

Remarkable Conformational Control of Photoinduced Charge Separation and Recombination in a Giant U-Shaped Tetrad

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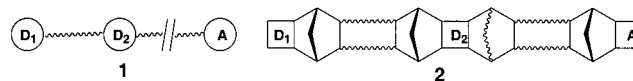
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Abstract: Intramolecular photoinduced electron transfer (ET) with rates greater than $2 \times 10^9 \text{ s}^{-1}$ has been observed in polar solvents for the U-shaped, *syn,syn* isomer (*syn,syn-4*) of a giant tetrad with porphyrin and methyl viologen termini (**4**). In contrast, no ET is observed in a sample containing the extended isomers *anti,syn* and *anti,anti* of **4**. Photoexcitation of the *syn,syn* isomer and subsequent ET leads to the formation of the charge-separated state which has an unusually long lifetime of 420 ns in acetonitrile and 230 ns in benzonitrile. Temperature-dependent fluorescence lifetime studies of *syn,syn-4* revealed the presence of a small (0.09 eV) activation barrier for the ET process and they indicate the presence of two ground-state conformers, one where the terminal porphyrin and methyl viologen chromophores are located close enough to facilitate ET and one where they are not. The experimental data and theoretical calculations support the proposal that ET occurs by a direct through-space process and that the observed slow charge recombination arises from an increase in the separation of the terminal chromophores due to electrostatic repulsion between the porphyrin and methyl viologen radical cations.

Introduction

The synthesis and study of multichromophoric structures containing electron donor (D) and acceptor (A) species has contributed much to the fundamental understanding of photoinduced electron transfer (ET) processes. By careful design of such systems, key issues in ET can be singled out for study.^{1–4} For example, the covalent attachment of chromophores to rigid bridges has provided valuable insight into the dependence of ET dynamics on the nature of D and A^{5–8} and their relative separation and orientation.^{9–11} More recently, multichromophoric systems of the type **1**, in which more than two redox centers are connected in series by rigid bridges, are being studied with the prime aim of generating long-lived charge-separated

(CS) states with high efficiency.^{12–15} These types of systems are also being used to probe other aspects of ET, such as superexchange^{16–19} mechanisms and solvent-mediated ET processes.^{20–22}



Recently, our group has investigated multichromophoric systems, of the general structure depicted by **2**, based on the

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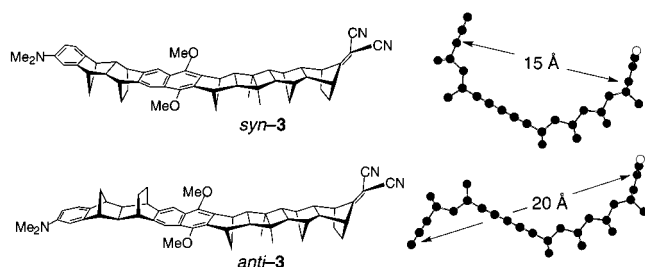
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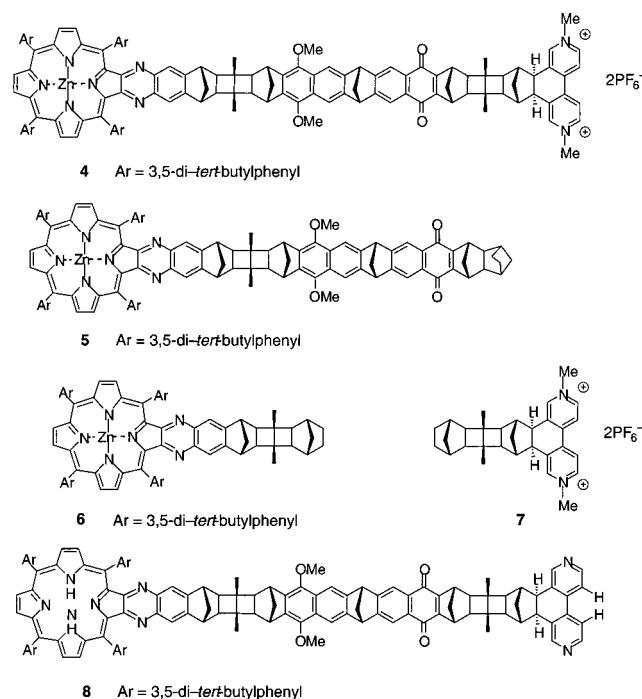
norbornylogous bridge.^{1,7,9,23,24} These systems offer a number of advantages, a particularly important one being the ability to modify dramatically the shape of the supramolecular assembly by fixing the central methano bridges of **2** to be either *syn* or *anti* with respect to each other. Such stereochemical control enables one to probe more intimately superexchange and solvent-mediated ET processes. For example, the spatial relationships between the two terminal chromophores in the *syn* and *anti* stereoisomers of **3** are quite different; in the former isomer, they are separated by a 15 Å U-shaped cavity, whereas in the latter this cavity is absent. Comparison of photoinduced rates of charge separation and subsequent charge recombination in *syn*-**3** and *anti*-**3** is providing interesting insights into the role of solvent-mediated ET in the U-shaped *syn* isomer.^{6,7,9,11,25} Subsequent studies on U-shaped systems possessing smaller cavity sizes are providing more definitive information concerning solvent-mediated ET and how the dynamics of such processes depend on solvent properties.^{26–29}



