Electronic Supplementary Information (ESI)

Fabrication and Transformation of Novel Two-Dimensional Tripod Structures: Structural Modulation by Alkyl Chain Length and Tandem Claisen Rearrangement

Kazuhiro Omori,[a, b, c] Yoshihiro Kikkawa,*[, b] Masatoshi Kanesato,[b] and Kazuhisa Hiratani*[, c]

[a] *Industrial Technology Center of Tochigi Prefecture, 367-1 Karinuma, Utsunomiya, Tochigi 321-3224, Japan,* [b] *Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan,* [c] *Department of Applied Chemistry, Utsunomiya University, 7-1-2 Youtou, Utsunomiya, Tochigi 321-8585, Japan,*

(y.kikkawa@aist.go.jp, hiratani@cc.utsunomiya-u.ac.jp)

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1. Detail of experimental procedure

1.1 Synthesis and characterization

Isobutenyl compounds were synthesized according to the previous literature.[s1] Characterization of each compounds were performed by ^{1}H NMR (Varian NMR System 500 spectrometer) operating at 500 MHz in $CDCl_3$ and FT-IR (Shimadzu IR Prestige-21) using a KBr disk.

C19-1

^{1}H NMR ($CDCl_3$): δ = 0.88(6H, t, *J* = 7.0 Hz, CH_3), 1.19(64H, broad, CH_2), 1.51(4H, m, CH_2), 3.40(4H, m, N-CH_2), 4.94(4H, s, =C-CH_2-O), 5.66(2H, s, CH_2=C), 7.24(2H, s, Naph-H), 7.41(2H, dd, *J* = 7.5 7.5 Hz, Naph-H), 7.50(2H, dd, *J* = 7.5 7.0 Hz, Naph-H), 7.66(2H, d, *J* = 8.0 Hz, Naph-H), 7.71(2H, t, *J* = 5.0 Hz, N-H), 7.89(2H, d, *J* = 8.0 Hz, Naph-H), 8.71(2H, s, Naph-H), IR (KBr): 743(Naph), 1182(C-O-C), 1626(C=C), 1644(C=O), 3308(N-H) cm^{-1}. Anal. Calcd for $C_{64}H_{98}N_2O_4$: C, 80.12; H, 10.30; N, 2.92. Found: C, 80.15; H, 10.85; N, 2.93.

C20-1

^{1}H NMR ($CDCl_3$): δ = 0.88(6H, t, *J* = 7.0 Hz, CH_3), 1.18(68H, broad, CH_2), 1.50(4H, m, CH_2), 3.40(4H, m, N-CH_2), 4.94(4H, s, =C-CH_2-O), 5.66(2H, s, CH_2=C), 7.24(2H, s, Naph-H), 7.41(2H, dd, *J* = 8.0 7.5 Hz, Naph-H), 7.50(2H, dd, *J* = 8.0 7.0 Hz, Naph-H), 7.66(2H, d, *J* = 8.0 Hz, Naph-H), 7.72(2H, t, *J* = 5.5 Hz, N-H), 7.88(2H, d, *J* = 8.0 Hz, Naph-H), 8.70(2H, s, Naph-H), IR (KBr): 744(Naph), 1180(C-O-C), 1623(C=C), 1642(C=O), 3338(N-H) cm^{-1}. Anal. Calcd for $C_{66}H_{102}N_2O_4 \cdot 1/2H_2O$: C, 79.55; H, 10.42; N, 2.81. Found: C, 79.18; H, 10.79; N, 2.82.

C21-1

^{1}H NMR ($CDCl_3$): δ = 0.88(6H, t, *J* = 7.0 Hz, CH_3), 1.19(72H, broad, CH_2), 1.50(4H, m, CH_2), 3.40(4H, m, N-CH_2), 4.94(4H, s, =C-CH_2-O), 5.66(2H, s, CH_2=C), 7.24(2H, s, Naph-H), 7.41(2H, dd, *J* = 7.0 7.5 Hz, Naph-H), 7.50(2H, dd, *J* = 8.0 7.0 Hz, Naph-H), 7.66(2H, d, *J* = 8.0 Hz, Naph-H), 7.72(2H, t, *J* = 5.5 Hz, N-H), 7.89(2H, d, *J* = 8.0 Hz, Naph-H), 8.71(2H, s, Naph-H), IR (KBr): 744(Naph), 1181(C-O-C), 1627(C=C), 1646(C=O), 3309(N-H) cm^{-1}. Anal. Calcd for $C_{68}H_{106}N_2O_4 \cdot 1/2H_2O$: C, 79.71; H, 10.53; N, 2.73. Found: C, 80.05; H, 10.96; N, 2.59.

