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Fullerenes in Solar Energy Cells

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Abstract:

This project involves controlling and characterizing the morphology of the active layer in a special type of organic photovoltaics (OPVs), consisting of porphyrin-fullerene composites, with emphasis on electron exchange interactions between the two components. The Vienna Ab Initio Simulation Package (VASP) is applied to model a variety of donor-acceptor complexes containing fullerene and porphyrin in terms of their stabilities as well as their geometric, electronic, and charge transfer features. The goal is to identify supramolecular chain structures with highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) that may serve as electron (hole) transfer channels in a photovoltaic device.

A stable structure, involving the planar adsorption of a porphyrin unit on a C60 hexagon, has been identified. The results for fullerene have been extended to phthalocyanine–fullerene dyads where the fullerene-derived unit Phenyl-C61-butyric acid methyl ester (PCBM) is connected to a porphyrin analogous electron donor through two oxygen-linked benzene rings. In both cases, the HOMO is located on the porphyrin segment, the LUMO on the fullerene component. As a fullerene, PCBM is a material of very high electron affinity, but it has better solubility properties than fullerene. It is often used in plastic solar cells or flexible electronics in conjunction with electron donor materials such as P3HT or other polymers. The results of our work contribute to the ongoing effort of using computational modeling to identify fullerene-based materials of potential relevance for organic photovoltaics.

Introduction:

Throughout the 21st century, it has become increasingly challenging to meet the global demand for power and electricity. As developing nations continue to advance, so too will their energy consumption. In addition to meeting the magnitude of future energy demand, a growing awareness for the environmental impact of power generation and the decreasing supply of fossil fuels has made it a national initiative to develop clean and sustainable alternative sources of energy.

One source of renewable energy that is being utilized and developed is solar energy. According to the Institute of Energy Research (IER), 0.5% of the energy consumed by the United States was from solar energy in 2015 [1]. Clearly, solar energy is not the most utilized energy source in the U.S. and it is not the most utilized renewable energy source either. But why is this the case?

The problem with utilizing current Photovoltaics (PVs) is the Levelized Cost of Energy (LCOE) and the Energy Payback Time (EPBT) attached to this type of renewable energy source. The LCOE is the total cost of producing, installing, and maintaining a source of energy over its life cycle divided by the energy it produces. The EPBT is the ratio of the energy consumed over the life of the module and the energy that it generates over its lifetime. While these figures are dependent on government regulations, they can be explained from a production standpoint. PVs compete for materials with the electronics industry and the production of silicon requires the utilization of costly clean rooms and hazardous etching chemicals with an environmental footprint. PVs are also composed of rigid, heavy materials that are cut from a substrate to meet a specific application design. These properties result in higher shipping costs, racking costs, installation costs, increased manipulation of the material in production, and fairly narrow

applications. In summation, the soft costs associated with the logistics of production limit the utilization of solar energy in renewable energy production [3]. Furthermore, PVs could have more applications if they had more advantageous mechanical properties.

With these disadvantages in mind, members of the scientific community are optimistic about Organic Photovoltaics (OPVs) and their potential to be a solution. OPVs currently operate at around 10% efficiencies but are expected to rise quickly as they are relatively new in their development [3]. The vision for OPVs is to realize high throughput production utilizing organic polymer chemistry to make production much faster and cheaper than silicon-based materials. Furthermore, utilizing the technique of roll-to-roll production could greatly increase the efficiency and volume at which we produce high surface areas of OPV materials. With roll-to-roll production [3], OPVs could be produced in a process similar to inkjet printing in which large surface areas of substrate can be rolled out continuously on conveyor belts, the cell could be printed, and then rolled back up for storage and shipping. The rolls could then be tailored to specific applications. With these attributes, there is optimism in OPVs having a lower levelized cost of energy and a faster energy payback time than current solar cells despite having significantly lower efficiencies at this time. New solar technology made from OPVs could have a payback time in days instead of the silicon EPBT of years [2]. This would make solar energy more economically competitive with fossil fuels and a convenient source of energy to be utilized residentially as well as in commercial and utility scale facilities.

