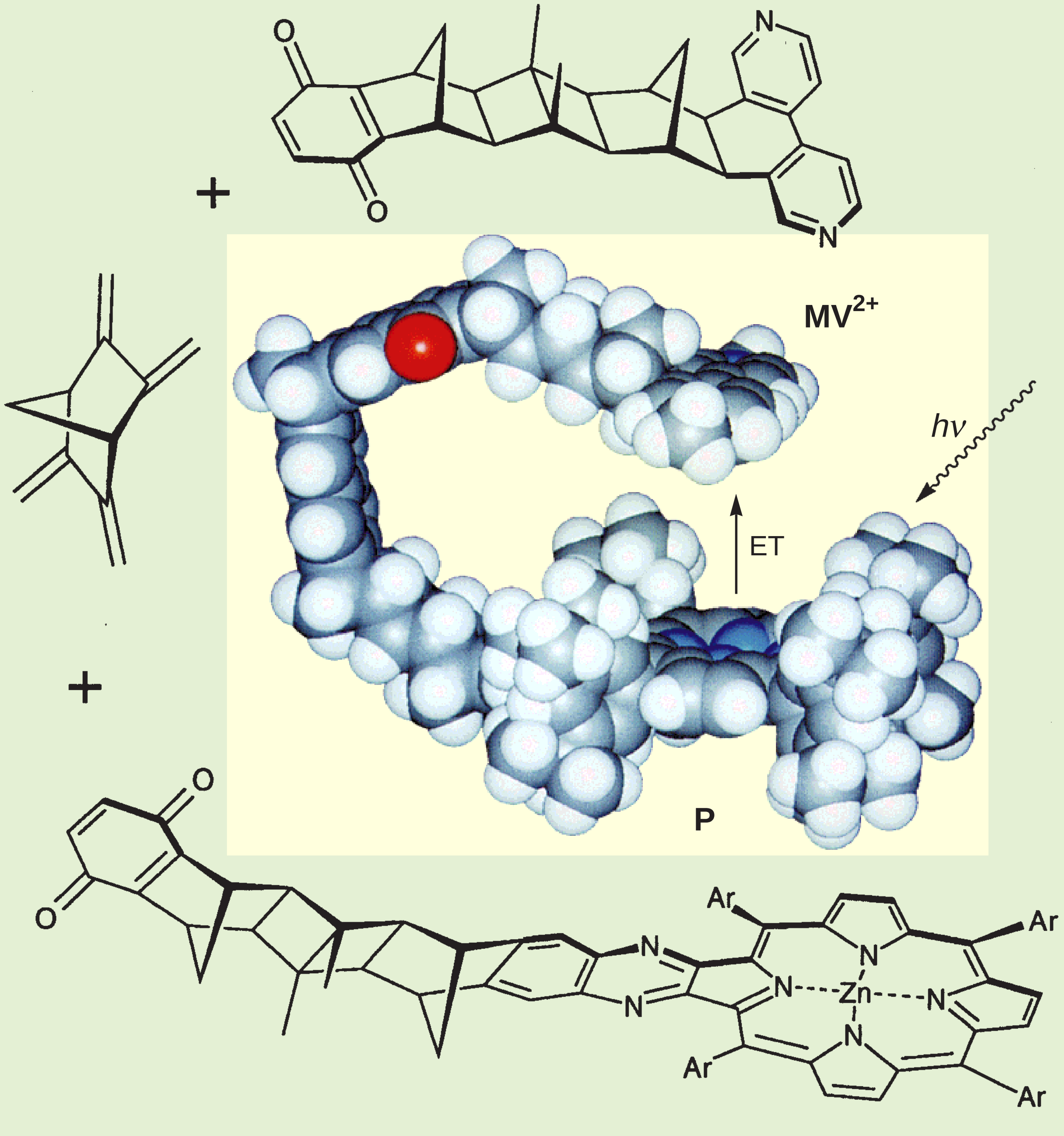

The giant U-shaped tetrad shown above as a space-filling model (and surrounded by the reagents needed for its synthesis) contains porphyrin (P) and methyl viologen (MV^{2+}) chromophores. The terminal P and MV^{2+} units are only about 10 Å apart. Photophysical measurements demonstrate that rapid electron transfer occurs between these units, and that the resulting charge-separated state is remarkably stable towards charge recombination. More details are reported by Paddon-Row et al. on the following pages.

