lutions containing the mixed oxidation state dimer shifts eq 3 in favor of the $Os^{II}(L)Ru^{III}$ isomer. From spectral studies, $Os^{II}(pz)Ru^{III}$ is slightly the predominant isomer in CH_3CN, but the two forms coexist and $\Delta G \sim O$ for reaction 3.[6]

As in related mixed-valence dimers,[1,4a,b,5,7] metal-to-metal charge-transfer (MMCT) bands appear in near-IR spectra of the mixed oxidation state dimer as shown in Figure 2 for CD_3NO_2, CD_3CN, and Me_2SO-d_6 as solvent. The origin of the relatively broad band ($\Delta\bar{\nu}_{1/2} = 1.3 \times 10^3$ cm^{-1} at $E_{max} = 9.0 \times 10^3$ cm^{-1}) in nitromethane is the MMCT transition.[8]

$$[(bpy)_2(Cl)Os^{III}(pz)Ru^{II}(NH_3)_5]^{4+} \xrightarrow{h\nu} [(bpy)_2(Cl)Os^{II}(pz)Ru^{III}(NH_3)_5]^{4+} \quad (4)$$

This band is somewhat narrower than commonly observed in localized mixed-valence dimers. The narrow band in Figure 2a at $\sim 5.6 \times 10^3$ cm^{-1} arises from the second of an expected two $d\pi \rightarrow d\pi$ spin–orbit transitions based on the d^5 Os^{III} site[7,9] and is a useful oxidation state marker. The transition appears in the Os^{III} monomer and $Os^{III}(pz)Ru^{II}$ dimer but not in the $Os^{II}(pz)Ru^{II}$ dimer nor in the mixed oxidation state dimer in Me_2SO-d_6 (Figure 2b). In Me_2SO, UV–visible spectra show that the oxidation state distribution is $Os^{II}(pz)Ru^{III}$ and the MMCT band arises from the transition.

$$[(bpy)_2(Cl)Os^{II}(pz)Ru^{III}(NH_3)_5]^{4+} \xrightarrow{h\nu} [(bpy)_2(Cl)Os^{III}(pz)Ru^{II}(NH_3)_5]^{4+} \quad (5)$$

The MMCT band has the broad featureless character of the reverse transition in CD_3NO_2 but is less intense and somewhat distorted by an underlying absorption feature at higher energy. An absorption increase for the $Os^{III}(L)Ru^{III}$ dimer below 5000 cm^{-1} (not shown) arises because of the onset of the lower energy of the two $d\pi \rightarrow d\pi$ transitions based at Os(III).

The low-energy absorption spectrum of the mixed oxidation state dimer in CD_3CN (Figure 2c) has some distinctive features when compared with the spectra in CD_3NO_2 or Me_2SO-d_6. The availability of a wider solvent spectral window allows both Os^{III} based spin–orbit bands to be observed, the lower at $E \leq 3.6 \times 10^3$ cm^{-1} and the higher, which appears in Figure 2c, at 5.6×10^3 cm^{-1}. Of more interest is the fact that the MMCT band becomes noticeably asymmetric, in a fashion somewhat reminiscent of the MMCT band for the Creutz and Taube ion, $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$.[1,5,10]

The results presented here show that variations in solvent can be used to control the oxidation state distribution within the Os–Ru mixed oxidation state dimer and, thus, to induce intramolecular electron transfer. The change in band shape in acetonitrile (which is *not* observed in the analogous dimer with 4,4′-bipyridine as the bridge) suggests that *the nature of the electronic delocalization between metals can be influenced by solvent variations* as well. A possible microscopic origin for the solvent effect is suggested by the spectral data. In CH_3CN, ΔG approaches zero for intramolecular electron exchange (eq 3). The combination of $\Delta G \sim O$, moderate electronic coupling across pyrazine, and relatively low vibrational trapping barriers[1] may lead to thermal intramolecular electron transfer rates which approach or even exceed the time scale of solvent dipole reorientations, 10^{-11}–10^{-12} s.[11] An exchange process in this time domain would diminish the ability of the solvent dipoles to trap the exchanging electron at a single site and explain the change in band shape for the MMCT band as arising from a partly "relaxed" solvent dipole environment around the ion. In nitromethane or Me_2SO, ΔG is positive for intramolecular electron transfer (either $Ru^{II} \rightarrow Os^{III}$ or $Os^{II} \rightarrow Ru^{III}$). In these solvents electron transfer may be slow compared to the time scale for solvent dipole reorientations, giving rise to the full width and symmetrical band shape expected for a MMCT transition in a "localized" dimer.[8]

Acknowledgments are made to Jeff Curtis for stimulating discussions and to the US Army Research Office—Durham under Grant DAAG29-85-K-0121 and the National Science Foundation under Grant CHE-8503092 for support of this research.

