C_{60} Molecular Chains on α-sexithiophene Nanostripes

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Abstract

We demonstrate the formation of highly ordered C_{60} molecular wire arrays with 2.31 nm inter-wire spacing by manipulating the intermixed phase of C_{60} and α-sexithiophene on Ag(111) surface. Our *in-situ* LT-STM results show that the delicate balance between molecule-molecule and molecule-substrate interactions facilitates the assembly of C_{60} into well-ordered molecular wire arrays. Due to the large inter-wire spacing and unique molecular structure, the C_{60} wire arrays could have useful electron transport properties or be used for 2D or 1D quantum confinement of surface electronic states.

Objective

Well-ordered two-dimensional molecular nanostructure arrays have potential uses in molecular electronics, solid-state quantum computation and biosensors. One of the challenging tasks is to effectively engineer the functional molecules into well-ordered nanostructure arrays. Surface nanotemplate-assisted molecular assembly represents a versatile approach towards the design of molecular architectures with high periodicity.

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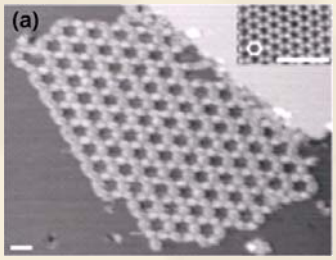
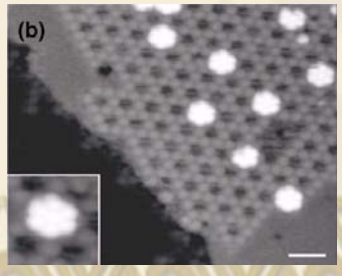
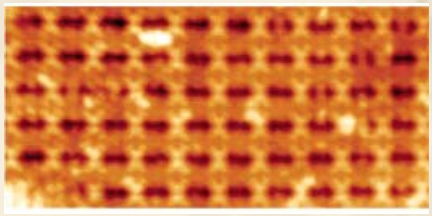


PTCDI–melamine honeycomb network



Fullerene fit in the honeycomb network



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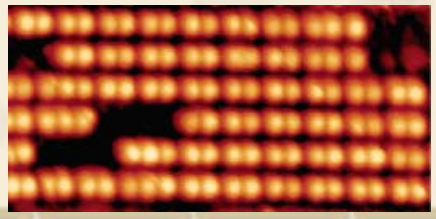
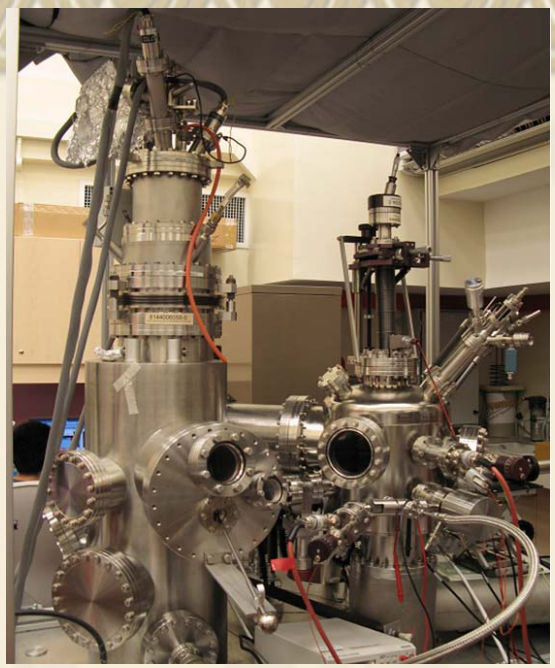
$SrTiO_3$(001)-(6x8) "waffle" surface



Fullerene molecules fit in the "waffle" sites

- ✓ Well-ordered 2D template
- ✓ Dominant molecule-substrate interaction

Experiment



Low-temperature STM system

Experiments were carried out in a home-built multichamber ultra-high vacuum system housed an Omicron low-temperature scanning tunneling microscope (LT-STM) with a pressure better than 6 ×10^{-11}mbar. The STM was imaged with a chemically etched tungsten tip at 77 K. Ag(111) was cleaned by repeated Ar^+ sputtering and annealing cycles. The 6T and C_{60} were thermally evaporated from Knudsen cells in the growth chamber with a deposition rate of 0.1 ML/min and 0.05 ML/min respectively.

