

**Intel STS 2014: The Effect of Electron Correlation on Excitonic Energy Transfer in a
Synthetic Chromophore System**

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Personal

My love for chemistry is largely because of my high school chemistry teacher, Mrs. Brucker. I have had the good fortune of knowing Mrs. Brucker for all four years of high school, having her for three chemistry classes and being her TA for two years. Both her engaging teaching style in the classroom and passion for chemistry motivated my own curiosity and excitement for the subject. As a result, I decided to explore chemistry outside of school and learn about it in a deeper way I had never encountered before. I wanted to find a place I could volunteer my time during the summer, and so, I searched the UChicago Chemistry Department's faculty page to see the different types of chemistry that these incredible professors were working on. The theoretical work in Professor Mazziotti's group caught my eye, as I had never worked with computationally modeling and representing with mathematics a variety of chemical systems before. And so, I worked with Professor Mazziotti and his group (mainly Andrew Valentine, a PhD student) over the summer of 2013 at UChicago, and had one of the coolest experiences in my entire life! I learned more about the complex mathematics and the quantum mechanics behind the way chemical systems work, and it made the relationship between mathematics and science much clearer to me than it ever was before. My advice to any student who would like to conduct research combining science and mathematics would be to not be afraid of the unknown because although we may not have a lot of experience with many mathematical concepts, there are lots of resources out there to help further understanding and people who will support you throughout the way, which makes things a whole lot less daunting.

Research

I. Introduction

Recent experimental studies have shown how the quantum mechanism of electronic coherence is essential in the efficient energy transfer systems of the photosynthetic Fenna-Matthews-Olson (FMO) complex found in green sulfur bacteria [1-3]. The FMO protein structure consists of a central magnesium atom surrounded by three identical monomers, each embedded with seven bacteriochlorophyll chromophore molecules, with an eighth additional bacteriochlorophyll chromophore between each of the three monomers [4]. The FMO acts as a mediator, efficiently facilitating the energy transfer from the light-harvesting antennae, known as chlorosomes, to the reaction center where the energy conversions of photosynthesis take place.

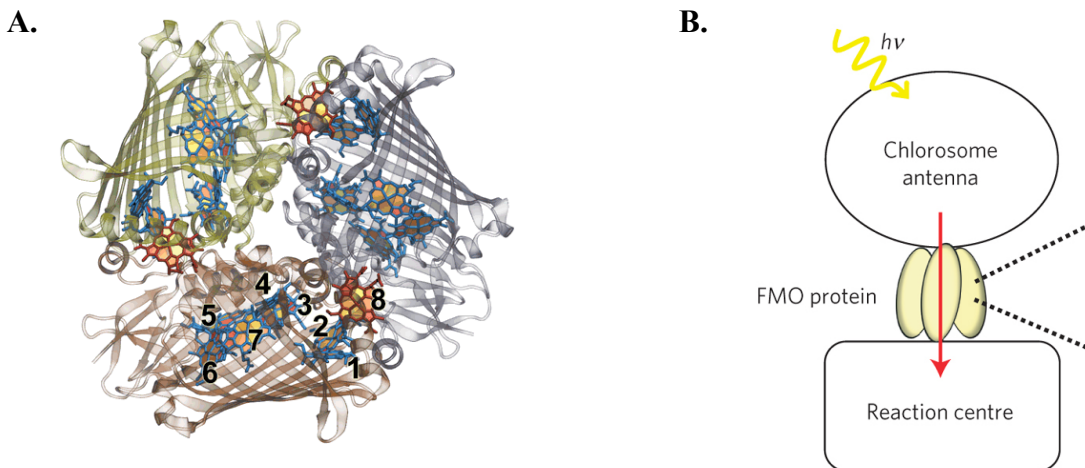


FIG 1: (A) The Fenna-Matthews-Olson (FMO) complex consists of three monomers with seven chromophores, and an additional eighth chromophore between the three monomers [4]. (B) The FMO is situated between the chlorosomes and the photosynthetic reaction center [5].

