

Link Foundation Fellowship Report:

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1. Organic photovoltaics have the potential to become an accessible form of alternative energy production because of their ease of manufacture via traditional printing techniques and consequent low cost.¹ However, the simplicity of device manufacture belies the complex cascade of processes that allow light to be efficiently converted into electrical power.² Electron transfer (ET) events constitute the most critical steps. ET is known to be governed by a complex function of many system-specific variables including distance, orientation, and energetics of the donor and acceptor species.³ This complexity is amplified by the amorphous nature of organic photovoltaics making exact characterization of relevant system parameters impossible.

To combat this second obstacle, we have synthesized model compounds: organic molecules with specific electron donors and acceptors fixed at a well defined distance about an intervening molecule that covalently bridges the donor and acceptor.⁴ In the past, we have been particularly concerned with the nature of the bridging medium between the donor and acceptor groups and have shown that energy-level matching between the donor and the bridge is particularly important for efficient ET.^{5,6} This research continues to be extended with a family of molecules with oligo-fluorene bridges for study of the distance dependence of ET.⁷ However, the support of the Link Foundation has allowed us to move past the study of a single polymeric linear bridge, to the study of multiple non-collinear bridges. Research in this area overlaps with an extremely rich field of quantum interference phenomena.

Is multiple spatial pathway ET relevant to organic photovoltaics? As there are many routes between the p and n junction interface and the electrode, many spatial pathways certainly exist. In the study of ET in biological systems, another area where exact spatial characterization is difficult, calculations have shown that many spatial pathways contribute to overall ET rates.⁸ Examples of destructive interference have been used to rationalize certain systems' amplified sensitivity to conformation.⁹ It seems plausible that multiple spatial pathway ET will be important in organic photovoltaics, and we are left with the task of understanding just how important.

Destructive interference can be costly in terms of reduction of the effective matrix elements that couple the electron donor and acceptor.¹⁰ However, interference is a coherent phenomenon, and is consequently only as important as the sustainability of wavefunction coherence. We undertook a theoretical investigation as to how environmental dephasing¹¹ modulates destructive interference where we employed a simple site model to simulate a molecular interferometer.¹² The interferometer has two paths, each with oppositely signed matrix elements, and results in destructive interference significantly reducing the ET efficiency. ET rate constants were calculated, dephasing was added, and ET rate constants were recalculated.

Our calculation methodology has previously been used in the Wasielewski group to show the transition from coherent superexchange, which operates well over short distances, to incoherent hopping, which operates efficiently over long distances, as a function of dephasing, bridge energetics, and distance.¹³ Briefly, the system connectivity is defined by a purely electronic Hamiltonian while dynamics are calculated within the density matrix formalism.¹⁴ Density matrices are useful here because site populations are contained in the diagonal elements while the off diagonal elements, the "coherences" reflect the phase relationships between sites. Alternatively, coherences can be seen as being reflective of the degree of delocalization of the electron wavefunction.¹⁵

Dephasing is added by reducing the coherences to zero with some characteristic time constant.

As the dephasing time constant (often referred to as T_2^* in magnetic resonance literature, here represented phenomenologically as the energy, γ) is increased, we found that all transport lost as a result of destructive interference was recovered. This observation makes sense, because dephasing reduces the coherences and causes localization,¹⁶ erasing interference between the two pathways. Moreover, only modest amounts of dephasing are required to effect this recovery. Estimates of dephasing times in conjugated polymers¹⁷ and photosynthetic reaction centers¹⁸ of hundreds of femtoseconds are fast enough to correspond to high enough values of γ to easily mask the effects of destructive interference. It seems that destructive interference will likely not significantly hinder ET in organic photovoltaics.

However, will the efficiency of ET in organic photovoltaics receive any advantage as a result of multiple spatial pathways? This question also has relevance to the field of molecular electronics, where conductance measurements made on several or many molecules are then used to extrapolate to values for single molecules.¹⁹ Models are shown in Fig 1 and results in Fig 2. With no dephasing present, we see an approximate quadratic dependence of rate on the number of degenerate pathways, or $k_{ET} \propto N^2$. The calculation agrees with previous theoretical investigations of molecular conduction scaling laws.²⁰ However, when we add dephasing, we see the system reach a state where k_{ET} is independent of N (the ratios go to 1), followed by an enhancement of the rate due to incoherent hopping. Just as previous studies supported by the Link Foundation have helped describe the distance dependence of ET via coherent superexchange and incoherent hopping mechanism,¹³ we have elucidated the dependence on the number of pathways involved: superexchange is enhanced by increasing N , while hopping is seen to be independent of N .

How does the loss of pathway additivity correlate with the onset of incoherent hopping? As seen in Fig 3, this onset occurs at values of γ several orders of magnitude past the point at which the rate ratios have approached unity. To help understand what determines the onset of both seemingly related phenomena, following previous studies of exciton coherence,²¹ we plotted “real space” pictures of the density matrices at different γ . Loss of pathway additivity requires reduction of the coherences (off-diagonal parts of the picture) to roughly 10% of their non-dephased values (green region) while the onset of hopping seems to require the coherences to have essentially infinitesimal magnitudes.

Our theoretical work has also been accompanied by experimental efforts. We designed molecules **1-4** to look experimentally at multiple pathway effects in photoinduced ET. **1** is a control compound and shows us the intrinsic ability of the bicyclooctane scaffold to perform ET. **2-4** have increasing numbers of phenyl pathways for ET. By plotting the ratio of ET rates from **3** and **4** to **2** at varying temperatures (to tune γ), we hope to trace out our theoretical curve in Fig 2. So far, **1** and **4** have been synthesized, while synthesis of **2** and **3** has proven to be more difficult than expected.

In summary, with the Link Foundation’s support, we have looked at multiple spatial pathway effects in ET that we believe to be relevant to ET in organic photovoltaics. We have shown that destructive interference is likely not a concern, as relatively small amounts of dephasing will recover the lost transport. Benefits of constructive interference may be present over small length scales before hopping

becomes dominant, but ultimately, hopping transport is independent of the number of pathways involved. Future work will focus on completing our experimental investigation of constructive interference in ET. By being able to present a unified theoretical and experimental investigation, we hope to continue to better our description of ET in organic photovoltaic materials.

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2. Published:

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Manuscripts in Preparation:

Scaling Laws and Dephasing in Electron Transfer in Donor-Bridge-Acceptor Molecules
Temperature Dependence of Charge Transport in Oligo-Fluorenes

3. Discretionary funds were used to allow the fellow to attend the Electron Donor Acceptor Interactions Gordon Research Conference. A poster was presented and much constructive input was obtained.

4. The Wasielewski group has looked almost exclusively at ET in linear systems.

Work with multiple spatial pathway systems represents a significant departure from

systems we have looked at in the past. More importantly, the synthesis of these systems

also represents a departure from the group's established areas of synthetic expertise. The

Link Foundation's support allowed the fellow and advisor to take a risk and move out of

the group's established comfort zone.

