Communication

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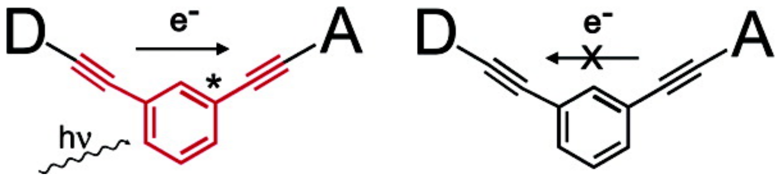

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Using Meta Conjugation To Enhance Charge Separation versus Charge Recombination in Phenylacetylene Donor−Bridge−Acceptor Complexes

Alexis L. Thompson,[†] Tai-Sang Ahn,[§] K. R. Justin Thomas,[‡] S. Thayumanavan,*[,‡]
Todd J. Martínez,*[,†] and Christopher J. Bardeen*[,§]
Departments of Chemistry, University of Illinois, Urbana, Illinois 61801, University of Massachusetts, Amherst, Massachusetts 01003, and University of California, Riverside, California 92521

Received July 8, 2005; E-mail: thai@chem.umass.edu (S.T.); tjm@spawn.scs.uiuc.edu (T.J.M.); christob@ucr.edu (C.J.B.)

A promising approach to high-efficiency solar energy conversion uses molecules consisting of an electron donor−acceptor pair separated by a chemical bridge as components of solar electrochemical cells.[1] Conjugated organic bridges in such donor−bridge−acceptor (DBA) compounds have been shown[2] to act as molecular "wires". However, the ideal bridge would be an *asymmetric* wire or "diode"—promoting electron transfer (ET) from donor to acceptor while resisting ET in the reverse direction and thus suppressing charge recombination. Our recent studies of excitation energy transfer (EET) in meta-linked phenylacetylene (PA) dendrons suggest a route to this goal. It is well-known that meta linkages lead to electronic decoupling of the substituents in the ground electronic state. We showed that this same meta linkage undergoes enhanced electronic coupling in the excited state.[3,4] The similarity of the electronic coupling matrix elements in EET and ET further suggests that DBA complexes with a meta-substituted bridge could act as gated wires. The bridge would be a wire or resistor when in its excited or ground electronic state, respectively. If de-excitation of the bridge coincides with the forward ET event, the effective result is a "one-electron wire". Here, we demonstrate that such an asymmetric wire can indeed be created. Both para- and meta-linked PA bridges act as good conduits for forward excited-state ET, but the meta bridge effectively prevents recombination, leading to the asymmetric behavior. While ET through para−meta linkages in model DBA compounds has been studied previously in terms of both through-bond[5] and through-space mechanisms,[6] these studies have focused on the ground state of the bridge.

The insets in Figure 1 show the two DBA molecules (denoted **Meta** and **Para**) that are the subject of this Communication. Carbazole (donor) and naphthalimide (acceptor) units are linked by a para- or meta-conjugated PA bridge. Steady-state spectral properties of both are shown in Figure 1, where the solvent polarity is tuned using mixtures of toluene and CH_2Cl_2. The PA bridge is partially conjugated to the donor−acceptor moieties, as can be seen from the fact that both absorptions are considerably red-shifted compared to those of naphthalimide (340 nm) and carbazole (365 nm). While absorption does not change with solvent composition, the emission red-shifts, broadens, and decreases in intensity with increasing solvent polarity. The different dependences of absorption and emission on solvent polarity indicate that they originate from two different electronic states. Multireference semiempirical quantum mechanical/molecular mechanical calculations (Table 1) show that absorption corresponds to a low-lying neutral excited state (DBA)* for both **Para** and **Meta** in low- and high-polarity solvents, cyclohexane and dimethylformamide (DMF). A higher excited state with charge-transfer (CT) character, D^+BA^-, becomes the lowest-energy emitting state after excited-state relaxation. Both the steady-state spectra and theoretical calculations suggest a three-state model where the initial absorption event between neutral states, DBA to (DBA)*, which are largely insensitive to solvent polarity, is followed by electron transfer to D^+BA^-, whose energy depends strongly on polarity. This is shown schematically in Figure 2.[7]

Table 1. Excited-State Properties at Absorption and Emission Geometries in Polar (DMF) and Nonpolar (Toluene/Cyclohexane) Solvents[a]

	Meta		Para	
	polar	nonpolar	polar	nonpolar
E_{abs} (eV)	3.77 (3.17)	3.79 (3.15)	3.51 (3.05)	3.56 (3.03)
TDM/DM	2.5/10	2.5/9	3.9/16	3.8/13
E_{em} (eV)	2.37 (n/m)	2.53 (2.65)	2.07 (1.86)	2.76 (2.56)
TDM/DM	0.5/63	0.3/60	3.4/53	4.8/26

[a] Experimental values in parentheses. Transition dipole moment (TDM) and dipole moment (DM) lengths are in debye.

