

Supporting Information

STM investigation of structural isomers: alkyl chain position induced self-assembly at liquid/solid interface

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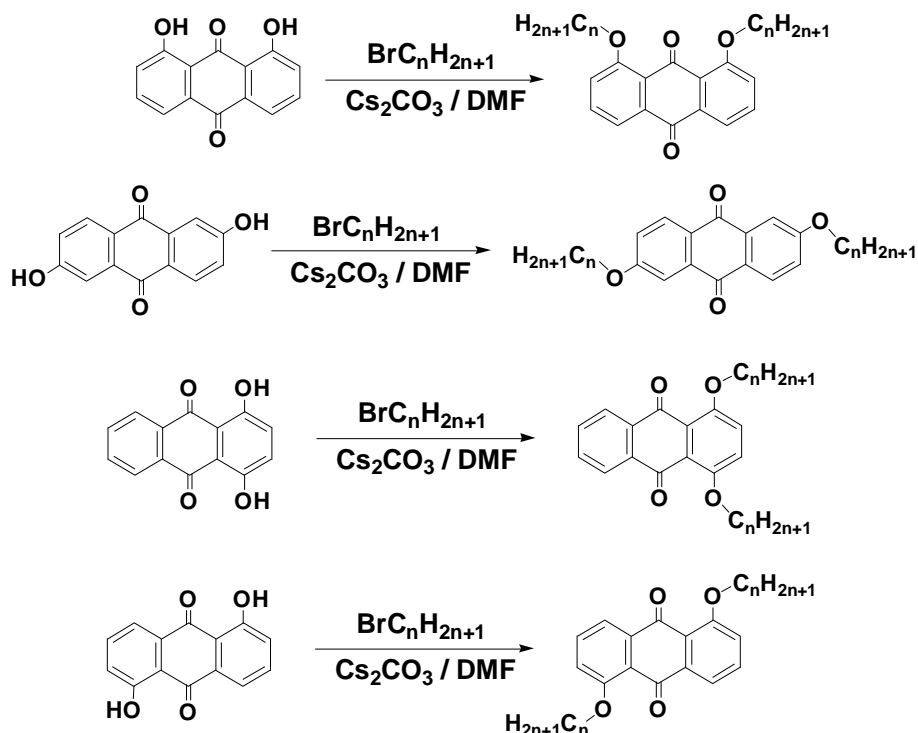
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Synthesize

1,8-A, 2,6-A, 1,5-A, 1,4-A ($n = 15, 16$) were synthesized from the commercially available 1,8-dihydroxyanthraquinone, 2,6-dihydroxyanthraquinone, 1,4-dihydroxyanthraquinone and 1,5-dihydroxyanthraquinone, in DMF (dry, 150 °C, 50mL) along with Cs_2CO_3 added (Scheme S1). The reaction finished thirty hours later and proved to be quite successful with a yield of 97%. The desired products were obtained by repeated recrystallization in view of high degree purity. All of the chemical reagents were purchased from Tokyo Chemical Industry without further purification. The products were dissolved in CH_2Cl_2 for observing their color (Figure S1).



Scheme S1. Synthesis of 1,8-A, 2,6-A, 1,5-A, 1,4-A ($n = 15, 16$) derivatives.

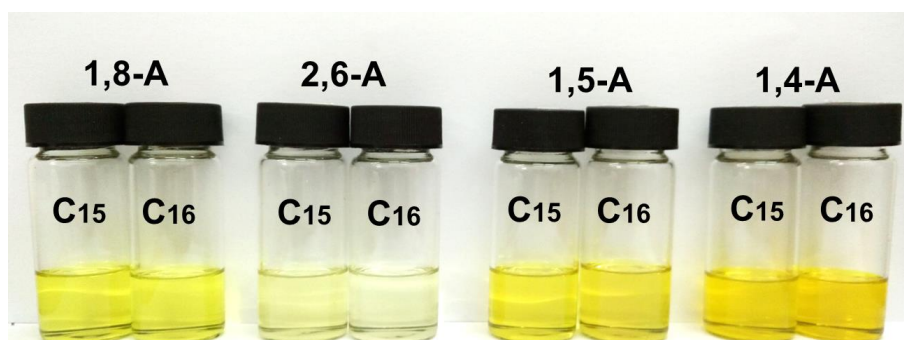


Fig. S1 Photography of the structural isomers of anthraquinone derivatives in CH_2Cl_2 (10^{-2} M).