In summation, OPVs could provide an attractive and cheaper alternative to the contemporary silicon solar cells controlling most of the solar energy market. Furthermore, OPVs could find an underdeveloped market niche of their own based on their lightweight and thin fabric-like properties when used in films. With these advantages, OPVs could increase the cost

efficiency of producing solar energy and provide a convenient way to increase surface areas of solar energy generation through their ability to extend the applications of solar technology.

But to improve upon this already promising start, capable molecular building blocks must be identified and further analyzed to increase the efficiency of OPVs. Organic supramolecular Donor-Acceptor (DA) complexes often form the basic component in the active layers of organic solar cells. Porphyrin-Fullerene dyads are a special type of DA complex suited for this purpose. Porphyrin acts as an electron donor molecule and Fullerene acts as an electron acceptor. Upon photoexcitation, Porphyrin-Fullerene dyads can transfer an electron from the Porphyrin part to the Fullerene part [4]. This is a called a photo-induced charge separated state, and it is crucial for the production of free, utilizable charge.

To efficiently reach this separated state, the molecule must exhibit certain properties. The Highest Occupied Molecular Orbital (HOMO) must be centered around the Porphyrin unit and the Lowest Unoccupied Molecular Orbital (LUMO) must be centered around the Fullerene or delocalized over the molecule. Thus there is a higher probability that the exciton is separated and available for collection at the cathode or anode of the solar cell [5].

In addition to having the correct electrical properties, OPV candidates are considered for their advantageous mechanical properties. For example, Phenyl-C61-butyric acid methyl ester (PCBM) is a popular fullerene derivative due to its solubility in contrast to the relative insolubility of traditional fullerenes which allows it to diffuse as it is being sprayed onto sheets during manufacturing. This forms an active layer configuration called a Bulk Heterojunction which effectively increases the surface area of the interface of the active layer responsible for solar collection and thus increases efficiency [6]. Another characteristic of PCBM that is of

importance is its ability to be assembled into supramolecular nanocables which are efficient at charge transfer as well as solar power generation [7].

All of these properties in the same material are valuable goals to be attained but to predict the potential of candidate complexes, one must deal with the intractable many-body Schrödinger Equation. To cope with this problem, a popular method is to use an approximation technique called Density Functional Theory (DFT). Instead of manipulating the wavefunction of the electrons, DFT operates with the electron density function and it reduces the problem of interacting electrons in a static external potential to the more tractable problem of non-interacting electrons in an effective potential.

After an initial geometry is specified, this technique can be utilized with high performance computing to move individual atoms one at a time according to the effective potential produced by the other atoms. After each movement, we can calculate the change in energy of the overall geometry. If the change results in a drop in energy that is above a preset threshold, the process continues. In this way over many iterations across all the atoms in the molecule, some geometries can approach a local minimum in energy. At this point we can say the molecule has converged to a stable geometry.

Programs like the Vienna Ab Initio Simulation Package (VASP) and the Atomistix Tool Kit (ATK) utilize this technique to optimize molecular geometries and generate output files that hold information about the characteristics of the final molecule [8][9]. This information can then be used to simulate how that molecule would react to outside influences in virtual experiments. It is important to note, however, that since the algorithm converges to a local minimum, there may be multiple optimized geometries depending on the starting point, and these isomers could also be of interest when studying molecular systems.

Another interesting application of the insights gained from studying Porphyrin-Fullerene complexes, is their application in nature. Specifically, we have known for years that birds navigate using the earth's magnetic field during their periodic migrations and it turns out that the mechanism for this ability can be explained by quantum biology. There has been of late an accumulating stack of evidence that birds have a chemical structure in their eyes that is responsible for their sensitivity to the inclination of earth's magnetic field. As a proof of concept for the existence of a molecular compass, studied a molecule composed of a linked carotenoid, porphyrin, and fullerene.

