

Supporting Information

Dynamic Covalent Chemistry of Imine Polymers at Liquid/solid Interfaces Investigated by Scanning Tunneling Microscopy

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1 Additional STM images

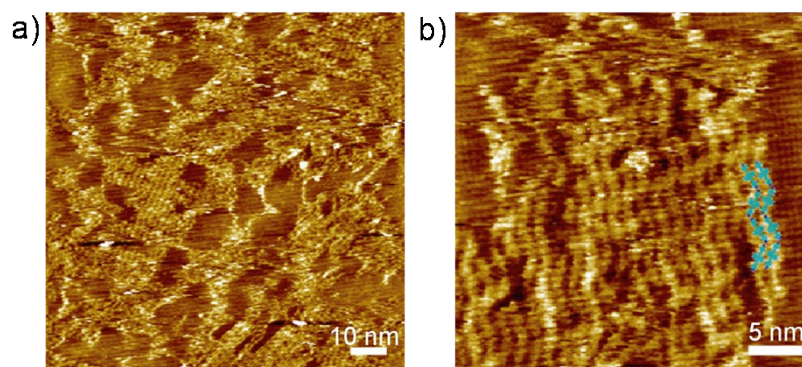


Figure S1. a) large-scale and b) high resolution STM images of the assembly of **4** (2.2×10^{-5} mol/L) at the octanoic acid/HOPG. Imaging conditions: (a) $I_{set} = 20$ pA, $V_{bias} = 0.66$ V; (b) $I_{set} = 25$ pA, $V_{bias} = 0.60$ V.

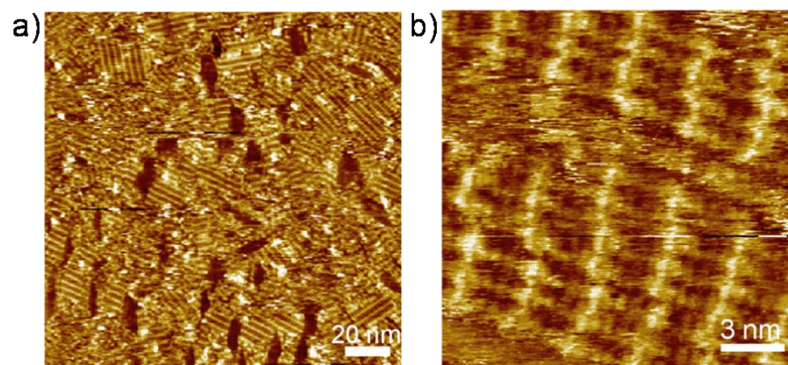


Figure S2. Large-scale and molecular-resolution STM images of 1DP derived from co-condensation of terephthalaldehyde with **4** at the octanoic acid/HOPG. Imaging conditions: (a) $I_{set} = 22$ pA, $V_{bias} = 0.77$ V; (b) $I_{set} = 28$ pA, $V_{bias} = 0.77$ V.

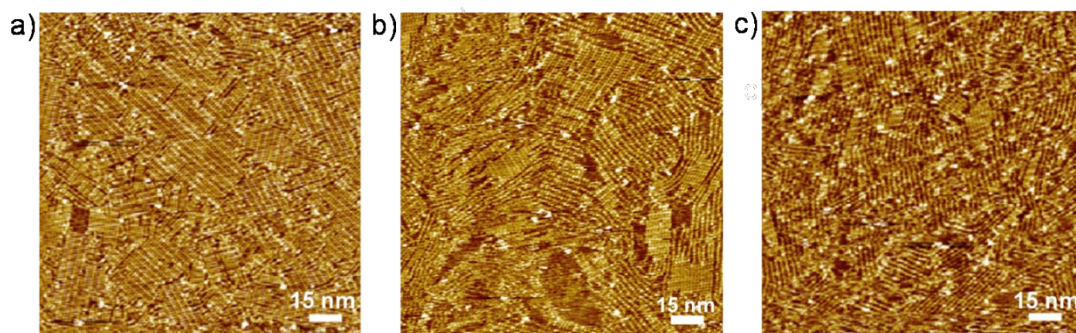


Figure S3. Typical wide-area STM images of the monolayer formed by a three-component mixture of **2**, **3** and **4** in octanoic acid in the ratio 3:1.5:1.5 (a), 3:2:1 (b), 3:2.5:0.5 (c), is dropcasted on the HOPG surface. Imaging conditions: (a) $I_{set} = 39$ pA, $V_{bias} = 0.60$ V; (b) $I_{set} = 22$ pA, $V_{bias} = 0.77$ V; (c) $I_{set} = 38$ pA, $V_{bias} = 0.38$ V.

