

Room Temperature On-Surface Synthesis of Two-Dimensional Imine Polymers at the Solid/Liquid Interface: Concentration Takes Control

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1. Materials and methods

All of the chemicals, except **6**, were purchased from J&K and used without further purification. The monomer **6** was synthesized with reported method.^[1]

For the synthesis of 2D polymers with moderate heating method, the monomers were dissolved in dimethylacetamide, and a droplet of the mixed solution of the two monomers was added to a freshly cleaved HOPG surface. The samples were put into a low vacuum oven and annealed at 200 °C for ~30 min with a pressure of <133 Pa. For the on-surface synthesis at the solid/liquid interface at room temperature, owing to the limited solubility of chemicals in octanoic acid, all building blocks were first dissolved in dimethylsulfoxide with a designated concentration and then the solution were dilute 5 or 10 times in octanoic acid. Then the aromatic amine and aromatic aldehyde were mixed in a mol ratio of about 2:3. A~5μL amount of the mixed solution was drop-cast on the freshly cleaved surface of HOPG at room temperature, then characterized by scanning tunneling microscopy (STM).

The HOPG samples for XPS experiment were prepared by depositing ~5μL amount of the mixing solution containing ~0.3 mg/g **1** and **3**, or ~0.3 mg/g **1** and **4**, or ~0.3 mg/g **1** and **5**, or ~0.2 mg/g **1** and **6**, or ~0.5 mg/g **2** and **5**, or ~0.5mg/g **2** and **6** on freshly cleaved HOPG surface and allow them to dry at room temperature.

STM measurements were performed with an Agilent 5100 scanning probe microscope with mechanically formed Pt/Ir (80/20) tips under ambient conditions. All images were taken with the constant current mode. The calibration of STM images were carried out by using an atomic resolution HOPG lattice. X-ray photoelectron spectroscopy (XPS) spectra were performed with ESCALAB 250Xi electron spectrometer with a monochromatized Al-Kα X-ray source (1486.7

eV). The base pressure was about 1×10^{-8} mbar. The C1s line was deconvoluted to two bands, the one with lower binding energy is attributed to the HOPG substrate and the binding energy is set as 284.4 eV^[2], all the binding energy of the other bands are calibrated against it.

2. Supplementary figures

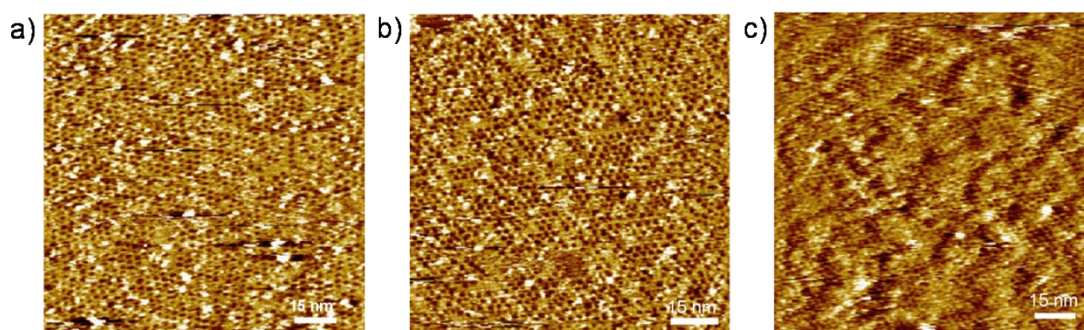


Figure S1. Effect of monomer concentration on the growth of $2DP_{1+3}$ at the octanoic acid/HOPG interface. STM images obtained at different monomer concentration of **3**: a) 2.5×10^{-5} mol/L, b) 4.2×10^{-5} mol/L, c) 4.2×10^{-4} mol/L. Imaging conditions: a) $I_{\text{set}} = 33$ pA, $V_{\text{bias}} = 0.66$ V; b) $I_{\text{set}} = 24$ pA, $V_{\text{bias}} = 0.60$ V; c) $I_{\text{set}} = 25$ pA, $V_{\text{bias}} = 0.60$ V.

