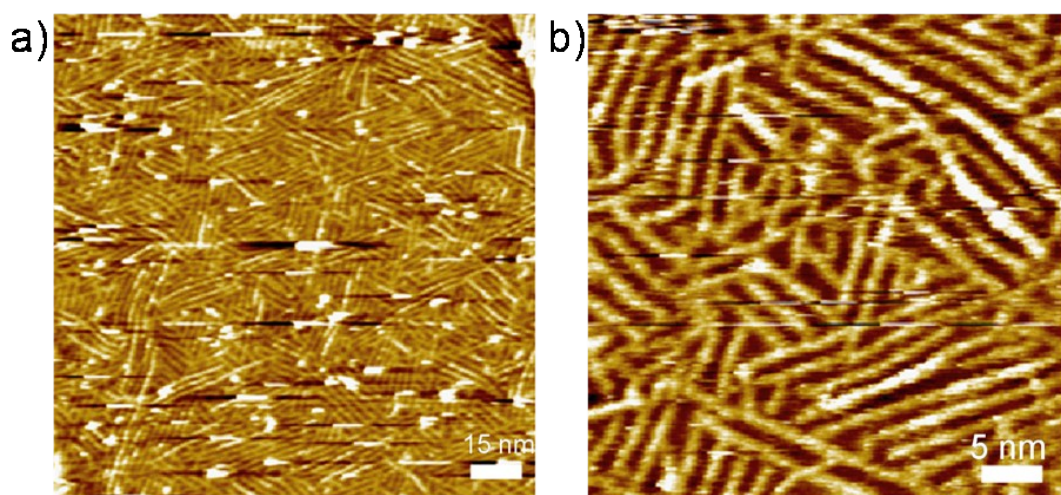

Figure S4. a) large-scale and b) high resolution STM image of polymers from Schiff-base coupling of **1** with **3** at 40 °C. Imaging conditions: (a) $I_{set} = 13$ pA, $V_{bias} = 0.52$ V; (b) $I_{set} = 13$ pA, $V_{bias} = 0.52$ V.
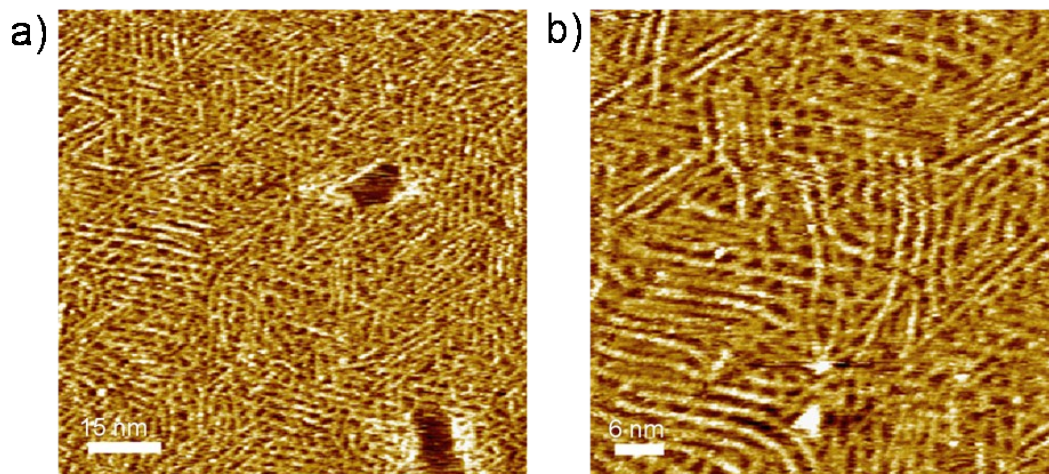
Figure S5. a) large-scale and b) high resolution STM image of polymers from Schiff-base coupling of **1** with **3** at 140°C in vacuum. Imaging conditions: (a) I_{set} =16 pA, V_{bias} =0.50 V; (b) I_{set} =14 pA, V_{bias} =0.52 V.

$1DP_{1+3}$(parallel)

$1DP_{1+3}$(cross)

