

Electronic Supplementary Information

Tuning the Formation of Discrete Coordination Nanostructures

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(1) Density functional theory calculations on the molecular adsorption

To confirm that the observed nanostructures are formed by metal coordination between gold adatoms and cyano functional groups, we performed density functional theory (DFT) calculations, comparing the adsorption of a cyanosexiphenyl molecule on the bare surface with the adsorption at a gold adatom. The relaxed configuration for a single cyanosexiphenyl molecule adsorbed on the bare Au(111) surface is shown in Figure S1a. The corresponding simulated STM image for the highest occupied molecular orbital (HOMO) is shown in Figure S1c. The bonding energy between the molecule and the substrate was calculated to be 6.27 eV.

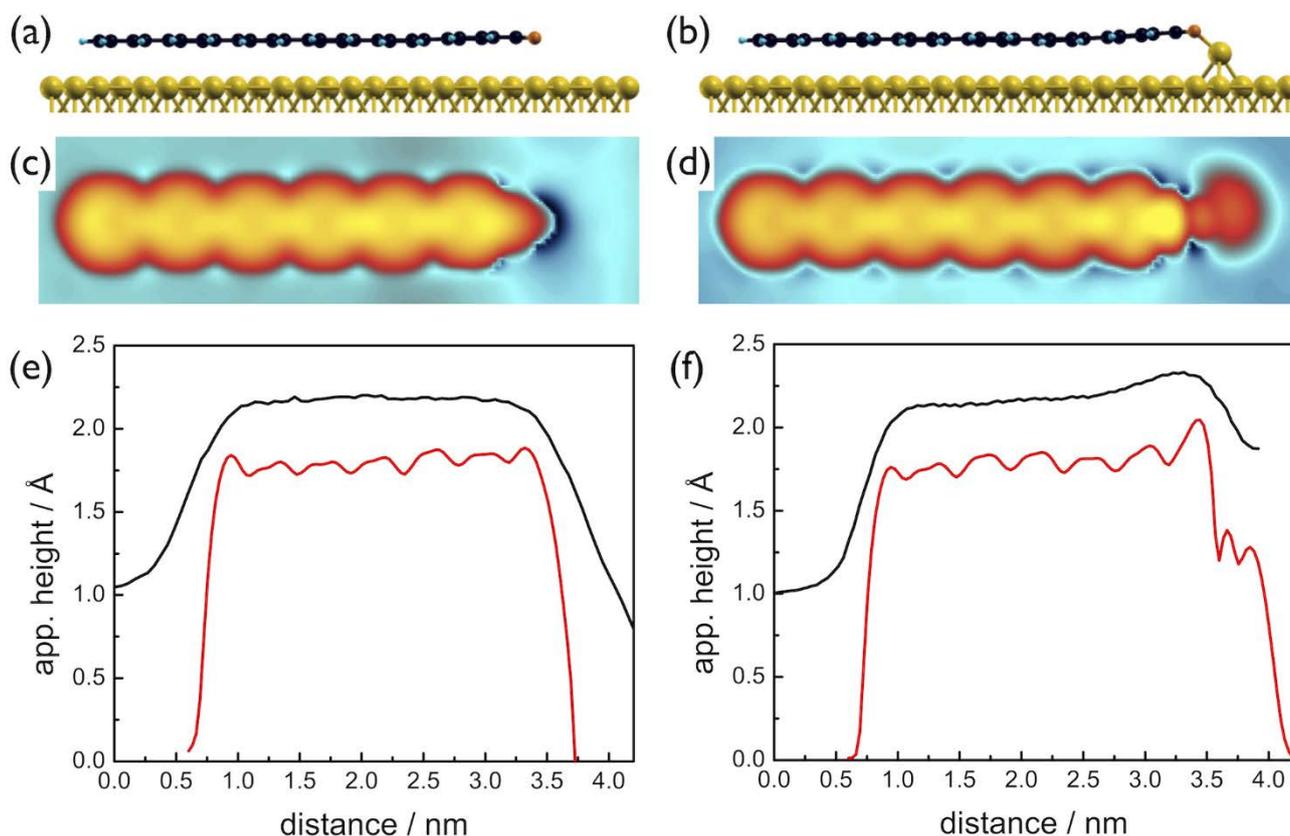


Figure S1. Adsorption of single molecules. (a) Side view of the calculated relaxed geometry of a single cyanosexiphenyl molecule adsorbed on the Au(111) surface and (b) adsorbed next to a Au adatom; (c) and (d) show simulated STM images corresponding to the two cases of (a) and (b), respectively. Images are simulated in an energy window between 0 V and -1.2 V, which corresponds to the HOMO; (e) and (f) show the comparison of line scans from simulated (red) and experimental (black) images of a molecule with and without a gold adatom, respectively. The experimental line scans have been shifted for clarity (upward by 1 Å). The experimental line scan in (e) was measured at a molecule adsorbed on the upper side of the step edge (like in Figure 1b). Accordingly, the apparent height drops on the right side of the molecule.