C19-2

^{1}H NMR ($CDCl_3$): δ = 0.88(6H, t, *J* = 7.0 Hz, CH_3), 1.25 (56H, broad, CH_2), 1.67(4H, m, CH_2), 3.50(4H, m, N-CH_2), 4.00(4H, s, =C-CH_2-O), 4.44(2H, s, CH_2=C), 6.53(2H, t, *J* = 5.5 Hz, N-H), 7.27(2H, dd, *J* = 8.5 7.5Hz, Naph-H), 7.40(2H, dd, *J* = 7.0 7.0 Hz, Naph-H), 7.72(2H, d, *J* = 8.5 Hz, Naph-H), 7.77(2H, d, *J* = 8.5 Hz, Naph-H), 7.84(2H, s, Naph-H), 12.0(2H, s, OH), IR (KBr): 742(Naph), 1617(C=C), 1647(C=O), 3303(OH), 3352(N-H) cm^{-1}. Anal. Calcd for $C_{64}H_{98}N_2O_4 \cdot H_2O$: C, 78.64; H, 10.31; N, 2.87. Found: C, 78.87; H, 10.61; N, 2.80.

C20-2

^{1}H NMR ($CDCl_3$): δ = 0.88(6H, t, *J* = 7.0 Hz, CH_3), 1.25 (60H, broad, CH_2), 1.67(4H, m, CH_2), 3.50(4H, m, N-CH_2), 4.00(4H, s, =C-CH_2-O), 4.43(2H, s, CH_2=C), 6.54(2H, t, *J* = 5.5 Hz, N-H), 7.28(2H, dd, *J* = 8.0 7.5Hz, Naph-H), 7.41(2H, dd, *J* = 8.0 7.5 Hz, Naph-H), 7.72(2H, d, *J* = 8.0 Hz, Naph-H), 7.77(2H, d, *J* = 8.5 Hz, Naph-H), 7.84(2H, s, Naph-H), 12.0 (2H, s, OH), IR (KBr): 741(Naph), 1616(C=C), 1642(C=O), 3338(OH, N-H) cm^{-1}. Anal. Calcd for $C_{66}H_{102}N_2O_4 \cdot H_2O$: C, 78.84; H, 10.43; N, 2.79. Found: C, 78.58; H, 10.61; N, 2.74.

1.2 STM observation

The 2D structures of each compound were observed by low-current STM (Veeco Instruments, CA: Nanoscope IIIa multimode SPM). The STM tip was prepared by mechanically cutting from Pt/Ir (90:10) wire. Compounds were dissolved in $CHCl_3$ (Kanto), then these solution were diluted by 1-phenyloctane (Aldrich) with a final concentration below 0.1 mM. The solution was dropped onto fleshly cleaved HOPG of ZYB grade (NT-MDT, Russia), and arrowed to evaporate the $CHCl_3$ before STM imaging. Then, STM observation was performed at the HOPG/ 1-phenyloctane interface. Samples were negatively biased. All STM images were obtained in the constant current mode. To check the reproducibility of the STM image, different tips, and samples were used. STM images of the molecules and HOPG lattice under the compounds were simultaneously obtained, and the HOPG lattice was used as an internal standard to correct the STM images as well as to determine the lattice constants of the compounds.

2. Additional STM images

2.1 2D structures of **C18-1**, **C18-2** and **C20-2**

Self-assembled monolayers of **C18-1** and **C18-2** were observed as reported previously.[S1] Figure S1 shows the STM images of **C18-1** (a) and **C18-2** (b) physisorbed at the HOPG/1-phenyloctane interfaces. **C18-1** and **C18-2** formed wavy and linear structures, respectively. Figure S1 (c) shows the STM image of **C20-2** physisorbed at the HOPG/1-phenyloctane interface. **C20-2** also formed linear structure. Therefore, as described in text, **Cn-1** (n = even: 18 and 20) displayed wavy structures, and **Cn-2** formed linear structure regardless of alkyl chain length. The unit cell parameters are summarized in Table S1.