We have recently extended our studies of multichromophoric systems to the giant tetrad **4** (Scheme 1), containing zinc porphyrin (P_{Zn}) and methyl viologen (MV^{2+}) as the terminal chromophores and dimethoxynaphthalene (DMN) and naphthoquinone (NQ) as intermediate chromophores.^{23,30,31} This system offers the promise of exploring the relative importance of three competing mechanisms for effecting photoinduced ET from locally excited P_{Zn} donor to MV^{2+} acceptor, namely: (1) superexchange through the bridge, (2) electron hopping through the bridge in which ET takes place via the intermediacy of DMN and NQ radical anions, and (3) direct ET between P_{Zn} and MV^{2+} , either through-solvent or through-space.

This mechanistic multiplicity could fruitfully be explored by comparing ET rates for various stereoisomers of **4** (Figure 1), since superexchange should be the sole mechanism responsible for ET in the S-shaped *anti* stereoisomers, if it occurs at all over such a large distance, whereas direct, or through-solvent-mediated ET may be the dominant mechanism operating in the U-shaped *syn,syn* isomer. Preliminary photophysical measurements carried out on *syn,syn*-**4** revealed that efficient intramo-

Scheme 1. Giant Tetrad **4** and Various Model Systems **5–7** for Photophysical Studies



lecular ET took place to give the giant CS state $^{++}P_{Zn}-MV^{+}$, but the mechanism responsible for this ET process, i.e., direct, solvent-mediated, or superexchange, could not be elucidated.³⁰ In an attempt to shed more light on the fascinating photophysical results for the U-shaped *syn,syn*-**4**, we have now synthesized the *anti* isomers of this system (Scheme 1). Herein, we present the results of photophysical studies on both *syn* and *anti* systems and the effect of solvent and temperature on the dynamics of photoinduced ET in these systems.

Experimental Section

The synthesis of the stereoisomers of **4** and the model compounds **5–7** has been reported elsewhere.^{23,30,31} An isomerically pure sample of *syn,syn*-**4** was used. Because it was difficult to separate the *anti* isomers, a 3:1 mixture of *anti,syn*-**4** and *anti,anti*-**4** was used in the photophysical studies (hereafter referred to as *anti*-**4**). This course of action should not compromise the interpretation of the photophysical data since the porphyrin–viologen (through-space) separation is very large in both *anti* stereoisomers: 32.2 and 34.9 Å for *anti,syn* and *anti,anti* isomers, respectively.³¹

Photophysical measurements were carried out as reported previously.³⁰ Solvents were spectroscopic grade and solutions were degassed by multiple freeze–pump–thaw cycles. Methyl viologen radical cation was generated by reduction of **7** with Na_2S in the absence of O_2 . The solution was purged with N_2 and sealed and a deep blue color was afforded indicating the formation of the radical cation of **7**. Steady-state absorption spectra were recorded on a Hitachi 150-20 spectrophotometer. Fluorescence decay profiles were obtained by the time correlated single photon counting technique using a mode-locked and cavity-dumped Spectra Physics 3500 dye laser as the excitation source. Temperature-dependent fluorescence measurements were conducted in an Oxford Instruments Optistat cryostat.

