*Electronic Supplementary Information for*

# Molecular Pentagonal Tiling: Self-Assembly of Pentagonal-Shaped Macrocycles at Liquid/Solid Interfaces

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## Contents

## 1. Details of STM Investigations.

All experiments were performed at 20–22 °C using a PicoSTM (Agilent) with negative sample bias. All STM images were acquired in the constant current mode. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.25 mm).

Prior to imaging, a compound under investigation was dissolved in commercially available anhydrous 1,2,4-trichlorobenzene (TCB, Aldrich) or 1-octanoic acid (Aldrich) at various solute concentrations, and a drop of this solution (4–7 μL) was applied on a freshly cleaved surface of HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH) or the surface of a flame annealed Au(111) substrate (Georg Albert PVD Company). Then the 2D networks were investigated at the liquid/solid interface. By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the substrate and the average tunneling current, it was possible to switch from the visualization of the adsorbate layer to that of the underlying HOPG substrate. This enabled us to correct for drift effects by the use of SPIP software (Image Metrology A/S). On the other hand, in-situ calibrations of image was not performed on Au(111) surface. The white colored axes shown in Figures indicate the direction of main symmetry axes of graphite underneath the molecular layers. In the case of Au(111) surface, the direction of the symmetry axes of the underlying substrate was determined by using the direction of the herringbone reconstructed lines or the step edge of gold.

## 2. Synthesis of Pentagonal-Shaped Macrocycles.

**General**. All manipulations were performed in an inert gas (nitrogen or argon) atmosphere. All solvents were distilled before use. Macrocycle **1c** and **1d** was prepared following the literatures.[1,2]

$^{1}$H (270 MHz) and $^{13}$C (67.5 MHz) NMR spectra were measured on a JEOL JNM-GSX-270 spectrometers, respectively. When chloroform-*d* was used as a solvent, the spectra were referenced to the residual solvent hydrogen in the $^{1}$H NMR spectra (7.26 ppm) and to the solvent carbons in the $^{13}$C NMR spectra (77.0 ppm). Preparative HPLC was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as the eluent. Other spectra were recorded by the use of the following instruments: IR spectra, JACSCO FT/IR-410; mass spectra, AXIMA-CFR for LD ionization mode.

**Ester Exchange Reactions**. Macrocycle **1c**[1] (27.0 mg, 27.0 μmol), $K_2CO_3$ (10.0 mg, 72.4 μmol), and 18-crown-6 (5.0 mg, 18.9 μmol) were suspended in a mixture of $CH_2Cl_2$ (1.0 mL) and hexadecanol or decanol (1.0 mL). After stirred at 40 °C for 3 d, the solvents were removed under vacuum. The crude mixture was subjected to silica gel column chromatography ($CH_2Cl_2$ as eluent), and recrystallization from $CH_2Cl_2$/MeOH afforded white-colored solids. Further purification was performed by using recycling HPLC to afford the ester-exchanged compounds (24% yield for **1a** and 16% yield for **1b**) as white solids.

**1a**. mp 91.5–93.5 °C; $^{1}$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 8.05 (d, *J* = 1.6 Hz, 10H), 7.98 (t, *J* = 1.6 Hz, 5H), 4.35 (t, *J* = 6.8 Hz, 10H), 1.83 (quint, *J* = 7.6 Hz, 10H), 1.55–1.20 (m, 130H), 0.88 (t, *J* = 6.8 Hz, 15H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 164.8, 141.0, 131.5, 131.1, 123.5, 89.7, 65.8, 33.7, 32.0, 29.80, 29.77, 29.75, 29.73, 29.65, 29.44, 29.42, 28.8, 26.1, 22.8, 14.2; IR (neat) 3071, 2924, 2854, 2214, 1724, 1594, 1450, 1322, 1238, 1008, 763, 673 cm$^{-1}$; MS (LDI) *m/z* 1841 ($M^-$).

**1b**. mp 87.0–89.0 °C; $^{1}$H NMR (270 MHz, $CDCl_3$, 30 °C) δ 8.12 (d, *J* = 1.6 Hz, 10H), 8.06 (t, *J* = 1.6 Hz, 5H), 4.37 (t, *J* = 6.8 Hz, 10H), 1.82 (quint, *J* = 7.6 Hz, 10H), 1.55–1.20 (m, 70H), 0.88 (t, *J* = 6.8 Hz, 15H); $^{13}$C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 164.9, 141.01, 131.6, 131.08, 123.5, 89.6, 65.8, 32.0, 29.7, 29.6, 29.4, 28.8, 26.1, 22.8, 14.2; IR (neat) 3072, 2917, 2851, 2214, 1726, 1595, 1469, 1450, 1324, 1238, 1010, 889, 763, 673 cm$^{-1}$; MS (LDI) $m/z$ 1421 ($M^-$).

