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Supporting Information

Side Chain Position, Length and Odd/Even Effects on 2D Self-Assembly of Mono-Substituted Anthraquinone Derivatives at Liquid/Solid Interface

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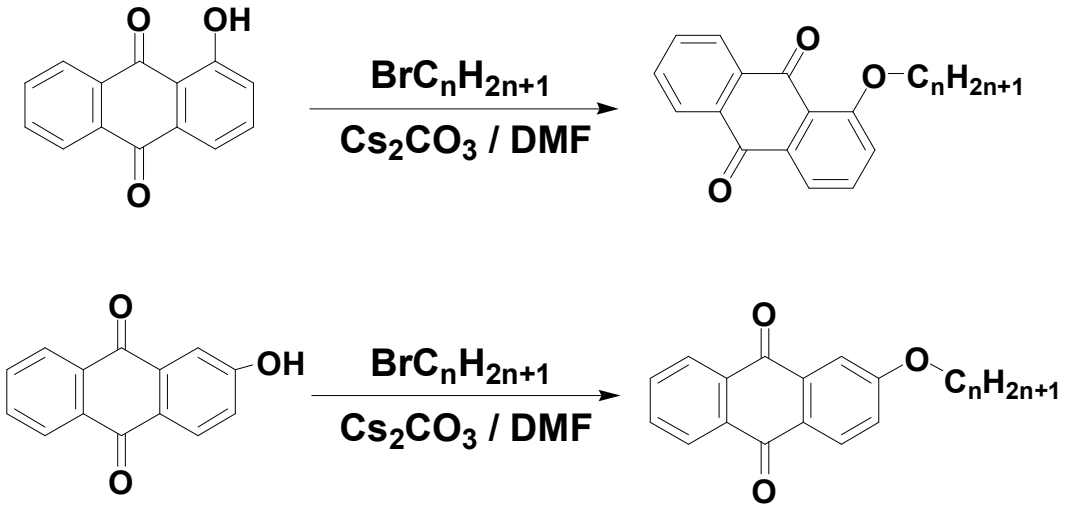
Synthesize

1-HA-OC_n (n = 15, 16) and 2-HA-OC_n (n = 12, 14–16) were synthesized from the commercially available 1-Hydroxyanthraquinone and 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 (four to six times) in view of high degree purity. The solvent was purchased from Tokyo Chemical Industry without further purification.



Scheme S1. Synthesis of 1-HA-OC_n (n = 15, 16) and 2-HA-OC_n (n = 12, 14–16) derivatives.

Characterization data：

1-HA-OC_{15}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.22 (d, 1H), 8.16 (d, 1H), 7.88 (d, 1H), 7.66 (m, 3H), 7.27 (d, 1H), 4.10 (t, 2H), 1.90 (t, 2H), 1.19 (m, 24H), 0.81 (t, 3H)

MS: 457 $[C_{29}H_{38}NaO_3]^+$.

1-HA-OC_{16}： ^{1}H NMR (400 MHz $CDCl_3$) δ 8.22 (d, 1H), 8.17 (d, 1H), 7.89 (d, 1H), 7.66 (m, 3H), 7.27 (d, 1H), 4.10 (t, 2H), 1.90 (t, 2H), 1.19 (m, 26H), 0.81 (t, 3H)

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

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_{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 $[C_{30}H_{41}O_3]^+$.