Results and Discussion

Preliminary results³⁰ reported the observation of fast efficient ET from P_{Zn} to MV^{2+} in *syn,syn*-**4** in acetonitrile. The resultant giant CS state showed remarkable longevity and the rate for the charge recombination process is ~ 1000 times slower than that for the forward ET process. Studies of this molecule have

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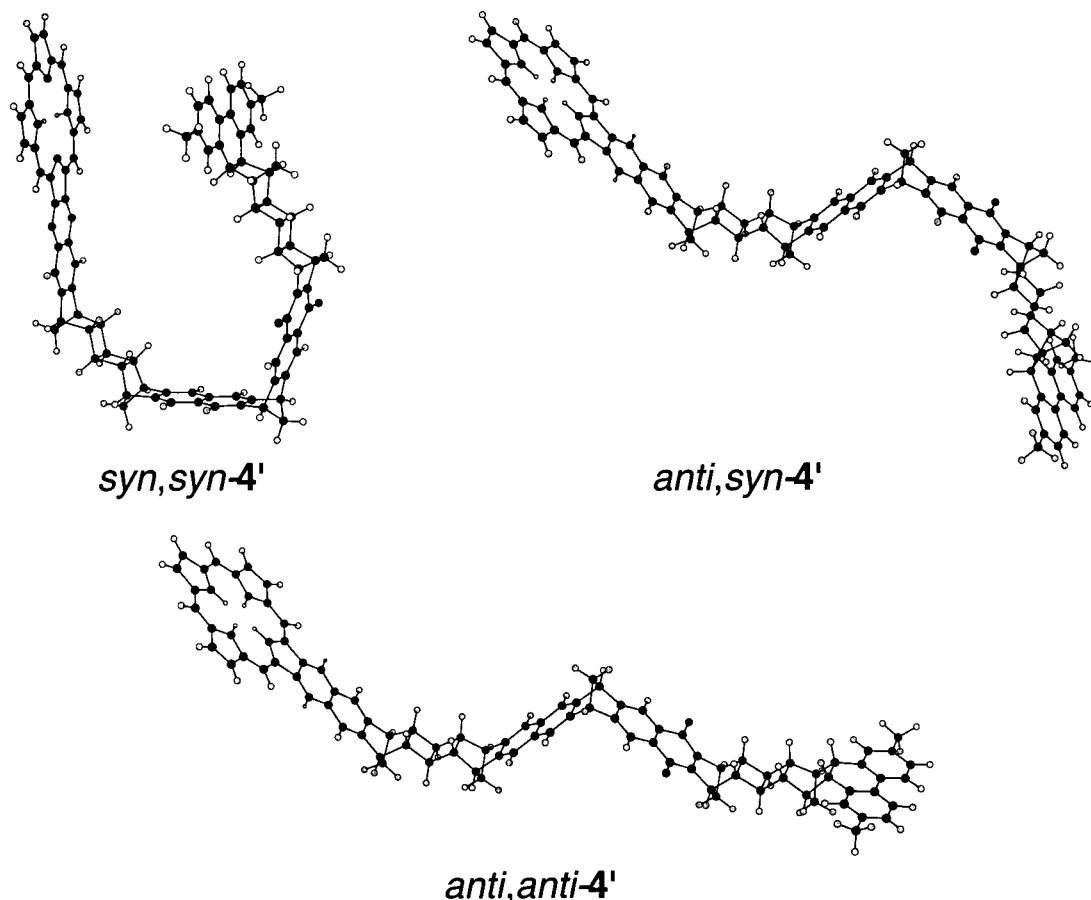


Figure 1. AM1 optimized structures for three stereoisomers of a simplified version of the tetrad, **4**, $P_{Zn}-(6\sigma)$ -DMN-(2 σ)-NQ-(7 σ)-MV $^{2+}$. The simplified molecules, designated by **4'**, differ from the unprimed ones in that each of the former series of molecules has free base porphyrin, rather than P_{Zn} , the DMN group is replaced with naphthalene, and the bicyclo[2.2.0] unit is not methylated.