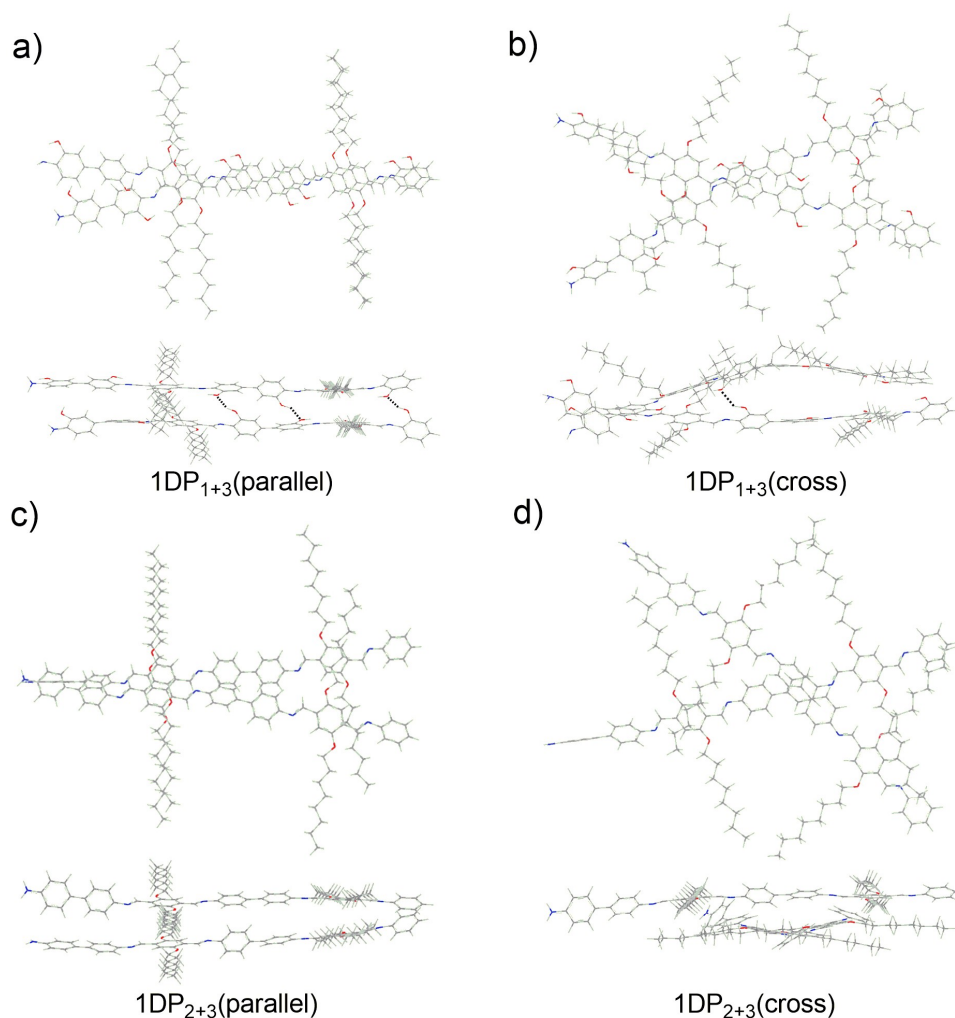$1DP_{2+3}$(parallel)

$1DP_{2+3}$(cross)

Figure S6. Top view and side view for the optimized geometries of the multi-layers without substrate, $1DP_{1+3}$ parallel (a) and cross junction (b), $1DP_{2+3}$ parallel (c) and cross junction (d).
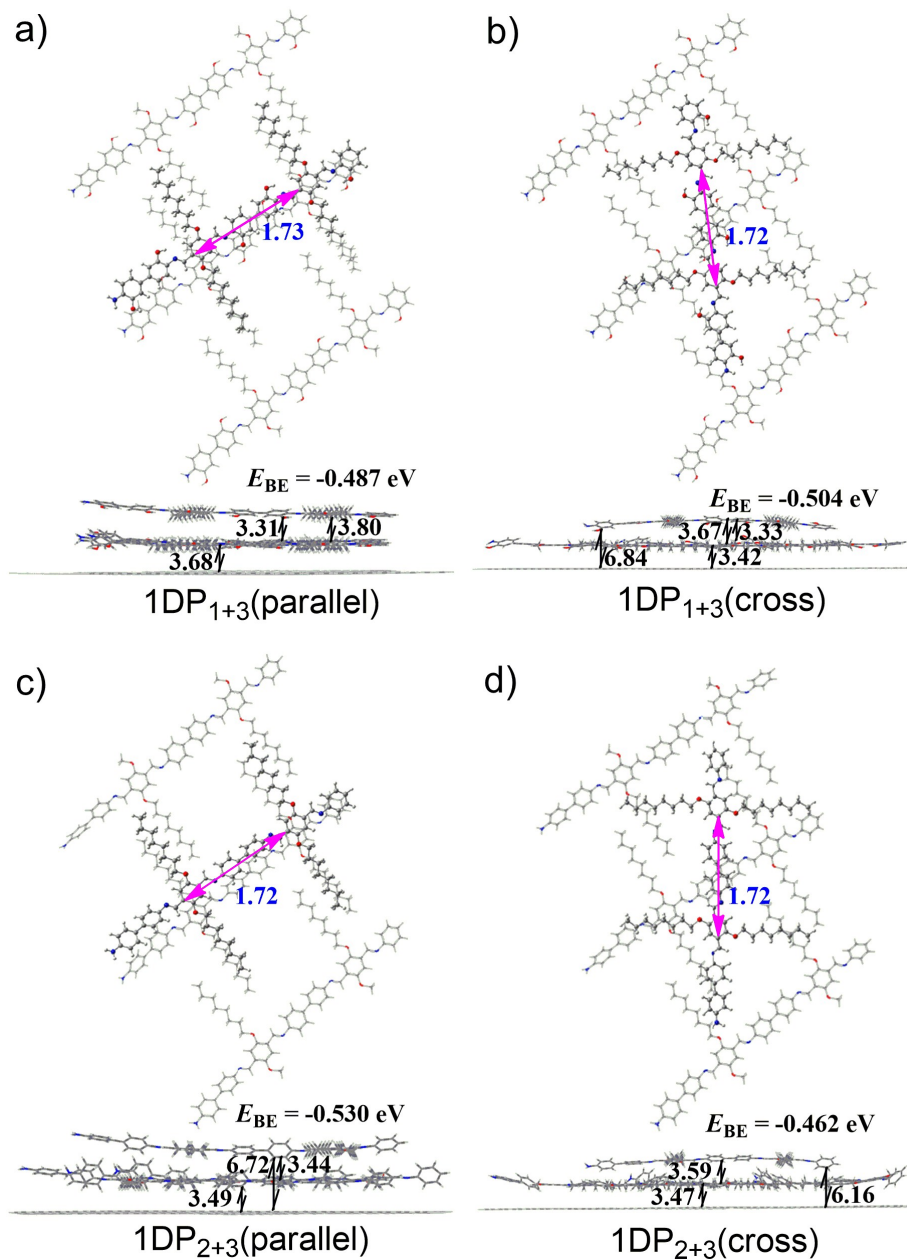
a)