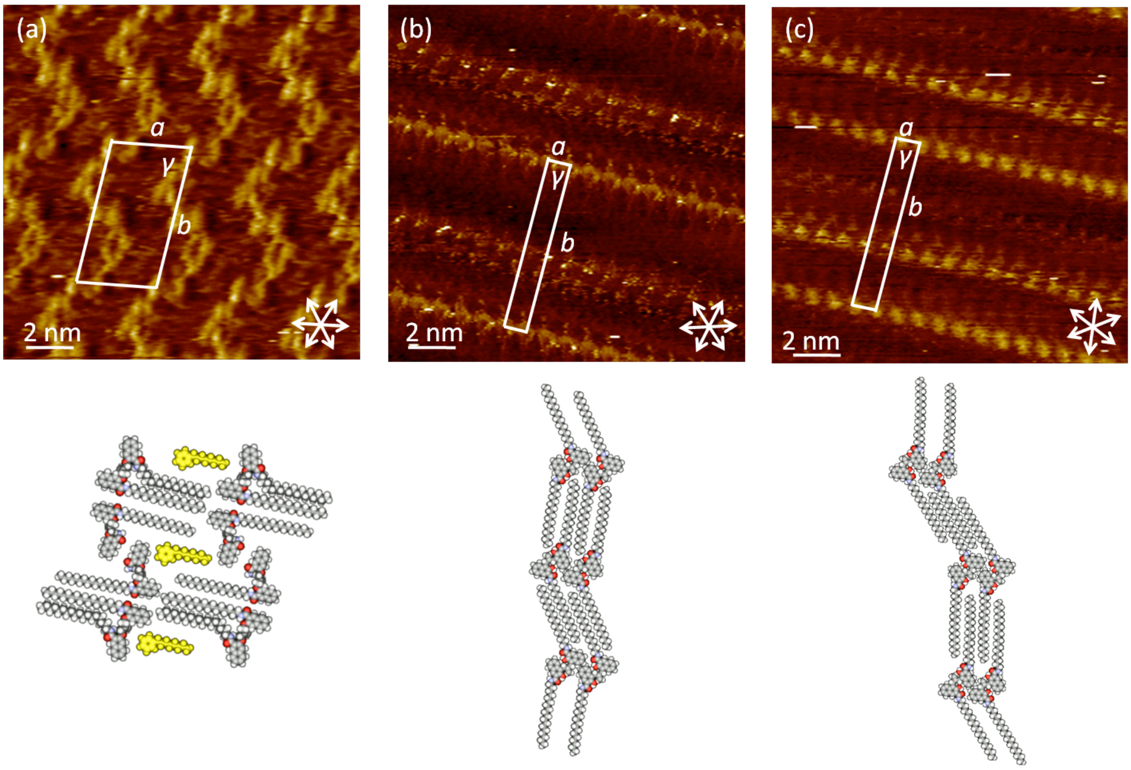

Figure S1 STM images of **C18-1** (a), **C18-2** (b) and **C20-2** (c) physisorbed at the HOPG/1-phenyloctane interface. Tunneling conditions: (a) I = 7.0 pA, V = -675 mV.; (b) I = 4.0 pA, V = -732 mV.; (c) I = 2.3 pA, V = -958 mV. Tentative molecular models are depicted on the basis of the STM images, and shown under each image.

2.2 Large-area STM images of C19 and C20

C19-1 and **C21-1** formed only tripod structures throughout the monolayers. Figure S2(a) shows the typical large-area STM image of **C19-1** physisorbed at the HOPG/1-phenyloctane interface. In contrast, there are both wavy and tripod structures in the **C20-1** monolayer. As shown in Figure S2(b), phase-separated wavy and tripod structures are visible in A and B regions, respectively. Detailed observations of A and B regions are shown in the text.