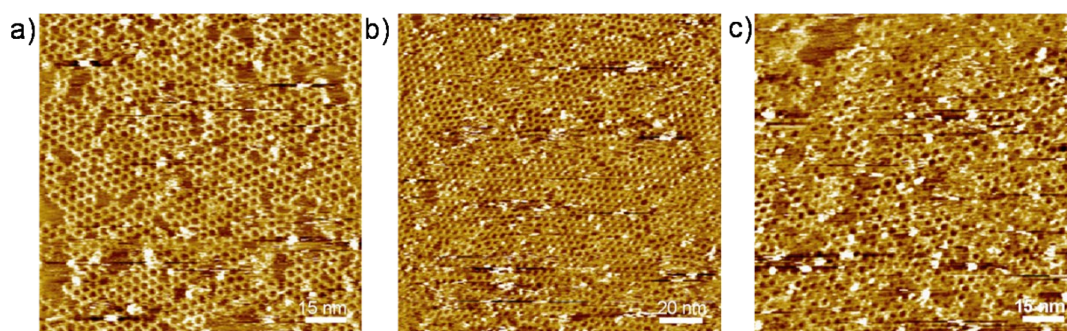


Figure S2. Effect of monomer concentration on the growth of $2DP_{1+4}$ at the octanoic acid/HOPG interface. STM images obtained at different monomer concentration of **4**: a) 9.36×10^{-6} mol/L, b) 1.3×10^{-5} mol/L, c) 6.2×10^{-5} mol/L. Imaging conditions: a) $I_{\text{set}} = 28$ pA, $V_{\text{bias}} = 0.86$ V; b) $I_{\text{set}} = 33$ pA, $V_{\text{bias}} = 0.62$ V; c) $I_{\text{set}} = 28$ pA, $V_{\text{bias}} = 0.60$ V.

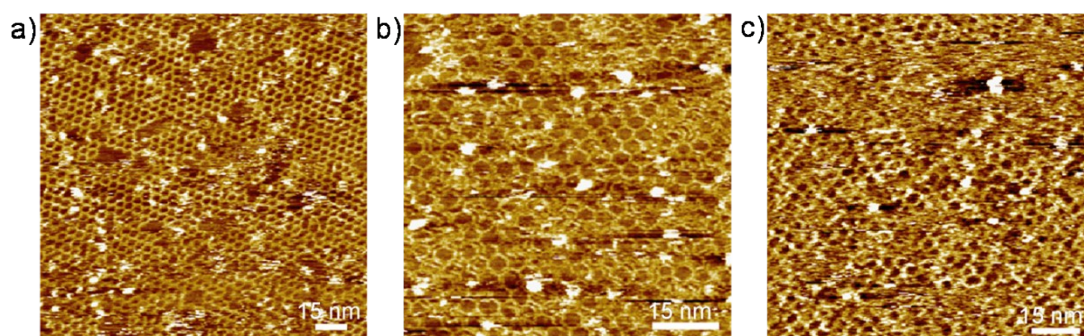


Figure S3. Effect of concentration of building blocks on the growth of $2DP_{1+5}$ at the octanoic

acid/HOPG interface. STM images obtained at different monomer concentration of **5**: a) 5.0×10^{-6} mol/L, b) 2.0×10^{-5} mol/L, c) 5.0×10^{-5} mol/L. Imaging conditions: a) $I_{\text{set}} = 26$ pA, $V_{\text{bias}} = 1.50$ V; b) $I_{\text{set}} = 39$ pA, $V_{\text{bias}} = 1.20$ V; c) $I_{\text{set}} = 49$ pA, $V_{\text{bias}} = 0.60$ V.

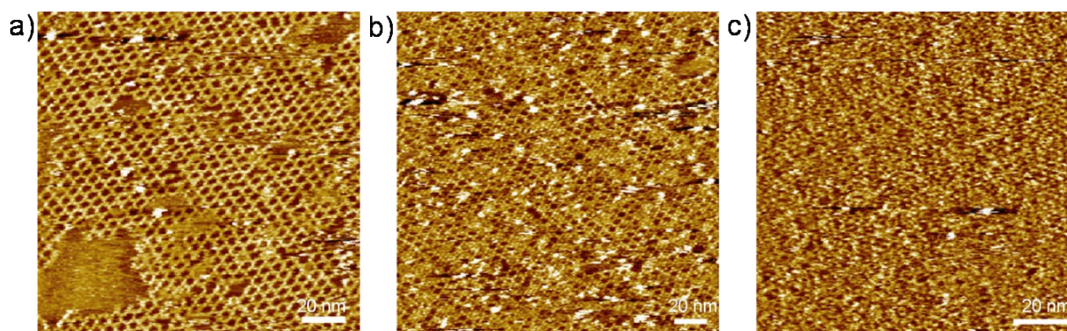


Figure S4. Effect of building blocks concentration on the growth of $2DP_{1+6}$ at the octanoic acid/HOPG interface. STM images obtained at different monomer concentration of **6**: a) 3.5×10^{-6} mol/L, b) 8.8×10^{-6} mol/L, c) 1.8×10^{-5} mol/L. Imaging conditions: a) $I_{\text{set}} = 67$ pA, $V_{\text{bias}} = 0.80$ V; b) $I_{\text{set}} = 40$ pA, $V_{\text{bias}} = 0.80$ V; c) $I_{\text{set}} = 28$ pA, $V_{\text{bias}} = 0.68$ V.