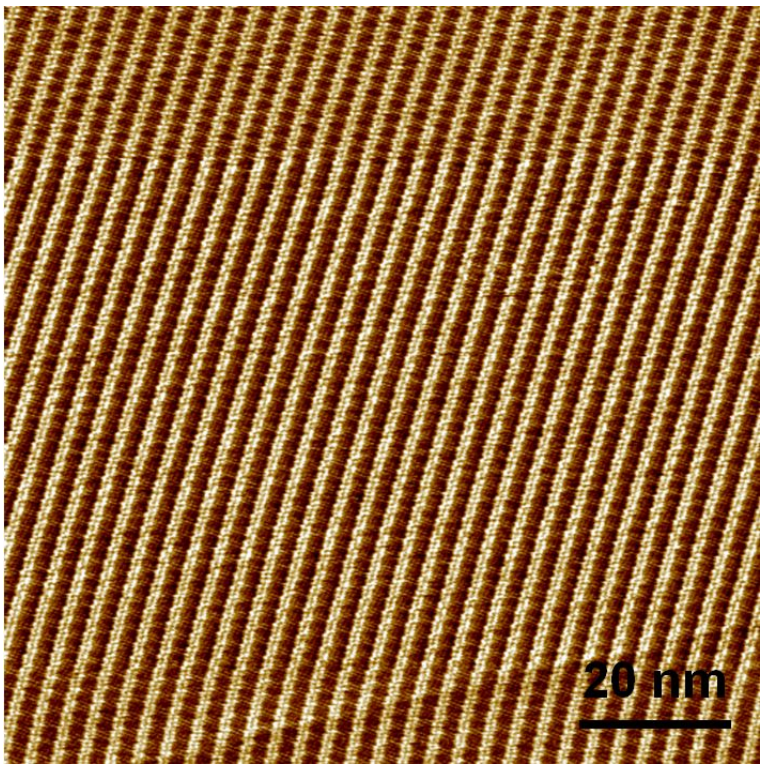


Figure S1. Large-scale STM image of 1-HA-OC_{16} physisorbed in 1-octanoic acid on HOPG. A uniform linear structure covers the substrate surface, exhibiting this Linear I packing fashion. Imaging conditions: I_t = 500 pA, V_{bias} = 750 mV.

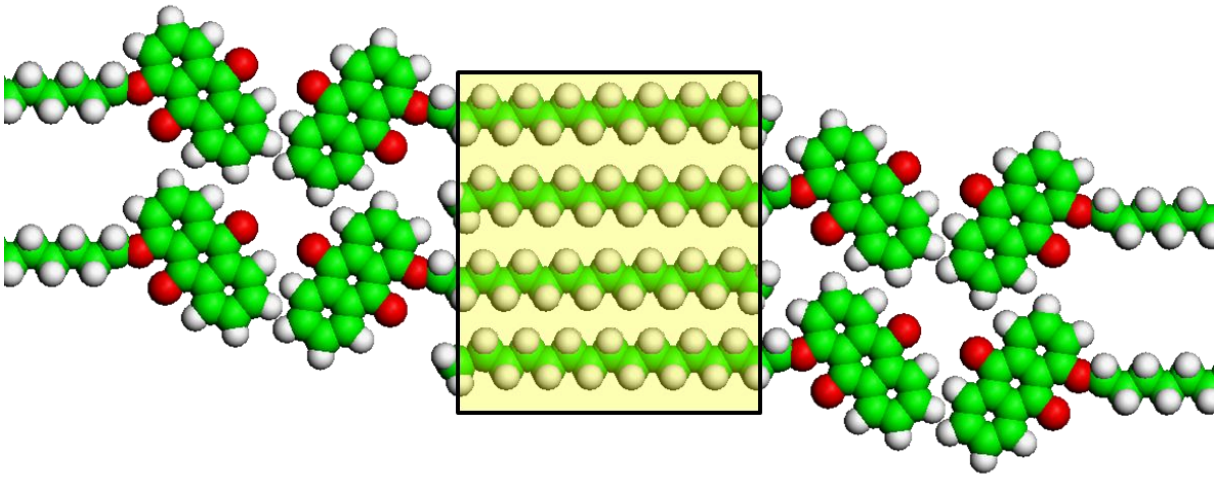


Figure S2. Space-filling spheres figure representation of the matched methyl and methylene groups in the side chains for 1-HA-OC_{16}. The interdigitated carbon atoms are enclosed by the yellow rectangle. For this linear packing fashion, alkyl chains are supposed to be not fully interdigitated. Only fifteen carbon atoms in a chain participate in the interdigitation between neighboring side chains. This dislocation by one atom is caused by the requirement for minimum steric repulsion.

