

Energy- and Electron-Transfer Quenching of Porphyrin Triplets by C₆₀¹

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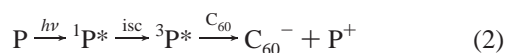
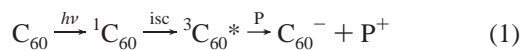
Energy- and electron-transfer from porphyrins in the triplet excited state to C₆₀ in toluene and benzonitrile has been studied with Fourier transform EPR (FT-EPR). Pulsed-laser excitation of the systems magnesium tetraphenylporphyrin (MgTPP)/C₆₀ and free-base octaethylporphyrin (OEP)/C₆₀ in toluene gives rise to a resonance peak from C₆₀ triplets (³C₆₀) generated primarily by the energy-transfer process ³MgTPP (³OEP) + C₆₀ → MgTPP (OEP) + ³C₆₀ as evident from the emissive spin polarization of the ³C₆₀ signal observed at early times. No FT-EPR signals from redox products could be detected. In benzonitrile, triplet energy transfer from ³MgTPP or ³OEP to C₆₀ is a minor process. In this polar solvent photoexcitation of MgTPP/C₆₀ produces FT-EPR spectra with signal contributions from MgTPP⁺ and C₆₀⁻ in addition to the ³C₆₀ resonance. From the spin polarization and time profile of the signal from the anion radical, it can be deduced that the primary route of electron transfer is oxidative quenching of the porphyrin triplets, ³MgTPP (³OEP) + C₆₀ → MgTPP⁺ (OEP⁺) + C₆₀⁻. The reduction in ³C₆₀ lifetime indicates that C₆₀⁻ is generated as well by the reductive triplet quenching reaction ³C₆₀ + MgTPP (OEP) → C₆₀⁻ + MgTPP⁺ (OEP⁺).

Introduction

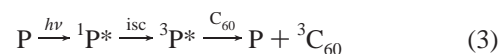
In recent years a number of studies concerned with the photophysics and photochemistry of porphyrin–fullerene systems have been reported. The investigations involved solutions of porphyrins and fullerenes (C₆₀ and C₇₀),^{2–4} solutions of C₆₀ covalently linked to a porphyrin,⁵ and an organized assembly of a porphyrin with C₆₀ in a lipid bilayer.⁶ Interest in these systems stems from possible applications in solar-energy conversion systems and optoelectronic devices.

Porphyrins and C₆₀ have a number of properties that make them suitable as components in artificial reaction centers and molecular-scale electronic devices. The molecules absorb light in the visible region of the spectrum, intersystem crossing (isc) to the relatively long-lived triplet excited state occurs with close to 100% quantum yield,^{7,8} and in the triplet state the porphyrins can be good electron donors,⁹ whereas C₆₀ is a good electron acceptor.^{10,11}

A transient optical absorption study of zinc tetraphenylporphyrin (ZnTPP) with C₆₀ or C₇₀ in polar solvents by Nojiri et al.² shows that photoexcitation results in electron transfer from ZnTPP to the fullerene independent of which chromophore is excited. The following mechanisms were proposed to account for the photoinduced electron-transfer process:



Fujisawa et al.³ demonstrated with the aid of time-resolved cw EPR (TREPR) that photoexcitation of porphyrins in the presence of C₆₀ in liquid solution (toluene) can also lead to triplet energy transfer according to



The authors also reported on a study of photoinduced electron and energy transfer from photoexcited porphyrins to C₆₀ in benzonitrile carried out with pulsed EPR and TREPR.⁴

As the work by Fujisawa et al.⁴ illustrates, for the study of porphyrin/C₆₀ systems where excited-state quenching can involve competing paths, the application of Fourier transform EPR (FT-EPR) has advantages over transient optical absorption measurements. First, the magnetic resonance spectra show well-resolved peaks due to ³C₆₀ as well as electron-transfer product-(s) that can be easily identified with the aid of information on *g* values and hyperfine splitting constants. This facilitates the study of the kinetics of electron- and energy-transfer processes. Second, spin polarization transfer accompanies the formation of ³C₆₀ by energy transfer. Since the resonance peak of C₆₀ triplets carries the spin polarization signature of the precursor porphyrin triplet, this energy-transfer route of triplet C₆₀ formation is readily identified. In the present study these features have been used to obtain information on the solvent dependence of electron- and energy-transfer quenching of porphyrin triplets by C₆₀.