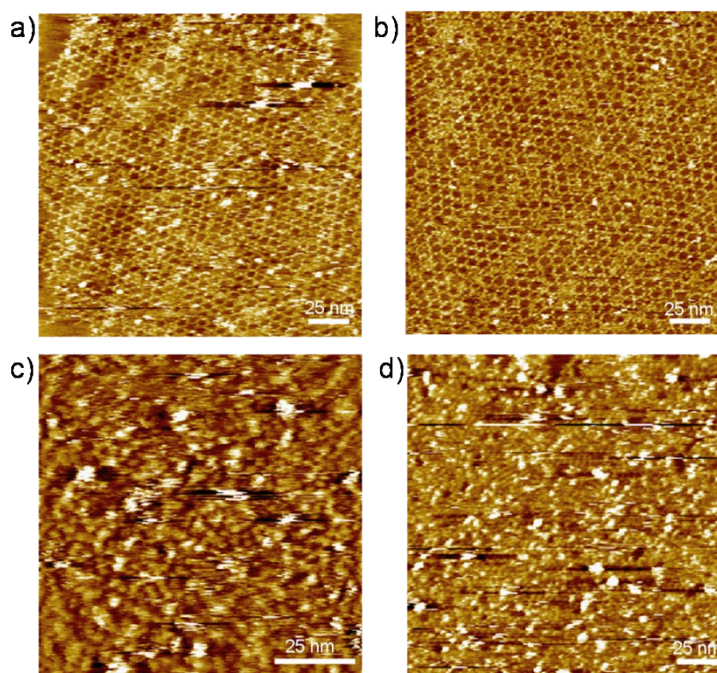


Figure S5. Effect of building blocks concentration on the growth of $2DP_{2+6}$ at the octanoic acid/HOPG interface. STM images obtained at different monomer concentration of **6**: a) 1.4×10^{-6} mol/L, b) 2.7×10^{-6} mol/L, c) 4.1×10^{-6} mol/L, d) 6.8×10^{-6} mol/L. Imaging conditions: a) $I_{\text{set}} = 26$ pA, $V_{\text{bias}} = 0.80$ V; b) $I_{\text{set}} = 39$ pA, $V_{\text{bias}} = 0.75$ V; c) $I_{\text{set}} = 24$ pA, $V_{\text{bias}} = 1.18$ V; d) $I_{\text{set}} = 24$ pA, $V_{\text{bias}} = 1.15$ V.

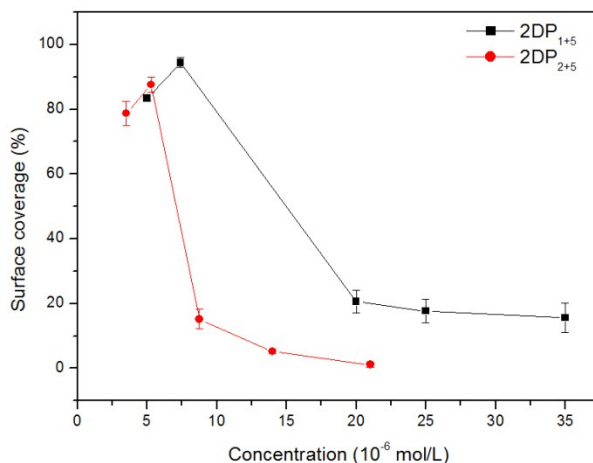


Figure S6. Dependence of the surface coverage of 2DP₁₊₅ and 2DP₂₊₅ on the monomer concentration. Please note that the decrease of surface coverage of well-defined 2DPs at the lowest concentration is due to the formation of submonolayer rather than densely packed linear polymer.

