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# One-dimensional chains of dye molecules on ultrathin insulating films

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R. Bretel *et al*, Phys. Rev. B **108**, 125423 (2023)

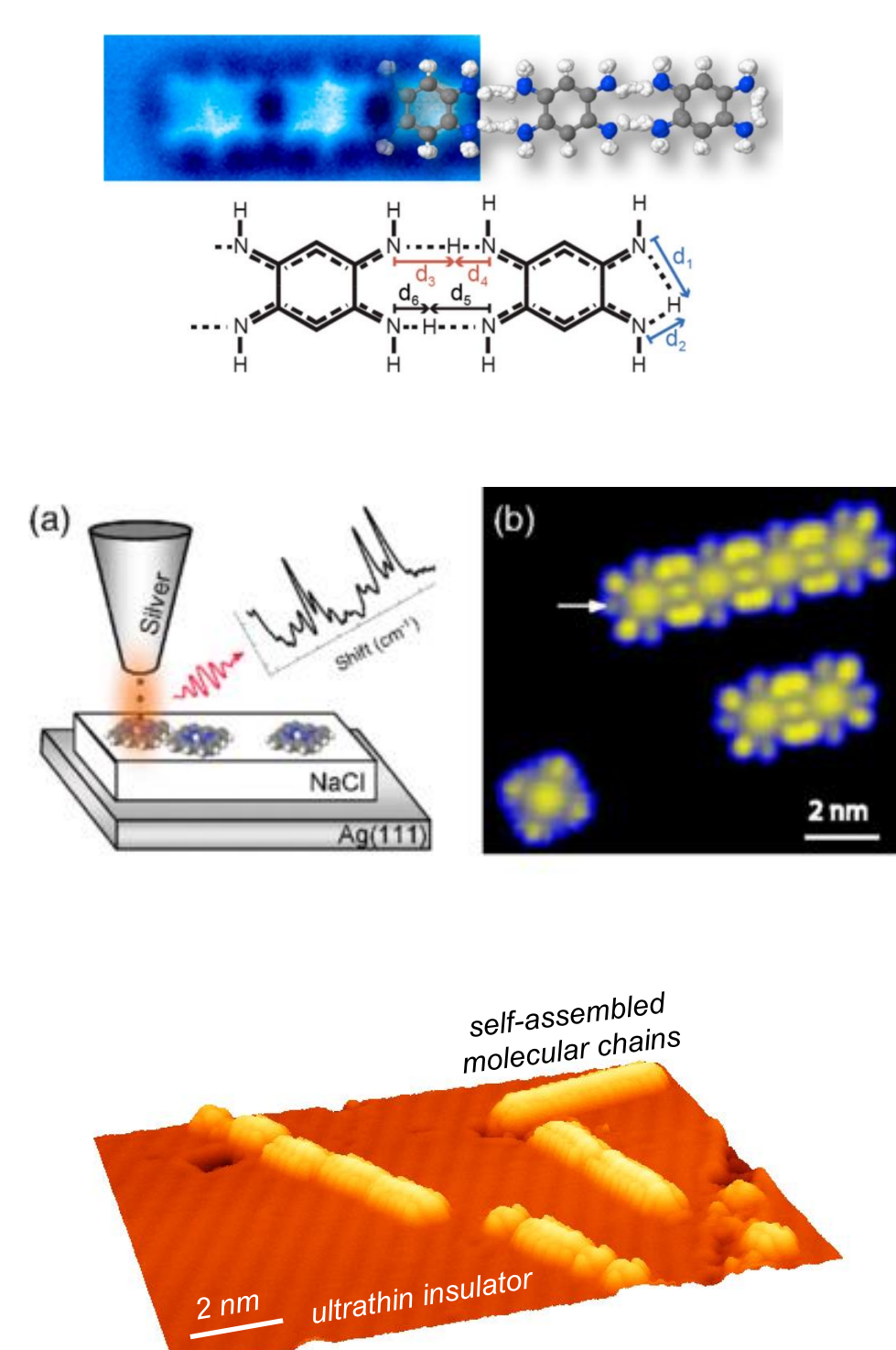
## 1. Motivations:

Linear chains of hydrogen-bonded organic molecules on insulating thin films may become essential for the study of electronic and excitonic effects in quantum-confined molecular systems using scanning tunneling microscopy (STM) [1].

