# Supporting information for:

# Surface Supported Supramolecular Pentamers

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# Role of the substrate

The lack of a preferred orientation on the Au(111) surface in contrast to the more reactive Ag(111) one, indicates the unimportance of the substrate interaction for the formation of the pentamers. In addition, the observed islands and arrays are not commensurable with the underlying substrate, which is also an indication of the limited interaction. On the other hand, the size of the arrays and the lack of commensurability of the islands prohibits a DFT calculation including the surface. However, test calculations have been done with low precision for individual molecules and dimers. From such calculations, we conclude that the interaction of molecules with the substrate is purely due to van der Waals forces, with charge transfers below 0.2 electrons for the whole molecule, which is around the accuracy of the calculation. We were also able to estimate the energy needed to separate two molecules on the surface, which is equal to 0.90 eV, very close to the value reported in Table 1 (0.85 eV). The lack of directional preference, the smallness of the molecule–surface interactions with negligible charge transfer, and the agreement of the dimer binding energy computed with and without surface give us confidence on the ability of the calculations without surface to capture the intermolecular behavior of the supported molecules.

# Optimized geometries of ReA hexamers
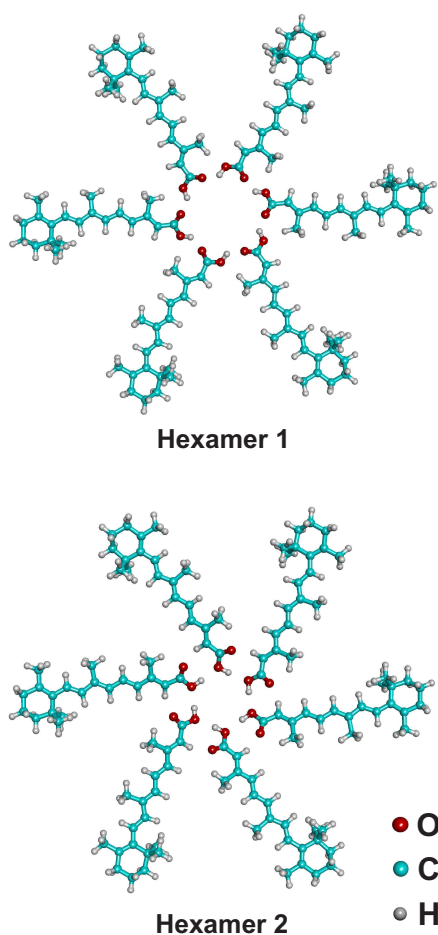


**Hexamer 1**

**Hexamer 2**

Figure S1: Two optimized geometries of six *all-trans*-retinoic acid (ReA) molecules in a plane. Hexamer 1 is obtained by requiring that the hexamer be obtained by inserting an additional ReA molecule into the optimized pentamer. It has a binding energy of 0.83 eV. The binding energy of the fully optimized Hexamer 2 is higher (1.15 eV). However, its formation requires a significant rearrangement of the pentamer. Both the structures have lower binding energies than a pentamer (1.45 eV).
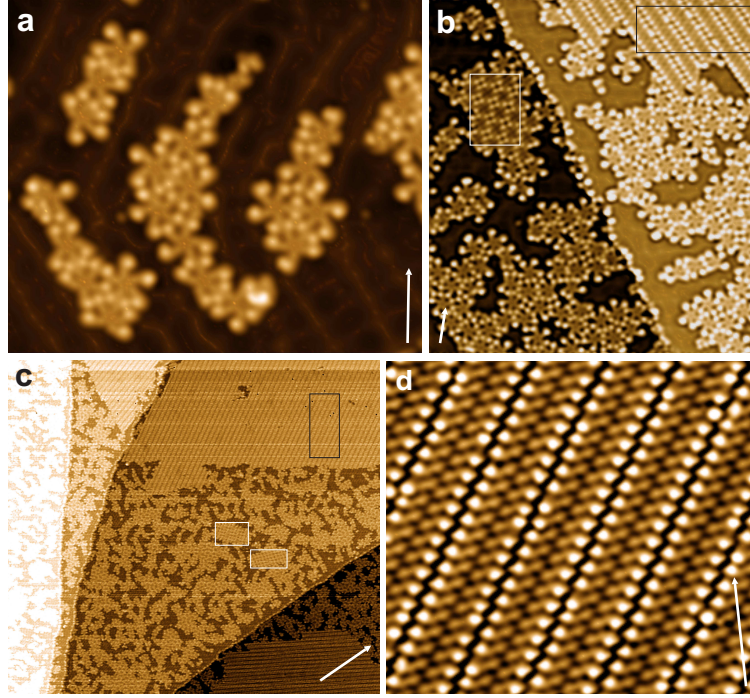
# Overview images of ReA on Au(111)



Figure S2: Constant current images of ReA on Au(111). Arrows indicate a $\langle 1\bar{1}0 \rangle$ direction. Their lengths indicate 5 nm in (a), (b), and (d) and 50 nm in (c). (a) Image at low coverage ($\theta \approx 0.4$ ML) showing essentially only pentamers. (b), (c) Coexistence of structures at intermediate coverage ($\theta \approx 0.75$ ML). Black and white rectangles indicate islands of dimers and tetramer, respectively. Most other structures are due to pentamers. (d) Close to $\theta = 1$ ML only dimer chains are observed.

Table S1: Fractions of structures observed. Values are based on more than 10 images of $(150 \text{ nm})^2$ for each coverage.

| coverage in ML | pentamers | tetramers | dimers |
|:---:|:---:|:---:|:---:|
| 0.25 | 100% | 0% | 0% |
| 0.4 | 100% | 0% | 0% |
| 0.6 | 87% | 1% | 12% |
| 1.0 | 0% | 0% | 100% |

# ReA trimer on Au(111)



Figure S3: Constant current images of ReA trimer on Au(111). Scale bar indicates 1 nm and a $\langle 1\bar{1}0 \rangle$ direction.