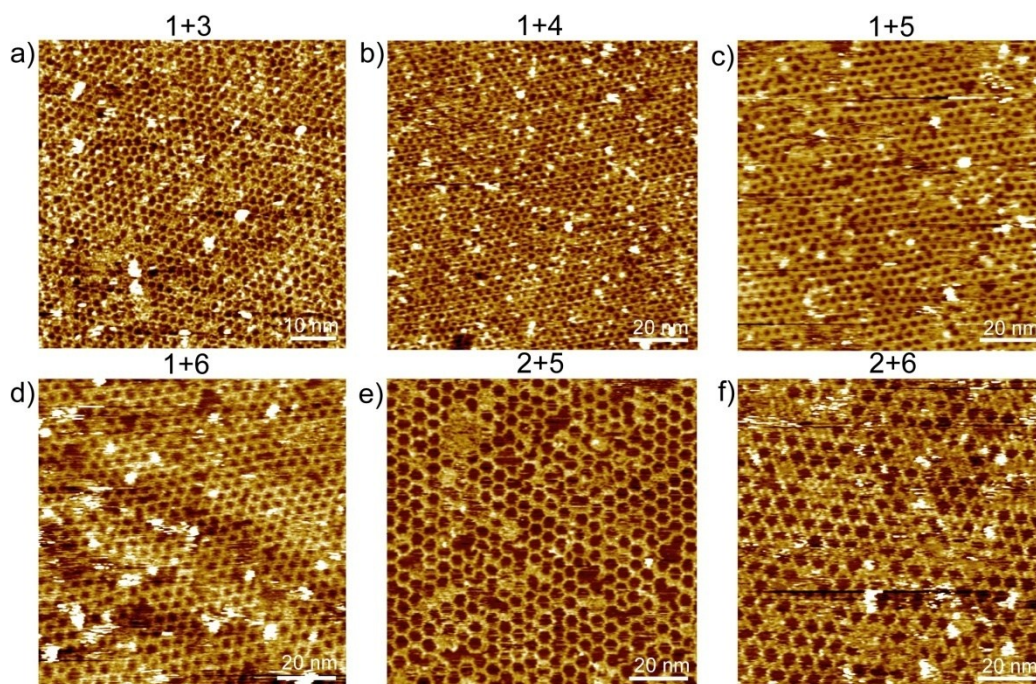


Figure S7. Large-scale STM images of 2DPs derived from co-condensation of the following monomers (the molar concentration of monomers were present in the bracket): (a) 2DP₁₊₃ (2.5×10^{-5} mol/L), (b) 2DP₁₊₄ (1.6×10^{-5} mol/L), (c) 2DP₁₊₅ (7.4×10^{-6} mol/L), (d) 2DP₁₊₆ (3.5×10^{-6} mol/L), (e) 2DP₂₊₅ (5.3×10^{-6} mol/L), (f) 2DP₂₊₆ (2.7×10^{-6} mol/L), at the octanoic acid/HOPG interface. a) $I_{\text{set}} = 36$ pA, $V_{\text{bias}} = 0.66$ V; b) $I_{\text{set}} = 70$ pA, $V_{\text{bias}} = 0.55$ V; c) $I_{\text{set}} = 30$ pA, $V_{\text{bias}} = 0.70$ V; d) $I_{\text{set}} = 62$ pA, $V_{\text{bias}} = 0.76$ V; e) $I_{\text{set}} = 45$ pA, $V_{\text{bias}} = 0.25$ V; f) $I_{\text{set}} = 30$ pA, $V_{\text{bias}} = 1.00$ V.

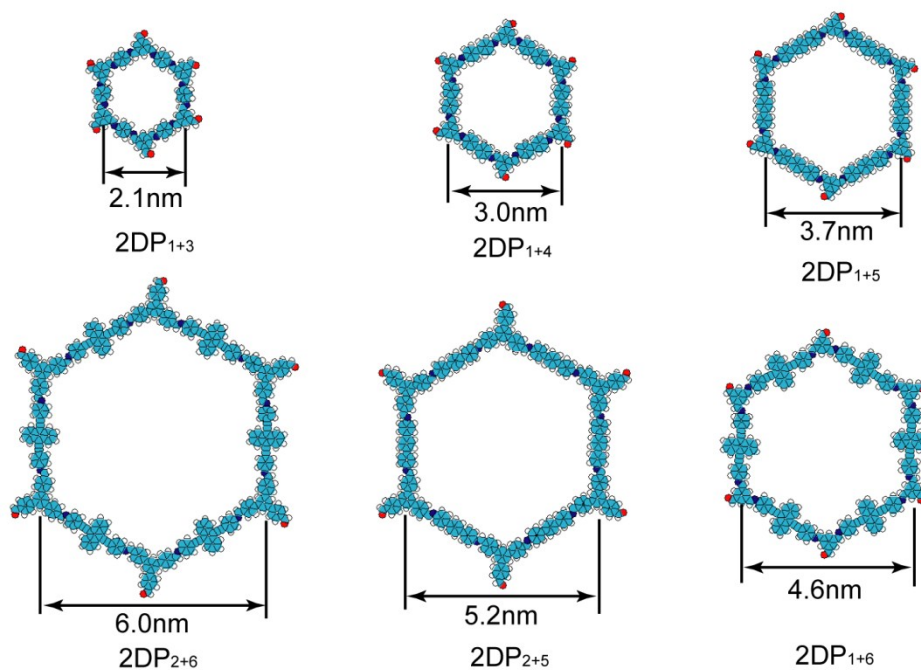


Figure S8. Optimized models of $2DP_{1+3}$, $2DP_{1+4}$, $2DP_{1+5}$, $2DP_{1+6}$, $2DP_{2+5}$, and $2DP_{2+6}$ and the repeating periods are 2.1 nm, 3.0 nm, 3.7 nm, 4.6 nm, 5.2 nm and 6.0 nm, respectively.