Characterization data:

- 1,8-A-2OC₁₆: ¹H NMR (400 MHz CDCl₃) δ 7.82 (d, 2H), 7.60 (t, 2H), 7.28 (d, 2H), 4.15 (t, 4H), 1.93 (m, 4H), 1.57 (m, 4H), 1.28 (m, 48H), 0.90 (t, 6H)
MS: 689 [C₄₆H₇₃O₄]⁺.
- 1,8-A-2OC₁₅: ¹H NMR (400 MHz CDCl₃) δ 7.82 (d, 2H), 7.60 (t, 2H), 7.28 (d, 2H), 4.15 (t, 4H), 1.93 (m, 4H), 1.59 (m, 8H), 1.28 (m, 40H), 0.90 (t, 6H)
MS: 661 [C₄₄H₆₉O₄]⁺.
- 2,6-A-2OC₁₆: ¹H NMR (400 MHz CDCl₃) δ 8.24 (d, 2H), 7.73 (s, 2H), 7.25 (d, 2H), 4.17 (t, 4H), 1.87 (m, 4H), 1.51 (m, 4H), 1.28 (m, 48H), 0.90 (t, 6H)
MS: [C₄₆H₇₃O₄]⁺.
- 2,6-A-2OC₁₅: ¹H NMR (400 MHz CDCl₃) δ 8.25 (d, 2H), 7.73 (s, 2H), 7.24 (d, 2H), 4.17 (t, 4H), 1.87 (m, 4H), 1.51 (m, 4H), 1.28 (m, 44H), 0.90 (t, 6H)
MS: [C₄₄H₆₉O₄]⁺.
- 1,4-A-2OC₁₆: ¹H NMR (400 MHz CDCl₃) δ 8.18 (m, 2H), 7.71 (m, 2H), 7.32 (s, 2H), 4.11 (t, 4H), 1.94 (m, 4H), 1.27 (m, 52H), 0.89 (t, 6H)
MS: 689 [C₄₆H₇₃O₄]⁺.
- 1,4-A-2OC₁₅: ¹H NMR (400 MHz CDCl₃) δ 8.18 (m, 2H), 7.71 (m, 2H), 7.32 (s, 2H), 4.11 (t, 4H), 1.94 (m, 4H), 1.27 (m, 48H), 0.89 (t, 6H)
MS: 683 [C₄₄H₆₈NaO₄]⁺.
- 1,5-A-2OC₁₆: ¹H NMR (400 MHz CDCl₃) δ 7.90 (d, 2H), 7.67 (t, 2H), 7.27 (d, 2H), 4.17 (t, 4H), 1.97 (m, 4H), 1.59 (m, 8H), 1.28 (m, 44H), 0.90 (t, 6H)
MS: 689 [C₄₆H₇₃O₄]⁺.
- 1,5-A-2OC₁₅: ¹H NMR (400 MHz CDCl₃) δ 7.89 (d, 2H), 7.67 (t, 2H), 7.25 (d, 2H), 4.17 (t, 4H), 1.97 (m, 4H), 1.57 (m, 8H), 1.26 (m, 40H), 0.90 (t, 6H)
MS: 661 [C₄₄H₆₉O₄]⁺.

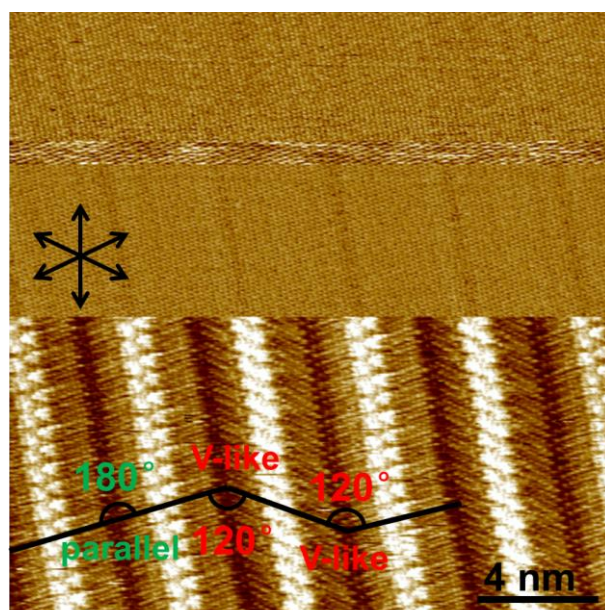


Fig. S2 STM image consists both of the 1,8-A-2OC₁₅ and the HOPG surface, indicating that alkyl chains extend along the orientation of the graphite lattice, no matter they are tail-to-tail in a parallel or V-like way. Concentration: 4.84×10^{-3} M. Imaging conditions: $I_t = 580$ pA, $V_{\text{bias}} = 100 \sim 790$ mV.

