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Structural transition control between dipole−dipole and hydrogen bonds induced chirality and achirality

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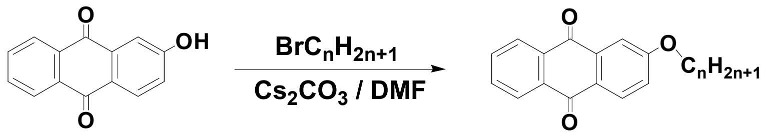
Synthesize:

2-HA-OC_n molecules were synthesized from the commercially available 2-Hydroxyanthraquinone with BrC_nH_{2n+1} in DMF (dry, 150 °C, 50 mL) along with Cs_2CO_3 added. The reaction finished twelve hours later and proved to be quite successful with a yield of 98%. The desired products were obtained by repeated recrystallization for the sake of high degree purity. The solvent was purchased from Tokyo Chemical Industry without further purification.



Scheme S1. Synthesis of 2-HA-OC_n derivatives.

Characterization data：

2-HA-OC_{11}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.32 (t, 2H), 8.27 (d, 1H), 7.80 (m, 2H), 7.74 (d, 1H), 7.29 (m, 1H), 4.17 (t, 2H), 1.88 (m, 2H), 1.30 (m, 16H), 0.90 (t, 3H)

MS: 379 $[C_{25}H_{31}O_3]^+$.

2-HA-OC_{12}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (t, 2H), 8.18 (d, 1H), 7.71 (m, 2H), 7.65 (d, 1H), 7.19 (m, 1H), 4.08 (t, 2H), 1.78 (m, 2H), 1.20 (m, 18H), 0.81 (t, 3H)

MS: 393 $[C_{26}H_{33}O_3]^+$.

2-HA-OC_{13}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.32 (t, 2H), 8.27 (d, 1H), 7.80 (m, 2H), 7.74 (d, 1H), 7.29 (m, 1H), 4.17 (t, 2H), 1.88 (m, 2H), 1.29 (m, 20H), 0.90 (t, 3H)

MS: 407 $[C_{27}H_{35}O_3]^+$.

2-HA-OC_{14}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (t, 2H), 8.18 (d, 1H), 7.71 (m, 2H), 7.65 (d, 1H), 7.19 (m, 1H), 4.08 (t, 2H), 1.78 (m, 2H), 1.19 (m, 22H), 0.81 (t, 3H)

MS: 421 $[C_{28}H_{37}O_3]^+$.

2-HA-OC_{15}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (t, 2H), 8.18 (d, 1H), 7.71 (m, 2H), 7.65 (d, 1H), 7.19 (m, 1H), 4.08 (t, 2H), 1.78 (m, 2H), 1.19 (m, 24H), 0.81 (t, 3H)

MS: 435 $[C_{29}H_{39}O_3]^+$.

2-HA-OC_{16}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (t, 2H), 8.18 (d, 1H), 7.71 (m, 2H), 7.65 (d, 1H), 7.19 (m, 1H), 4.08 (t, 2H), 1.78 (m, 2H), 1.19 (m, 24H), 0.81 (t, 3H)

MS: 449 $[C_{30}H_{41}O_3]^+$.

2-HA-OC_{17}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.32 (t, 2H), 8.27 (d, 1H), 7.80 (m, 2H), 7.74 (d, 1H), 7.29

(m, 1H), 4.17 (t, 2H), 1.87 (m, 2H), 1.28 (m, 28H), 0.90 (t, 3H)

MS: 463 $[C_{31}H_{43}O_3]^+$.

2-HA-OC_{18}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.32 (t, 2H), 8.27 (d, 1H), 7.80 (m, 2H), 7.74 (d, 1H), 7.29 (m, 1H), 4.17 (t, 2H), 1.88 (m, 2H), 1.28 (m, 30H), 0.90 (t, 3H)

MS: 477 $[C_{32}H_{45}O_3]^+$.

2-HA-OC_{20}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.32 (t, 2H), 8.27 (d, 1H), 7.80 (m, 2H), 7.74 (d, 1H), 7.29 (m, 1H), 4.17 (t, 2H), 1.88 (m, 2H), 1.28 (m, 34H), 0.90 (t, 3H)

MS: 505 $[C_{34}H_{49}O_3]^+$.