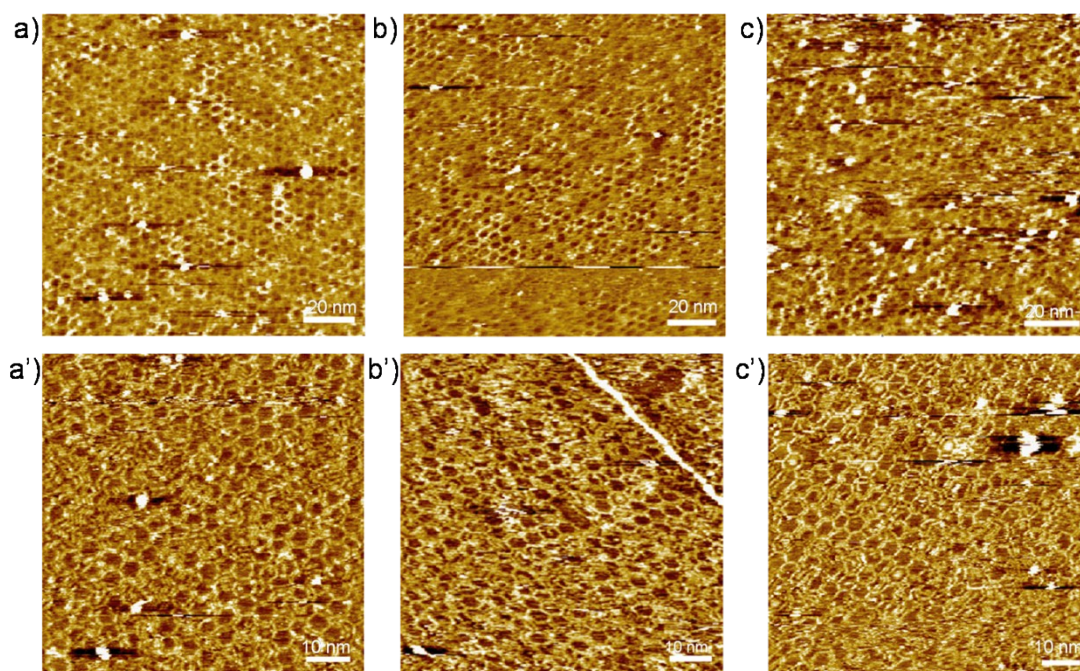


Figure S9. STM images show the top (a, b, c) and bottom (a', b', c') layer of $2DP_{1+5}$ at the octanoic acid/HOPG interface at room temperature: concentration of **5**, a, a') 3.5×10^{-5} mol/L; b, b') 2.5×10^{-5} mol/L; c, c') 2.0×10^{-5} mol/L. Imaging conditions: a) $I_{\text{set}} = 17$ pA, $V_{\text{bias}} = 0.60$ V; a') $I_{\text{set}} = 24$ pA, $V_{\text{bias}} = 0.60$ V; b) $I_{\text{set}} = 36$ pA, $V_{\text{bias}} = 0.60$ V; b') $I_{\text{set}} = 45$ pA, $V_{\text{bias}} = 0.68$ V; c) $I_{\text{set}} = 26$ pA, $V_{\text{bias}} = 0.65$ V; c') $I_{\text{set}} = 49$ pA, $V_{\text{bias}} = 0.80$ V.