[10]
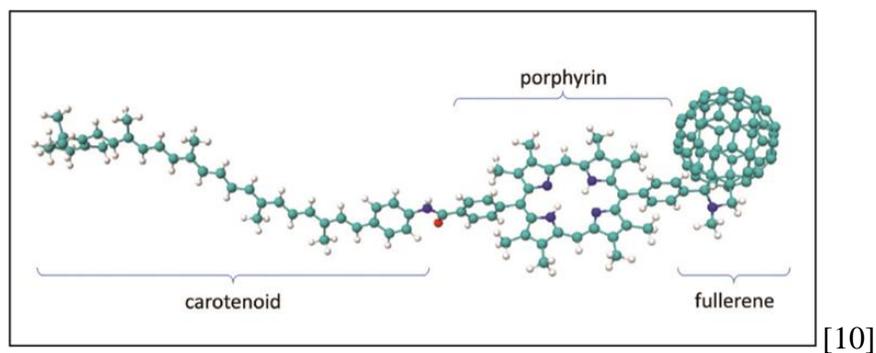
Although Carotenoid-Porphyrin-Fullerene (CPF) is not expected to be found in biological systems, it is similar geometrically and chemically to proteins found within the retinas of birds and the individual subunits are common structures in the broader frame of biology excluding the Fullerene. Timmel et al. found experimentally that when CPF was excited with green laser light, the time it spent in its excited state was directly dependent on the orientation of an outside magnetic field [10].

The effect can be explained by radical pair reactions and spin chemistry. When CPF is excited, a bond within the carotenoid chain is effectively broken and the two electrons that were part of that bond are separated to opposite ends of the molecule similarly to the previously

discussed charge separated state, but these two electrons are a radical pair. When they are moved to opposite ends of CPF, one on the fullerene end and the other on the carotenoid end, these two electrons exist in two different local magnetic environments.

We know from quantum mechanics that electrons precess in magnetic fields in a process called Larmor Precession. When the electron spins are aligned (parallel) they are in a triplet state. When they are not aligned (anti-parallel) they can be in a singlet state. By experiencing these different magnetic environments, the precessions of both electrons are no longer in phase with each other. This out of phase precession in addition to an outside magnetic field can result in the singlet and triplet state population being shifted in one direction or the other [10].

By altering the spin population, the electrons have a differing probability depending on the magnetic field to transition back and forth between spin forbidden (parallel) and spin-allowed (anti-parallel) pathways. These pathways directly determine the chemical outcome of the reaction. In this case, these pathways determine the lifetime of the excited state of CPF before it relaxes back into its ground state [10]. So, in addition to the PF part of CPF potentially having solar applications, modeling CPF could lead to applications in magnetic sensing technology.

Methods:

In this research, the Vienna Ab Initio Simulation Package (VASP) is applied to model a variety of Porphyrin-Fullerenes on East Tennessee State University's computer cluster, Knightrider. For the purposes of this research, 2 nodes with a total of 24 processors were used for all optimizations. Each optimization had a duration of 1-2 days depending on how close the starting geometry was to the converged geometry and on how large the system was. All operations were performed through an SSH client called Putty with no graphical user interface, and all interactions and troubleshooting were done using Unix code.

VASP uses a plane wave basis for its electronic structure calculations. Plane-wave DFT was used in conjunction with Projector Augmented Wave (PAW) pseudopotentials and the Generalized Gradient Approximation (GGA) within periodic boundary conditions consistent with the Monkhorst-Pack scheme implemented in the VASP code [8]. This was the method chosen in this research in contrast to the localized basis sets used by ATK. ATK uses a variety of DFT functionals in conjunction with norm-conserving pseudopotentials of the Troullier-Martins type. ATK also utilizes an electronic basis with local atomic orbitals at double-ς-plus polarization precision [9].

Initial configurations for the starting configuration were assembled using pre-defined units such as C60, porphyrin, and benzene rings. The resulting structures defined the VASP input files. If the geometries did not converge they were redesigned and submitted again. If the geometries converged, they were then visualized using the program Moldraw. After the molecules were visualized, other output files of VASP were analyzed for information regarding each structure's electronic properties focusing on the energy difference between the HOMO and LUMO (energy gap) and other molecular orbitals (MOs).

Overall, the process involved inspired trial and error that explored different parameters to find new converging geometries to analyze for potential as an OPV material. Each geometry was also checked for consistency with the localized basis set DFT (ATK) methods employed in the literature. The purpose of this research was to contribute to the computational documentation of materials that can reach a photo-induced charge-separated state and investigate their electric characteristics. This documentation allows chemists and engineers to choose the most favorable molecules for implementation in more efficient solar cells, and these configurations might find more general application in nanotechnology.

