Comparative Study of the Self-Assembly of Pentacene Derivatives on Gold Surfaces for Photovoltaic Applications

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Abstract

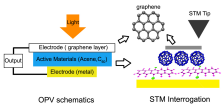
The self-assembly of organic molecules, such as pentacenes, have technological potential for organic photovoltaic (OPV) applications. Pentacene derivatives have been developed that overcome some of the shortcomings of pure pentacene, many of which inhibit the efficiency of its use in electronic devices. Increased solubility, high photo-oxidative resistance, thermal stability, and tailor-able HOMO-LUMO gaps make pentacene derivatives enticing for further study.

Scanning tunneling microscopy and density functional theory was used to examine the atomic interface between gold and the pentacene derivatives: 6,13-dichloropentacene (DCP) and 5,6,7-trithiapentacene -13-one (TTPO), electron donors exhibiting self assembled monolayer (SAM) structures on gold surfaces. This is exemplified by DCP's observed long-range, highly-ordered SAM of a brick-wall pattern along the length of the stepped Au (788) surface. TTPO was observed to form chain-like structures anchored to the surface at low coverage, as well as a more ordered SAM at close to monolayer coverage.

By studying the self assembly of organic molecules on metallic surfaces, we are developing novel pathways toward **molecular control of the organic-metal interface** as a means of addressing efficiency problems at the nanoscale for OPV devices. It is the understanding of the structure of photovoltaic heterojunctions that can allow for **tailoring of interfaces with improved electrical transport and energy-conversion efficiency**.

Molecular Self-Assembly and Organic Photovoltaics

Molecular self-assembly is governed by molecule-molecule and molecule-substrate interactions and allows for efficient production of molecular-scale architectures.



Heterojunctions between small molecules and metal electrodes are important in terms of OPV efficiency.

Small molecule photovoltaics can utilize self-assembly - *vacuum deposited small organic molecule solar cells exhibit 12% efficiency*[1]

Understanding electrical transport across interfaces is necessary to make better devices.

At metal-organic interface, differing band gaps can form a barrier to charge transport affecting efficiency.

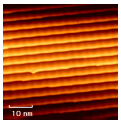
Materials and Methods

Methods:

Organic molecules (powder) are deposited *in-situ* onto surfaces *via* a Physical Vapor Deposition (PVD) process in ultrahigh vacuum (UHV) chamber.

Scanning Tunneling Microscopy (STM) is used to examine structure properties of the bulk heterojunctions at the molecular level at RT.

Density Functional Theory (DFT) is used for theoretical modeling to unravel molecular interaction hierarchies.



Materials:

Single crystal Au (788) substrate

Pentacene derivatives synthesized at UNH by Chemistry group of Professor Glen P. Miller

-TTPO developed in-house[2]

Au (788) – vicinal surface of Au(111) terraces terminated by monatomic steps

-notable Au(111) herringbone surface reconstruction on terraces

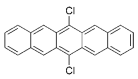
References

[1] Heliatek. Press Release, January 16, 2013. www.heliatek.com

[2] Miller, G.P., Kintigh, J. TTPO (5 6,7-trithiapentacene-13-one) and its derivatives: a new class of thermally stable, photooxidatively resistant organic semiconductors. U.S. Patent 8,389,744 B1, October 11, 2011.

6,13-dichloropentacene (DCP)

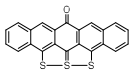
5,6,7-trithiapentacene-13-one (TTPO)

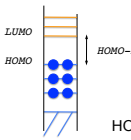


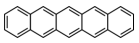
DCP

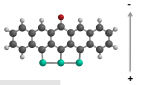
Pentacene Derivatives :
Electron donors
Increased solubility
High photo-oxidative resistance
Thermal stability

TTPO









Differences:
Polar species of pentacene
Melting point ~390°C
Asymmetrical molecule

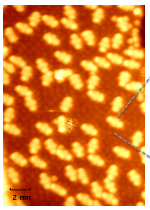
	DCP (bulk)	PENTACENE	TTPO (bulk)
HOMO-LUMO Gap (calc)	2.16 eV	2.21 eV	1.90 eV

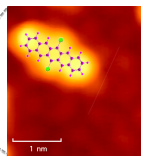
In general, band gap reduction increases absorption efficiency of the solar spectrum in OPV applications

DCP and TTPO can be thermally evaporated or used in low cost methods like blade coating, spin coating, ink-jet printing *--appealing*

