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ABSTRACT Organic semiconductors are often used as light-absorbers in photovoltaic devices, and studying the energy flow through these materials is an important field of research. The energy flow is controlled by electronic coupling between the organic semiconductor molecules, which is affected by the distance between the molecules and their relative orientation. Here we calculated the couplings as a function of distance and relative orientation based on semi-empirical calculations of the low-lying excited states of pairs of organic semiconductor molecules. We showed that as distance increased, electronic couplings approach zero. Electronic couplings calculated as a function of rotation were maximized as the rotation brought the molecules to their minimum separation, while electronic couplings were minimized as the molecules approached their maximum separation.

INTRODUCTION

The study of resonance energy transfer (RET) focuses on the energy transfer that occurs between a donor and acceptor molecule (Scholes 2003). RET, also referred to as electronic energy transfer, occurs when electronic coupling between an energy donating molecule and an energy accepting molecule allows for the de-excitation of the donor and the excitation of the acceptor (Hwang and Scholes 2011). Electronic coupling and resonance between donor emission

and acceptor absorption affect the electronic energy transfer rate between the two molecules (Voityuk 2014). This type of energy flow is common in molecular aggregates, and coupling is therefore a key consideration when attempting to control electronic energy flow in these materials. Electronic couplings have a wide range of applications in the field of electrochemistry and photochemistry (Ramon and Bittner 2006).

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For RET to occur, an external energy source must excite the donor molecules. Molecules that form molecular aggregates that strongly absorb light and can effectively transmit the energy over nanoscale distances are frequently used to create solar cells (Marsh, et al. 2010). Many recent studies have focused on the use of polyfluorenes in photovoltaic cells due to their favorable optical properties (Donley, et al. 2005). One of these polyfluorene molecules is Poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) also referred to as F8BT (Figure 1).
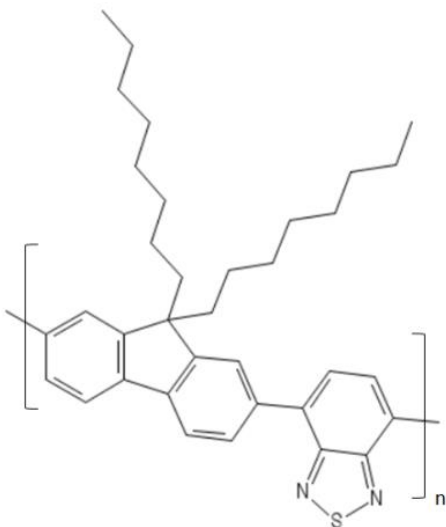
Figure 1. F8BT is a fluorene copolymer made of alternating dioctylfluorene, F8, and benzothiadiazole, BT, components. (Donley, et al. 2005)

Recent studies have found that, due to the benzothidiazole unit being polarized, F8BT is ideal for energy transfer. The study also showed that F8BT behaves differently from other conjugated polymers due to having a strong localized charge (Donley, et al. 2005). Because F8BT is so frequently used to make devices, F8BT is an ideal candidate for closer study of the spatial characteristics that affect electronic coupling.

Theoretical calculations of couplings can be performed in several ways, including both *ab initio* methods and various approximations (Beenken and Pullerits 2004, Slater 1951). The semi-empirical method for quantum chemistry calculations is a fast computational method that employs Hartree-Fock Roothan approach to

calculate electronic structure (Ridley and Zerner 1973). These methods have been shown to create accurate representations of the coupling as compared to experimental data (Slater 1951). We employed this method to calculate the electronic structure of pairs of F8BT-analogs arranged at various distances and relative orientations. We then used the results to examine the way electronic coupling between molecules depends on these parameters.

A study has found that coupling strong enough to drive useful energy flow typically occurs between molecules within 100 nm in organic semiconductors (Voityuk 2014). Our computational chemistry approach offers a way in which to examine how controlled environment coupling varies in this distance range, where experimental control is extremely difficult. A computational chemistry approach provides complete control over relative orientation of the molecules, and also completely defines the observed ensemble. In this article we employ a combination of custom built software and the commercial program Gaussian 16 to explore the relationship between coupling and spatial orientation (Frisch, et al. 2016).

