

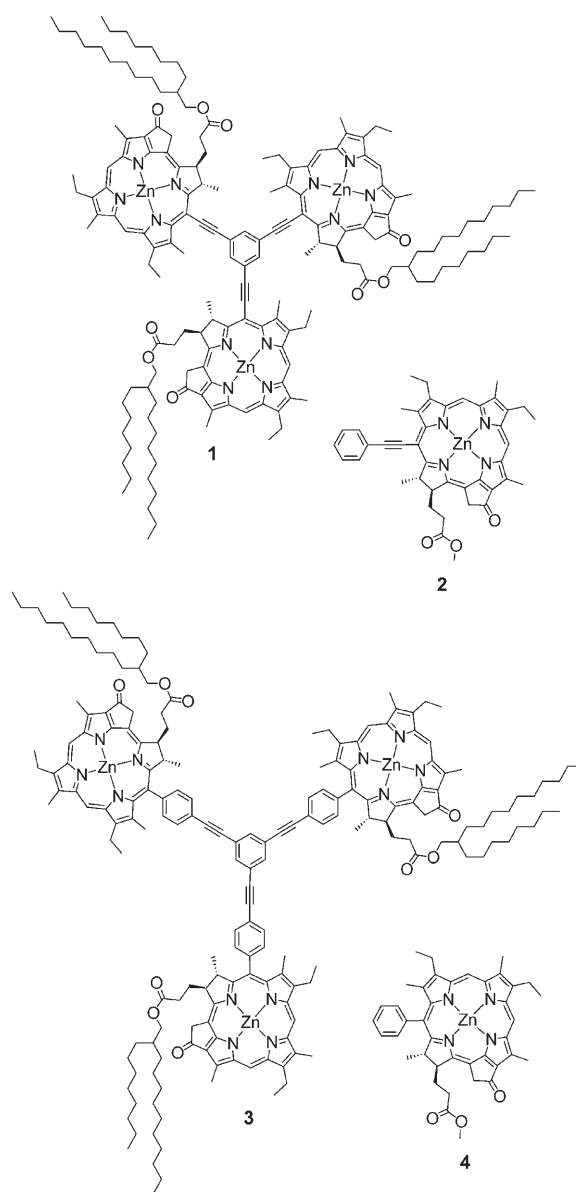
Linker-Controlled Energy and Charge Transfer within Chlorophyll Trefoils**

Richard F. Kelley, Michael J. Tauber, and Michael R. Wasielewski*

Dedicated to Professor Klaus Möbius on the occasion of his 70th birthday

Photosynthetic organisms frequently use chemically identical chlorophylls (Chls) as donors and acceptors of both energy and charge. The specific tasks that these Chls carry out are differentiated largely by their interactions with other Chls, nearby redox cofactors, and the surrounding protein.^[1–3] To mimic this versatility in artificial photosynthetic systems, we have prepared Chl trefoil arrays **1** and **3**, in which both energy and charge transfer are controlled by the structure of the rigid linker between three identical Chls. These molecules use the 20-position of Chl as the point of attachment to the linkers,^[4] thereby leaving the central metals and the 13¹ carbonyl groups available for self-assembly of these building blocks into larger structures for light harvesting as well as charge separation and transport.^[5–10]

Molecules **1–3** were synthesized in 10–20 % overall yields (see the Supporting Information), and **4** was reported previously.^[4] The 20-ethynylchlorophyll linkages were made by using a copper-free Sonogashira reaction^[11] in DMF/Et₃N at room temperature, whereas the 20-phenylchlorophyll linkages were made by using Suzuki coupling. The UV/Vis spectra of **1–4** in THF (Figure 1) show that both the Soret and Q bands of trefoil **1** and its monomeric reference **2** are red-shifted by approximately 10 nm relative to those of the corresponding molecules **3** and **4**. This is because of the small increase in π conjugation afforded by direct attachment of the ethynyl group to the Chl. Excitation of **1** and **2** in THF with 665-nm, 120-fs laser pulses yields transient absorption spectra



of their respective lowest excited singlet states ¹**1** (Figure 2 a) and ¹**2** (see the Supporting Information). The spectra are nearly identical, yet the decay of ¹**2** is monoexponential with

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

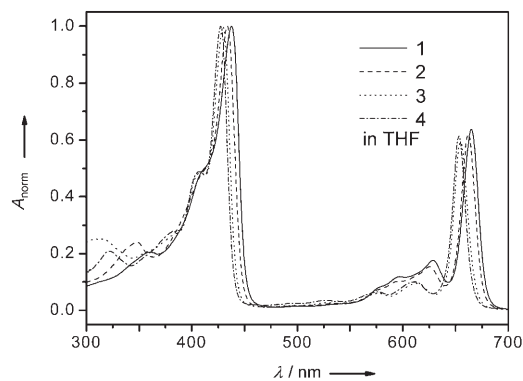


Figure 1. Ground-state electronic absorption spectra of **1–4**. A_{norm} = normalized absorbance.