Results:

All structures that were examined were based on C60 or PCBM. All of them were found to be stable. As a starting point, simpler Porphyrin-Fullerene dyads were analyzed, but the research progressed to larger and more applicable geometries. Energy gaps were recorded for all convergent geometries and later geometries were analyzed for the spatial characteristics of their MOs.

Porphyrin and Fullerene

Energy Gap: 1.1555 eV by DFT plane-wave analysis
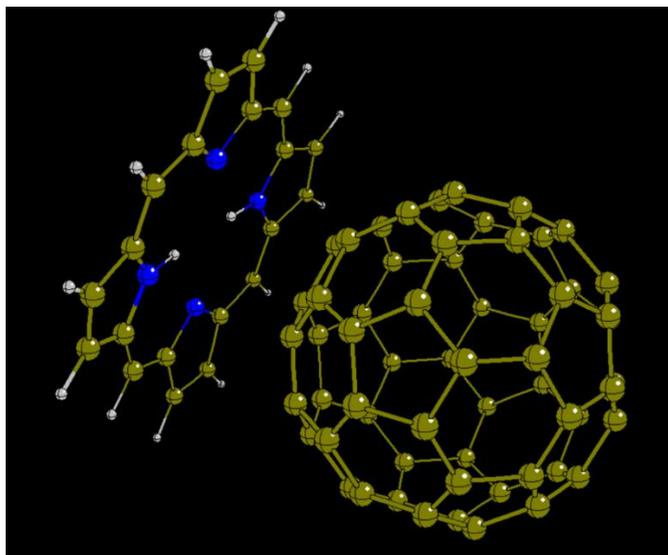
Porphyrin-Fullerene was the simplest dyad simulated. This configuration will result in a photo-induced charge separated state but its lifetime will not be long due to the proximity of the excited electron to its starting point in the ground state. Next, we modified the Porphyrin by introducing transition metals to the center and removing the hydrogen atoms that were in the center beforehand.

Left to Right: HEME-Fullerene, Porphyrin metallized with Mg and Fullerene

Energy Gaps: 0.7535 eV, 0.9468 eV
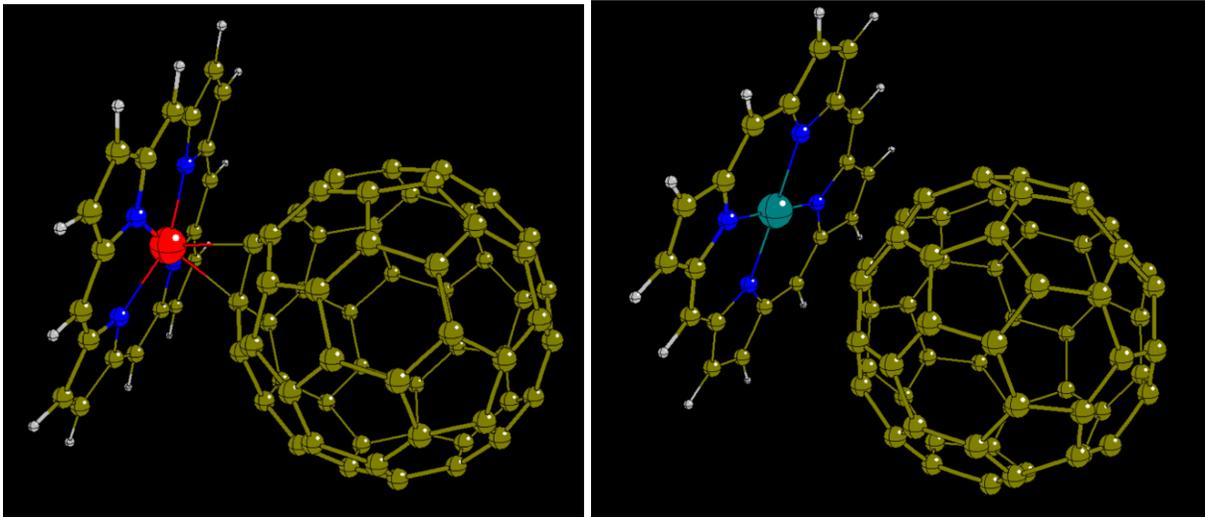
These metal-containing systems still exhibit the same behavior of charge seperation and have the the same weaknesses with respect to lifetimes. However, these structures show slight structural changes in the Porphyrin unit influenced by the metals which become more important in later structures. The most important thing to notice with these configurations is the change in the energy gap. The energy gap is significantly lower. After this, the distance between the Porphyrin and the Fullerene was increased.