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Efficient Photoinduced Electron Transfer in a Rigid U-Shaped Tetrad Bearing Terminal Porphyrin and Viologen Units**

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Kenneth P. Ghiggino, Steven J. Langford, and
Michael N. Paddon-Row*

Molecules constructed through the covalent attachment of donor and acceptor chromophores to rigid, saturated hydrocarbon bridges continue to provide important and fundamental insights into the characteristics of long-range intramolecular electron transfer (ET) processes.[1] By way of example, our experimental studies on diads involving the norbornyl bridge revealed that these bridges not only serve as a highly rigid scaffold that fixes the chromophores at well-defined separations and orientations with respect to each other, but they also play a crucial role in mediating the ET process by a superexchange or through-bond (TB) coupling mechanism.[1d, 2]

Recently, we extended these studies to the construction of novel trichromophoric compounds such as **1**, which exist in two rigid, noninterconverting diastereomeric *syn* and *anti* forms (Figure 1).[3] Interestingly, the charge recombination (CR) rate constants k_{CR} for the giant charge-separated (CS) states of **1** (i.e., $^{+\bullet}$DMA-bridge-DMN-bridge-DCV$^{\bullet-}$), generated following photoinduced ET, are at least an order of magnitiude different for the *syn* and *anti* diastereomers ($k_{CR}^{syn} > k_{CR}^{anti}$).[4] This behavior is probably a consequence of the fact that the *syn* diastereomer possesses a U-shaped geometry with the terminal chromophores facing each other at a distance of about 15 Å. The orientation of chromophores in the *syn* diastereomer is conducive to a facile solvent-mediated CR process that is not available to the *anti* diastereomer.[4]

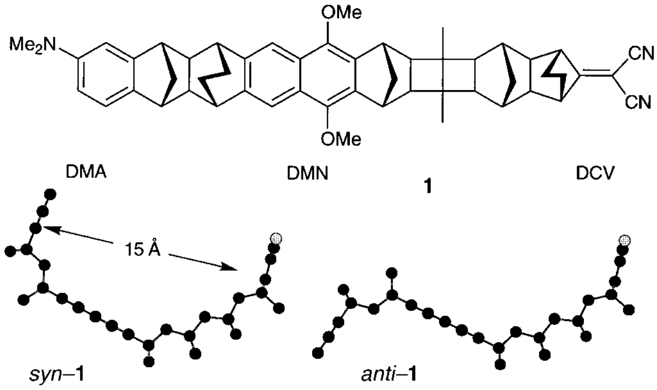

Figure 1. Calculated structures (AM1) of the *syn* and *anti* diastereomers of **1**. The *syn* and *anti* terms refer to the relative disposition of the methano or ethano groups in one bridge with respect to those on the other bridge. DMA = dimethylaminobenzene, DMN = 1,4-dimethoxynaphthaline, DCV = dicyanovinylidene.

To gain a better understanding of the importance of solvent-mediated ET processes, we and others[5] are presently designing and synthesizing rigid systems possessing U-shaped cavities of various dimensions. Here we describe the synthesis and photophysical properties of the *syn,syn*-tetrad $\mathbf{2}\cdot 2\,PF_6$ (Figure 2).[6] This compound is endowed with several features which make it well suited for studying photoinduced ET processes: 1) The porphyrin and methyl viologen chromophores serve as acceptable mimics of redox chromophores which participate in biological ET processes; 2) the synthetic strategy adopted to prepare $\mathbf{2}\cdot 2\,PF_6$ follows a "building-block" approach in which more than ten different types of chromophores[2, 7] can be incorporated into the methodology; 3) most importantly, the geometry-optimized structure (AM1) for *syn,syn*-$\mathbf{2}\cdot 2\,PF_6$ reveals that the porphyrin and viologen chromophores lie in roughly parallel planes approximately 10 Å apart. The near cofacial alignment of the two chromophores provides an excellent opportunity for exploring the role of solvent-mediated ET processes.