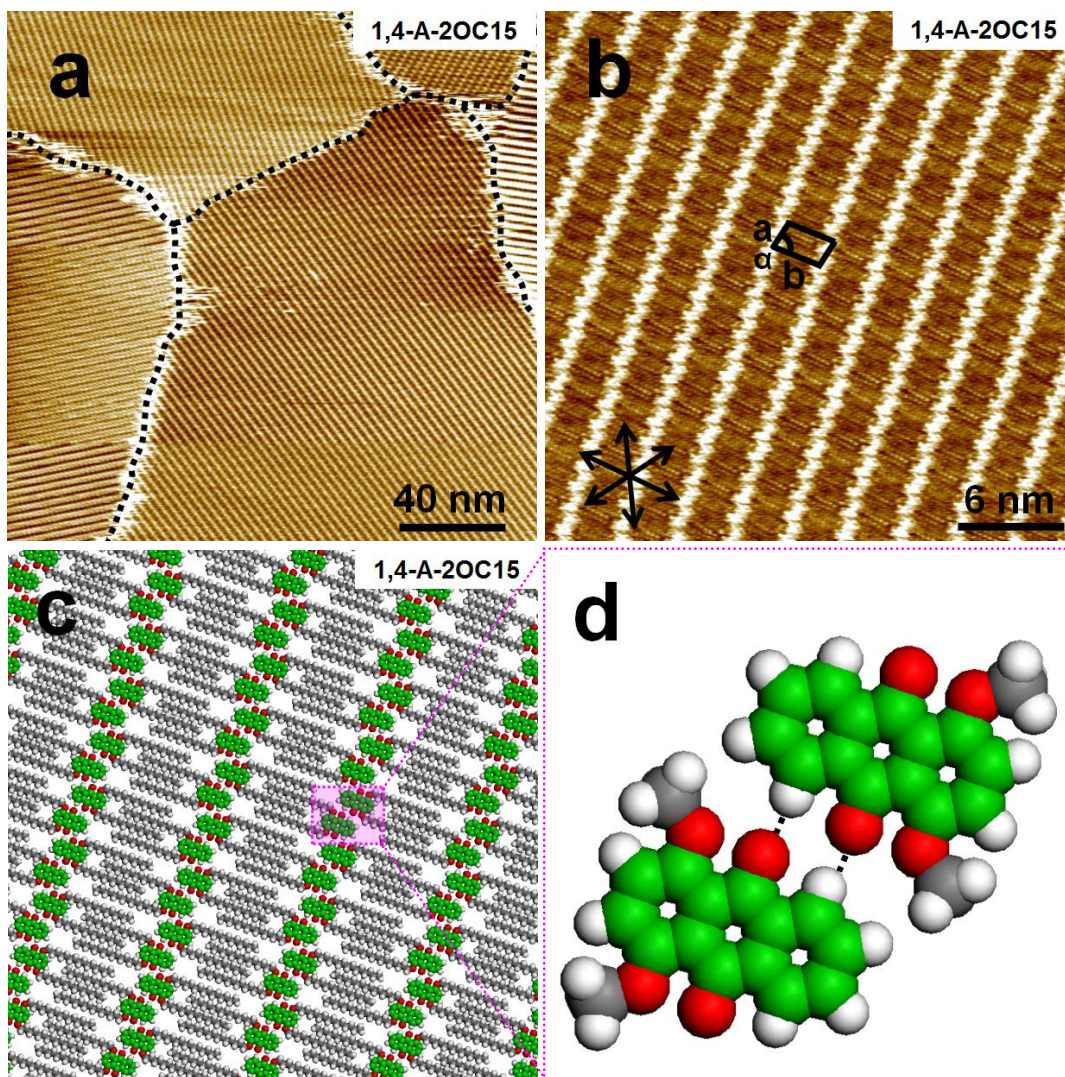


Fig. S3 (a) Large-scale and (b) high-resolution STM images of 1,4-A-2OC₁₅ self-assembled monolayer on HOPG surface. Concentration: 5.34×10^{-3} M. A unit cell consists two molecules is overlaid in (b), with the measured parameters of $a = 1.5 \pm 0.1$ nm, $b = 3.5 \pm 0.1$ nm and $\alpha = 74 \pm 1^\circ$. The calculated area density is 2.52 nm^2 per molecule. A set of black arrows in (b) show the basic symmetry axis of the graphite substrate. (c) Molecular model of the dimer zigzag structure (Z-like II). (d) Illustration of C=O \cdots H-C hydrogen bonding interactions within the dimer aggregations. The long alkyl chains are replaced by methyl groups. Imaging conditions: $I_t = 560$ pA, $V_{\text{bias}} = 630$ mV.

