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Computational Chemistry in Rational Material Design for Organic Photovoltaics

Introduction

The acceleration in global population growth, combined with worldwide economic development, have together dramatically increased the demand for energy. This demand has been filled by fossil fuels. The reliance on fossil fuels as a cheap and convenient means of energy is leading to adverse, and perhaps irreversible, ramifications for the entire planet. Many potential alternative energy sources have been explored to alleviate the dependence upon fossil fuels. The use of solar energy as a renewable energy source has been a key area of investigation to many scientists and engineers looking to solve this problem. Among current solar cell design paradigms, organic photovoltaic cell technology shows significant potential due to its potential low cost, flexibility, and manipulability. While scientific research has led to progress in organic photovoltaics, significant issues remain that must be addressed in order for organic photovoltaic cells to become a more feasible option. The purpose of this paper is to expound the crucial role of computational chemistry in novel material discovery and optimization as it pertains to organic photovoltaics.

The Problem

Current data indicates energy consumption increased from 238 Exajoules (EJ) in 1972 to 464 EJ in 2004, with an additional 65% increase projected by the year 2030.^[1] Over the same time period, global population grew from 3.85 billion to 6.44 billion people with a projected 8.5 billion in 2030. With an ever growing appetite for energy, the environmental consequences will become more evident at an ever faster rate. Scientists suggest a multitude of observations as evidence of global climate change. For example, the last three decades have been successively warmer than any preceding decade since 1850. Average surface temperature has increased 0.85°C from 1880 to 2012. Global average sea rise grew from 1.7 to 3.2 mm/yr and the upper 75 m of oceans have warmed by

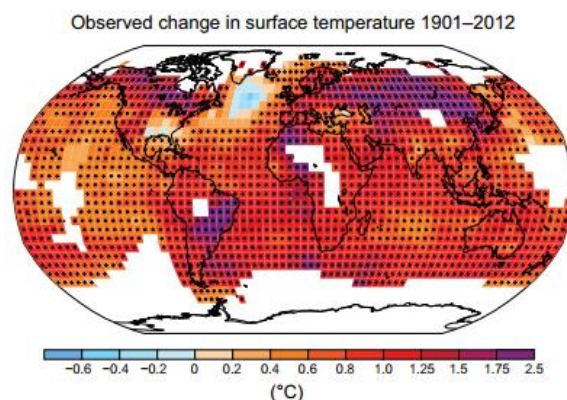


Figure 1. Map of observed surface temperature change from 1901 to 2012.^[1]

0.11°C/decade from 1971–2005.^[1] Humanity has done more than affect Earth's surface temperatures, we have also had staggering impact on atmospheric composition, and ocean acidity.

Anthropogenic greenhouse gases have accumulated in our atmosphere. Concentrations of carbon dioxide, methane, and nitrous oxide have increased by 40%, 150%, and 20% respectively since 1750. These concentrations are the highest in the past 800,000 years as recorded by ice cores and their rates of increase are unprecedented in the last 220,000 years. Humanity has emitted over 555 Gigatonnes of carbon cumulatively, of which 315 GtC has been absorbed by our oceans and ecosystems while the rest remains in the atmosphere. The absorption of carbon compounds, particularly carbon dioxide, into our oceans has rendered our oceans more acidic. Since the industrial era, there has been a 26% increase in hydronium ion concentration in the oceans and a corresponding decrease of 0.1 pH.^[1] This pH shift solubilizes calcium carbonate, a molecule that makes up the structure of coral reefs and other marine calcifying organisms. By solubilizing this vital mineral, dissolved oxygen levels decrease by the killing of algae, thus risking the health of entire ecosystems.

Our energy usage needs improvement, to continue utilizing fossil fuels means the irreversible destruction of the environment. This provides some of

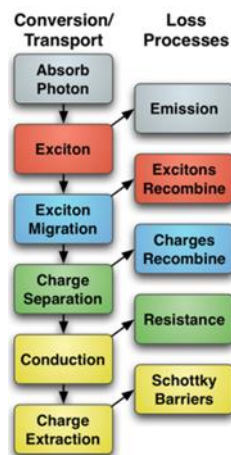
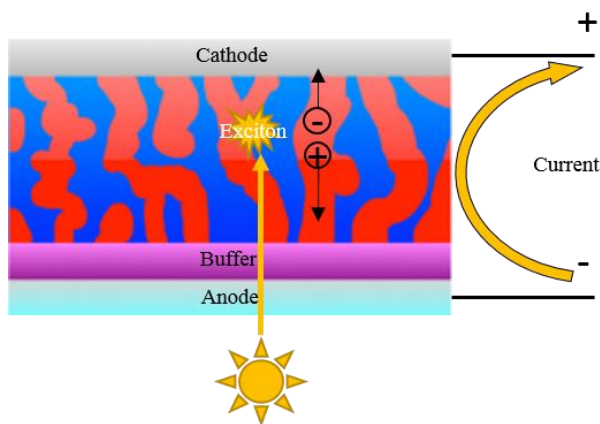


Figure 2. (a) Schematic of light absorbance converted to current in a bulk heterojunction architecture. (b) Energy conversion, transport and loss processes. ^[14]

the motivation behind solar cell research. The potential benefit from solar energy is tremendous, as the total energy absorbed by the Earth is about 3,850,000 EJ per year. ^[2] In 2002, one hour of sunlight absorption was more energy than the entire world used in that year. ^[3] Inexhaustible and import-independent energy is an extremely tempting idea, and it is why so many researchers have gone to work on harnessing solar energy.