Until now, such linear chains on thin insulators have only been obtained by assembling molecules one by one using the STM tip [2], which strongly limits the field of possible investigations and hampers the potential applications in device technology.

Here, we demonstrate the spontaneous growth of these linear chains via molecular self-assembly on insulating thin films (1 to 3 atomic layer thick) [3].

- [1] Cahlik *et al*, ACS Nano 15, 10357 (2021)
- [2] Doppagne *et al*, Phys. Rev. Lett. 118, 127401 (2017)
- [3] Bretel *et al*, Phys. Rev. B 108, 125423 (2023)



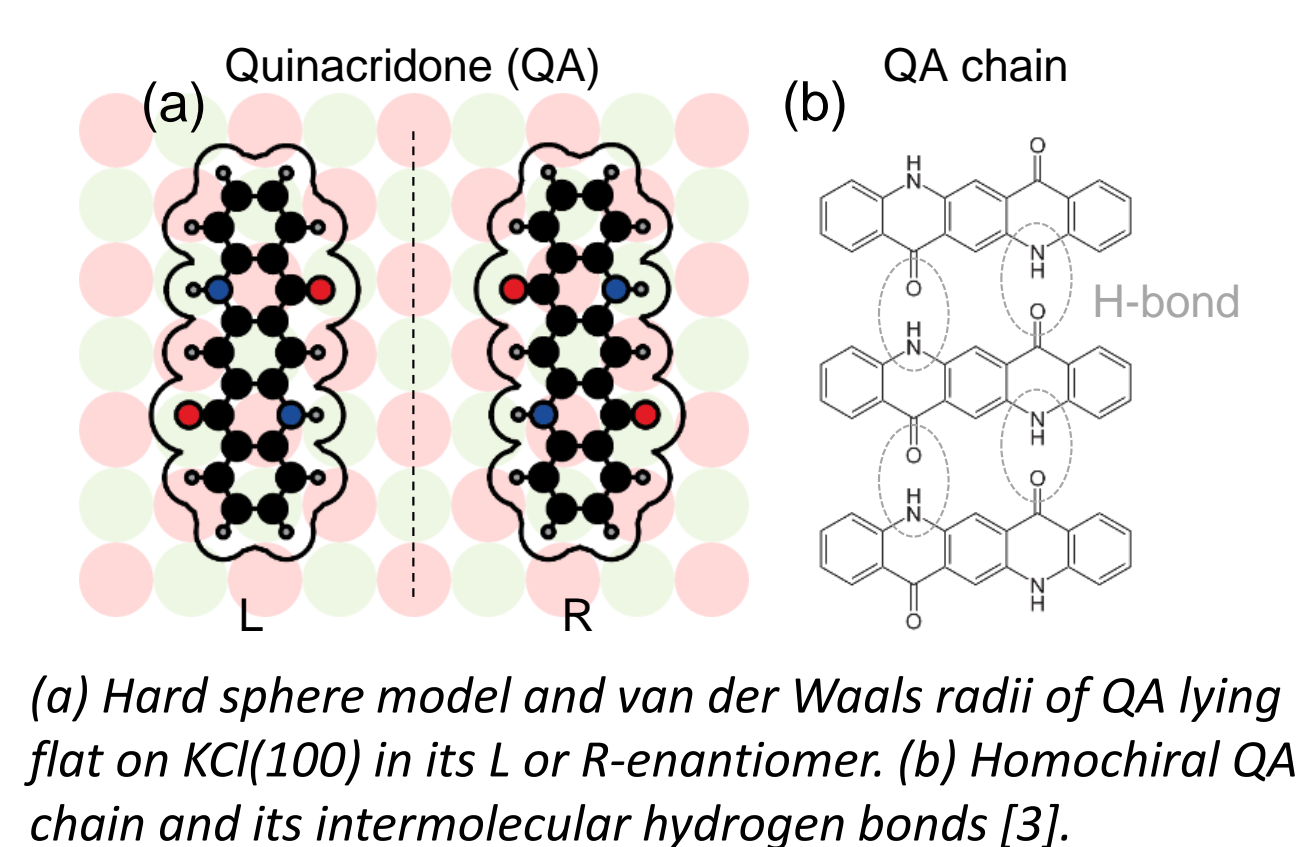
## 2. Strategy / Methods:

