

2023

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Etnyre, Christian D. (2023) "Modeling Exciton Migration in Two-Dimensional Space," *DePaul Discoveries*: Volume 12, Article 4.

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Acknowledgements

This research would not have been possible without the help of my faculty advisor, Dr. Graham Griffin. I especially want to thank him along with the DePaul University Department of Chemistry for supporting me since I began this project in the spring of 2020.

Modeling Exciton Migration in Two-Dimensional Space

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ABSTRACT Computational analysis through density matrix quantum mechanics was performed to model exciton migration in two-dimensional space for a zinc-substituted tetraazaphthalocyanine. The model produced resembles a two-dimensional sheet of molecules. Energy transport mechanisms, controlled by point dipole couplings, were evaluated while altering the size of the crystal lattice. It was determined that energy transport was much more significant with a decreasing size of the crystal lattice. Likewise, the result of increasing the size of the crystal lattice had the effect of dampening the rate of energy transport. It was of interest to determine, with varying crystal lattice dimensions, the time that it would take for an excitation placed at one site to migrate across the lattice and back to its original site.

INTRODUCTION

Phthalocyanines are a group of molecules that are of interest for their possible industrial use in photovoltaic cells. Specifically, these compounds are used in many forms of dye-containing materials such as paint, printers, or markers (Liebold et. al, 2018). Another aspect of this class of molecules that is of interest is their self-assembly into a crystal lattice structure. This crystal lattice structure allows for a modeling of exciton migration which was performed in this study. Molecules which assemble into a crystal lattice structure are especially useful for modeling exciton migration due to the close packing that allows for interactions between the components of the crystal lattice.

Exciton migration is defined as the downhill flow towards lower energy sites of an electron-hole pair that originates at a certain molecule (Zhou

et. al, 2020). An exciton corresponds to a neutral pseudoparticle that consists of an excited electron and its associated hole. The hole comes from the idea that the electron in the lower energy level will be “missing” when it is excited to a higher, empty orbital or energy level. Essentially, an exciton will travel in the direction that is most energetically favorable, from one site to another while being restricted by the dimensions of the lattice. Two-dimensional systems are of interest particularly due to their presence in biological light-harvesting processes such as photosynthesis (Cao et. al, 2017). In two-dimensional systems, there is more restriction on the directionality that exciton migration can have. Exciton migration is also dependent on the transfer rate of the system (Demin et. al, 2010). For systems that have high transfer rates, the resulting energy flow rate of the

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Research Completed in Winter 2023

system will be increased as well. In contrast, systems with low transfer rates are prone to slower energy flow rates.

The most efficient systems of exciton migration are those in which there is restriction on travel. Therefore, linear or two-dimensional models have the most efficient processes of exciton migration as there is clear directionality as to where an exciton may flow (Nakano et. al, 2009). When there is more opportunity for divergence in the path that an exciton may take, there is a decrease in efficiency for the route taken from one point to another in a lattice. The model generated in this study allows for the analysis of various points of excitation along varying crystal lattice dimensions. Therefore, an excitation can be placed anywhere within the matrix and its effect on neighboring points can be measured over a defined period of time. It can be of interest to determine for various compounds the optimal dimensional orientations that will allow for effective electronic couplings between molecular substituents. Electronic couplings refer to the electronic interactions that exist between sites of possible excitation. These couplings are dependent on both the relative orientation and the magnitude of the transition dipole moment for

excitation at each site. The transition dipole moment is a vector quantity representing the change in electron density upon excitation of the corresponding site. The transition dipoles thus determine the interaction strength between sites. Information regarding optimal dimensional orientations and their relationship to point dipole couplings can give valuable insight as to the efficiency of use for various photovoltaic cells as potential energy sources.