Anatomy of an OPV

While there have been a variety of attempts to capture the energy from the sun, organic photovoltaics (OPV) are one method. Essentially, an OPV works by absorbing a photon emitted by the sun. The photon carries energy that is used to excite an electron off of a donor layer, often comprised of a semiconducting polymer. Complimentary to the donor polymer is the acceptor, which accepts the excited electron. The donor and acceptor form a heterojunction along which charges can migrate. When the electron is excited it leaves the ground-state energy level and leaves behind an electron hole: the space the electron used to occupy. This space and the now excited electron are referred to as a quasi-particle, called an exciton. The exciton begins to migrate and once at the donor-acceptor interface, the exciton can be split into a separate free electron and hole. As the charges separate further, they are able to reach electrodes which, upon becoming charged, generate current. In practical devices, almost every step in the process is affected by inefficiency. To effectively render electricity from sunlight solar cells need to have an optimal mechanism and be composed of efficient materials.

Typically, OPV's feature four layers of materials that have different functions: an active layer, a buffer layer, a cathode layer, and an anode layer.

The active layer is constituted by the donor and acceptor materials. The interface, called the junction, between the acceptor and donor materials has undergone serious change to optimize efficiency. Circa 1960, the active layer was only a single organic electronic material. ^[4] This architecture had an efficiency of <0.1% and so alternative measures were considered. With the advent of donor and acceptor materials, the bilayer was considered. Here, each layer was separated in a planar heterojunction; this model improved efficiency, but could not effectively separate charges because they would recombine. Recently, a bulk heterojunction (BHJ), a single bi-continuous network of donor and acceptor, is utilized by many research groups. BHJs are shown to be proficient at charge separation because the domain sizes are similar to exciton diffusion lengths, and can be made thick enough to absorb a large amount of photons yielding a higher output. While modes of architecture are explored and continually improved, research has also revealed the nature of ideal solar cell materials. Researchers have begun to highlight properties that individual layers and materials must exhibit to optimize efficiency.

Subject to much research is the electron donor. Donors are p-type semiconductors that are often polymers. While there are a plethora of donor molecules, researchers look for a donor to have broad absorption spectrum, ideally with a red-shifted absorption maximum to effectively make use of the visible and UV light that the sun emits. ^[4] The wavelength max should

be about 800 nm; this has been found to relate to an excitation energy of 1.5 electron volts (eV), which many consider optimal for the transfer to the acceptor. Donors should have relatively low excitation energy so electrons are easily excited and can form excitons. The donor needs to have about a 0.3 eV energy offset to the acceptor to provide the driving force behind exciton separation.^[5] The highest occupied molecular orbital (HOMO) needs to have electronic stability to avoid oxidation and to enhance voltage. Semiconducting polymer donors must have an extended π -system to favor charge separation and transport. Additionally, the donor needs thermal, chemical, and morphological stability. For many years POV's with the highest power conversion efficiency (PCE) have been made of poly(3-hexylthiophene) (P3HT) donor material, obtaining efficiencies around 5%.

The electron acceptor almost ubiquitously adheres to a fullerene theme. While not as researched as the donor, there are three consistent choices in the literature: Phenyl-C61-butyric acid methyl ester (PCBM), Phenyl-C71-butyric acid methyl ester (PC₇₁BM), and indenylC60-bisadduct.^[4] Fullerenes are commercially available and are useful electron acceptors because they do not have to distort to take on electron; they also have several low-lying excited states that the accepted electron has a probability of occupying. Of the three, PCBM remains the most economically viable; although PC₇₁BM has been shown to make polymers with low excitation energy.^{[6][7][8]}

The driving force behind the all-important charge migration is the electrode layer that inevitably creates the electron current through the collection and extraction of charges. In the literature, Tin doped Indium Oxide (ITO) is often used as the anode because of its transparency and conductivity. Aluminum or Calcium/Aluminum is used frequently for the cathode.^[9] Some of the issues facing the electrode layer include its instability against undesired redox reactions resulting in reduced lifetimes. To alleviate this issue, an inverted cell

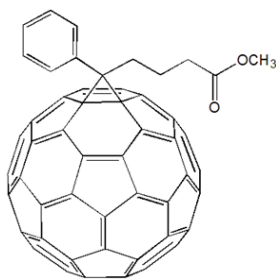
geometry has been suggested^[10] in which, the electrode positions are switched and ITO is used as the cathode and usually silver is used as the anode. The inverted geometry is a much more stable architecture. Additionally, Indium is a scarcely available material and as such there has been a push to develop more Earth abundant electrode materials.^[11] Some potential alternatives are conductive polymers and metal grids, thin metal films, and graphene.^[12] Electrode materials require further advancement particularly in conductive and optical transmittance properties.

