

Supporting information for:

Surface Control of Alkyl Chain Conformations and 2D Chiral Amplification

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S1. Details of the calculation

All density functional theory (DFT) calculations were performed with Turbomole 6.2^{S1} modified with the Grimme D3^{S2} dispersion energy correction. The SVP Ahlrichs basis set^{S3} and the gradient-corrected correlation functional of Perdew, Burke and Ernzerhof (PBE)^{S4} were used. A D_{3d} symmetric gold cluster consisting of 170 gold atoms (ECP 60) was used as the substrate (Fig. S1a). Calculations including plane wave methods and periodic boundary conditions are expensive as the lateral distance between two neighboring TATA molecules is more than 10 Å. Further, the adsorption of a molecule on each extended Au(111) facet leads to cancellation of induced dipole errors because of the inherent C_i symmetry, and saves computational costs because of the

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higher symmetry of the system as shown in a previous work.^{S5} The herring bone reconstruction is neglected in the calculation since it does not significantly affect the TATA island growth as observed in STM images.

After optimizing the gold cluster geometry the gold atom coordinates were fixed and a *tri-propyl*-TATA molecule was optimized on top of the (111) surface of the gold cluster. Calculations on adsorbed *tri-octyl*-TATA were not feasible because of its size. After the optimization of *tri-propyl*-TATA an all *anti pentyl* chains were attached and optimized at the PBE/SV(P) level of density functional theory. The gold cluster model was employed for both single molecules in the gas phase and on the surface at the same level of theory.

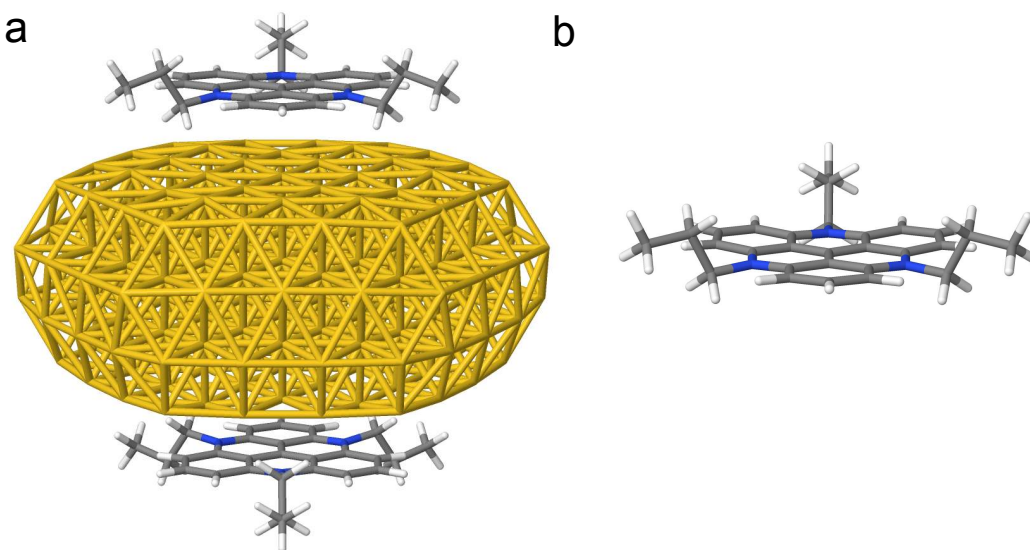


Figure S1: (a) The Au cluster with *tri-propyl*-TATA as used in the calculations. (b) Calculated structure of gas phase *tri-propyl*-TATA.

The adsorption energy of molecules at different surface sites (Fig. S2) was calculated with a methyl group attached to the nitrogen atoms instead of an octyl chain. As extracted from STM images and mass spectra, the *tri-octyl*-TATA ion adsorbs on the Au(111) without tetrafluoroborate which is the counter ion in solution. The bulk gold acts as a counter ion for the *tri-octyl*-TATA ion. Therefore, any influence of the counter ion is neglected in our calculations. The obtained energetic levels of the gold atom orbitals are close enough to each other that our discrete molecular orbital model cluster is acting almost like bulk gold.

