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# Photoinduced Charge Separation and Charge Recombination to a Triplet State in a Carotene–Porphyrin–Fullerene Triad

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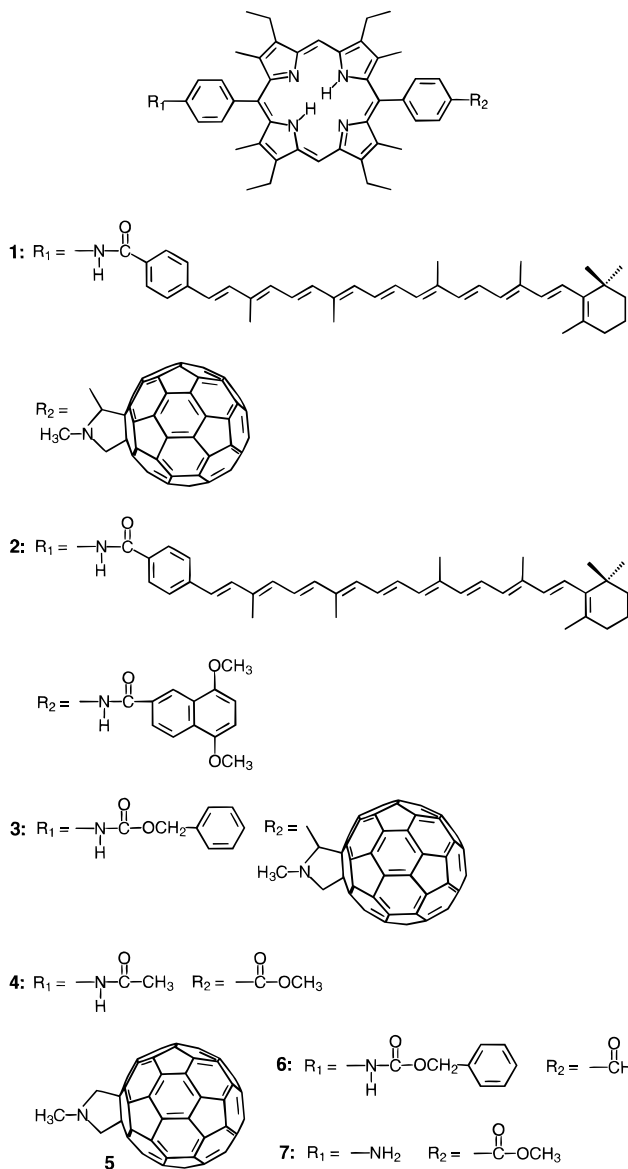
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**Abstract:** A molecular triad consisting of a diarylporphyrin (P) covalently linked to a carotenoid polyene (C) and a fullerene (C<sub>60</sub>) has been prepared and studied using time-resolved spectroscopic methods. In 2-methyltetrahydrofuran solution, the triad undergoes photoinduced electron transfer to yield C–P<sup>•+</sup>–C<sub>60</sub><sup>•–</sup>, which evolves into C<sup>•+</sup>–P–C<sub>60</sub><sup>•–</sup> with an overall quantum yield of 0.14. This state decays by charge recombination to yield the carotenoid triplet state with a time constant of 170 ns. Even in a glass at 77 K, C<sup>•+</sup>–P–C<sub>60</sub><sup>•–</sup> is formed with a quantum yield of ~0.10 and again decays mainly by charge recombination to give <sup>3</sup>C–P–C<sub>60</sub>. The fullerene triplet, formed through normal intersystem crossing, is also observed at 77 K. The generation in the triad of a long-lived charge separated state by photoinduced electron transfer, the low-temperature electron transfer behavior, and the formation of a triplet state by charge recombination are phenomena previously observed mostly in photosynthetic reaction centers.

## Introduction

Fullerenes absorb light throughout the visible spectrum. Although their extinction coefficients at visible wavelengths are small, their low-lying first excited singlet states may be sensitized by energy transfer from better absorbers. Fullerenes are excellent electron acceptors and potential electron accumulators. Recently, the interaction of fullerenes with a variety of covalently attached chromophores has been investigated.<sup>1–11</sup> Such dyads undergo singlet energy transfer from the pigment to the fullerene and/or photoinduced electron transfer to the fullerene, generating a charge-separated state. Therefore, fullerenes might be useful electron acceptors in more complex molecular systems that can demonstrate multiple electron transfer pathways. In order to investigate this possibility, we have prepared molecular triad **1**, consisting of a diarylporphyrin (P) covalently linked to a carotenoid polyene (C) and a fullerene (C<sub>60</sub>), and model compounds **2–5**. As described in detail below, **1** demonstrates curious photochemical behavior. It undergoes photoinduced electron transfer not only in solution at ambient



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temperatures but also in a glass at 77 K to yield  $C-P^+-C_{60}^{\bullet-}$ , which evolves into  $C^{\bullet+}-P-C_{60}^{\bullet-}$ . This long-lived charge-separated state decays by radical pair recombination to yield the carotenoid triplet state, rather than the molecular ground state.

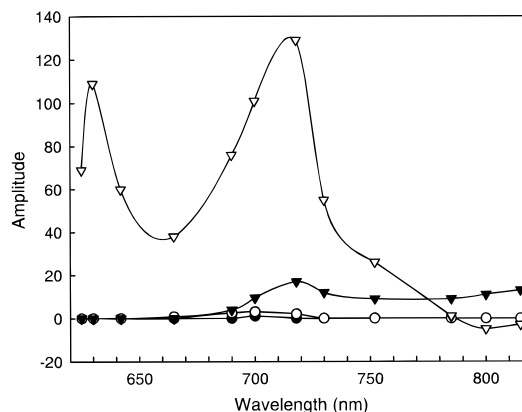
## Results

**Synthesis.** The synthesis of triad **1** commenced with the preparation of porphyrin **6** from **7**<sup>12</sup> via protection of the amino group as the (benzyloxy)carbonyl derivative, reduction of the ester with lithium aluminum hydride, and oxidation of the resulting alcohol with manganese dioxide. Reaction<sup>13</sup> of **6** with  $C_{60}$  and sarcosine gave **3**. This reaction is known to produce only a single isomer; an adduct to a double bond at a 6,6-ring fusion in  $C_{60}$ . Dyad **3** was deprotected with boron tribromide and allowed to react with the appropriate carotene acid chloride<sup>14</sup> to give **1**. The triad and intermediates were characterized by mass spectrometry and <sup>1</sup>H NMR spectroscopy, as detailed in the Experimental Section. The <sup>1</sup>H NMR spectra of **1** and **3** displayed broadening of porphyrin and aryl resonances for protons near the fullerene, suggesting slow conformational interconversion on the NMR time scale involving single bonds in the porphyrin–fullerene linkage.