The quantum beating signals among the excitons in the 2D electronic spectra of the FMO illustrate the sustained quantum coherence of the FMO [1]. This allows for greater energy transfer efficiency because the FMO is now able to survey large phase space regions to locate the most efficient path for energy transfer [1]. Using the FMO and its quantum properties as

inspiration, researchers have engineered a heterodimer system that allows for this same sustained quantum coherence [6]. The heterodimer comprises of two halofluorescein monomers linked together by rigid piperazine molecules. The 2D electronic spectra of the heterodimer shows the same quantum beating signals necessary for persistent electronic coherence, as observed in the FMO, suggesting that this synthetic chromophore is able to transfer energy as efficiently as the FMO [6]. The study also proposes that long-lived quantum coherence, and therefore, efficient energy transport, are general properties of closely positioned, electronically coupled chromophores in a fixed orientation [6]. However, another significant property of this efficient energy transport has been overlooked. Strong and enhanced electron correlation, which is defined as the increased interactions between all the electrons in a given quantum system, has been shown by recent theoretical studies by Mazziotti [7] to be employed by the FMO in order to maximize the efficiency of energy transfer from the chlorosomes to the photosynthetic light harvesting reaction center. The study found that by increasing the number of electrons per chromophore from one to four into the N-electron Lipkin-Meshkov-Glick (LMG) model, thereby incorporating strong electron correlation as a variable, the efficiency of energy transfer from the chlorosomes to the reaction center by the FMO increases by more than 100% [7]. In my project, the effect of strong electron correlation on energy transfer efficiency is analyzed by substituting different electron-donating and electron-withdrawing groups on the synthetic chromophoric system engineered by Hayes *et al.* [6]. After changing the electronic structure with different substituent groups, the different rates of excitonic energy transfer from each substitution can then be compared.