Porphyrin-Fullerene portion of CPV

Energy Gap: 0.2478 eV
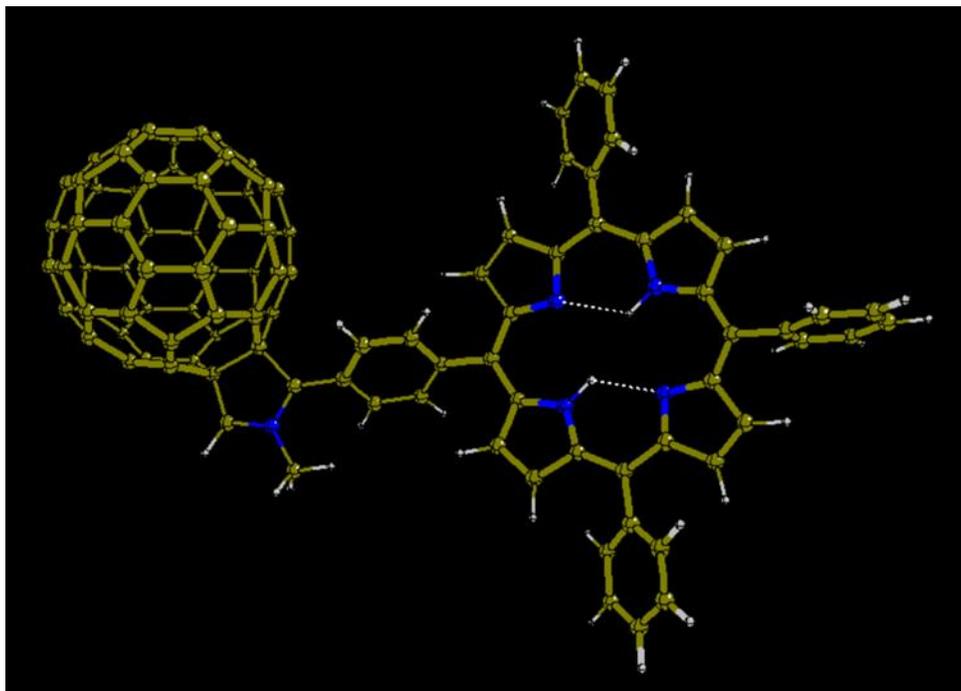
This structure is the Porphyrin-Fullerene part of CPF. The Porphyrin was attached to benzene rings on four sides and connected to the Fullerene directly. In addition to the previously discussed magnetic properties, this configuration has a much lower energy gap than the previous configurations and a longer separation lifetime. If this structure proves to be inconvenient for solar enegy, it could still yet prove useful in nanotechnology applications like magnetic sensing. At this point in the research, Fullerene was substituted for its derivative, PCBM.
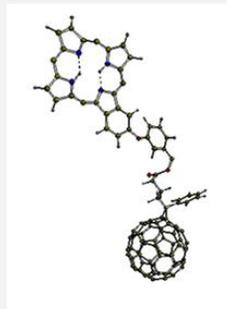
Porphyrin-PCBM and Pthalocyanine-PCBM