Table 1. Fluorescence Lifetimes (τ_{fl}) and Rate Constants for Electron Transfer (k_{ET}) and Charge Recombination (k_{CR}) for Molecules Studied

	τ_{fl} (ns)		rate constants for <i>syn,syn-4</i>		
	aceto-nitrile	benzo-nitrile		aceto-nitrile	benzo-nitrile
<i>syn,syn-4</i>	0.33 ^b	0.35 ^b	k_{ET} (10^9 s $^{-1}$)	2.3	2.1
<i>anti-4</i> ^a	1.28	1.26	k_{CR} (10^6 s $^{-1}$)	2.3	4.2
5	1.22	1.28	k_{ET}/k_{CR}	1000	500
6	1.33	1.35			

^a 3:1 mixture of *anti,syn-4* and *anti,anti-4*, respectively. ^b Major (85% contribution) short lifetime component.

now been carried out in benzonitrile, a polar aromatic solvent that other studies suggest can play an active role in mediating ET processes.²⁹ Considerable quenching of the fluorescence emission occurs for *syn,syn-4* in both acetonitrile and benzonitrile when compared to the model porphyrin **6**, whereas no quenching is observed for the *anti-4* mixture. The fluorescence lifetimes extracted from the fluorescence decay profiles of the compounds studied and the corresponding rates for photoinduced ET are presented in Table 1. In the case of *syn,syn-4*, in addition to the quenched lifetime component there is a smaller (15%) component having the same fluorescence lifetime as that of the excited state of the model porphyrin **6**. The fluorescence quenching observed for *syn,syn-4* is accompanied by the formation of new transient absorptions associated with radical ion pair formation.

Figure 2 shows the transient absorption spectrum of *syn,syn-4* in benzonitrile and exhibits two broad transient absorptions at

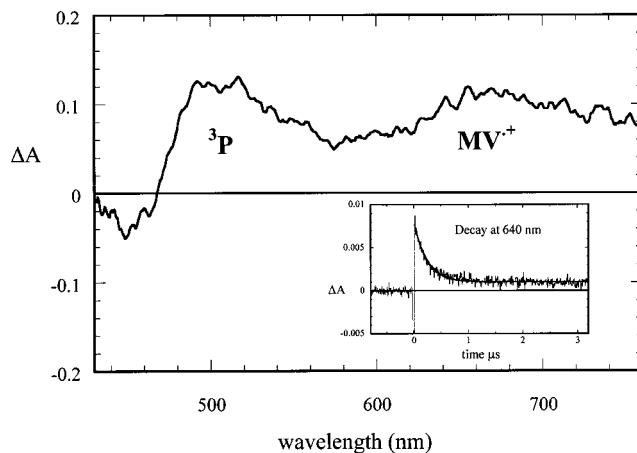


Figure 2. Transient absorption spectrum of *syn,syn-4* in benzonitrile recorded 100 ns after photoexcitation. Absorbing species, methyl viologen radical cation (MV $^{+}$), and porphyrin triplet state (3P) are indicated. The inset shows the decay of the transient absorption at 640 nm. The data were fitted to a single-exponential function with a baseline offset, $\Delta A = Be^{(-t/\tau)} + C$; $\tau = 233$ ns, $B/C = 6.83$.

480–560 and 600–700 nm. The longer wavelength transient absorption (600–700 nm) can be attributed to MV $^{+}$, formed following photoinduced ET from the photoexcited P_{Zn} chromophore. The identification of this species was confirmed by comparison with the absorption spectrum of authentic MV $^{+}$, generated by the chemical reduction of the MV $^{2+}$ model compound **7**. The transient absorption decay profile at 640

could be fitted with one exponential lifetime of 233 ns and a second much longer lived component that is best represented over the time frame of the decay of the shorter component by a small baseline offset of some 13%. This longer lifetime component and the shorter wavelength transient band (480–560 nm) may be assigned to the residual porphyrin triplet state since the triplet state of the model porphyrin compound **6** absorbs strongly around 500 nm and weakly throughout the red end of the visible spectrum with a lifetime of 350–400 μ s. Table 1 summarizes the kinetic data for all compounds in both benzonitrile and acetonitrile.