The buffer layer is an essential layer within the OPV cell. Buffer layers play a prominent role by having a direct effect on the electrical, optical, and mechanical aspects of the cell. Buffers assist the electrode in both charge collection and extraction. Usual architectures now include both an anode and cathode buffer layer.^[13] They have strong influence over the properties of the organic/electrode interface by inducing interfacial charge redistributions, geometry modifications, and chemical reactions.^[4] The anode buffer has to provide substantial ohmic contact with the donor; it has to transport positive charge carriers while blocking negative ones. In addition to having stability, it should not increase device resistance and must be transparent in the conventional device architecture. The Cathode buffer has the same requirements, but involves the acceptor and negative charges, and must be transparent in the inverted device architecture.^[13]

Computational Screening of OPVs

The high specificity of properties required to create an optimal solar cell produces a difficult problem of sorting through candidate materials. Traditionally, an expert in the field uses his or her chemical intuition as to the suitability of molecules to a certain task. To explore molecular space, an alleged $\sim 10^{60}$ molecules that can potentially exist, such a slow pace is inadequate to make viable decisive change for the environment.^[14] With the advent of high-throughput computational screening, research into candidate molecules happens at a much improved rate.

Scheme 1. Phenyl-C61-butyric acid methyl ester (PCBM)



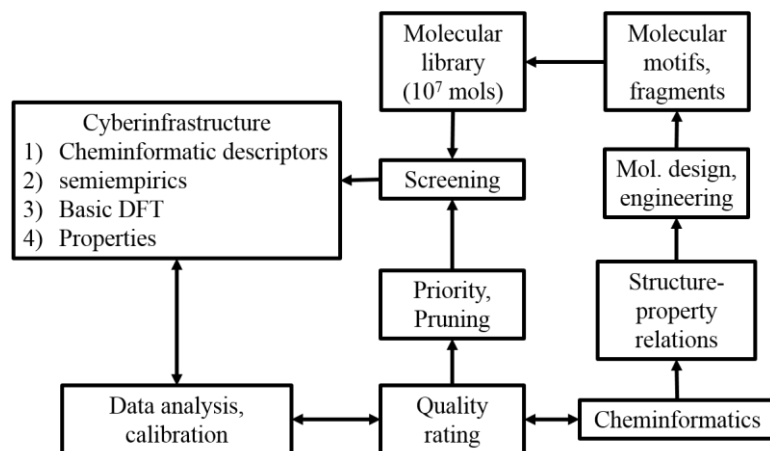
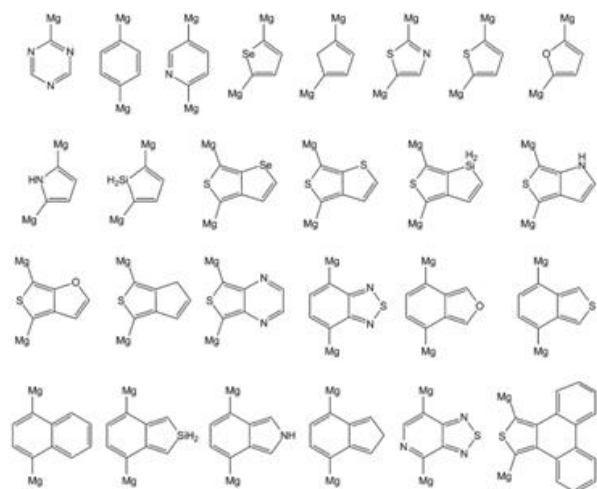


Figure 3. (a) The 26 building blocks used for generating the CEP molecular library. The Mg atoms represent chemical handles, i.e., the reactive sites in the generation process. We introduce simple links between two moieties (by means of substituting two Mg for a single C-C bond) as well as the fusion of two rings. ^[15] (b) Structure and flow chart of CEP.

One research project taking advantage of such methodology is the Harvard Clean Energy Project (CEP). ^[15] To investigate OPV materials, CEP categorizes molecules and their properties into motifs; the necessary chemical/structural elements for a successful OPV that take the form of molecular fragments. Motifs are stored in the molecular candidate library that is produced by a combinatorial molecule generator. By swapping and combining molecular substituents, sidechains, and fragments, and using 1,000,000 guiding molecular motifs, the generator creates the candidate library. Motifs are based upon 26 building blocks and connectivity rules, and by linking 4 or 5 units together a candidate molecule is formed.

An automated, *in silico*, and high-throughput infrastructure is utilized to screen the primary library's oligomers for optimal properties. ^[16] This approach is excellent for an exhaustive search of a well-defined chemical space. Currently, the CEP is investigating candidate OPV donor polymers, but the software can be geared to produce other libraries by changing chemical fragments, motifs and connection parameters. In principle, any p-type organic semiconductor can be a suitable OPV electron donor. To effectively sort through 20,000 oligomer sequences daily, the CEP uses a calculation hierarchy, in which a successive characterization of relevant structural and electronic aspects is performed. This hierarchy is designed to successively address pertinent issues and provide characterization at an increasing level of theory. Early stages focus on molecular properties and hence are

useful for assessing macroscopic quantities like open circuit voltage. Later stages move to intermolecular and condensed phase characteristics that are indispensable to understanding exciton and charge transportation.

