# Influence of Energetics and Electronic Coupling on Through-Bond and Through-Space Electron Transfer within U–Shaped Donor-Bridge-Acceptor Arrays<sup> $\dagger$ </sup>

## Emily A. Weiss, Louise E. Sinks, Aaron S. Lukas, Erin T. Chernick, Mark A. Ratner,\* and Michael R. Wasielewski<sup>\*</sup>

Department of Chemistry and Center for Nanofabrication and Molecular Self-Assembly, Northwestern University, Evanston, Illinois 60208-3113

Received: December 8, 2003; In Final Form: February 23, 2004

We present here a study of multistep electron transfer mechanisms within donor-bridge-acceptor arrays consisting of functionalized aromatic imide and diimide donors and acceptors arranged in rodlike linear structures and in U-shaped folded structures on xanthene scaffolds. Femtosecond and nanosecond transient absorption spectroscopy is used to explore the relative efficiency of through-bond and through-space electron transfer in these molecules. The magnitude of the electronic coupling between the oxidized donor and the reduced acceptor is probed specifically by direct measurements of the singlet—triplet splitting, 2*J*, within the radical ion pairs using magnetic field effects on the yield of triplet states resulting from radical ion pair recombination. These data are used to quantitatively assess the effects of both energetics and electronic coupling on the electron transfer mechanism. Through-space electron transfer is found to be a viable mechanism in the U-shaped structures when reduction of the acceptor that is folded back toward the donor is energetically more favorable than reduction of the acceptor directly bonded to the donor.

#### Introduction

The ability of photosynthetic reaction center proteins to convert photon energy into chemical potential with near unity quantum yield and the availability of crystal structures for these proteins have resulted in an extensive effort to decipher and mimic elements of the complex series of electron-transfer reactions that occur within them.<sup>1-3</sup> An important feature of these proteins that differs from most model systems is the fact that none of their energy or electron transport cofactors are covalently linked to one another. The protein structure provides specific distances and orientations between the cofactors as well as an electronic environment that is critical to proper functioning of the system. Thus, it is important to understand electron transfer between donors and acceptors that are not covalently linked to one another as well as the more typical situation in which they are covalently linked by a bridging molecule. In the noncovalent case, electron transfer occurs by the interaction of the molecular orbitals of the electron donor with those of the acceptor, whereas in the covalent case, the interaction involves participation of the orbitals of bridging molecules in a superexchange interaction.<sup>4-6</sup> A corollary to the noncovalent case is electron transfer using the orbitals of solvent molecules or nonbonded protein functional groups positioned between the donor and the acceptor.<sup>7-19</sup> The possibility that the highly efficient electron-transfer reactions in the reaction center may involve all of these mechanisms has motivated the synthesis and study of a host of model compounds designed to probe the relative efficiency of such mechanisms under specific structural and environmental conditions.<sup>4–6,20–28</sup>

We present here a series of donor-bridge-acceptor arrays, Figure 1, designed to explore the effects of both energetics and



Figure 1. Structures of the donor-acceptor arrays.

electronic coupling on the pathway utilized for electron transfer. These arrays consist of functionalized aromatic imide and diimide donors and acceptors arranged in rodlike structures and in U-shaped structures on xanthene scaffolds.<sup>29</sup> The xanthene scaffold provides a means of folding the structure so that specific electron acceptors are spatially proximate to the electron donors, yet have many covalent bonds between them. Since electron transfer via the long through-bond pathway is expected to be very slow,<sup>4</sup> these structures provide a means to study the through-space interaction between the donor and the nearby

<sup>&</sup>lt;sup>†</sup> Part of the special issue "Gerald Small Festschrift".

<sup>\*</sup> To whom correspondence should be addressed. E-mail: wasielew@ chem.northwestern.edu.

acceptor in the folded leg of the structure. Specifically, radical ion pairs (RPs) are created in these systems through a series of rapid, nonadiabatic charge separation reactions starting from the lowest excited singlet state of their common chromophore, 4-(*N*-piperidinyl)naphthalene-1,8-dicarboximide (6ANI).<sup>28</sup> The through-space and through-bond charge separation and recombination mechanisms between the donor and the acceptor vary throughout the series.

The 6ANI molecule serves as the photoexcited chromophore within all of the donor-acceptor arrays presented here. In some arrays <sup>1\*</sup>6ANI is the primary electron donor, whereas in others, it is the primary electron acceptor. p-Methoxyaniline (MeOAn), acts as the primary or secondary electron donor, whereas naphthalene-1,8:4,5-bis(dicarboximide) (NI) and pyromellitimide (PI) are primary or secondary electron acceptors. The NI and PI acceptors are covalently linked to 6ANI either directly using a N-N single bond or 2,5-dimethylphenyl (dmp) or 4,5disubstituted xanthene (xan) spacers.<sup>30</sup> Energy minimized ground-state structures calculated using the semiempirical AM1 method show that the  $\pi$  systems of the NI and PI acceptors adopt a nearly cofacial arrangement when they are linked through their imide bonds to the 4 and 5 positions of the xanthene spacer in 5-8, 12, and  $13.^{31}$  Direct linkage of 6ANI to NI or PI in 1, 3, 5, 7, and 10-13 using N-N single bonds at their imide groups results in a near perpendicular orientation of their respective  $\pi$  systems, minimizing electronic communication, whereas linkage of 6ANI to NI or PI through the dmp spacer in 2, 4, 6, and 8 results in a nearly coplanar arrangement of their  $\pi$  systems. The nature of the amino group functionality within 4-diakylaminonaphthalene-1,8-dicarboximides is known to play a critical role in the photophysics of this chromophore.<sup>32</sup> The conformational effects of 4-cycloalkylamino rings on the photophysics of 6ANI derivatives in Debye solvents has been explored in detail.<sup>33</sup> All molecules in this series have either piperidine or piperazine derivatives attached to the 4-position of the naphthalene-1,8-dicarboximide to produce the 6ANI chromophore, so that conformational effects on the electron-transfer rates will be similar across the set.