The kinetic data obtained provide insights into the nature of the ET mechanism occurring in *syn,syn-4*. The observation that no photoinduced ET takes place in either the *anti-4* mixture of stereoisomers or the model triad, **5**, which lacks the terminal MV²⁺ acceptor moiety, is convincing evidence that the observed photoinduced ET in *syn,syn-4* does not occur by way of the intervening bridge, either by a through-bridge superexchange mechanism or by a multistep process involving electron hopping via the intermediate chromophores. (A stepwise mechanism involving the transfer of an electron from photoexcited P_{Zn} to the NQ chromophore is feasible as there is a small calculated negative free energy change for this process in the solvents studied.)

The results therefore strongly suggest that intramolecular photoinduced ET in *syn,syn-4* occurs directly from the locally excited donor (P_{Zn}) to the acceptor (MV²⁺), perhaps involving solvent mediation. In previous work by Zimmt et al.²⁸ on a rigid U-shaped bichromophoric molecule possessing dimethoxyanthracene (DMA) donor and dicyanovinyl (DCV) acceptor groups, it was concluded that a solvent molecule occupying the U-shaped cavity could mediate direct electron transfer between the redox couple. In support of this argument, a strong correlation between the vertical electron affinity, EA_v, of the solvent and the observed rate of ET in this system was found.²⁹ In particular, benzonitrile (EA_v = 0.2 eV) assisted ET considerably, whereas acetonitrile (EA_v = -2.8 eV) did not promote ET (the estimated electronic coupling matrix element for ET in the system in benzonitrile is about an order of magnitude greater than that in acetonitrile).

In marked contrast, we find that the photoinduced ET rate in *syn,syn-4* is approximately the same in both benzonitrile and acetonitrile. This lack of dependence of ET rate in *syn,syn-4* on solvent EA_v suggests that the solvent is *not* mediating ET from P_{Zn} to MV²⁺. It is tempting to explain this surprising finding in terms of the much lower excitation energy for the P_{Zn} donor than that for the dimethoxyanthracene group in the DMA-DCV system. This would reduce the magnitude of the electronic coupling between the locally excited reactant state of P_{Zn} and the virtual anionic states of the solvent molecule for *syn,syn-4*, compared to that for the DMA-DCV system. However, the problem with this explanation is that rapid, efficient, photoinduced ET nevertheless takes place in *syn,syn-4* in both acetonitrile and benzonitrile solvents.

An alternative explanation that accommodates the facts is that ET in *syn,syn-4* takes place by way of direct, through-space interaction between the P_{Zn} and MV²⁺ chromophores. This would require the chromophores to be no further than about 6 Å apart. Intriguingly, ¹H NMR spectra showed strong upfield shifts in the resonances of some bipyridyl (bipy) protons in *syn,syn-8*, the free base bipyridyl precursor of *syn,syn-4*. Specifically, the bipy protons shown in the structure of *syn,syn-8* appear at 3.3 ppm (δ , CDCl₃), representing a 4.4 ppm upfield shift, relative to a model bipy system.³¹ This observation implies