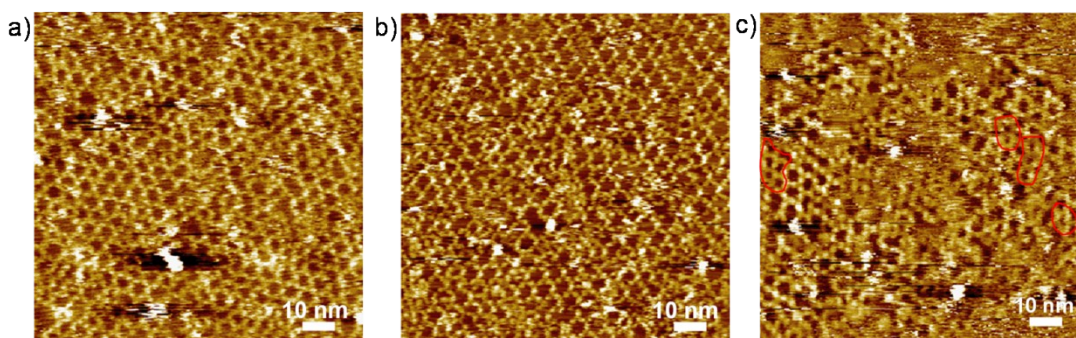


Figure S4. Typical STM images of the monolayer formed by a three-component mixture of **1**, **3** and **4** with the molar ratio 4:3:3 (a), 2:3:3 (b) and 4: 5: 1 (c). The domains of $2DP_{1+3}$ are marked by the red circles. Imaging conditions: (a) $I_{set} = 24$ pA, $V_{bias} = 0.66$ V; (b) $I_{set} = 28$ pA, $V_{bias} = 0.60$ V; (c) $I_{set} = 28$ pA, $V_{bias} = 0.66$ V.

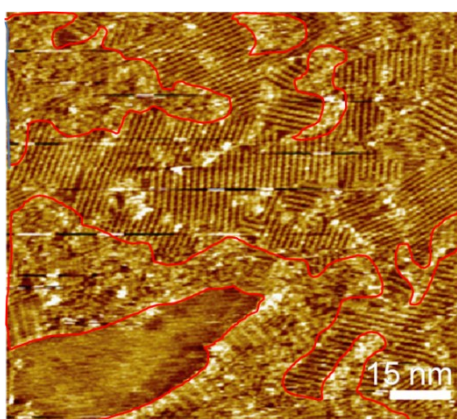


Figure S5. Representative STM images show the coexistence of $1DP_{2+3}$ and $1DP_{2+4}$ after about 780 minutes of the addition of **4** on top of a pre-existing monolayer of $1DP_{2+3}$ ($I_{set} = 19$ pA, $V_{bias} = 0.60$ V). Domains of $1DP_{2+4}$ are marked by the red curves.

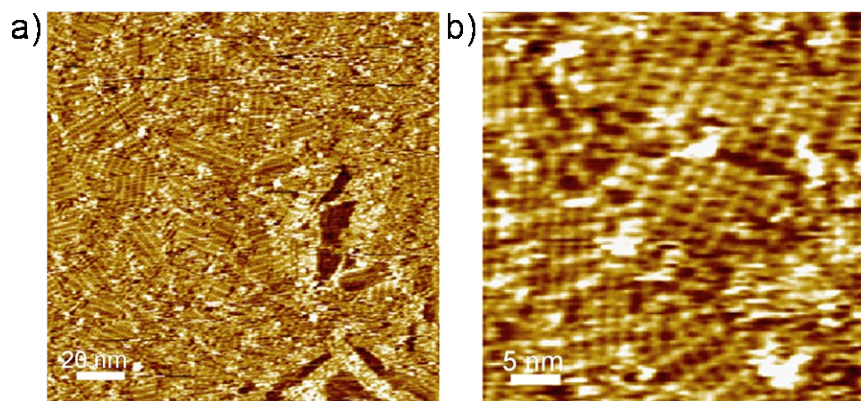


Figure S6. STM images showing that the amine exchange in $1DP_{1+3}$ by **4** was accomplished after annealing at $100\text{ }^{\circ}\text{C}$ for 30 minutes. (a) $I_{set} = 22\text{ pA}$, $V_{bias} = 0.60\text{ V}$; (b) $I_{set} = 20\text{ pA}$, $V_{bias} = 0.60\text{ V}$.