The electron transfer dynamics in the molecules presented here are investigated in both nonpolar toluene and polar 2-methyltetrahydrofuran (MTHF). Charge separation and recombination rates are measured using femtosecond and nanosecond transient absorption spectroscopy. In addition, the magnitude of the electronic coupling between the oxidized donor and the reduced acceptor is probed specifically by direct measurements of the RP singlet-triplet splitting, 2*J*, using magnetic field effects (MFEs) on the yield of triplet states resulting from radical ion pair recombination. The MFEs are due to the radical pair intersystem crossing (RP–ISC) mechanism, which is well-known to account for triplet production within photosynthetic reaction centers<sup>34–39</sup> and has been described in detail elsewhere.<sup>40–48</sup>

### **Experimental Section**

The synthesis and characterization of compounds  $1,^{46} 2,^{28}$  $3,^{33} 4,^{46} 9,^{28} 10,^{49} 11,^{50}$  and  $13^{29}$  have been reported previously, and those of 5-8 and 12 can be found in the Supporting Information. Characterization was performed with a Gemini 300 MHz, Varian 400 MHz, or INOVA 500 MHz NMR and a PE BioSystems MALDI-TOF mass spectrometer. All solvents were spectrophotometric grade or distilled prior to use. Immediately before use, the 2-methyltetrahydrofuran was additionally purified over a basic alumina column.

Absorption measurements were made on a Shimadzu (UV-1601) spectrophotometer. The optical density of all samples was maintained between 0.3 and 1.0 at 416 nm, ( $\epsilon_{6ANI, 416 nm} = 7000$ cm<sup>-1</sup> M<sup>-1</sup>).<sup>28</sup> Femtosecond and nanosecond transient absorption data, as well as MFE experiments were obtained with apparatus described elsewhere.<sup>33,46,47,51</sup> For the femtosecond experiments, cuvettes with a 2 mm path length were used and the samples were irradiated with 80 fs, 400 nm 0.5–1.0  $\mu$ J laser pulses focused to a 200  $\mu$ m diameter spot. The optical density at 400 nm was typically 0.4-0.8. The total instrument response function (IRF) for the pump-probe experiments was 130 fs. For the nanosecond experiments, samples were placed in a 1 cm path length quartz cuvette equipped with a vacuum adapter and subjected to five freeze-pump-thaw degassing cycles prior to transient absorption measurements. The samples were excited with 5 ns, 1 mJ, 416 nm laser pulses focused to a 5 mm diameter spot and the IRF was 7 ns. Between 50 and 80 shots were averaged for each kinetic trace with a LeCroy 9384 digital oscilloscope and sent to a microcomputer, which calculated the  $\Delta A$ . Kinetic analyses were performed at several wavelengths using a nonlinear least-squares fit to a general sum-of-exponentials using the Levenberg-Marquardt algorithm accounting for the presence of the finite instrument response.

For the MFE experiment, the sample cuvette was placed between the poles of a Walker Scientific HV-4W electromagnet powered by a Walker Magnion HS-735 power supply. The field strength was measured by a Lakeshore 450 gaussmeter with a Hall effect probe. Both the electromagnet and the gaussmeter were interfaced with the data collection computer, allowing measurement and control of the magnetic field to  $\pm 1 \times 10^{-5}\, T$ during data acquisition. Kinetic traces at the characteristic wavelength of the localized triplet state were taken at each magnetic field, which was changed by a constant increment depending on desired resolution. Due to the length of the sample runs (>5 h), a small amount of sample degradation was observed, resulting in a decrease in the triplet yield at zero field,  $\Delta A(\mathbf{B} = 0)$ , over the course of the experiments. To compensate for this, the magnetic field was reset to  $\mathbf{B} = 0$  mT every five kinetic traces for increments of 5 mT and every three kinetic traces for increments of 0.5 mT and 1 mT and  $\Delta A(\mathbf{B} = 0)$  was plotted and fit with a polynomial or series of polynomials. These functions were used to calculate the relative triplet yield as a function of applied field strength. The relative triplet yield is thus

$$\frac{T}{T_0} = \frac{\Delta A(\mathbf{B})}{\Delta A(\mathbf{B}=0)} \tag{1}$$

The results presented are an average of two or more experiments conducted on separate days with freshly prepared samples.

#### Results

The photophysics of rodlike donor-acceptor arrays containing the 6ANI chromophore have been characterized previously in detail.<sup>28</sup> The oxidation potential of 6ANI (1.2 V vs SCE) is similar to that of piperidine, whereas its reduction potential (-1.4 V vs SCE) is similar to that of naphthalene-1,8dicarboximide. The oxidation potential of the MeOAn electron donor (0.79 V) is substantially less positive than that of 6ANI due to resonance stabilization of the aniline radical cation by the *p*-methoxy group. Greenfield et al.<sup>28</sup> found that attachment of the MeOAn electron donor to 6ANI via a piperazine bridge results in strong quenching of the 6ANI emission, consistent with the rapid electron-transfer reaction: MeOAn-1\*6ANI  $\rightarrow$ MeOAn<sup>+</sup>-6ANI<sup>-</sup>. The reduction potentials of the NI and PI chromophores are -0.5 and -0.79 V vs SCE, respectively.<sup>52</sup>

TABLE 1: Reorganization Energies ( $\lambda$ ) and  $\Delta G$ 's for Each Electron Transfer Step in Toluene and MTHF<sup>a</sup>