II. Methods

A. The Synthetic Chromophoric System

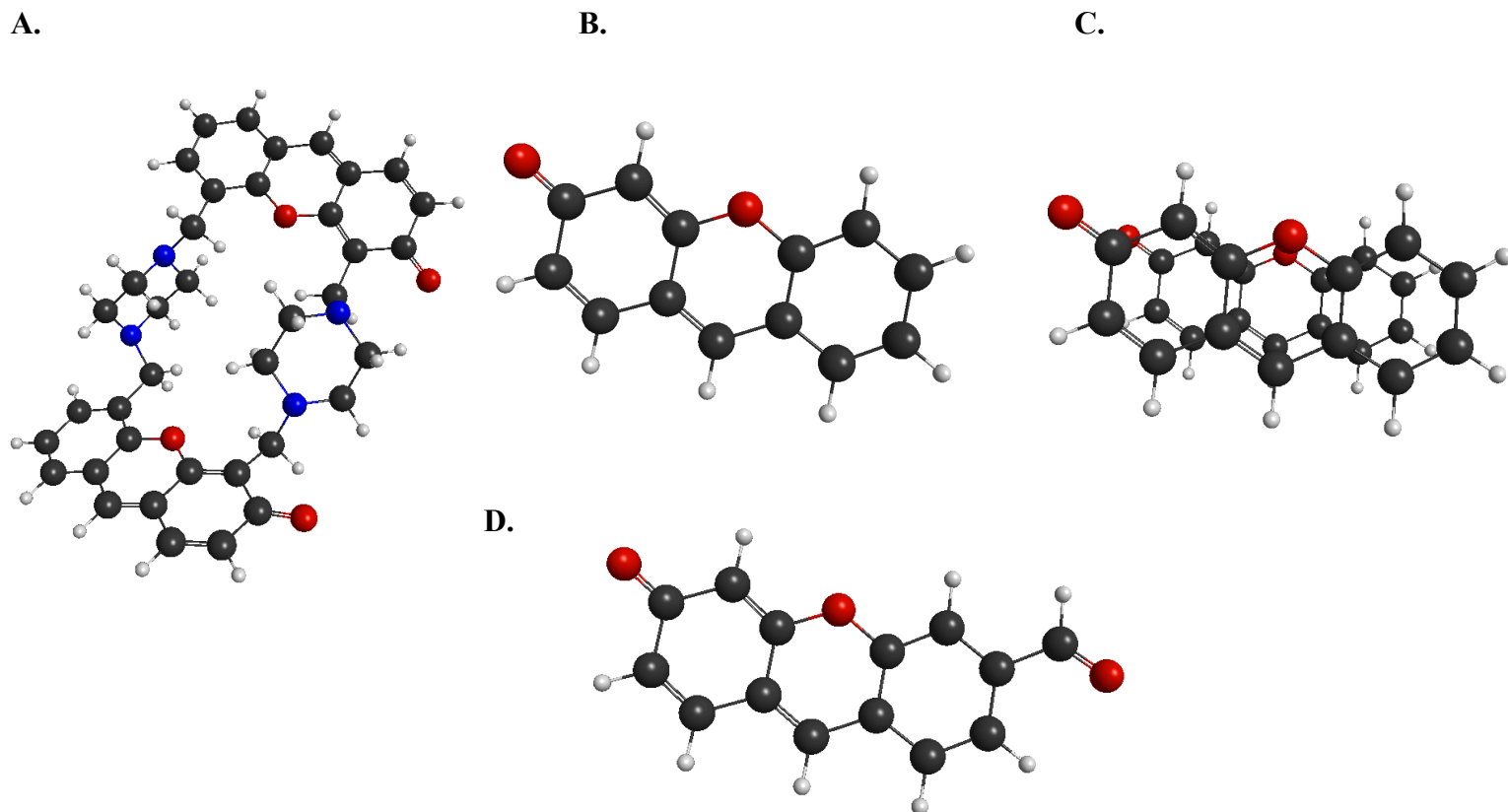


FIG 2: (A) The fluorone dimer with piperazine linkers. (B) The fluorone monomer. (C) The fluorone dimer without the piperazine linkers in a parallel-0° orientation. (D) The fluorone monomer with an aldehyde substituent group.

The monomer and dimer structures used in this study, shown in FIG 2, are modified structures derived from the synthetic heterodimer exhibiting long-lived quantum coherence, engineered by Hayes *et al* [6]. The modifications are as follows: the two rigid piperazine linkers between the two monomers and the two benzene rings at the ends of the heterodimer are removed, leaving two fluorone monomers. The geometry of a single fluorone monomer is optimized using the Becke 3-Parameter Lee-Yang-Parr (B3LYP) functional with a Dunning/Hay (DH) atomic orbital basis set, shown in FIG 2 (B). Two geometry-optimized fluorone monomers

are then placed in a parallel- 0° orientation, shown in FIG 2 (C), to create a fluorone dimer. To examine electron correlation changes, different functional groups, an aldehyde, amine, and a hydroxyl, are substituted onto the fluorone dimer, shown in FIG 2 (C). An aldehyde-substituted fluorone monomer is shown in FIG 2 (D). These substituted functional groups are either electron-withdrawing or electron-donating, which is how the electron correlation strength is changed. Electron-donating groups increase the electron density of the overall chemical system, therefore increasing and strengthening electron correlation, while electron-withdrawing groups decrease the electron density of the overall chemical system, and therefore decreasing and weakening electron correlation. All ground-state and excited-state energy calculations were conducted using time-dependent density functional theory (TDDFT) with the B3LYP functional and a DH atomic orbital basis set. The General Atomic and Molecular Electronic Structure System (GAMESS) was used to perform all of the geometry optimizations and energy calculations in this report [8].

B. Theory

To model the synthetic chromophoric dimer system, a 2x2 excitonic Hamiltonian is introduced, as shown below:

$$\hat{H} = \begin{pmatrix} \epsilon_1 & V \\ V & \epsilon_2 \end{pmatrix} \quad (1)$$

The individual chromophores are represented as single-electron sites with both their excitation energies and couplings. The matrix elements are then generated by the *ab initio* calculations derived from the Davydov splitting method [9]. At infinite separation, the energies of the two identical fluorone monomers are equal to each other, but as they move closer together and start to interact with each other, the degenerate excited states begin to split into two. When this

splitting occurs, the energy state of one chromophore is raised an equal amount as the other energy state of the other chromophore is lowered. Because of this property, the energy of the two excited states of the chromophores relative to the ground state energy of each chromophore can be calculated. The 2x2 Hamiltonian at a given monomer separation distance of “r” can now be written as this:

$$\hat{H} = \begin{pmatrix} (\epsilon_1 + \epsilon_2)/2 & V \\ V & (\epsilon_1 + \epsilon_2)/2 \end{pmatrix} \quad (2)$$

The diagonal elements of the Hamiltonian are now the average excitation energies of the two excited states, and the off-diagonal elements are half of the energy splittings of the two excited states, known as the coupling energies. After diagonalizing the Hamiltonian, as shown below:

$$\hat{H} = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \quad (3)$$

the resulting eigenvalues are then representative of the lowest excitation energies of the chromophoric dimer system.