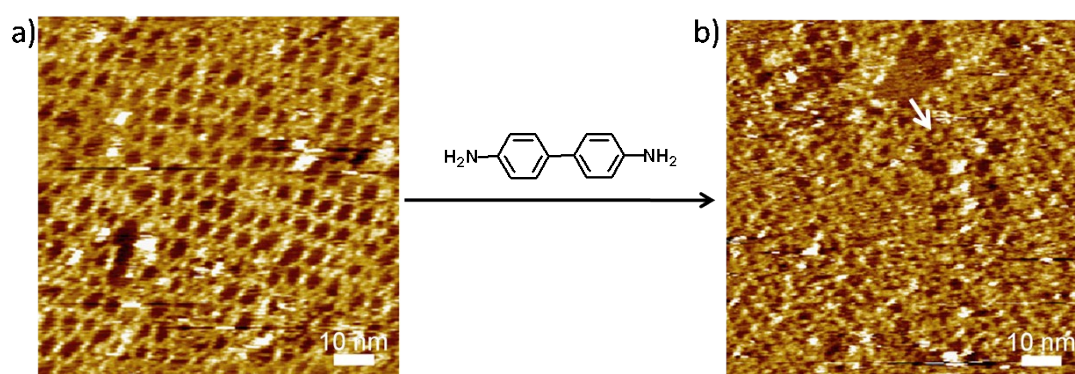


Figure S7. STM representative images of *in situ* amine exchange process in case of $2DP_{1+4}$. On the *in situ* addition of **3** on top of a pre-existing monolayer of $2DP_{1+4}$ (a), a large portion of the cavities of the $2DP_{1+4}$ network appear filled (b). Imaging conditions: (a) $I_{set} = 26\text{ pA}$, $V_{bias} = 0.60\text{ V}$; (b) $I_{set} = 26\text{ pA}$, $V_{bias} = 0.60\text{ V}$.

