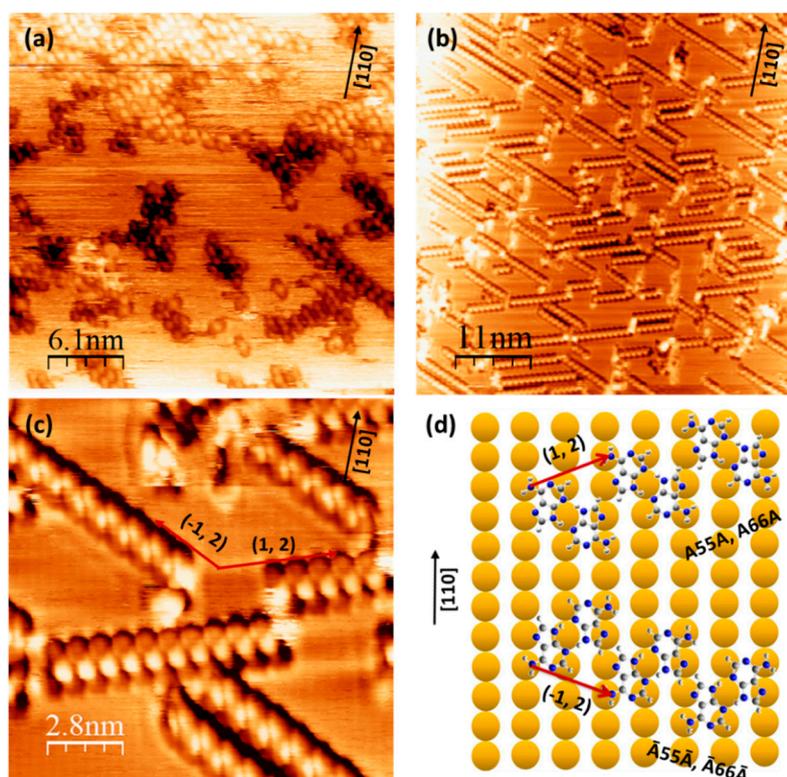


## Supplementary Materials: Role of Hydrogen Bonding in the Formation of Adenine Chains on Cu(110) Surfaces

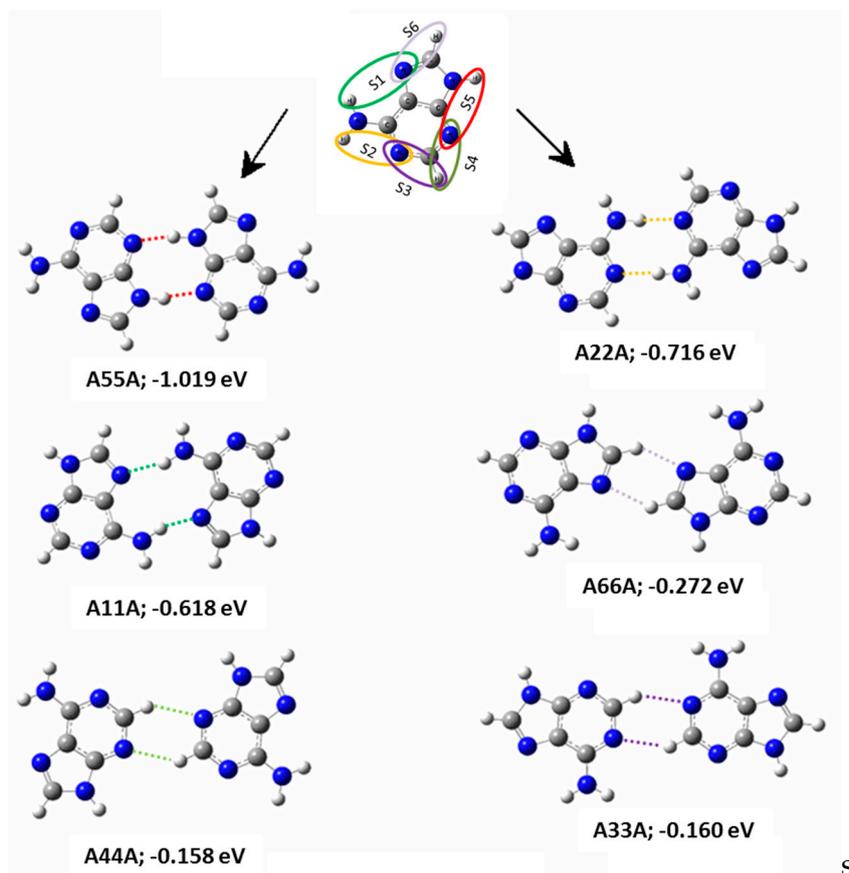
Lanxia Cheng

When deposition is performed at a deposition rate of  $\sim 0.041$  ML/min and at room temperature, adenine molecules aggregate into small islands and short molecular arrays on the copper terraces, as shown in Figure S1a. Figure S1b,c show ordered adenine dimer chains aligning along the  $(\pm 1, 2)$  directions, obtained after annealing to 490 K, in agreement with that reported by Qiao et al. [1] and Zhang et al. [2]. A model of these chains is proposed in Figure S1d.



**Figure S1.** STM images of adenine adsorbed on Cu(110) surfaces showing the evolution of the superstructures as a function of the annealing temperature. (a) Room temperature (0.314 nA,  $-1.2$  V,  $30 \times 30$  nm<sup>2</sup>); (b,c) annealing to 490 K (0.51 nA,  $-1.15$  V,  $55 \times 55$  nm<sup>2</sup> and  $14 \times 14$  nm<sup>2</sup>); (d) Proposed model of adenine chiral chains adsorbed in the registry on the Cu(110) substrate.  $\bar{A}$  indicates an enantiomer of A, obtained by reflecting A on a mirror plane normal to the page.

Figure S2 shows the six binding sites for adenine and the possible centro-symmetric dimers discussed in the text, with respective dimerization energies,  $\Delta E_{dim}$ .



**Figure S2.** (Top) Adenine molecular configuration labeled with the six sites that can participate in the formation of hydrogen bonding between adenine molecules to form dimers; (Bottom) Six centrosymmetric adenine pairs and the corresponding stabilization energies are given. Proposed adenine gas-phase dimers were geometrically optimized using the Gaussian-03 software package [3] with the 6-31G basis set using the hybrid density functional theory (DFT) with the non-local Becke's three parameter functional (B3LYP) [4,5].

Table S1 reports stabilization energy per molecule of the adenine  $n$ -mer species calculated.  $\Delta E_{n\text{-mer}}$  are calculated as:

$$\Delta E_{n\text{-mer}} = \frac{1}{n} (E_{n\text{-mer,relaxed}} - n \times E_{\text{adenine,relaxed}})$$

where  $n$  is the number of molecules considered,  $E_{n\text{-mer,relaxed}}$  is the energy of the relaxed  $n$ -mer, and  $E_{\text{adenine,relaxed}}$  is the energy of a relaxed adenine molecule.

**Table S1.** Stabilization energy per molecule of adenine  $n$ -mer species.

| $n$ -mer | $E_{n\text{-mer,relaxed}}$ /Hartree | $\Delta E_{n\text{-mer}}$ /eV | $\Delta E_{n\text{-mer}}$ per Molecule/eV |
|----------|-------------------------------------|-------------------------------|---|
| A        | -467.15988800                       | -                             | -   |
| A55A     | -934.35722133                       | -1.0189                       | <b>-0.5094</b>                            |
| A22A     | -934.34608626                       | -0.7159                       | -0.3579                                   |
| A11A     | -934.34249141                       | -0.6181                       | -0.3090                                   |
| A66A     | -934.32976414                       | -0.2718                       | -0.1359                                   |
| A44A     | -934.32557915                       | -0.1579                       | -0.0789                                   |
| A33A     | -934.32567288                       | -0.1605                       | -0.0802                                   |
| A15A     | -934.34974199                       | -0.8154                       | -0.4077                                   |
| A55A15A  | -1401.54879459                      | -1.8812                       | <b>-0.6270</b>                            |
| A55A11A  | -1401.54115235                      | -1.6732                       | -0.5577                                   |

## References

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