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Photonic Switching of Photoinduced Electron Transfer in a Dihydropyrene−Porphyrin−Fullerene Molecular Triad

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Abstract: Photonic control of photoinduced electron transfer has been demonstrated in a dimethyldihydropyrene (DHP) porphyrin (P) fullerene (C_{60}) molecular triad. In the DHP−P−C_{60} form of the triad, excitation of the porphyrin moiety is followed by photoinduced electron transfer to give a DHP−$P^{•+}$−$C_{60}^{•-}$ charge-separated state, which evolves by a charge shift reaction to DHP$^{•+}$−P−$C_{60}^{•-}$. This final state has a lifetime of 2 μs and is formed in an overall yield of 94%. Visible (≥300 nm) irradiation of the triad leads to photoisomerization of the DHP moiety to the cyclophanediene (CPD). Excitation of the porphyrin moiety of CPD−P−C_{60} produces a short-lived (<10 ns) CPD−$P^{•+}$−$C_{60}^{•-}$ state, but charge shift to the CPD moiety does not occur, due to the relatively high oxidation potential of the CPD group. Long-lived charge separation is not observed. Irradiation of CPD−P−C_{60} with UV (254 nm) light converts the triad back to the DHP form. Thermal interconversion of the DHP and CPD forms is very slow, photochemical cycling is facile, and in the absence of oxygen, many cycles may be performed without substantial degradation. Thus, light is used to switch long-lived photoinduced charge separation on or off. The principles demonstrated by the triad may be useful for the design of molecule-based optoelectronic systems.

Introduction

After 25 years of research, chemists can now design and prepare porphyrin-based molecules containing electron donors and acceptors that undergo photoinduced electron transfer to produce high-energy, long-lived charge-separated states with quantum yields approaching unity.[1−16] Information obtained from the study of such molecules is of interest not only for understanding photosynthesis and devising new approaches to solar energy conversion, but also for the design of molecule-based optoelectronic systems. For such possible applications, it is of interest not only to use light to generate charge separation, but also to use light to switch electron transfer on or off. Photochromic molecules, which can be isomerized between two thermally stable molecular structures using light, are good candidates for light-activated control units in molecule-based devices of various types.[17−22] Recently, we have reported two different approaches to controlling photoinduced electron transfer using photochromic moieties. We have shown that it is possible to use photochromic units to control singlet energy transfer quenching of a porphyrin excited state,[23] thereby turning

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Chart 1

1a

1b
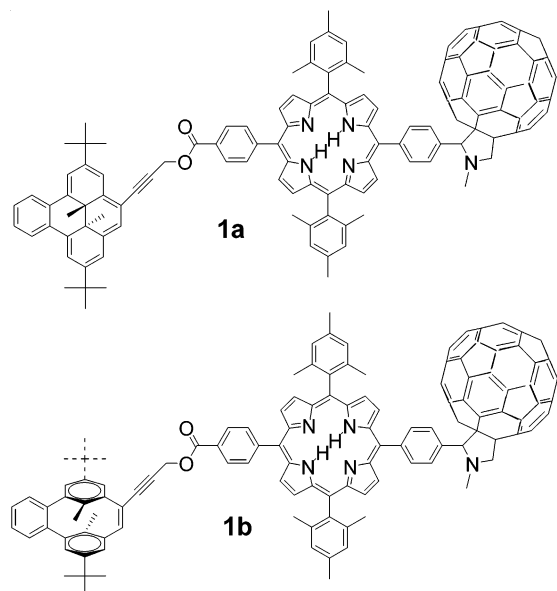
photoinduced electron transfer to an attached acceptor on or off.[24] Additionally, we have used the light-induced changes in reduction potential of a photochromic dihydroindolizine to switch photoinduced electron transfer in a porphyrin−dihydroindolizine dyad.[25]

In the current work, we have investigated a third approach by synthesizing and studying [*e*]-annelated dimethyldihydropyrene (DHP) porphyrin (P) fullerene (C_{60}) triad **1** (Chart 1) and related model compounds (Charts 2 and 3). By photonically switching the photochromic dihydropyrene moiety of **1**, we reversibly control the oxidation potential of the switching element, and through this, the lifetime of a charge-separated state generated following excitation of the porphyrin. In the closed, DHP form of the triad (**1a**), excitation of the porphyrin is followed by photoinduced electron transfer to yield DHP−P$^{\bullet+}$−$C_{60}{}^{\bullet-}$. The DHP rapidly reduces the porphyrin radical cation through a charge shift reaction to generate a DHP$^{\bullet+}$−P−$C_{60}{}^{\bullet-}$ charge-separated state that has a lifetime of 2.0 μs. Visible irradiation of **1a** converts the DHP moiety to the cyclophanediene (CPD) form, yielding triad **1b**, in which the oxidation potential of the CPD group is much higher than that of the DHP isomer. Excitation of the porphyrin of CPD-P−C_{60} leads to CPD−P$^{\bullet+}$−$C_{60}{}^{\bullet-}$, but charge shift does not occur, and the charge-separated state collapses to the ground state in a few ns. UV irradiation of **1b** converts it back to **1a**.

Dimethyldihydropyrene photochromic molecules (e.g., model compound **8**, Chart 3) have been investigated by several groups,[18,26−33] and shown to be inverse photochromes, wherein

Chart 2

2: $R_1 = R_3 = CH_3$, $R_2 =$

3: $R_1 =$ $R_2 = R_3 = H$

4: $R_1 =$ $R_2 =$ $R_3 = H$

5: $R_1 = R_3 = CH_3$, $R_2 = H$

6: $R_1 = R_2 = R_3 = CH_3$

Chart 3

a   **b**

7: R = ══─OH

8: R = H

9: R = ══─H
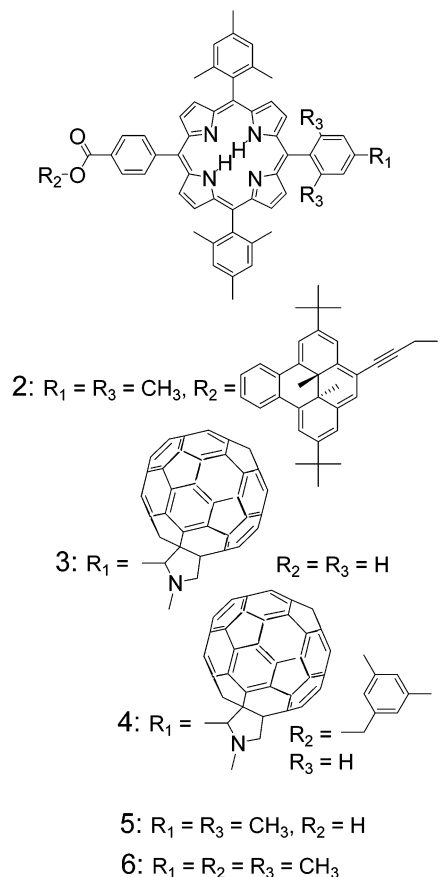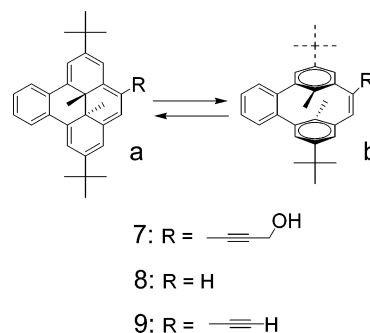
the thermally stable isomer is the closed, DHP form (e.g., **8a**), which absorbs strongly in the visible region of the spectrum. The DHP isomer can be converted to the open, CPD form (e.g., **8b**) with visible light. The CPD does not absorb significantly in the visible, but does absorb in the UV, and ultraviolet irradiation converts it back to the DHP isomer. Thermal reversion of CPD to DHP also occurs, albeit very slowly. The photochemical ring opening of the DHP form occurs from the first excited singlet state.[31] Despite reasonably long excited singlet state lifetimes for DHP molecules (1−6 ns), ring opening generally occurs with relatively low quantum yields (<10%); the quantum yield is highest with [*e*]-annelated DHPs such as **8**.[31] The photochemical ring closing of the CPD form with UV light is more facile (Φ ≈ 30%).