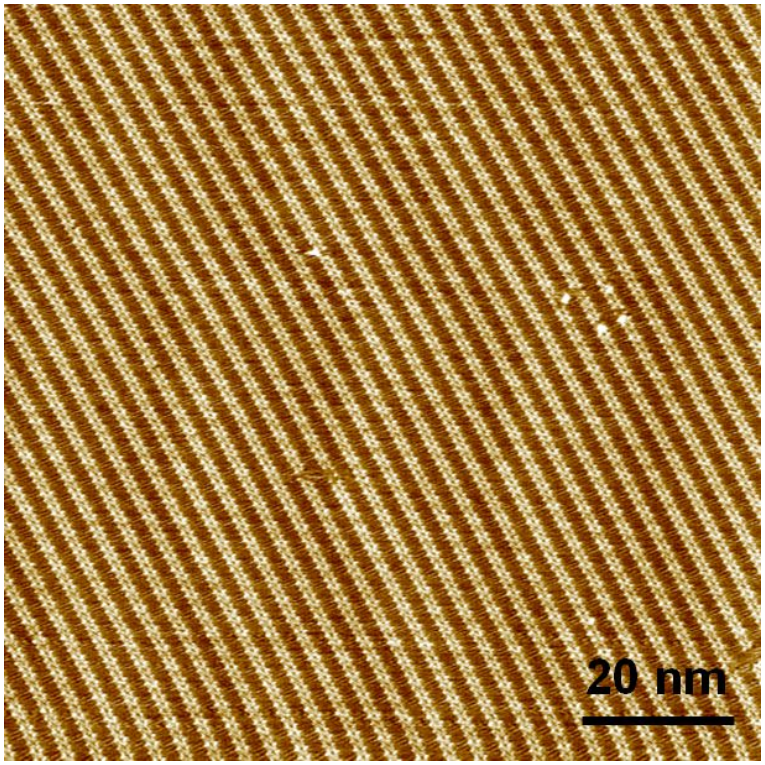


Figure S3. Large-scale STM image of 1-HA-OC_{15} physisorbed in 1-octanoic acid on HOPG surface, showing the Linear II packing fashion. Imaging conditions: I_t = 450 pA, V_{bias} = 600 mV. The HOPG surface is covered with orderly molecular adlayer.