Table S1. Concentration for 100% saturated solutions (C_0, mol L^{-1}) of 2-HA-OC_n molecules.

n	11	12	13	14	15	16	17	18	20
1-octanoic acid	2.9×10^{-2}	1.1×10^{-2}	9.9×10^{-3}	9.5×10^{-3}	9.2×10^{-3}	8.9×10^{-3}	7.6×10^{-3}	4.2×10^{-3}	3.9×10^{-3}
n-tetradecane	-	2.6×10^{-6}	-	2.1×10^{-6}	-	1.4×10^{-6}	-	7.1×10^{-7}	5.6×10^{-7}
n-phenyloctane	-	-	-	1.43×10^{-2}	-	-	-	-	-

Surface coverage:

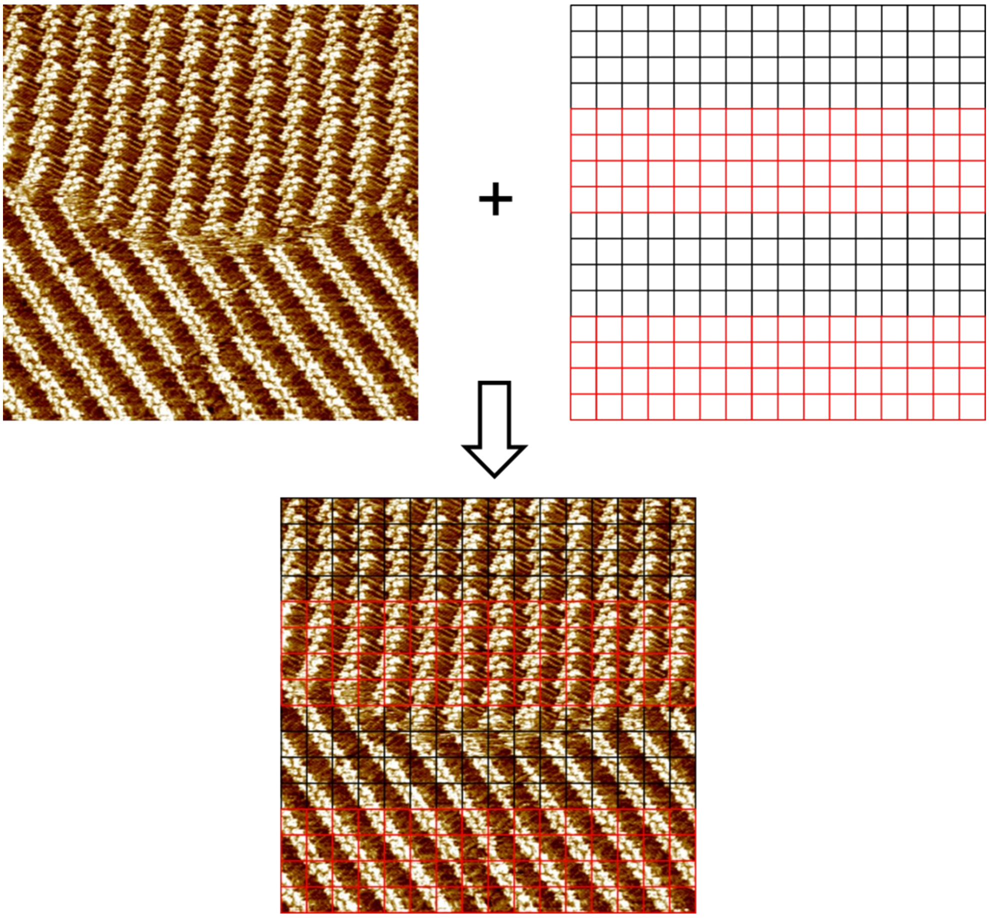


Fig. S1: The method for calculating the surface coverage.

