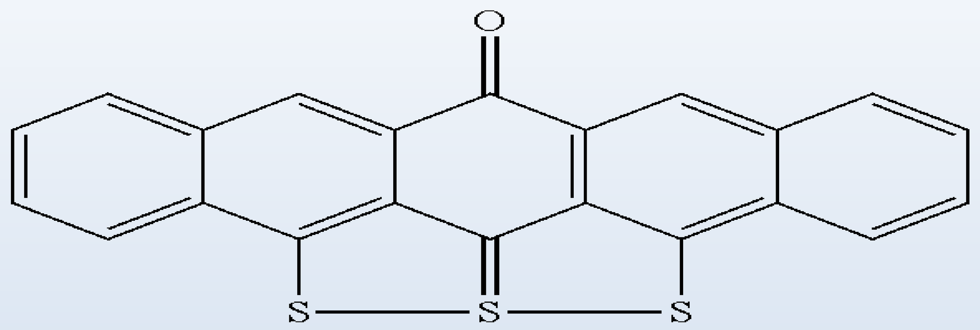
High-Performance Simulations of the Diffusion Characteristics of a Pentacene Derivative on Gold Surfaces



Ryan Miller, Amanda Larson, Karsten Pohl

Department of Physics, University of New Hampshire, Durham, NH

Introduction

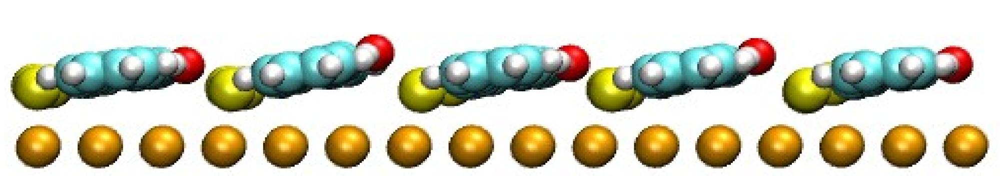
Organic semiconducting molecules show increasing promise for providing a relatively low-cost, easy to manufacture, and tailorable option for applications such as high-temperature photovoltaic devices.

5 6,7-trithiapentacene-13-one (TTPO) is an interesting and unique new semiconducting molecule that possesses attractive qualities for photovoltaic devices, such as thermal stability at temperatures up to 450°C, ease of preparation, solubility in organic solvents, high charge-carrier mobility, and more [1].

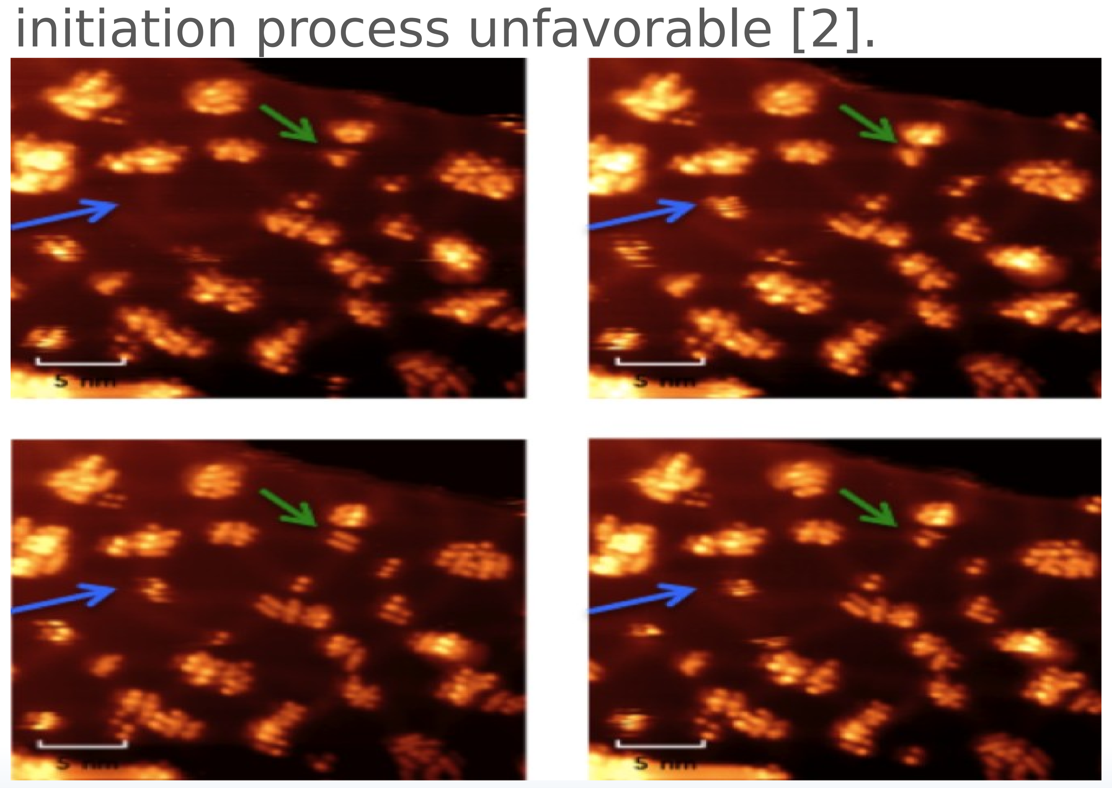
With top-down visualization methods such as scanning-tunneling microscopy (STM) providing limited resolution of atomic behavior, molecular dynamics (MD) simulations are needed to get more detailed profile of molecular traits.