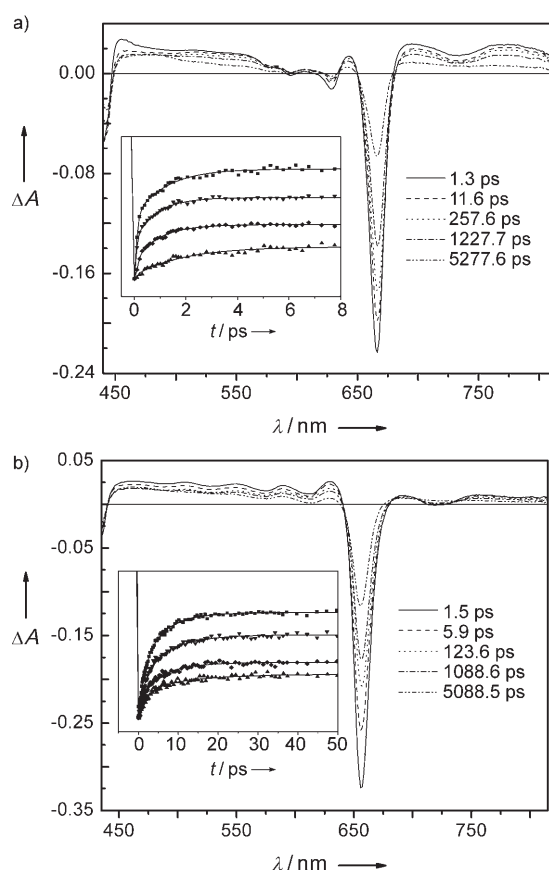


Figure 2. Transient absorption spectra for **1** and **3** in THF. a) Spectra of **1** following excitation with 665-nm, 120-fs laser pulses. Inset: power-dependent transient absorption kinetics of **1** monitored at 658 nm using 1.00 μJ (\blacksquare), 0.66 μJ (\blacktriangledown), 0.33 μJ (\blacklozenge), and 0.11 μJ (\blacktriangle) per pulse. Nonlinear least-squares fits to the kinetic data are also shown. b) Spectra of **3** following excitation with 655-nm, 120-fs laser pulses. Inset: power-dependent transient absorption kinetics of **3** monitored at 658 nm using 1.00 μJ (\blacksquare), 0.33 μJ (\blacktriangledown), 0.11 μJ (\blacklozenge), and 0.06 μJ (\blacktriangle) per 655-nm excitation pulse.

a lifetime of $\tau = 4.1$ ns, whereas that of $^1\mathbf{1}$ is biexponential with $\tau = (0.9 \pm 0.1)$ ps and 4.1 ns. Excitation of **3** and **4** with 655-nm, 120-fs laser pulses yields transient absorption spectra of $^1\mathbf{3}$ (Figure 2b) and $^1\mathbf{4}$ (see Reference [4]). Again, the spectra are nearly identical and the decay of $^1\mathbf{4}$ is monoexponential with $\tau = 4.0$ ns, whereas the decay of $^1\mathbf{3}$ is biexponential with $\tau = (3.0 \pm 0.1)$ ps and 4.0 ns. The components with $\tau \approx 4$ ns in the transient absorption decay kinetics of $^1\mathbf{1}$ – $^1\mathbf{4}$ match their fluorescence lifetimes in THF measured by using an apparatus with an instrument response time of 20 ps (data not shown). The amplitudes of the 0.9 and 3.0 ps components in the decay of $^1\mathbf{1}$ and $^1\mathbf{3}$, respectively, are laser-power dependent and indicative of singlet–singlet annihilation (see insets to Figure 2a and b, respectively). Assuming annihilation is the result of random exciton transfer between adjacent chromophores, the time constant for exciton hopping (energy transfer) within the trefoil, τ_h , can be derived from the annihilation lifetime, τ_a , by using the formula developed for cyclic arrays of N chromophores:^[12] $\tau_a = \tau_h / (8 \sin^2(\pi/2N))$. By using this model, $N = 3$, and the measured values of τ_a , $\tau_h = (1.8 \pm 0.1)$ ps and (6.0 ± 0.1) ps for **1**

and **3**, respectively. To verify this approach for analysis of the exciton hopping rates in the trefoils, we prepared a derivative of **3** with only one Zn Chl and two free-base pheophorbides (Pheo), **3-1Zn**. As the lowest excited singlet state of Pheo is slightly lower in energy than that of the Zn Chl, selective excitation of the Zn Chl with 645-nm, 120-fs laser pulses results in a singlet–singlet energy-transfer rate to Pheo of $((14 \pm 1) \text{ ps})^{-1}$. This rate is only about a factor of two slower than that obtained for **3** by using the annihilation rate. Although we do not expect the energy-transfer rates for **3-1Zn** and **3** to be the same because they are not chemically identical, this result shows that energy transfer within these structurally related chlorophyll trefoil molecules is much faster than that observed for analogous porphyrin systems, which are discussed below, and that the annihilation analysis is reasonable.