N_{sum}: the total number of cells

$N_{\text{Knot-like}}$: number of cells for the Knot-like structure

$N_{\text{Wheat-like}}$: number of cells for the Wheat-like structure

Surface coverage for Knot-like structure: $N_{\text{Knot-like}} / N_{\text{sum}}$

Surface coverage for Wheat-like structure: $N_{\text{Wheat-like}} / N_{\text{sum}}$

Surface coverage for defects: $1- (N_{\text{Knot-like}} + N_{\text{Wheat-like}}) / N_{\text{sum}}$

Error:

We denote the surface coverage as S, the average surface coverage as S_{aver}, the error as σ.

$S_{aver} = (S_1 + S_2 + \cdots + S_n) / n \qquad \sigma = \left(\frac{\sum_{i}^{n} (S_i - S_{aver})^2}{n}\right)^{\frac{1}{2}}$

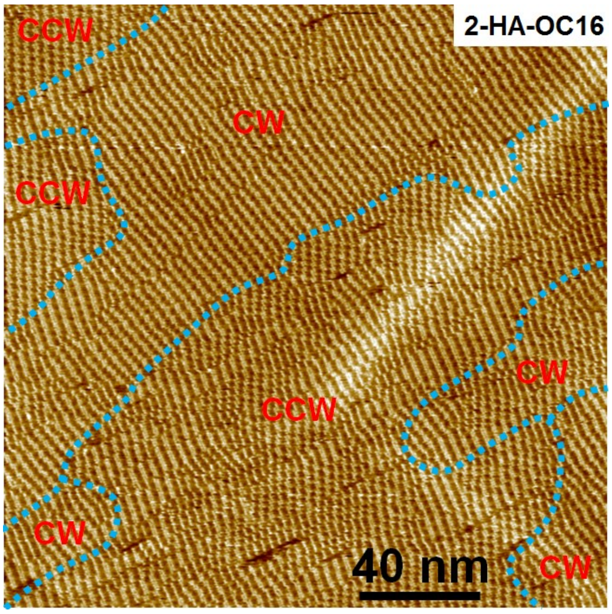


Fig. S2 Large-scale STM image of 2-HA-OC_{16} molecules self-assembled monolayer at 1-octanoic acid/HOPG interface under the concentration of 50% saturation (4.5×10^{-3} mol L^{-1}). The CW and CCW domains are separated by blue dotted lines. Imaging condition: $I_t = 640$ pA, $V_{bias} = 750$ mV.

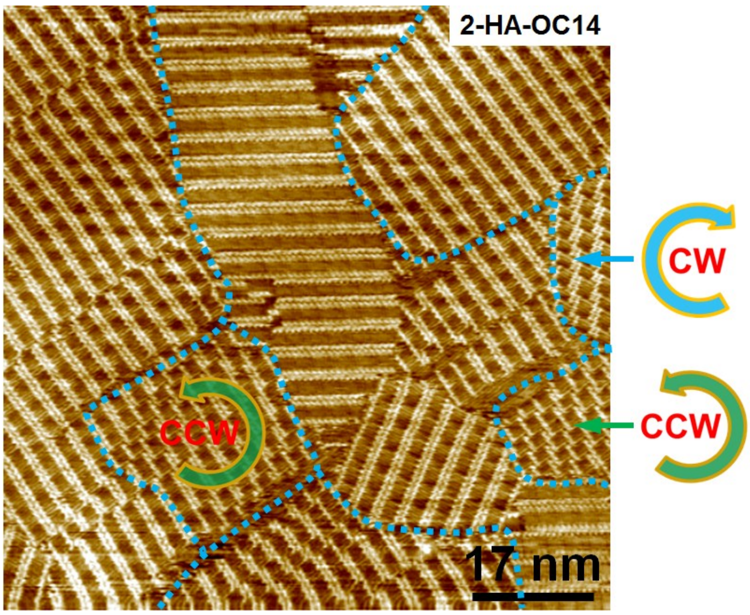


Fig. S3 Large-scale STM image of 2-HA-OC_{14} molecules self-assembled monolayer at 1-octanoic acid/HOPG interface under the concentration of 50% saturation (4.8×10^{-3} mol L^{-1}). The blue and green open-circle arrows indicate the CW and CCW patterns. As the adlayer consists of coexistent Knot-like and Wheat-like structures, chirality with good consecutiveness was usually broken by Wheat-like structure. Imaging condition: I_t = 630 pA, V_{bias} = 800 mV.