TTPO on Gold Surfaces

TTPO's ground-state angular assembly on close-packed Au(111) is unique from other pentacene derivatives. This allows tight packing of molecules, favorable for molecular chain growth.



TTPO diffuses on flat, pristine Au(111) and Au(788) terraces, making the self-assembly initiation process unfavorable [2].

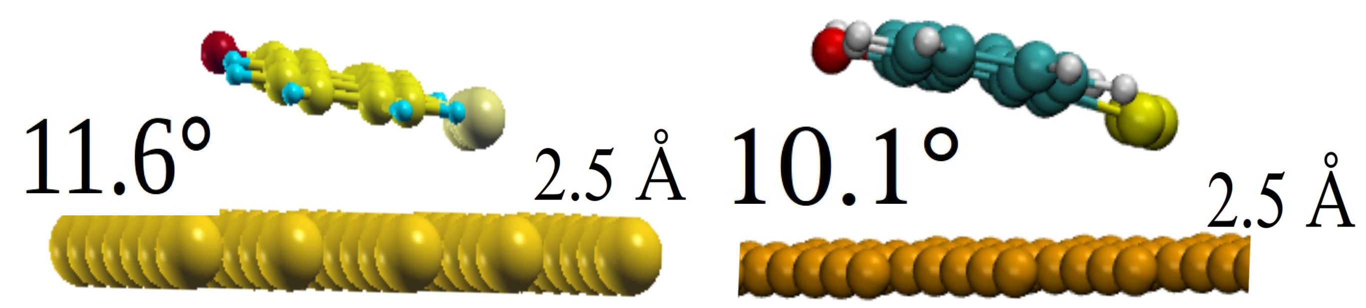


Four consecutive STM images showing the Instability of TTPO molecules that are not in a chain

DFT-Based Calculations in Quantum Espresso (QE)[3]

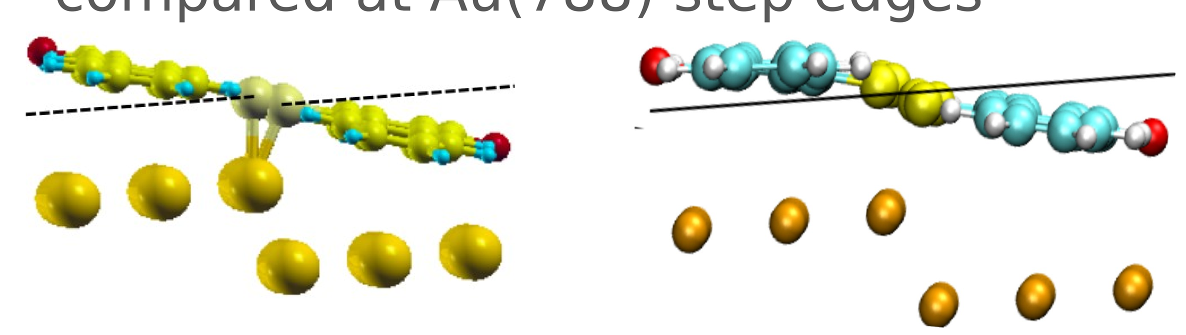
Quantum mechanical MD simulations are most accurate, but expensive computationally.