This growth is particularly difficult due to the generally weak interactions between the adsorbed molecules and the insulating surface. We overcome this difficulty by using a prochiral molecule (quinacridone, QA) and an ionic insulator (potassium chloride, KCl).

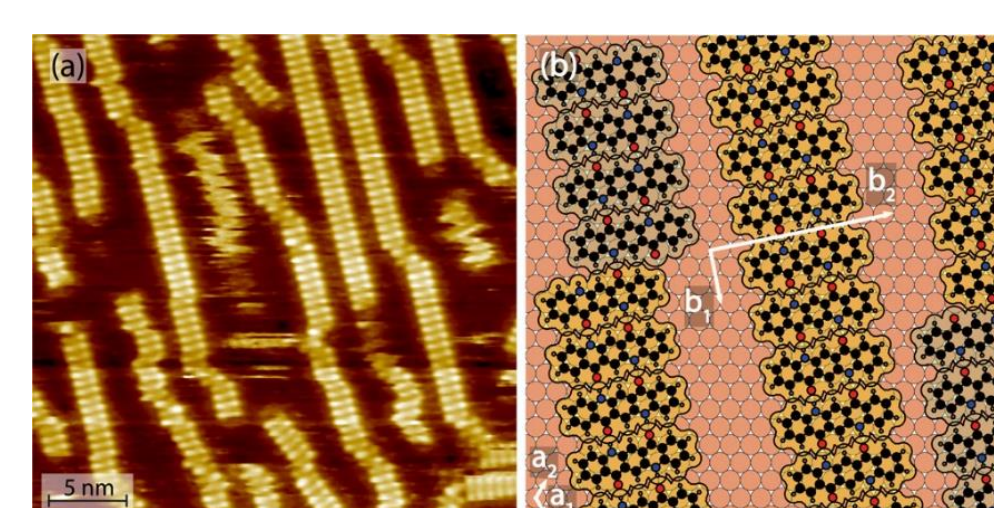
QA has been shown to self-assemble into homochiral hydrogen-bonded chains on metals [4]. Here, we take advantage of the electrostatic interactions between the (partially charged) functional groups of QA and the ions of the KCl layer to stabilize the molecular chains.

QA/KCl/Cu(111) is both of fundamental and technological interest. QA is a unique model system for the study of current driven optical transitions at the sub-molecular scale [5]. QA is actively considered for future organic-based (opto)electronic devices. Alkali-halide thin films are increasingly used as buffer layers at the electrode/semiconductor interfaces to enhance the performance of such devices [6,7].

Using low-temperature STM in ultrahigh vacuum, we determine the molecular arrangement of these chains and their relation of epitaxy with the substrate.



(a) Hard sphere model and van der Waals radii of QA lying flat on KCl(100) in its L or R-enantiomer. (b) Homochiral QA chain and its intermolecular hydrogen bonds [3].



(a) STM image of submonolayer structures of QA on Cu(111) after deposition at 300 K and (b) corresponding structure model [4].