Tetrads of the type $\mathbf{2}\cdot 2\,PF_6$ may be synthesized[8] by a convergent pathway (Scheme 1 on page 918) involving the cycloaddition of tetraenes such as **3**[9] with dienophiles such as **4**[7b,c, 10] and **5**. Quinone **5** is formed by the reaction of **6**[11] with BBr_3 followed by oxidation[12] of the resulting hydroquinone (AgO/Ag_2O). When tetraene **3** is heated with **4** (0.3 equiv) in toluene at reflux under an inert atmosphere, the corresponding mono-adduct **7** is formed in nearly quantitative yield as a mixture of inseparable diastereomers. That no bis-adduct was produced clearly indicates the difference between the rates for the first and second cycloadditions,[13] thereby making it possible for **3** (or analogues thereof) to react sequentially with a range of dienophiles to yield the backbone of a range of tetrachromophoric systems.

Adduct **7** was converted in two steps into a mixture of *syn*- and *anti*-**8**. Separation of the two diastereomers by preparative thin-layer chromatography (TLC) gave pure *syn*- and *anti*-**8** in a ratio of 70:30. Although we cannot assign *syn* or *anti* stereochemistry to either stereoisomer with absolute certainty, precedence from similar Diels–Alder reactions[3, 14] strongly suggests that the major isomer has *syn* stereochemistry. Diene *syn*-**8** was heated with a large excess of quinone **5** (40 h/Δ/Ar/toluene) in the dark to give directly *syn,syn*- and *syn,anti*-**9**. Separation of the two newly formed diastereomers was achieved by column chromatography upon demetalation of the zinc compounds (2 M HCl/CH_2Cl_2) to give *syn,syn*-[15] and *syn,anti*-**10**. Matrix-assisted laser desorption and ionization (MALDI) mass spectrometry of both fractions yielded a parent ion peak at 2097 mass units, which is consistent with the calculated value for $[\mathbf{10}+2]^+$. Metalation of porphyrin *syn,syn*-**10** with $Zn(OAc)_2\cdot 2\,H_2O$, methylation of the bipyridyl unit (MeI/MeCN/Δ), and exchange of the counterion

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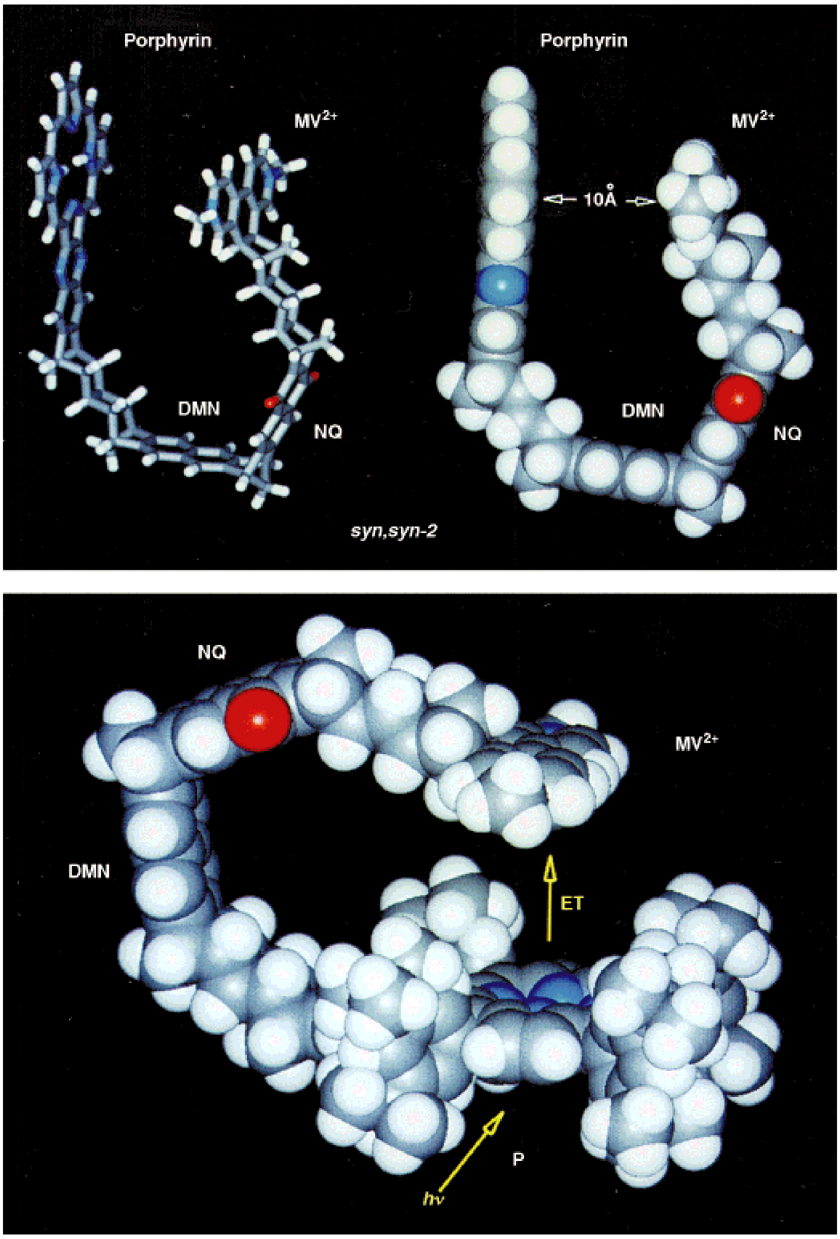
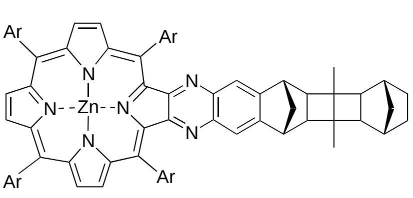