When the molecule binds to an adatom (Figure S1b), the configuration of the adsorbed molecule changes and the cyano group is raised up. The simulated image for the HOMO of this configuration is shown in Figure S1d. As one can see, the image is now brighter around the carbon atom in the cyano group. The bonding energy of the molecule adsorbed at an adatom was calculated to be 6.64 eV. This is almost 0.4 eV larger than in the case without the Au adatom and confirms that the molecule

preferentially adsorbs at gold adatoms on the surface. In Figure S1e and S1f, line scans of the simulated images are compared to experimental topography profiles. The apparent height for the two calculated configurations is in good agreement with the experimental line scans. As one can see in Figure S1f, the presence of the gold adatom induces a peak in the calculated apparent height at the one end of the molecule, corresponding to the position of the C atom in the cyano group. This peak is experimentally observed on the molecule in the trimer and dimer geometry (Figure S1f, black curve). On the other hand, molecules adsorbed at step edges have a flatter profile, similar to the calculated structure without the adatom. This indicates that the molecules adsorbed on top of a step edge (Figure 1b in the manuscript) are directly bound to the Au(111) surface and not to a gold adatom.

(2) Stability of dimer pairs

To better understand the formation of dimer pair, we performed DFT calculations. To reduce the computational effort, molecules with only two phenyl rings (i.e. cyanobiphenyl) instead of six as in the case of cyanosexiiphenyl are considered. The results show that there is an attractive interaction between the dimers. In Figure S2, we present the calculated energy of a dimer pair for different distances between dimers. The minimum of the energy is achieved for a coupled dimer pair, as shown also in Figure 3a. The coupling energy is found to be of about 0.4 eV with an energy barrier about 0.8 eV, explaining why at low temperatures all single dimers form pairs or structures with a larger number of dimers.