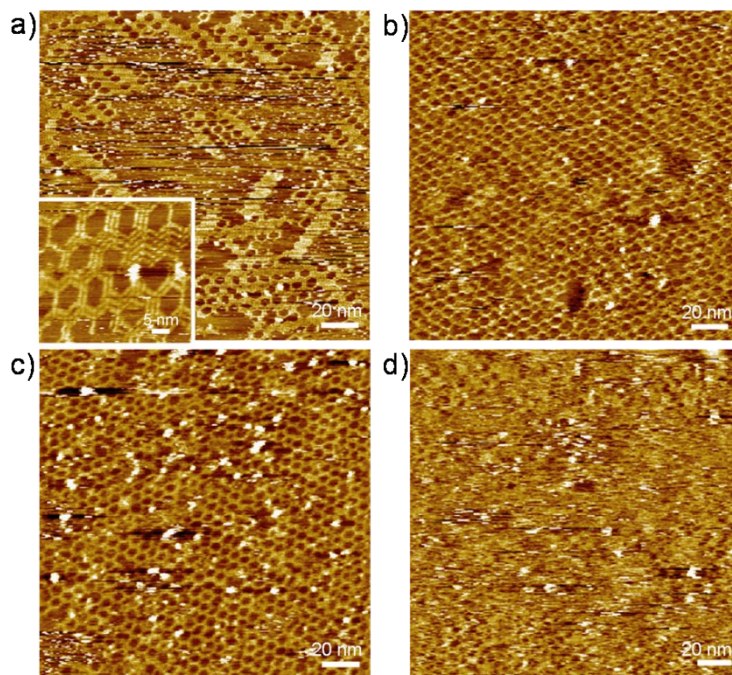


Figure S10. Effect of the molar ratio of monomers on the growth of $2DP_{2+5}$. STM images obtained at different molar ratio of **2** and **5**: a) 3:1, b) 1:3, c) 1:5, d) 1:10. Imaging conditions: a) $I_{\text{set}} = 73$ pA, $V_{\text{bias}} = 1.04$ V ($I_{\text{set}} = 58$ pA, $V_{\text{bias}} = 1.04$ V, inset); b) $I_{\text{set}} = 39$ pA, $V_{\text{bias}} = 0.68$ V; c) $I_{\text{set}} = 28$ pA, $V_{\text{bias}} = 0.80$ V; d) $I_{\text{set}} = 36$ pA, $V_{\text{bias}} = 0.66$ V.

3. XPS and XRD of the precipitations

XPS were conducted on samples obtained with two different methods: thin films formed by deposition of mixture solutions on a HOPG surface, and precipitations obtained by mixing the high concentration monomers, both at room temperature. The Schiff base condensation already happens in solution upon mixing at room temperature, which can be inferred from the color change of the solution, and even precipitates when the monomer concentration is high enough. These precipitations were allowed to age at room temperature for 12h and then isolated by centrifugation, washed with *N,N*-dimethylformamide (3×10 mL) and tetrahydrofuran (3×10 mL), and dried at 25 °C under vacuum for 24 h to yield powders.^[3] XPS of these participations (Figure S11) are consistent with that obtained with the thin film on HOPG surface, confirms the formation of imine polymers. X-ray diffraction (XRD) analysis of these powders indicates that the structure are amorphous rather than crystalline. Besides confirming the covalent nature of the 2D networks observed by STM, these data also indicate that the epitaxy effect of the HOPG surface plays an important role in the formation of well defined 2D polymers.

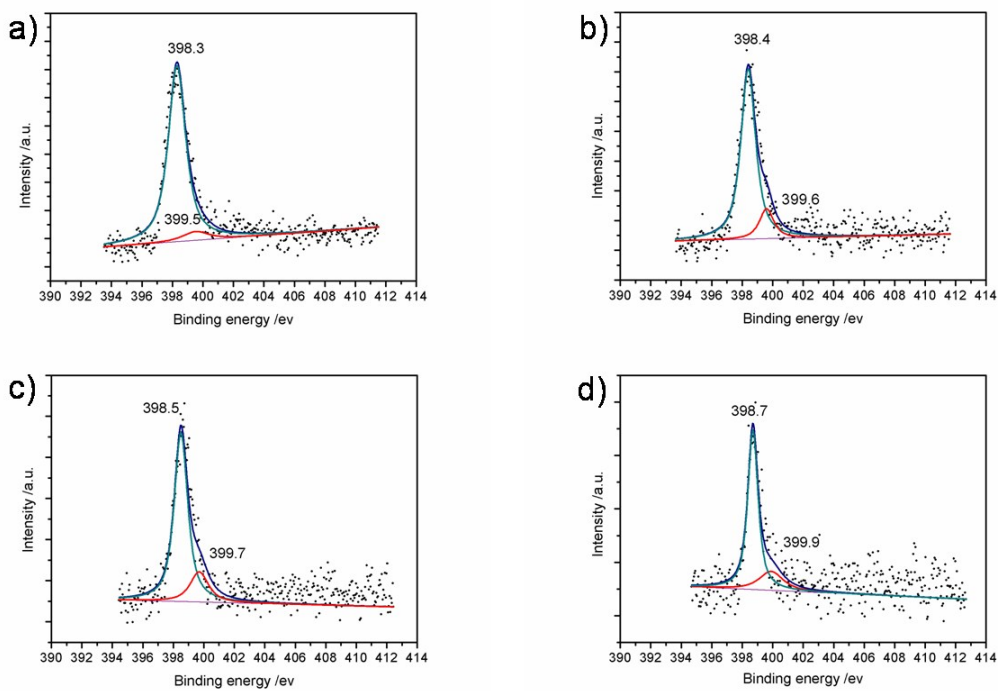


Figure S11. N1s XPS signals of the powders of (a) 1+3, (b) 1+4, (c) 1+5 and (d) 1+6.