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Designing a DHP-based molecular switch for photoinduced electron transfer presented several challenges. The oxidation potential of the DHP isomer of the photochromic moiety had to be low enough so that this species could readily donate an electron to the porphyrin radical cation of DHP−P$^{•+}$−C$_{60}$$^{•−}$, but the oxidation potential of the CPD form needed to be high enough so that it could not serve as a viable electron donor. The DHP form of the photochrome could not absorb to the red of the porphyrin moiety, to prevent quenching of the porphyrin excited singlet state by energy transfer to the photochrome. The electronic interaction between the DHP and the porphyrin was required to be strong enough to permit rapid electron transfer from DHP to the porphyrin radical cation, before DHP−P$^{•+}$−C$_{60}$$^{•−}$ decayed by charge recombination. At the same time, energy transfer quenching of DHP or CPD excited singlet states by the porphyrin had to be slow enough to prevent competition with photoisomerization. Finally, the DHP and CPD moieties should not interfere with porphyrin-to-fullerene photoinduced electron transfer by taking part in competing electron-transfer processes. On the basis of these criteria, synthetic feasibility, and the results for model compounds (see below), the DHP, porphyrin and fullerene moieties and interchromophore linkages for **1** were chosen.

Experimental Section

Synthesis. The preparation of porphyrin-fullerene dyads **3**[34] and **4**,[35] porphyrins **5** and **6**,[36] and dihydropyrenes **8** and **9**,[31] have been previously reported. The DHP, CPD, and fullerenopyrrolidine moieties are chiral. No attempt was made to separate the various stereoisomers arising from this situation.

3-{4′-(2′,7′-Di-*tert*-butyl-*trans*-12c′,12d′-dimethyl-12c′,12d′-dihydrobenzo[*e*]pyrenyl}prop-2-ynol (7a). *n*-Butyllithium (1.0 mmol, 0.6 mL of a 1.8 M solution in hexane) was added to a solution of ethynyldihydropyrene **9a**[31] (250 mg, 0.60 mmol) in dry tetrahydrofuran (10 mL) at 0 °C under argon. After 5 min, the cooling bath was removed and dry gaseous formaldehyde (generated by pyrolysis of paraformaldehyde at 200 °C in a stream of argon) was passed into the flask, just above the surface of the solution, with vigorous stirring. The mixture was allowed to stir for a further 30 min, and then diethyl ether and water were added. The organic layer was separated, dried over anhydrous MgSO$_4$, and evaporated to dryness. The red residue was chromatographed on silica gel (60−200 mesh, deactivated with 3 wt. % NH$_4$OH) using first diethyl ether−hexanes (1:10) as eluant to elute unchanged **9a**, and then diethyl ether−hexanes (1:1) to elute 132 mg (49%) of the red alcohol **7a**. Recrystallization from cyclohexane yielded intense red crystals, mp 83−84 °C: ^{1}H NMR (500 MHz, CDCl$_3$) δ −1.46 (3H, s), −1.44 (3H, s), 1.47 (9H, s), 1.51 (9H, s), 4.67 (2H, s), 7.13 (1H, d, J = 1 Hz), 7.27 (1H, t, J = 1 Hz), 7.64−7.58 (2H, m), 7.85 (1H, d, J = 1 Hz), 8.21 (1H, d, J = 1 Hz), 8.26 (1H, d, J = 1 Hz), 8.73−8.68 (2H, m); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 17.69, 17.81, 30.51, 30.56, 35.19, 35.38, 35.79, 36.43, 52.09, 85.60, 91.76, 112.16, 117.11, 117.35, 117.84, 119.26, 122.77, 124.47, 124.58, 126.03, 126.21, 129.17, 129.43, 134.94, 136.62, 137.73, 141.87, 145.32, 147.32; FAB−MS *m/z* 448.2; HRMS calcd for C$_{33}$H$_{36}$O, 448.2766, obsd, 448.2766; UV (λ$_{max}$, nm (ε$_{max}$), cyclohexane) 310 (16 140), 325 (16 100), 345 (15 800), 380 (17 600), 400 (22 700), 505 (3220); IR (KBr) ν 3439 (br), 3060, 2960, 2924, 2867, 1463, 1367, 1256, 872, 754 cm^{-1}.

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DHP−P−C$_{60}$ triad (1a). To a flask containing 60 mg (0.039 mmol) of dyad **3**[34] was added 5 mL of dichloromethane and 7.0 μL (0.063 mmol) of *N*-methylmorpholine. The solution was cooled to 0 °C, and 8.0 mg (0.043 mmol) of 2-chloro-4,6-dimethoxy-1,3,5,-triazine was added. Stirring was continued for 10 min at 0 °C and then at room temperature for an additional 60 min. At this point TLC (toluene/7% ethyl acetate) indicated that all the acid dyad had been converted into a less polar material. To the reaction mixture was added 18 mg (0.039 mmol) of alcohol **7a** and 5.0 mg (0.039 mmol) of 4-(dimethylamino)-pyridine. After 1 h TLC (toluene/1% ethyl acetate) indicated that the reaction was complete; the solvent was evaporated and the residue was chromatographed on a silica gel column (toluene/10% hexanes) to give 57 mg (74% yield) of triad **1a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ −2.63 (2H, s), −1.40 (3H, s), −1.38 (3H, s), 1.50 (9H, s), 1.57 (9H, s), 1.82 (6H, s), 1.84 (6H, s), 2.61 (6H, s), 3.12 (3H, s), 4.43 (1H, d, J = 9 Hz), 5.12 (1H, d, J = 9 Hz), 5.28 (1H, s), 5.52 (2H, s), 7.19 (1H, s), 7.26 (4H, m), 7.33 (1H, s), 7.62−7.65 (2H, m), 8.00 (1H, s), 8.20 (2H, brd s), 8.26−8.30 (4H, m), 8.34 (2H, d, J = 8 Hz), 8.55 (2H, d, J = 8 Hz), 8.64−8.76 (10H, m); MALDI-TOF−MS *m/z* calcd for C$_{147}$H$_{81}$N$_5$O$_2$ 1949, obsd 1949; UV/vis (dichloromethane) 312, 328, 345, 420, 516, 550, 592, 648, 702 nm.

