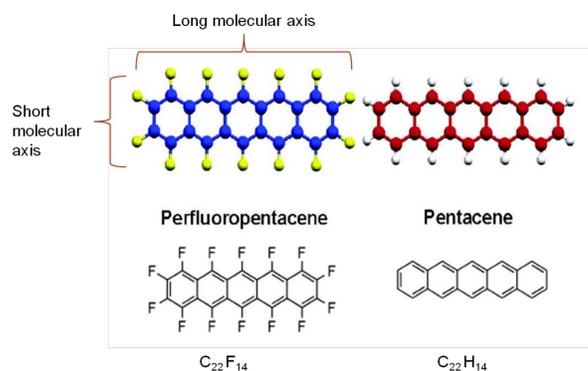


The growth of perfluoropentacene (PFP) and pentacene (PEN) ultrathin films on Ag (111) has been investigated using low temperature scanning tunneling microscopy. To understand the influence that perfluorination of the parent molecule has on its resultant packing structure, the results are compared against each other in the framework of morphological differences. Perfluorination leads to a different packing structure in the first monolayer. We observed only one closely packed arrangement with periodic dislocation lines observed for PFP molecules; while for PEN molecules, there are two co-existing arrangements in the first monolayer. Monolayers of each molecule are commensurate with the underlying substrate with long axes of both molecules aligned in the direction along the silver surface. The disparity in arrangements is attributed to the difference in peripheral atoms of the two molecules. Additional photoemission spectroscopy studies reveal that PFP physisorbs on Ag (111).

## Introduction

Molecular thin films of organic compounds have garnered considerable interest in recent years due to their applicability in low-cost and flexible devices such as organic field-effect transistors, organic photovoltaic cells and organic light emitting diodes.

Among these organic molecules, pentacene (C<sub>22</sub>H<sub>14</sub>) has been widely studied as a p-type semiconductor for OFETs because the pentacene (PEN) thin film transistor has the highest field-effect hole mobility recorded amongst organic materials (in excess of 5 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> on SiO<sub>2</sub>/Si substrates) [1]. Its functionalized n-type counterpart, perfluoropentacene (C<sub>22</sub>F<sub>14</sub>, PFP), which has similar physical dimensions and electron mobility in OFETs of more than 0.2 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> [2] is a suitable candidate for a complementary circuit as it minimizes lattice mismatch with PEN.



**Fig. 1** Diagram of perfluoropentacene and pentacene with their respective chemical formula.

However, the change in atomic make up of the molecule is expected to alter the intermolecular and molecule-substrate interactions and thus the resultant packing structure, which is crucial to its implementation and compatibility in devices. Thus, this study aims to investigate the morphological differences between the two molecular networks on the Ag (111) substrate and also its origin.

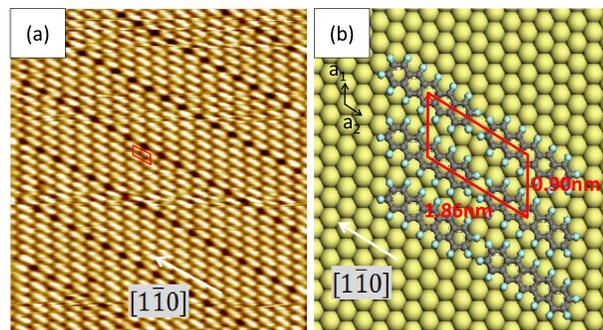
## Methodology

LT-STM experiments were carried out in a custom-built multichamber ultrahigh vacuum system with base pressure lower than  $6.0 \times 10^{-11}$  mbar, housing an Omicron LT-STM. STM imaging was carried out in constant current mode with a chemically etched tungsten tip at 77K.

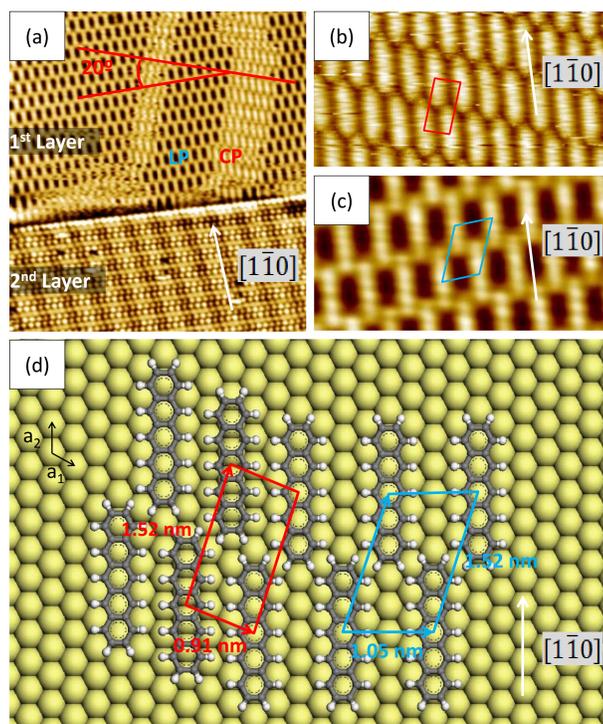
PFP (99.9%, sublimed) [3] and PEN (Sigma-Aldrich, 99.9%, sublimed) are deposited from different Knudsen cells (MBE Komponenten, Germany) at 400K and 420K respectively onto the Ag (111) substrate at room temperature. The deposition rates of PFP and PEN were measured by a quartz crystal microbalance and further calibrated from molecular coverages in the LT-STM images. In our experiments, the deposition rates were kept constant at approximately 0.15 monolayer (ML) min<sup>-1</sup> for PFP and 0.20 ML min<sup>-1</sup> for PEN on Ag (111).