**Steady State Absorption and Emission.** The visible absorption spectrum of **1** in toluene solution is essentially a linear combination of the spectra of model carotenoporphyrin **2** and fullerene **5**, with maxima at 412, 455 (sh), 485, 510, 575, 628, and 706 nm. The spectrum in 2-methyltetrahydrofuran solution is similar, with maxima at 409, 450 (sh), 475, 506, 575, 630, and 705 nm.

In toluene, porphyrin **4** and carotenoporphyrin **2** have fluorescence maxima at 631 and 699 nm, whereas fullerene **5** has emission maxima at 715 and 796 nm. Triad **1**, excited at 590 nm, yields an emission spectrum with features characteristic of both the porphyrin and the fullerene moieties. However, the porphyrin emission is strongly quenched relative to that of the fullerene. In 2-methyltetrahydrofuran, porphyrin **4** has emission maxima at 630 and 699 nm, whereas fullerene **5** has maxima at 714 and ~800 nm. The emission of **1** in this solvent with excitation at 590 nm also features spectral shapes characteristic of both the porphyrin and the fullerene components, but in this case, the emission from both components is strongly quenched relative to emission from the model compounds.

**Time-Resolved Emission Studies.** In order to investigate further the fluorescence quenching, time-resolved fluorescence measurements were performed using the single-photon timing technique. A  $\sim 1 \times 10^{-5}$  M solution of **1** in toluene was excited at 590 nm, and the fluorescence decay was monitored at 12 wavelengths in the 625–815 nm region. The results of global analysis of these data as four exponential processes ( $\chi^2 = 1.12$ ) are shown in Figure 1. The major decay component, with a lifetime of 12 ps, has maxima characteristic of porphyrin emission and represents the decay of  $C-P-C_{60}$ . The negative amplitude of this decay component in the 800 nm region, where the fullerene moiety emits, signifies an increase in the amplitude of fullerene emission with time after the laser pulse. This is due to singlet–singlet energy transfer from the porphyrin to the fullerene, yielding  $C-P-C_{60}^{\bullet}$ . The first excited singlet state



**Figure 1.** Decay-associated fluorescence emission spectrum obtained by exciting a  $\sim 1 \times 10^{-5}$  M solution of triad **1** in toluene with 590 nm,  $\sim 9$  ps laser pulses. Global analysis of the data at the indicated wavelengths gave four exponential decay components with time constants of 0.012 ( $\nabla$ ), 1.52 ( $\blacktriangledown$ ), 0.201 ( $\circ$ ), and 6.12 ( $\bullet$ ) ns.

of the porphyrin in model carotenoporphyrin **2** decays as a single exponential with a lifetime of 7.34 ns ( $\lambda_{ex} = 590$  nm,  $\lambda_{em} = 700$  nm,  $\chi^2 = 1.07$ ). The time-resolved fluorescence results for **1** are thus compatible with the strong quenching of the porphyrin fluorescence noted in the steady state measurements, and the quenching can be attributed at least in part to singlet–singlet energy transfer to the fullerene.

The only other significant decay component in the decay-associated spectrum of triad **1**, with a lifetime of 1.52 ns, has the shape of fullerene emission. Model fullerene **5** has a fluorescence lifetime of 1.40 ns. Thus, in toluene, the fullerene first excited singlet state is unquenched.

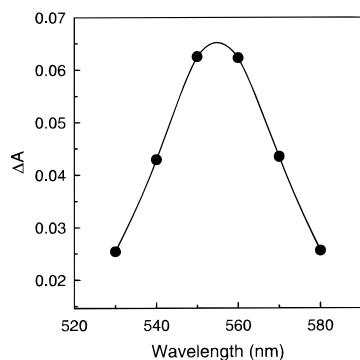
Similar time-resolved fluorescence measurements were performed on  $\sim 1 \times 10^{-5}$  M solutions of **1** in 2-methyltetrahydrofuran. With 600 nm excitation, global analysis ( $\chi^2 = 1.12$ ) of decays at 772, 787, and 795 nm yielded one significant exponential decay component of 0.032 ns. At these wavelengths, emission is due to the fullerene moiety; the porphyrin emission is very weak and causes no interference. Thus, the lifetime of  $C-P-C_{60}$  is 32 ps. Excitation at 590 nm, where the porphyrin is the major absorber, gave porphyrin fluorescence decays at 625, 630, 635, and 640 nm whose global analysis ( $\chi^2 = 1.10$ ) yielded one significant lifetime of 10 ps for  $C-P-C_{60}$ , which is approaching the time resolution of the spectrometer. As the singlet-state lifetime of **2** is 7.22 ns ( $\lambda_{ex} = 590$  nm,  $\lambda_{em} = 630$  nm,  $\chi^2 = 1.11$ ) and that of **5** is 1.35 ns ( $\lambda_{ex} = 590$  nm,  $\lambda_{em} = 712$  nm,  $\chi^2 = 1.15$ ) in 2-methyltetrahydrofuran, the short lifetimes for **1** are consistent with the strong steady state fluorescence quenching of both the porphyrin and fullerene moieties.