Phthalocyanines of particular interest for their photodynamic capabilities are those with strong metal to ligand interactions, as these allow for the most efficient exciton transfer mechanisms (Vivas et. al, 2014). Literature phthalocyanine comparison has focused on the effect of changing the center metal atom to evaluate the subsequent conducting capabilities of the phthalocyanine after undergoing a change in its central atom. The way in which a phthalocyanine is organized in space is of interest in determining efficacy as an organic semiconductor (Alkhamisi et. al, 2018). This, along with evaluating the effect of point dipole coupling on exciton migration, can assist in evaluating various phthalocyanine systems for real-world use as an energy source.

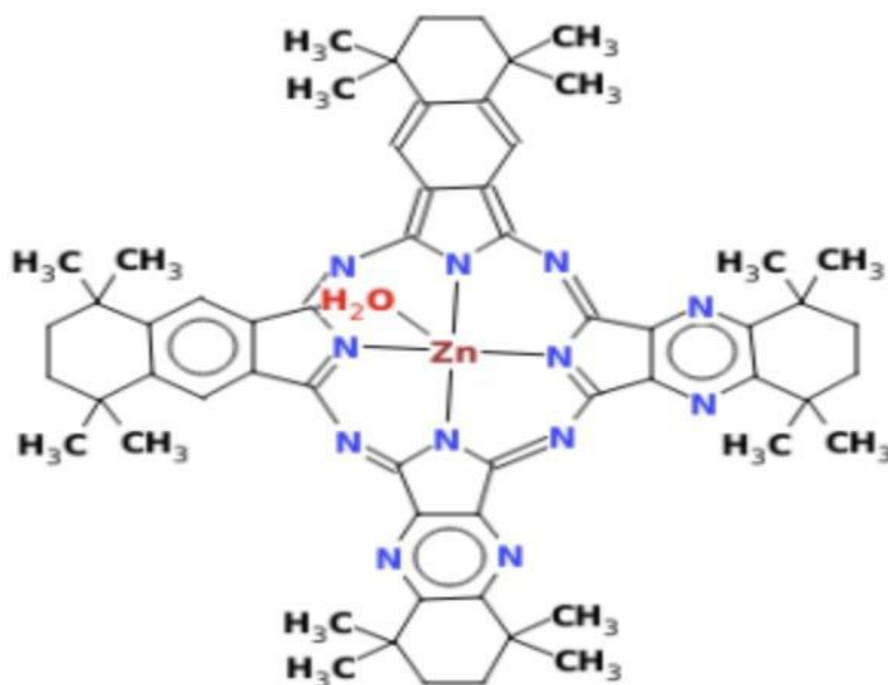


Figure 1. Chemical structure of $A_2B_2; N_4-Pc^*Zn$
(A: isoindoline, B: pyrrolopyrazine)

METHODS

The crystal structure for the zinc-substituted tetraazaphthalocyanine (Figure 1) used in this study was analyzed to determine the site spacings in the molecule's arrangement into a crystal lattice. Literature values for site spacings in two-dimensional space were used (short axis: 6.0419 Å, long axis: 31.008 Å).¹ These site spacings were used geometrically to create a model of the crystal lattice, from which exciton migration was modeled. The site spacings were also used to calculate an original transition dipole magnitude (38.3260 D) and excitation energy (1.5876 eV) which were used to perform Hamiltonian mechanics (Eq. 1) on the system (Bednarz, et. al

2017).

$$H = \sum_{m=1}^N [\varepsilon] |m\rangle \langle m| + \sum_{m \neq n} [J_{TS}] |m\rangle \langle n| \quad (1)$$

In the context of this equation 1, the variables “m” and “n” refer to the dimensions of the matrix. The Hamiltonian equation incorporates site energies (ε , 1.5876 eV) as the diagonal matrix elements of the Hamiltonian for the system. These terms represent the energy of exciting each tetraazaphthalocyanine represented in the model. The equation also incorporates through-space electronic couplings (J_{TS}) as the off-diagonal elements of the Hamiltonian ($m \neq n$). The couplings were calculated using the point dipole approximation, resulting in values vary from magnitudes of 0.00272 to 2.72 eV. Using the calculated Hamiltonian (H) incorporating the point dipole couplings measured for this system,

