Electric Supplementary Information (ESI)

Odd-even effect in two-dimensions induced by the bicomponent blends of isobuenyl compounds

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- S1. Characterization of isobutenyl compounds newly prepared in this study
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S1. Characterization of isobutenyl compounds newly prepared in this study

The previously prepared OC_n (n=15-18) and CC_n (n=15,16) were used for STM studies, whereas CC_n (n = 17, 18) and $OC_{15}F$ were newly prepared in this study.

CC₁₇: ¹H NMR (CDCl₃): $\delta = 0.88$ (t, 6H, J = 6.9 Hz, CH₃), 1.25 (broad, 60H, CH₂), 1.62 (m, 4H, CH₂), 2.24 (m, 4H, O-CH₂), 4.91 (s, 4H, =C-CH₂-O), 5.58 (s, 2H, CH₂=C), 7.18 (s, 2H, Naph-H), 7.35 (d, 2H, *J* = 6.1 Hz, Naph-H), 7.36 (d, 2H, *J* = 6.3 Hz, Naph-H), 7.58 (dd, 2H, *J* = 6.0 6.0 Hz, Naph-H), 7.77 (dd, 2H, *J* = 6.1 6.1 Hz, Naph-H), 7.91 (s, 2H, N-H), 8.88 (s, 2H, Naph-H), IR (KBr): 743(Naph), 1180(C-O-C), 1622(C=C), 1641(C=O), 3340(N-H) cm⁻¹, Anal. Calcd for C60H90N2O4 \cdot 1/2 H₂O: C, 78.98; H, 10.05; N, 3.07. Found: C, 78.85; H, 10.06; N, 2.85.

CC₁₈: ¹H NMR (CDCl₃): $\delta = 0.88$ (t, 6H, J = 6.8 Hz, CH3), 1.25 (broad, 60H, CH₂), 1.62 (m, 4H, CH₂), 2.24 (m, 4H, O-CH₂), 4.91 (s, 4H, =C-CH₂-O), 5.57 (s, 2H, CH₂=C), 7.18 (s, 2H, Naph-H), 7.35 (d, 2H, J = 6.0 Hz, Naph-H), 7.36 (d, 2H, J = 6.3 Hz, Naph-H), 7.58 (dd, 2H, J = 6.1 6.1 Hz, Naph-H), 7.77 (dd, 2H, J = 6.2 6.2 Hz, Naph-H), 7.91 (s, 2H, N-H), 8.88 (s, 2H, Naph-H), IR (KBr): 743(Naph), 1180(C-O-C), 1622(C=C), 1641(C=O), 3340(N-H) cm⁻¹, Anal. Calcd for C62H94N2O4 \cdot 1/2 H₂O: C, 79.18; H, 10.18; N, 2.98. Found: C, 79.37; H, 10.13; N, 2.85.

1-Iodononafluorobutene (20.8 g, 0.06 mol), undecyl-10-en-1-ol (10.2 g, 0.06 mol) and azobis-*iso*-butyronitrile (0.16 g, 0.002 mol) as an initiator were heated in a sealed glass tube filled with nitrogen gas for 12 h at 60-70 °C while gentle stirring. 15,15,15,14,14,13,13,12,12-Nonafluoro-10iodopentadeca-1-ol was isolated by vacuum distillation of the reaction mixture (bp: 120-125 °C /0.1 mmHg, 27 g).^{S1} The iodide in 50 ml of ethanol was refluxed with a solution of sodium hydroxide (8.4 g, 0.21 mol) and water 15 ml for 3 h to give an olefinic product, 15,15,15,14,14,13,13,12,12nonafluoropentadeca-10-en-1-ol (bp: 85-90 °C /0.1 mmHg, 19.2 g).^{S2} Hydrogenation^{S3} of the olefinic fluorohydrocarbon in 40 ml of ethanol over palladium-carbon (1.0 g) under normal pressure at room temperature for 12 h gave a saturated fluorohydrocarbon, 15,15,15,14,14,13,13,12,12nonafluoropentadeca-1-ol (bp: 85-90 °C/ 0.1 mmHg, white solid),^{S4} which was connected to isobutenyl binaphthyl di(acid chloride) for the preparation of **OC**₁₅**F**. **HO-(CH₂)₁₁C₄F₉:** ¹H NMR (CDCl₃): $\delta = 1.29$ (broad, 14H, (CH₂)₇ and s, 1H, OH), 1.58 (m, 4H, <u>CH₂</u>CH₂OH and <u>CH₂CH₂CF₂), 2.05 (m, 2H, <u>CH₂CF₂), 3.64 (t, 2H, *J* = 6.6 Hz , <u>CH₂OH)</u>. IR (KBr): 1224 (C-F), 3374 (OH) cm⁻¹.</u></u>