Suitable for high-temp electronics >100°C operation

Gold (111)

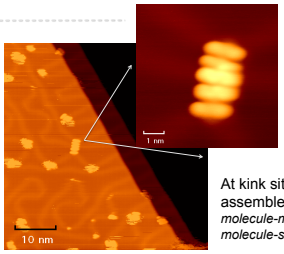




Atomically resolved STM image of dispersed DCP on Au(111)

A high resolution STM image of a single DCP molecule

Individual DCP molecules stable on Au(111) at room temperature



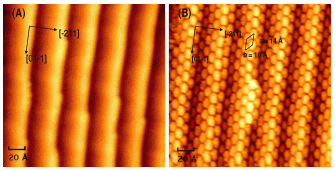
STM image of dispersed TTPO on Au (111), with visible herringbone reconstruction

Highly mobile TTPO forms clusters at energetically-favorable herringbone kink sites

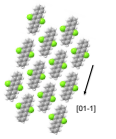
At kink sites TTPO starts to self-assemble
molecule-molecule interaction > molecule-substrate interaction

TTPO is stable as molecule chains on the Au(111) substrate

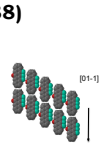
Self-Assembled Monolayers on Vicinal Gold (788)



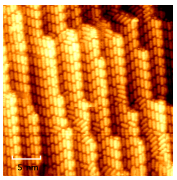
(A) STM image of clean Au(788) surface.
(B) STM image of DCP SAM on the stepped Au(788) surface at RT



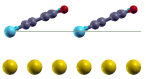
Unit cell: 14 Å X10 Å



Unit cell: 17.1 Å X 7.5 Å, θ = 68°



STM image of TTPO SAM on the stepped Au(788) surface at RT



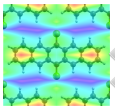
Angle of assembly cannot be determined by STM imaging, DFT will be used to model *angular assembly*

leads to

- **Symmetric brick-wall structure**
- **Flat-lying molecules**
- **5 molecules on 3.9 nm wide terrace**
- **Long range order**
- **Asymmetric offset structure**
- **3-D laterally standing molecules**
- **6 molecules on 3.9 nm wide terrace**
- **Offset structure directions can change between rows**

DFT Modeling and C_{60} Co-deposition

DFT modeling concludes that the observed structure minimizes intermolecular hydrogen-bonding energies while maintaining favorable molecule-step interactions.

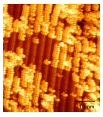


Single C_{60} adsorption energy landscape on DCP SAM

higher energy

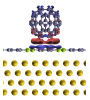
lower energy

Unique C_{60} double chain geometry in STM investigation verified as low-energy minimum for DFT calculations



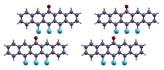
STM image of C_{60} on DCP on Au(788)

Theoretical model C_{60} on DCP on Au (788)



Wang, J., et al., *Highly Ordered Assembly of Single-Domain Dichloropentacene over Large Areas on Vicinal Gold Surfaces*. ACS Nano, 2011. **5**(3): p. 1792-1797.
Wang, J., et al., *Sharp Organic Interface of Molecular C_{60} Chains and a Pentacene Derivative SAM on Au(788): A combined STM & DFT study*. Surface Science, 2013. 618: p.78-82.

Further Work

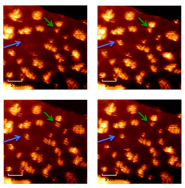


DFT modeling will be used to examine possible angles of assembly as well as the sulfur interaction of the molecule with the Au substrate.

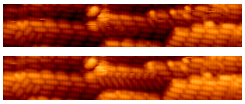
Other areas to address:

- High mobility of TTPO at room temp
- Effect of dipole on assembly
- Molecular switching between self assembled structures

High mobility



TTPO rotation in room-temp STM images



Subsequent STM images where TTPO moves overcoming anticipated gold-sulfur interaction

Conclusions

DCP and TTPO are promising donor layers for use in OPVs due to their robust natures and self assembly on Au(788) which, exemplifying molecular interaction with the surface, can be favorable in terms of charge transport.

Both DCP and TTPO exhibit unique SAMs on Au(788) which are unlike conventional pentacene assemblies

- DCP: Long range, highly ordered, *center-shifted* brick-wall structure
- TTPO: *Laterally-standing* angular assembly of an offset structure

DFT examination of DCP has lead to better understanding of this system, and will be beneficial for understanding the more complex angular assembly of TTPO.

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