In combination with techniques from data mining, cheminformatics, and machine learning, the CEP uses descriptors to rapidly gauge the quality of the candidate serving as the preliminary ranking. ^[15] These cheminformatic descriptors: current density, open circuit voltage, and PCE are the measures comprising the first step in the calculation hierarchy and are key quantities in the assessment of photovoltaic performance.

Electronic structure theory is subsequently utilized to probe the candidate donor's properties, therefore the first intensive calculation performed is Density Functional Theory ^{[17][18]} (DFT) to reveal the electronic states of the candidate. A set of functionals such as BP86 ^{[18][19]}, B3LYP ^{[20][21][22]}, PBE0 ^[19-24], M062X ^{[25][26]}, in addition to Hartree-Fock theory, ^{[27][28]} are used. Information gathered from this step includes molecular geometry, electronic ground state and total energies, electron spin density, electrostatic potentials, multipole moments, Mulliken and natural populations, and molecular orbitals and their eigenvalues. The CEP uses this data to rate and compare candidates. Calculated ionization potentials, electron affinity and gaps, and partial density of state are compared because the electron levels have to be tuned for the complex interplay between the donor, acceptor, and atmospheric stability. Exciton and charge mobilities are predicted by delocalization of frontier orbitals in addition to transition

character and probability of excitation. Charge maps can be created utilizing the multipole moments data to reveal chemically active sites and can predict organization in bulk structure. Finally, a wave function analysis is performed to find property trends and relations. Beyond DFT, vibrational and partition functions are calculated to gauge photon scattering and trapping in vibrational nodes. Additionally, candidate ionic states are computed for improved e- affinity and ionization potential values, and for optimized geometry in the ionic state to gather reorganization during charge migration. Other groups have used a similar method, as is the case for the Curtiss group who utilized a computation hierarchy to down-select a large pool of potential electrolytes for use in an advanced electrical energy storage system. Results of the screening are optimized for redox potentials, solvation energies, and structural changes. ^[29]

During each stage of the calculation donor candidates are prioritized according to the score they receive. Molecules that score higher earlier in the calculation hierarchy are characterized faster and are screened at a higher rate. Scoring is freely customizable so as to assess different properties. Comparison of computed data and experimental results are a way of finding systematic error. Obtained data can also be used to create novel quantum chemical descriptors allowing for the development of more advanced models founded on a more physically rigorous basis. Some groups suggest logging the parameters under which a solar cell is synthesized for use as a descriptor. Asserting that the variation in production parameters is correlated to variation in PCE, and as such production conditions ought to be computationally optimized. ^{[30][31]}

Of the screened compounds 0.3% of 2,600,000 compounds have the required energetic levels to obtain OPV PCE of 10% or greater. ^[6] This highlights the need for computational analysis to assist and expedite the task, as an unassisted search has a smaller probability of success. The DFT calculations have illuminated the wide range of electronic properties contained in the CEP library. Successful discovery of OPV materials with specific features will rely on the electronic versatility of the screened compounds. CEP's contributions to the field of material optimization are computational in nature and do not give definitive quantitative results. However, the real world applications of these contributions are useful, as the qualitative analysis of data relative to structural motifs reveal global trends.

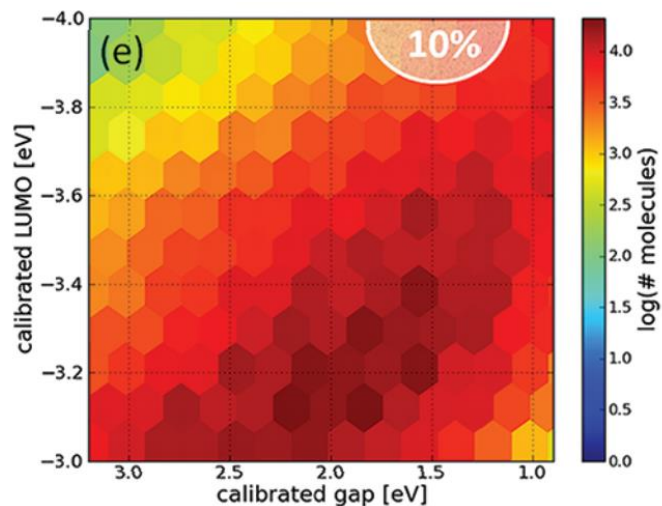


Figure 5. OPV relevant parameter space with the 10% PCE region (with respect to a PCBM acceptor). About 0.3% of the screened compounds fall in this high-efficiency region. ^[14]

With these trends leaps are made in material optimization that would otherwise be a laggard field.

The results of all calculations are used to build a database accessible to the public which serves as the hub for data mining, analysis, and scoring to facilitate study of trends and OPV design results. The CEP library is not intended for the sole use of OPVs, but to organic electronics in general. Calculations like DFT are a computationally intense process. To offset the processing strain the CEP employs the IBM world community grid (WCG). ^{[32][33]} The WCG allows anyone with idle computing power to loan it to scientific research. In 2014, the WCG consisted of 650,000 volunteers worldwide donating the use of 2.7 million computational platforms equating to 880,000 years of computation. This way, everyone has the ability to connect electronically to assist in the development of solutions for the issues of today.