Results and Discussion

➢ Formation of monolayer 6T nanostripe superstructure on Ag(111)

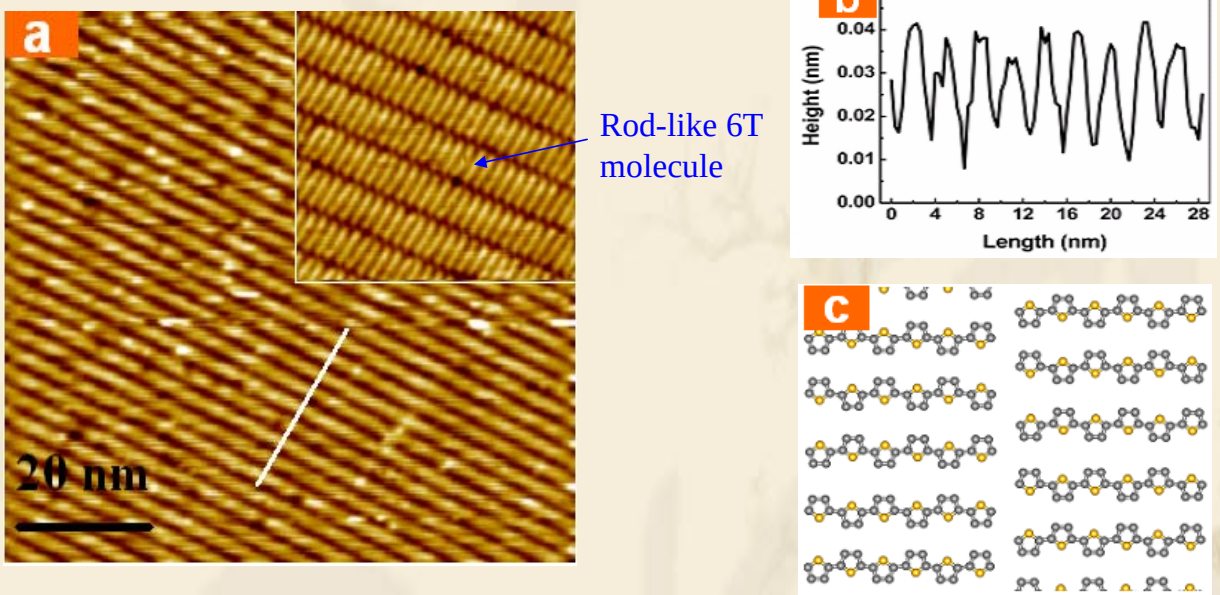


Figure 1. α **-*sexithiophene (6T) nanostripes on Ag (111): a****, *STM image of the long-range ordered 6T nanostripes formed by annealing the Ag(111) covered with 1 ML RT deposited 6T at 400 K. Inset: a high resolution view of molecular structure on 6T nanostripes(I_t=150 pA, V_{tip}=-1.70 V);* ***b****, Cross-sectional profile along the diagonal white line in panel a; and* ***c****, Proposed model for 6T nanostripes on Ag(111).*

- ***A side-by-side packing structure with a periodicity of 0.63 nm (van der Waals distance)***
- ***6T lies flat on Ag(111): π electrons in 6T and metal d-bands interaction***