## 3. An Additional STM Images at the TCB/Au(111)Interface.

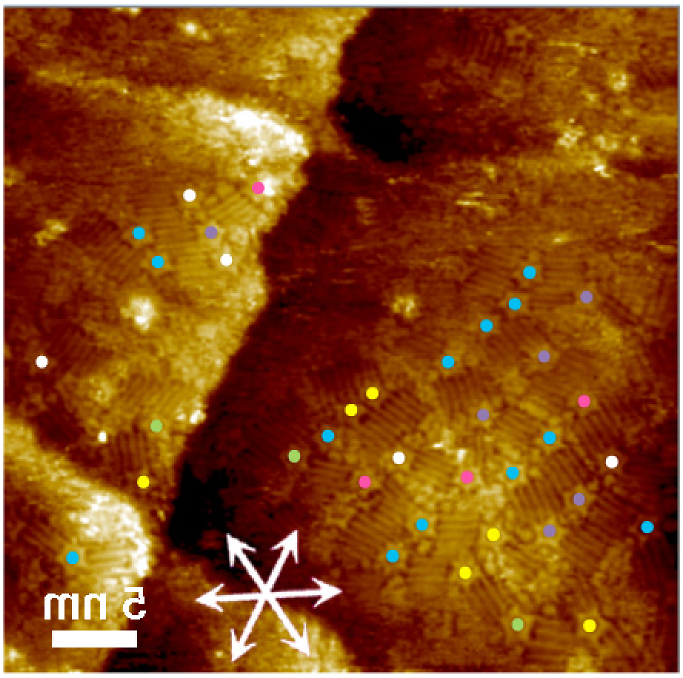

**Fig. S1** Large scale STM image of **1a** at the TCB/Au(111) interface (the tunneling parameters; $I_{set}$= 278 pA, $V_{bias}$ = –354 mV). The white arrows correspond to the NN direction of the Au(111) surface. The six orientations of the π-cores are highlighted by different colors.

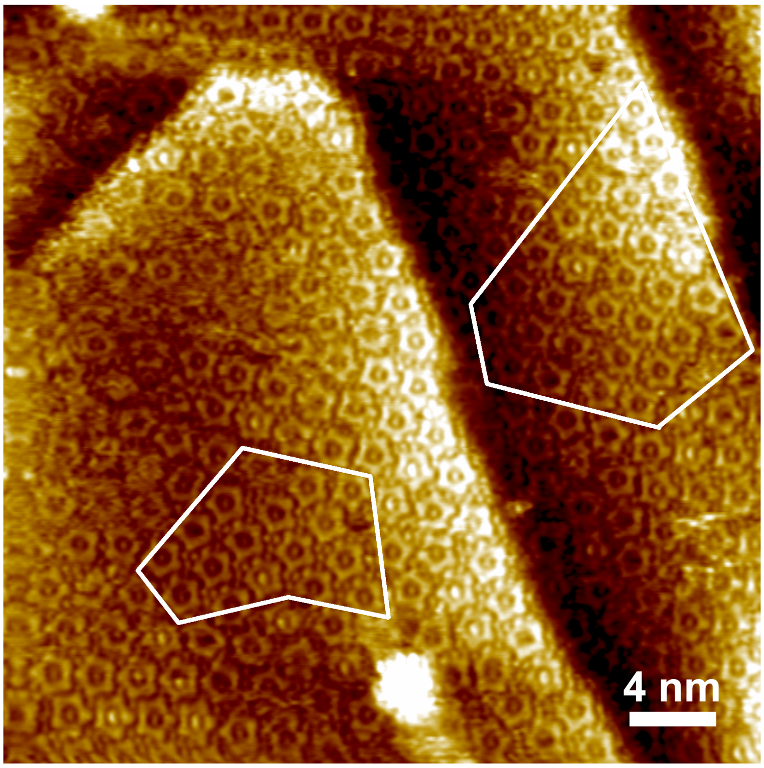

**Fig. S2** Large scale STM image of **1d** at the 1-octanoic acid/Au(111) interface (the tunneling parameters; $I_{set}$= 278 pA, $V_{bias}$ = –354 mV). The areas surrounded by the white lines correspond to domains of the parallel type linear structure.

## 4. References.

1. (a) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227–4239. (b) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019–1027.
2. Yamakawa, J.; Ohkoshi, M.; Takahashi, F.; Nishiuchi, T.; Kuwatani, Y.; Nishinaga, T.; Yoshida, M.; Iyoda, M. *Chem. Lett.* **2008**, *37*, 784–785.