Figure 2. Top: Calculated structure (AM1) of metal-free base *syn,syn*-**2**$\cdot 2PF_6$ showing the near parallel orientation of the porphyrin and methyl viologen units. The 3,5-di-*tert*-butylphenyl and methoxy groups have been omitted for clarity. Bottom: A possible orientation of the *meso* aryl groups in the structure of basic *syn,syn*-**2**$\cdot 2PF_6$. MV = methyl viologen, NQ = naphthoquinone

(NH_4PF_6/aq Me_2CO) gave the desired tetrad *syn,syn*-**2**$\cdot 2PF_6$ in 72% yield. A MALDI mass spectrum of *syn,syn*-**2**$\cdot 2PF_6$ showed a parent ion at 2188 mass units, which corresponds to the molecular mass of $[\mathbf{2} - 2PF_6]^+$.

Evidence for photoinduced ET from the porphyrin to the viologen unit was obtained from time-resolved fluorescence and laser flash photolysis studies. The fluorescence lifetime of porphyrin emission from *syn,syn*-**2**$\cdot 2PF_6$ ($\tau = 330$ ps) was shorter than that of the porphyrin model compound **11** ($\tau = 1.16$ ns; Ar = 3,5-di-*tert*-butylphenyl). This indicates the presence of an additional nonradiative process occurring in *syn,syn*-**2**$\cdot 2PF_6$ with a rate constant of $3 \times 10^9\ s^{-1}$ following photoexcitation. Laser flash photolysis of **11** resulted in a long-lived transient absorption ($\lambda_{max} \approx 500$ nm, $\tau = 400\ \mu s$), which was attributed to the formation of a triplet state by intersystem crossing from the porphyrin singlet state. The transient spectrum of *syn,syn*-**2**$\cdot 2PF_6$ (Figure 3) was markedly different from that of **11** and exhibited additional transient absorptions in the 580–690 nm and 700–800 nm spectral regions. Comparison with the spectrum of chemically reduced **12** enabled the assignment of the band at 580–690 nm to the methyl viologen radical ion, $MV^{\bullet +}$.



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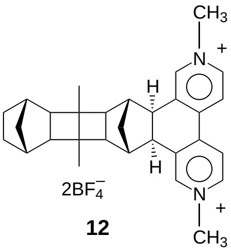