DHP−P dyad (2a). To a flask containing 60 mg (0.076 mmol) of 5(4-carboxyphenyl)-10,15,20-tris(2,4,6-trimethylphenyl) porphyrin (**5**)[36] was added 8 mL of dichloromethane and 13 μL (0.12 mmol) of *N*-methylmorpholine. The solution was cooled to 0 °C, and 15 mg (0.084 mmol) of 2-chloro-4,6-dimethoxy-1,3,5-triazine was added. Stirring was continued at 0 °C for 10 min, and then at room temperature for 2 h. TLC (dichloromethane/1% acetone) indicated that all the porphyrin acid had been consumed. To the reaction mixture was added 34 mg (0.076 mmol) of alcohol **7a** and 9 mg (0.076 mmol) of 4-(dimethylamino)pyridine. Stirring continued for 2 h after which time TLC (toluene/30% hexanes) showed that the reaction was complete. The solvent was evaporated and the residue was chromatographed on a silica gel column (toluene/hexanes, 2:1 to 4:1) to give 71 mg (76% yield) of dyad **2a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ −2.53 (2H, s), −1.38 (3H, s), −1.36 (3H, s), 1.52 (9H, s), 1.59 (9H, s), 1.88 (18H, s), 2.64 (9H, s), 5.55 (2H, s), 7.20 (1H, s), 7.29 (6H, s), 7.35 (1H, s), 7.64−7.67 (2H, m), 8.02 (1H, s), 8.27 (1H, s), 8.32 (1H, s), 8.34 (2H, d, J = 8 Hz), 8.56 (2H, d, J = 8 Hz), 8.66 (4H, s), 8.71−8.78 (6H, m); MALDI-TOF-MS *m/z* calcd for C$_{87}$H$_{82}$N$_4$O$_2$ 1216, obsd 1216; Uv/vis (dichloromethane) 329, 346, 418, 516, 550, 592, 648 nm.

Spectroscopic Measurements. The solvent for all measurements was freshly distilled 2-methyltetrahydrofuran, unless otherwise stated. All samples were deoxygenated by bubbling with argon for 20 min.

Steady state and time based UV−vis ground-state absorption measurements were performed using a Shimadzu UV-3101PC UV−Vis−NIR spectrometer. Steady-state fluorescence emission spectra were measured using a Photon Technology International MP-1 fluorometer and corrected. Excitation was produced by a 75 W xenon lamp and single grating monochromator. Fluorescence was detected at 90° to the excitation beam via a single grating monochromator and an R928 photomultiplier tube having S-20 spectral response operating in the single photon counting mode.

Fluorescence decay measurements were performed on ~1 × 10^{-5} 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. Fluorescence emission was detected at a magic angle using a single grating monochromator and microchannel plate photomultiplier (Hamamatsu R2809U-11). The instrument response time was ca. 35−50 ps, as verified by scattering from Ludox AS-40. The spectrometer was controlled by software based on a LabView program from National Instruments.[37]

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Nanosecond transient absorption measurements were made with excitation from the second harmonic of a Continuum Surelight Nd: YAG laser (532 nm). The pulse width was ∼5 ns, and the repetition rate was 10 Hz. The detection portion of the spectrometer has been described elsewhere.[38]

The femtosecond transient absorption apparatus consisted of a kilohertz pulsed laser source and a pump−probe optical setup. The laser pulse train was provided by a Ti:sapphire regenerative amplifier (Clark-MXR, Model CPA-1000) pumped by a diode-pumped CW solid-state laser (Spectra Physics, Model Millennia V). The typical laser pulse was 100 fs at 790 nm, with a pulse energy of 0.9 mJ at a repetition rate of 1 kHz. Most of the laser energy (80%) was used to pump an optical parametric amplifier (IR−OPA, Clark−MXR). The excitation pulse was sent through a computer-controlled optical delay line. The remaining laser output (20%) was focused into a 1.2 cm rotating quartz plate to generate a white light continuum. The continuum beam was further split into two identical parts and used as the probe and reference beams, respectively. The probe and reference signals were focused onto two separated optical fiber bundles coupled to a spectrograph (Acton Research, Model SP275). The spectra were acquired on a dual diode array detector (Princeton Instruments, Model DPDA-1024).[39]

To determine the number of significant components in the transient absorption data, singular value decomposition analysis[40,41] was carried out using locally written software based on the MatLab 5.0 program (MathWorks, Inc.). Decay-associated spectra were then obtained by fitting the transient absorption change curves over a selected wavelength region simultaneously as described by eq 1

$$\Delta A(\lambda,t) = \sum_{i=1}^{n} A_i(\lambda) \exp(-t/\tau_i) \tag{1}$$

where $\Delta A(\lambda,t)$ is the observed absorption change at a given wavelength at time delay t and n is the number of kinetic components used in the fitting. A plot of $A_i(\lambda)$ versus wavelength is called a decay-associated spectrum, and represents the amplitude spectrum of the ith kinetic component, which has a lifetime of τ_i. Transient absorption experiments on the DHP-containing compounds were done under continuous UV irradiation at 254 nm with a UVP UV lamp Model UVGL-25 in order to reduce laser-induced conversion of the sample to the CPD form.

The photoinduced closing and opening kinetics of the CPD/DHP chromophore were studied using, respectively, a UVP UV lamp Model UVGL-25 and a Xe/HgXe-lamp (ORIEL Corp. Model 66028). Before sample illumination with the Xe-lamp, the IR portion of the light was reduced by passing the beam through two water-cooled IR filters ($A = 5$ and $A = 9$ at 900 and 1060 nm, respectively). Furthermore, one of two different cutoff filters was used to remove wavelengths shorter than 590 or 300 nm, as required. The absorption as a function of time was monitored at 560 nm through an interference filter to exclude the Xe-lamp light from entering the detection portion of the spectrometer.