	toluene						MTHF								
	$\lambda_{s}^{*}$	$\lambda_{CS1}^{a}$	$\lambda_{CS2}{}^{b}$	$\lambda_{\rm CR}$	$\Delta G_{CS1}$	$\Delta G_{CS2}$	$\Delta G_{\text{CRS}}$	$\Delta G_{CRT}$	$\lambda_{s}^{*}$	$\lambda_{CS1}^{a}$	$\lambda_{CS2}{}^{b}$	$\lambda_{CR}$	$\Delta G_{CS1}$	$\Delta G_{CS2}$	$\Delta G_{CRS}$
1	0.08	0.74	1.11 <sup>c</sup>	0.54	-0.53	-0.36	-1.91	0.12	1.10	1.64	1.19 <sup>c</sup>	1.56	-0.78	-0.43	-1.51
2	0.09	0.19	0.34	0.55	-0.32	-0.47	-2.01	0.02	1.19	0.93	0.69	1.65	-0.41	-0.76	-1.60
3	0.08	0.19	0.40	0.61	-0.32	-0.28	-2.20	-0.15	1.10	0.89	0.67	1.63	-0.41	-0.51	-1.85
4	0.09	0.19	0.41	0.79	-0.32	-0.18	-2.30	-0.25	1.19	0.93	0.76	1.72	-0.41	-0.47	-1.89
5	0.08	0.74	1.11 <sup>c</sup>	0.54	-0.53	-0.41	-1.86	0.17	1.10	1.64	1.19 <sup>c</sup>	1.56	-0.78	-0.48	-1.59
6	0.09	0.19	0.34	0.55	-0.32	-0.50	-1.98	0.05	1.20	0.93	0.70	1.66	-0.41	-0.81	-1.55
7	0.08	0.19	0.40	0.61	-0.32	-0.35	-2.13	-0.08	1.10	0.89	0.67	1.63	-0.41	-0.58	-1.78
8	0.09	0.19	0.34	0.55	-0.32	-0.53	-1.95	0.08	1.18	0.93	0.68	1.64	-0.41	-0.82	-1.54
9	0.06	0.19		0.29	-0.32		-2.48		0.81	0.93		1.24	-0.41		-2.36
10	0.07	0.74		1.05	-0.56		-2.24		1.01	1.64		1.99	-0.83		-1.94
11	0.07	0.81		1.12	-0.27		-2.53		1.01	1.71		2.06	-0.54		-2.23
12	0.07	0.74		1.05	-0.62		-2.18		1.01	1.64		1.99	-0.88		-1.89
13															
(PI)	0.07	0.81		1.12	-0.33		-2.47		1.03	1.73		2.08	-0.61		-2.16
(NI)	0.08	0.75		1.06	-0.55		-2.25		1.07	1.70		2.05	-0.86		$-1.91^{+}$

<sup>*a*</sup> All values are in eV. Charge recombination in MTHF takes place too fast for RP intersystem crossing and so all CR is from the singlet RP. The methods and schemes used to calculate the reorganization energies, denoted by superscripts a, b, and c in the table entries, are provided in the Supporting Information.



Figure 2. Femtosecond transient spectra for compound  $\mathbf{8}$  in toluene illustrating through-space electron transfer; inset: kinetic trace of compound  $\mathbf{8}$  at 480 nm.

Redox potentials for all relevant chromophores within compounds 1-13 can be found in Table S1. The electronic spectra of all NI-containing compounds in toluene, Figure S1, exhibit a broad charge transfer (CT) absorption centered near 400 nm in both toluene and MTHF due to the 6ANI chromophore, and a second band displaying vibronic structure at 343, 363, and 382 nm arising from a  $\pi$ - $\pi$ \* transition of the NI acceptor. The ground-state absorption maximum of PI occurs at 307 nm and overlaps higher energy absorption bands of 6ANI. The charge separation and charge recombination free energies for 1-13, calculated using the spectroscopic method outlined by Greenfield et al.,<sup>28</sup> which is based on the Weller's dielectric continuum treatment for the energy of an RP in an arbitrary solvent,<sup>53</sup> as well as the solvent reorganization energies calculated for the various electron-transfer reactions using the Marcus formulation,<sup>54</sup> are listed in Table 1. Internal reorganization energies,  $\lambda_{I}$ , calculated from DFT-energy minimized structures of both the neutral and charged donors and acceptors are given in the Supporting Information, Table S1.

Figure 2 illustrates the time evolution of the transient spectra observed following photoexcitation of **8** in toluene and is representative of similar data obtained for 1-13. At early times the transient bleach at 500 nm is due to stimulated emission from <sup>1\*</sup>6ANI and is followed by rapid formation of an absorption band at 520 nm due to the formation of MeOAn<sup>++</sup>-6ANI<sup>-+</sup>. The 520 nm feature is due principally to MeOAn<sup>++.55,56</sup> At longer times, the 520 nm feature persists and is accompanied by formation of an intense band with maxima at 480 and 610 nm



Figure 3. Normalized nanosecond kinetic traces at radical anion peaks (480 nm for NI<sup>-</sup> and 720 nm for PI<sup>-</sup>) for compounds in toluene, (A) 1, 3, 5, and 7; (B) 2, 4, 6, and 8.

characteristic of NI<sup>-•.57</sup> The inset to Figure 2 shows the transient kinetics at 480 nm. Figure 3 shows the corresponding nanosecond transient kinetics for 1-8 in toluene monitoring either NI<sup>-•</sup> at 480 nm or PI<sup>-•</sup> at 720 nm. The transient absorption kinetics show a single-exponential decay component followed by a residual low amplitude absorption which decays on a much longer time scale. This long-lived absorption is due to formation of <sup>3\*</sup>6ANI in molecules having only a PI acceptor and <sup>3\*</sup>NI in those that have a NI acceptor.<sup>58</sup> The transient absorption kinetics for 1-13 are summarized in Table 2.

The data in Figure 4 show the relative triplet yields resulting from radical ion pair recombination for 1-8 in toluene as a function of applied magnetic field. These MFE plots exhibit



Figure 4. MFE plots for compounds in toluene: (a) 5, inset: 1; (b) 6, inset: 2; (c) 7, inset: 3; (d) 8, inset: 4. The value of 2J is given by the field at which the maximum triplet yield  $(T/T_0)$  is achieved.

 TABLE 2: Charge Recombination Time Constants and in

 Toluene and MTHF

	$\tau_{\rm CR}$ (ns) toluene	$\tau_{\rm CR}$ (ps) MTHF
1	28	150
2	210	$57^{a}$
3	18	280
4	73	53 <sup>a</sup>
5	27	170
6	350	57 <sup>a</sup>
7	14	280
8	230	53 <sup>a</sup>
9	5.0	$52^{a}$
10	12	100
11	19	230
12	21	88
13	12 (NI)	250 (NI)
	10 (PI)	250 (PI)

 $^a\,\tau_{\rm CR}$  is for recombination from the MeOAn<sup>+</sup>-6ANI<sup>-</sup> ion pair.