**Nanosecond Transient Absorption in Toluene.** The products resulting from decay of the porphyrin and fullerene excited singlet states of **1** were investigated by nanosecond transient absorption spectroscopy. Excitation of an argon-purged,  $\sim 1 \times 10^{-4}$  M solution of **1** in toluene with a 590 nm, 5 ns laser pulse led to the observation of a transient absorption with a maximum at  $\sim 550$  nm (Figure 2). This transient grows in after the laser flash with a time constant of 85 ns and decays with a lifetime of  $\sim 4.2 \mu s$ , which decreases in the presence of increasing amounts of oxygen. This transient species is assigned to the carotenoid triplet state,  $^3C-P-C_{60}$ , by comparison with spectra of related compounds.<sup>14</sup> The yield of  $^3C-P-C_{60}$  was determined by the comparative method and found to be essentially unity, using the *meso*-tetraphenylporphyrin triplet state ( $\phi_T = 0.67$ ,  $(\epsilon_T - \epsilon_G)_{440} = 6.8 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) as the standard and  $(\epsilon_T - \epsilon_G) = 1.4 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup> for the

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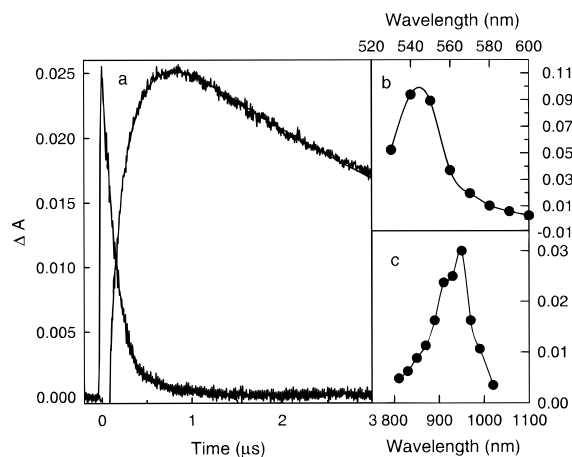
**Figure 2.** Transient absorption spectrum of the carotenoid triplet state determined 200 ns after excitation of a  $\sim 1 \times 10^{-4}$  M solution of **1** in toluene with a 590 nm,  $\sim 5$  ns laser pulse.

carotenoid. The fullerene triplet state of **5** has an absorption maximum at  $\sim 700$  nm.<sup>7,9</sup> Under the experimental conditions used for observation of  ${}^3\text{C-P-C}_{60}$  in **1**, recovery of the detection system from saturation at 700 nm precluded observation of the decay of  $\text{C-P-}{}^3\text{C}_{60}$ .

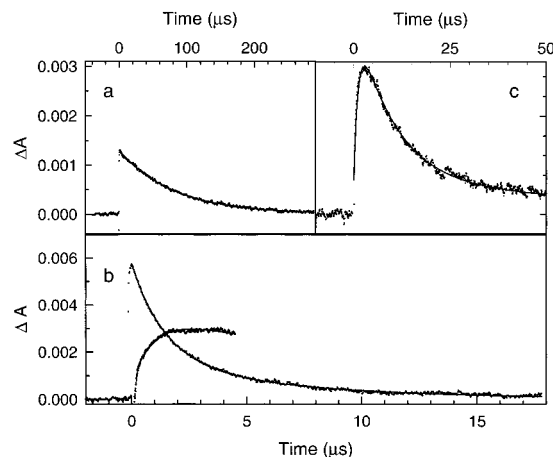
By analogy with other porphyrin–fullerene dyads,<sup>1,9,10</sup> the very short lifetime of  $\text{C-}^1\text{P-C}_{60}$  in toluene is consistent with decay not only by singlet–singlet energy transfer to yield  $\text{C-P-}^1\text{C}_{60}$  but also by photoinduced electron transfer to give  $\text{C-P}^{\bullet+}-\text{C}_{60}^{\bullet-}$ . As has been observed in other triads,<sup>15</sup> any  $\text{C-P}^{\bullet+}-\text{C}_{60}^{\bullet-}$  that is formed might evolve by electron transfer from the carotenoid to give  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$ . In order to investigate this possibility, transient absorption measurements were also carried out in the 800–1100 nm region, where the carotenoid radical cation<sup>16</sup> and fullerene radical anion<sup>7,17,18</sup> absorb. No significant transients were observed in this spectral region.

**Nanosecond Transient Absorption in 2-Methyltetrahydrofuran and Benzonitrile.** In contrast to the results in toluene, excitation of **1** in argon-purged 2-methyltetrahydrofuran with a 590 nm pulse led to the observation of a strong transient absorption at  $\sim 940$  nm (Figure 3). Similar results were obtained with excitation at 630 and 650 nm. Both the carotenoid radical cation and the fullerene radical anion absorb in the 940 nm region, although the extinction coefficient of the carotenoid radical cation is  $\sim 10$  times larger than that of the fullerene radical anion.<sup>16–18</sup> Therefore, the observed transient is assigned to  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$ . The charge-separated state has a lifetime of 170 ns and is formed with an overall quantum yield of 0.14, as determined by the comparative method with the *meso*-tetraphenylporphyrin triplet state as a standard, and using an extinction coefficient of  $1.6 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the carotenoid radical cation at its absorption maximum. The decay of  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$  is correlated with the growth ( $\tau = 170$  ns) of an absorption band at 550 nm characteristic of the carotenoid triplet state (Figure 3). The quantum yield of  ${}^3\text{C-P-C}_{60}$  is 0.13, and its (oxygen sensitive) lifetime is 4.9  $\mu\text{s}$ . Thus,  ${}^3\text{C-P-C}_{60}$  is formed by charge recombination of  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$ .

Similar behavior was observed in benzonitrile solution. Excitation of an argon-purged solution of **1** at 590 nm resulted in the formation of  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$  with a quantum yield of 0.12. This charge-separated state decayed with a time constant of 770 ns, with the concurrent formation of  ${}^3\text{C-P-C}_{60}$ . The quantum yield of  ${}^3\text{C-P-C}_{60}$  was 0.12. The carotenoid triplet state



**Figure 3.** Transient absorption results for a  $\sim 1 \times 10^{-4}$  M solution of **1** in 2-methyltetrahydrofuran at ambient temperature following excitation with a 5 ns, 590 nm laser pulse. (a) Decay at 950 nm of the absorption of  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$  ( $\tau = 170$  ns) and rise ( $\tau = 170$  ns) and decay ( $\tau = 4.9 \mu\text{s}$ ) of the carotenoid triplet absorption at 550 nm. The smooth curve is a simulation using the rate constants in the text. (b) Transient absorption spectrum of  ${}^3\text{C-P-C}_{60}$ . (c) Transient absorption spectrum of  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$ .