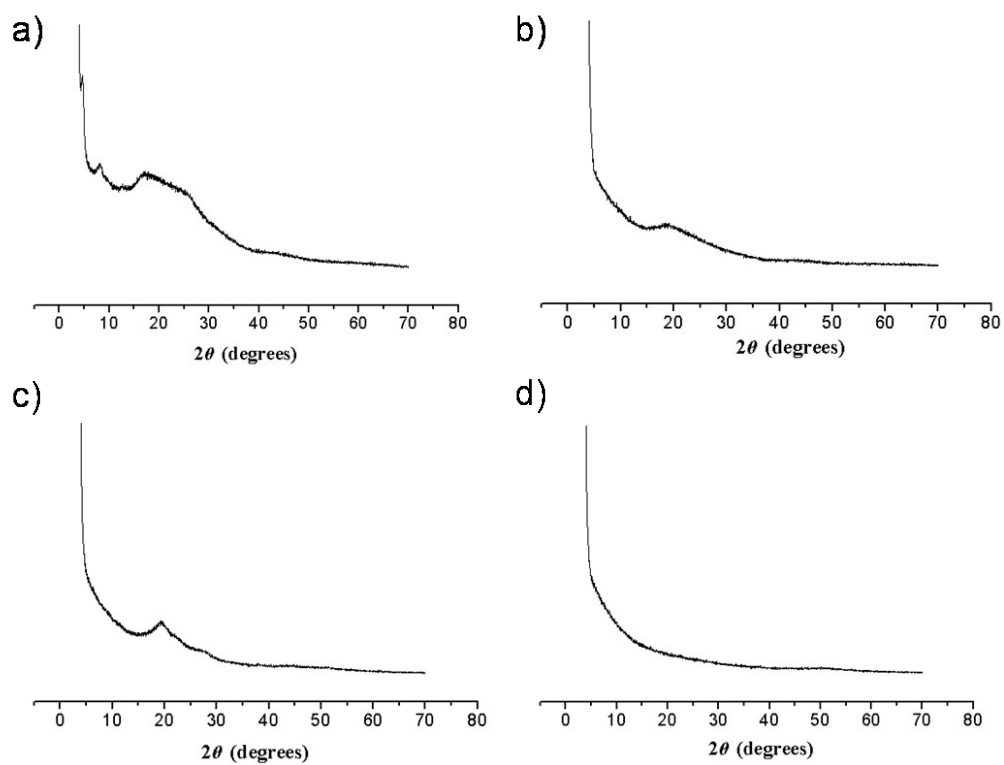
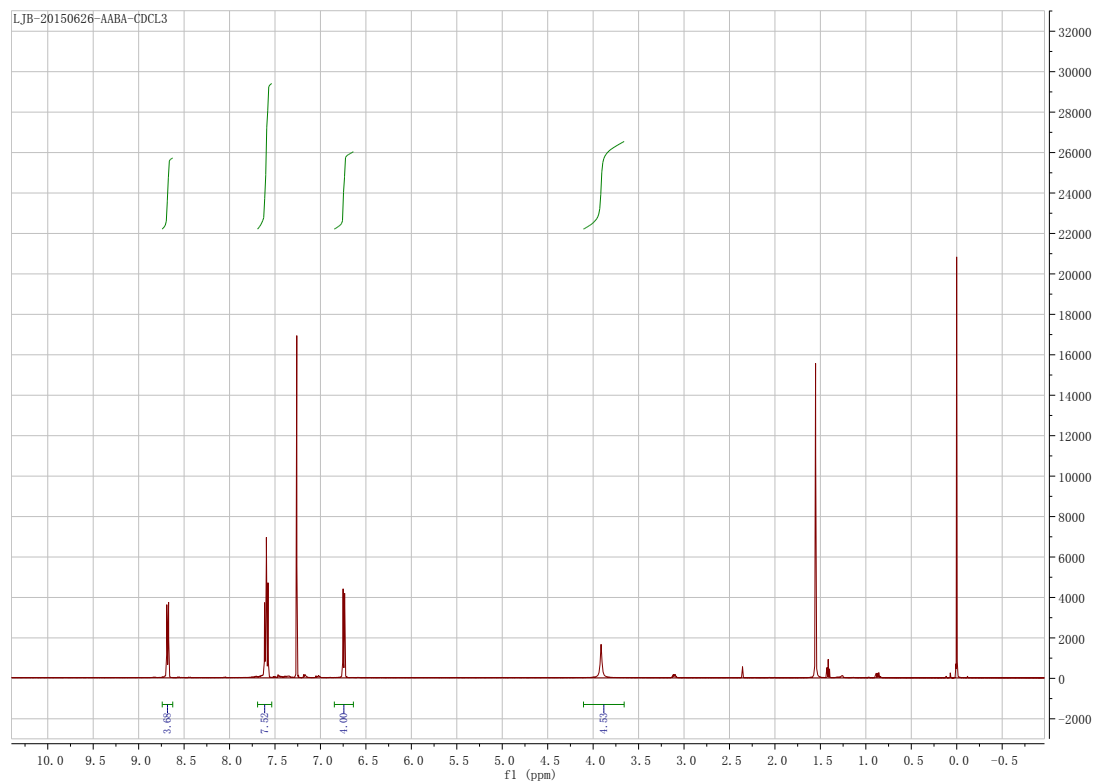
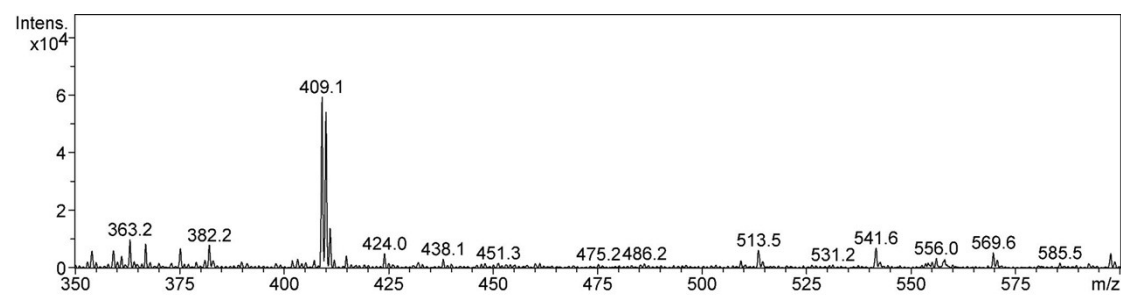