METHODS

Building Models of Theoretical Donors

As an analog for interacting portions of an F8BT aggregate, we selected an F8BT-based oligomer constructed from four monomer units of the structure shown in Figure 1. This F8BT tetramer was modeled in GaussView (Dennington, et al. 2016). To reduce calculation time the tetramers were modeled with methyl instead of octyl sidechains. The length of the alkyl side chains do not have significant impact on the low-lying excited states of polymeric organic semiconductors. The F8BT tetramer was then structurally optimized via the semi-empirical PM6 method using the Gaussian 16 program. The optimized structure is shown in Figure 2.

To create the pair of tetramers, a custom built program was created that read the optimized structure of the molecule from the Gaussian output file and created a new Gaussian input file
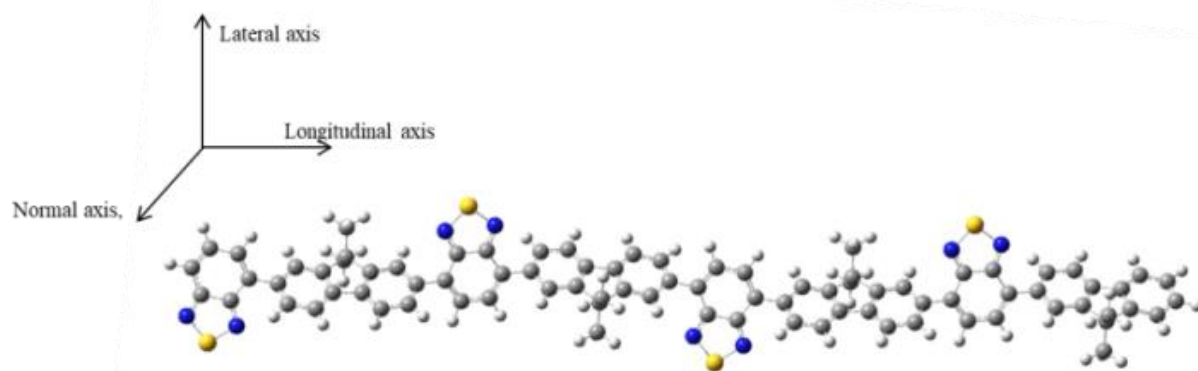
Figure 2. The F8BT tetramer was used as the source file to be duplicated from. All files created for the purpose of the experiment used the F8BT tetramer to create a second tetramer moved along the normal axis. Rotation along the normal axis is referred to as ϕ, rotation along the lateral axis is referred to as ω_{psr} and rotation along the longitudinal axis is ω_{per}.

containing two tetramers at a user-specified center of mass distance and relative orientation. We found that the molecules would collide when rotating along the lateral axis at a distance below 28 Å, so rotation was studied at larger distances.

For each pair of tetramers an excited state calculation was performed using Gaussian 16 and the ZIndo method. Custom built software extracted the excitation energies of both single tetramers and these tetramer pairs from the appropriate Gaussian output files. Electronic coupling was then calculated as:

$$J = \frac{E_{tetramer} - E_{tetramer\ system}}{2} \qquad (1)$$

The coupling, J, was calculated by taking the excited state energy of the tetramer, $E_{tetramer}$, and subtracting the excited state energy of the two tetramers, $E_{tetramer\ system}$. The values were collected in millivolts.

The angular dependence of couplings calculated via the point dipole approximation which is entirely reliant on the rotational constant, κ.

$$V^{dd} = \frac{1}{4\pi\varepsilon_0} \frac{\kappa\mu_D\mu_A}{R^3} \qquad (2)$$

$$\kappa = 2\cos\theta_D\cos\theta_A - \sin\theta_D\sin\theta_A\cos\varphi \qquad (3)$$

The dipole-dipole interaction can be used to approximate the coupling based on Föster theory (Scholes 2003). The program calculated κ based on the dipole-dipole interaction vectors to determine both θ_D and θ_A, and ϕ was determined based on the relative orientation of the two tetramers.