TABLE 3: Singlet—Triplet Splitting (2J) and Full Width at Half Maximium of the 2J Distribution for Compounds with MeOAn Donors ( $\pm 0.2 \text{ mT}$ )

		· /			
	2J	$\Delta 2 J_{ m fwhm}$		2J	$\Delta 2 J_{ m fwhm}$
1 2 3 4	48 mT 1 mT 66 mT	12 mT <1 mT 48 mT 15 7 mT	5 6 7	44 mT <1 mT 63 mT ≤1 mT	22 mT <1 mT 48 mT <1 mT
4	2, 19 m I	1.5, / m1	8	<1 m1	<1 m1

resonances whose maxima directly give the singlet-triplet splitting of the RP, 2J. The magnitude of 2J changes considerably as the electronic coupling between the radical ions within the RPs varies as a function of molecular structure. The values of 2J measured for 1-8 in toluene are listed in Table 3 along with the full width at half-maximum of the resonances. As has been discussed previously,<sup>46,47</sup> the strength of the magnetic superexchange interaction between the spins of the RP, as indicated by the position of the 2J resonance in the MFE plot, Figure 4, is a good gauge of the overall contribution of the

donor-acceptor electronic coupling to the rate of charge recombination within these systems. The compounds with MeOAn donors attached to the 6ANI chromophore (1-8) have 2J values within the range measurable by our magnet (0-1.2 T), but for those where 6ANI serves as the electron donor (10-13), the stronger coupling between the radical cation and radical anion spins results in a short-lived RP and presumably a S-T splitting that is much larger than 1.2 T.

#### Discussion

In the following discussion, the influence of reaction free energy, reorganization energy, and electronic coupling on the electron-transfer dynamics within the multiple donor-acceptor arrays 1-8 are examined by focusing on the competition between (1) reduction of <sup>1\*</sup>6ANI by the adjacent MeOAn donor and oxidation of 1\*6ANI by PI or NI acceptors in the primary charge separation step, (2) secondary charge separation and primary RP charge recombination, and (3) through-bond and through-space charge separation/charge recombination pathways. Compounds 9-13 serve as reference molecules that allow us to dissect the contributions of competing electron-transfer processes to the overall charge separation and recombination within 1-8. The free energies for the electron-transfer reactions are changed by using acceptors with different reduction potentials, NI and PI, as well as solvents having different polarities, toluene and MTHF. The donor-acceptor electronic coupling is altered by changing both the distance and orientation between the donor and acceptor. Scheme 1 outlines the primary charge separation steps and, depending on the compound, either the subsequent secondary charge separation step or the charge recombination of the primary RP for 1–13, as discussed below. Table 1 gives charge recombination time constants for the RPs formed in these systems.

**Primary Charge Separation.** Following photogeneration of  $1^{*}6ANI$  in 1-8, a competition occurs between oxidation of

SCHEME 1: Primary and Secondary Charge Transfer Steps for Compounds 1–13 in Toluene (Black) and MTHF (Red)<sup>*a*</sup>



<sup>*a*</sup>  $\mathbf{D}$  = MeOAn and  $\mathbf{C}$  = 6ANI and  $\mathbf{A}$ ,  $\mathbf{A1}$ , and  $\mathbf{A2}$  refer to acceptors in the positions indicated in the diagram.

<sup>1\*</sup>6ANI by NI or PI and reduction of <sup>1\*</sup>6ANI by MeOAn. Electron transfer from <sup>1\*</sup>6ANI to NI to form MeOAn-6ANI<sup>+•</sup>-NI<sup>-•</sup> occurs in  $\leq 1$  ps in toluene within MeOAn-6ANI-NI (1) and MeOAn-6ANI-NI-xan-PI (5), as noted by observing the formation of NI<sup>-•</sup>, which matches the time constant for charge separation in the model compound 6ANI-NI (10). Formation of the initial RP is followed by electron transfer from MeOAn to 6ANI<sup>+•</sup> to yield the final RPs, MeOAn<sup>+•</sup>-6ANI-NI<sup>-•</sup> (1) and MeOAn<sup>+•</sup>-6ANI-NI<sup>-•</sup>-xan-PI (5), in  $\tau_{CS} = 1.3$  ps. Measurements on reference molecule 9 show that the time constant for the alternative process MeOAn-<sup>1\*</sup>6ANI-NI → MeOAn<sup>+</sup>•-6ANI<sup>-</sup>•-NI should be about 11 ps,<sup>59</sup> which is therefore not kinetically competitive with the initial reduction of NI by <sup>1\*</sup>6ANI. The Marcus energy gap law<sup>60</sup> states that the electron-transfer rate is fastest when  $-\Delta G$  for the reaction is equal to  $\lambda$ , the total nuclear reorganization energy. Calculations of  $\Delta G$  and  $\lambda$  for these reactions (see Table 1 and the Supporting Information) show that the reaction MeOAn- $1^{*}$ 6ANI-NI  $\rightarrow$  MeOAn $^{+\bullet}$ -6ANI $^{-\bullet}$ -NI in toluene is in the Marcus inverted region ( $-\Delta G = 0.32 \text{ eV} >$  $\lambda = 0.19 \text{ eV}$ ), whereas the opposing reaction, MeOAn-<sup>1\*</sup>6ANI- $NI \rightarrow MeOAn-6ANI^{+\bullet}-NI^{-\bullet}$ , is in the normal region ( $-\Delta G =$ 0.53 eV  $< \lambda = 0.74$  eV). Neither mechanism is conclusively favored based on these calculations. However, electronic coupling is most likely not responsible for the preference to reduce NI because, in general, the PI acceptor, having greater torsional freedom around the imide-imide linkage, is more strongly coupled to 6ANI than NI (see Table 3 and ref 46). We must therefore conclude that the errors in our calculations of  $\Delta G$  and  $\lambda$  are too great to predict the observed mechanism in this case, where one mechanism is not significantly energetically favored over the other. When the same experiment is carried out in MTHF, the data for compounds 1 and 5 show that the formation of MeOAn<sup>+</sup>• and NI<sup>-</sup>• both occur with the same time constants (<1ps), so that both reactions occur simultaneously. In MTHF,  $-\Delta G \approx \lambda/2$  for both mechanisms, so that both reactions are in the normal region and should have similar rates.

