SUPPORTING INFORMATION

2D analogues of the inverted hexagonal phase self-assembled from 4,6-dialkoxylated isophthalic acids at solid-liquid interfaces

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1. Self-assembly on Au(111) under potential control

Video S1. Ordering of ISA-D10 at Au(111)-water (0.1 M $HClO_4$) interface as a function of time. A sequence of 18 frames, recorded approx. every 1 min, are presented. While the ordering of cyclic structures remains intact, the bright spots in the middle of these cycles show dynamics. Substrate potential, E_w = 350 mV vs SCE; tunneling current, I_t = 1 nA; bias voltage, U_{bias} = -300 mV.

Video S2. Ordering of ISA-D7 at Au(111)-water (0.1 M $HClO_4$) interface as a function of time. A sequence of 15 frames, recorded approx. every 1 min, are presented. Similarly to ISA-D10, the ordering of cyclic structures remains intact, while the bright spots in the middle of these cycles show dynamics. E_w = 350 mV vs SCE; I_t = 1 nA; bias voltage, U_{bias} = -300 mV.

2. Self-assembly at the Au(111)-tetradecane interface

STM images were obtained by using a PicoSPM with a tip mechanically cut from a Pt/Ir wire (80/20, diameter 0.25 mm).

2.1 Self-assembly of ISA-D7 on Au(111).

Similar to the results obtained with EC-STM at the Au(111)-water (0.1 M $HClO_4$) interface, ISA-D7 at the Au(111)-tetradecane interface shows both pentameric cyclic and zig-zag type patterns (Figure S1). The pentameric cyclic structure is the dominant one.

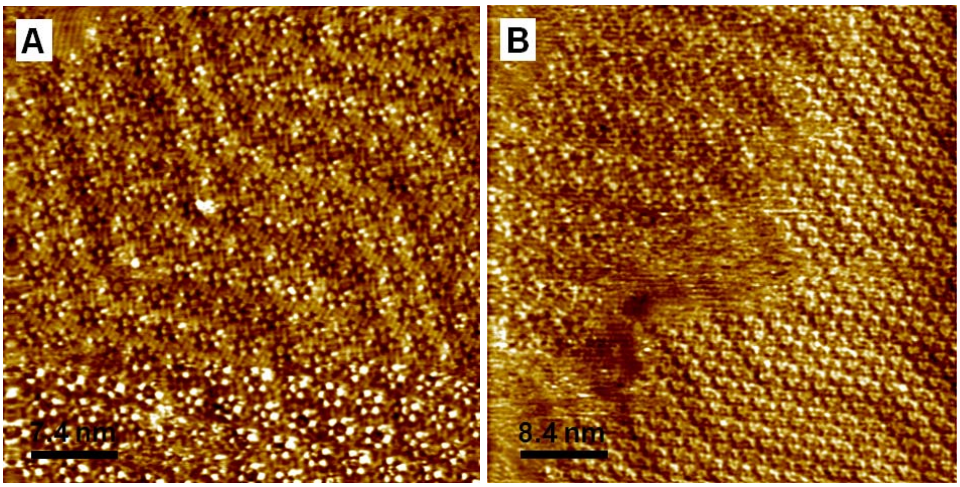

Figure S1. Representative STM images of ISA-D7 at the Au(111)-tetradecane interface: coexistence of two patterns. a) I = 100 pA, V = -340 mV; b) I = 100 pA, V = -340m V.

2.2 Self-assembly of ISA-D10 on gold (111).

Similar to ISA-D10 measured with EC-STM at the Au (111)-water (0.1 M $HClO_4$) interface, predominantly pentameric cyclic structures are formed and the degree of long-range ordering is limited. “Defect” clusters of more than five ISA-D10 molecules are common. A typical STM image of ISA-D10 at the Au(111)-tetradecane interface is shown in Figure S2.

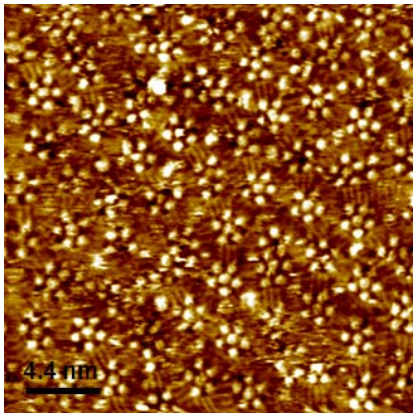

Figure S2. STM image of ISA-D10 at Au(111)-tetradecane interface: I = 271 pA, V = -248 mV.