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[6] Because of the large potential difference between $E_{1/2}(1)$ and $E_{1/2}(2)$, 0.37 V in CH_3CN, disproportionation, $2[(bpy)_2(Cl)Os(pz)Ru(NH_3)_5]^{4+} \rightarrow [(bpy)_2(Cl)Os^{III}(pz)Ru^{III}(NH_3)_5]^{5+} + [(bpy)_2(Cl)Os^{II}(pz)Ru^{II}(NH_3)_5]^{3+}$, is disfavored by $\sim 10^6$ and cannot be the origin of the appearance of transitions associated with Ru^{II} in the spectrum.

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Charge Separation and Energy Transfer in Carotenopyropheophorbide–Quinone Triads

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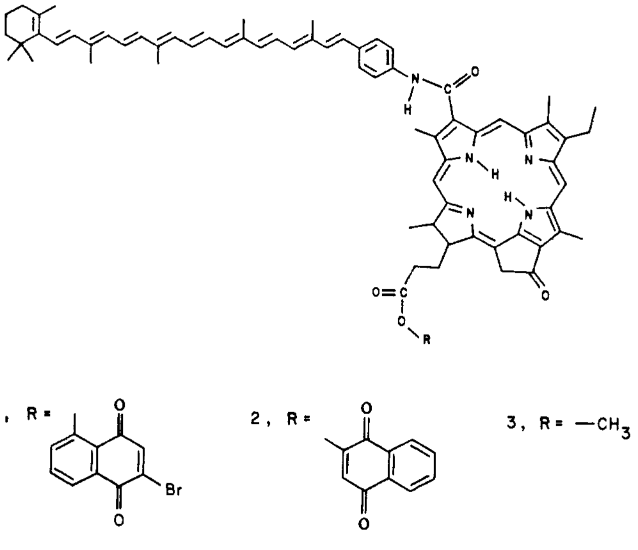
In natural photosynthetic membranes, chlorophyll molecules serve as the site of the initial photodriven charge separation. In addition, they play a role in subsequent electron-transfer steps, accept singlet excitation energy from carotenoid antenna molecules, and transfer triplet energy to carotenoid acceptors (thereby preventing sensitized singlet oxygen production and subsequent photodamage to the organism). We report herein the synthesis and study of chlorophyll-based carotenopyropheophorbide–quinone triad molecules which mimic all of these natural processes. Irradiation of **1** in solution initiates a two-step electron transfer leading to the formation of an energetic charge-separated state with a quantum yield of ca. 4% and a lifetime of 120 ns. Carotenopyropheophorbide **3** demonstrates singlet–singlet energy transfer from the carotenoid moiety to the pyropheophorbide with 50% efficiency. The carotenoid moiety of **3** also provides photoprotection from singlet oxygen formation by quenching the pyropheophorbide triplet state within 50 ns of its formation.



The syntheses of **1** and **2** were achieved by coupling 2-devinyl-2-(carboxymethyl)pyropheophorbide *a* to the appropriate aminocarotenoid via the acid chloride to yield **3**, cleaving the methyl ester with potassium carbonate and esterifying with 2-bromojuglone or lawsone, respectively. Information concerning the solution conformations of **1**–**3** was deduced from 400-MHz ^{1}H NMR spectra by analyzing[1] tetrapyrrole aromatic-ring-cur-