Results

Electrochemistry and Energetics. Cyclic voltammetric measurements were made in order to obtain redox potentials that could be used to estimate the energies of the various charge-separated states. The measurements were made in benzonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. The counter electrode was platinum, the reference electrode Ag/ 0.1 M AgNO₃, and the working electrode glassy carbon. The measurements employed ferrocene as an internal reference redox system, and are reported vs SCE. Model compound **7** in the DHP form (**7a**) featured a reversible oxidation wave at 0.60 V
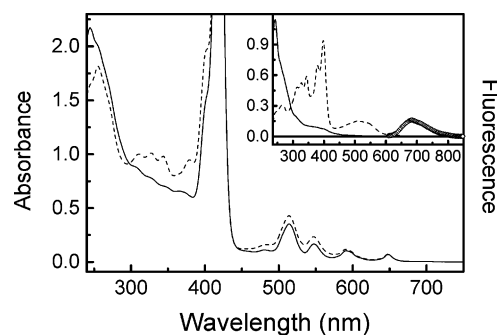
Figure 1. Absorption spectra of 2-methyltetrahydrofuran solutions of the closed, dihydropyrene-bearing DHP−P−C₆₀ triad **1a** (- - -) and the open, CPD−P−C₆₀ cyclophanediene-containing isomer **1b** (—). The inset shows absorption spectra in the same solvent of model DHP compound **7a** (- - -) and CPD isomer **7b** (—). Also shown in the inset is the emission spectrum of **7a** obtained with excitation at 510 nm (◊).

vs SCE, and irreversible reduction waves at −1.75 and −1.91 V (peak potentials). The CPD form (**7b**), prepared by VIS irradiation of the compound, showed oxidation at 0.96 V and reduction at −1.76 and −1.93 V (all irreversible, peak potentials). The first oxidation potential of the porphyrin moiety of **1**, **3**, and **4** is taken as 1.02 V vs SCE, its first reduction potential as −1.17, and the first reduction potential of the fullerene portion of these three compounds as −0.56 V vs SCE, based on potentials for closely related molecules.[42] Using these data, the energies of DHP−P•⁺−C₆₀•⁻, DHP•⁺−P−C₆₀•⁻, DHP•⁺−P•⁻− C₆₀, CPD−P•⁺−C₆₀•⁻, CPD•⁺−P−C₆₀•⁻, and CPD•⁺−P•⁻−C₆₀ may be estimated as 1.58, 1.16, 1.77, 1.58, 1.52, and 2.13 eV above the ground states, respectively. Similarly, the energy of P•⁺−C₆₀•⁻ in dyad **4** is estimated to be 1.58 eV. These estimates make no corrections for Coulombic stabilization in the charge-separated states.

Absorption and Emission Spectroscopy. The absorption spectrum of **7a**, the closed, DHP form of a model dihydropyrene, is shown in the inset in Figure 1. The compound has absorption maxima at 263, 314, 327, 344, 379, 398, and ∼513 nm. The corrected fluorescence emission spectrum (with excitation at 510 nm, Figure 1 inset) resembles the mirror image of the longest-wavelength absorption band, with a maximum at 692 nm, indicating a large Stokes shift. Irradiation of **7a** with ≥ 300 nm light converts it to the open, CPD form **7b**. The absorption spectrum of **7b** (Figure 1 inset) features maxima at 245 and 380 (sh) nm. CPD **7b** could be converted back to DHP **7a** by 254-nm irradiation.

Figure 1 shows the absorption spectrum of DHP−P−C₆₀ triad **1a** in 2-methyltetrahydrofuran. Maxima are observed at 255, 314, 327, 344, 379, 398 (sh), 417, 481 (sh), 514, 548, 591, 648, and 704 nm. The first six maxima correspond mainly to the absorption of the DHP moiety, although the porphyrin and fullerene contribute to the overall absorption in this region. The bands from 417 to 648 nm are ascribed to the porphyrin, with some underlying broad absorption by the fullerene, and from the DHP in the 513-nm area. There is a very weak band at 704 nm due to the fullerene.

Irradiation of **1a** with ≥300 nm light causes spectral changes wherein some of the 513-nm region absorption and much of

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the fine structure in the 300–400 nm region due to the DHP have disappeared. Irradiation of the resulting sample at 254 nm returns the spectrum to its original state. This demonstrates that the photochromic moiety can be photoisomerized between the DHP and CPD forms even when it is attached to the porphyrin. The spectrum of CPD triad **1b** still shows bands at 245, 417, 481 (sh), 514, 548, 591, 648, and 704 nm that are characteristic of the porphyrin and fullerene components. In general, the spectra of **1** resemble linear combinations of the spectra of the component chromophores, suggesting that there are no strong electronic interactions among these chromophores that impact the spectral properties.

Thermal Isomerization and Photoisomerization. Figure 1 shows that photoisomerization of the photochromic moieties is possible even when they are attached to the porphyrin, indicating that any energy or electron-transfer reactions involving the porphyrin or fullerene do not prevent isomerization. The thermal closing of the CPD to yield the DHP form was investigated for **1** and **7**. At 25 °C in 2-methyltetrahydrofuran, the closing rate constant for **7b** is 6.2×10^{-6} s^{-1} (lifetime = 45 h). The corresponding rate constant for **1b** is 1.0×10^{-5} s^{-1} (lifetime = 27 h). The reason for this difference in lifetimes is unknown. However, the activation energy for thermal isomerization in other DHP/CPD systems has also been shown to be a sensitive function of the substituents.[28]

Photoinduced closing of both **1b** and **7b** was readily achieved; with 254 nm irradiation ($\sim$700 μW/cm^2), the time constants were 50 s for **1b** and 19 s for **7b**. The quantum yield for closing of the closely related CPD molecule **9b** in cyclohexane is 28%, and the rate constant for the isomerization reaction from ^{1}CPD is 2.0×10^7 s^{-1}.[31]

Opening of the DHP forms of model **7**, dyad **2** and triad **1** can be achieved with $\geq$300 nm radiation. When using a 590-nm long pass filter ($\sim$40 mW/cm^2), **7a** opens with a lifetime of 137 s, DHP–P **2** with a lifetime of 62 s, and **1a** with a time constant of 90 s. The corresponding experiment using a 300-nm long pass filter ($\sim$300 mW/cm^2) results in time constants about 50 times smaller, but the percentage of the DHP form present in the photostationary state is larger. The quantum yield for opening of **9a** in cyclohexane is 7.5%, and the rate constant for the isomerization reaction from ^{1}DHP is $\sim$2.5 $\times 10^7$ s^{-1}.[31]

Time-Resolved Fluorescence Measurements. Fluorescence decay data in 2-methyltetrahydrofuran solution at ambient temperatures were gathered by the time-correlated single photon counting technique, with excitation at 590 nm. The solutions were bubbled with argon to remove dissolved oxygen. Model DHP **7a** fluorescence decays at 685 nm as a single exponential with a lifetime of 1.02 ns (goodness-of-fit parameter $\chi^2 = 1.08$). Comparable lifetimes have been observed for related compounds.[31]