2.3 Self-assembly of ISA-D15 on Au(111).

Very similar to the experiments obtained with EC-STM at the Au (111)-water (0.1 M $HClO_4$) interface, ISA-D15 forms more disordered patterns compared to ISA-D7 and ISA-D10 at the Au(111)-tetradecane interface as well. ISA-D15 shows a tendency to form tetramers, hexamers, and even octamers, involving the interdigitation of alkyl chains (Figure S3).

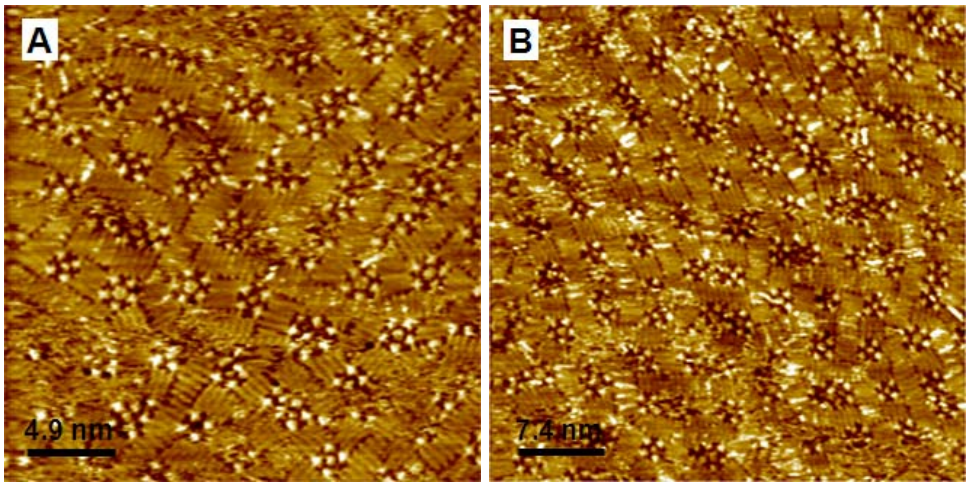

Figure S3. STM images of ISA-D15 at Au(111)-tetradecane interface. a) I = 225 pA, V = -128 mV; b) I = 237 pA, V =- 245m V.

3. Self-assembly at the HOPG-tetradecane interface

3.1. Self-assembly of ISA-D10 on HOPG.

ISA-D10 at the HOPG-tetradecane interface forms a regular network of pentameric cyclic structures (Figure S4). The degree of order is higher than for ISA-D10 on Au(111).

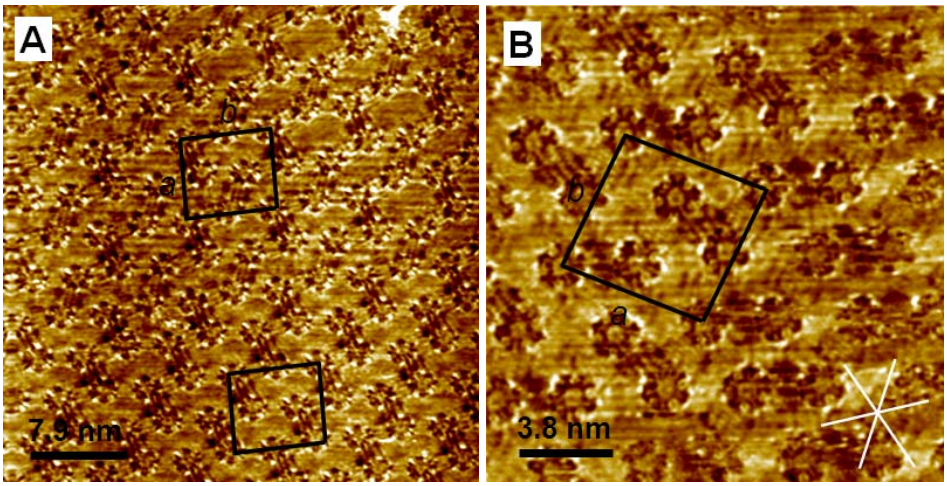

Figure S4. STM images obtained at HOPG/tetradecane interface for the monolayer of ISA-D10. a) I = 214 pA, V = -800 mV, b) I = 111 pA, V = -883 mV. Unit cells are indicated: a = 6.4±0.1 nm, b = 6.8±0.1 nm, α = 89±1°.