All other compounds, 2-4 and 6-8, show exclusive formation of MeOAn<sup>+•</sup>-6ANI<sup>-•</sup> as the initial RP with time constants given in Scheme 1. This includes 3 and 7 in which 6ANI is covalently bound directly to PI using an N-N bond. The formation of MeOAn<sup>+•</sup>-6ANI<sup>-•</sup> in both **3** and **7** in toluene occurs with  $-\Delta G = 0.32$  eV, whereas  $\lambda$  is only 0.19 eV, Table 1, so that the reaction lies near the maximum of the Marcus rate vs free energy profile. On the other hand, the data for reference molecule 11 shows that  $-\Delta G = 0.27$  for electron transfer from <sup>1\*</sup>6ANI to PI is comparable to that for the oxidation of MeOAn, yet  $\lambda$  for the reduction of PI is 0.81 eV, resulting in a relatively slow rate of PI reduction compared to the rate of MeOAn oxidation. The energy gap law is therefore most likely responsible for determining whether 1\*6ANI is either oxidized or reduced by the adjacent acceptor or donor, respectively, in these compounds.

Secondary Charge Separation vs Primary RP Recombi**nation.** As discussed above, 1 and 5 within the series 1-8generates a primary RP in which 6ANI<sup>+•</sup> forms. This implies that the secondary electron-transfer step for these two molecules MeOAn-6ANI<sup>+</sup>•-NI<sup>-</sup>• → MeOAn<sup>+</sup>•-6ANI-NI<sup>-</sup>• must compete with charge recombination within MeOAn-6ANI<sup>+•</sup>-NI<sup>-•</sup>. For both 1 and 5, the charge shift reaction is more than 10 times faster than the charge recombination of 6ANI<sup>+</sup>·-NI<sup>-</sup>, as indicated by the data for reference molecule 10, Scheme 1, leading to a high yield of the distal RP MeOAn<sup>+</sup>·-6ANI-NI<sup>-</sup>·. In addition, following photogeneration of the primary RP, MeOAn<sup>+•</sup>-6ANI<sup>-•</sup> in 2-4 and 6-8, secondary charge separation from 6ANI<sup>-•</sup> to the adjacent NI or PI acceptor competes well with charge recombination within the primary RP. The data for reference molecule 9 in toluene show that the charge recombination reaction, MeOAn<sup>+</sup>·-ANI<sup>-</sup>·  $\rightarrow$  MeOAn-6ANI, occurs with  $\tau_{CR} = 5$  ns. As a consequence of the relatively long lifetime of this RP in toluene, secondary charge separation from 6ANI<sup>-4</sup> to NI or PI, for 2-4 and 6-8 in toluene, even for the slowest case ( $\tau_{\rm CS} = 410$  ps for 7), occurs with >90% yield. In contrast, the secondary electron transfer does not occur at all in MTHF for the compounds having the dmp spacer between 6ANI and the acceptor (2, 4, 6, and 8), because it cannot compete kinetically with charge recombination of the primary RP, which occurs in 53–57 ps, closely matching  $\tau_{CR} = 52$  ps for model compound 9. However, the secondary charge shift reaction in MTHF is competitive with charge recombination of the primary RP within the compounds in which 6ANI is directly linked to NI or PI via a N-N bond (1, 3, 5, and 7). Once again, the slowest time constant for the secondary electron transfer is 4.7 ps (7), which implies that the yield of the secondary RP is >90%in 1, 3, 5, and 7. The solvent reorganization energies for the electron-transfer reactions in these molecules, 0.8 eV  $< \lambda_{\rm S} <$ 1.2 eV, in MTHF ( $\epsilon = 6.97^{61}$ ) are much larger than those in toluene, 0.06 eV <  $\lambda_{\rm S}$  < 0.09 eV. In addition, the RP is stabilized in the more polar solvent, which makes the charge recombination reaction of MeOAn<sup>+</sup>·-6ANI<sup>-</sup> lie much further in the Marcus inverted region in toluene than in MTHF resulting in a much slower recombination rate in toluene.

Through-Space vs Through-Bond Electron Transfer. The folded donor-acceptor molecules 5-8, 12, and 13 offer the possibility of competitive through-space electron transfer to a second adjacent NI or PI that is part of the folded leg of the xanthene structure. The term "through-space" is meant to encompass both a direct transfer from 6ANI-• to the distal NI or PI as well as a superexchange interaction involving toluene or MTHF positioned between them. We have presented evidence previously implicating aromatic solvents in such an interaction in related molecules.<sup>29</sup> In both toluene and MTHF, the electrontransfer dynamics of MeOAn-6ANI-NI-xan-PI (5) and MeOAn-6ANI-PI-xan-NI (7) are very similar to those of the linear model compounds, MeOAn-6ANI-NI (1) and MeOAn-6ANI-PI (3), respectively. There is no evidence of through-space electron transfer to the "opposite-side" acceptors in 5 (PI) and 7 (NI). In addition, there is no evidence of a charge shift equilibrium between NI and PI attached to the xanthene scaffold.

Comparing the results for MeOAn-6ANI-dmp-NI-xan-PI (6) to those for the linear model compound MeOAn-6ANI-dmp-NI (2), the formation of the primary RPs occur with similar time constants, whereas the secondary charge separation from  $6ANI^{-\bullet}$  to NI across the dmp spacer is somewhat faster for 6 than it is for 2. There is no evidence for electron transfer to PI in any of the electron-transfer dynamics of 6. In MTHF, the primary RP recombines in only 57 and 54 ps in 6 and 2, respectively, so that secondary electron transfer to NI does not occur.

The situation is more interesting in the case of MeOAn-6ANIdmp-PI-xan-NI (8) in toluene, where the secondary charge separation results in formation of NI<sup>-•</sup> with  $\tau_{CS} = 360$  ps. In fact, there is no evidence of formation of PI-• at any time during the electron-transfer dynamics leading to MeOAn<sup>+•</sup>-6ANI-dmp-PI-xan-NI<sup>-•</sup>. The corresponding data for model compound 4 shows that electron transfer from 6ANI<sup>-•</sup> to PI across the dmp spacer does in fact occur, albeit slowly with  $\tau_{CS} = 5$  ns. Thus, the reduction of NI in 8 is more than 10 times faster than the reduction of PI in 4. It is unlikely that the energetically accessible MeOAn+•-6ANI-dmp-PI-•-xan-NI intermediate is a precursor to NI reduction because the formation of this intermediate would be rate limiting, which is not consistent with the observed rapid formation of NI<sup>-•</sup>. Thus, the formation of NI<sup>-•</sup> in 8 most likely occurs by through-space electron transfer either directly from 6ANI<sup>-•</sup> to NI or through a superexchange interaction involving the orbitals of solvent molecules between 6ANI-• and NI. The free energy for electron transfer from 6ANI<sup>-•</sup> to NI within 8 is more negative by 0.35 eV than that for transfer to PI, Table 1. Even though the energetics favor through-space electron transfer from 6ANI-• to NI in 8, the electronic coupling matrix element for this process should be smaller than that for through-bond transfer to PI. Nevertheless, the dominance of electron transfer to NI implies that the electronic coupling between 6ANI-• and NI cannot be significantly smaller, otherwise the free energy advantage for the reduction of NI would be canceled out.