Similar to Harvard's CEP is the Hutchinson group, which also uses virtual molecular synthesis to find donor materials matching an ideal target value. ^[14] However, instead of using DFT alone, the Hutchinson group concurrently uses a genetic algorithm (GA) for additional refinement.

A calculation hierarchy is also used by the Hutchinson group; early calculations used include AM1 ^[34], PMG ^[35] and ZINDO/S ^[36] which are characterized by their relative speed, and find electronic structure and properties of oligomers. These calculations need not be perfect because they only need to remove

the worst candidates. Higher efficiency oligomers are then used as a frame work for the GA to develop upon with the goal of minimizing the HOMO-LUMO gap of isolated molecules in the gas phase. While these parameters optimize speed of calculation they leave out bulk phase considerations. The GA rewards the oligomers with desired optoelectronic properties like a large oscillator strength that corresponds to a high extinction coefficient yielding a stronger absorbance at a given wavelength. The GA works by crossing over two stochastically selected oligomers from the fittest set, determined by initial calculations, and swapping component monomers. Children of these crossovers were then mutated by swapping their monomers with randomly selected, high-scoring, similar monomers. This process is allowed to run for one hundred generations, and the fittest oligomers produced were predicted to have efficiencies of 8% and dozens were predicted to have >10%. For the top oligomers DFT is used to further characterize and screen donor candidates, removing several top candidates due to high activation barriers for charge mobility.

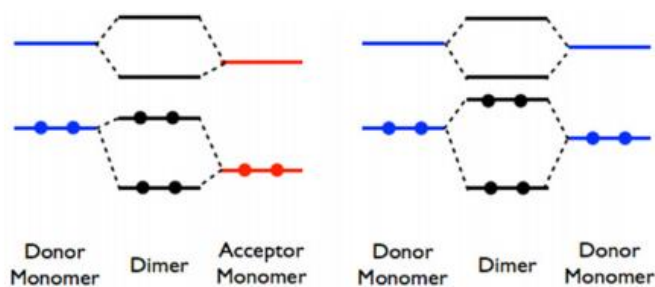
The key to the Hutchinson group's screening is to utilize the GA to save computational investigation for a small fraction of candidate materials. More accurate parameters can be used by the GA that would include redox potentials using the Δ SCF procedure. Also, open circuit voltage can be considered further by considering molecular and interfacial geometries and calculation of intermolecular charge state energies. However, these calculations are computationally and time intensive.

The Hutchinson group's methodology is proven effective by new design principles unlocked by their research. For example, most donor polymers investigated in the literature feature donor-acceptor (DA) monomers as an attempt to tailor optimal band gap. Band gap energies are important because they determine exciton separation and charge migration. However, top oligomers from the GA feature donor-donor (DD)

monomers. The DD architecture yields smaller band gaps than their DA counterparts because of greater electron delocalization across the π -conjugated backbone. This delocalization creates a large amount of energetic splitting from monomer orbitals. This may have positive impact on charge mobility and separation, and may be a new paradigm in improved p-type OPV semiconductors. Although highly optimized DA polymers exist due to thorough research, the potential benefit from the DD architecture is promising.

Additionally, it was found that modifying monomer sequence has large effects on the HOMO and LUMO energies and thus changes the band gap. Generally, there has been little research into investigation of purposely sequenced oligomer π -systems and most are joined randomly (AABABA), alternating (ABABAB) or blocked (AAABBB). The Hutchinson group names this the sequence effect; the ability to change donor material's band gap energies by an average of 0.2 eV creates more opportunity to optimize donor materials beyond synthesizing new monomers. To find the average sequence effect across all monomers, not just efficient ones, the group created a pool of 1056 tetramers from monomers of different HOMO-LUMO energies. Orbital energies and lowest-energy optical excitations were calculated for each tetramer and surprising trends were found by comparing band gap energies among all sequences. For example, regardless of its coupling agent trithieno[3,4-b:2',3'-f:3'',2''-h]-quinoxaline consistently produced the lowest band gap energy across all different sequences. On the other hand, coupled 4,4'-difluoro-[1,1'-bi(cyclopentane)]-1,1',4,4'-tetraene raised the band gap of its associated tetramer. Outside of particular monomers, HOMO-LUMO and band gap energies were also averaged across each sequence pattern for each tetramer. It was found that for LUMO and band gap energies there is a large increase between ADDD and DAAA. The opposite is true for the HOMO where there is a large decrease between ADDD and DAAA. Furthermore, the average DDDD sequence is a consistent outlier from other averages lying at 2.6 eV. An increase in HOMO energy of ~ 0.2 eV going from ADDA to DAAD sequences was found and a related decrease in LUMO and band gap energy of ~ 0.2 eV, again going from ADDA to DAAD. This finding allows room for the optimization of traits other than electronic property such as stability or synthetic accessibility by picking species with different sequences and similar electronic properties.