**Figure 4.** Transient absorption results for a  $\sim 1 \times 10^{-4}$  M solution of **1** in a 2-methyltetrahydrofuran glass at 77 K following excitation with a 5 ns, 590 nm laser pulse. (a) Decay at 700 nm of the fullerene triplet state ( $\text{C-P-}^1\text{C}_{60}$ ). The smooth curve is an exponential decay with a time constant of 81  $\mu\text{s}$ . (b) Decay of the carotenoid and fullerene radical ions at 980 nm (smooth curve is the sum of two exponential decays with time constants of 1.5  $\mu\text{s}$  (73%) and 7  $\mu\text{s}$  (27%)) and rise of the carotenoid triplet state monitored at 550 nm (smooth curve has a time constant of 1.4  $\mu\text{s}$  for the rise). (c) Decay of the carotenoid triplet absorption at 550 nm. The smooth curve is the sum of a 1.4  $\mu\text{s}$  rise time and 10  $\mu\text{s}$  (87%) and 83  $\mu\text{s}$  (13%) decay lifetimes.

lifetime was  $\sim 5.7 \mu\text{s}$  in the argon-purged solution and was strongly quenched by oxygen.

**Nanosecond Transient Absorption at 77 K.** Excitation of a  $\sim 1 \times 10^{-4}$  M solution of **1** in a 2-methyltetrahydrofuran glass at 77 K with a 590 nm, 5 ns laser pulse gave rise to several transient species (Figure 4). The  $\text{C}^{\bullet+}-\text{P-C}_{60}^{\bullet-}$  charge-separated state was detected via observation at 980 nm of the carotenoid radical cation absorption (Figure 4b) and was formed with a quantum yield of  $\sim 0.10$  based on total light absorbed. The decay of this transient at 77 K is not a true single exponential, probably due to conformational or environmental heterogeneity. The decay at 980 nm can be fitted as two exponentials with a major component (73%) having a 1.5  $\mu\text{s}$  lifetime and a minor,  $\sim 7 \mu\text{s}$  component. The 1.5  $\mu\text{s}$  decay is accompanied by a corresponding rise of the carotenoid triplet

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absorption in the 550 nm region, with a major component of 1.4  $\mu$ s (Figure 4b). The  $^3\text{C-P-C}_{60}$  species is formed with a quantum yield of 0.07. Its decay can be fit with a lifetime of 10  $\mu$ s (Figure 4c). The decay also features a small component with a lifetime of 83  $\mu$ s. A transient with a maximum absorbance at 700 nm, corresponding to  $\text{C-P-}^3\text{C}_{60}$ , forms with the excitation pulse in a yield of 0.17 and decays with a time constant of 81  $\mu$ s (Figure 4a).

## Discussion

**Energetics.** The photochemical behavior of **1** may be discussed in terms of Figure 5, which indicates the relevant high-energy states and kinetic pathways. The energetics of the excited singlet states in the figure are estimated from the average of the long-wavelength absorption maxima and short-wavelength emission maxima of relevant model systems. The energies of the charge-separated states are estimated from cyclic voltammetric measurements in polar solvents of appropriate model fullerenes,<sup>5</sup> porphyrins,<sup>12</sup> and carotenoids.<sup>16</sup> The triplet state energies are estimated from those of **5**<sup>8</sup> and model octaalkylporphyrins<sup>19</sup> and carotenoids.<sup>20</sup> No corrections have been made for any Coulombic effects.

**Photochemistry in Toluene.** In toluene, excitation of the porphyrin is followed by singlet–singlet energy transfer to the fullerene. Since no charge-separated state was observed in this solvent, it can be postulated that energy transfer is the only significant decay pathway for  $\text{C-}^1\text{P-C}_{60}$  (*vide infra*). It is conceivable that some  $\text{C-P-}^1\text{C}_{60}$  is formed from very rapid charge recombination of  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$ , which in turn might be produced by photoinduced electron transfer from  $\text{C-}^1\text{P-C}_{60}$ . There is no experimental evidence for such a process in **1**. However, charge recombination to excited singlet states has been observed in other molecules. For example, we recently reported the observation of dual fluorescence resulting from charge recombination in porphyrin dyads.<sup>21</sup> Picosecond transient absorption studies may reveal more concerning this possibility. Thus,  $k_1$  is taken as the reciprocal of the observed 12 ps lifetime:  $8.3 \times 10^{10} \text{ s}^{-1}$ .

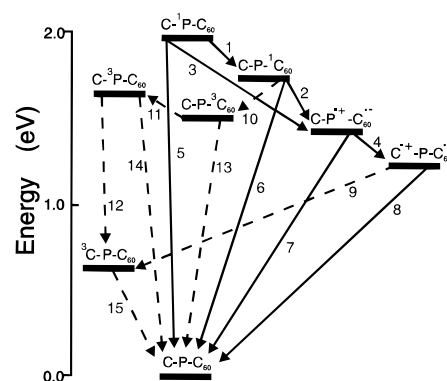
The  $\text{C-P-}^1\text{C}_{60}$  state lifetime is not quenched relative to the corresponding state of model fullerene **5**. Fullerenes including **5**<sup>8</sup> are known to undergo intersystem crossing to give the triplet with quantum yields of essentially unity. Thus,  $\text{C-P-}^1\text{C}_{60}$  decays in 1.52 ns, presumably by intersystem crossing to give  $\text{C-P-}^3\text{C}_{60}$  with  $k_{10} = 6.6 \times 10^8 \text{ s}^{-1}$ . However, the carotenoid triplet, rather than the fullerene triplet, is observed spectroscopically. Carotenoids such as this one have negligible yields of intersystem crossing, and  $^3\text{C-P-C}_{60}$  is formed with a time constant of 85 ns. Thus,  $^3\text{C-P-C}_{60}$  must form from  $\text{C-P-}^3\text{C}_{60}$  by triplet–triplet energy transfer. It is postulated that  $\text{C-P-}^3\text{C}_{60}$  undergoes endergonic triplet energy transfer to the porphyrin to give  $\text{C-}^3\text{P-C}_{60}$  ( $k_{11} = 1.2 \times 10^7 \text{ s}^{-1}$  based on the 85 ns rise time of  $^3\text{C-P-C}_{60}$ ). This species in turn transfers triplet excitation to the carotenoid ( $k_{12} > 1 \times 10^8 \text{ s}^{-1}$  based on the rise time of the carotenoid triplet absorption in **2** following porphyrin excitation). A similar triplet energy transfer relay has been observed in a carotenoid–porphyrin–pyropheophorbide triad<sup>22</sup> and in bacterial photosynthetic reaction centers.<sup>23–25</sup>