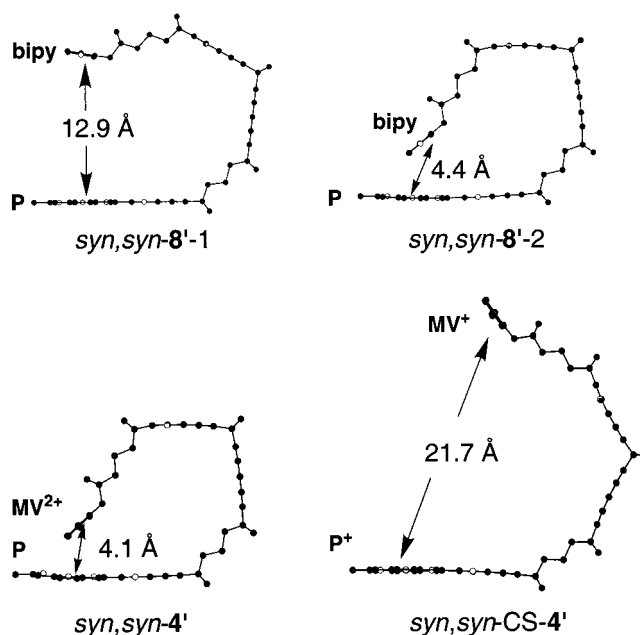


Figure 3. Profiles of gas-phase (U)HF/3-21G optimized structures for *syn,syn-8'*, *syn,syn-4'*, and the giant triplet CS state of the latter, *syn,syn-CS-4'*. The primed molecules differ from the unprimed ones in that each of the former series of molecules has free base porphyrin, rather than P_{Zn}, the DMN group is replaced with naphthalene, and the bicyclo-[2.2.0] unit is not methylated. Two stable conformations were located for *syn,syn-8'*, with *syn,syn-8'-2* being 0.4 kcal mol⁻¹ more stable than *syn,syn-8'-1*.

that the bipy group is lying well within the shielding zone of the porphyrin moiety and that the bipy–porphyrin separation is probably no more than 4 Å in *syn,syn-8*. This conjecture receives support from gas-phase ab initio RHF/3-21G calculations carried out on a slightly simplified version of this molecule, denoted by *syn,syn-8'*.³¹ Two stable conformations were located (Figure 3), *syn,syn-8'-1* and *syn,syn-8'-2*. The porphyrin–bipy separation in the former conformer is about 13 Å and corresponds to relaxed geometry of the bridge framework with the terminal chromophores not interacting with each other. On the other hand, the porphyrin–bipy separation in the slightly more stable conformer, *syn,syn-8'-2*, is only 4.4 Å, a feat that is achieved by out-of-plane bending of the internal naphthalene and NQ chromophores. Attractive Coulombic forces between the porphyrin and bipy moieties are the driving forces for this geometric distortion.³¹

Only modest upfield shifts (ca. 1 ppm) for the MV²⁺ protons were observed for *syn,syn-4* in the more polar acetone solvent, suggesting that the porphyrin and the MV²⁺ groups are now further apart than they are in *syn,syn-8*, but that they may still lie within 6 Å separation of each other. Gas-phase HF/3-21G calculations on *syn,syn-4'*, a simplified version of *syn,syn-4*, led to only one stable structure, in which the porphyrin and viologen groups are only 4.1 Å apart (Figure 3).³¹ While the separation between the terminal chromophores in *syn,syn-4* in the condensed phase will almost certainly be greater than the calculated gas-phase value of 4 Å, the favorable near face-to-face orientation of P_{Zn} and MV²⁺ in this system, combined with the promotion of electron density into the spatially diffuse LUMO of photoexcited P_{Zn}, should enhance direct orbital overlap between locally excited P_{Zn} and MV²⁺. The close approach of the donor and acceptor thus facilitates the through-space transfer without the requirement for any solvent mediation.

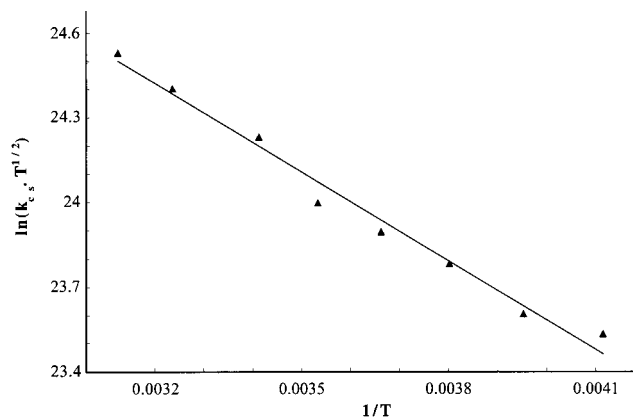


Figure 4. Plot of $\ln(k_{\text{ET}}T^{1/2})$ vs $1/T$ for the photoinduced charge separation rate for *syn,syn-4* in acetonitrile over the temperature range 243–320 K. The data were fitted to a straight line, $\ln(k_{\text{ET}}T^{1/2}) = mT + c$; $m = -1050$, $c = 27.8$. The activation barrier, $\Delta G_{\text{ET}}^{\ddagger}$, for ET derived from the gradient is 0.09 eV.