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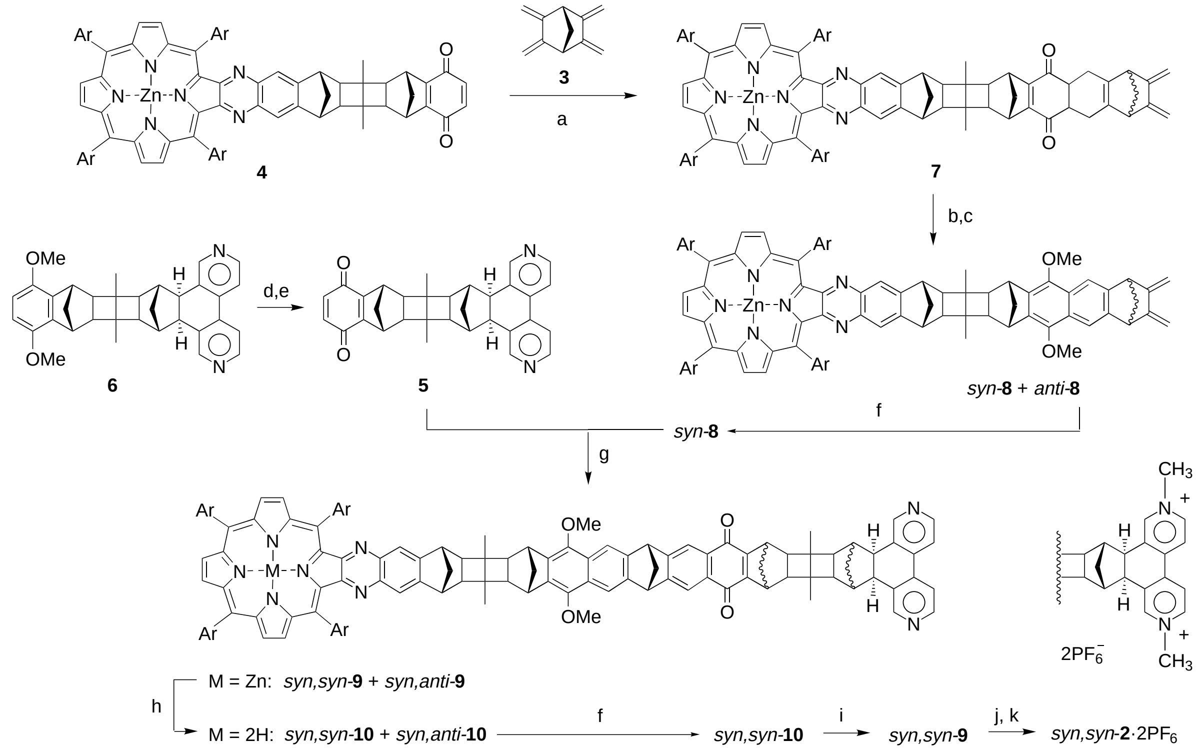
There remains an additional transient absorption above 690 nm. Previous work on other linked, porphyrin-based donor–acceptor molecules carried out by ourselves[16a] and others[16c] has assigned absorption in this spectral region to the



Scheme 1. Synthesis of tetrad *syn,syn*-**2**$\cdot 2PF_6$. a) Toluene, 80°C, 99%; b) K_2CO_3, Me_2CO, MeI, 86%; c) DDQ, CH_2Cl_2, 83%, separate isomers; d) BBr_3, CH_2Cl_2, 83%; e) AgO, Ag_2O, CH_2Cl_2, 85%; f) **5** (7 equiv), 40 h, reflux, $CH_3C_6H_5$; g) 2M HCl, CH_2Cl_2, 60% over two steps, separate isomers; h) $Zn(OAc)_2 \cdot 2H_2O$, MeOH, $CHCl_3$; i) MeI, MeCN, reflux; j) NH_4PF_6, H_2O, Me_2CO, 72% over three steps. DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone.

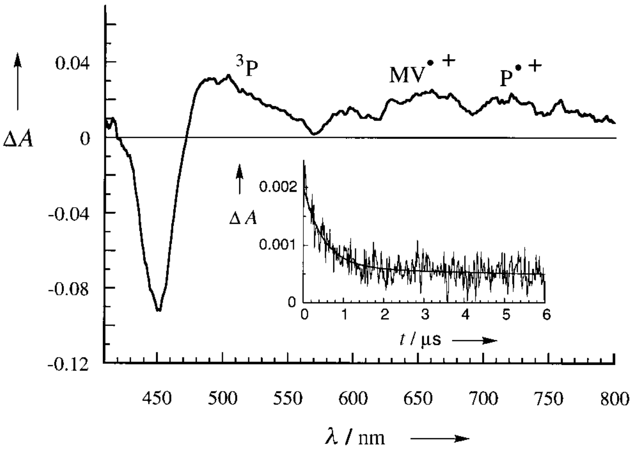


Figure 3. Transient absorption spectrum of *syn,syn*-**2**$\cdot 2PF_6$ in MeCN recorded 700 ns after photoexcitation along with assignments of the absorbing species. The inset shows the decay of the transient absorption at 650 nm. The data were obtained by fitting to Equation (1); $\tau_1 = 500$ ns, $\tau_2 = 32$ µs, $B/C = 2.33$.

$$\Delta A = B\,e^{(-t/\tau_1)} + C\,e^{(-t/\tau_2)} \tag{1}$$

porphyrin radical cation, $P^{•+}$. Thus, the transient absorption spectra provide convincing evidence for photoinduced ET from locally excited porphyrin, P*, to MV^{2+} in *syn,syn*-**2**$\cdot 2PF_6$. The additional absorption near 500 nm (Figure 3) can be assigned to residual formation of a triplet state, whereas there is strong bleaching of the ground state in the region of the porphyrin Soret band at 450 nm.