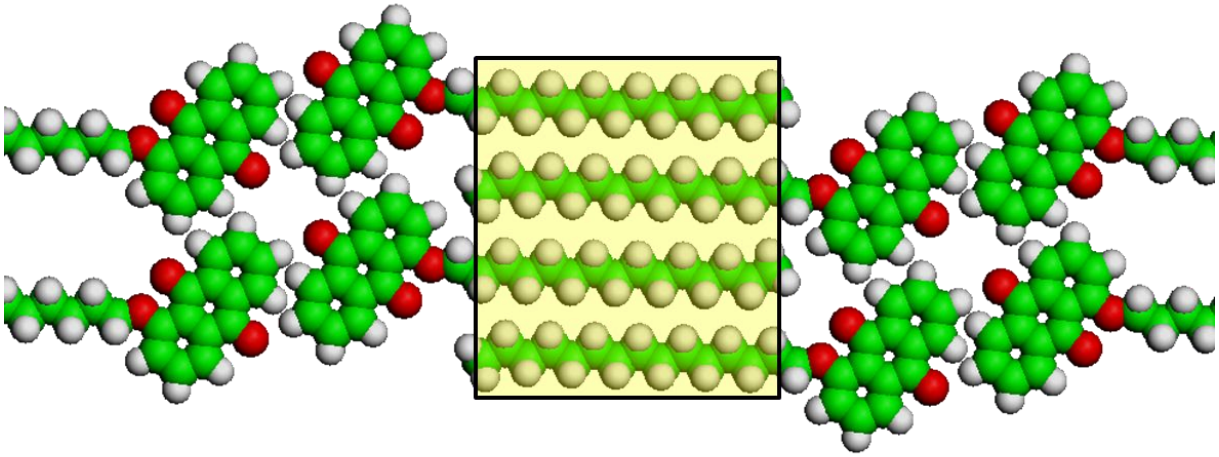


Figure S4. Space-filling spheres figure representation of the matched methyl and methylene groups in the side chains for 1-HA-OC_{15}. The interdigitated carbon atoms are enclosed by the yellow rectangle. For this linear packing fashion, alkyl chains are supposed to be not fully interdigitated. Only fourteen carbon atoms in a chain participate in the interdigitation between neighboring side chains. This dislocation by one atom is caused by the requirement for minimum steric repulsion.

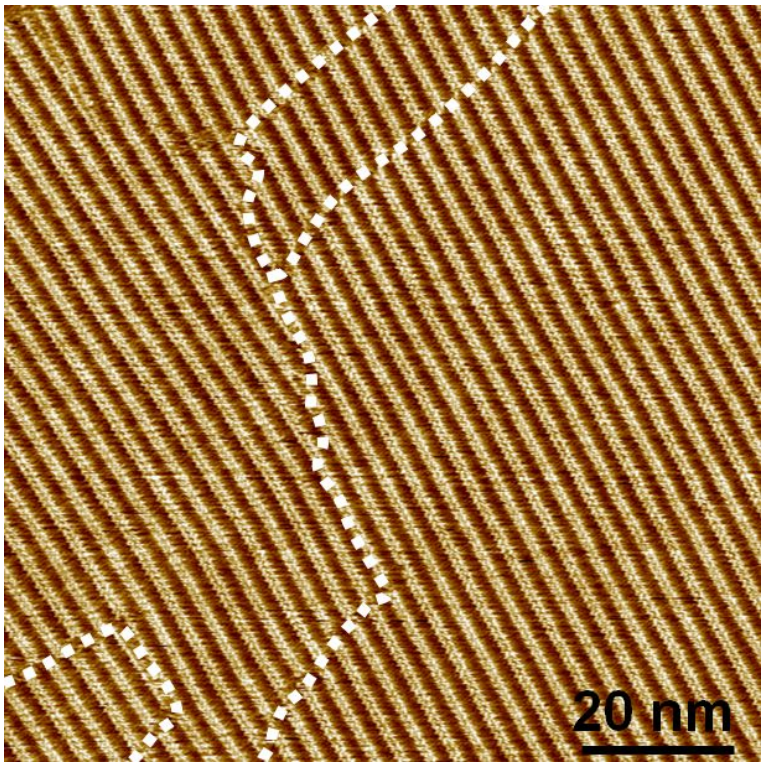


Figure S5. Large-scale STM image of 2-HA-OC_{12} physisorbed on 1-octanoic acid/HOPG surface, showing the Linear IV packing fashion. It can be clear seen that the 100 × 100 nm^2 area is not uniform, with several domains separated by white dotted lines. Imaging conditions: I_t = 600 pA, V_{bias} = 800 mV.