QE was used as a basis for verification that classical MD simulations were well-parameterized.



DFT-Based Relax *Classical MD*

In addition to close-packed, single layer Au(111) above, DFT results[2] were also compared at Au(788) step edges



QE *Classical*

Classical Simulation in LAMMPS[4]

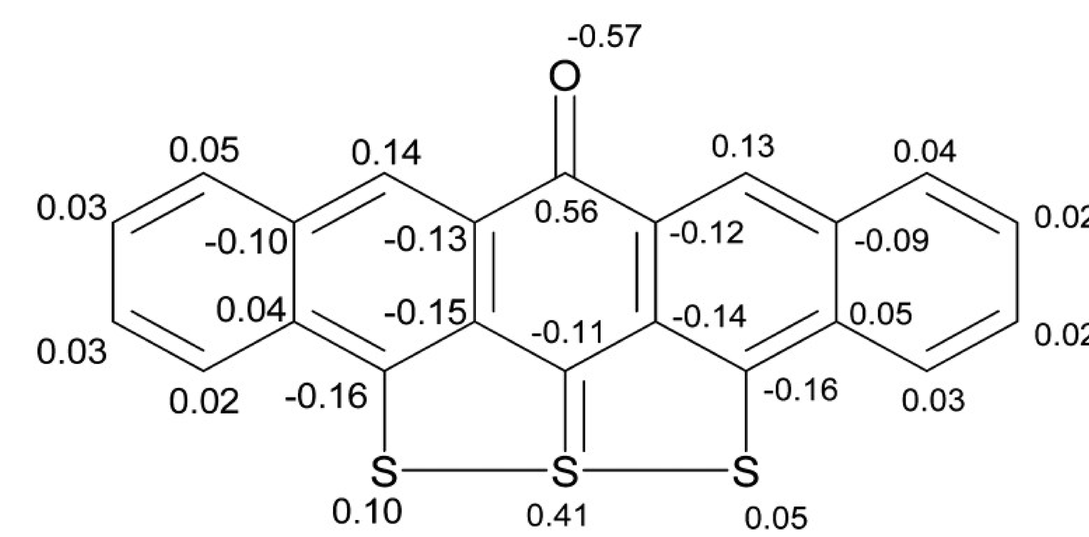
The system evolves according to the Hamiltonian

$$H = \sum_{i,j} U_{ij,int} + \sum_{bonds} \frac{1}{2} K_B(\vec{r} - \vec{r_0})^2 + \sum_{angles} \frac{1}{2} K_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} K_D(1 + d\cos(n\phi)) + \sum_{i,j} 4\epsilon((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6) + \sum_{atoms} \frac{Cq_iq_j}{r_{ij}}$$

All pairwise interactions are Lennard-Jones except gold-gold, which follows the Embedded Atom Model, and gold-sulfur, gold-hydrogen, and gold-carbon, which adhere to a Morse potential:

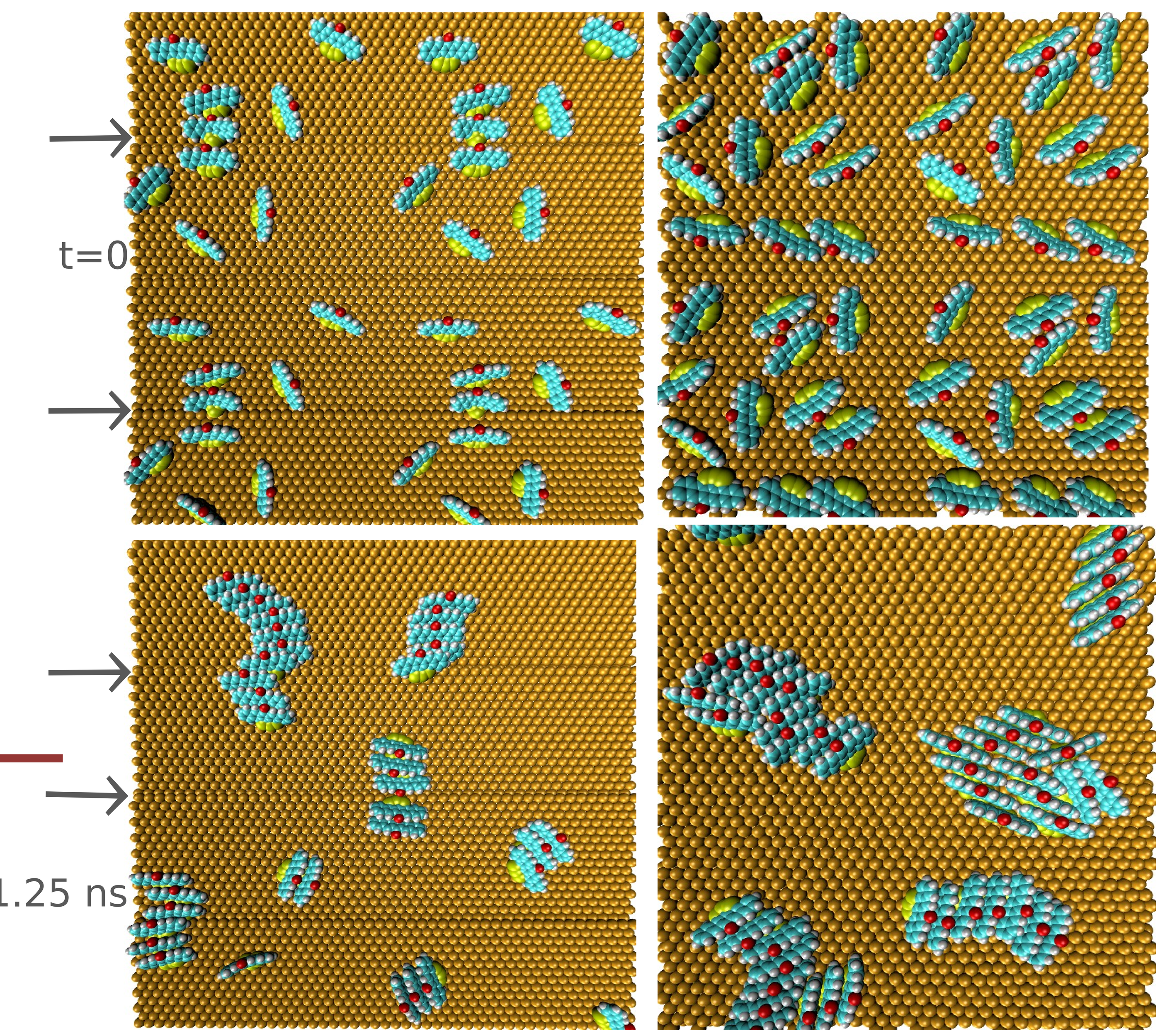
$$E = D_0[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}]$$

The partial charges for the Coulombic potential were assigned based on the DFT NBO population analysis performed in [5].