The experimental data show that the Chl–Chl energy-transfer rate within **1** is only three-times faster than in **3**. Energy transfer within covalently linked chromophore arrays can occur by the through-space Förster mechanism and the through-bond Dexter mechanism.^[13] Calculated Förster energy-transfer rates for **1** ($(3 \text{ ps})^{-1}$) and **3** ($(31 \text{ ps})^{-1}$) predict a 10:1 ($1/3$) ratio for the rate (see the Supporting Information). These calculations primarily reflect the significant change in the Chl–Chl distances, r , between **1** (15.1 Å) and **3** (21.5 Å) owing to the $1/r^6$ dependence of the dipole–dipole interaction. The values are only approximate owing to the size of the Chl macrocycles and the resultant length of their transition dipoles relative to the distances between them. Energy-transfer rates have been measured for analogous phenyl–ethynyl–phenyl and phenyl–ethynyl linked porphyrin and oxochlorin dyads.^[14,15] In that work, placing an additional phenyl in the linkage results in a 10-fold slowing of the energy-transfer rate. The energy-transfer rates for the oxochlorin dyads with both linkages agree with the predictions of Förster calculations, whereas the rates for the corresponding porphyrin dyads support a substantially faster through-bond contribution. The similarity of the energy-transfer rates between **1** and **3** suggests that a through-bond or Dexter-type energy-transfer mechanism may be an important contributor in both trefoils. Efficient through-bond energy transfer within threefold-symmetric porphyrin arrays with a 1,3,5-triphenylbenzene linker has also been reported.^[16] Although the porphyrin electron density at the site of the linker attachment is larger than that for **1** and **3** owing to the difference between the porphyrin (a_{2u})^[17] and Chl (a_2)^[18] highest occupied molecular orbitals (HOMOs), the energy-transfer rates for **1** and **3** are 150- and 45-times faster, respectively, than those of the porphyrin trefoils. This results from relatively poor orbital overlap between the porphyrin π systems owing to the large dihedral angles between the porphyrins and the phenyls attached to them as well as between these same phenyls and the benzene core.^[16] The differences in energy-transfer rates displayed among all these examples highlight the importance of through-bond electronic coupling between chromophores in organized covalent arrays.^[19,20]

Charge transport within the Chl trefoils was studied by generating their radical cations, which were characterized by

using electron nuclear double resonance (ENDOR) spectroscopy. Solutions of **1–4** ($2\text{--}5 \times 10^{-4}\text{ M}$) in a mixture of $\text{CH}_2\text{Cl}_2/\text{THF}$ (9:1)^[18] were generated by the addition of a solution of I_2 and AgClO_4 dissolved in acetonitrile. The oxidation of **1** and **3** was carried out to approximately 30% completion to produce the singly oxidized species. The extent of the oxidation was monitored by using UV/Vis spectroscopy (e.g. see the spectra for **1**⁺ and **2**⁺ and the Supporting Information). Oxidized samples were loaded into quartz tubes and sealed under vacuum after successive freeze–pump–thaw cycles. Electron paramagnetic resonance (EPR) and ENDOR^[21] spectra were acquired at 290 K and 140 K by using a Bruker E-580 spectrometer fitted with an EN801 resonator, and a RF power amplifier (ENI A-500). A spline fit baseline correction was applied to the spectra. The EPR spectra of **1**⁺–**4**⁺ are inhomogeneously broadened into single unresolved lines owing to the large number of electron–nuclear hyperfine interactions within each molecule. In such cases, the number of sites over which the radical ion hops or is delocalized can be estimated from EPR line-width changes.^[6,22,23] For example, charge hopping within a linear multiporphyrin array was studied recently by using this method.^[24] The peak-to-peak Gaussian line widths of **2**⁺–**4**⁺ are all 0.73 mT, whereas that of **1**⁺ is only 0.45 mT (see the Supporting Information). The line-width ratio of **2**⁺/**1**⁺ is 1.6, which is very close to the value predicted for charge sharing over three sites by using the treatment of Norris et al.^[22]