RESULTS AND DISCUSSION

Figure 3 shows how coupling changes as a function of distance, for two relative orientations of the tetramers.
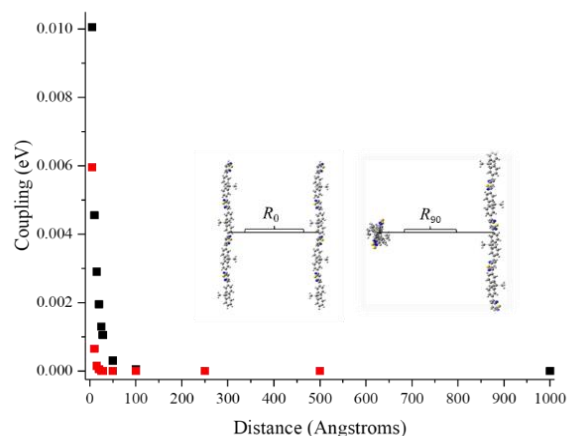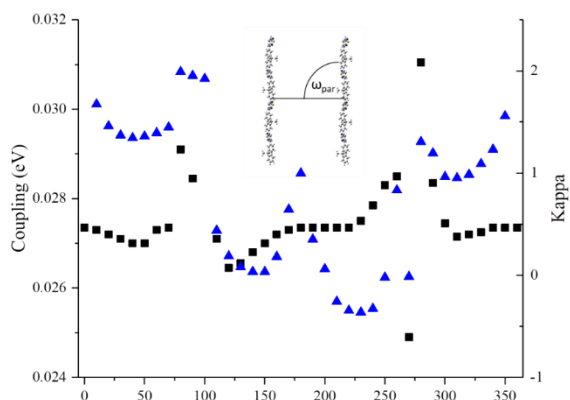

Figure 3. F8BT tetramers were separated by distances, R, in angstroms. Red squares match with molecules separated by distances of R_{90} while black squares represent molecules separated by distances of R_0. These distances were plotted as a function of coupling. The data presented is the couplings calculated from the first excited state over distance.

Couplings decreased as distance increases for both orientations becoming effectively zero by 100 Å. Couplings for tetramers with a rotation of 90° are shown to be smaller than those that were parallel when at the same distance. As the molecules become closer together the couplings exponentially increase approaching infinity until zero separation. These results are consistent with the patterns observed for couplings calculated using the point dipole approximation, which predicts that coupling is inversely proportional to the cube of distance.

Next we investigated the dependence of the coupling on relative spatial orientations by rotating one tetramer and calculating the coupling as a function of the rotation angle. These couplings were calculated for one full rotation due to the non-symmetrical nature of F8BT.

Figure 4 shows data collected from the rotation through angle ω_{par}. At $\omega_{par}=0$ the two tetramers are parallel and coplanar, and as ω_{par} increases one tetramer tips towards the other while remaining coplanar. The coupling shows peaks at 90 and 270 degrees. These rotations correspond to the two tetramers being perpendicular. They show that as distance between the nearest atoms

of the two molecules decreases, the coupling will see an increase. Proximity of the two molecules may have caused issues in running the Gaussian calculations as evident by the point at 260 degrees, which is a negative deviation in the coupling.

Values of κ are co-plotted in Figure 4 for comparison with the more exact semi-empirical calculation. Similar trends are observed from 0-80 degress and 270-360 degrees.

Figure 5 shows the data collected from rotation through angle ϕ. At $\phi=0$ the two tetramers are parallel and co-planar, and as ϕ increases the tetramers remain parallel. Figure 4 show that as ϕ approaches 90 and 270 degrees coupling energy is approximately zero.

Figure 5. The angle, ϕ, corresponded to two parallel molecules 28 angstroms apart, based on center of mass, from each other. Molecules were made at ten degree intervals going from 0 to 360 degrees. The couplings shown were calculated from the second excited state because the first excited state had an oscillation strength that was too low. Rotational constants, κ, were compared to couplings as ϕ changed. The couplings are represented by the black squares while the blue triangles represent κ.