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**Figure 5.** Transient states of triad **1** and their relevant interconversion pathways. Spin multiplicities for radical pair states are not indicated.

The quantum yield of  $^3\text{C-P-C}_{60}$  in toluene is essentially unity, and no  $\text{C}^+-\text{P-C}_{60}^{\bullet-}$  state is observed. Thus, the quantum yields of steps 2, 3, 13, and 14 in Figure 5 must be negligible.

Figure 5 indicates a significant thermodynamic driving force in polar solvents (0.31 eV) for photoinduced electron transfer from  $\text{C-P-}^1\text{C}_{60}$  to give  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  (step 2). This does not occur in toluene, as  $\text{C-P-}^1\text{C}_{60}$  is unquenched relative to the model compound. The probable reason for this is the low dielectric constant of toluene. Loss of dielectric stabilization of  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  in this solvent reduces the driving force to the point that the electron transfer is endergonic or only slightly exergonic, and electron transfer cannot compete with intersystem crossing. The driving force for electron transfer from  $\text{C-}^1\text{P-C}_{60}$  to yield  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  (step 3) is substantially larger (0.54 eV in polar solvents). This electron transfer process may well be energetically feasible in toluene, but the very rapid singlet–singlet energy transfer to yield  $\text{C-P-}^1\text{C}_{60}$  is evidently the dominant decay process for  $\text{C-}^1\text{P-C}_{60}$  (barring rapid charge recombination to yield  $\text{C-P-}^1\text{C}_{60}$ , as discussed above).

**Photochemistry in 2-Methyltetrahydrofuran.** In 2-methyltetrahydrofuran at ambient temperatures,  $\text{C-}^1\text{P-C}_{60}$  decays in 10 ps by some combination of singlet–singlet energy transfer to the fullerene and electron transfer to give  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  ( $k_1 + k_3 = 1.0 \times 10^{11} \text{ s}^{-1}$ ). The fullerene excited singlet state  $\text{C-P-}^1\text{C}_{60}$ , whether formed by energy transfer or direct excitation, accepts an electron from the porphyrin to yield  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  ( $k_2 = 3.1 \times 10^{10} \text{ s}^{-1}$  as determined from the fullerene fluorescence decays of **1** (32 ps) and **5** (1.35 ns). The overall quantum yield of  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  by the two paths is essentially unity. Competing with charge recombination of  $\text{C-P}^+-\text{C}_{60}^{\bullet-}$  (step 7) is electron transfer (step 4), giving  $\text{C}^+-\text{P-C}_{60}^{\bullet-}$  with an overall yield of 0.14. This final long-lived charge-separated state decays in 170 ns, mainly by charge recombination to produce the carotenoid triplet state ( $k_9 = 5.9 \times 10^6 \text{ s}^{-1}$ ). The  $^3\text{C-P-C}_{60}$  formed with a quantum yield of 0.13 in this unusual manner returns to the ground state in 4.9  $\mu$ s ( $k_{15} = 2.0 \times 10^5 \text{ s}^{-1}$ ).

**Photochemistry at 77 K.** In a glass at 77 K,  $\text{C-P-}^3\text{C}_{60}$  is formed by intersystem crossing within 10 ns of excitation with a quantum yield of 0.17 and decays to the ground state with  $k_{13} = 1.2 \times 10^4 \text{ s}^{-1}$ . Relay of triplet energy to the carotenoid via the porphyrin does not occur. This is expected for energetic reasons, given the estimated triplet energy levels in Figure 5. With 590 nm excitation, ~19% of the absorbed light excites the fullerene directly. As the yield of intersystem crossing in

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5 and other fullerene model compounds is essentially unity, this suggests that at 77 K the observed fullerene triplet state ( $\phi = 0.17$ ) arises mainly from light absorbed directly by the fullerene moiety and that C-P-<sup>1</sup>C<sub>60</sub> is not quenched by electron transfer but decays by intersystem crossing (as occurs in toluene). This being the case, the majority of the C-<sup>1</sup>P-C<sub>60</sub> states must decay by the photoinduced electron transfer step 3 to give C-P<sup>•+</sup>-C<sub>60</sub><sup>•-</sup>, which goes on to yield C<sup>•+</sup>-P-C<sub>60</sub><sup>•-</sup> via step 4 with an overall yield of 0.10 (0.12 based on light absorbed by the porphyrin). As that which occurs at ambient temperatures, C<sup>•+</sup>-P-C<sub>60</sub><sup>•-</sup> slowly recombines, mainly to the carotenoid triplet ( $k_8 + k_9 = 6.7 \times 10^5 \text{ s}^{-1}$ ,  $\phi = 0.07$ ), which decays with  $k_{15} = 1.0 \times 10^5 \text{ s}^{-1}$ . The small 83  $\mu\text{s}$  decay component observed at 550 nm is likely due to absorption of C-P-<sup>3</sup>C<sub>60</sub>.