- [4] Humberg *et al*, J. Phys. Chem. C 124, 24861 (2020)
- [5] Jiang *et al*, Phys. Rev. Lett. 130, 126202 (2023)
- [6] Wang *et al*, J. Mater. Chem. C 4, 9918 (2016)
- [7] Wang *et al*, Adv. Mater. 26, 925 (2014)

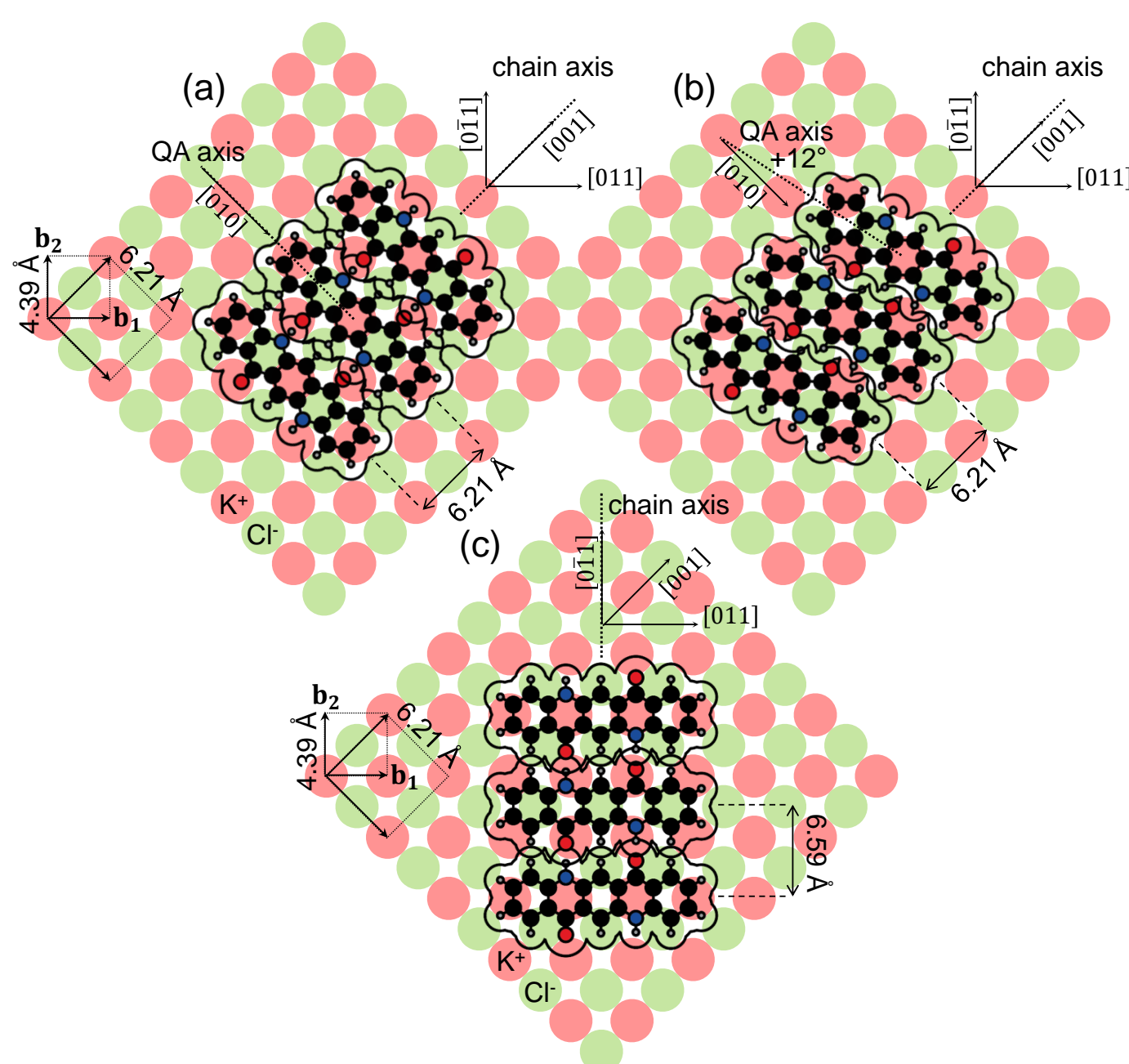
## 4. Discussion:

The commensurate growth of QA chains along KCl <100> directions is hindered by QA-QA intermolecular interactions, either due to too short hydrogen bonds or excessive overlapping of neighboring molecules.