Energy Gaps: 0.9646 eV and 1.1555 eV
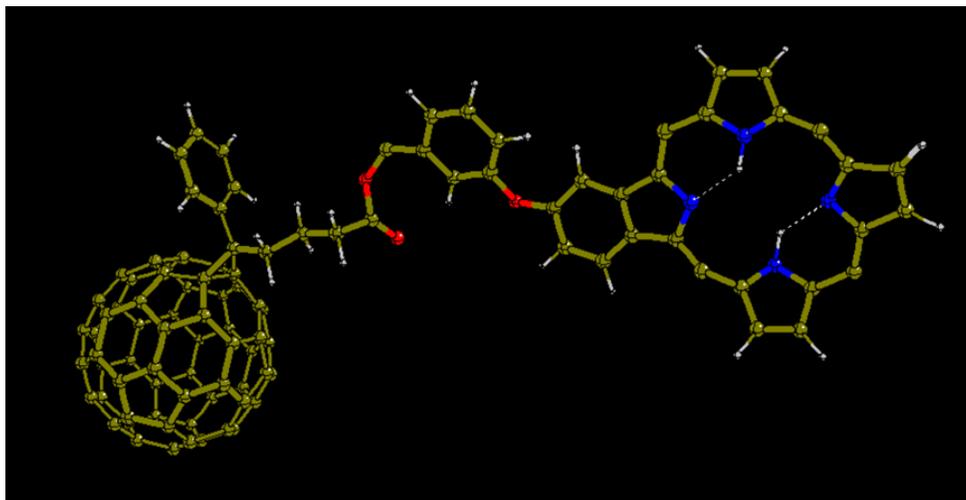
Comparison between two isomers of the PCBM dyad
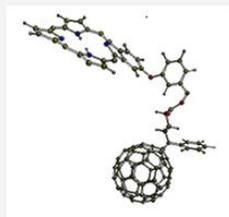
A

B

Total energies: $\Delta E = E_A - E_B = 1.19$ eV

HOMO-LUMO gaps:
$$\Delta E_{HL,A} = 0.49 \text{ eV}, \quad \Delta E_{HL,B} = 0.96 \text{ eV}.$$

By both criteria, B emerges as the more stable geometric variant.

When modeling this geometry, it was found to converge to two different isomers. The bent isomer had a lower energy gap but a higher total energy. This meant that the straight geometry was the more stable of the two. PCBM allows for greater charge separation allowing for longer lifetimes for the charge separated state, and it also makes the entire structure soluble which is a useful property for manufacturing. One side effect of introducing PCBM was that the

Porphyrin unit converged into a nonplanar configuration with antisymmetric warping across the initial plane of Porphyrin. This would reduce its surface area and stability which affects the efficiency of Porphyrin's absorption of light. To solve this problem and retain a planar geometry, Phthalocyanine was substituted for Porphyrin and it produced the following more optimal result.
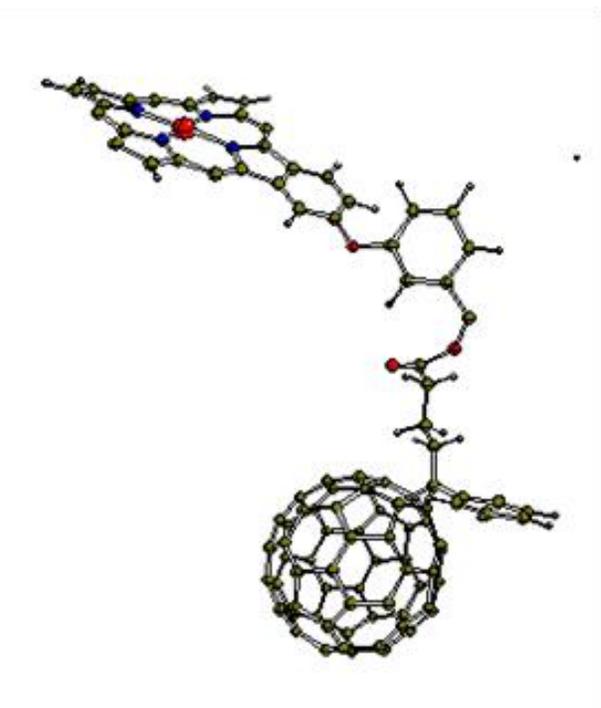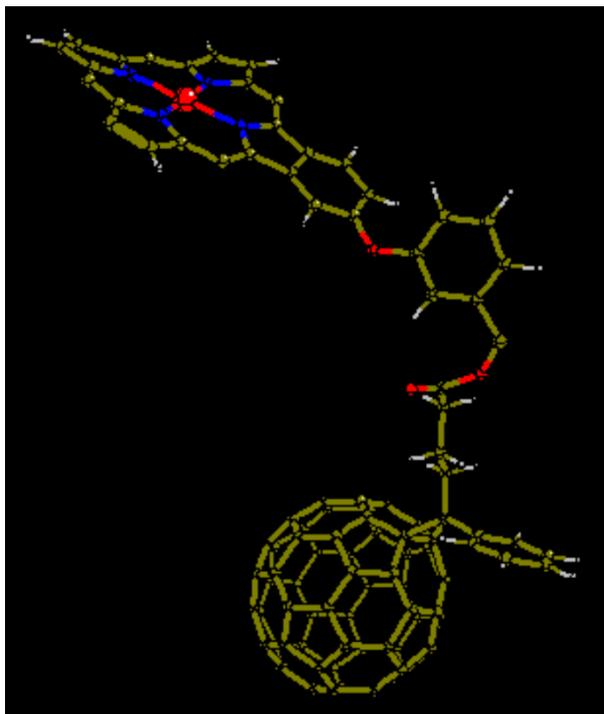
Phthalocyanine-PCBM