In order to model the time-dynamics of the chromophoric dimer system, the quantum Liouville equation is utilized:

$$\frac{d}{dt}D = -\frac{i}{\hbar}[\hat{H}, D] \quad (4)$$

where D is the 2x2 Hamiltonian of Equation (2). The time-independent Hamiltonian has an initial excitation on chromophore 1, and is then allowed to evolve under Equation (4), leading to an oscillatory representation of the excitations of each chromophore. Noise from the

environment, including dephasing, dissipation, and the transfer of energy to the reaction center (sink), has also been shown by recent theoretical studies to assist excitonic energy transfer [5, 10-15]. In order to represent these environmental effects, a Lindblad operator, L , can be added to the quantum Liouville equation, resulting in:

$$\frac{d}{dt}D = -\frac{i}{\hbar}[\hat{H}, D] + L(D) \quad (5)$$

where the Lindblad operator can be divided into three more operators:

$$L(D) = L_{deph}(D) + L_{diss}(D) + L_{sink}(D) \quad (6)$$

By incorporating these environmental effects into the quantum Liouville equation, there is now an accurate model to represent the time-dynamics of the synthetic chromophoric dimer system.

III. Data and Results

TDDFT calculations for excitation energies of the fluorone dimer and all of its substituted variations, as a function of monomer separation, are presented in Figures 3 and 4. The fifth and sixth excitations are the lowest excitation energies for each chromophoric dimer structure.

FIG 3: 5th and 6th Excitation Energies (Hartree) for the aldehyde-substituted fluorone dimer and fluorone dimer.

Distance (angstrom)	Aldehyde 5th Excitation	Aldehyde 6th Excitation	Fluorone 5th Excitation	Fluorone 6th Excitation
6	0.096743	0.098946	0.1064662	0.1087399
6.5	0.09698	0.098877	0.1067446	0.1086741
7	0.097187	0.098819	0.1069784	0.1086216
7.5	0.097359	0.098771	0.1071697	0.1085783
8	0.097502	0.098729	0.1073271	0.1085422
8.5	0.09762	0.098694	0.1074573	0.1085119
9	0.09772	0.098664	0.1075658	0.1084862

9.5	0.097804	0.098638	0.1076568	0.1084642
10	0.097876	0.098615	0.1077336	0.1084454
10.5	0.097937	0.098596	0.1077989	0.1084291
11	0.09799	0.098579	0.1078546	0.108415
11.5	0.098036	0.098564	0.1079025	0.1084027
12	0.098075	0.098551	0.1079438	0.108392
12.5	0.09811	0.09854	0.1079796	0.1083826
13	0.09814	0.09853	0.1080108	0.1083743
13.5	0.098167	0.098521	0.108038	0.1083669
14	0.098191	0.098513	0.1080619	0.1083604
14.5	0.098212	0.098506	0.108083	0.1083546
15	0.098231	0.0985	0.1081016	0.1083494
15.5	0.098247	0.098494	0.1081182	0.1083448
16	0.098262	0.098489	0.1081329	0.1083406
16.5	0.098276	0.098485	0.108146	0.1083369
17	0.098288	0.098481	0.1081577	0.1083335
17.5	0.098298	0.098477	0.1081683	0.1083305