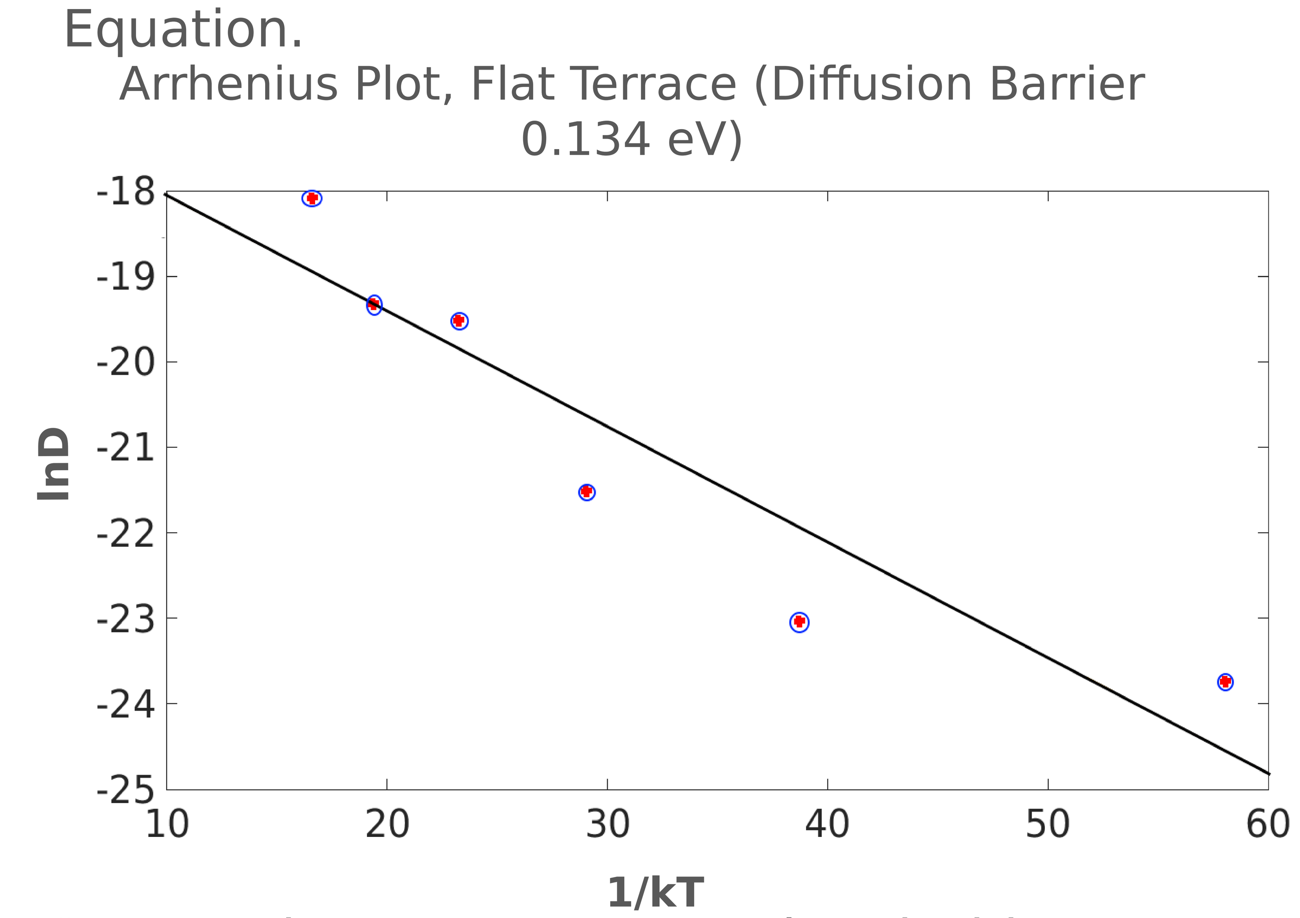
Results

Partially-covered flat Au(111) terraces and Au(788) were thermalized at various temperatures to analyze diffusion properties.