OC₁₅**F**: ¹H NMR (CDCl₃): $\delta = 1.25$ (broad, 24H, CH₂), 1.40 (m, 4H, CH₂), 1.57 (m, 4H, CH₂), 1.75 (m, 4H, CH₂), 2.03 (m, 4H, CH₂), 4.31 (t, 4H, J = 6.9 Hz , O-CH₂), 4.91 (s, 4H, =C-CH₂-O), 5.59 (s, 2H, C=CH₂), 7.29 (s, 2H, Naph-H), 7.37 (dd, 2H, J = 7.5 7.5 Hz, Naph-H), 7.49 (dd, 2H, J = 7.5 7.5 Hz, Naph-H), 7.69 (d, 2H, J = 8.2 Hz, Naph-H), 7.82 (d, 2H, J = 8.1 Hz, Naph-H), 8.30 (s, 2H, Naph-H), IR (KBr): 745(Naph), 1071 (C-O-C), 1234 (C-F), 1631(C=C), 1727 (C=O) cm⁻¹. MALDI-TOF MS: m/z 1195.48 [M + Na]⁺, calcd for C56H62F18O6Na 1195.42.

References

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S2. STM images of mono-component system

The naphthalene units in the OC_n (n ≤ 17) formed dumbbell structure (Fig. S1A – C), whereas those in the OC_n (n = 18) showed linear structure (Fig. S1D). In contrast, only linear structure was found for CC_n (n = 15 – 18), as shown in Fig. S1E – H.



Fig. S1 STM images of **OCn** (A–D) and **CCn** (E–H) at the HOPG/1-phenyloctane interface. Tunneling conditions: (A) I = 2.2 pA, V = -620 mV, (B) I = 2.0 pA, V = -880 mV, (C) I = 2.3 pA, V = -1500 mV, (D) I = 2.0 pA, V = -1200 mV, (E) I = 1.5 pA, V = -530 mV, (F) I = 3.7 pA, V = -270 mV, (G) I = 2.0 pA, V = -1000 mV, (H) I = 2.1 pA, V = -1100 mV.

S3. Wide area and proposed molecular models in the blend system

Basically, the 2D structures in the blend system showed star shaped ($OC_n > CC_n$: n = odd), lozenge ($OC_n < CC_n$: n = odd), twist-like ($OC_n > CC_n$: n = even), and linear structures ($OC_n < CC_n$: n = even). In the case of $OC_n \ge CC_n$ (n = 17), knot-like structure was coexisted with the star shaped structure.



Fig. S2 Wide area STM images of OC_n/CC_n blends. The alkyl chain length (n) and blend ratio are shown on the left and the top of images, respectively. (A) I = 2.0 pA, V = -200 mV, (B) I = 2.0 pA, V = -540 mV, (C) I = 2.5 pA, V = -400 mV, (D) I = 1.8 pA, V = -600 mV, (E) I = 2.0 pA, V = -100 mV, (F) I = 1.6 pA, V = -630 mV, (G) I = 2.5 pA, V = -620 mV, (H) I = 2.0 pA, V = -940 mV, (I) I = 1.7 pA, V = -100 mV, (J) I = 2.0 pA, V = -680 mV, (K) I = 2.3 pA, V = -750 mV, (L) I = 1.8 pA, V = -870 mV, (M) I = 3.3 pA, V = -660 mV, (N) I = 2.5 pA, V = -800 mV, (O) I = 1.7 pA, V = -850

mV, (P) *I* = 2.0 pA, *V* = -1000 mV, (Q) *I* = 2.0 pA, *V* = -800 mV, (R) *I* = 2.0 pA, *V* = -1000 mV, (S) *I* = 2.0 pA, *V* = -570 mV, (T) *I* = 3.0 pA, *V* = -650 mV.

2D structural characteristics could be recognized from the enlarged STM images. Then, molecular models are proposed and superimposed on the typical STM images for the OC_n/CC_n blends (n = 17 and 18), as shown in Fig. S3. Although the location of naphthalene and alkyl chain units can be determined from the STM images, it was difficult to distinguish the two components because the they only contain the different chemical linkages between the naphthalene and alkyl chain units. Therefore, the molecular models are constructed by only OC_n molecules.



Fig. S3 Proposed molecular models superimposed on the typical STM images of OC_n/CC_n blends. The panels A-E are corresponding to the Figs. 2K, K', Q and R' in the main text, respectively. Note that bright contrast was observed at the central part of star shaped structure surrounded by the naphthalene units, possibly due to the loosely trapped solvent molecules with some mobilities. This is also the case for lozenge shaped structure indicated by an arrow.