Figure S12. XRD pattern for powder (a) 1+3, (b) 1+4, (c) 1+5 and (d) 1+6.

4. ^1H NMR and MS of AABA



^1H NMR (500 MHz, CDCl_3) δ 8.70 – 8.67 (m, 4H), 7.62 – 7.57 (m, 8H), 6.74 (d, $J = 8.5$ Hz, 4H), 3.91 (s, 4H).



MS(ESI) m/z 409.1 [M^+]

5. Estimation of the adsorption energy

The estimation of the adsorption energy in the linear and 2D polymers is based on parameterization referring to some theoretical simulations.^[4] This estimation is rough and qualitative but helpful to understand in an energetic aspect the difference of these two polymorphs at the level of total system, and could not be considered as a quantitative measurement.

A. Parameterization

Interaction of the molecule with the HOPG substrate

Aromatic parts: -65 ± 5 meV/sp² carbon

The nitrogen atoms are considered as aromatic carbon when estimate the adsorbate-substrate interaction.

B. Assumptions

The estimation take into account only the interactions between the adsorbate-substrate, but not the adsorbate-adsorbate and interaction between the molecule and solvent, neither the interaction between solvent and substrate.

Based on the above parameterization, the adsorption energy for the linear and 2D polymers could be estimated as:

$E_{\text{ads}} = n*65/A$, where n is the number of carbon and nitrogen atoms in each unit cell, and A is the area of the unit cell.

References:

- [1] M. Imoto, M. Takeda, A. Tamaki, H. Taniguchi, K. Mizuno, *Res. Chem. Intermed.* 2009, **35**, 957.
- [2] X. H. Liu, C. Z. Guan, S. Y. Ding, W. Wang, H. J. Yan, D. Wang, L. J. Wan, *J. Am. Chem. Soc.* 2013, **135**, 10470.
- [3] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, *J. Am. Chem. Soc.* 2011, **133**, 19816.
- [4] R. Zacharia, H. Ulbricht and T. Hertel, *Phys. Rev. B*, 2004, **69**, 1555406; S. Yin, C. Wang, X. Qiu and C. L. Bai, *Surf. Inter. Analysis*, 2001, **32**, 2248; A. J. Gellman and A. R. Paserba, *J. Phys. Chem. B*, 2002, **106**, 13231.