3.2. Self-assembly of ISA-D15 on HOPG.

At the HOPG-tetradecane interface ISA-D15 forms two types of domains both coexisting on the surface (Figure S5). One type of pattern consists of cyclic pentamers (unit cell values are *a* = 6.8±0.4 nm, *b* = 8.3±0.1 nm, α = 90±0.5°), a motif which is quite typical for this class of molecules. The second type resembles a linear network (*a* = 2.4±0.1 nm, *b* = 3.3±0.1 nm, α = 90±1°). For the latter network, only 3 out of 4 alkyl chains are adsorbed.

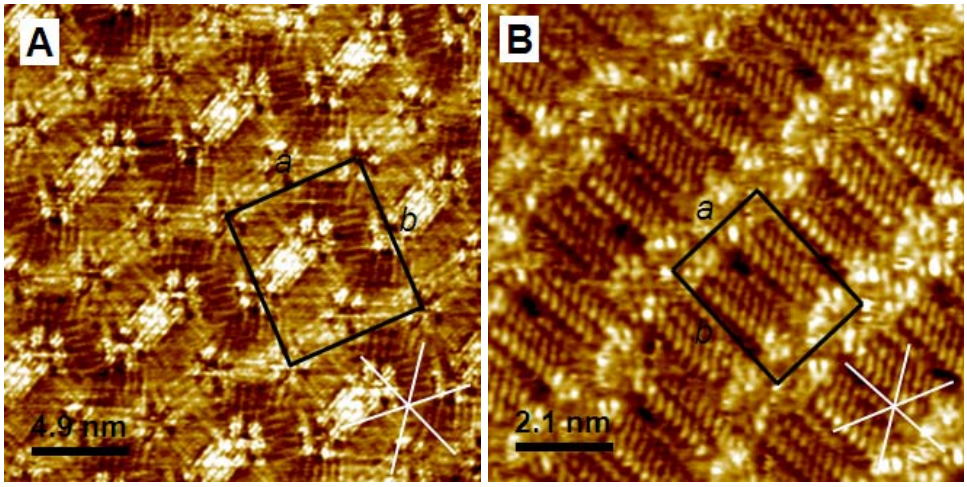

Figure S5. STM images of ISA-D15 at the HOPG-tetradecane interface, I = 135 pA, V = -800 mV. Two types of networks are observed: a) pentameric cyclic, where pentamers are well-ordered into parallel rows; b) high resolution image of the linear type pattern.

4. Cyclic voltammetry on Au(111) substrate in $HClO_4$

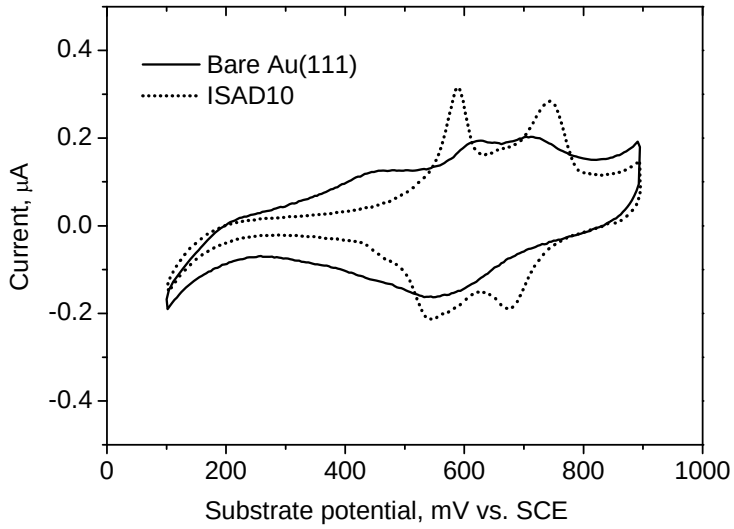

Figure S6. Cyclic voltammograms of bare Au(111) electrode in 0.1 M $HClO_4$ (solid line) and in the presence of ISA-D10 (dotted line) obtained using the EC-STM setup. Platinum wire was used as a reference electrode. The potential scan rate was 10 mV/s.