S4. Blend system at an extremely different blend ratio

In order to compare the stability of homo- (OC_n) and hetero-dimers (OC_n-CC_n) , STM observation was performed for the monolayer with the single component (OC_n) and blend system (OC_n/CC_n) . First, the physisorbed monolayer of OC_n was formed at the HOPG/1-phenyloctane interface, and then the small amount of CC_n solution was added to be the blend ratio of OC_n : $CC_n=5:1$. On adding the CC_n solution, star-shaped structure (*St*) surrounded by the dumbbell-shaped structure (*Du*) was observed, as shown in Fig. S4A. Then, the domain size of *St* gradually increased with time to cover the whole area of STM imaging (Figs. 4B and 4D). This result suggests that the hetero-dimers (OC_n-CC_n) in the *St* domain are thermodynamically more stable than homo-dimers (OC_n) in *Du* even if the quite larger amount of OC_n is included in the blend system than the CC_n .



Fig. S4 Time-dependent 2D structural change in the OC_n/CC_n blend ($OC_n:CC_n=5:1$). The OC_n solution was first placed on the HOPG surface to form the monolayer. Then, a small amount of CC_n solution was added *in situ* to the already existing OC_n solution on the HOPG surface to be the blend ratio of $OC_n:CC_n=5:1$. STM observation at the same position was performed to follow the gradual 2D structural change due to blending. Tunneling condition: I = 1.8 pA, V = -470 mV.

S5. Assumed orientation of hetero-dimers

The hetero-dimer formation (OC_n-CC_n) is specific for the bicomponent blend, and therefore, this is one of the possible reasons for the emergence of odd-even effect because homodimers $(OC_n-OC_n \text{ and } CC_n-CC_n)$ in the single component system did not show odd-even effect. In the 2D structures of blend system, the structural unit seems to be composed of a paired hetero-dimer, as indicated in Fig. S5A-D.

In order to obtain a stable structure in a pair of hetero-dimers, MM2 calculation was performed under the following assumptions: (1) a pair of hetero-dimers take an arrangement that maximizes the dispersion interactions between all-*trans* alkyl chains; (2) the hetero-dimers take an ordering observed in Fig. 3, namely the same type of molecule (OC_n or CC_n) are arranged to be adjacent to each other. Figs. S5E and S5F show orientations in a pair of hetero-dimers with odd and even numbers of carbon atoms in the alkyl chain unit, respectively. In both cases, the total shape of a paired hetero-dimer is parallelogram, but a parallelogram structural unit with n = even has a steeper angle than that with n = odd. The odd-even effect had been discussed in terms of the direction of terminal methyl group.^{S5} In the present study in Fig S5E and S5F, the direction of terminal methyl group is opposite with each other (Fig. S5E and F), resulting in the formation of different shape of a structural unit.

Basically, the hetero-dimer with n = odd orients in the same direction. The star-shaped structure ($OC_n > CC_n$; n = odd: Fig. S5A) is composed of 6 parallelogram structural units (Figs. S5E) formed by the hetero-dimers only, whereas the lozenge-shaped structure ($OC_n < CC_n$; n = odd: Fig. S5B) is constructed by the mixture of parallelogram structural units for hetero-dimer and CC_n - CC_n , as evidenced by the STM image in Fig. 3. Therefore, the linear structure cannot be appeared, but the lozenge-shaped structure, whose shape is dominated by the parallelogram structural unit of hetero-dimer, is formed.

In the case of twist-like structure ($\mathbf{OC}_n > \mathbf{CC}_n$; n = even: Fig. S5C), the hetero-dimer unit can be distorted by the periodic voids with different size, which are filled with co-adsorbed solvent molecules, resulting that parallelogram structural units seems to alternately orient in opposite directions (Fig. S5C). For the blends in the $\mathbf{OC}_n < \mathbf{CC}_n$ (n = even), the hetero-dimer unit with a shape close to a rectangle (Figs. S5F) may be assimilated with the orientation of \mathbf{CC}_n - \mathbf{CC}_n , resulting in the formation of linear structure (Fig. S5D), in which the long axis of alkyl chain is almost perpendicular to that of naphthalene rings' alignment. Thus, the orientation of hetero-dimers, parallelogram structural unit, would play important role for the emergence of odd-even effect after the bicomponent blend.



Fig. S5 Structural units overlapped on the STM images for star-shaped (A), lozenge (B), twist-like (C) and linear structures (D). The panels (E) and (F) shows the optimized structure of a pair of hetero-dimers possessing odd and even numbers of carbon atoms in the alkyl chain part, respectively. The yellow arrows indicate the direction of terminal methyl groups of alkyl chains. The green and pink frames show a structural unit composed of a pair of hetero-dimers.

References

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