Model porphyrin **6** has a typical porphyrin emission spectrum with maxima at 650 and 718 nm. The fluorescence, monitored at 650 nm, decays as a single exponential ($\chi^2 = 1.03$) with a lifetime of 13.4 ns. When the porphyrin moiety is linked to a fullerene, the porphyrin fluorescence is quenched due to photoinduced electron transfer to generate P$^{\bullet+}$–C$_{60}$$^{\bullet-}$. In model P–C$_{60}$ dyad **4**, the fluorescence decay features one significant decay component with a lifetime of 34 ps, and three minor ($\leq$5% of the decay) components due to small amounts of impurity ($\chi^2 = 1.16$).[35]
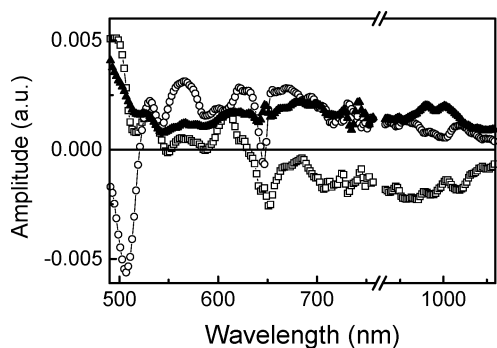
Turning now to dyad **2**, it was found that when the photochromic moiety was in the open, CPD–P form, normal porphyrin emission was observed as a single-exponential process, with a lifetime of 13.3 ns ($\chi^2 = 1.07$). Thus, the CPD has no effect on the porphyrin first excited singlet state. The dyad was converted to the DHP–P form with UV light, and the fluorescence investigated. Because the 590-nm excitation light causes opening of the DHP to the CPD form, the sample was irradiated at 254 nm every 10 s during the experiment in order to limit the effects of this isomerization. Under these conditions, two exponential emission components were observed at 650 nm, where essentially all of the emission is due to the porphyrin (with 590 nm excitation). The lifetimes are 1.76 ns (80%) and 13.0 ns (20%); $\chi^2 = 1.03$. The major component is ascribed to DHP–^{1}P and the minor to some CPD–^{1}P formed by the excitation laser.

At $\sim$680 nm, where the DHP moiety has its fluorescence maximum (Figure 1), a third decay component (in addition to the 1.76 ns and 13.0 ns decays) was detected. The lifetime of this component is 335 ps, and its amplitude is as much as 60% of the total fluorescence amplitude at some wavelengths >650 nm. This component represents decay of ^{1}DHP–P, and shows that the DHP excited singlet state is quenched somewhat, relative to model compound **7a**.

The fluorescence emission of the triads was also investigated. DHP–P–C$_{60}$ triad **1a**, with excitation at 590 nm, featured decay curves at 640 nm (mainly porphyrin emission) that could be satisfactorily fit ($\chi^2 = 1.06$) with four components: 34 ps (93% of the decay), 240 ps (6%), 1.7 ns (0.6%), and 13.4 ns (0.4%). At $\sim$680 nm, where the DHP moiety fluoresces most strongly, fitting the decay required components of 32 ps (81%), 330 ps (17%), 1.9 ns (1.5%), and 13.4 ns (0.5%) ($\chi^2 = 1.17$). At both wavelengths, the major, $\sim$33 ps component is assigned to decay of the porphyrin first excited singlet state. The 330 ps component at 680 nm is due to the emission of the DHP first excited singlet state (see results for dyad **2**). The other components are assigned to minor impurities and decomposition products.

Excitation of CPD–P–C$_{60}$ triad **1b** at 590 nm led to a fluorescence decay at 640 nm that could be fitted with three exponentially decaying components ($\chi^2 = 1.08$): 32 ps (99% of the total amplitude), 1.05 ns (0.4%), and 13.4 ns (0.6%). The two minor components are assigned to impurities.

Transient Absorption Measurements. Triad **1** in 2-methyltetrahydrofuran solution was investigated in the closed, DHP form using transient absorption spectroscopy with $\sim$100 fs excitation pulses. The results, with excitation at 650 nm where absorption is mainly by the porphyrin, are shown in Figure 2 as decay-associated spectra. That is, the spectral features in each spectrum are all associated with the reported exponential time constant. The best fit to the entire data set was achieved with three components: 35 ps, 150 ps, and a component that does not decay significantly on the time scale of the instrument (i.e., τ >5 ns). The 35 ps component has features corresponding to ground-state bleaching of the porphyrin Q-bands at $\sim$514, 548, 591, and 648 nm. In addition, porphyrin stimulated emission bands are seen in the 650 and 720 nm regions. There is negative amplitude at wavelengths >650 nm, representing the grow-in of a new transient species with induced absorption in this region. Such absorption is characteristic of the porphyrin radical cation.[43–45] The fullerene radical anion has absorption in the
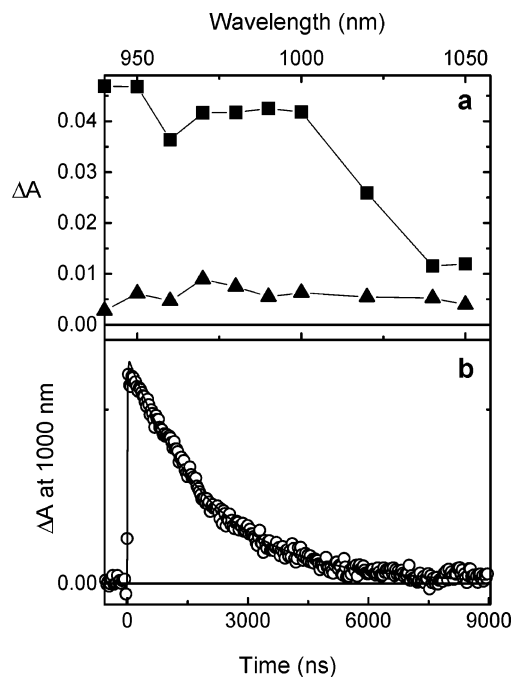
Figure 2. Decay-associated transient absorption spectra for DHP−P−C_{60} triad **1a** obtained by analysis of spectra obtained following excitation of a 2-methyltetrahydrofuran solution with a ∼100 fs laser pulse at 650 nm. The analysis gave decay components with lifetimes of 35 ps (□) and 150 ps (○), and a component that did not decay on the time scale of the instrumentation (▲).

1000 nm region, where grow-in of a new transient is also observed.[46,47] The 150 ps component also has features characteristic of porphyrin Q-band bleaching, but the stimulated emission is absent, as indicated by the change in ratio of the negative features at 650 and 720 nm. The large negative feature at ∼510 nm is due to the decay of ground state bleaching of a Q-band of the porphyrin radical cation superimposed on negative amplitude due to the growing in of a new transient, ascribed to the DHP radical cation. There is also a broad absorption at wavelengths greater than 650 nm which is assigned to decay of the porphyrin radical cation with a time constant of 150 ps. Note that this spectrum does not have features characteristic of the fullerene radical anion, so this anion does not decay on this time scale. The spectrum of the nondecaying component shows induced absorption in the 1000 nm region due to the fullerene radical anion, and induced absorption in the blue part of the spectrum which we ascribe to the dihydropyrene radical cation. Porphyrin ground state bleaching has nearly disappeared, but some small porphyrin features are still evident.

The interpretation of these data is that the initial laser pulse forms mainly DHP−^{1}P−C_{60}, which decays by photoinduced electron transfer to give DHP−$P^{\bullet+}$−$C_{60}^{\bullet-}$ with a time constant of 35 ps. This intermediate charge-separated state evolves with a time constant of 150 ps by charge shift from the DHP, yielding DHP$^{\bullet+}$−P−$C_{60}^{\bullet-}$. The final state lives much longer than the time window available with the spectrometer. The very small porphyrin features observed in the nondecaying component are ascribed to some CPD−$P^{\bullet+}$−$C_{60}^{\bullet-}$, as irradiation in the UV does not convert 100% of the CPD−P−C_{60} to the DHP form.