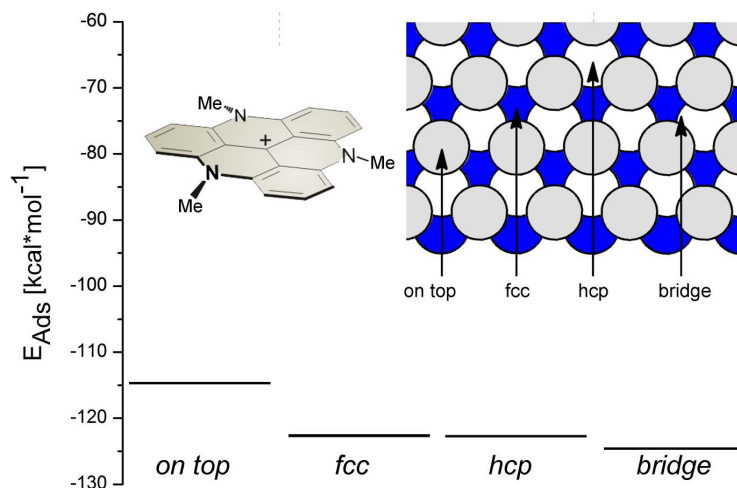


Figure S2: Adsorption energies of *methyl*-TATA with nitrogen atoms adsorbed at different sites. Inset shows the possible binding sites of nitrogen atoms on Au(111).

The calculated adsorption energies should be at the upper limit due to two following computational limitations. First, a Basis Set Superposition Error (BSSE) that is expected from an incomplete basis set such as the SVP Ahlrichs base. It was technically not feasible to perform a BSSE correction for the model system. Further, the Grimme D3 dispersion correction is known to overestimate the dispersion energies and might be another cause for an overestimation of the binding energies.^{S2} Nevertheless, a comparison of binding energy between different surface sites within the model is qualitatively correct.

The geometrical arrangement of three nitrogen atoms of TATA coincides with Au(111) lattice so as to consider surface sites with all nitrogen atoms adsorbed at top, fcc, hcp and bridge sites (Fig. S2). While the adsorption energies of TATA for the fcc, hcp, and bridge sites are comparable, the adsorption at the top site is weaker by $\approx 5 \text{ kcal mol}^{-1}$. TATA molecules are preferably adsorbed on either hcp, fcc, or bridge sites. The energy difference between these sites are within the error margin of the used method. Therefore, the exact binding site cannot be determined but the calculated adsorption energies strongly suggest a non-directional binding mode dominated mainly by dispersive interactions. In addition the calculations reveal that the TATA ion is aligned with its axis (dashed line in Fig. 1c) along the compact directions of Au(111) as observed in the experiment (see Fig. 1f).