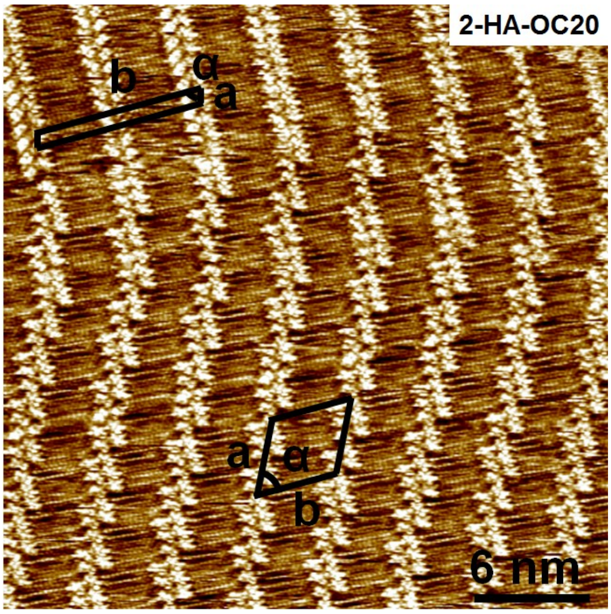


Fig. S4 High-resolution STM images of 2-HA-OC_{12} molecules at 1-octanoic acid/HOPG interface under the concentration of 50% saturation (5.5×10^{-3} mol L^{-1}), indicating the coexistent Knot-like and Wheat-like configurations. The basic unit cells are superimposed and the parameters are measured to be $a = 5.1 \pm 0.3$ nm, $b = 4.5 \pm 0.3$ nm, $\alpha = 79 \pm 1°$ for Knot-like pattern and $a = 0.9 \pm 0.1$ nm, $b = 9.2 \pm 0.1$ nm, $\alpha = 87 \pm 2°$ for Wheat-like pattern. The area density is calculated to be 2.25 nm^2 per molecule for the former and 2.07 nm^2 per molecule for the latter. Imaging condition: $I_t = 570$ pA, $V_{bias} = 710$ mV.