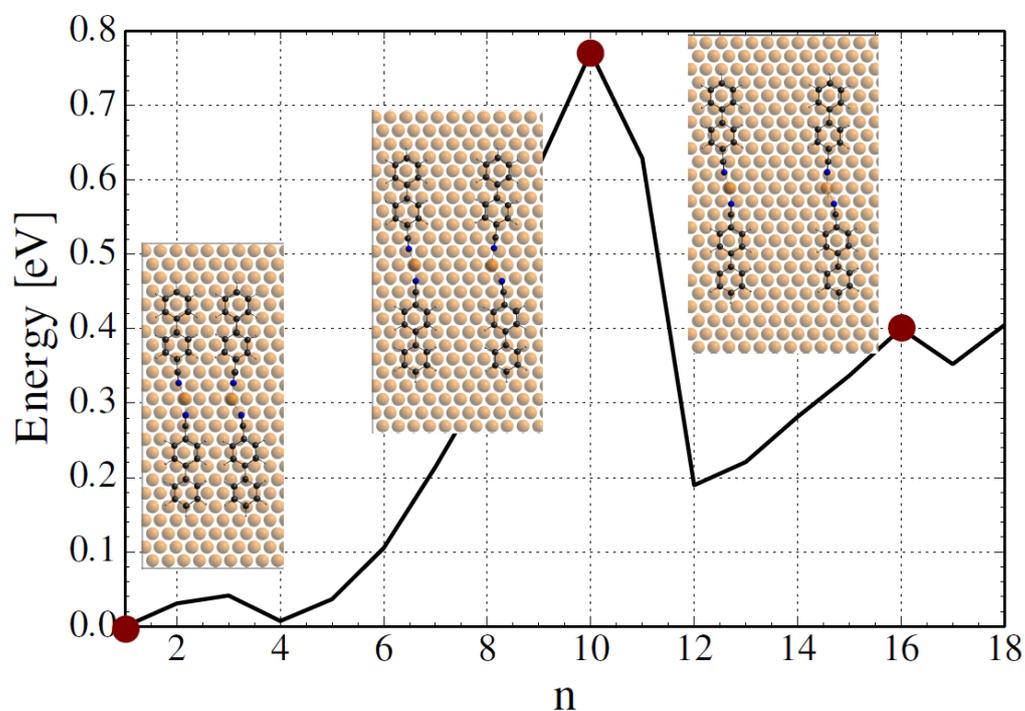


Figure S2. Calculated energy of dimer pairs. Energy of a dimer pair for 18 different distances between dimers. Three atomic configurations are shown corresponding to three positions marked by red circles. From this energy profile, it follows that single dimers are bound in pairs at low temperature.

(3) Overview STM images

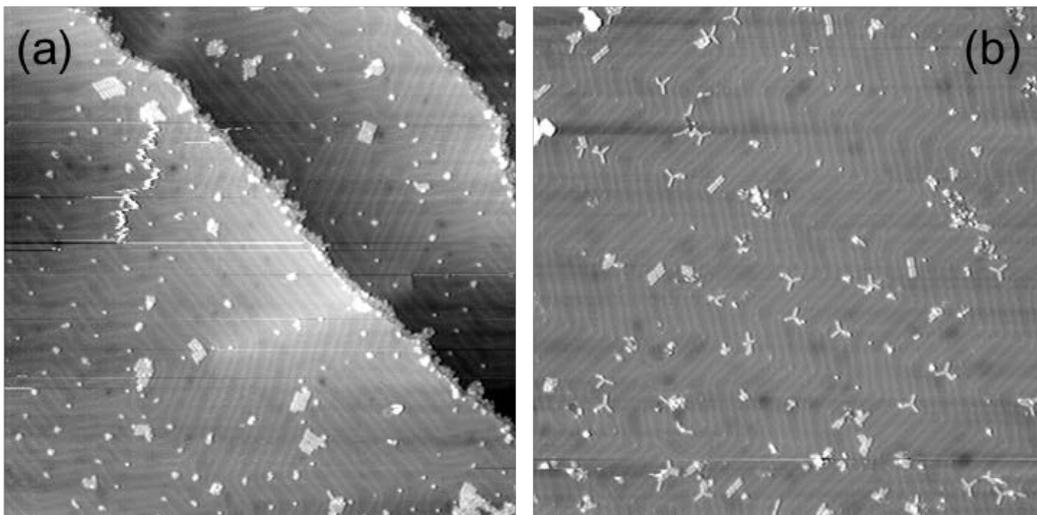


Figure S3. Overview STM images. STM images of the self-assembled structures formed at low coverage at a surface temperature of (a) 20° C and (b) 80° C. Image parameters: $V=0.1$ V, $I=0.2$ nA, images size 160×160 nm. As one can see, after the preparation at room temperature mainly dimer islands are visible on the surface (a), while after the preparation at 80°C, trimer structures dominate (b). Defects can be identified at step edges and at the elbows of the herringbone reconstruction.

