Supporting Information

Exploration of alkyl chain number and position effects towards 2D self-assembly

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Method for density functional theory (DFT) calculations

We use four unit cells for the calculation of the binding energies for the self-assembled structures. The hydrogen bonds and van der Waals interactions are calculated separately.

$E$ represent the calculated total energy, then

$E_1 = \text{total energy for one molecule}$

$E_2 = \text{total energy for the four unit cells}$

$N = \text{number of molecules in the unit cell}$

$\Delta E = \text{the binding energy}$

$\Delta E = E_2 - 4N \cdot E_1$
Results

Fig. S1 High-resolution STM images for (a) 1-A, (b) 2-A, (c) 1.8-A, (d) 1.5-A, (e) 1.4-A, (f) 2.6-A and (g) 1.2.4-A at the 1-octanoic acid/HOPG interface, showing the Linear I, Linear II, Linear III, Linear IV, Zigzag, Linear V and Dimer-Linear structures, respectively. Imaging conditions: $I_t = 450–700$ pA, $V_{bias} = 550–900$ mV.
**Fig. S2** Structural model for the dimer in Dimer-Linear structure for 1,2,4-A molecules from the (a) top view and (b) side view. In the Linear rows, the three chains belong to one 1,2,4-A molecule are fully interdigitated with the chains from the adjacent rows. However, in the dimer rows, we can only observe two chains, which means the other chain is directing to the liquid phase.

**Fig. S3** Large-scale STM images for 1,2,3-A at the 1-octanoic acid/HOPG interface. Scanning conditions: $I_t = 610$ pA, $V_{bias} = 780$ mV.
**Fig. S4** Surface coverage distribution of aggregations with different number of molecules (measuring area: 50 × 50 nm²). *N* represents number of a certain aggregation. *N’* represents total number of molecules in a certain aggregation.

**Table S1.** Phase-transition temperatures and UV absorption peaks for the anthraquinone derivatives.

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<th>mono-</th>
<th>bis-</th>
<th>tri-</th>
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<tr>
<td></td>
<td>1-A</td>
<td>2-A</td>
<td>1,8-A</td>
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<td>phase-transition</td>
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