Temperature-dependent fluorescence lifetime studies were conducted over the temperature range of 233–320 K for *syn,syn-4* and the porphyrin model **6** in acetonitrile. The short lifetime component of the fluorescence decay of *syn,syn-4* exhibited a significant temperature dependence. When the D–A electronic coupling is weak ($\ll kT$), ET may be considered to occur nonadiabatically³² and the rate, k_{ET} , is well described by application of Fermi's Golden Rule:

$$k_{\text{ET}} = \text{FCWDS} |V^*|^2 \frac{4\pi^2}{h} \quad (1)$$

where V^* is the electronic coupling matrix element and FCWDS is the Frank Condon weighted density of states. In the high-temperature limit the FCWDS can be represented classically:^{33,34}

$$\text{FCWDS} = \frac{1}{(4\pi\lambda k_{\text{b}}T)^{1/2}} \exp\left[-\frac{(\Delta G_{\text{ET}}^{\circ} + \lambda)^2}{4\lambda k_{\text{b}}T}\right] \quad (2)$$

where λ = total reorganization energy (solvent plus internal), k_{b} = Boltzmann's constant, and $\Delta G_{\text{ET}}^{\circ}$ = free energy change for ET. Marcus theory^{35,36} relates the activation barrier, $\Delta G_{\text{ET}}^{\ddagger}$, to the free energy:

$$\Delta G_{\text{ET}}^{\ddagger} = \frac{(\Delta G_{\text{ET}}^{\circ} + \lambda)^2}{4\lambda} \quad (3)$$

A plot of $\ln(k_{\text{ET}}T^{1/2})$ vs $1/T$ (where $k_{\text{ET}} = 1/\tau_{\text{syn,syn-4}} - 1/\tau_{\text{c}}$) gave a linear relationship (Figure 4) consistent with the behavior predicted from eqs 1 and 2 resulting in a gradient of -1050 and an ordinate intercept of 27.8. Assuming that the conformation of the molecule and the reaction exergonicity remains temperature independent and that the solvent reorganization energy is also insensitive to temperature, a value for $\Delta G_{\text{ET}}^{\ddagger}$ of 0.09 eV can be derived from the gradient.³⁷ This quantity can be used to calculate λ and, with the ordinate intercept, V^* for the electron-transfer process by simple substitution into eqs

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1–3.^{8,38} The calculated values for λ and V^* using this approach are 1.5 eV and 18 cm^{-1} , respectively.³⁹ The reorganization energy is of similar magnitude to values reported for other intramolecular ET reactions in acetonitrile,³⁸ while the electronic coupling is much greater than would be expected if through-bond interaction was the mechanism operating for a donor/acceptor pair separated by a nonbonylogous bridge of this length.⁸ Zimmt and co-workers^{40,41} have examined the factors affecting the temperature dependence of intramolecular photoinduced electron transfer rates in considerable detail which indicate that the assumptions made in the above analysis may not be rigorous. Nevertheless, the low activation barrier and strong electronic coupling are consistent with the conclusion that a direct (i.e. through-solvent or through-space rather than through-bond) ET mechanism is operative. It has been reported previously that electronic coupling through acetonitrile solvent in a U-shaped DMN-DCV dyad possessing a 10 Å wide cavity is quite small, $< 2 \text{ cm}^{-1}$.²⁹ The much larger value of 18 cm^{-1} for the electronic coupling for *syn,syn-4* in acetonitrile found in this work suggests that a direct, through-space mechanism is operating in this system in which the cavity size is quite small (≈ 7 Å). Model HF/6-31+G calculations on a complex comprising two ethene molecules lying in parallel planes and separated by 7 Å gives a through-space π,π splitting of 72 cm^{-1} .⁴² The coupling of 18 cm^{-1} calculated from the experimental data for *syn,syn-4* is therefore not inconsistent with a through-space ET process.

