May 18th, 12:00 AM - May 22nd, 12:00 AM

Modeling Adsorption of Molecular Semiconductors on an Ionic Substrate: PTCDA and CuPc on NaCl

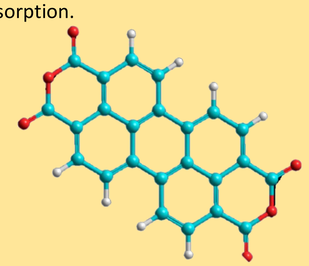
Julia Thorpe
Western Washinton University

Modeling Adsorption of Molecular Semiconductors on an Ionic Substrate: PTCDA and CuPc on NaCl

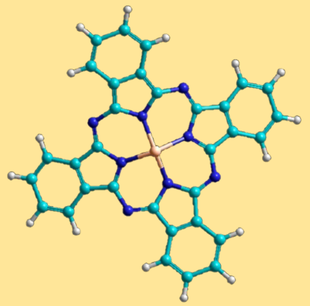
Julia Thorpe, Andreas Riemann
Department of Physics & Astronomy –
Western Washington University, Bellingham, WA.

Abstract

Molecular adsorption can be accurately studied using computational chemistry methods. Experimental results suggest that molecular geometry and energies can be influenced by the presence of thin film substrates as well as surrounding molecules. In our study, Density Functional Theory (DFT) and Molecular Mechanics (MM) are used to model the configurations of the organic semiconducting materials, Perylene Tetracarboxylic Dianhydride, $C_{24}H_8O_6$ (PTCDA), and Copper Phthalocyanine, $C_{34}H_{16}CuN_8$ (CuPc), as adsorbed on single and double layer NaCl substrates of various dimensions and charge settings. After geometry and charge optimization of the molecules using DFT, the molecular geometries are optimized under different environments using computational calculations with specific force field settings in HyperChem software using MM. Energies and geometries of the molecules are then recorded and results are compared to experimental results as detailed in Burke et al, 2018. As we evaluate our computational findings, we can see that our results directly reflect those found experimentally by Burke et al, 2018. This supports the idea that this method of simulation can produce reliable models in the field of physical chemistry of molecular adsorption.



PTCDA, as modeled in HyperChem



CuPc, as modeled in HyperChem

Background

- The geometries of PTCDA and CuPc can be greatly influenced by the environments they are exposed to. By adsorbing these materials on different variations of NaCl substrates, we can measure the geometric change and subsequent binding energies as they adsorb to the surface.
- Different configurations and energies occur as the molecule is rotated about the z-axis in 15-degree intervals on the substrate. Finding a global minimum in energy as a function of configuration yields results about optimal geometries and locations for the adsorbed molecules.
- We can see how these molecules react when more than one is present on the substrate and create plots to represent where the lowest molecular energy is located. This shows where the molecules optimally adsorb in relation to one another.
- Comparing these optimizations to the experimental work in Burke et al, 2018, allows us to understand the resilience and legitimacy of our computational methodology.

References

Burke, S., Cochrane, K., Marsell, E., Roussey, T., Tom, G., Yuan, B., "Molecularly Resolved Electronic Landscapes of Differing Acceptor-Donor Interface Geometries" *J. Phys. Chem. C,* 2018, 122, 15, 8437-8444.

Manz, T., Sholl, D., "Chemically Meaningful Atomic Charges That Reproduce the Electrostatic Potential in Periodic and Nonperiodic Materials" JCTC, 2010, 6, 8, 2455-2468.

Segall, R., Shah, C., Pickard, J., Payne, M., "Population Analysis of Plane-Wave Electronic Structure Calculations of Bulk Materials" PRB, 1996, B **54**, 16317.