Energy Gap: 1.1555 eV
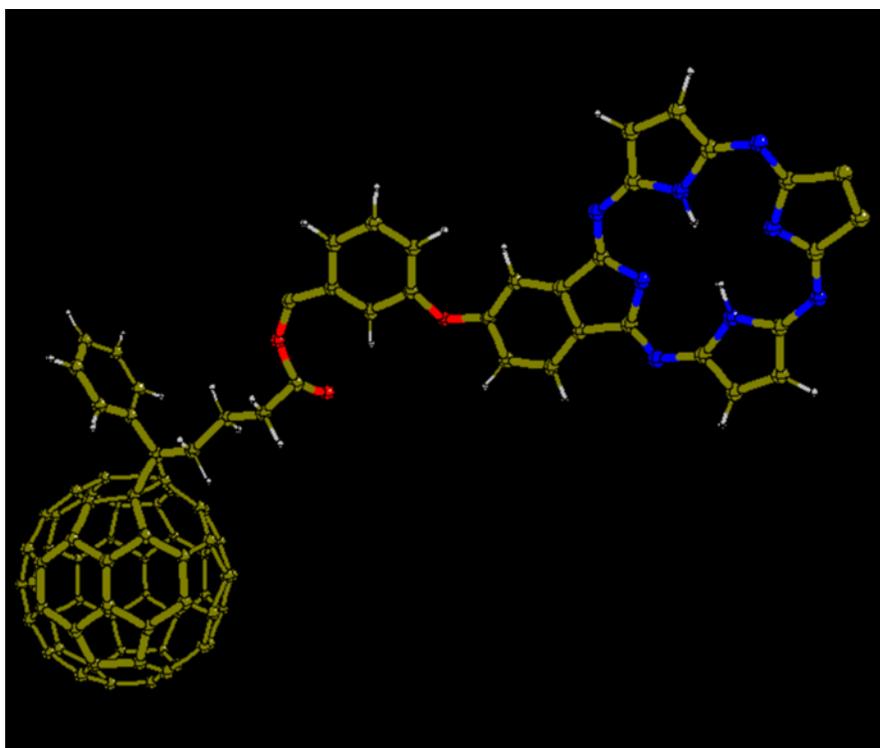
This Porphyrin derivative raised the energy gap and resulted in a more stable molecule. After introducing PCBM, the fullerene unit was modified.

HEME-PCBM

Energy Gap: 0.1671 eV

This geometry had the lowest energy gap of all the converged geometries we found. The HEME group produced a bent geometry similar to the isomer of Porphyrin-PCBM generated earlier. As an example, this structure was consistent with the structure produced by use of a localized basis. In addition to the optimized geometry, the spatial characteristics of the HOMO and LUMO of this structure were also visualized and yielded promising results.