Alternatively, ENDOR spectroscopy has been shown to provide a substantial improvement in spectral resolution of the hyperfine splittings of tetrapyrrole macrocycle radical cations.^[18,21,25–28] The proton ENDOR spectra of **2**⁺–**4**⁺ at 290 K each exhibit four line pairs with average isotropic hyperfine splittings of 7.6, 6.5, 3.3, and 0.4 MHz (see Figure 3 and the Supporting Information). The similarity between the spectra of **2**⁺ and **4**⁺ indicates that the attachment of an ethynyl linker directly to the Chl macrocycle only slightly affects the spin (charge) distribution in **2**⁺. Earlier work has shown that the presence of the phenyl in **4**⁺ does not change the spin distribution within the Chl macrocycle.^[4] The similar hyperfine splittings for **3**⁺ and **4**⁺ confirm that the radical cation is localized on a single Chl within trefoil **3**⁺. In contrast, the proton ENDOR spectrum of **1**⁺ at 290 K exhibits four line pairs with hyperfine splittings that correspond to those of **2**⁺, but are reduced by a factor of three. This indicates that, on the ENDOR timescale ($>10^7\text{ Hz}$), the unpaired electron is shared between all three Chls in the assembly. The weak additional lines at 12.2 and 16.8 MHz (4.6 MHz hyperfine splitting) observed in the spectrum of **1**⁺ at 290 K may be due to the 17- and 18-position protons on the reduced rings within a minor conformer of **1**⁺. These lines disappear when the temperature is lowered to 250 K (see the Supporting Information). ENDOR spectra of **1**⁺–**4**⁺ were also obtained in frozen solution at 140 K and show that the hyperfine splittings for **1**⁺–**4**⁺ are essentially identical (Figure 3). The observed localization of the radical cation in **1**⁺ in frozen solution is most likely due to the inability of the counter anion to move between the Chls sufficiently fast to accommodate hopping of the positive charge on the ENDOR timescale.

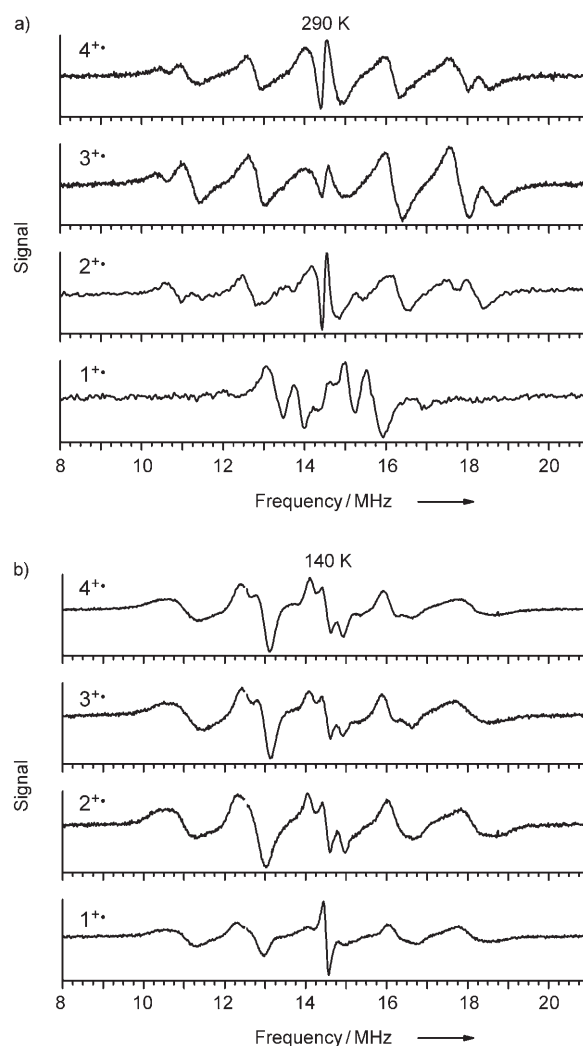


Figure 3. Proton ENDOR spectra in $\text{CH}_2\text{Cl}_2/\text{THF}$ (9:1). Radiofrequency (RF) power was 400 W with a frequency modulation depth of 50 kHz. Microwave power was 100 mW at 290 K (a) and 20 mW at 140 K (b).

Charge sharing in **1**⁺ most likely results from an increase in through-bond electronic coupling between its Chls relative to those in **3**⁺. Overlap of the π orbital of the ethynyl group with that of the Chl HOMO is greater in **1**⁺ relative to that of the 20-phenyl group in **3**⁺ because of the relatively large dihedral angle between the π systems of the Chl and the phenyl.^[4] Thus, attaching an ethynyl group to the 20-position of Chl provides both a means of generating rigid chromophore arrays and increasing the electronic interaction between the Chls. These qualities will be exploited to generate new building blocks for the self-assembly of artificial photosynthetic systems.

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