The decay behavior of the transient spectrum is complex. Analysis of the decay kinetics in the region of the radical-ion absorbance yielded two components (inset of Figure 3). The contribution of the shorter component dominates (≈70%) and decays with a lifetime of 500 ns (±15%) at 650 nm and 710 nm, whereas the longer component decays over tens of microseconds!

These results indicate that photoinduced ET occurs in *syn,syn*-**2**$\cdot 2PF_6$ with a quantum efficiency of 78% and formation of the giant CS state $P^{•+}$-DMN-NQ-$MV^{•+}$. The ratio of the rates of charge separation to charge recombination is greater than 1400. The observation of efficient photoinduced ET from locally excited P* to MV^{2+} is surprising because, although the process is calculated[17] to be strongly exoergic (−0.77 eV), the P and MV^{2+} chromophores are remote in terms of spatial separation (10 Å) and connectivity (23 σ bonds). Three mechanisms could explain the observed ET dynamics: 1) direct, solvent-mediated ET from P* to MV^{2+}; 2) direct TB-mediated ET from P* to MV^{2+} through the orbitals of the bridge and the DMN and NQ units; 3) a two-step ET process in which TB-mediated ET from P* to NQ occurs first to generate the CS intermediate $P^{•+}$\{bridge\}$NQ^{•-}$ followed by thermal ET from $NQ^{•-}$ to MV^{2+}. Both steps are estimated to be exoergic, the first by about 0.25 eV,[7h, 17] and the second by about 0.52 eV[17]. The present experimental data are unable to discriminate between these mechanisms, although the solvent-mediated mechanism would appear to be more plausible than the other two mechanisms.[18] Further investigations are in progress to resolve both the matter of mechanisms and the origin of the complex decay kinetics of the CS species.

Experimental Section

Photophysical measurements were carried out at room temperature on solutions in MeCN which were thoroughly degassed by freeze-pump-thaw cycles. Transient decay experiments were performed with a laser flash photolysis apparatus that used the second harmonic of a Nd-YAG laser (Continuum) for photoexcitation at 530 nm. Transient species generated by the absorption of 5-mJ excitation pulses (pulse width 7 ns) were monitored at right angles to the excitation with a pulsed 150-watt high-pressure xenon lamp, a photomultiplier tube, and a digital oscilloscope. For transient spectra, the flash photolysis system (CSIRO Division of Molecular Sciences) incorporated an excimer laser excitation source (351 nm) and a gated diode array/optical multichannel analyser detector (Princeton Applied Research).

syn,syn-**10**: M.p. > 300 °C; ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = -2.64$ (brs, 2H), 0.45 (m, 1H), 0.52 (s, 6H), 0.92 (m, 1H), 1.11 (s, 6H), 1.34 (m, 1H), 1.41 (s, 18H), 1.46 (s, 18H), 1.54 (s, 36H), 1.60 (s, 2H), 1.63 (m, 1H), 1.70 (s, 2H), 1.75 (m, 1H), 1.79 (m, 1H), 1.83 (s, 2H), 1.90 (s, 4H), 1.97 (m, 1H), 2.03 (m, 1H), 2.28 (s, 2H), 2.66 (AB q, 2H), 3.31 (d, $J = 5.1$ Hz, 2H), 3.34 (s, 2H), 3.46 (s, 2H), 3.67 (s, 2H), 3.94 (s, 6H), 4.56 (s, 2H), 6.01 (d, $J = 5.1$ Hz, 2H), 7.32 (s, 2H), 7.36 (t, $J = 1.5$ Hz, 2H), 7.67 (s, 2H), 7.82 (t, $J = 1.5$ Hz, 2H), 7.83 (t, $J = 1.8$ Hz, 2H), 7.86 (m, 2H), 7.89 (s, 2H), 7.91 (s, 2H), 8.12 (t, $J = 1.8$ Hz, 2H), 8.18 (t, $J = 1.8$ Hz, 2H), 8.86 (s, 2H), 9.03 (AB q, 4H); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 8.8$, 9.5, 31.8, 31.9, 34.9, 35.1, 40.0, 40.7, 40.8, 41.0, 42.8, 43.0, 43.5, 43.8, 48.4, 48.6, 50.5, 50.6, 51.0, 52.6, 62.0, 63.2, 113.4, 115.0, 118.1, 119.2, 120.6, 121.2, 122.4, 126.4, 126.8, 128.0, 128.1, 128.6, 129.4, 129.5, 130.5, 131.7, 133.8, 134.1, 135.4, 137.6, 139.6, 140.3, 140.6, 141.2 144.7, 144.8, 145.7, 146.0, 148.4, 148.6, 148.8, 150.0, 150.7, 151.6, 152.6, 154.7, 155.8, 181.8; MS (MALDI): *m/z*: 2097 $[M+2]^+$.