RESULTS

It was of interest to determine the effect of altering the transition dipole magnitude on exciton migration rates. Particularly of interest was the evaluation of the ways in which an excitation placed at one corner of a square lattice would migrate to the opposite corner of the lattice (Figure 2).

time propagation was performed using the quantum Liouville equation (Eq. 2) (Mukamel, 1999). This equation incorporated the previously calculated Hamiltonian (Eq. 1) along with the density matrix (ρ). The density matrix gives information about the state of a system, either existing in a pure or a mixed state. Diagonal elements of the density matrix represent normalized population at each tetraazaphthalocyanine molecule, while off-diagonal elements report on coherent behavior. Time derivatives were approximated using the 4th-order Runge Kutta method.

$$\frac{d\rho}{dt} = -\left(\frac{i}{\hbar_{bar}}\right) [H, \rho] \quad (2)$$

Excitations were placed at various points among the matrix to determine effects on neighboring substituents over time. Plots were generated which depicted the time vector as a function of the change in the density matrix over time at the excitation point to determine the point-dipole coupling effects on the system. Measurements were performed over a series of varying parameters, such as a change in the transition dipole magnitude as well as a change in lattice dimension.

The software used to generate this model was GNU Octave. This program is designed by the developers to be compatible with the programming language used in MATLAB. The software is free to download and accessible to anyone.

By monitoring exciton migration patterns diagonally across a square lattice, the maximum coupling effect was experienced as the excitation was allowed to transverse the longest possible distance of the lattice. Placing an equivalent excitation at one corner (1,1) of an equally spaced, 3x3 matrix, plots were generated to model migration rates as a function of time using various transition dipole magnitudes (Figure 3).

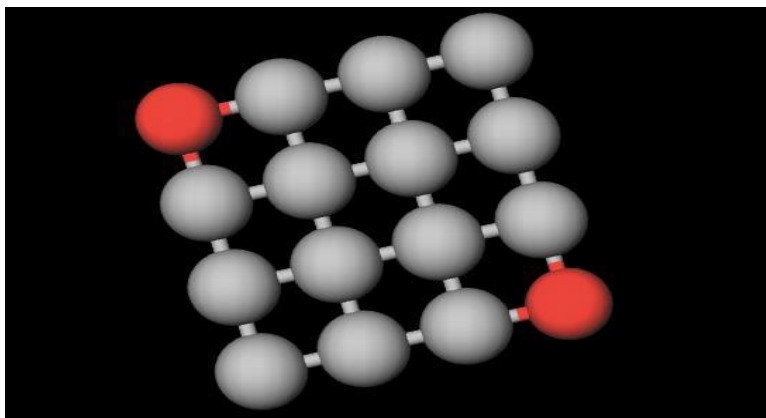


Figure 2. Representative 4x4 lattice depicting sites which were monitored. An excitation would be placed at one site while monitoring both sites over time.