In the reference compound 6ANI-PI-xan-NI (13), spectroscopic signatures of both PI<sup>-•</sup> and NI<sup>-•</sup> are observed. We will discuss the MTHF case first, where these features develop with the same time constants,  $\tau = 3.2$  ps. Formation of the radical anion can occur via two pathways: 1) direct electron transfer through the covalent bonds to form PI<sup>-•</sup> and 2) through-space electron transfer to form NI<sup>-•</sup>. The electron can then move back and forth between the NI and PI, resulting in detectable populations of both radical anions. The rate observed is most likely a composite rate consisting of all electron-transfer pathways, plus the equilibrium constant. From model compound 6ANI-PI (11), we know that formation of the radical pair  $6ANI^+PI^-\bullet$  occurs in 11 ps in MTHF. This is significantly slower than the rate of radical anion formation in 13, indicating that the formation of the radical anion is dominated by a fast through-space rate. The situation is similar in toluene, though the charge separation in 13 is biphasic, with a 1.5 ps component (30%) and a 7.6 ps component (70%). This may represent a separation of the observed rates into intrinsic rates, but assignment of the components to particular processes is difficult. Again, through comparison with the reference compound 11, it is appears that the dominate electron-transfer pathway is through-space.

Charge recombination can also occur via these two pathways, and therefore, the observed charge recombination rates are composite rates. In MTHF, both radical anion signals decay in 250 ps, which is very similar to the 230 ps time constant observed in 11 for the decay of PI-. This indicates that the covalent pathway is the major recombination route. In toluene, however, the recombination time constant in 13 is approximately 11 ns for both anions, which is significantly shorter than the 19 ns recombination time constant seen in 11. This may indicate that a faster through-space recombination pathway is accessible in toluene and not in MTHF. However, the MFE indicates that covalent pathway must still be important. In compound 8, the value of 2J decreases sharply as the through-space pathway is utilized. In compound 13, no magnetic field effect was observed, indicating that the strongly coupled through-bond pathway is a major component of the overall recombination process.

Electronic Coupling. The charge recombination reactions within 1-8 take place in a single kinetically resolvable step in both toluene and MTHF. We have shown previously that the overall charge recombination process is dominated by the electronic coupling matrix element for recombination to the lowest excited triplet state of the system in other compounds of this type,<sup>46</sup> so that that the singlet-triplet splitting within the RP, 2J, accurately reflects the relative electronic coupling for charge recombination. The magnitude of 2J depends exponentially on distance, so that as mentioned earlier, the short distances between the RPs generated within 9-13 result in larger values of 2J than we can measure. However, values of 2J are readily obtained for 1-8 in which the distances between the radical ions in the final RPs are a minimum of 13.5 Å, Table S2. The insertion of the dmp spacer between the 6ANI chromophore and the NI or PI acceptor greatly increases  $r_{DA}$  to an average of about 18 Å resulting in a sharp decrease in 2J in all cases, Table 3. The value of 2J goes from 48 mT for MeOAn<sup>+•</sup>-6ANI-NI<sup>-•</sup> (1) to <1 mT for MeOAn<sup>+•</sup>-6ANI-dmp-NI<sup>-•</sup> (2) and MeOAn<sup>+•</sup>-6ANI-dmp-NI<sup>-•</sup>-xan-PI (6), within which NI serves as the only acceptor. The value of 2J drops from 66 mT for MeOAn<sup>+</sup>•-6ANI-PI<sup>-</sup>• (3) to either 2 or 19 mT for MeOAn<sup>+•</sup>-6ANI-dmp-PI<sup>-•</sup> (4) depending on the conformation of the 6ANI piperazine ring.46 The values of 2J are exquisitely sensitive to changes in RP structure which, in turn, modulate the electronic interaction between the two radical ions. For example, comparing the data for 1 and 3, the larger value of 2J for **3** relative to that of **1** most likely results from the greater torsional freedom of PI around the imide-imide linkage with 6ANI as compared to NI.46

The values of 2*J* observed for the MeOAn<sup>+•</sup>-NI<sup>-•</sup> and MeOAn<sup>+•</sup>-PI<sup>-•</sup> RPs within 5-7 are very similar to those observed in the corresponding linear model compounds 1-3. This is reasonable given that the transient kinetic data shows that the electron transfer rates, RP intermediates, and final RP

products are essentially the same for a given donor-acceptor array in both the linear series, **1**-**3**, and the folded series, **5**-**7**. Once again, MeOAn-6ANI-dmp-PI-xan-NI (8) proves to be the exception. The value of 2J observed for the MeOAn<sup>+•</sup>-6ANIdmp-PI-xan-NI<sup>-•</sup> RP within **8** is < 1 mT, significantly less than the 2 or 19 mT interaction observed for MeOAn<sup>+•</sup>-6ANI-dmp-PI<sup>-•</sup> (4) (please see ref 46 for a detailed discussion of this double resonance and an additional MFE plot for this compound), consistent with having the electron strongly localized on NI as indicated by the transient absorption data.

Structural Effects of the Xanthene Spacer on Electron **Transfer.** Finally, it is important to comment on the potential effects of single bond rotations within these structures on the observed electron-transfer reactions. Attaching the bulky xanthene-acceptor moiety to the linear donor-acceptor segment containing 6ANI most likely changes the torsional motions of the PI or NI acceptor on the linear segment. This may change the electronic coupling matrix elements for the various electrontransfer reactions, altering the reaction rates. The kinetic data in Table 2 show that the presence or absence of the xantheneacceptor moiety attached to the linear donor-acceptor segment containing 6ANI has a significant effect the primary or secondary charge separation time constants in toluene and MTHF. For example, comparing the data for MeOAn-6ANIdmp-NI-xan-PI (6) and MeOAn-6ANI-dmp-NI (2) in toluene, the secondary charge separation reaction producing NI<sup>-•</sup> occurs faster in 6 (270 ps) as opposed to 2 (410 ps). A similar comparison between 8 and 4 is not valid because different acceptors are reduced to form the final RP in each molecule.