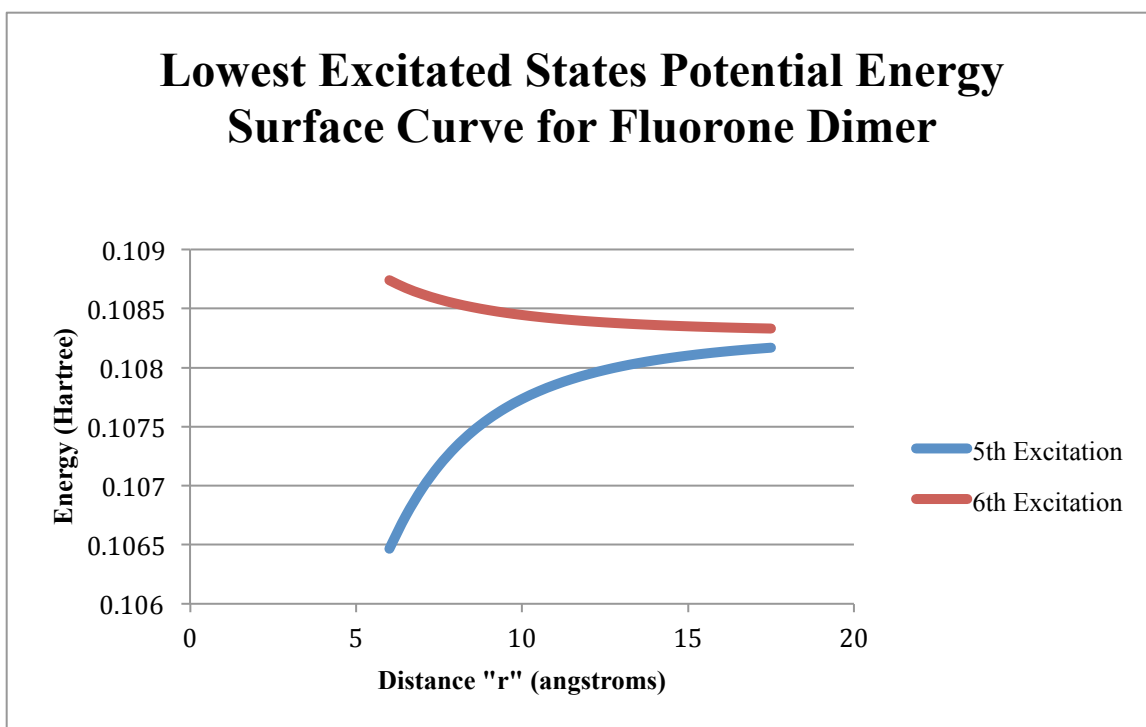
FIG 4: 5th and 6th Excitation Energies (Hartree) for the amine-substituted and hydroxyl-substituted fluorone dimers.

Distance (angstrom)	Amine 5th Excitation	Amine 6th Excitation	Hydroxyl 5th Excitation	Hydroxyl 6th Excitation
6	0.107755	0.111642	0.108609	0.11163
6.5	0.108144	0.111481	0.108939	0.111517
7	0.108465	0.111342	0.109212	0.111421
7.5	0.108725	0.111221	0.109434	0.111338
8	0.108939	0.111116	0.109615	0.111266
8.5	0.109116	0.111025	0.109764	0.111205
9	0.109263	0.110944	0.109889	0.111151
9.5	0.109387	0.110874	0.109993	0.111105
10	0.109492	0.110812	0.11008	0.111064
10.5	0.109581	0.110758	0.110155	0.111029
11	0.109657	0.11071	0.110218	0.110998
11.5	0.109723	0.110668	0.110272	0.11097
12	0.10978	0.110631	0.110319	0.110946
12.5	0.109829	0.110598	0.11036	0.110925
13	0.109872	0.110568	0.110395	0.110906
13.5	0.109909	0.110542	0.110426	0.110889
14	0.109942	0.110518	0.110453	0.110874
14.5	0.109971	0.110497	0.110477	0.110861

15	0.109997	0.110479	0.110498	0.110849
15.5	0.11002	0.110462	0.110517	0.110838
16	0.11004	0.110446	0.110534	0.110829
16.5	0.110059	0.110433	0.110549	0.11082
17	0.110075	0.11042	0.110562	0.110812
17.5	0.11009	0.110409	0.110574	0.110805

These excitation energies are then plotted into a potential energy surface (PES) curve. The PES of the fluorone dimer is shown in Figure 5. Similar curves were plotted for all the substituted variations of the fluorone dimer.

FIG 5: 5th and 6th Excitation Energies for the fluorone dimer.