The ratio of the preexponential factors for the short lifetime and long lifetime (unquenched) components of the fluorescence decay of *syn,syn-4* in acetonitrile was found to be markedly temperature dependent with the relative contribution from the long-lived component increasing from 15% at room temperature to over 50% at 233 K. This behavior is consistent with a temperature-dependent equilibrium between two conformations of *syn,syn-4* in solution where only one conformation, characterized by the short lifetime component, is capable of undergoing ET.^{43,44} The two conformers are likely to resemble the “collapsed” conformation of *syn,syn-4'* and the “extended” conformation of *syn,syn-8'* (Figure 3). The barrier between these conformers must be significant to account for the apparent slow interconversion during the fluorescence lifetime and arises from the two opposing effects of increased Coulombic stabilization and out-of-plane ring bending of the DMN and NQ rings in the backbone. Both HF/3-21G and AM1 calculations predict the existence of the collapsed conformer for *syn,syn-4'*. As well, AM1 calculations predict the existence of the extended conformer at about 12 kcal/mol higher in energy than the collapsed conformer.³¹ These are gas-phase calculations and in polar solvents it might be expected that the relative energies of the conformers could be quite different. The AM1 calculated center-to-center distance between the porphyrin and viologen chromophores in the extended and collapsed conformers of *syn,syn-4'* is 9.98 and 5.26 Å, respectively. AM1 calculations on the

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collapsed conformer of *syn,syn-4* (i.e. the complete molecule including the 3,5-di-*tert*-butylphenyl groups) show that there is no steric congestion between the *tert*-butyl groups and the viologen group in the gas phase which would interfere with the approach of the end groups indicated in Figure 3.

UHF/3-21G calculations also indicate possible reasons why the charge recombination (CR) rate from the giant CS state of *syn,syn-4* is 3 orders of magnitude slower than the rate for the forward charge separation reaction (Table 1).⁴⁵ Even though the CR process for *syn,syn-4* undoubtedly lies within the Marcus inverted region, it is unusually slow, by as much as 3 orders of magnitude, compared to similar CR processes in other systems.⁴⁶ The UHF calculations revealed that in the optimized geometry of *syn,syn-CS-4'*, the giant charge-separated state for *syn,syn-4'* differs markedly from that of the ground state in that the $^{+}P_{Zn}-MV^{+}$ separation is about 22 Å (Figure 3). Thus, the porphyrin–viologen separation has increased by some 17 Å following charge separation (in the gas phase), a consequence of strong Coulombic repulsion existing between the positively charged terminal chromophores.⁴⁵

If a similar increase in the interchromophore separation were to occur in solution, then it would explain the slow rate of charge recombination, since direct, through-space, or through-solvent mediated-CR would be unfavored and, consequently, the CR process would now be forced to take place through the long bridge. Enhancement of the CS lifetime via a conformational change due to electrostatic repulsion between the oxidized donor and the reduced acceptor has also been reported in a flexibly linked phenothiazine–Ru(bpy)₃²⁺–diquat system.^{47–50}

Conclusion

The remarkable electrostatically driven conformational changes in *syn,syn-4* which are believed to accompany photoinduced electron transfer and charge recombination processes open up interesting possibilities for the design of molecular systems with

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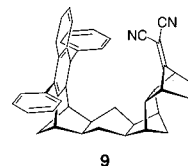
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more effective formation of photoinduced charge gradients. In particular, the increased spatial separation of like charges following electron transfer offers the prospect of dramatically increasing the lifetime of the CS state while still maintaining a high forward ET rate via direct overlap of the D and A orbitals.

On the other hand, the use of supposedly rigid U-shaped redox systems for studying solvent-mediated superexchange coupling mechanisms should be treated circumspectly until more experimental data are amassed. For example, as discussed recently by Paddon-Row and Shephard,⁵¹ geometry changes accompanying charge separation or charge recombination processes in redox systems, on the scale similar to that predicted for *syn,syn-4*, will markedly influence the interpretation of rate data using semiclassical ET theories.



Recent experimental studies on another U-shaped system, namely **9**, by Paddon-Row and Verhoeven⁵² have provided the most convincing confirmation that large geometric distortions may occur in rigid bichromophoric systems. The CS state of **9** was found to display charge transfer (CT) fluorescence in a wide range of solvent polarity which enabled the dipole moment of the CS state to be determined. The surprisingly small dipole found for the CS state of **9** is consistent with the predicted⁴⁵ very small interchromophore separation (4.2 Å), resulting from electrostatically induced attraction between the oppositely charged chromophores.

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