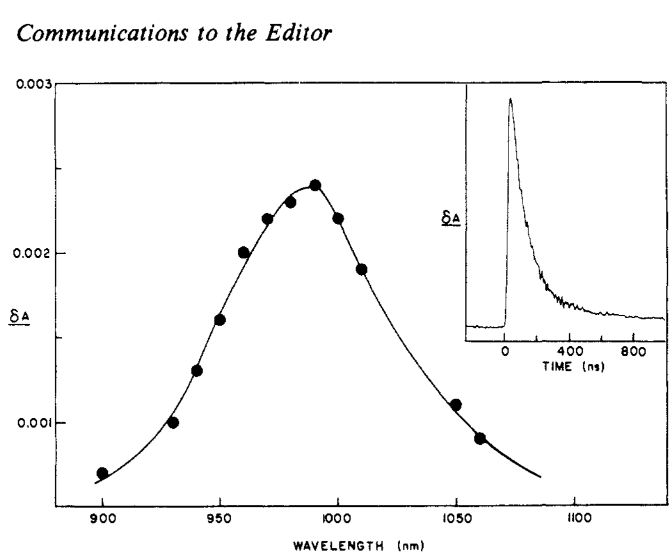


Figure 1. Spectrum of transient carotenoid radical cation obtained 50 ns after excitation of a 1 × 10^{-4} M solution of triad **1** in methylene chloride with a 30-ns pulse of 590-nm light. The inset is the decay of the absorption at 990 nm (207 K).

rent-induced chemical shift changes. In the three cases, the carotenoid moieties were found to be in essentially identical conformations and extended away from the pyropheophorbide, rather than folded back over it.

Although the absorption spectra of **1**–**3** are essentially unperturbed relative to those of the appropriate model compounds, the tetrapyrrole fluorescence of **1** is strongly quenched. In addition, excitation of a methylene chloride solution of **1** at 207 K with a 30 ns, 590-nm laser pulse gives rise to a transient carotenoid radical cation absorption with a maximum at 990 nm and a lifetime of 120 ns (Figure 1). By analogy to recent work with porphyrin-based triad molecules,[2-7] the following scheme is proposed to account for these results. Excitation of the carotenoid–pyropheophorbide–quinone (C–P–Q) triad leads to the pyropheophorbide excited singlet state (C–^{1}P–Q) which then donates an electron to the quinone to form C–$\mathrm{P^{\bullet+}}$–$\mathrm{Q^{\bullet-}}$. The decay of this intermediate charge-separated state is partitioned between the back-reaction to yield C–P–Q and a second forward electron transfer (from the carotenoid) to yield a final charge-separated state $\mathrm{C^{\bullet+}}$–P–$\mathrm{Q^{\bullet-}}$, which lives for 120 ns. The extremely long lifetime for this final state is a result of the biomimetic two-step electron transfer which rapidly separates the positive and negative charges in space.

The quantum yield of $\mathrm{C^{\bullet+}}$–P–$\mathrm{Q^{\bullet-}}$, estimated by using the yield of carotenoid cation in previously studied porphyrin-based triads[2-5] as a standard, was ca. 0.04 for **1** at 207 K. At ambient temperatures the yield could not be determined accurately because the lifetime of the carotenoid radical cation drops to ~50 ns, and the decay is therefore convoluted into the instrumental response function. Similar experiments at 207 K demonstrated that **2** also undergoes two-step photodriven charge separation with a yield of 0.007 and a lifetime of 120 ns for the final $\mathrm{C^{\bullet+}}$–P–$\mathrm{Q^{\bullet-}}$ state. Dyad **3** yields no detectable carotenoid cation under similar conditions.

Biomimicry of carotenoid antenna function (singlet energy transfer)[8-10] was also observed. The fluorescence excitation spectrum of **3** in toluene was obtained while monitoring the pyropheophorbide emission at 680 nm. The corrected[8,9] spectrum, normalized to the absorption spectrum over the wavelength range 600–630 nm, revealed a 50% quantum yield of singlet transfer, which is considerably higher than that reported in other model systems.[8-10]

Excitation of **3** in deoxygenated methylene chloride at 295 K with a 30-ns, 590-nm laser pulse resulted in the immediate ($\leq$50 ns) formation of a carotenoid triplet state with an absorption maximum at 550 nm and a lifetime of 6.5 μs in the absence of oxygen. The carotenoid triplet, which cannot be formed by intersystem crossing, represents rapid triplet–triplet energy transfer from the pyropheophorbide. The rate of transfer (>10^7 s^{-1}) indicates that the carotenoid moiety of **3**, and by analogy those of **1** and **2**, can compete favorably with molecular oxygen for the pyropheophorbide triplet and thus mimic the natural photoprotective function of carotenoids.[11-15]

The results presented above demonstrate that chlorophyll-based triads are very successful mimics of carotenoid function in natural photosynthesis. Previous model studies have shown that singlet and triplet energy transfer requires contact of the carotenoid and tetrapyrrole π-electron systems.[8-13] In the present instance, the exchange interaction is evidently provided by the amide linkage, rather than a stacked arrangement of the pigments. In natural photosynthetic membranes where the pigments are not covalently liked but are held in suitably close proximity by proteins, measured singlet energy transfer efficiencies range from 100% to <50%[15,16] and the triplet–triplet energy transfer rates are $\gtrsim 10^8$ s^{-1}.[14,15]