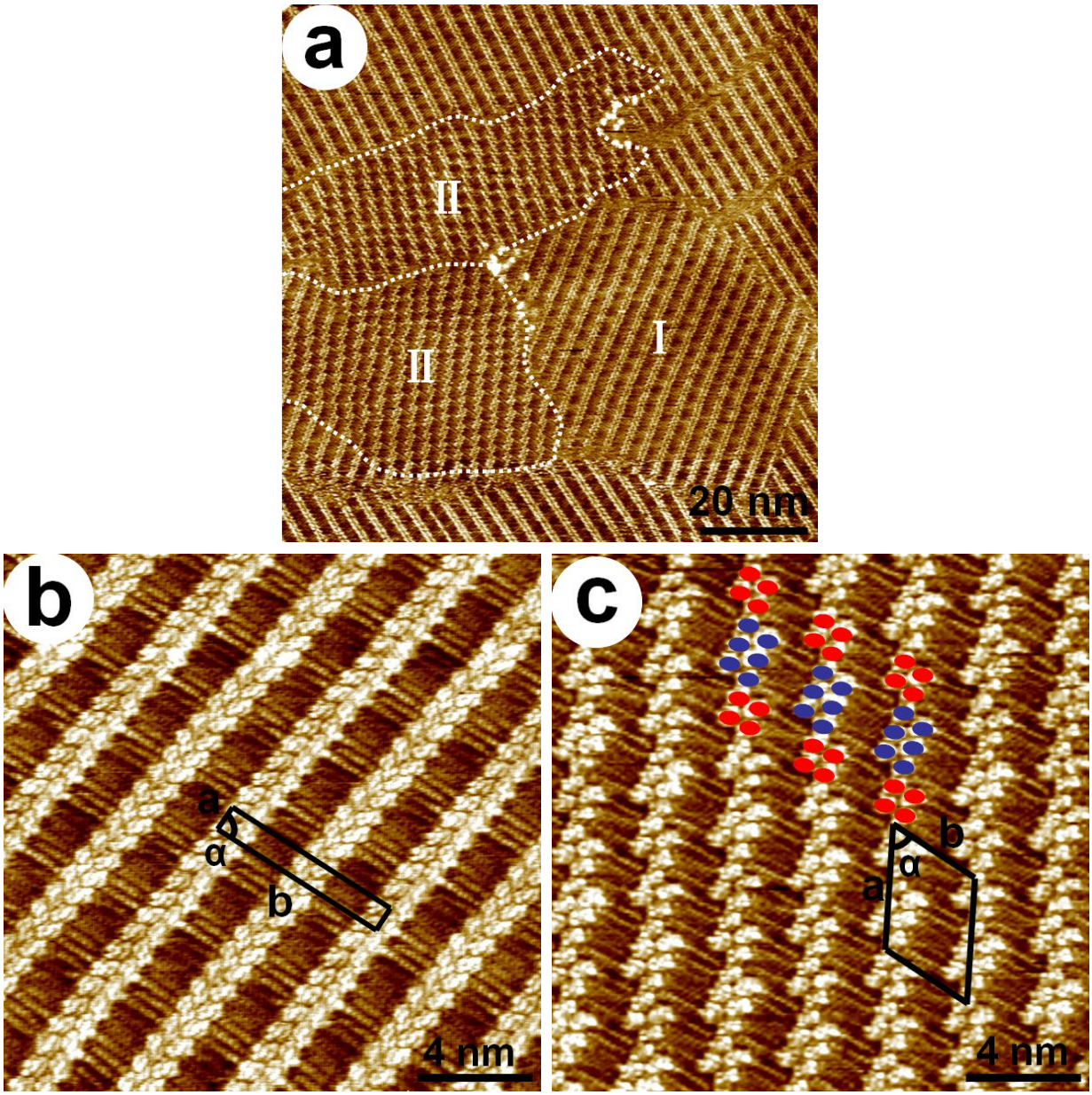


Figure S6. STM images of 2-HA-OC_{14} physisorbed on 1-octanoic acid/HOPG interface. (a) Large-scale STM image consists of both Linear IV (domain I) and Z-Like (domain II) structures. (b) High-resolution STM image of the Linear IV packing fashion. (c) High-resolution STM image of the Z-Like packing fashion. Imaging conditions: I_t = 500 pA, V_{bias} = 600 mV. The parameters for basic unit cell imposed in (b) are: a = 0.9 ± 0.1 nm, b = 6.3 ± 0.1 nm and α = 84 ± 1°. The parameters for basic unit cell imposed in (c) are: a = 5.5 ± 0.2 nm, b = 3.6 ± 0.2 nm and α = 67 ± 2°. According to the unit cell parameters, the calculated area densities are 1.41 nm^2 per molecule for Linear IV and 1.82 nm^2 per molecule for Z-Like structure.