Methods

- Begin by creating the molecules in HyperChem and exporting the files to ORCA software to calculate molecular charge assignments using Density Functional Theory (DFT).
- NaCl substrates are created using fixed geometric parameters of a=5.64Å, imported into HyperChem. These substrates will function as a local environment for the adsorption of the molecules.
- Three separate charge assignments for the NaCl substrates:
  - **Pauling**, based on empirical data. Percent ionic according to $\left(1 - e^{(-1/4(X_a - X_b)^2)}\right)$.
  - **DDEC**, Density Derived Electrostatic and Chemical (Manz & Sholl, 2010).
  - **Plane Wave** (Segall et al, 1996).
- One single layer and one double layer NaCl substrate created for each charge assignment, giving us six types of substrates in total. For each type of substrate, different sizes are created: 8x8, 16x16, 32x32, and 64x64 (atoms).
- Want to avoid molecules being influenced by the edge of the substrate. We run models for the adsorption of the molecule on each substrate and settled on the 64x64 atom substrate being the ideal size for the adsorption of the molecules based on consistency of data, suggesting lack of influence from the environmental boundaries.
- For both the single layer and double layer substrates and for each charge type, the molecules are individually adsorbed in 15- degree rotation intervals about the z-axis. Energy calculations are recorded each time, and the lowest energy configuration is considered optimized (see Fig. 1. and Fig. 2).
- The optimized molecule is then replicated. One is placed central on the substrate and the other is moved at small interval time steps through the program IGOR Pro. For each time step, a single point energy is taken and recorded. These single point energies are compiled into a plot that show where the optimal configuration lies.
- From these plots, images of the modeled molecules are scaled and overlaid at the lowest energy points (See Fig 3.).

Fig. 1: We observe a global minimum of energy for PTCDA adsorbed at a 135° rotation about its z-axis on an NaCl substrate.

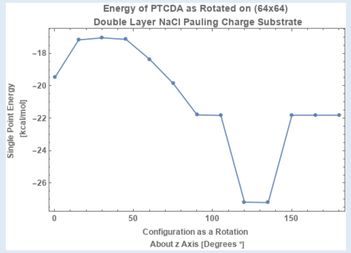
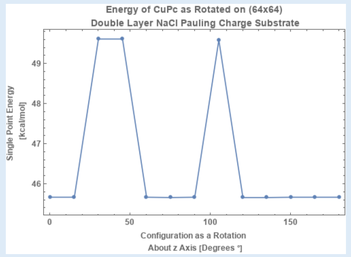


Fig. 2: Recorded energies for CuPc adsorbed at a 120° rotation about its z-axis and 180° rotation about the x-axis on an NaCl substrate.



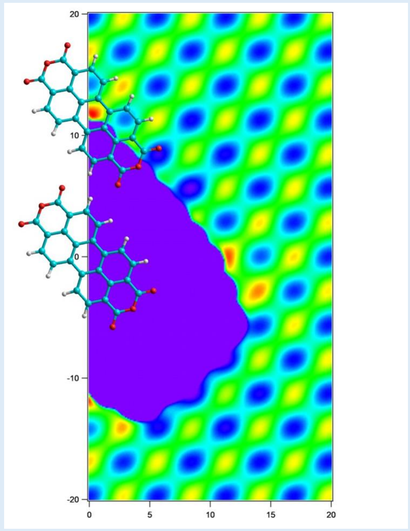


Fig. 3: Two PTCDA molecules shown on a double layer NaCl Pauling Charge substrate at a 20Å x 20Å range. The upper molecule sits at its lowest energy state relative to the molecule below it. The red spot indicates a minimum single point energy location.

Results

From our visual models of the adsorbed molecules (Fig. 4 and Fig. 5), we can compare to what we expect to see from experimental results (Fig. 6). We observe that our computational results mirror the experimental results of Burke et al, 2018. The double layer Pauling charge substrate especially gives us results that reflect the experimental work. This can be seen in the central sodium molecule under the adsorbed PTCDA being present in both the computational model and the experimental image. This gives confidence in our method of optimizing these molecules and adsorbing them onto NaCl substrates.

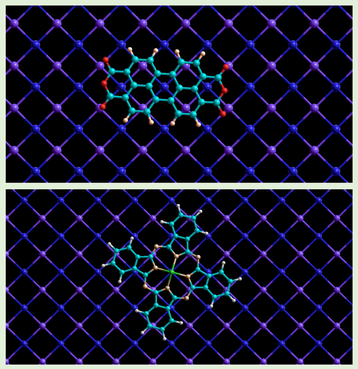


Fig. 4: PTCDA adsorbed at a global minimum energy configuration on a double layer NaCl Pauling charge substrate.

Fig. 5: CuPc adsorbed at a global minimum energy configuration on a double layer NaCl Pauling charge substrate.

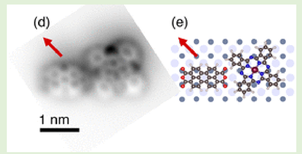


Fig. 6: Experimental image,(d), and subsequent model, (e), of PTCDA and CuPc adsorbed onto a bilayer NaCl substrate, taken from the Burke et al, 2018 study.