The charge recombination data also shows that attachment of the xanthene spacer has an impact on the time constants. Comparing the data for 6 and 2, the time constant for recombination reaction in 6 (350 ns) is significantly slower than that for 2 (210 ns). Once again, no valid comparison can be made between 8 and 4 as mentioned above. Comparisons between compounds 5 vs 1 and 7 vs 3 in toluene as well as MTHF show that the presence of the xanthene-acceptor moiety has less of an impact on the rates of charge recombination. Large amplitude torsional motions about the single bonds joining the redox components in 1, 3, 5, and 7 should have higher barriers due to significant steric interactions between the carbonyl groups of 6ANI with those of NI or PI at their point of attachment. The torsional barriers should be somewhat lower for 2, 4, 6, and 8 in which 6ANI and NI or PI are attached to dmp. Thus, attachment of the bulky xanthene-acceptor moiety with its own steric requirements is more likely to influence the torsional motion about single bonds which have lower torsional barriers. This model is consistent with our observation that the time constants for both the secondary charge separation and charge recombination reactions in 6 vs 2 differ significantly, whereas those for charge recombination in 5 vs 1 and 7 vs 3 do not. In summary, the variations that we see depend both on torsional barriers and on the time scales at which large amplitude torsions occur relative to the observed electron-transfer rates.

#### Conclusions

We have examined the influence of energetics and electronic coupling on electron transfer rates and mechanisms within a series of both linear and U-shaped donor-bridge-acceptor arrays. Femtosecond and nanosecond transient absorption spectroscopy were used to explore the relative efficiency of through-bond and through-space electron transfer in these molecules. The magnitude of the electronic coupling between the oxidized donor and the reduced acceptor is probed specifically by direct measurements of the RP singlet-triplet splitting, 2J, using magnetic field effects (MFEs) on the yield of triplet states resulting from radical ion pair recombination. These data were used to quantitatively assess the effects of both energetics and electronic coupling on the electron transfer mechanism. Throughspace electron transfer was found to be a viable mechanism in the U-shaped structures when reduction of the acceptor that is folded back toward the donor is energetically more favorable than reduction of the acceptor directly bonded to the donor. Future work will focus on developing a better understanding how residual structural motions, such as rotations about single bonds joining the donors and acceptors influence the electrontransfer reactions, as well as elucidating the role of potential "antennae" in electron-transfer processes, e.g., the alkyl chain attached to the opposite-side acceptor in the xanthene molecules. Preliminary rate and coupling measurements suggest that the alkyl chains may play a role in mediating through-space electron transfer in these molecules, a result that could clarify longstanding speculation regarding the contribution of the phytyl chain of the bacteriochlorophyll in the initial charge separation events of photosynthesis.

Acknowledgment. M.R.W. acknowledges support by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Grant No. DE-FG02-99ER-14999. M.A.R. acknowledges support from the National Science Foundation, and E.A.W. acknowledges a Fellowship from the Link Energy Foundation.

**Supporting Information Available:** Details regarding the synthesis and characterization of the molecules used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. J. Mol. Biol. 1984, 180, 385.

(2) Witt, H. T. Adv. Photosyn. 1996, 4, 363.

(3) Fromme, P.; Kern, J.; Loll, B.; Biesiadka, J.; Saenger, W.; Witt, H. T.; Krauss, N.; Zouni, A. *Philos. Trans. R. Soc. London, B* **2002**, *357*, 1337.

(4) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. J. Am. Chem. Soc. **1987**, 109, 3258.

(5) Rodriguez, J.; Kirmaier, C.; Johnson, M. R.; Friesner, R. A.; Holten, D.; Sessler, J. L. J. Am. Chem. Soc. **1991**, 113, 1652.

(6) Wasielewski, M. R. Chem. Rev. 1992, 92, 435.

(7) Gosztola, D.; Wang, B.; Wasielewski, M. R. J. Photochem. Photobiol. A: Chem. 1996, 102, 71.

(8) Jolliffe, K. A.; Bell, T. D. M.; Ghiggino, K. P.; Langford, S. J.; Paddon-Row: M. N. Angew. Chem., Int. Ed. Engl. **1998**, *37*, 916.

(9) Seischab, M.; Lodenkemper, T.; Stockmann, A.; Schneider, S.; Koeberg, M.; Roest, M. R.; Verhoeven, J. W.; Lawson, J. M.; Paddon-Row: M. N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1889.

(10) Lokan, N. R.; Paddon-Row, M. N.; Koeberg, M.; Verhoeven, J.
 W. J. Am. Chem. Soc. 2000, 122, 5075.

(11) Armspach, D.; Matt, D.; Harriman, A. Eur. J. Inorg. Chem. 2000, 6, 1147.

(12) Hu, Y.-Z.; Bossmann, S. H.; van Loyen, D.; Schwarz, O.; Durr, H. Chem. Eur. J. 1999, 5, 1267.

(13) Linke, M.; Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. J. Am. Chem. Soc. 1997, 119, 11329.

(14) Kumar, K.; Lin, Z.; Waldeck, D. H.; Zimmt, M. B. J. Am. Chem. Soc. 1996, 118, 243.

(15) Han, H.; Zimmt, M. B. J. Am. Chem. Soc. 1998, 120, 8001.

(16) Lawson, J. M.; Paddon-Row, M. N.; Schuddeboom, W.; Warman,

J. M.; Clayton, A. H. A.; Ghiggino, K. P. J. Phys. Chem. 1993, 97, 13099.
 (17) Head, N. J.; Oliver, A. M.; Look, K.; Lokan, N. R.; Jones, G. A.;
 Paddon-Row: M. N. Angew. Chem., Int. Ed. Engl. 1999, 38, 3219.

(18) Bell, T. D. M.; Jolliffe, K. A.; Ghiggino, K. P.; Oliver, A. M.; Shepard, M. J.; Langford, S. J.; Paddon-Row, M. N. J. Am. Chem. Soc. **2000**, *122*, 10661.