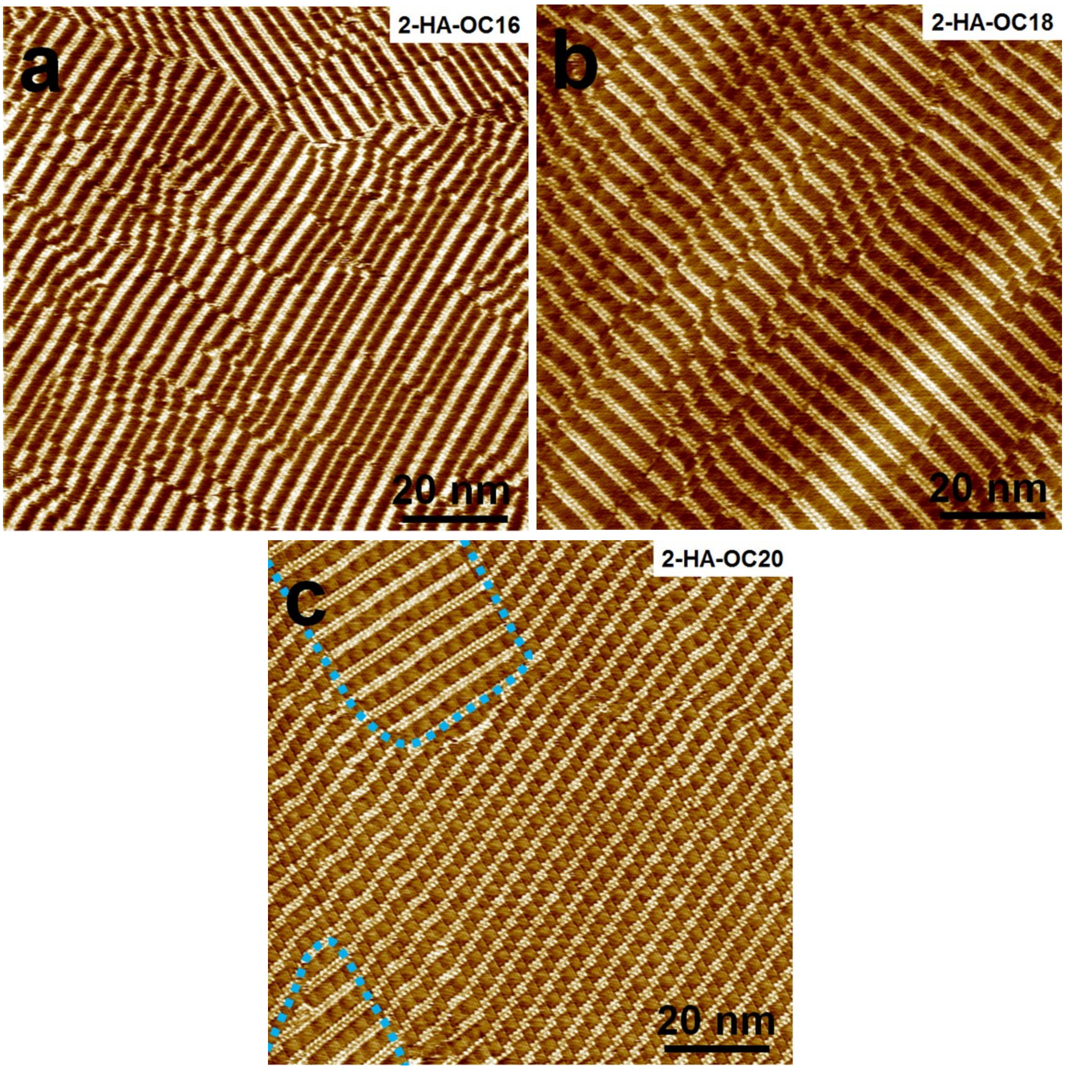


Fig. S5 Large-scale STM image of 2-HA-$OC_{16,18,20}$ molecules self-assembled monolayer at *n*-tetradecane/HOPG interface under the concentration of 50% saturation. 7×10^{-7} mol L^{-1} for (a), 3.6×10^{-7} mol L^{-1} for (b), 2.8×10^{-7} mol L^{-1} for (c). As the length of alkyl chain increases, surface coverage for Knot-like structure increases. Imaging condition: I_t = 560 pA, V_{bias} = 700 mV for (a), I_t = 590 pA, V_{bias} = 680 mV for (b), and I_t = 610 pA, V_{bias} = 740 mV for (c).

Table S2. Surface coverage of Knot-like pattern, Wheat-like pattern and the defects in 1-octanoic acid under the concentration of 50% saturation for 2-HA-OC_n molecules.

n	Knot-like	Wheat-like	Defects
12	0	99.5%	0.5%
14	49.7%	50.1%	0.2%
16	99.5%	0	0.5%
18	72.1%	27.7%	0.2%
20	82.8%	17.0%	0.2%

Table S3. Surface coverage of Knot-like pattern, Wheat-like pattern and the defects in *n*-tetradecane under the concentration of 50% saturation for 2-HA-OC_n molecules.

n	Knot-like	Wheat-like	Defects
12	0	99.4%	0.6%
14	0	99.5%	0.5%
16	5	94.6%	0.4%
18	17.2%	82.5%	0.3%
20	89.7%	10.0%	0.3%