syn,syn-**2** $\cdot$ 2PF$_6$: M.p. > 300 °C; ^{1}H NMR (500 MHz, [D$_6$]acetone): $\delta = 0.68$ (s, 6H), 0.92 (m, 1H), 1.09 (m, 1H), 1.17 (s, 6H), 1.40 (s, 18H), 1.48 (s, 18H), 1.54 (s, 36H), 1.70 (m, 2H), 1.92 (m, 3H), 2.19 (m, 3H), 2.30 (s, 2H), 2.58 (AB q, 2H), 3.09 (s, 2H), 3.32 (s, 2H), 3.60 (s, 2H), 3.75 (s, 2H), 3.92 (s, 6H), 4.15 (s, 6H), 4.69 (s, 2H), 7.55 (m, 4H), 7.73 (m, 2H), 7.89 (s, 2H), 7.90 (m, 2H), 7.93 (m, 2H), 7.96 (s, 2H), 7.97 (m, 2H), 8.07 (m, 6H), 8.86 (AB q, 4H), 8.90 (brs, 2H); ^{13}C NMR (75.5 MHz, [D$_6$]acetone): $\delta = 8.4$, 8.8, 31.1, 31.3, 34.6, 34.7, 34.8, 40.7, 40.8, 40.9, 41.0, 42.8, 43.0, 43.6, 43.8, 47.9, 48.3, 49.6, 50.8, 50.9, 52.4, 61.1, 114.8, 118.0, 118.6, 120.3, 120.5, 121.1, 122.0, 123.7, 126.3, 127.7, 128.4, 128.9, 129.3, 131.1, 131.2, 131.5, 131.7, 135.0, 138.7, 139.6, 140.5, 141.5, 142.1, 142.3, 142.5, 144.6, 145.2, 147.9, 148.4, 148.6, 148.7, 148.8, 149.7, 149.8, 150.9, 152.1, 152.9, 156.3, 181.1; MS (MALDI): *m/z*: 2188 $[M - 2\mathrm{PF}_6]^+$.

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[15] Interestingly, the ^{1}H NMR spectrum of *syn,syn*-**10** exhibits a pair of doublets at $\delta = 3.31$ and 6.01 which was not seen for the other isomer. Based on COSY and TOCSY experiments, these resonances are attributed to the ring-fused bipyridyl protons. The upfield nature ($\Delta\delta > 2.5$) of these resonances is most likely a result of an intramolecular porphyrin ring current, which supports the presence of the U-shaped cavity in this molecule. This is reasonable since NOESY experiments indicated that NOEs exist between the signals at $\delta = 6.01$ and 3.31 and those of the inner peripheral protons, the β-pyrrolic protons, and several *tert*-butyl protons within the porphyrin unit. The only other option, that of an intermolecular interaction, can be ruled out on the basis of both ^{1}H NMR and UV dilution studies. Dilution experiments (10^{-2} to 10^{-5} M) resulted in no observable changes in the NMR spectrum or diversion from the Beer–Lambert law for *syn,syn*-**10**.

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[18] Mechanism 2 is unfavored because P and MV^{2+} are separated by 23 σ bonds; superexchange coupling through these bonds is expected to be weak. The first step of mechanism 3 involves a weakly exoergic process taking place over a comparatively large connectivity distance; it is expected to be inefficient. Mechanism 1 involves solvent-mediated ET between chromophores that are about 10 Å apart. There is experimental precedence that this mechanism is efficient for this interchromophore separation.[3, 5]

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