The singlet and triplet energy transfer results for **3** are consistent with our previous observations: if the electron exchange interaction is sufficient for ultrafast (7 ps)[18] singlet energy transfer from the cartenoid to the tetrapyrrole, then there will necessarily be very rapid triplet transfer as well.[8-13] From these model studies we can predict that in pigment-bearing proteins in photosynthetic membranes, the cartenoid will be found at or near van der Waals contact with a specific chlorophyll for which it acts as both antenna and triplet quencher.

The quantum yield of long-lived charge separation in **1** is comparable to that observed in porphyrin-based triads in the same solvent.[2-5] The yield of $\mathrm{C^{\bullet+}}$–P–$\mathrm{Q^{\bullet-}}$ for **2**, however, is considerably lower. Although the quantum yield is a function of the rates of a number of photophysical steps, this difference is certainly due in part to the enhanced rate of the initial electron transfer step in **1**, which is a result of the greater exergonicity of electron donation to a quinone which is a better acceptor. Thus, the initial electron transfer step can compete more favorably with other paths for the decay of the pyropheophorbide singlet.

There is no good evidence for the involvement of carotenoids in electron transfer in vivo, although carotenoid radical cations have been observed upon excitation of certain PSII preparations.[17] However, carotenoid polyenes have the dimensions necessary to

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span a phospholipid bilayer and are well suited for transmembrane electron transfer in artificial photosynthetic membranes. In fact, porphyrin-based triads have been found to demonstrate photodriven transmembrane electron transfer.[6] The chlorophyll-based triads have a much larger effective absorption cross section due to the efficient singlet energy transfer and the greatly increased oscillator strength in the Q-bands and therefore are potentially much more effective in model photosynthetic systems.

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Absolute Configuration of (−)-Botryococcene

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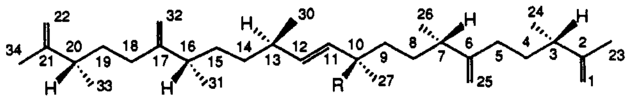
The green alga *Botryococcus braunii* (Kützing) is found throughout the world under a wide range of climatic conditions.[1] The unusual morphology and composition of this organism has been investigated and its involvement in the formation of a variety of carboniferous deposits, including petroleum, has been postulated.[2] Of particular chemical interest is the finding that *B. braunii* produces a mixture of C_{30}–C_{36} hydrocarbons of terpenoid origin that constitutes up to 90% of the dry weight of the alga.[3] The major component of this mixture, botryococcene, was shown by Eglinton et al. through degradation and spectral analysis to possess the gross structure depicted in **1**.[4] Our interest in the total synthesis of **1**, as well as the biosynthetic events leading to incorporation of the four non-mevalonoid methyl groups and the unusual coupling of the farnesyl moieties, required that we establish the configuration of the six stereogenic centers in the molecule. We now report that the absolute configuration of botryococcene is 3*S*,7*S*,10*S*,13*R*,16*S*,20*S*.

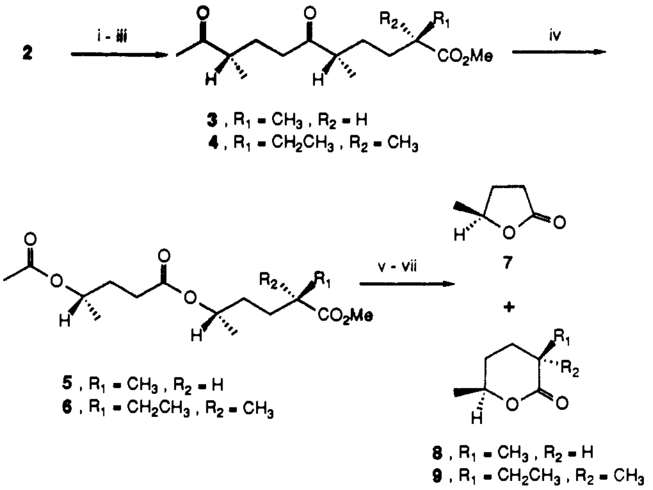


1, R = $\overset{28}{C}H{=}\overset{29}{C}H_2$
2, R = CH_2CH_3

Selective reduction of botryococcene (**1**) with diimide afforded the known dihydro derivative **2**[4] which, upon exhaustive ozonolysis followed by an oxidative workup and treatment with diazomethane, gave **3** and **4**. After chromatographic separation, these diketo esters were each subjected to Baeyer–Villiger oxidation to furnish triesters **5** and **6**, respectively. Saponification of **5**, followed by acidification, afforded a pair of hydroxy acids which were converted to a 1:1 mixture of γ- and δ-lactones **7** and **8**. Similar treatment of **6** yielded **7** and the δ-lactone **9** (Scheme I).