2 NMR experiment

2.1 2+3 condensation

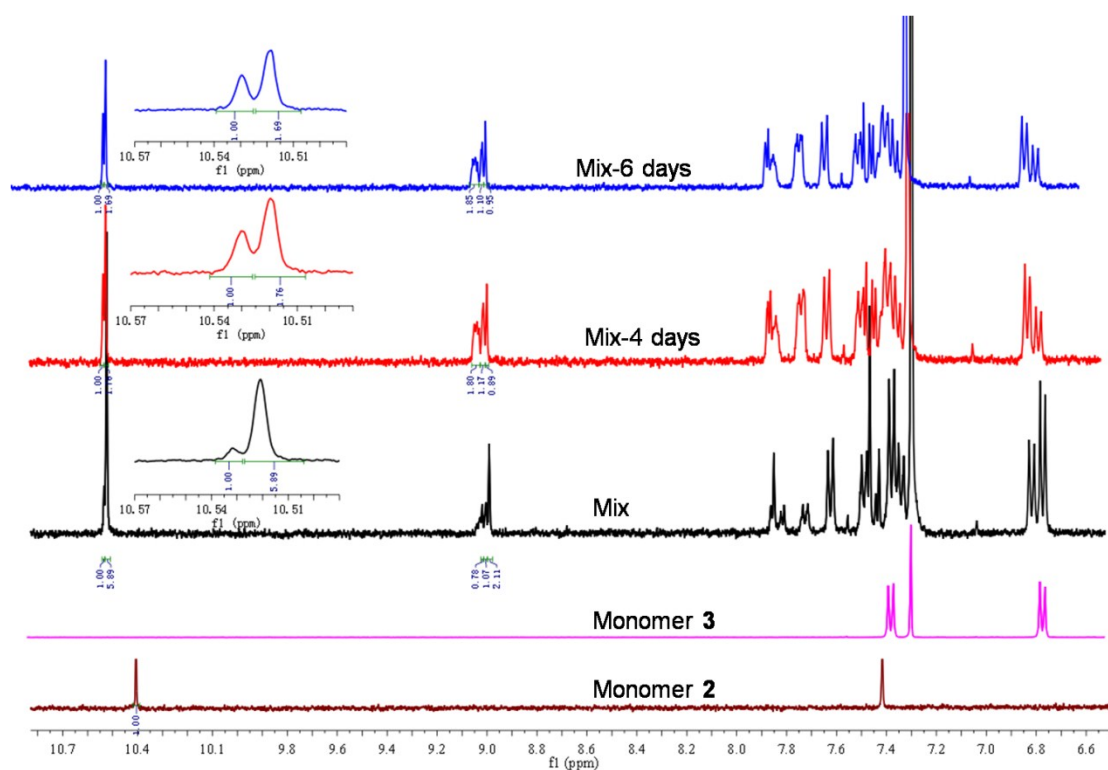


Figure S8. The ¹H-NMR spectrums (400 MHz, 298K) of monomer **3** in CDCl₃, monomer **2** in DMSO-*d*₆ and the mixture of aldehyde **2** with **3** (molar ratio: 1:1, C₃=2.3×10⁻³ mol/L) in CDCl₃ after lay aside for 0 day, 4 days and 6 days, respectively.

2.2 2+4 condensation

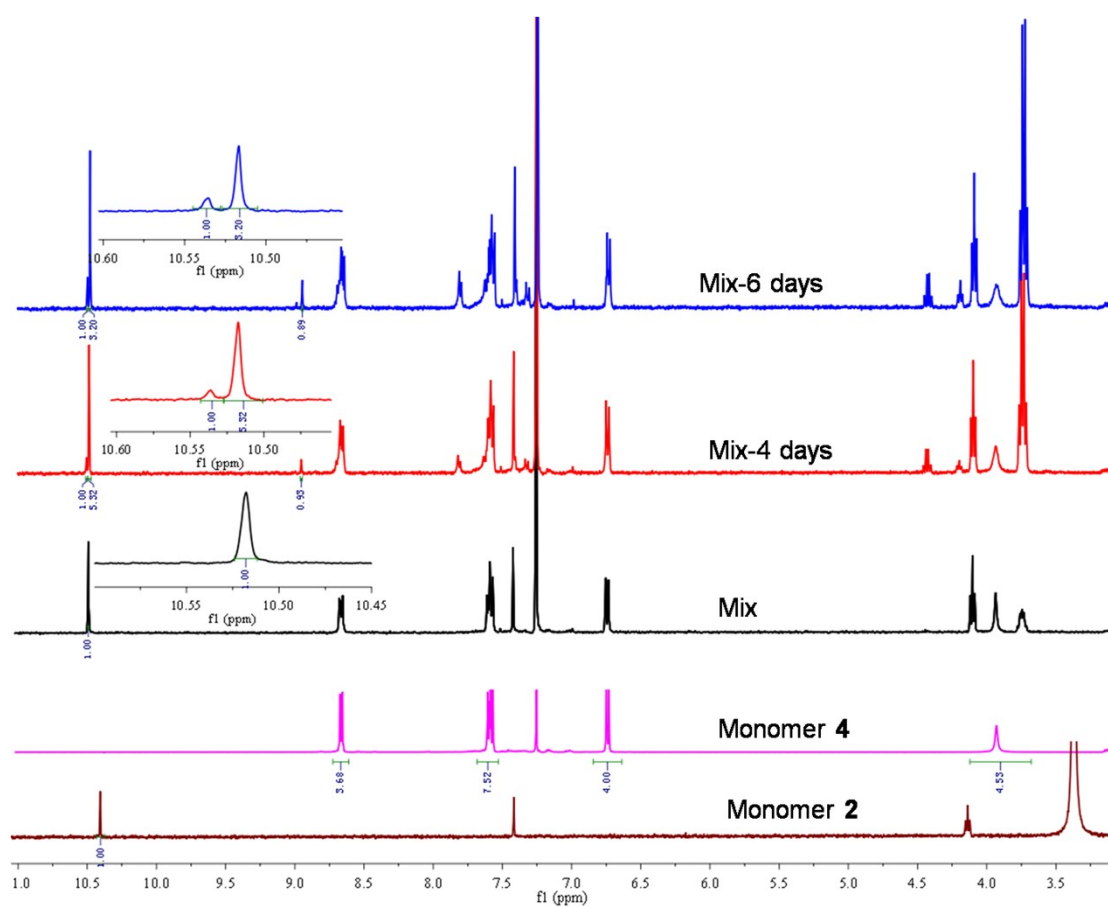


Figure S9. The ¹H-NMR spectrums (400 MHz, 298K) of monomer **4** in CDCl₃, monomer **2** in DMSO-*d*₆ and the mixture of aldehyde **2** with **4** (molar ratio: 1:1, C₄=1.9×10⁻³ mol/L) in CDCl₃ after lay aside for 0 day, 4 days and 6 days, respectively.