➢ Warm-like C60 on 6T nanostripes at room temperature

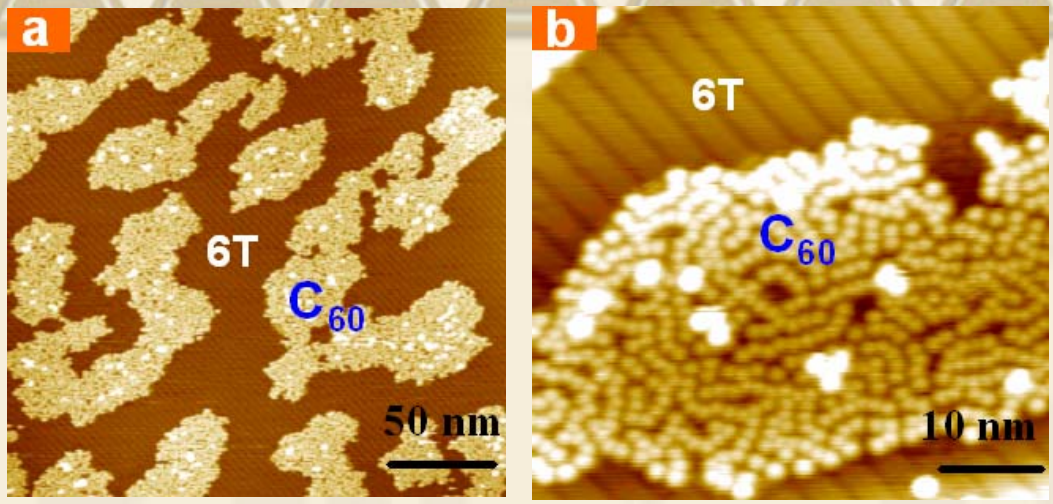
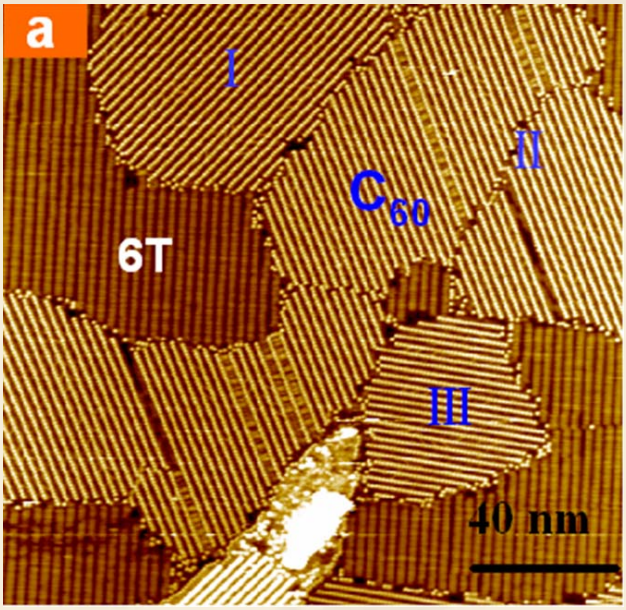
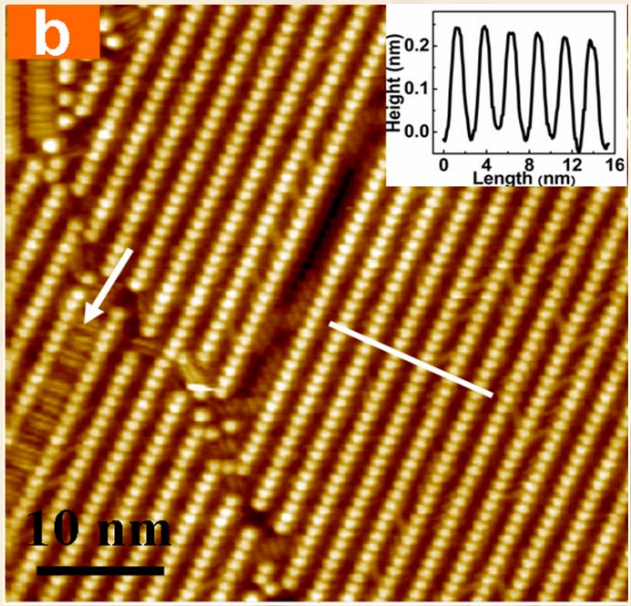