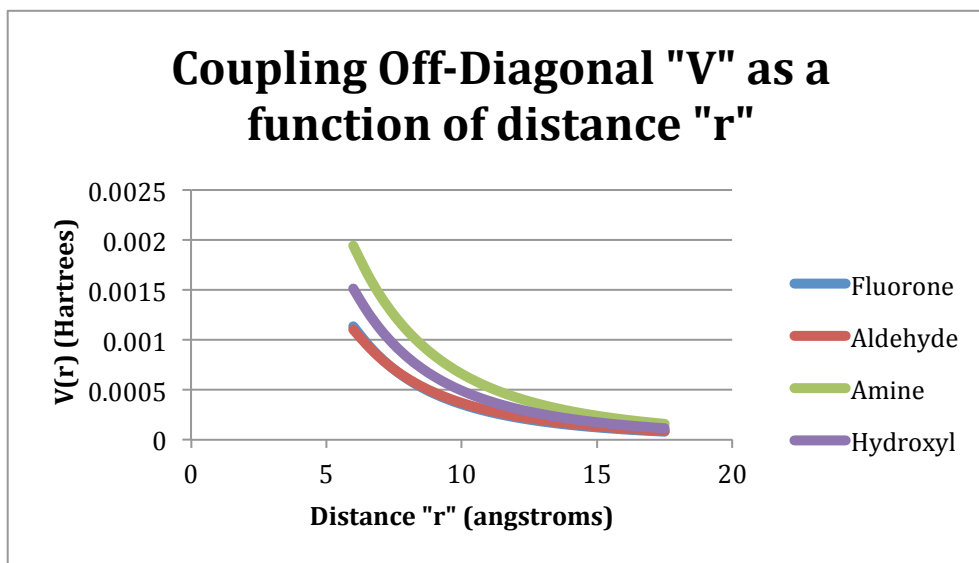
The amine-substituted and hydroxyl-substituted dimers, both comprised of electron-donating functional groups, and therefore, the most strongly electron correlated, display the greatest excitonic splitting of the four systems.

After calculating the excitation energies for each dimer, the coupling energies “V” are then calculated as a function of monomer separation. The coupling values are presented in Figure 6. Similar to the excitonic splitting, the amine-substituted and hydroxyl-substituted dimers also display the greatest coupling, due to the strong electron correlation. The coupling terms are then plotted for all four dimers in Figure 7.

FIG 6: Coupling “V” values for all dimers as a function of monomer distance “r”

Distance “r” (Angstrom)	Fluorone V(r) (Hartree)	w/ Aldehyde V(r) (Hartree)	w/ Amine V(r) (Hartree)	w/ Hydroxyl V(r) (Hartree)
6	0.0011368	0.001101208	0.00194344	0.00151082
6.5	0.0009648	0.000948492	0.001668453	0.001289091
7	0.0008216	0.000815987	0.001438556	0.001104132
7.5	0.0007043	0.000705705	0.001248077	0.00095203
8	0.0006075	0.000613637	0.001088396	0.000825535
8.5	0.0005273	0.000536849	0.000954403	0.000720238
9	0.0004602	0.000471952	0.000840549	0.000631415
9.5	0.0004037	0.00041689	0.000743505	0.000556211
10	0.0003559	0.000369848	0.00066028	0.00049211
10.5	0.0003151	0.000329441	0.000588591	0.0004372
11	0.0002802	0.00029457	0.000526571	0.000389938
11.5	0.0002501	0.000264324	0.000472675	0.000349057
12	0.0002241	0.000237972	0.000425642	0.000313533
12.5	0.0002015	0.000214916	0.000384459	0.000282549
13	0.0001818	0.000194684	0.000348261	0.000255411
13.5	0.0001644	0.000176846	0.000316336	0.000231555
14	0.0001492	0.000161062	0.000288088	0.000210509
14.5	0.0001358	0.000147074	0.000263009	0.000191877
15	0.0001239	0.000134619	0.000240688	0.000175334
15.5	0.0001133	0.000123502	0.00022076	0.0001606
16	0.0001039	0.000113548	0.000202917	0.000147436
16.5	0.0000955	0.000104612	0.000186906	0.000135646
17	0.0000879	9.65743E-05	0.000172498	0.000125057
17.5	0.0000811	8.93214E-05	0.000159501	0.000115521

FIG 7: Coupling values "V" curves for each dimer.



The excitation energies and coupling terms generate the 2x2 Hamiltonian of Equation (2), which is then allowed to evolve under Equation (5). Oscillatory graphs are produced for each dimer case, at 13 Å separation, in Figures 8, 9, 10, and 11, showing the evolution of the excitonic population through a given period of time, therefore, representing the time dynamics and the efficiency of energy transfer of the synthetic chromophoric systems. The amine and hydroxyl-substituted dimers exhibit faster oscillations than the aldehyde-substituted and fluorone dimer, due to their larger coupling values, which is a direct result of stronger electron correlation.