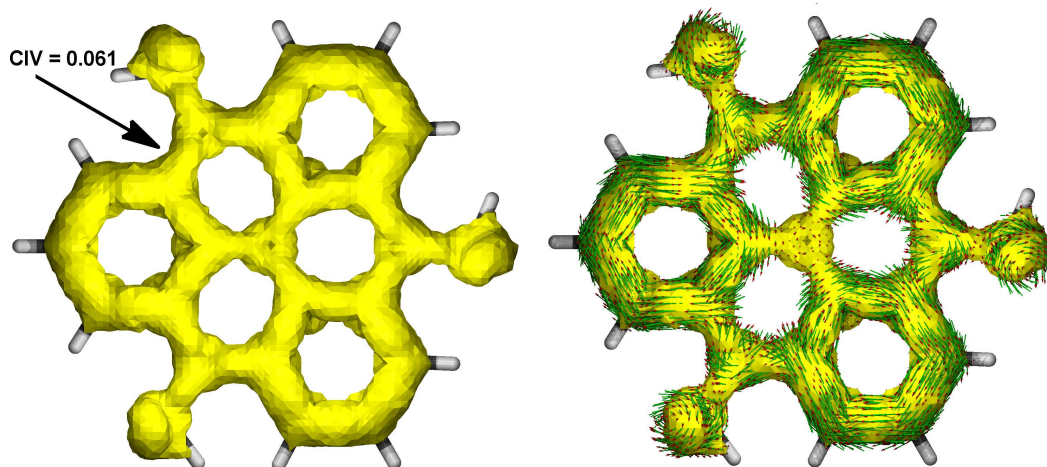


Figure S3: ACID plot of the TATA cation with methyl side chains at an isosurface value of 0.03 without (left) and with (right) depicted current density vectors. The external magnetic field vector is applied orthogonal to the molecular plane pointing towards the viewer.

Further, the anisotropy of the induced current density (ACID) ^{S6} of the TATA cation with methyl side chains was calculated (Fig. S3). Only π -orbitals were included to investigate the π -electron delocalization of the TATA molecule. The isosurface plot predicts a distinctive delocalization of the π system. The current density vectors, which are depicted on the isosurface, exhibit a diamagnetic (clockwise) ring current along the peripheral bonds. Moreover, the critical isosurface value (CIV) is very high throughout the whole molecule. The ACID plot of the TATA cation leads to the conclusion that the lone pairs of the nitrogen atoms are part of the aromatic system and, therefore, are not likely to form covalent bonds with the atoms of the gold surface. As a result, the adsorption of the TATA molecule on the substrate is mainly based on a dispersive interaction in agreement with the calculated adsorption geometries.

S2. Proposed adsorption geometry of TATA on Au(111)

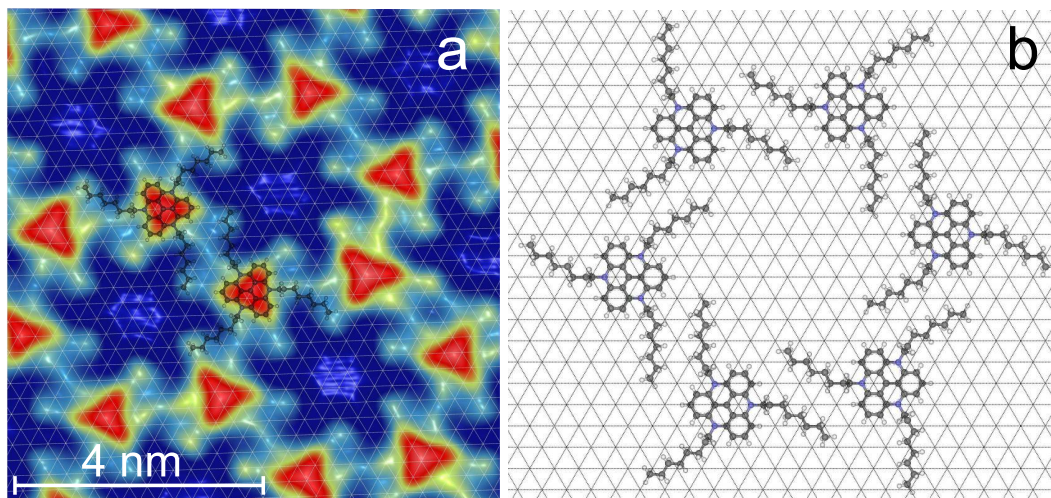


Figure S4: (a) STM topograph (100 mV, 100 pA) of the hexagonal pattern of *tri-octyl*-TATA. The overlaid molecules show their relative orientation within the pattern. A white hexagonal grid depicts the Au(111) lattice. The distance between the nitrogen atoms of TATA (4.86 Å) fairly matches with the Au(111) lattice constant along the $\langle 112 \rangle$ direction. Thus they adsorb at equivalent positions. (b) Proposed adsorption geometry of *tri-octyl*-TATA on Au(111) based on experimental findings and with the nitrogen atoms kept at the bridge sites, which have the lowest adsorption energy according to Fig. S2.