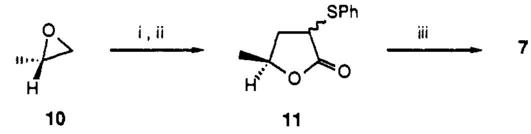
The absolute configurations of **7**–**9** were determined by correlation with the optically pure substances synthesized from (*S*)-(−)-propylene oxide (**10**).[5] Thus, opening of **10** with the dilithio dianion of 2-thiophenoxyacetic acid,[6] followed by lactonization, gave **11** which was desulfurized with Raney nickel to yield (4*S*)-**7** (Scheme II).[7] For synthesis of the δ-lactones **8** and **9**, (*S*)-propylene oxide was reacted with lithium trimethylsilylacetylide to afford **12** which was converted to its tetrahydropyranyl

Scheme I[a]



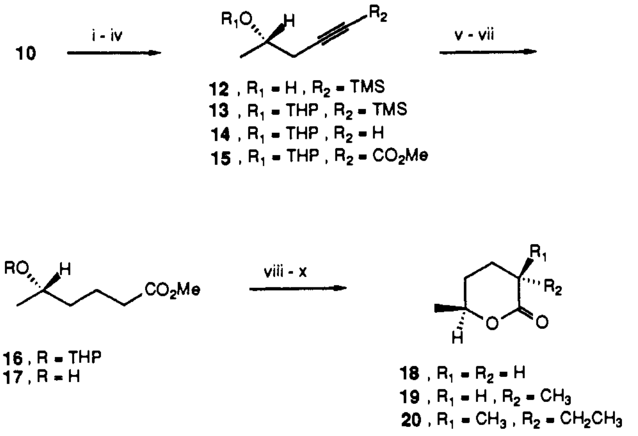
[a] (i) O_3, CH_2Cl_2/MeOH/EtOAc (10:5:1), −78 °C; (ii) CrO_3, H_2SO_4, Me_2CO, 0 °C, 2 h; (iii) CH_2N_2, Et_2O, 25 °C (**3**, 38%; **4**, 40% from **2**); (iv) mCPBA, $NaHCO_3$, CH_2Cl_2, 25 °C, 5 days then Δ, 24 h (**5**, 64%; **6**, 83%); (v) KOH, aqueous THF, 25 °C, 24 h; (vi) aqueous HCl; (vii) C_6H_6, 4-Å sieves, Δ, 3 h, (**7**,**8** (1:1), 80%; **7**,**9** (1:1), 86% from **5** and **6**, respectively).

Scheme II[a]



[a] (i) $PhSCH_2CO_2H$, 2 equiv of LDA, THF, −78 °C; (ii) C_6H_6, *p*-TsOH, Δ (80% from **10**); (iii) Raney nickel (W6), MeOH, Δ, 6 h (78%).

Scheme III[a]



[a] (i) $Me_3SiC{\equiv}CH$, *n*-BuLi, THF, −78 °C, 6 h (97%); (ii) DHP, *p*-TsOH, CH_2Cl_2, 25 °C, 3 h (90%); (iii) *n*-Bu_4NF, THF, 25 °C, 1 h (78%); (iv) *n*-BuLi, $ClCO_2Me$, THF, −78 → 25 °C, 2 h (92%); (v) H_2, 10% Pd/C, EtOAc, 25 °C (97%); (vi) *p*-TsOH, MeOH, 40 °C, 1.5 h; (vii) K_2CO_3, azeotropic removal of MeOH with C_6H_6, 25 °C; (viii) *P*-TsOH, C_6H_6, 4-Å sieves, Δ, 2 h (78% from **16**); (ix) LDA, MeI, THF, HMPA, −78 → −40 °C, 4 h (92%); (x) LDA, EtI, THF, HMPA, −78 → −40 °C, 4 h (87%).

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