The growth of QA chains oriented along KCl <110> directions is hindered by QA-KCl electrostatic interactions, possibly because only second-next-neighbour molecules have equivalent adsorption sites.

QA-KCl interactions govern the in-plane orientation of the chain axis relative to KCl directions and the in-plane orientation of the QA long axis with respect to the chain axis, whereas QA-QA interactions determine the intermolecular distance.

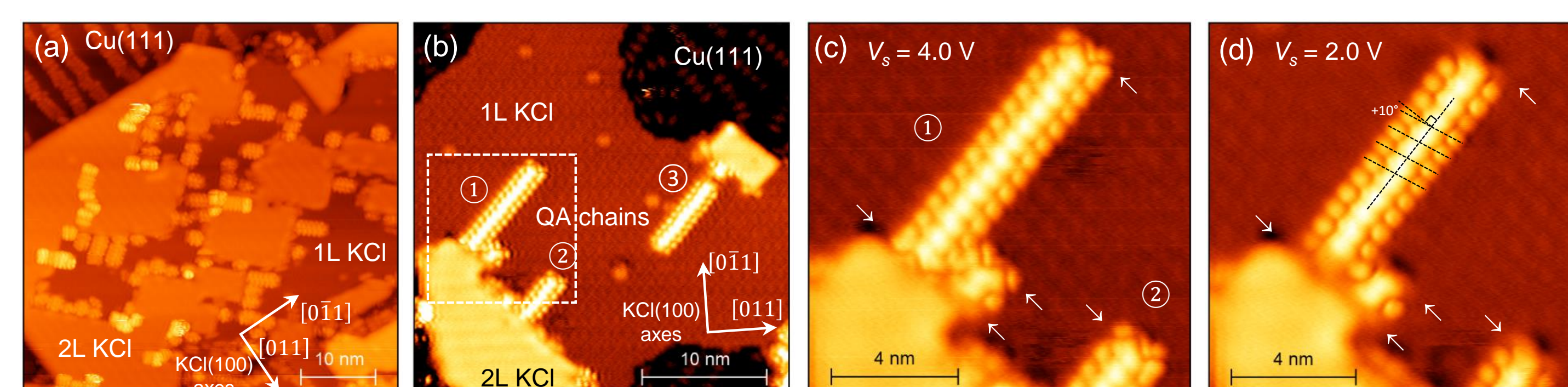
Hypothetical (not experimentally observed) adsorption models for QA chains on KCl(100), where (a,b) the chain axis is oriented parallel to a KCl <100> direction and the intermolecular distance is commensurate with KCl lattice parameter (all molecules have identical adsorption sites) and (c) the chain axis is oriented parallel to a KCl <110> direction. In (a), QA long axis is orthogonal to the chain axis (shortest hydrogen bonds). In (b), the carbonyl oxygen is equidistant from the closest hydrogen atoms of the neighboring molecule (longest hydrogen bonds, but stronger spatial overlapping of neighboring molecules). In (c), the intermolecular distance is chosen such that all second-nearest-neighbour molecules have identical adsorption sites (higher-order commensurability).