S3. Ratio of C_3 symmetric molecules in an island for Au(111)

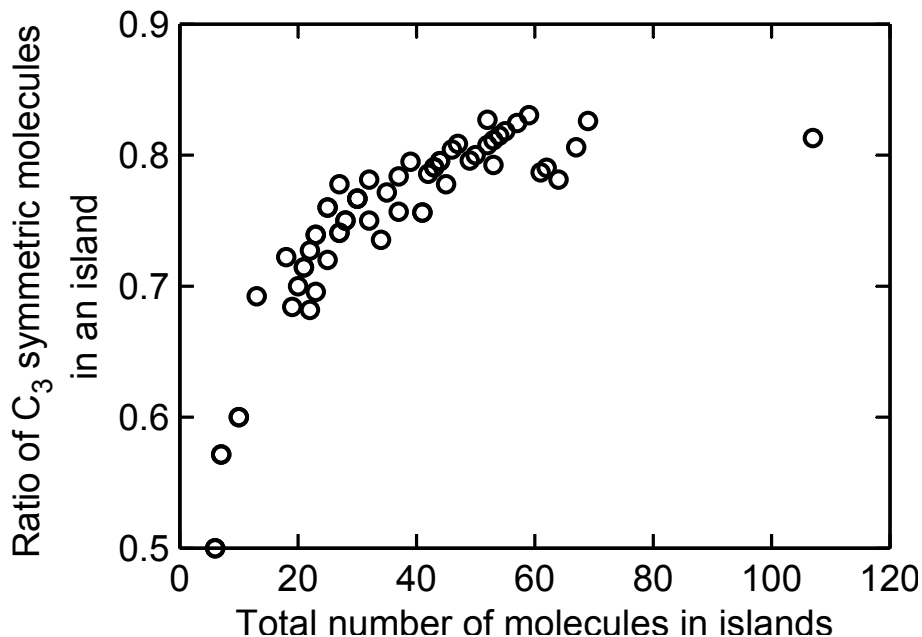


Figure S5: Ratio of C_3 symmetric molecules to the total number of molecules in islands on Au(111) vs island size extracted from various islands.

S4. Estimation of the flipping rate of *octyl* groups

The flipping process is considered to consist of two energy-costly processes: A desorption of the *octyl* group and a rotation process along $C_{(2)}-C_{(3)}$. According to Fig. 1e only five out of eight carbon atoms are attached to the surface. Hence, the desorption energy may be compared to that of a pentane. In Ref. S7 desorption energies for different hydrocarbons on Au(111) are determined where 40.5 kJ/mol and 55.9 kJ/mol are obtained for butane and hexane, respectively. As an explicit desorption energy for pentane is not given, we use that of butane or hexane. The energy for a S-*gauche* to R-*gauche* transition via the totally eclipsed conformation for the example of a butane chain is ($E_{rot} = 17.2$ kJ/mol ^{S8}) used for the rotational barrier between $C_{(2)}-C_{(3)}$. The flipping rate f can be described by an Arrhenius law as:

$$f = \nu \exp \left[-\frac{(E_p + E_{rot})}{k_B T} \right] \quad (1)$$

where k_B is the Boltzmann's constant, T the temperature, and ν the pre-exponential factor which can be expected to be in the range $10^{13} \leq \nu \leq 10^{19}$ according to previous works.^{S9-S12} This yields flipping rates for *octyl* chain at room temperature of $f \sim 800$ to 10^8 s^{-1} with desorption energy of butane and $f \sim 2$ to 10^6 s^{-1} with desorption energy of hexane. Therefore suggesting that flipping does occur at room temperature for *octyl* chain.

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S5. Complete list of Publications that are shortened to the first author name followed by “et al.” in the manuscript

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