The lack of charge separation from C-P-<sup>1</sup>C<sub>60</sub> at 77 K is ascribed mainly to loss of Coulombic stabilization of C-P<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> in the 2-methyltetrahydrofuran glass (dielectric constant = 2.60<sup>26</sup>). This makes the free energy change for electron transfer small or positive. Electron transfer from C-<sup>1</sup>P-C<sub>60</sub> to yield C-P<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> has a substantially larger driving force, as mentioned above, and this photoinduced electron transfer reaction still occurs. It is interesting to note that, in the glass at 77 K, the electron transfer step 3 is the dominant decay mechanism, rather than energy transfer step 1, whereas in toluene step 1 predominates. This apparent reversal of behavior could be rationalized by electron transfer in toluene from C-<sup>1</sup>P-C<sub>60</sub> to yield C-P<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> followed by rapid charge recombination to give C-P-<sup>1</sup>C<sub>60</sub>. However, as mentioned above, the time-resolved fluorescence and nanosecond transient absorption experiments reported here give no evidence for this process.

## Conclusions

The photochemistry of triad **1** has a number of unusual features. The results demonstrate that fullerenes can act as effective primary electron acceptors in multicomponent systems that generate long-lived charge-separated states with reasonable quantum yields. Secondly, two-step photoinduced electron transfer to generate long-lived charge separation in **1** occurs even at 77 K in a glass. The vast majority of systems based on other electron acceptors fail to undergo charge separation under these conditions.<sup>15,27,28</sup> It is generally thought that this failure is due mainly to the fact that upon freezing, the effective solvent dielectric constant decreases dramatically because the solvent dipoles cannot reorient to stabilize the newly-formed ions. (Photosynthetic electron transfer in natural reaction centers does not suffer from this problem.) Studies of porphyrins linked to quinones and related acceptors have shown that the loss of stabilization in going from liquid butyronitrile to a 2-methyltetrahydrofuran glass at low temperatures is ~0.8 eV and that only dyads with a greater driving force for electron transfer can still function at these temperatures.<sup>29</sup> The free energy change for formation of C-P<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> from C-<sup>1</sup>P-C<sub>60</sub> is only 0.54 eV, based on cyclic voltammetry in benzonitrile. Thus, the fullerene anion in **1** may be less susceptible to destabilization in nonpolar solvents than these other organic ions. The effect of solvent reorganization may also be different for fullerenes.

Finally, the C<sup>•+</sup>-P-C<sub>60</sub><sup>•-</sup> charge-separated state recombines to yield the carotenoid triplet state, rather than the molecular ground state. In related carotenoid-porphyrin-quinone systems, only recombination to the ground state is observed. Charge recombination to triplet states is well-known in photosynthetic reaction centers<sup>30-33</sup> and has been observed at low temperatures in liquid crystalline media for a model system consisting of non-photosynthetic pigments that absorb in the blue spectral region.<sup>34</sup> Recombination of a short-lived charge-separated state to a local triplet state has been inferred, but not observed directly, in two fullerene-containing dyads.<sup>7,8</sup> The triplet state in **1** presumably forms by radical pair recombination wherein most of the initially-formed C<sup>•+</sup>-P-C<sub>60</sub><sup>•-</sup> singlet radical pair state evolves into the triplet radical pair, which then recombines to yield <sup>3</sup>C-P-C<sub>60</sub>. It will be of interest to investigate **1** using time-resolved EPR spectroscopy in order to learn more about the birth of this unusual triplet state.

## Experimental Section

**Synthesis.** Model carotenoporphyrin **2**,<sup>12</sup> model porphyrin **4**,<sup>12</sup> and model fullerene **5**<sup>13</sup> were prepared as previously described.

**5-(4-(((Benzyloxy)carbonyl)amino)phenyl)-15-(4-(methoxycarbonyl)phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (8).** To a stirred solution of 5-(4-aminophenyl)-15-(4-(methoxycarbonyl)phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**7**)<sup>12</sup> (300 mg, 0.43 mmol) in 100 mL of dichloromethane under a nitrogen atmosphere was added 94  $\mu\text{L}$  (0.85 mmol) of *N*-methylmorpholine, followed by 80  $\mu\text{L}$  (0.55 mmol) of carbo(benzyloxy) chloride. After 4 h of stirring, a second portion of carbo(benzyloxy) chloride was added, and stirring was continued for a total of 24 h. Dilute aqueous sodium bicarbonate was added to the reaction vessel, and the resulting mixture was stirred vigorously for 2 h. The organic phase was separated, washed with dilute aqueous citric acid, washed with dilute aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and filtered. The filtrate was distilled under reduced pressure to remove the solvent. The residue was chromatographed on silica gel (toluene containing 5% ethyl acetate) to give 0.331 g of porphyrin **8** (92% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  -2.43 (2H, brs, -NH), 1.76 (12H, t, *J* = 8 Hz, 2-CH<sub>3</sub>, 8-CH<sub>3</sub>, 12-CH<sub>3</sub>, 18-CH<sub>3</sub>), 2.46 (6H, s, 13-CH<sub>3</sub>, 17-CH<sub>3</sub>), 2.53 (6H, s, 3-CH<sub>3</sub>, 7-CH<sub>3</sub>), 4.01 (8H, q, *J* = 8 Hz, 2-CH<sub>2</sub>, 8-CH<sub>2</sub>, 12-CH<sub>2</sub>, 18-CH<sub>2</sub>), 4.13 (3H, s, -OCH<sub>3</sub>), 5.36 (2H, s, -CH<sub>2</sub>Ar), 7.04 (1H, s, -NH), 7.3-7.6 (5H, m, -CH<sub>2</sub>ArH), 7.79 (2H, d, *J* = 8 Hz, 5Ar-3,5-H), 7.99 (2H, d, *J* = 8 Hz, 5Ar-2,6-H), 8.19 (2H, d, *J* = 8 Hz, 15Ar-3,5-H), 8.44 (2H, d, *J* = 8 Hz, 15Ar-2,6-H), 10.23 (2H, s, 10-CH, 20-CH); MS *m/z* 837 (*M*<sup>+</sup>); UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 408, 508, 542, 576, 628 nm.