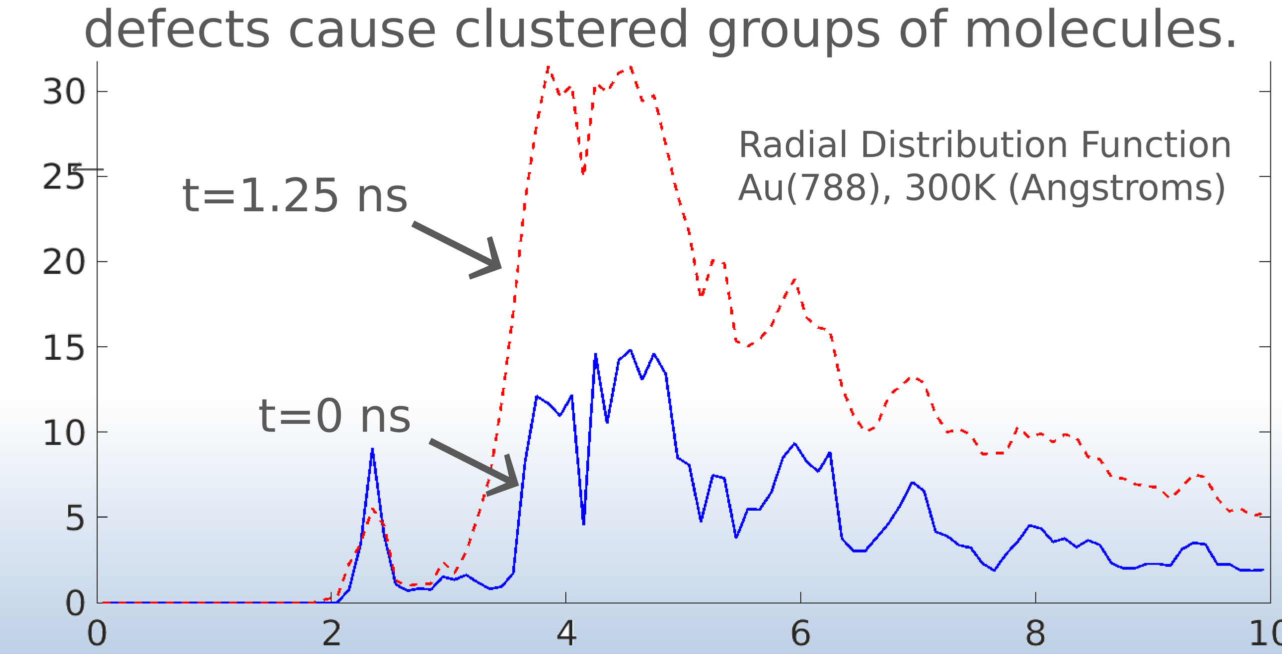


Stepped Surface Flat Terrace

An activation energy for diffusion for TTPO on gold was calculated from the Arrhenius Equation.



Systems become more correlated with or without step defects, but chains are far more stable at step edges, and align in ordered rows, whereas pristine surfaces and point defects cause clustered groups of molecules.



Conclusions

Molecular dynamics simulations in the DFT and classical frameworks were used to model TTPO on Au surfaces.

While molecules become correlated through intermolecular attraction on smooth terraces (forming disorganized and mobile clusters), Au(788) steps offer more stability and organization for molecular chains to form and stay localized.

The energy barrier needed for diffusion on a gold terrace was calculated to be 0.134 eV from analyzing the Arrhenius Plot formed by the diffusion coefficients at various temperatures up to near the thermal breakdown temperature.

References

- [1] Miller, Glen P., and Jeremy Kintigh. *TTPO (5 6,7-trithiapentacene-13-one) and Its Derivatives: A New Class of Thermally Stable, Photooxidatively Resistant Organic Semiconductors*. University of New Hampshire, assignee. Patent 8389744. 11 Oct. 2011. Print.
- [2] Larson, Amanda. *The Directed Molecular Self-Assembly of a Novel Pentacene Derivative on Gold Surfaces: An Experimental and Computational Study.* Dissertation, University of New Hampshire. May, 2015.
- [3] http://www.quantum-espresso.org/
- [4] http://lammps.sandia.gov
- [5] *Jeremy T. Kintigh, Jennifer L. Hodgson, Anup Singh, Chandrani Pramanik, Amanda M. Larson, Lei Zhou, Jonathan B. Briggs, Bruce C. Noll, Erfan Kheirkhahi, Karsten Pohl, Nicol E. McGruer, and Glen P. Miller. A Robust, High-Temperature Organic Semiconductor. The Journal of Physical Chemistry C 2014 118 (46), 26955-26963DOI: 10.1021/jp505011x*