(4) Structure models of trimer and dimer-pair

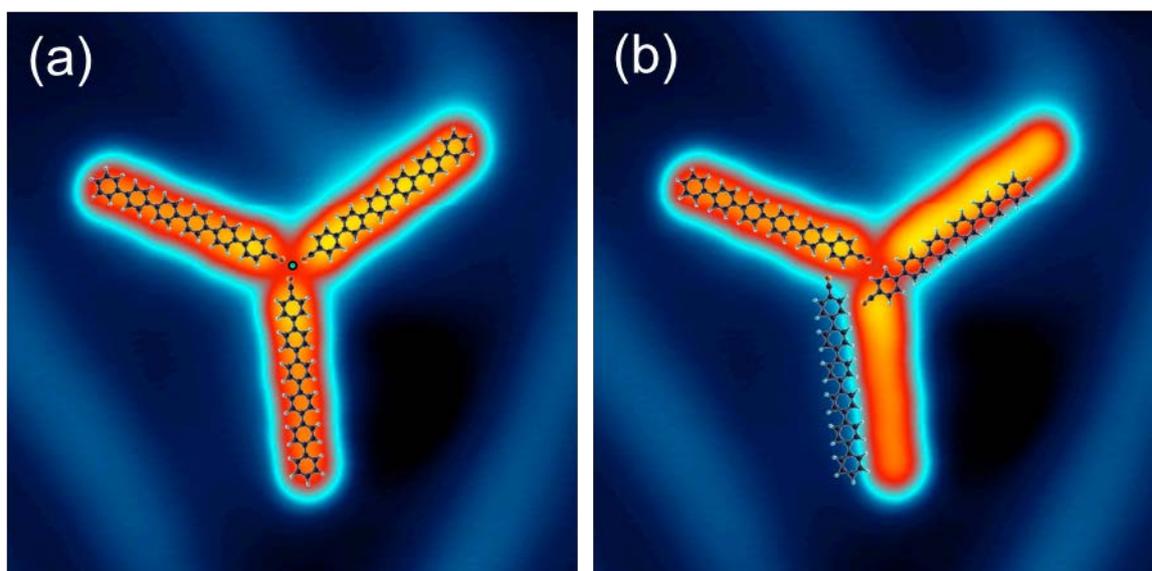


Figure S4. Possible structure models of a trimer cyanosexiiphenyl nanostructure. (a) Surface coordination structure (CN-Au-NC), (b) CN-NC dipolar bond structure based on ref. 3a. Both models are superposed to a STM image of a trimer nanostructure on Au(111). Image parameters: $V = -0.5$ V, $I = 0.2$ nA, image size 7.5×7.5 nm². As one can see, the surface coordination structure fits nicely with the experimental STM image, while a dipolar bond based structure is not compatible with the observed molecular arrangement. Based on the model in (a), we estimate a CN-Au bond length of about 2 Å.

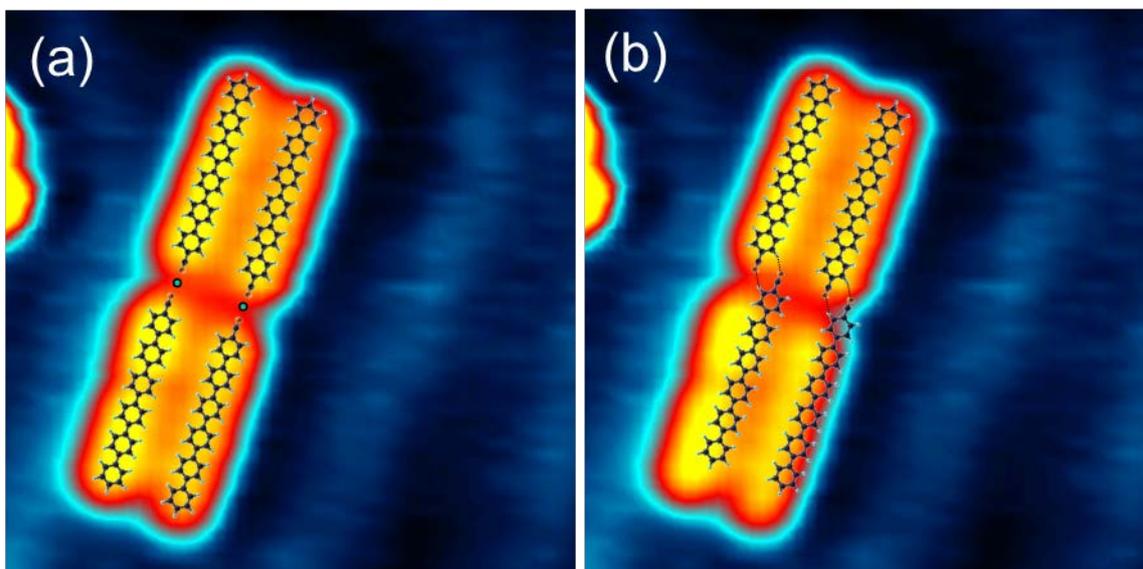


Figure S5. Possible structural models of a dimer pair of cyanosexiphenyl molecules. (a) Surface coordination structure (CN-Au-NC), (b) CN-NC dipolar bond structure based on ref. 3a . Both models are superposed to a STM image of a dimer pair on Au(111). Image parameters: $V = 0.5$ V, $I = 0.2$ nA, image size 7.5×7.5 nm². As one can see, the surface coordination structure nicely fits with the experimental STM image, while a dipolar bond based structure is not compatible with the observed molecular arrangement. Based on the model in (a), we estimate for the dimers a bond length of about 2 Å.