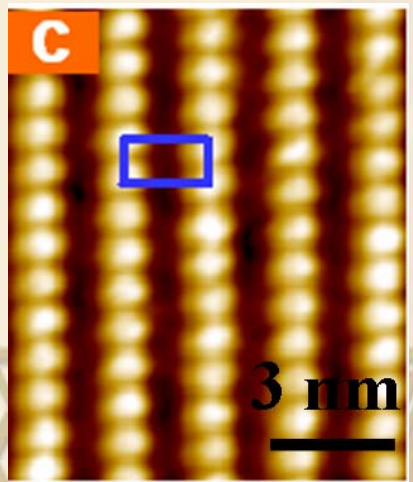
Figure 2 RT deposition of C_{60} on 6T nanostripes: a, *Large-scale image of 0.5ML C_{60} deposited on 6T nanostripes at RT. C_{60} molecules aggregate to form irregular shaped single-layer islands on 6T nanostripes.* ***b,*** *A detailed image indicates C_{60} molecules form disordered worm-like structures.*

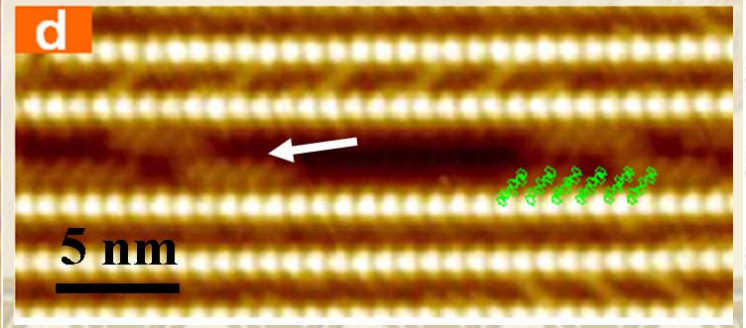
No template effect at room temperature

➢ Self-assembly of C_{60} molecular chain array









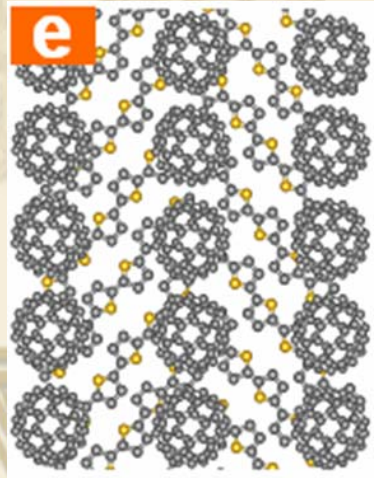


Figure 3. Ordered C_{60} molecular wire arrays. *a, Large-scale STM image of C_{60} molecular chain arrays produced by annealing 6T nanostripes covered with 0.5 ML C_{60} at 380K; Three domains are highlighted as I , II and III; b, Corresponding detailed image of C60 molecular chain arrays; Inset: cross-sectional profile along the diagonal white line. The inter-chain distance is 2.31 nm; c, A high resolution image of C_{60} molecular chain arrays. The C_{60}-C_{60} periodicity along the chain is 1.00 nm; d, A higher resolution image showing a C_{60} molecular chain vacancy in the middle; and e, Proposed molecular packing model for C_{60} molecular chain arrays on 6T nanostripes. (Imaging parameters: I_t=85 pA, V_{tip}=-1.90 V)*

Driving forcing:

Delicate balance between *molecule-molecule* and *molecule-substrate* interactions

Molecule-Molecule interactions

- **C_{60}-6T heteromolecular interaction**

  Charge transfer *(C_{60} acceptor and 6T donor)*
- **C_{60}-C_{60}, 6T-6T intermolecular interaction**

  Van der Waals interaction

Ag(111)-Molecule interactions

- **C_{60}-Ag interaction**

  Charge transfer
- **6T-Ag interaction**

  π electrons and metal d-interaction

Conclusion

In conclusion, we demonstrate the formation of highly ordered C_{60} molecular chain arrays by using α-sexithiophene monolayer nanostripes on Ag(111) as a molecular surface nanotemplate. The formation of ordered C_{60} molecular chain arrays is ascribed to the subtle balance between the molecule-molecule and molecule-substrate interactions. By carefully tuning the molecular ratio of C_{60}:6T as well as the annealing temperature, the inter-chain distance of the C_{60} molecular chain arrays can be adjusted. Controlling the intermixed phase of this binary molecular system can lead to the assembly of ordered functional nanostructure arrays, and offer a versatile route towards the fabrication of novel molecular interconnects and devices. In particular, it could be a possible route towards fullerene based quantum computer.

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