Supporting Information

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

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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\(_2\)CO\(_3\) 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\(_2\)Cl\(_2\) 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\(_2\)Cl\(_2\) (10\(^{-2}\) M).
Characterization data:

1,8-A-2OC₁₆: $^1$H 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: $^1$H 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: $^1$H 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: $^1$H 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: $^1$H 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: $^1$H 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 [C₄₄H₆₉NaO₄]$^+$.  

1,5-A-2OC₁₆: $^1$H 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: $^1$H 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]$^+$.  

MS data taken from solvent and temperature.
**Fig. S2** STM image consists both of the 1,8-A-2OC$_{15}$ 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: $4.84 \times 10^{-3}$ M. Imaging conditions: $I_t = 580$ pA, $V_{bias} = 100 \sim 790$ mV.
**Fig. S3** (a) Large-scale and (b) high-resolution STM images of 1,4-A-2OC_{15} self-assembled monolayer on HOPG surface. Concentration: $5.34 \times 10^{-3}$ 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···H-C hydrogen bonding interactions within the dimer aggregations. The long alkyl chains are replaced by methyl groups. Imaging conditions: $I_t = 560$ pA, $V_{bias} = 630$ mV.
Fig. S4 (a) Large-scale and (b) high-resolution STM images of 1,5-A-2OC\textsubscript{15} self-assembled monolayer on HOPG surface. Concentration: $1.96 \times 10^{-3}$ 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···H-C hydrogen bonding interactions within the dimer aggregations. The long alkyl chains are replaced by methyl groups. Imaging conditions: $I_t = 590$ pA, $V_{bias} = 760$ mV.
**Table S1.** The maximum absorbance peaks of anthraquinone isomers.

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<th>molecules</th>
<th>1,8-A</th>
<th>2,6-A</th>
<th>1,4-A</th>
<th>1,5-A</th>
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<tr>
<td></td>
<td>C_{16}</td>
<td>C_{15}</td>
<td>C_{16}</td>
<td>C_{15}</td>
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<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>385</td>
<td>350</td>
<td>380</td>
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**Table S2.** Phase transition temperature of anthraquinone isomers

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<th>2,6-A</th>
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<th>1,5-A</th>
<th>1,4-A</th>
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<tr>
<td>point (°C)</td>
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<td>&gt;</td>
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<td></td>
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<td>97</td>
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