Scheme 2. Comparison of (left) Conventional D-A and (right) D-D Synthetic Strategies to Tailor the HOMO- LUMO Gap ^[14]



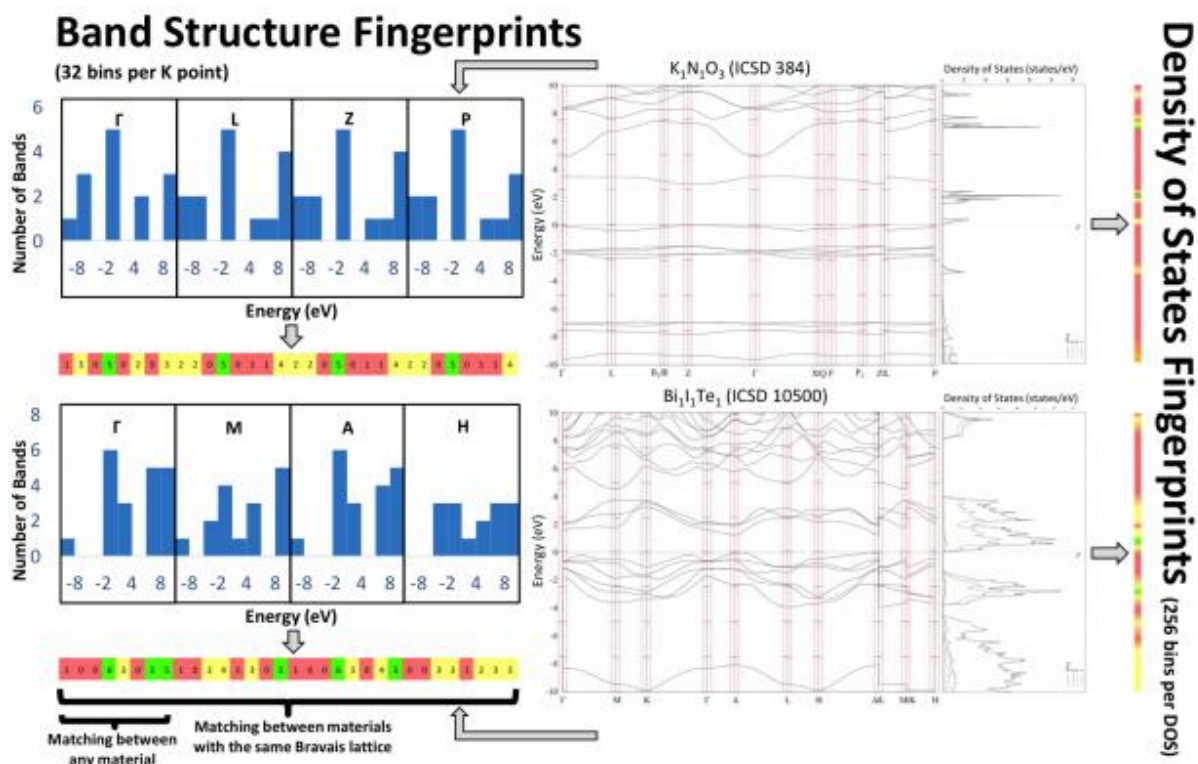


Figure 6. Construction of materials fingerprints from the band structure and the density of states. For simplicity, B-fingerprints are presented with only 8 bins. ^[37]

Cheminformatics and material fingerprints

Although the Tropsha group does not work on OPVs their advancements in cheminformatic descriptors, material's space visualization, and structure-property models is exciting, and can be applied to OPV materials. ^[37] As the gap between derived information and experimentally obtained knowledge widens, the group introduces new data analysis in the form of structural and electronic fingerprinting to make sense of the data and alleviate this issue. Material fingerprints were motivated by the need to find materials that match target material properties. Finger prints follow the assumptions that the properties of the material is a direct function of its structure and that materials with similar structure are likely to have similar physical-chemical character. The group uses the AFLOWLIB database, a collection of DFT calculations managed by the AFLOW software package, to collect data on optimized geometries, symmetries, band structures, and densities of states. In 2014, AFLOWLIB contained the results of over 20,000 different materials. This data is then converted into two distinct types of finger print: band structure fingerprints (B-FP) and density of states fingerprints (D-FP). The B-FP is defined as a combined histogram of energy eigenvalues with 32 bins and the D-FP is a string covering 256 4-byte real numbers, each number

characterizing the strength of the density of states in 256 bins across the $[-10\text{eV}, 10\text{eV}]$ interval. Encoding material characteristics in fingerprints takes the form of numerical arrays and enables the use of classical cheminformatics and machine-learning tactics to mine, visualize, and model any set of materials because of the condensed representation of chemical properties. One important cheminformatic technique the group concentrated on was similarity searches. These searches allow for the rapid and effective identification of compounds with similar properties but different compositions. As an added benefit, similarity searches also detect redundant material records in databases, which is essential for data curation on large scales. ^[29]

Some of the test cases the Tropsha group did were for barium titanate (BaTiO_3) with perovskite structure which is widely used as a ferroelectric ceramic. ^[38] Perovskite structure is the structure that calcium titanium oxide exhibits and has been identified as a possible inexpensive base material for high efficiency photovoltaics. The group found that of the six most similar matches five were well studied, although one remained, cubic YbSe , and is largely unresearched. Even though most DFT calculations do not take spin orbit coupling into effect, the test cases showed exceptionally high band structure similarities, a tour de force of B-FPs

and proof of the power of fingerprint based searches in large databases. Fingerprinting used in this way allows the discovery of unresearched materials with target properties and also succinctly displays the link between structure and property.

