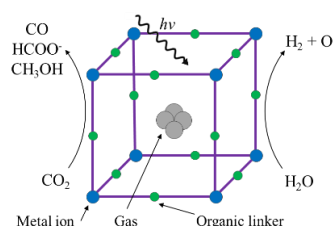


Overview: The proposed project utilizes *ab initio* non-adiabatic molecular dynamics, in order to determine the feasibility of metal-organic frameworks (MOFs) being used as new semiconductor materials for applications such as transistors, diodes, solar cells, and photoelectrochemical cells, as well as applications in catalysis. MOFs are an improvement over current semiconductor technology, based on the limitations that MOFs are able to overcome. The current limitations of semiconductor materials are numerous: bulky and inconsistent and randomly-assembled structures give rise to the inefficiency of charge transfer, unstable in moist environments and sometimes not even air stable.¹ MOFs have been shown to have stable, self-assembled, three-dimensional structures that are robust, even in varied environments.² The ability for self-assembly fabrication is key to a reduction in the size of the materials because it eliminates the need to rely on macroscopic production methods. Their periodic nature keeps the metal ions fixed between organic linkers at constant mutual distances.

The coordination between organic linkers and transition metal ions could prolong the electron-hole recombination time. Prolonging electron-hole recombination time is essential for charge separation. If the electrons can be collected after the separation, an electric potential is created which can be used to do work. The greater the charge separation, the greater the ability to generate a current of useful magnitude. In addition to the prospect of novel semiconductor materials, MOFs are ideal candidates for photocatalysis due to their construction with metal centers that can easily be used in catalysis. Since MOFs have cavities employed in gas storage



applications,³ MOFs could easily be altered for use in catalysis, due to tunable cavity size that could house catalytic sites. Constructing a MOF with titania and doping with various photosensitizers/dyes will make them tunable to several applications, including photocatalytic water splitting. Due to a record surface-to-volume ratio, MOF photocatalysis would become the leader in the efficiency of converting and storing sunlight's energy. (Image adapted.⁴)

Intellectual Merits: Prediction and control of photoexcitation dynamics are possible through time-dependent theoretical methodologies, such as non-adiabatic coupling, energy transfer, charge transfer, recombination, and carrier multiplication processes in photo-catalytic MOF materials. Electron-phonon dynamics are an important analysis that has not yet been applied to MOFs. Once you excite a material, it has vibrational modes; these modes are the phonons. Charge carrier recombination can release light or heat energy as a phonon vibration of the material. Modes of relaxation can be calculated and used to determine electronic properties of materials. Performing these calculations can be a challenge, considering that examining molecules in excited states is difficult. It is often necessary to make some assumptions and simplifications in order to reduce the number of degrees of freedom (DOF). For example, Redfield's theory of an electron's relaxation includes the influence of vibrational DOF on electronic DOF and also removed vibrational DOF from explicit consideration. Upon building reliable atomistic models, electron-phonon dynamics can be computed and then converted into typical observables such as time-resolved spectra and frequency-dependent response functions, surface photovoltage measurements, and current-voltage characteristics of the nanostructures in the ground and photoexcited states. Observables I plan to calculate and compare to experimental results are oxygen and hydrogen evolution rates, UV-Vis and X-ray diffraction spectra, and lifetimes of photoexcitation.

One of the main challenges in this project is the presence of transition metal ions throughout the MOF structure. Computation involving these atoms becomes increasingly difficult with the increasing mass of atoms due to non-negligible relativistic effects and spin-orbit coupling, which increases computing time because spin up and spin down must be calculated in a coupled way in order to maintain an acceptable level of accuracy. Moreover, the presence of a metal center which has the ability to produce multiple oxidation states and coordination numbers in conjunction with the periodic nature of MOFs makes locating absolute minima difficult due to the high number of local minima scattered throughout the potential energy surface.⁵ Multiple coordinate scans may need to be performed in order to find the local minima.

An inspection of MOFs as a future photocatalyst involves modeling reactions. Modeling a reaction mechanism is challenging when considering side reactions and equilibria. Overcoming this challenge requires a deep understanding of the reaction mechanism, in order to predict these side reactions. During the proposed catalysis reaction utilizing MOFs, a molecule such as H₂O, forms a temporary bond with the titania complex, causing a chemical reaction which breaks apart the water molecule into O₂ and H₂ gases. A primary benefit of modeling MOFs is the ability to optimize the structures based on modifying all the building blocks. For example, the size of the titania dopants, length and shape of organic linkers, amount and type of dyes could all be optimized considering the calculated optoelectronic properties.

Broader Impacts: Light-harvesting materials are necessary for reducing dependence on fossil fuels. Solar cells and water-splitting are promising frontiers to attain this goal. A deeper understanding of optoelectronic properties of MOFs, gained through theoretical studies, can guide material engineering efforts toward improving, for example, the efficiency of solar conversion energy. Studies of surface exciton transfer between nanostructures and photosensitizers (MOFs manufactured with titania and dyes respectively) will assist the design process for photovoltaic and photoelectrochemical devices.

Uniform construction via self-assembly leads to quantum states of ions that would serve to process information in a parallel way. This property could lead to improvements in quantum computing, due to the highly conjugated *pi*-metal system that would allow electrons to be found anywhere within the system (superposition).⁶ Exploiting this possible application will result in the need to develop new methodology and write code, thereby furthering computational chemistry as a field.

References:

1. Ameri, T.; Khoram, P.; Min, J.; Brabec, C. J., *Adv. Mater.* **2013**, 25 (31), 4245-4266.
2. Wu, C.-M.; Rathi, M.; Ahrenkiel, S. P.; Koodali, R. T.; Wang, Z., *Chem. Commun. (Cambridge, U. K.)* **2013**, 49 (12), 1223-1225.
3. Wang, Z.; Tanabe, K. K.; Cohen, S. M., *Chem. - Eur. J.* **2010**, 16 (1), 212-217, S212/1-S212/29.
4. Zhang, T.; Lin, W., *Chemical Society Reviews* **2014**, 43 (16), 5982-5993.
5. De Angelis, F.; Fantacci, S.; Sgamellotti, A., *Coordination Chemistry Reviews* **2006**, 250 (11-12), 1497-1513.
6. Kloeffer, C.; Loss, D., *Annu. Rev. Condens. Matter Phys.* **2013**, 4, 51-81.