E_{BE} = -0.487 eV

3.31 / 3.80
3.68

1DP$_{1+3}$(parallel)

b)

E_{BE} = -0.504 eV

3.67 / 3.33
6.84 / 3.42

1DP$_{1+3}$(cross)

c)

E_{BE} = -0.530 eV

6.72 / 3.44
3.49

1DP$_{2+3}$(parallel)

d)

E_{BE} = -0.462 eV

3.59
3.47 / 6.16

1DP$_{2+3}$(cross)

Figure S7. Top view and side view for the optimized geometries of the multi-layers with a single layer graphene as substrate, 1DP$_{1+3}$ parallel (a) and cross junction (b), 1DP$_{2+3}$ parallel (c) and cross junction (d). The graphene substrate were omitted in the top view for clarity. The numbers in the side view graphics indicate the interlayer distances.
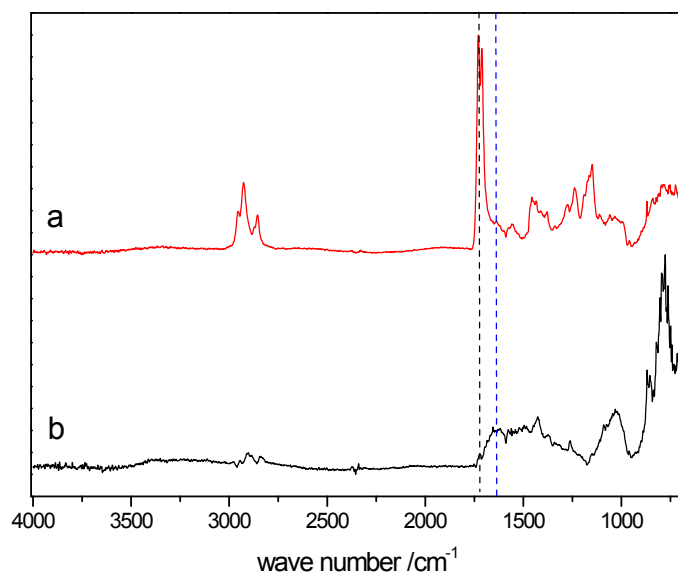
Figure S8. ATR-FTIR of $1DP_{1+3}$ samples prepared at room temperature (a) and after annealing at 140 °C under Argon protection (b). The black and blue dashed lines correspond to wave number of 1720 and 1640 cm^{-1}, resulted from vibration of aldehyde and imine groups, respectively. The data indicate the sample prepared at room temperature contains significant amount of monomers, while the reaction is much more complete after annealing. In the spectra no significant signal at ~1680 cm^{-1} was observed, which means no significant transformation from imine to oxzaline, [8] which may happen as a side reaction when oxygen presents in the system.

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