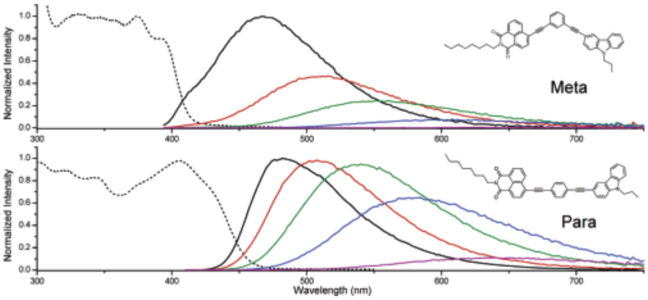

Figure 1. Absorption and emission spectra of **Meta** (top) and **Para** (bottom) molecules. Emission in neat toluene (black), 10% CH_2Cl_2 (red), 25% CH_2Cl_2 (green), 50% CH_2Cl_2 (blue), and 100% CH_2Cl_2 (violet).

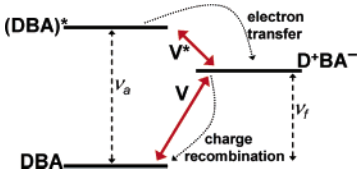

Figure 2. Three-state model for the DBA compounds used in this study. The variables are as defined in eqs 1 and 2 in the text.

We use time-resolved spectroscopy to determine the forward and backward ET rates for **Para** and **Meta** in toluene. Using femtosecond transient absorption measurements, with 150 fs time resolution and excitation at 400 nm, we observe a broad excited-state absorption ranging across the visible spectrum in both molecules. This spectrum, shown in Figure 3a for **Meta**, rapidly converts into a double-peaked spectrum. A global fit of the data at probe wavelengths from 475 to 775 nm reveals two principal components, shown in Figure 3b, which interconvert with a single-exponential time: 4.5 ps in **Meta** and 5.4 ps in **Para**. We take this to be the formation time of the D^+BA^- state after excitation to the (DBA)* state. After this initial rapid decay, we observe only very

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[†] University of Illinois.
[‡] University of Massachusetts.
[§] University of California, Riverside.

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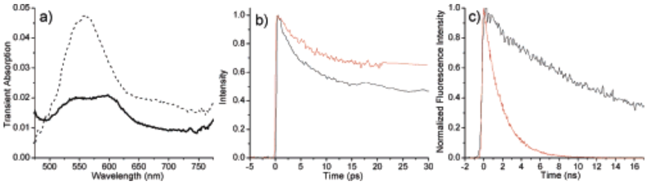

Figure 3. (a) Pump−probe transient signals at 200 fs (---) and 200 ps (—) for **Meta**. (b) Pump−probe transient signals monitoring the decay of the neutral excited-state absorption for **Meta** (555 nm, black) and **Para** (614 nm, red). The decay times from a global fit are 4.5 ps for **Meta** and 5.4 ps for **Para**. (c) Fluorescence decays for **Meta** (black, lifetime = 16.8 ns) and **Para** (red, lifetime = 1.8 ns).

minor changes in the spectral shape over the course of hundreds of picoseconds. Preliminary pump−probe experiments in more polar solvents such as CH_2Cl_2 and DMF show the same initial decay, accelerated by at least a factor of 2, providing further evidence that it reflects the forward electron-transfer event.

Figure 3c shows the measured fluorescence decays of **Meta** and **Para** in toluene. In both molecules, fluorescence measurements in toluene reveal emission from the initially excited neutral state which disappears within the 15 ps instrument response time, replaced by a much longer-lived, red-shifted CT emission. Unlike the forward charge separation times, the charge recombination times extracted from these data are quite different: 16.8 ns for **Meta** and 1.8 ns for **Para**. Thus, the ratio of forward/backward ET rates is ∼300 in **Para** and ∼3500 in **Meta**, making **Meta** better suited for photovoltaic applications.