The Tropsha group goes on to create material cartograms which are the visual representations of library materials.^[37] Encoded by its fingerprint, each material exists as a node where similarity dictates location. The result is an accurate and informative representation of material space. While the group made a few different cartograms using AFLOWLIB, the most relevant to OPV's is the band gap map. Built using B-FPs, four large clusters appear labeled A-D. Group A is dominated by insulators and some semi-conductors. Group B consists of materials with polymetallic character. Group C features compounds with zero band gap and often feature non-metal atoms like halogenides, carbides, and silicides. Group D is characterized by having a mixed population with around 300 materials having a band gap at or below 1.5 eV and around 500 semimetals and semiconductors.^[37] With cartograms to navigate materials and fingerprints to describe them a model that aids the prediction of structure-property relationships can be created to guide novel material design. Advances in the analysis and exploration of databases may become foundational for sensibly designing new compounds with desired characteristics.

Full device modeling

A three-pronged alternative model is utilized by the Koster group to detect different pathways to efficient OPV materials, sometimes predicted to be in excess of 20% efficiency.^[39] This particular group looks at radiation limits that reveal the nature of the charge-transfer (CT) state. By looking for materials with a weak CT action, OPV's are projected to be as efficient as their inorganic counterparts. Next, exciton generation is considered by using Marcus theory modeling, which gives insight onto reorganization energies allowing the group to reduce recombination. Finally, the introduction of dielectric parameterization by means of a drift-diffusion model, is used to further PCE.

In consideration of the CT state, Shockley and Queisser introduced a fundamental thermodynamic parameter.^[40] Operating at a finite temperature, the OPV radiates black-body radiation, implying no excess

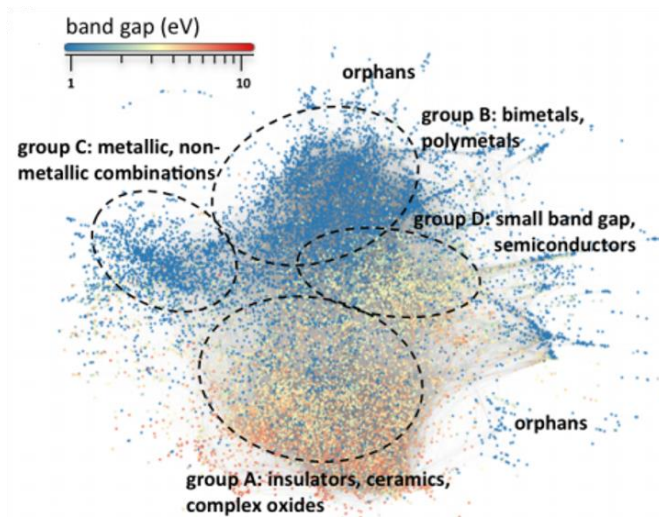


Figure 7. Mapping band gaps of materials. Points colored in deep blue are metals; insulators are colored according to the band gap value. Four large communities are outlined.^[37]

recombination takes place other than emissions. Shockley and Queisser assert this constitutes the limit to exciton generation. An ideal OPV is then projected to have 33% efficiency for optimized band gap energy. In the current state of OPV's, efficiencies are significantly lower than this projected limit due to non-radiative recombination. To approach the efficiency limit two directions can be taken, by either moving toward zero radiative recombination or toward unity CT radiative recombination. Because BHJ's operate nearer the left hand side of the minimum efficiency, it is more pragmatic to reduce the CT action. **Figure 8** shows PCE (η), open circuit voltage (V_{OC}), and current density (J_{SC}) as a function of CT action (α_{CT}).

Further analysis using Marcus theory description develops a qualitative model of exciton dissociation in addition to charge carrier recombination to the ground state. The purpose of Marcus theory description is to look at device efficiency as a function of reorganization energy reduction and the utility of both donor and acceptor as optical absorbers. Essentially, the Koster group aims to create a more realistic model of exciton/charge carrier dissociation and recombination. For example, much research does not consider the ability of acceptors to absorb light.^[41] PC₇₀BM is particularly successful in this and contributes about 25% of short circuit current. Using Marcus theory expressions for CT