HOMO   LUMO
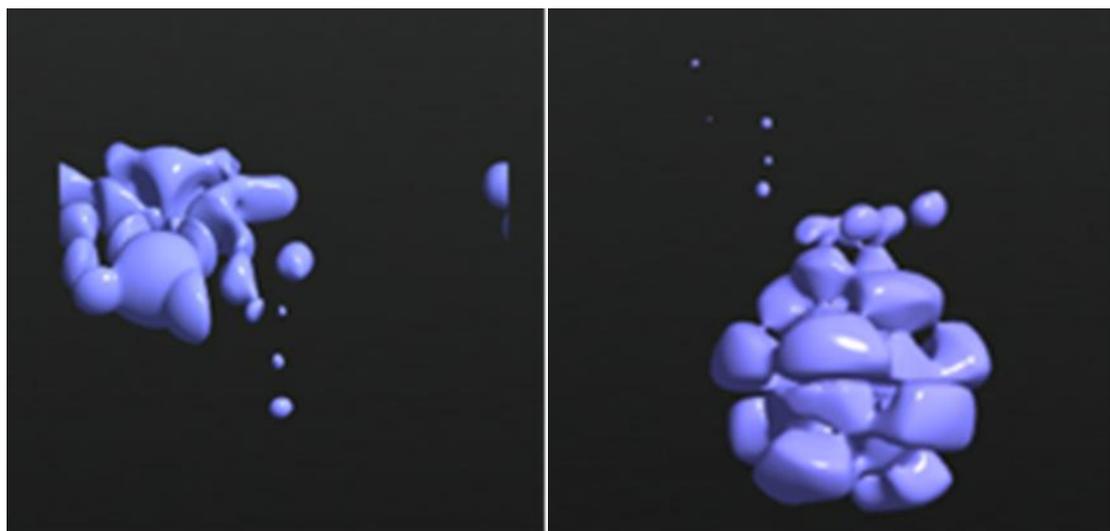
The HOMO was centered around the HEME unit and the LUMO was centered around the

Fullerene unit with almost no delocalization elsewhere in the molecule. This structure shows

very good probability for a charge separated state which would make for an efficient active layer

material.

Conclusion:

In summation, a variety of Porphyrin-Fullerene dyads were investigated in terms of

geometry and stability. Stability was obtained for various arrangements involving C60 and

PCBM. The tested geometries favored the formation of a photo-induced charge-separated state.

The HOMO-LUMO gaps were found to lie typically in the optical regime. Finally, the

DFT/plane-wave and the DFT/localized-basis approach turned out to be consistent in terms of

molecular structure.

The mechanical properties, energy gaps, and the models of the spatial characteristics of

the MOs are also very important considerations in the engineering of the active layers of OPVs.

Not many specific advantages and disadvantages with regards to the active layer were discussed on a molecule to molecule basis in the results section because it would be short-sighted to comment on the dynamics of macroscopic systems based on a small part of it. Nevertheless, it should be noted that the energy gaps are important because they determine the frequency of light absorbed by the solar cell, the stability of the dyad, and they can determine the voltage output of the cell [2][11]. These factors and more stemming from the supramolecular interaction within the active layer must be weighed and optimized in the construction of OPVs from a quantum scale all the way to the macroscopic manufacturing scale to maximize the cost efficiency of solar energy cells and improve our supply of clean sustainable energy.

Future Research:

After identifying these candidates for use in manufacturing OPVs, it would be enlightening to first analyze the HOMOs and LUMOs of the rest of the converged geometries already listed to determine the spatial characteristics of the band gap. After that, tweaking geometries to examine isomers could yield further knowledge with the goal of attaining a HOMO concentrated around the porphyrin and a LUMO concentrated around the fullerene.

Primary long term goals would be to continue this approach to analyze supramolecular structures made from the subunits optimized in this work. For example, the Porphyrin-PCBM nanocable described in the study by Buldum et al.

Fullerene-porphyrin staircase
(Buldum et al., Nanotechnology 25 (2014) 235201)

Further research could also be simulating molecular responses to outside forces using the information attained from converged geometries. For example, one could simulate the potential differences across the molecule. In regards to the CPF molecule, simulations of the electron density function under the influence of magnetic fields would contribute to exploring the interface between quantum biology and nanotechnology. The overall idea is to continue to apply this computational approach as far as possible into the subject of supramolecular interactions. This effort is in pursuit of knowledge that chips away at the grey area separating the atomic scale and large polymer morphologies.

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