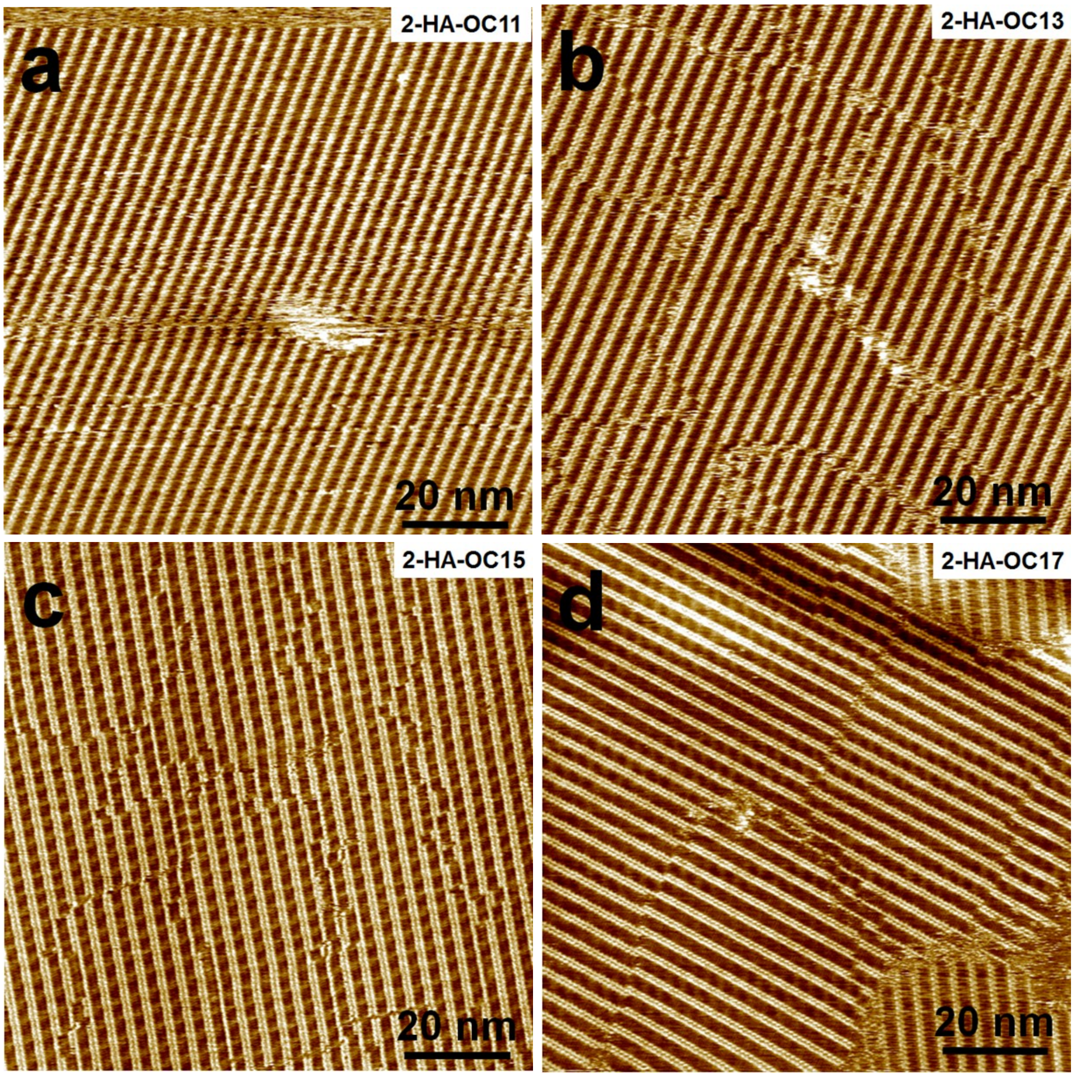


Fig. S6 Large-scale STM image of 2-HA-OC$_{11,13,15,17}$ molecules self-assembled monolayer at 1-octanoic acid/HOPG interface under the concentration of 50% saturation, showing the Wheat-like′ pattern. Imaging condition: I_t = 500 pA, V_{bias} = 660 mV for (a), I_t = 450 pA, V_{bias} = 620 mV for (b), I_t = 550 pA, V_{bias} = 800 mV for (c), and I_t = 630 pA, V_{bias} = 780 mV for (d).