To observe the decay of the long-lived transient, transient absorption measurements on the nanosecond time scale were undertaken. Solutions of DHP−P−C_{60} triad **1a** in 2-methyltetrahydrofuran were excited with ∼5 ns laser pulses at 532 nm, with argon bubbling of the sample to remove dissolved oxygen. Figure 3a shows the transient spectrum in the 940−1050 nm region. The absorption is due mainly to the fullerene radical anion of the DHP$^{\bullet+}$−P−$C_{60}^{\bullet-}$ charge-separated state. Figure 3a also shows the results of an identical experiment with CPD−
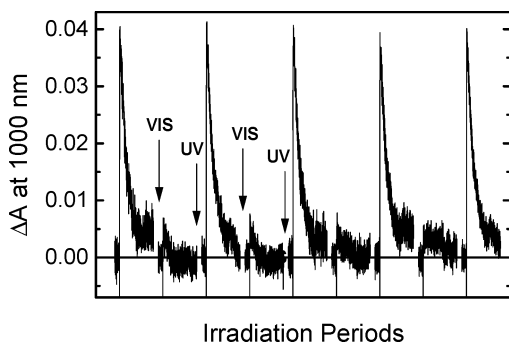
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Figure 3. (a) Transient absorption spectra of DHP−P−C_{60} triad **1a** (■) and CPD−P−C_{60} triad **1b** (▲) in 2-methyltetrahydrofuran solution 20 ns after excitation with a 5 ns, 532 nm laser pulse. The absorbance of the long-lived DHP$^{\bullet+}$−P−$C_{60}^{\bullet-}$ state seen in **1a** is absent in **1b**. (b) Decay of the absorbance observed for **1a** at 1000 nm. Fitting of averaged data for multiple pulses with an exponential function (solid line) yields a time constant of 2.0 μs for the decay.

P−C_{60} triad **1b**, which was generated from the solution of **1a** by 8 s of irradiation with visible light (≥300 nm, ∼300 mW/cm^2). In this case, virtually no fullerene radical anion was observed. Figure 3b shows the decay of the transient absorption for DHP−P−C_{60} triad **1a** at 1000 nm. The decay was fitted with a single-exponential component having a time constant of 2.0 μs. This is the lifetime of DHP$^{\bullet+}$−P−$C_{60}^{\bullet-}$.

Information necessary for interpretation of the transient absorption results for **1** was obtained from similar experiments with model dyads **2** and **4**. Excitation of a 2-methyltetrahydrofuran solution of the DHP−P form of **2** with ∼100 fs pulses at 600 nm yielded decay-associated spectra with two components. One component had a lifetime of 1.7 ns, and the second did not decay on the time scale of the instrument. Both spectra had spectral features characteristic of a porphyrin. The 1.7 ns component represents quenching of the porphyrin first excited singlet state by the DHP moiety. The second component is ascribed to unquenched porphyrin excited singlet state in some of the CPD form of the dyad which is present. It was not possible to identify with certainty any additional spectral features that could be ascribed to other transient species.

Previously, we have reported transient absorption results for P−C_{60} dyad **4** in 2-methyltetrahydrofuran.[35] Excitation with ∼100 fs pulses was into the porphyrin moiety at 600 nm, and transient spectra were recorded in the 450−760 nm and 930 − 1070 nm regions. Global fitting of the data yielded two components. The first of these, with a time constant of 32 ps, featured decay of the porphyrin first excited singlet state absorption and rise of absorption of the fullerene radical anion and porphyrin radical cation, verifying that ^{1}P−C_{60} undergoes 32 ps photoinduced electron transfer to yield $P^{\bullet+}$−$C_{60}^{\bullet-}$. The second component, with a time constant of 3.3 ns, contains the

Figure 4. Photochemical cycling of triad **1**. The triad in 2-methyltetrahydrofuran solution at 25 °C was switched between the DHP−P−C$_{60}$ triad **1a** (generated by illumination for 30 s with 254 nm light ($\sim$700 μW/cm^2)) and the CPD-P−C$_{60}$ triad **1b** (generated by illumination for 8 s with $\geq$ 300 nm light ($\sim$300 mW/cm^2)). The data shown are the decays of the transient absorption of the fullerene radical anion at 1000 nm, following excitation with a single 532-nm laser pulse (see Figure 3). The results show that the DHP−P−C$_{60}$ isomer gives rise to a long-lived charge-separated state upon excitation of the porphyrin moiety, but that virtually no long-lived state is produced when the sample enriched in the CPD−P−C$_{60}$ isomer is irradiated.

spectral signatures of P$^{\bullet+}$−C$_{60}^{\bullet-}$, and represents the decay of this state to the ground state.

Photochemical Cycling of the Photochromic Moiety. The experiments described above show that the photochromic moiety of triad **1** can be cycled between the DHP and CPD forms, and that light absorption by the porphyrin moiety of the DHP−P−C$_{60}$ triad **1a** leads to the formation of a long-lived charge-separated state, whereas similar excitation of the CDP−P−C$_{60}$ triad **1b** does not. To investigate the stability of this system, photochemical cycling experiments were undertaken, and the results are shown in Figure 4. A solution of the triad in 2-methyltetrahydrofuran was irradiated for 30 s with UV light (254 nm) in order to convert the sample to a photostationary state containing mainly the DHP chromophore. Next, the sample was excited with a single 532-nm laser pulse, and the transient decay at 1000 nm (fullerene radical anion absorption) was measured. This decay represents charge recombination of DHP$^{\bullet+}$−P−C$_{60}^{\bullet-}$. The sample was then irradiated for 8 s with visible light ($\geq$300 nm) to convert it to CPD−P−C$_{60}$, and excitation with a single pulse of laser light was again performed. It is apparent from Figure 4 that when the molecule is in the DHP−P−C$_{60}$ form, excitation produces the long-lived (2.0 μs) DHP$^{\bullet+}$−P−C$_{60}^{\bullet-}$ charge-separated state. After conversion to the CPD−P−C$_{60}$ form with visible light, no significant long-lived charge separation is observed. As is evident from the Figure, where photochemical cycling was repeated several times, photoinduced electron transfer to form a long-lived charge-separated state may be switched on or off many times without significant degradation of the sample. After 15 UV−vis photochemical cycles, less than 15% of the initial signal intensity was lost. This fatigue resistance is very sensitive to the presence of oxygen. Introduction of air into the solutions leads to significant degradation during each photochemical cycle. It is likely that at least part of this photodamage results from reaction of oxygen with the DHP radical cation.[48]

Discussion

Photoisomerization. A key finding of this research, upon which the other phenomena are based, is that the photochromic

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moiety of triad **1** readily photoisomerizes from the DHP form to the CPD isomer, and vice-versa, even when it is covalently linked to the porphyrin−fullerene dyad. In the case of the DHP isomer in particular, the irradiation conditions necessary for opening to the CPD forms are similar for the model compound **7a** and triad **1a** despite the facts that the lifetime of the DHP first excited singlet state in **7a** is relatively long (1.02 ns) and the quantum yield of opening in closely related compounds is only $\sim$7.5%,[31] opening the door to interference by other processes. Thus, interchromophore processes do not significantly impede photoisomerization.