**5-(4-(((Benzyloxy)carbonyl)amino)phenyl)-15-(4-(hydroxymethyl)phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (9).** A stirred solution of porphyrin **8** (320 mg, 0.38 mmol) in 200 mL of tetrahydrofuran under a nitrogen atmosphere was cooled in an ice bath, and an excess of lithium aluminum hydride was added. After 20 min, the mixture was poured into 150 mL of dichloromethane, and the resulting mixture was washed with water, followed by dilute aqueous sodium bicarbonate. After drying over anhydrous sodium sulfate, the solution was filtered, and the solvent was removed by distillation at reduced pressure. Chromatography of the residue on silica gel (toluene containing 15% ethyl acetate) gave **9** in 93% yield (290 mg): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  -2.42 (2H, brs, -NH), 1.76 (12H, t, *J* = 8 Hz, 2-CH<sub>3</sub>, 8-CH<sub>3</sub>, 12-CH<sub>3</sub>, 18-CH<sub>3</sub>), 2.48 (6H, s, 13-CH<sub>3</sub>, 17-CH<sub>3</sub>), 2.53 (6H, s, 3-CH<sub>3</sub>, 7-CH<sub>3</sub>), 4.01 (8H, q, *J* = 8 Hz, 2-CH<sub>2</sub>, 8-CH<sub>2</sub>, 12-CH<sub>2</sub>,

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18-CH<sub>3</sub>), 5.06 (2H, s, -CH<sub>2</sub>OH), 5.35 (2H, s, -CH<sub>2</sub>Ar), 7.03 (1H, s, -NH), 7.3–7.6 (5H, m, -CH<sub>2</sub>ArH), 7.72 (2H, d, *J* = 8 Hz, 15Ar-3,5-H), 7.76 (2H, d, *J* = 8 Hz, 5Ar-3,5-H), 7.98 (2H, d, *J* = 8 Hz, 5Ar-2,6-H), 8.05 (2H, d, *J* = 8 Hz, 15Ar-2,6-H), 10.22 (2H, s, 10-CH, 20-CH); MS *m/z* 809 (M<sup>+</sup>); UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 408, 508, 542, 576, 628 nm.

**5-(4-((Benzyloxy)carbonyl)amino)phenyl)-15-(4-formylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (6).** Porphyrin **9** (270 mg, 0.33 mmol) was dissolved in 200 mL of dichloromethane, and the solution was stirred under nitrogen while excess manganese dioxide was added. After 1 h of stirring, the solution was filtered through Celite. A mixture of chloroform and methanol (4:1) was washed through the filter cake until all of the porphyrin was extracted. The solvent was removed from the combined filtrates by distillation at reduced pressure, and the residue was chromatographed on silica gel (toluene containing 4% ethyl acetate) to give 204 mg of aldehyde **6** (76% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ -2.43 (2H, brs, -NH), 1.77 (12H, t, *J* = 8 Hz, 2-CH<sub>3</sub>, 8-CH<sub>3</sub>, 12-CH<sub>3</sub>, 18-CH<sub>3</sub>), 2.45 (6H, s, 13-CH<sub>3</sub>, 17-CH<sub>3</sub>), 2.53 (6H, s, 3-CH<sub>3</sub>, 7-CH<sub>3</sub>), 4.01 (8H, q, *J* = 8 Hz, 2-CH<sub>2</sub>, 8-CH<sub>2</sub>, 12-CH<sub>2</sub>, 18-CH<sub>2</sub>), 5.36 (2H, s, -CH<sub>2</sub>Ar), 7.04 (1H, s, -NH), 7.3–7.6 (5H, m, -CH<sub>2</sub>ArH), 7.78 (2H, d, *J* = 8 Hz, 5Ar-3,5-H), 7.98 (2H, d, *J* = 8 Hz, 5Ar-2,6-H), 8.26 (2H, d, *J* = 8 Hz, 15Ar-3,5-H or 15Ar-2,6-H), 8.27 (2H, d, *J* = 8 Hz, 15Ar-2,6-H or 15Ar-3,5-H), 10.24 (2H, s, 10-CH, 20-CH), 10.39 (1H, s, -CHO); MS *m/z* 807 (M<sup>+</sup>); UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 410, 508, 542, 576, 628 nm.

**Porphyrin–Fullerene 3.** Porphyrin aldehyde **6** (100 mg, 0.12 mmol), *N*-methylglycine (55 mg, 0.62 mmol), and C<sub>60</sub> (107 mg, 0.15 mmol) were added to 200 mL of toluene under a nitrogen atmosphere, and the resulting suspension was heated at reflux for 18 h. The mixture was cooled to room temperature and applied directly to a silica gel chromatography column. Elution with toluene containing 4% ethyl acetate gave an impure product, which was dissolved in carbon disulfide, diluted with toluene, and chromatographed on silica gel (toluene containing 3% ethyl acetate) to give pure dyad **3** (119 mg, 62% yield): <sup>1</sup>H NMR (500 MHz, 1:1 CDCl<sub>3</sub>/CS<sub>2</sub>) δ -2.46 (2H, brs, -NH), 1.79 (12H, t, *J* = 8 Hz, 2-CH<sub>3</sub>, 8-CH<sub>3</sub>, 12-CH<sub>3</sub>, 18-CH<sub>3</sub>), 2.4 (6H, brs, 13-CH<sub>3</sub>, 17-CH<sub>3</sub>), 2.52 (6H, s, 3-CH<sub>3</sub>, 7-CH<sub>3</sub>), 3.06 (3H, s, -NCH<sub>3</sub>), 4.00 (8H, q, *J* = 8 Hz, 2-CH<sub>2</sub>, 8-CH<sub>2</sub>, 12-CH<sub>2</sub>, 18-CH<sub>2</sub>), 4.27 (1H, d, *J* = 8 Hz, -CH<sub>2</sub>N-), 5.04 (1H, d, *J* = 8 Hz, -CH<sub>2</sub>N-), 5.11 (1H, s, -CHN-), 5.33 (2H, s, -CH<sub>2</sub>Ar), 6.97 (1H, s, -NH), 7.3–7.6 (5H, m, -CH<sub>2</sub>ArH), 7.78 (2H, d, *J* = 8 Hz, 5Ar-3,5-H), 7.96 (2H, d, *J* = 8 Hz, 5Ar-2,6-H), 8.13 (4H, brs, 15Ar-3,5-H, 15Ar-2,6-H), 10.14 (2H, s, 10-CH, 20-CH); MS *m/z* 1555.6 (M + 1)<sup>+</sup>; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 410, 508, 542, 576, 628 nm.