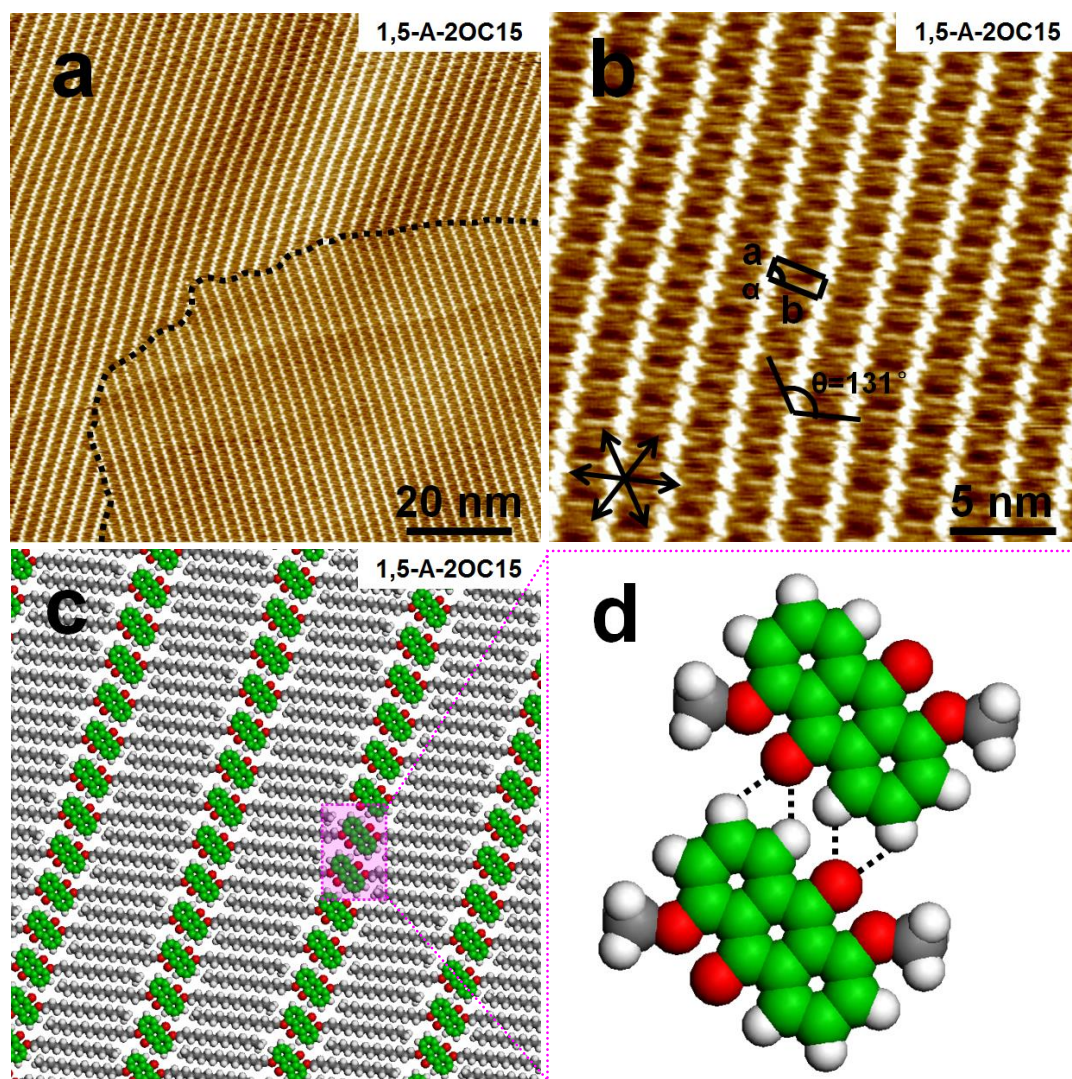


Fig. S4 (a) Large-scale and (b) high-resolution STM images of 1,5-A-2OC₁₅ self-assembled monolayer on HOPG surface. Concentration: 1.96×10^{-3} M. A unit cell consists one molecules is overlaid in (b), with the measured parameters of $a = 1.1 \pm 0.1$ nm, $b = 2.7 \pm 0.1$ nm and $\alpha = 88 \pm 2^\circ$. Area density is calculated to be 2.97 nm^2 per molecule. A set of black arrows in (b) show the basic symmetry axis of the graphite substrate. (c) Molecular model of the linear structure (Linear IV). (d) Illustration of C=O \cdots H-C hydrogen bonding interactions within the dimer aggregations. The long alkyl chains are replaced by methyl groups. Imaging conditions: $I_t = 590$ pA, $V_{\text{bias}} = 760$ mV.

Table S1. The maximum absorbance peaks of anthraquinone isomers.

molecules	1,8-A		2,6-A		1,4-A		1,5-A	
	C ₁₆	C ₁₅	C ₁₆	C ₁₅	C ₁₆	C ₁₅	C ₁₆	C ₁₅
λ_{max} (nm)	385		350		380		420	

Table S2. Phase transition temperature of anthraquinone isomers

	2,6-A		1,8-A		1,5-A		1,4-A	
melting	C ₁₆	117	>	112	>	102	>	91
point (°C)	C ₁₅	111	>	109	>	104	>	97