Synchrotron photoemission measurements were carried out at the Surface, Interface and Nanostructure Science (SINS) beam line in the Singapore Synchrotron Light Source (SSLS) with resolution of 0.05 eV.

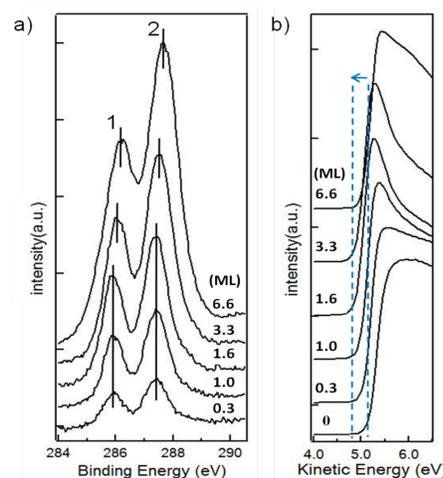
## Results



**Fig. 2** STM image of the 1<sup>st</sup> monolayer (a) of PFP deposited on Ag (111) (30 x 30 nm<sup>2</sup>, V<sub>tip</sub> = -1.80V) (b) Schematic drawing for the proposed molecular packing structure of lying-down PFP on Ag (111) with the unit cell indicated. Lattice vectors of substrate are indicated by vectors **a**<sub>1</sub> and **a**<sub>2</sub>.



**Fig. 3** STM image of (a) 1.4 ML PEN on Ag (111) (35 x 35 nm<sup>2</sup>, V<sub>tip</sub> = -1.44 V). CP and LP indicate the areas of closely and loosely packed arrangement respectively. (b) STM image of corresponding detailed 5 x 10 nm<sup>2</sup> image of the CP structure (V<sub>tip</sub> = 1.81 V) and (c) 5 x 10 nm<sup>2</sup> image of the LP structure (V<sub>tip</sub> = -1.50 V). (d) Schematic drawing for the proposed molecular packing structure of lying-down PEN on Ag (111) with the unit cell indicated (blue for CP arrangement and red for LP arrangement). Lattice vectors of substrate are also indicated by vectors **a**<sub>1</sub> and **a**<sub>2</sub>.



**Fig. 4** a) Spectra of C1s electron binding energy levels of increasing thickness of PFP deposited at room temperature on Ag (111). b) Spectra at photoemission secondary electron cutoff with a -5.0V bias applied of increasing thickness of PFP deposited on Ag (111) at room temperature. Nominal thicknesses for each spectrum are labeled at the side.

## Discussion

### Similarities between the molecular networks in the first monolayer

- Flat lying molecules for maximum exposure of their extended conjugated  $\pi$  plane of electrons to the substrate surface.
- Commensurate molecular superlattices, indicating substantial molecule-substrate interaction.

### Differences between the first monolayer molecular networks

PFP	PEN
Only one type of arrangement (Close packed).	Presence of coexisting dual phases (Close packed and Loosely packed).
Commensurate matrix: $\begin{bmatrix} 6 & 0 \\ 0 & 3 \end{bmatrix}$	Commensurate matrix: For CP: $\begin{bmatrix} 4 & 2 \\ 2 & 6 \end{bmatrix}$ For LP: $\begin{bmatrix} 3 & 1/2 \\ 2 & 6 \end{bmatrix}$
Dislocation lines running through network.	Absence of dislocation lines

- Peripheral fluorine atoms being much more electrostatically negative than hydrogen result in greater electrostatic repulsion between PFP molecules than PEN molecules.

- Results in only one stable configuration for PFP as compared to two for PEN.

- Substrate-molecule interactions results in a site-specific adsorption for both PEN and PFP molecules, as evidenced by the commensurability for both molecular superlattices.

- Due to increased intermolecular repulsion present between PFP molecules together with its inherent molecular anisotropy, i.e: PFP having more fluorine molecules at the long molecular edges, there is a significant buildup of stress which is released by the formation of dislocation lines.

- Closely packed network of PEN on Ag (111) does not display dislocation lines due to the reduced electrostatic repulsion between hydrogen atoms.

### Photoelectron Emission Spectroscopy

- No shift in Peak 1 (C bonded to fluorine) and Peak 2 (C not bonded to fluorine), indicating no bond formation (physisorption of molecule to substrate).

- Maximal work function shift of 3 eV at 6.6 ML due to electron pushback effect of PFP on substrate.

## Conclusion

Change in periphery atoms result in marked difference in morphology of thin films and should be noted in hybrid structures, especially at the interface.

## References

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