On the other hand, such processes do occur. The lifetime of the DHP first excited singlet state is quenched from 1.02 ns to $\sim$330 ps in both DHP−P dyad **2** and triad **1a**. Conceivable quenching processes are singlet energy transfer from the DHP to the porphyrin, photoinduced electron transfer, and enhanced decay due to an increase in the rate of photoisomerization or any of the usual photophysical processes. Energy transfer is expected to be slow because the fluorescence emission of ^{1}DHP (λ_{max} = 692 nm) does not overlap well with the longest-wavelength porphyrin absorption band (λ_{max} = 650 nm), and because the fluorescence quantum yield of DHP molecules of this type is low ($\sim$5 $\times$ 10^{-4}).[31] In fact, significant energy transfer does not occur, as the 330 ps decay of ^{1}DHP in the DHP form of dyad **2** was not accompanied by a corresponding rise in porphyrin emission.
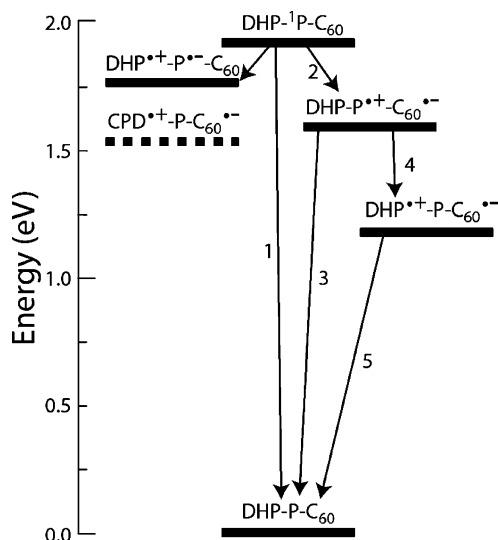
The energy of the DHP first excited singlet state is $\sim$2.10 eV (from the average of the energies of the absorption and emission maxima). Photoinduced electron transfer from ^{1}DHP−P−C$_{60}$ to yield DHP$^{\bullet+}$−P$^{\bullet-}$−C$_{60}$ (1.77 eV) is one possible explanation for the small amount of quenching of the DHP excited singlet state in these molecules. An enhanced quantum yield of photoisomerization is also a viable explanation, as the photochemical ring opening is faster for dyad **2** and triad **1** than for model DHP **7a** under similar irradiation conditions.

The singlet lifetime of the CPD isomer of [*e*]-annelated dimethyldihydropyrene **9b** is 14 ns, and the quantum yield of photoisomerization ($\sim$28%) is much higher than that for opening of the DHP form.[31] Despite this long lifetime, which could allow relaxation of ^{1}CPD−P−C$_{60}$ by competing processes, photoisomerization of CPD−P−C$_{60}$ **1b** is slower than that of CPD **7b** by a factor of only $\sim$2.5, indicating that any competing processes are relatively slow. Thus, for both DHP−P−C$_{60}$ **1a** and CPD−P−C$_{60}$ **1b**, the yield of photoisomerization is high enough that interconversion using light is facile, while thermal reversion of CPD-P−C$_{60}$ to the DHP form takes days.

Photoinduced Electron Transfer. The electron-transfer behavior of **1** and associated model compounds may be discussed in terms of Figure 5, which shows the relevant high-energy states of the triads and some interconversion pathways. The energy of the porphyrin first excited singlet state is estimated as 1.91 eV, based on the wavenumber average of the longest-wavelength absorption and the shortest-wavelength emission maxima. The energies of the various charge-separated states are estimated from cyclic voltammetric results, as discussed above.

P−C$_{60}$ dyad 4. The first excited singlet state of model porphyrin **6** has a lifetime of 13.4 ns, whereas the lifetime of ^{1}P−C$_{60}$ in dyad **4**, determined from time-resolved fluorescence studies, is only 34 ps. This quenching is due to photoinduced

Figure 5. High-energy states and interconversion pathways for triad **1**. Each numbered transformation (e.g., step 1) has an associated rate constant (e.g., k_1).

electron transfer from the porphyrin to the fullerene to yield a $P^{\bullet+}-C_{60}^{\bullet-}$ charge-separated state. This charge-separated state was characterized spectroscopically by the transient absorption measurements, which showed a formation time of 32 ps and a decay time of 3.3 ns.[35] On the basis of these values, the rate constant for photoinduced electron transfer from $^1P-C_{60}$, k_{ET}, may be calculated from eq 2,

$$1/\tau_s = k_{ET} + k_s \tag{2}$$

where τ_s is the lifetime of the porphyrin first excited singlet state in the dyad (average = 33 ps) and k_s is the rate constant for decay of the first excited singlet state by all processes other than electron transfer. A value of 7.5×10^7 s^{-1} may be calculated for k_s from the 13.4 ns lifetime of the first excited singlet state of porphyrin **6**. These data yield a value of 3.0×10^{10} for k_{ET}. The quantum yield of $P^{\bullet+}-C_{60}^{\bullet-}$ equals $k_{ET}\tau_s$, or 99%. From the 3.3 ns lifetime of $P^{\bullet+}-C_{60}^{\bullet-}$, the rate constant for charge recombination, k_{CR}, is 3.0×10^8 s^{-1}.

DHP–P dyad 2. The first excited singlet state of the porphyrin moiety of **2** in the DHP form has a lifetime of 1.76 ns based on fluorescence data, and transient absorption experiments gave a similar lifetime. Thus, the porphyrin excited state is quenched by some interchromophore process involving the DHP moiety. The rate constant for this process, k_q, is calculated to be 4.9×10^8 s^{-1}, using an equation similar to eq 2. The transient absorption experiments did not allow determination of the product of this quenching. Singlet energy transfer to DHP is unlikely; the overlap of the porphyrin emission and DHP absorption spectra is poor for this endergonic process. Electron transfer to form $DHP^{\bullet+}-P^{\bullet-}$ is thermodynamically possible, with a driving force of 140 meV, although no convincing evidence for the charge-separated state was seen in the transient absorption results for the DHP form of dyad **2**. This explanation is consistent with the quenching of ^1DHP in **1a** and the DHP form of **2**, which could also be the result of photoinduced electron transfer. It may be that the rate constant for recombination of the charge-separated state is higher than that for its formation (leading to a very low concentration at all times), or that any characteristic absorption features are obscured by the

absorption of the long-lived porphyrin first excited singlet state of CPD−P which is also present. In any event, the quenching process is too slow to contribute significantly to the decay of the porphyrin singlet state in the DHP−P−C_{60} triad **1**, and it does not impede photoisomerization. Therefore, it has no significant impact on the function of the triad molecular switch.