**Triad 1.** The protecting group of **3** was removed by adding 2 mL of a 1.0 M solution of boron tribromide in dichloromethane to a stirred mixture of **3** (80 mg, 0.051 mmol) in 20 mL of toluene and 20 mL of dichloromethane under a nitrogen atmosphere. After 2 h of stirring, the solution was diluted with 200 mL of toluene, washed with dilute aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and filtered. The filtrate was applied to a silica gel column and eluted with toluene containing 3% ethyl acetate. The fraction containing the fullerene-aminoporphyrin product was concentrated to ~25 mL and retained for the coupling reaction.

A mixture of 27 mg (0.51 mmol) of 7'-apo-7'-(4-carboxyphenyl)-β-carotene<sup>14</sup> (Car) in 20 mL of benzene and 42 μL (0.51 mmol) of pyridine was stirred under a nitrogen atmosphere, and 19 μL (0.26 mmol) of thionyl chloride was added. After 20 min, the solvent was removed by distillation at reduced pressure, and an additional 20 mL of benzene was added and removed in a similar manner. The residue

was dissolved in 20 mL of dichloromethane containing 42 μL (0.51 mmol) of pyridine, and the resulting solution added to the solution of fullerene-aminoporphyrin. After the reaction mixture was stirred for 1 h, it was diluted with toluene, washed with dilute aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate, and the volume was reduced to 100 mL by distillation of the solvent at reduced pressure. The resulting solution was applied to a silica gel column and eluted with toluene containing 3% ethyl acetate to give 48 mg of triad **1** (48% yield): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ -2.40 (2H, brs, -NH), 1.04 (6H, s, Car 16-CH<sub>3</sub>, Car 17-CH<sub>3</sub>), 1.44–1.54 (2H, m, Car 2-CH<sub>2</sub>), 1.58–1.68 (2H, m, Car 3-CH<sub>2</sub>), 1.73 (3H, s, Car 18-CH<sub>3</sub>), 1.78 (12H, t, *J* = 8 Hz, 2-CH<sub>3</sub>, 8-CH<sub>3</sub>, 12-CH<sub>3</sub>, 18-CH<sub>3</sub>), 1.98 (3H, s, Car 19-CH<sub>3</sub>), 2.00 (3H, s, Car 20-CH<sub>3</sub>), 2.02 (3H, s, Car 20'-CH<sub>3</sub>), 2.03 (2H, m, Car 4-CH<sub>2</sub>), 2.10 (3H, s, Car 19'-CH<sub>3</sub>), 2.55 (12H, brs, 3-CH<sub>3</sub>, 7-CH<sub>3</sub>, 13-CH<sub>3</sub>, 17-CH<sub>3</sub>), 2.93 (3H, s, -NCH<sub>3</sub>), 3.94–4.00 (8H, brm, 2-CH<sub>2</sub>, 8-CH<sub>2</sub>, 12-CH<sub>2</sub>, 18-CH<sub>2</sub>), 3.91 (1H, d, *J* = 8 Hz, -CH<sub>2</sub>N-), 4.73 (1H, s, -CHN-), 4.82 (1H, d, *J* = 8 Hz, -CH<sub>2</sub>N-), 6.0–6.8 (13 H, m, Car = CH-), 7.06 (1H, d, *J* = 16 Hz, Car 8'-H), 7.61 (2H, d, *J* = 8 Hz, Car 1',5'-H), 7.99 (2H, d, *J* = 8 Hz, Car 2',4'-H), 8.02 (2H, d, *J* = 8 Hz, 5Ar-3,5-H or 5Ar-2,6-H), 8.05 (2H, d, *J* = 8 Hz, 5Ar-2,6-H or 5Ar-3,5-H), 8.1 (4H, brs, 15Ar-3,5-H, 15Ar-2,6-H), 8.16 (1H, s, -NH), 10.21 (2H, s, 10-CH, 20-CH); MS(FAB) *m/z* 1938.7703 (calcd for (M + H)<sup>+</sup>, 1938.7755); UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) 410, 482, 510, 574, 628, 702 nm.

**Instrumental Techniques.** The <sup>1</sup>H NMR spectra were recorded on Varian Unity spectrometers at 300 or 500 MHz. Unless otherwise specified, samples were dissolved in deuteriochloroform with tetramethylsilane as an internal reference. High-resolution mass spectra were obtained on a Kratos MS 50 mass spectrometer operating at 8 eV in FAB mode. Other mass spectra were obtained on a Varian MAT 311 spectrometer operating in ET mode or a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). Ultraviolet-visible spectra were measured on a Shimadzu UV2100U UV/vis Spectrometer, and fluorescence spectra were measured on a SPEX Fluorolog using optically dilute samples and corrected.

Fluorescence decay measurements were performed on ~1 × 10<sup>-5</sup> M solutions by the time-correlated single-photon counting method. The excitation source was a cavity-dumped Coherent 700 dye laser pumped by a frequency-doubled Coherent Antares 76s Nd:YAG laser.<sup>35</sup> The instrument response function was 35 ps, as measured at the excitation wavelength for each decay experiment with Ludox AS-40.

Nanosecond transient absorption measurements were made with excitation from an Opotek optical parametric oscillator pumped by the third harmonic of a Continuum Surelight Nd:YAG laser. The pulse width was ~5 ns, and the repetition rate was 10 Hz. The detection portion of the spectrometer has been described elsewhere.<sup>36</sup>

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