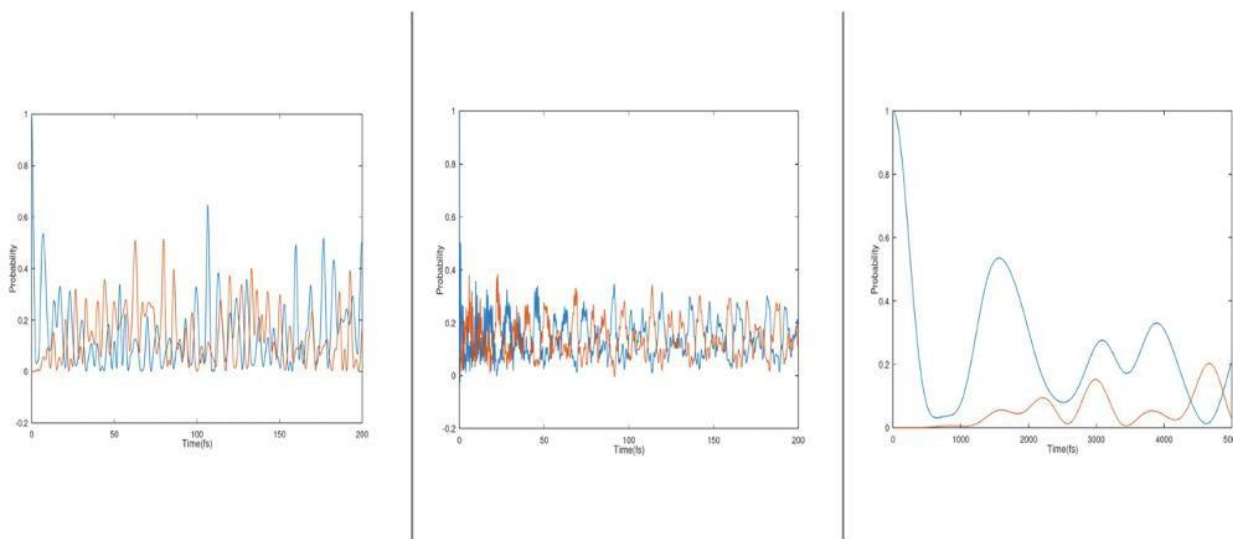


Figure 3. Site populations at point (1,1) (blue) and point (9,9) (red) as a function of time with transition dipole magnitudes of 38.3270 D (3a), 127.079 D (3b), and 0.393456 D (3c), respectively. An excitation was placed at point (1,1).

Based on the plots generated, an alteration of the transition dipole magnitude of this system has a significant effect on the exciton migration rates of this system. In fact, when altering the

transition dipole magnitude to 127.079 D, the time in which it takes for the excitation to populate significantly at point (9,9) decreases significantly from approximately 30 fs to approximately 10 fs. When the transition dipole magnitude is increased, the point dipole coupling of the system increases as well, stimulating further the interaction potential of sites in the lattice. Conversely, a decrease in transition dipole magnitude has the effect of reducing

interaction potential between sites in the lattice. As depicted in Figure 3c, when altered to 1 au, this change in transition dipole magnitude leads to no significant population in point (9,9) for a relatively long period of time (1000 fs) before any population begins to occur. Another factor of interest for its potential effect on exciton migration rates was the size of the crystal lattice. Theoretically, with uniform site spacings the

crystal structure of ZnPc could extend in all directions infinitely. Therefore, it was of interest to determine, based on the calculated transition dipole magnitude from the structure of the compound, whether certain arrangements were more efficient than others. Plots were generated (Figure 4) which depict migration rates as a function of time for varying lattice dimensions.