DHP−P−C_{60} triad 1a. The transient absorption experiments with **1a** yielded lifetimes for three processes, the shortest of which was 35 ps. The 35 ps event represents the decay of DHP−$^1P-C_{60}$ and formation of a $DHP-P^{\bullet+}-C_{60}^{\bullet-}$ charge-separated state, as shown by the transient absorption spectra. A similar time constant for the decay of DHP−$^1P-C_{60}$ was determined from the time-resolved fluorescence measurements. This photoinduced electron transfer is process 2 in Figure 5. The rate constant, k_2, may be estimated using eq 3

$$1/\tau_s = k_s + k_q + k_2 \tag{3}$$

with $\tau_s = 35$ ps, and equals 2.8×10^{10} s^{-1}, which is very close to the rate constant for charge separation in $P-C_{60}$ dyad **4**. The quantum yield of $DHP-P^{\bullet+}-C_{60}^{\bullet-}$ equals $k_2\tau_s$, or 0.98. Therefore, all other processes depopulating the porphyrin first excited singlet state, including quenching by the DHP, are insignificant.

The 150 ps component of the decay-associated spectra of triad **1a** is associated with the charge shift reaction of $DHP-P^{\bullet+}-C_{60}^{\bullet-}$ to form $DHP^{\bullet+}-P-C_{60}^{\bullet-}$. This process, step 4 in Figure 5, competes with decay of $DHP-P^{\bullet+}-C_{60}^{\bullet-}$ to the ground state by charge recombination step 3. The reciprocal of the 150-ps lifetime is the sum of k_3 and k_4. The value of k_3 is assumed to be identical to k_{CR} in $P-C_{60}$ dyad **4**; 3.0×10^8 s^{-1}. Thus, charge shift rate constant k_4 equals 6.4×10^9 s^{-1}. The yield of the charge shift reaction is $k_4/(k_3 + k_4)$, and equals 96%. The overall quantum yield of the long-lived $DHP^{\bullet+}-P-C_{60}^{\bullet-}$ state is the product of the yields of steps 2 and 4, and equals 94%.

The $DHP^{\bullet+}-P-C_{60}^{\bullet-}$ state has a lifetime that is too long to measure using the transient absorption instrument built around the 100-fs laser, and was measured instead using nanosecond transient spectroscopy. Because no new transient states were observed to form concurrently with the decay of $DHP^{\bullet+}-P-C_{60}^{\bullet-}$, it is assumed that decay is by recombination to the ground state (step 5 in Figure 5). The rate constant for this process, k_5 (the reciprocal of the 2.0 μs lifetime of the charge-separated state), is 5.0×10^5 s^{-1}.

CPD−P−C_{60} triad 1b. The time-resolved fluorescence studies of CPD-P dyad **2** showed that the porphyrin first excited singlet state is not quenched at all by the attached CPD group, as its lifetime (13.3 ns) is identical to that of the model porphyrin **6**, within experimental error. It is assumed that a similar situation obtains in triad **1b**. The time-resolved fluorescence results for triad **1b** showed quenching of the porphyrin first excited singlet state with a time constant of 32 ps. By analogy with dyad **4** and triad **1a**, this quenching is ascribed to photoinduced electron transfer from CPD−$^1P-C_{60}$ to yield the CPD−$P^{\bullet+}-C_{60}^{\bullet-}$ charge-separated state. The rate constant for this process is 3.1×10^{10} s^{-1}, and the quantum yield of charge separation is essentially unity. However, the nanosecond transient absorption studies show that no long-lived charge-separated state is produced in **1b**. The CPD−$P^{\bullet+}-C_{60}^{\bullet-}$ state recombines to the ground state, rather than undergoing a charge shift reaction

analogous to that in **1a** to form a CPD$^{\bullet+}$–P–C$_{60}^{\bullet-}$ charge-separated state. Transient absorption decays measured on the ns time scale show that recombination is essentially complete within 5–10 ns. It is assumed that recombination occurs with approximately the same time constant as in dyad **4** (3.3 ns).

Evolution of CPD–P$^{\bullet+}$–C$_{60}^{\bullet-}$ to form CPD$^{\bullet+}$–P–C$_{60}^{\bullet-}$ does not occur primarily for thermodynamic reasons. On the basis of the electrochemical data discussed above, CPD–P$^{\bullet+}$–C$_{60}^{\bullet-}$ lies 1.58 eV above the ground state, and CPD$^{\bullet+}$–P–C$_{60}^{\bullet-}$ is at 1.52 eV. The very small driving force for charge shift of 0.06 eV would result in slow electron transfer that could not compete well with charge recombination. In addition, we noted earlier that the energy estimates based solely on cyclic voltammetric data do not take into account differences in Coulombic effects, including differences in stabilization of the two charge-separated states in solvent. Coulombic attraction between charges would stabilize both CPD–P$^{\bullet+}$–C$_{60}^{\bullet-}$ and CPD$^{\bullet+}$–P–C$_{60}^{\bullet-}$, but stabilization would be greatest for CPD–P$^{\bullet+}$–C$_{60}^{\bullet-}$, in which the charges are closer together.[49] In a relatively nonpolar solvent like 2-methyltetrahydrofuran ($\epsilon = 7.6$), this would tend to equalize or reverse the energies of the two states.

Photochemical Stability. The results in Figure 4 show that unlike some photochromic systems, triad **1** can be photochemically cycled between the DHP and CPD forms many times. In argon-purged solutions, minimal decomposition was noted after 15 UV–vis cycles. In the presence of oxygen, significant decomposition does occur, and it is possible that the small amount of decomposition observed in the argon-purged solutions was due to residual oxygen. Results with rigorous degassing using freeze–pump–thaw cycles are not yet available.

(49) Weller, A. *Z. Physik. Chem. NF* **1982**, *133*, 93–98.

Conclusions

Triad **1** comprises a photochemically activated molecular switch for photoinduced electron transfer. In the DHP form **1a**, porphyrin excitation leads to formation of a DHP–P$^{\bullet+}$–C$_{60}^{\bullet-}$ state with a quantum yield of 98%. Charge shift from the DHP moiety gives DHP$^{\bullet+}$–P–C$_{60}^{\bullet-}$ in an overall yield of 94%. The lifetime of this species, 2 μs, is long enough to make the state readily detectable spectroscopically, through diffusional reactions in solution, or via coupling to electronically active surfaces. Visible irradiation of **1a** converts it to CPD–P–C$_{60}$ isomer **1b**. Excitation of the porphyrin moiety of **1b** again yields a porphyrin-fullerene charge-separated state, but charge shift to the CPD moiety is not observed, and no long-lived charge-separated state is produced. Isomer **1b** may be converted back to **1a** using UV light. Photochemical cycling of the switch is facile, thermal isomerization is slow, even at ambient temperatures, and excitation of the active form of the molecule gives long-lived charge separation in high yield. Furthermore, photochemical stability is reasonably high. The principles demonstrated by **1** may be useful for the design of molecule-based optoelectronic systems for data processing, transmission and storage, chemical sensing, and similar applications.