(19) Kaplan, R. W.; Napper, A. M.; Waldeck, D. H.; Zimmt, M. B. J. Am. Chem. Soc. 2000, 122, 12039.

- (20) Osuka, A.; Marumo, S.; Mataga, N.; Taniguchi, S.; Okada, T.; Yamzaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. J. Am. Chem. Soc. 1996, 118, 155.
- (21) Osuka, A.; Mataga, N.; Okada, T. *Pure Appl. Chem.* 1997, 69, 797.
  (22) Wiederrecht, G. P.; Watanabe, S.; Wasielewski, M. R. *Chem. Phys.* 1993, *176*, 601.
- (23) Johnson, D. G.; Niemczyk, M. P.; Minsek, D. W.; Wiederrecht, G. P.; Svec, W. A.; Gaines, G. L., III; Wasielewski, M. R. J. Am. Chem. Soc. **1993**, 115, 5692.
- (24) Kuciauskas, D.; Liddell, P. A.; Hung, S.-C.; Lin, S.; Stone, S.; Seely,
   G. R.; Moore, A. L.; Moore, T. A.; Gust, D. J. Phys. Chem. B 1997, 101,
   429.
- (25) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y. Tetrahedron 1989, 45, 4767.
- (26) Wasielewski, M. R.; Niemczyk, M. P.; Johnson, D. G.; Svec, W. A.; Minsek, D. W. *Tetrahedron* **1989**, *45*, 4785.
- (27) Lee, S.-J.; DeGraziano, J. M.; Macpherson, A. N.; Shin, E.-J.; Kerrigan, P. K.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *Chem. Phys.* **1993**, *176*, 321.
- (28) Greenfield, S. R.; Svec, W. A.; Gosztola, D.; Wasielewski, M. R. J. Am. Chem. Soc. **1996**, 118, 6767.
- (29) Lukas, A. S.; Bushard, P. J.; Wasielewski, M. R. J. Phys. Chem. A 2002, 106, 2074.
- (30) Hamann, B. C.; Branda, N. R.; Rebek, J., Jr. *Tetrahedron Lett.* **1993**, *34*, 6837.
- (31) AM1 calculations were performed using HyperChem(TM), Hypercube, Inc.: Gainesville, FL.
  - (32) Saha, S.; Samanta, A. J. Phys. Chem. A 2002, 106, 4763.
  - (33) Sinks, L. E.; Wasielewski, M. R. J. Phys. Chem. A 2003, 107, 611.
  - (34) Haberkorn, R.; Michel-Beyerle, M. E. Biophys. J. 1979, 26, 489.
- (35) Haberkorn, R.; Michel-Beyerle, M. E.; Marcus, R. Proc. Natl. Acad. Sci. U.S.A. 1979, 76, 4185.
- (36) Hoff, A. J. Photochem. Photobiol. 1986, 43, 727.
- (37) Hoff, A. J.; Rademaker, H.; Van Grondelle, R.; Duysens, L. N. M. Biochim. Biophys. Acta 1977, 460, 547.
- (38) Michel-Beyerle, M. E.; Scheer, H.; Seidlitz, H.; Tempus, D. FEBS Lett. 1979, 110, 129.
- (39) Hore, P. J.; Hunter, D. A.; McKie, C. D. Chem. Phys. Lett. 1987, 137, 495.
- (40) Blankenship, R. E.; Schaafsma, T. J.; Parson, W. W. Biochim. Biophys. Acta 1977, 461, 297.

- (42) Schulten, K.; Staerk, H.; Weller, A.; Werner, H.; Nickel, B. Z. Phys. Chem. N.F. 1976, 101, 371.
  - (43) Till, U.; Hore, P. J. Mol. Phys. 1997, 90, 289.
- (44) Weller, A.; Nolting, F.; Staerk, H. Chem. Phys. Lett. 1983, 96, 24.
  (45) Weller, A.; Staerk, H.; Treichel, R. Faraday Discuss., Chem. Soc.
- 1984, 78, 271.
  (46) Weiss, E. A.; Ratner, M. A.; Wasielewski, M. R. J. Phys. Chem. A 2003, 107, 3639.
- (47) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. J. Am. Chem. Soc. 2004, 126, 5577.
- (48) Lukas, A. S.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R. J. Am. Chem. Soc. 2003, 125, 3921.
- (49) Debreczeny, M.; Svec, W. A.; Wasielewski, M. R. New J. Chem. 1996, 20, 815.
- (50) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H. J. Am. Chem. Soc. **1999**, *121*, 7726.
- (51) Giaimo, J. M.; Gusev, A. V.; Wasielewski, M. R. J. Am. Chem. Soc 2002, 124, 8530.
- (52) Wiederrecht, G. P.; Niemczyk, M.; Svec, W.; Wasielewski, M. R. J. Am. Chem. Soc. **1996**, 118, 8.
  - (53) Weller, A. Z. Z. Phys. Chem. 1982, 133.
- (54) Marcus, R. A.; Sutin, N. Biochim. Biophys. Acta 1985, 811, 265.
   (55) Kimura, K.; Yoshinaga, K.; Tsubomura, H. J. Phys. Chem. 1967, 71, 4485.
- (56) Hester, R. E.; Williams, K. P. J. J. Chem. Soc., Perkin Trans. 2 1982, 559.
- (57) Gosztola, D.; Niemczyk, M. P.; Svec, W. A.; Lukas, A. S.; Wasielewski, M. R. J. Phys. Chem. A **2000**, 104, 6545.
- (58) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H. J. Am. Chem. Soc. **2000**, *122*, 9715.
- (59) The biexponential nature of the formation kinetics of MeOAn<sup>+•-</sup>  $6ANI^{-•}$  in 9 is most likely due to low amplitude torsional motions about the C–N bond at the 4-position of 6ANI, ref 33, and cannot be easily resolved in most other cases discussed here, so that monoexponential charge separation kinetics are usually observed.
  - (60) Marcus, R. J. Chem. Phys. 1965, 43, 679.
- (61) CRC handbook of chemistry and physics., 81 ed.; CRC Press: Boca Raton, FL.

<sup>(41)</sup> Mori, Y.; Sakaguchi, Y.; Hayashi, H. J. Phys. Chem. A 2000, 104, 4896.