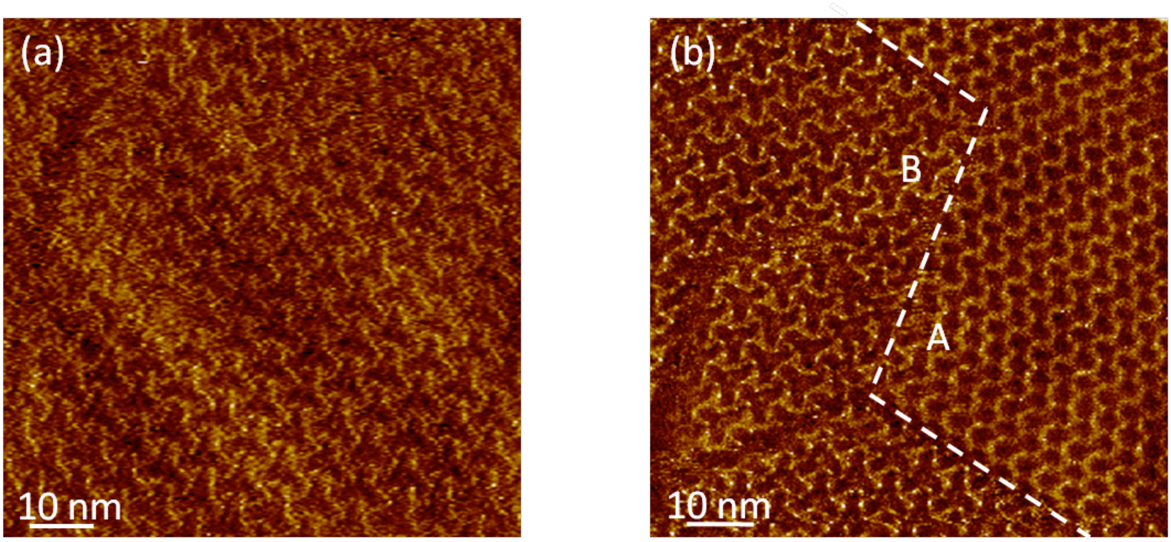

Figure S2 Large-area STM images of **C19-1** (a) and **C20-1** (b). Tunneling conditions: (a) I = 1.4 pA, V = -1000 mV.; (b) I = 2.4 pA, V = -954 mV.

2.3 Effect of solvent

The 1-phenylnonane was used to study the effect of solvent on the 2D structure formation. Figure S3 shows the STM images of **C18-1** (a) and **C19-1** (b) physisorbed at HOPG/1-phenylnonane interfaces. The **C18-1** and **C19-1** formed wavy structure and tripod structure, respectively. These 2D structures were completely same as those at HOPG/1-phenyloctane interfaces. This result suggests that the carbon numbers of solvent do not affect the 2D structure formation in the present system.

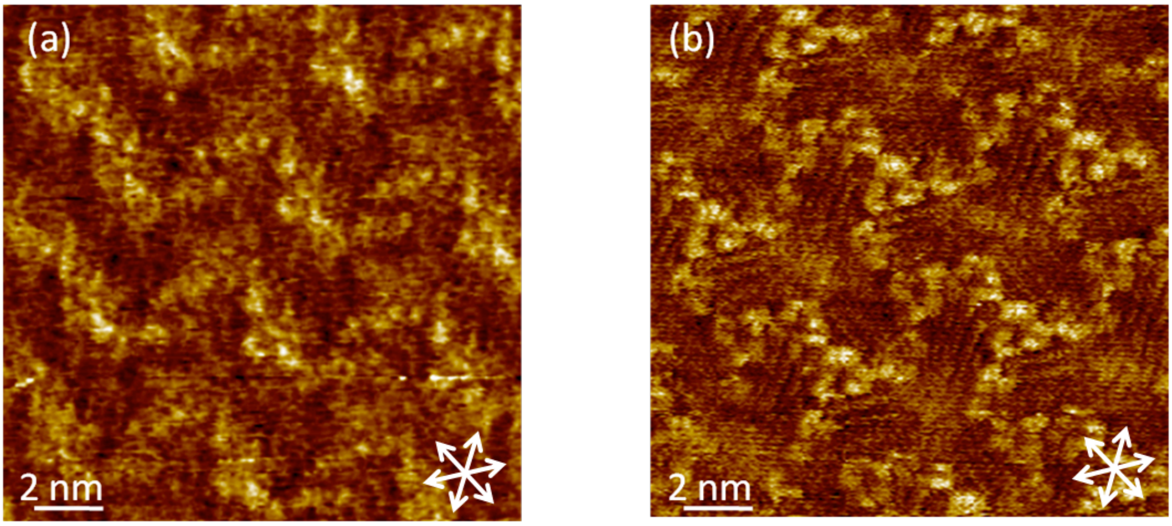

Figure S3 STM images of **C18-1** (a) and **C19-1** (b). Tunneling conditions: (a) I = 4.2 pA, V = -756 mV.; (b) I = 1.0 pA, V = -183 mV).

3. Unit cell parameters

The unit cell parameters measured from STM images are summarized in Table S1.

Table S1 Unit cell parameters of isobutenyl compounds

	a (nm)	*b* (nm)	γ (degree)
C18-1[S1]	3.5 ± 0.1	5.4 ± 0.1	80 ± 1
C19-1	5.3 ± 0.1	5.4 ± 0.1	68 ± 1
C20-1(wavy structure)	4.1 ± 0.1	5.4 ± 0.1	70 ± 1
C20-1(tripod structure)	5.4 ± 0.1	5.5 ± 0.1	67 ± 1
C21-1	5.4 ± 0.1	5.5 ± 0.1	60 ± 1
C18-2 [S1]	1.0 ± 0.1	6.3 ± 0.3	80 ± 3
C19-2	1.0 ± 0.1	6.7 ± 0.1	87 ± 1
C20-2	1.0 ± 0.1	7.2 ± 0.1	87 ± 1

Reference

S1 K. Omori, Y. Kikkawa, H. Tokuhisa, M. Kanesato, K. Hiratani, *Colloids Surf. A*, 2010, **356**, 58.