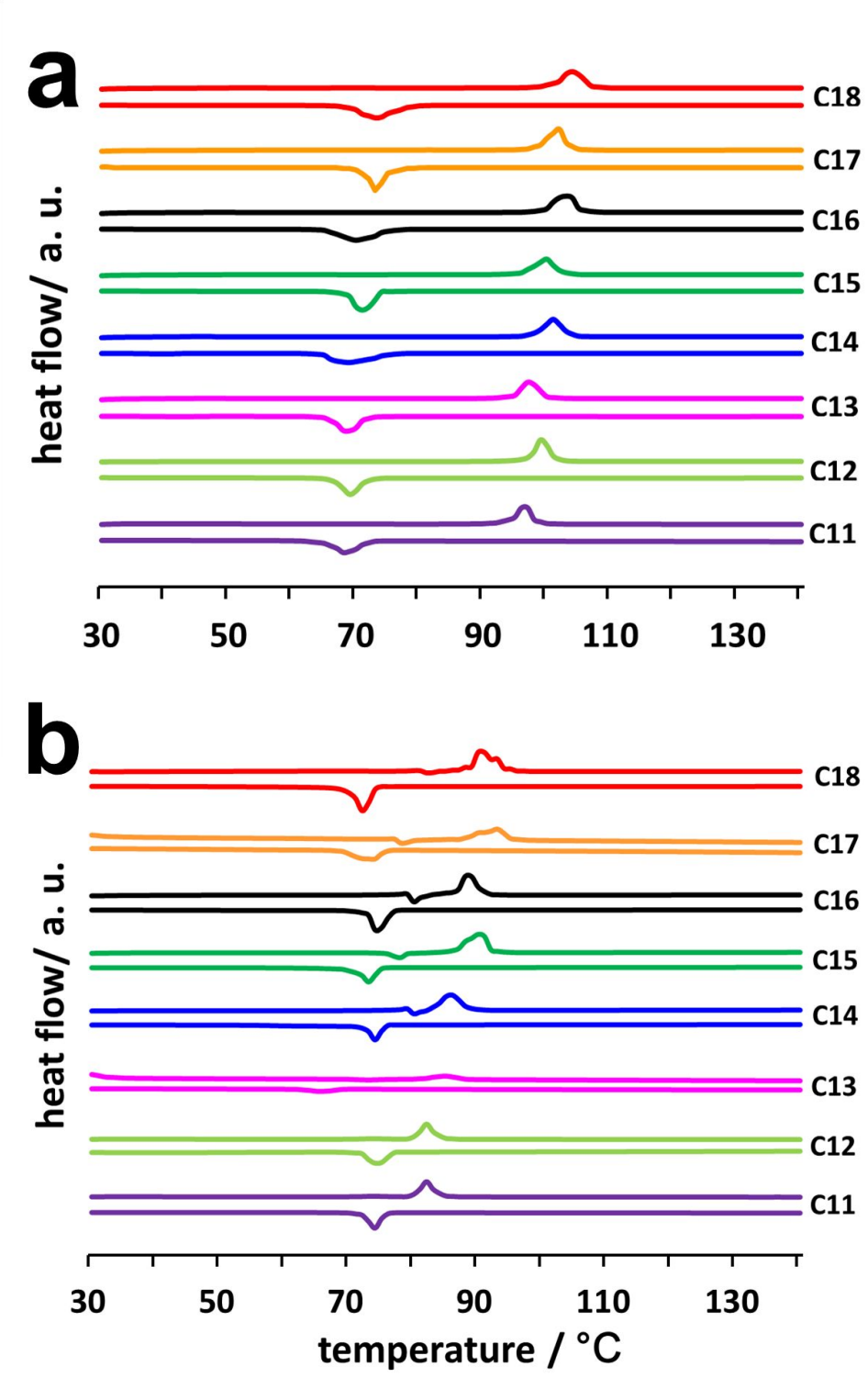


Figure S7. DSC thermograms of compounds 1-HA-OC_n (a) and 2-HA-OC_n (b) for the trace of heating (the above line) and cooling (the below line).