Rotational constants do correlate to couplings in Figure 5. The values collected follow a nearly symmetrical pattern with slight deviations with equivalent rotations. The similar trends do appear throughout the whole rotation.
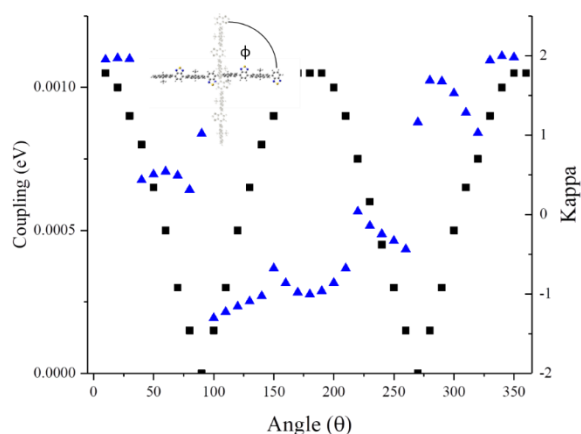

Figure 4. Two F8BT tetramers were modeled at 28 angstroms apart. The couplings were calculated from the second excited state energies because the first excited state had an oscillator strength that was too low. The tetramers were initially parallel with ω_{par} being equal to 0. Rotational constants, κ, were compared to couplings as ω_{par} changed. The couplings are represented by the black squares while the blue triangles represent κ.

Figure 6 shows the data collected from rotation through ω_{per}. The second tetramer was initially parallel but not co-planar instead it starts where ϕ=90. The rotation showed data that did not follow expected coupling values at 180 degrees. Couplings did follow expected trends at 90 and 270 degrees by reaching relative maxima.

The rotational constants showed a similar trend to that of the coupling showing that both values followed a similar trend. The increased value at 180 degrees may have been caused by the proximity of the two molecules affecting the Gaussian calculations.
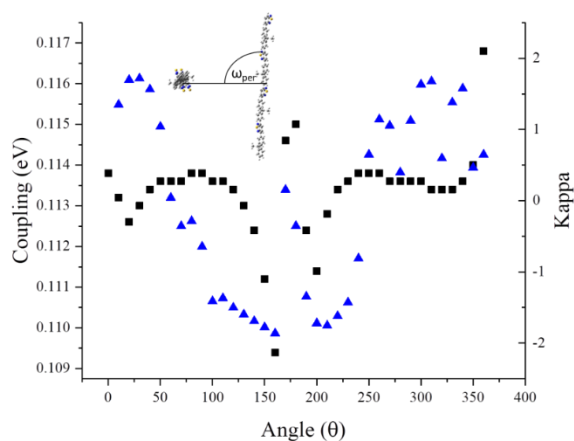
Figure 6: Rotation was plotted as a function of coupling. The tetramers were modeled 28 angstroms away based on the center of mass. Couplings were compared to the angle of the donor tetramer, ω_{per}. Data was collected based on the excited state energies from rotation from ω_{per}.

CONCLUSION

Calculated data showed that coupling decreases as distance increases. Couplings are shown to be effectively zero at 100 Å. Rotation is shown to increase coupling as one tetramer rotates toward the other tetramer. When rotating at angles of ϕ the couplings become zero as ϕ=90, 270 showing that the limited surface to interact at causes interactions to decrease. The deviations from expected coupling values show that to collect a complete set of rotational data the tetramers need to be separated at a distance larger than 28 Å.

The experimental data indicates that different basis sets and methods should be applied. This is evident in Figure 4 and Figure 6. Both figures have data points that appear to not follow the trends that the data was following. To determine if those data points are accurate other computational methods should be applied. The limitations of the semi empirical method show that the data from the semi empirical method should be compared to data collected using other methods such as hartree-fock or DFT. After testing these methods the process should then be applied to other organic semiconductors to see if the computational methods can serve as a generic method for large organic semiconductors or if further testing is necessary. Additional studies should then begin to focus on systems that have more than one type of organic semiconductor.

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