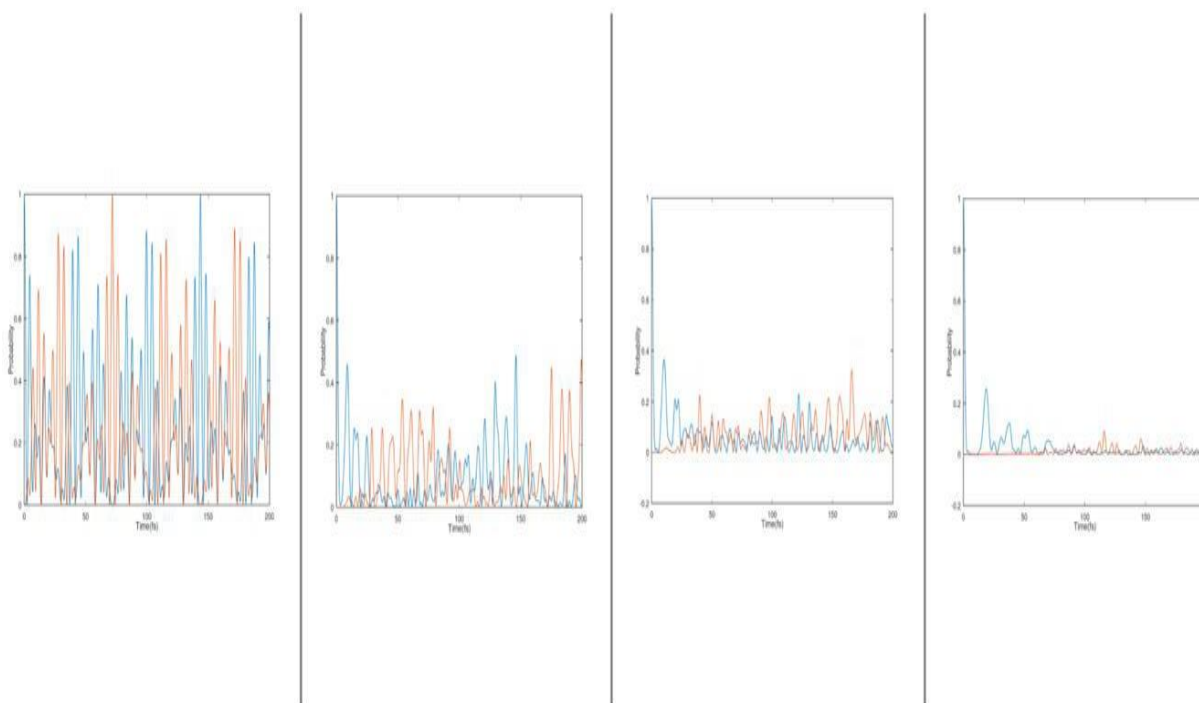


Figure 4. Site populations at point (1,1) (blue) and point (n,n) (red) as a function of time with matrix sizes of 2x2 (4a), 4x4 (4b), 5x5 (4c), and 10x10 (4d), respectively. An excitation was placed at point (1,1) with a transition dipole magnitude of 38.3270 D.

It is evident that when the size of the crystal lattice is decreased, the effect of a transition dipole on exciton migration is greatly increased. For example, for a 2x2 matrix where there is an equal relationship between diagonal and off-diagonal elements in the matrix, the coupling factors are significant and as a result the exciton migration between corner sites is in almost

perfect oscillation. Conversely, an increase in crystal lattice size has a negative effect on the ability of a transition dipole to influence interactions between sites on the lattice. As depicted in Figure 4, when the size of the lattice is increased, it is apparent that over a time period of 200 fs that the excitation does not reach the opposite corner in significant capacity. With increasing lattice size, the number of off-diagonal elements of the matrix greatly exceeds the number of diagonal elements, leading to significant dissipation of the original excitation. It is clear that exciton migration is both heavily influenced by both the coupling factor present in

a compound as well as the spatial arrangement that a compound assembles into.

DISCUSSION

Generation of this model allows for comparison of various organic molecules for use as potential photovoltaic cells. Through evaluation of point dipole coupling effects over time, information such as a compound's packing efficiency and interaction lifespan can be gained. Future work which may originate from this model is an evaluation of dephasing rates over time to determine the rates at which interactions between sites degrade over time. The limiting factor of this model is the processing ability of the machine used to calculate the time propagation step; however, it would also be of interest to apply this model to large-scale structures to determine the point that the model breaks down. Future work could also include the determination of directionality with respect to the way that coupling progresses through a system. This could be accomplished through the use of non-square lattice structures and an examination of the

resulting Hamiltonian matrix that is created. From this, it can be evaluated whether there is a preferred direction that the couplings tend to move in while acting on a system.

CONCLUSION

The model generated in this study allows for the possibility of future work surrounding exciton migration in a lattice. There are a variety of parameters, such as random noise and a dephasing function that can be incorporated into the model to mimic a “real-world” system at work. Conversely, “random” parameters can be turned off as well in order to simply compare the expected behaviors of multiple structures. The importance of this study is not focused on the exact compound used, rather it is focused on the model which allows for the examination of various compounds. This model will allow for the real-world analysis of various photovoltaic cell candidates, and it is the objective of this study to showcase a clear example of how this model can be applied.

ACKNOWLEDGEMENTS

The author would like to acknowledge Dr. Graham Griffin, as without his guidance and support this research would not be possible.

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