The greater rate asymmetry in **Meta** results from two factors: the similar forward ET rates and the more rapid recombination in **Para**. The fact that the rates of CT state formation differ by only about 20% is surprising considering the conventional picture that meta conjugation prevents electronic communication. But when the donor and/or acceptor is electronically coupled to the bridge moiety, as is the case here, the excited-state properties of the bridge must be taken into account. Both theory and experiment have demonstrated that phenyl compounds in their lowest excited state exhibit much stronger coupling between meta substituents than in the ground state.[8] Recent ab initio calculations showed how excitonic coupling between meta-linked PA segments is enhanced by a factor of 7.3 in the excited state, versus a factor of 1.3 for para-linked PAs.[4] This provides a qualitative explanation of why **Meta**'s forward ET rate is comparable to that of **Para**.

The second factor is the slower recombination rate in **Meta**. After forward ET, the bridge is presumably no longer in its excited state, and the electronic coupling decreases. Neglecting vibrational Franck−Condon effects, this decreased coupling results in a smaller recombination rate. To confirm this decreased electronic coupling in **Meta**, we need to determine the electron-transfer matrix elements between the D^+BA^- state and the ground state and the neutral excited state (denoted V and V^*, as shown in Figure 2). By measuring the fluorescence quantum yields, we determine the radiative and nonradiative components of the total fluorescence decay rate, k_r and k_{nr}. For **Para**, $k_r = 4.2 \times 10^8\ s^{-1}$ and $k_{nr} = 1.1 \times 10^8\ s^{-1}$, and for **Meta**, $k_r = 1.4 \times 10^7\ s^{-1}$ and $k_{nr} = 4.7 \times 10^7\ s^{-1}$. k_r for **Para** is 30 times larger than that of **Meta**, while the k_{nr} values differ only by a factor of 2.2, and this larger k_r leads to rapid radiative recombination. The radiative rate of a CT state is determined by its coupling to both the ground state and nearby neutral excited states, and the most general expression is quite complicated.[9] We examine two limiting cases where the solutions are well-known and show that in either one, the factor of 30 increase in k_r can be explained only by a larger electronic matrix element V or V^*. In the first case, $V \gg V^*$ and k_r is given by[10]

$$\frac{k_r}{n^3} = 3.137 \times 10^{-7}(V\Delta\mu)^2\nu_f \tag{1}$$

while in the second case, $V^* \gg V$ and k_r is given by

$$\frac{k_r}{n^3} = \frac{3.137 \times 10^{-7}(V^*\mu^*)2\nu_f^{\,3}}{(\nu_a - \nu_f)^3 + V^{*2}} \tag{2}$$

where n is the refractive index, ν_a and ν_f are the peaks of the absorption and fluorescence spectra, respectively, $\Delta\mu$ is the change in permanent dipole between the DBA and D^+BA^- states, and μ^* is the transition dipole between DBA and (DBA)*. Using either measured or calculated values for ν_a, ν_f, μ^*, and $\Delta\mu$ in eqs 1 and 2, only modest changes in k_r less than a factor of 2 can be obtained. Therefore, the 30-fold enhancement in k_r for **Para** cannot be solely due to variations in ν_a, ν_f, μ^*, or $\Delta\mu$, but must result from either V or V^*, or both, being larger for **Para** than for **Meta**. In other words, the enhanced radiative rate that leads to fast charge recombination in **Para** is a direct result of its larger ET matrix elements between the CT state and at least one neutral state.

In conclusion, we have shown that the two isolectronic DBA compounds have similar forward but very different backward ET rates. The origin of this difference lies in the excited-state enhancement of electronic coupling through the meta bridge: it acts like a wire in the excited state, allowing facile forward ET, while in its ground state the meta linkage acts like an insulator, preventing electronic communication. To exploit the asymmetry of the meta bridge, the initially absorbed photon must both provide energy for the CT event and place the bridge in its excited state. In our molecules, this is accomplished by having the bridge partially conjugated to the donor−acceptor groups. It is an interesting question whether more weakly coupled bridge structures can exhibit similar behavior.

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Supporting Information Available: Synthetic details, transient spectra, calculation details, and optimized geometries (PDF, PDB). This material is available free of charge via the Internet at http://pubs.acs.org.

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