FIG 8: Population time-dynamics for the fluorone dimer at 13 Å separation.

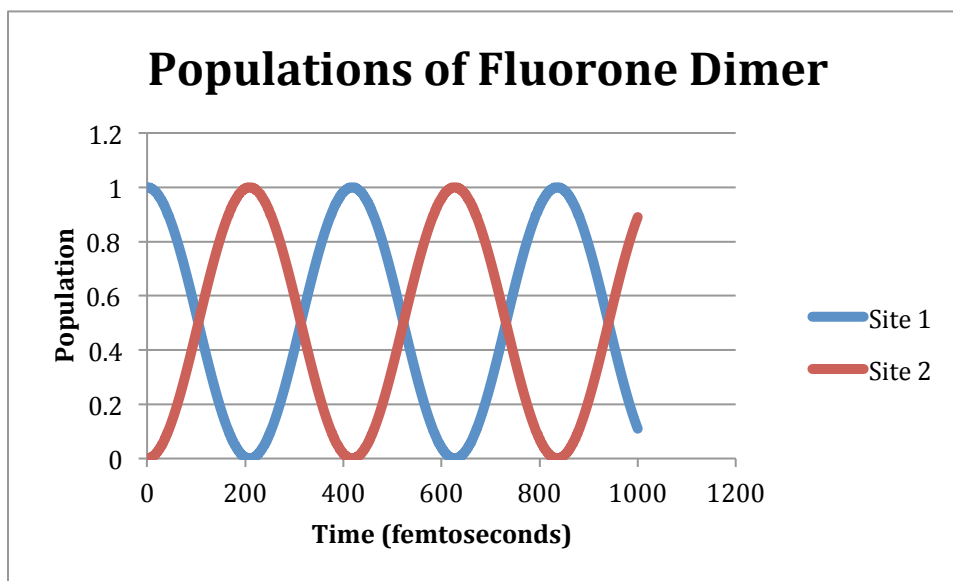


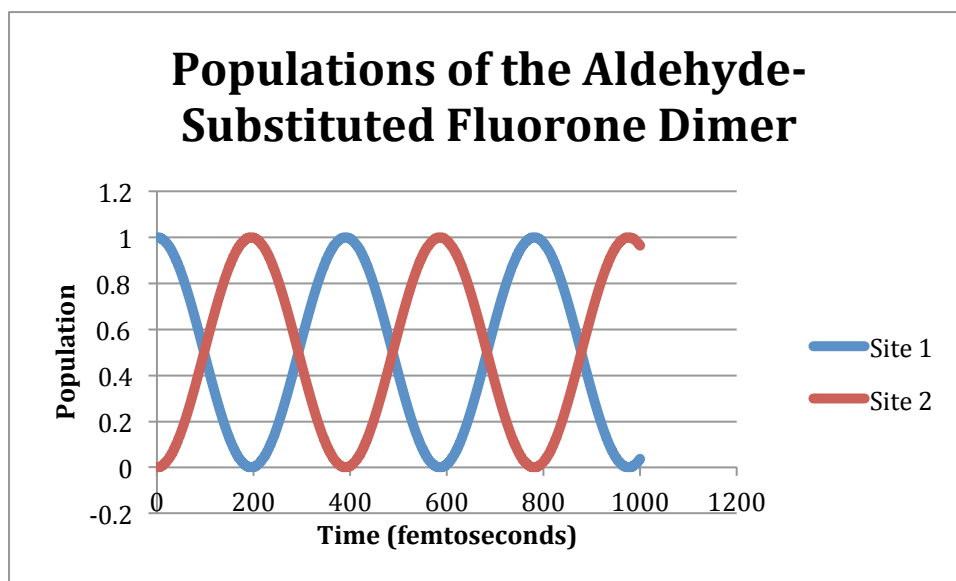
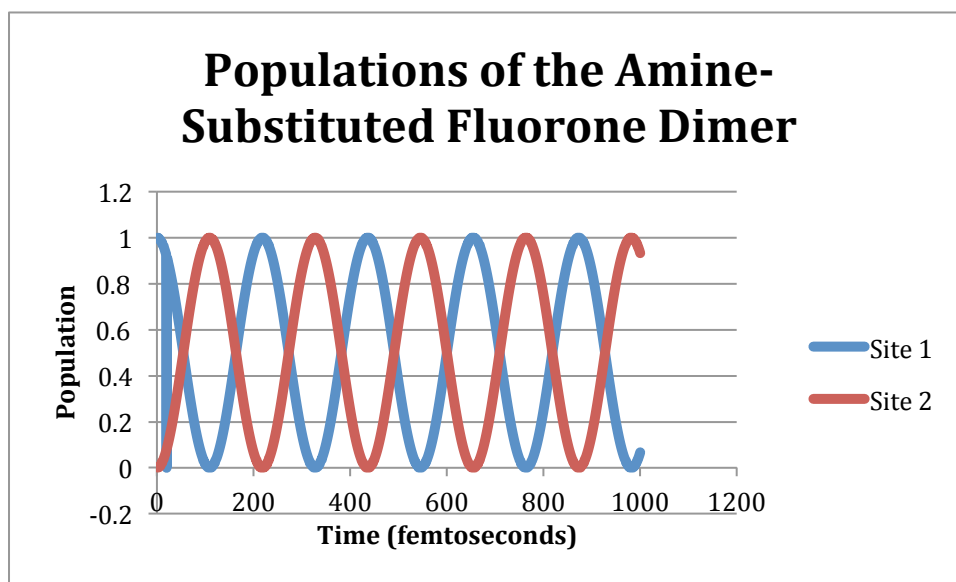
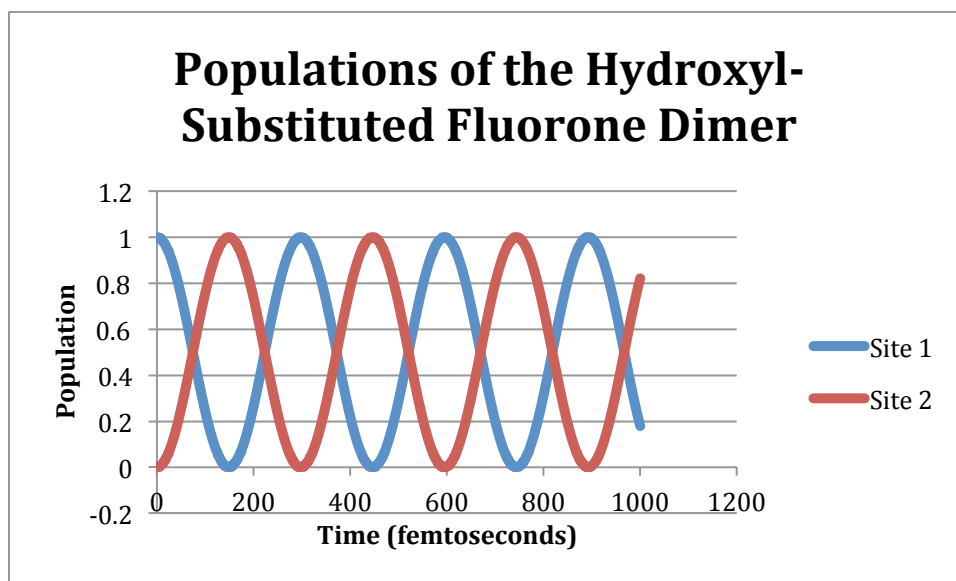
FIG 9: Population time-dynamics for the aldehyde-substituted fluorone dimer at 13 Å separation.**FIG 10: Population time-dynamics for the amine-substituted fluorone dimer at 13 Å separation.**

FIG 11: Population time-dynamics for the hydroxyl-substituted fluorone dimer at 13 Å separation.



IV. Discussion and Conclusions

The changing of the electronic structure of the synthetic chromophoric system with various substituents has an immediate effect on the electron correlation of the system: electron-donating functional groups, such as amines and hydroxyls, increase electron correlation, while electron-withdrawing groups, such as aldehydes, decrease the electron correlation of the system. The results presented for this synthetic chromophoric system are consistent with the results presented for the FMO complex by Mazziotti [7], in that strong electron correlation increases the efficiency of excitonic energy transfer, as it opens supplementary passages between the chromophores to accelerate energy transfer.

This theoretical study of electron correlation and its effect on the efficiency of excitonic energy transfer offers promising results for future experimental studies into the research and design of new artificial light-harvesting devices. Improved designs of these devices can help make solar energy a more viable source of energy for our society, reducing dependence on fossil fuels and other environmentally damaging energy sources.

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