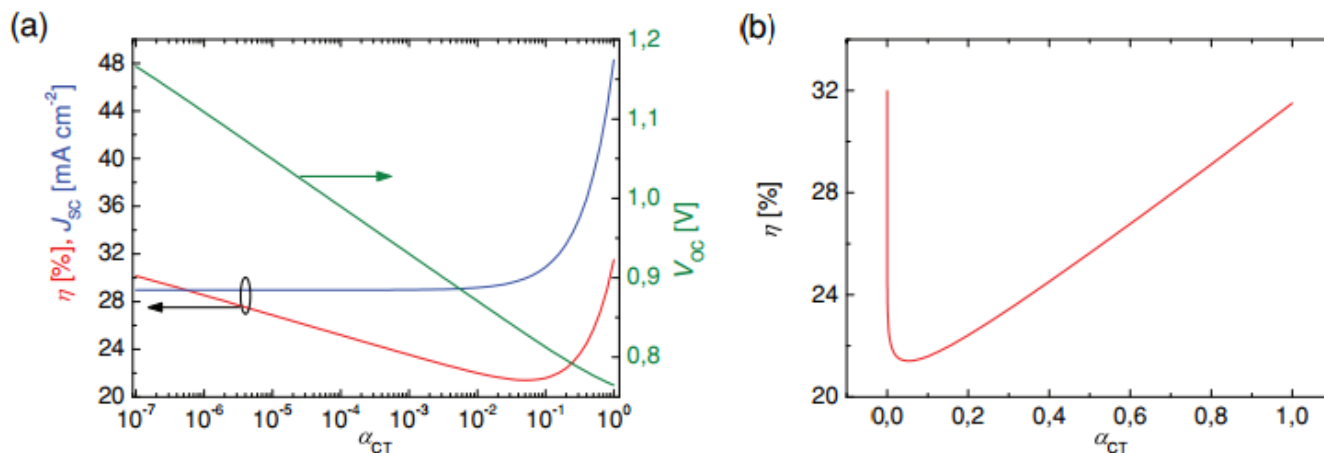


Figure 8. a) Efficiency (red), short-circuit current density (blue), and open-circuit voltage (green) calculated for $E_{gap} = 1.5$ eV and $\Delta = 0.5$ eV. b) The efficiency on a linear scale showing the two limits of zero and unity α_{CT} .^[36]

and recombination rates as functions of LUMO band offset energy; the Koster group is able to compare material parameters to find the optimal relations between materials. By minimizing Marcus reorganization energies for charge transfer in both phases, optimal band gap alignment between the phases can be created.

In another approach, the Koster group employs a drift-diffusion of charge carriers model to analyze semiconductor properties *in silico*. A BHJ model is used and treated as a one dimensional medium on which the transport of holes and electrons occur in the valence band. All recombination mechanisms take place at a slower rate if the coulomb interaction between the two carriers is reduced. With high dielectric materials, it may be possible to approach the Shockley and Queisser limit and thus increase PCE. Given such parameters a computational pipeline can be made to find optimized bang gap, followed by screening for low reorganization energies and predicted dielectric constants.

Conclusions

In summary, the problem space of OPV renewable energy research is extraordinarily complex and nuanced. However, computational chemistry, which combines a modern cyberinfrastructure paradigm with computational materials science, is a useful approach to explore this problem space. As proven, design of successful OPV materials is a multifaceted problem as a myriad of different properties and structures are required. Through the use of combinatorial libraries, vast numbers of molecules with interesting and electronically relevant characteristics can be rendered. The description

of candidate molecules, identified using rapid and effective cheminformatic descriptors, allows candidate screening based upon optimal properties, and for the visualization of material space through cartography. DFT and other more intensive characterization is the basis upon which predictive models are created and serve to predict the properties and behaviors of candidate materials. Coveted structure-property relations are discovered from patterns in the data and in turn inform rules for combinatorial libraries as a feedback loop. Computational chemistry, leveraging processing power and computational methods, plays an essential role in the expediting of rational systematic design of high efficiency OPV materials, and holds significant promise as a potential solution to future energy needs.

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Dear members of the award review committee,

It is a pleasure for me to recommend Andrew Hoffman for a 2015 WWU Libraries Undergraduate Research Award. During the preparation of his paper "Computational Chemistry in Rational Material Design for Organic Photovoltaics" for CHEM 405: Intensive Writing in Chemistry or Biochemistry, Andrew developed and demonstrated proficient use of library resources. Thanks to his access to the primary literature in topics ranging from computational chemistry to energy and climate change, Andrew was able to prepare a paper that draws important connections between computational screening methods and their role in photovoltaic materials research.

Andrew approached me about an intensive writing project after taking the first quarter of the physical chemistry sequence with me in Fall 2014. Once we settled on a topic area, Andrew took ownership of the subsequent literature search, seeded only by a few articles I selected as literature guideposts. Thereafter, the identification of research articles whose content supports his thesis was his task alone. The discussion of both seminal works and state-of-the-art studies within the report reflects his use of online tools for tracking backward and forward citations of key articles. WWU libraries' online access to journal collections such as ACS Publications makes these citation searches especially convenient. Still, it is evident from Andrew's paper that his search was not publication-biased because he also made use of cross-publisher, cross-platform search tools such as Web of Science to identify important related work. In at least one instance, when a critical article was not held within the library's collection, Andrew took advantage of PDF delivery through InterLibrary Loan (ILLiad) to continue his study.

The completion of Andrew's paper did not require substantial utilization of physical resources at the library. While most every field of study at Western can find value within the physical holdings of the library, in the case of Andrew's study I believe his near-exclusive use of digital resources reflects the high level of efficiency that can be obtained with the modern library resources available to us at WWU. The resulting paper makes a convincing argument for the value of computational screening in organic photovoltaic materials discovery, an argument that relies on Andrew's success in the retrieval, analysis, and interpretation of information from his library research.

Best regards,



Tim Kowalczyk