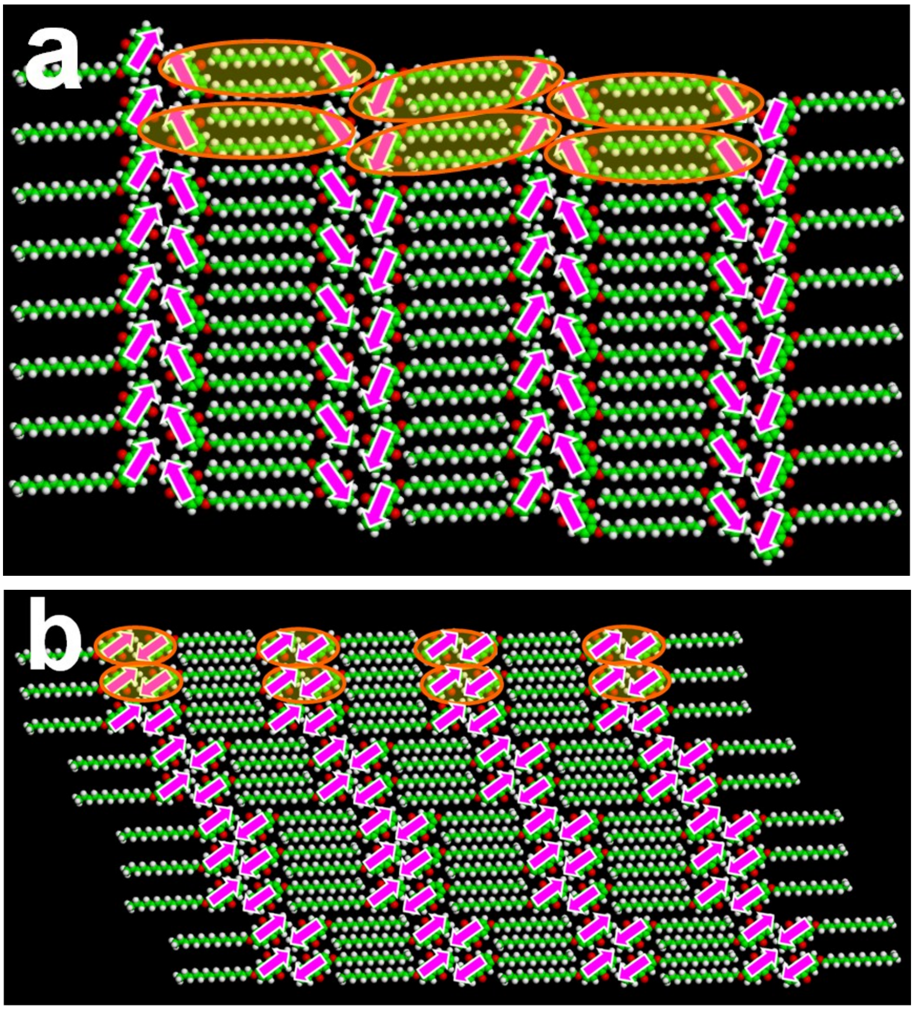


Fig. S7 Schematic diagrams with dipole alignments for Wheat-like (a) and Knot-like (b) structures. The dipole directions in these two patterns are depicted by pink arrows and the paired anthraquinone cores are denoted by orange ovals.

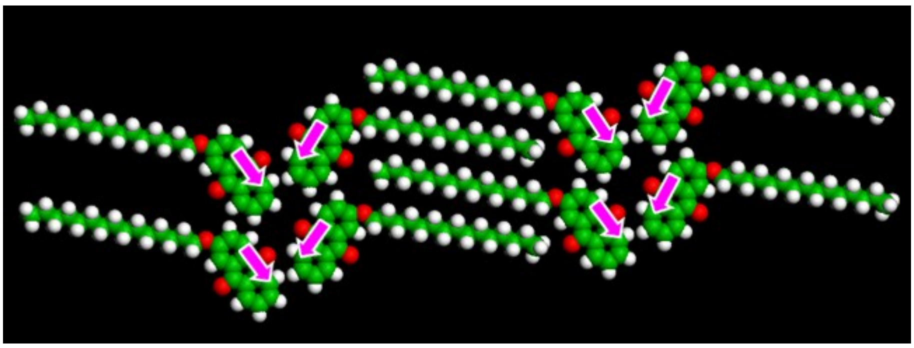


Fig. S8 Schematic diagrams with dipole alignments for Wheat-like′ structures. The dipole direction is depicted by pink arrows. No antiparallel pairs form to reduce the polarity of single molecule. This may be attributed to the competition of dipole−dipole interactions between the anthraquinone cores versus van der Waals interactions between the side chains, and the latter ones play the dominant role.