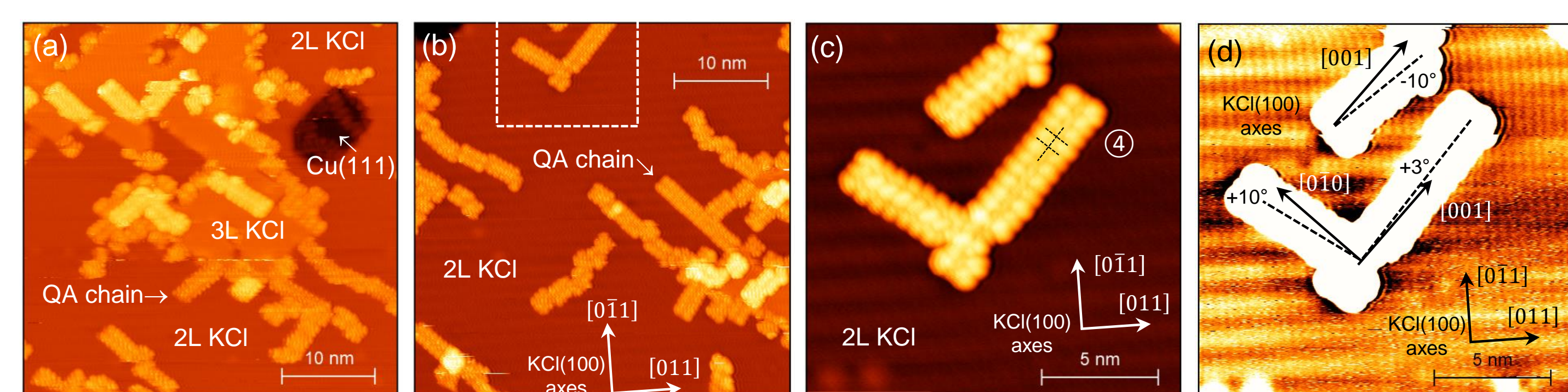
## 3. Results and models:

We observe straight homochiral 1D chains of QA molecules on one (1L), two (2L), and three (3L) atomic layer thick (100)-terminated KCl islands. QA chains can nucleate at step edges or on top of KCl terraces without assistance of step edges. In both cases, the longest straight QA chains observed grow along the KCl <100> directions or slightly rotated (typically less than 10°) from them.

Intermolecular distances ranging from 6.4   to 6.8   are measured for QA chains on KCl/Cu(111), which is compatible with hydrogen bonds between neighboring flat-lying QA molecules. These intermolecular distances being larger than the measured KCl lattice parameter (i.e., 6.21   at 78 K), QA chain growth on KCl/Cu(111) is incommensurate.



STM topography images of QA on 1L and 2L-thick KCl on Cu(111). (a-c) 4.0 V, 4 pA; (d) 2.0 V, 4 pA. (c,d) show QA chains on 1L-thick KCl. The white arrows help visualize the position of the molecules. (e) DFT calculations of the frontier orbitals of the neutral molecule and corresponding maps of their partial density of states at constant height. (f,g) Models for the molecular arrangement of the QA chains on 1L-thick KCl: (f) chains 1 and 2, (g) chain 3.



STM topography images of QA on 2L and 3L-thick KCl on Cu(111). (a,b) 4.6 V, 2 pA; (c,d) 4.0 V, 4 pA. (c,d) show QA chains on 2L-thick KCl. (e,f) Models for the molecular arrangement of the QA chains on 2L-thick KCl: two possible models for chain 4. In (d), the vertical scale is saturated in order to highlight the moir  pattern and the atomic resolution on KCl.

## 5. Conclusions:

The long-sought goal of growing linear chains of hydrogen-bonded organic molecules on thin insulating films via molecular self-assembly has been achieved. QA molecules vacuum-deposited on ultrathin KCl films spontaneously arrange into straight homochiral 1D chains. Irrespective of the in-plane orientation of the KCl islands relative to the underlying Cu(111) substrate, the longest straight QA chains observed are oriented with the chain axis parallel to or rotated less than 10° from the closest KCl <100> direction. We have highlighted the effects of molecule-substrate and molecule-molecule interactions on the in-plane orientation of the molecular chains with respect to the substrate, on the relative orientation of the molecules, and on the intermolecular distance within the chains.

Overall, our results introduce QA/KCl/Cu(111) as a self-assembled nanoscale model system of pi-conjugated molecules on thin insulating layers, for the study of emergent physics in nanophotonics, nanoelectronics and excitonics. Such investigations could be carried out on the nanometer scale using tip-enhanced Raman scattering (TERS) and photoluminescence (TEPL) and STM-induced luminescence (STML) spectroscopy and microscopy.

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