Experimental Section

C₆₀ (99.9%, SES Research), magnesium tetraphenylporphyrin (MgTPP, Aldrich), octaethylporphyrin (OEP, Aldrich), benzonitrile (99.9%, HPLC grade, Aldrich), and toluene (99.8%, HPLC grade, Aldrich) were used as received. In all solutions, the concentration of C₆₀ (2 × 10⁻⁴ M) was kept constant and the porphyrin concentration was varied (2 × 10⁻⁴, 4 × 10⁻⁴, and 8 × 10⁻⁴ M). Under the experimental condition where the porphyrin concentration was 4 × 10⁻⁴ M, the ratio of laser light (532 nm) absorbed by porphyrin over that absorbed by C₆₀ is 4 (4) and 9 (9.5) for MgTPP/C₆₀ and OEP/C₆₀ in toluene (benzonitrile), respectively. Porphyrin/C₆₀ samples in toluene and benzonitrile were degassed on a high-vacuum line by several

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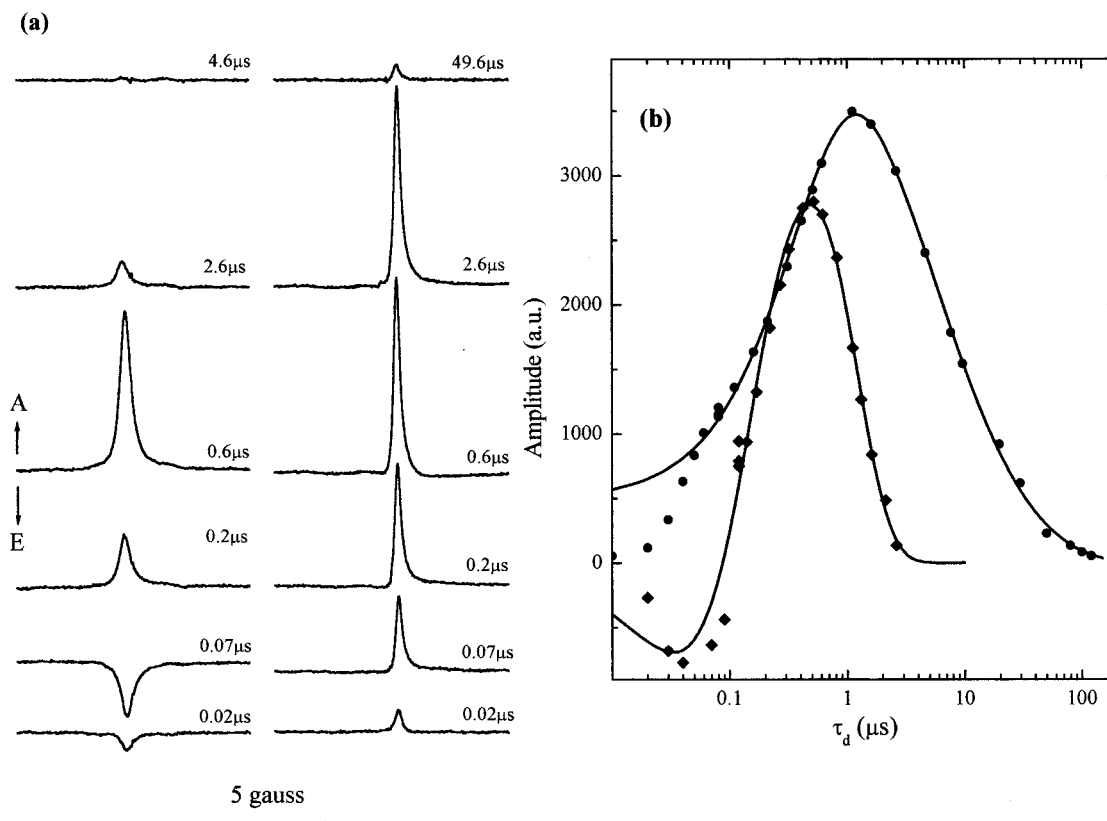


Figure 1. (a) FT-EPR spectra of ${}^3\text{C}_{60}$ produced by excitation of deaerated MgTPP (4×10^{-4} M)/ C_{60} (2×10^{-4} M) (left) and C_{60} (2×10^{-4} M) (right) in toluene, for a series of delay times (τ_d) between laser and microwave pulses. (b) Time profiles of the ${}^3\text{C}_{60}$ signal intensity given by (\blacklozenge) MgTPP/ C_{60} and (\bullet) C_{60} in toluene. Solid lines represent least-squares fits; see the text for the models used.

freeze–pump–thaw cycles and sealed off. Sample degradation over the time course of a series of measurements was negligible, establishing that the photoinduced processes studied are reversible.

FT-EPR measurements were performed with a home-built spectrometer.¹² The response of the sample to the $\pi/2$ microwave pulse was detected in quadrature with application of a CYCLOPS phase-cycling routine. Solutions held in the microwave cavity were excited with the second harmonic (532 nm) of a Quanta Ray GCR12 Nd:Yag laser (pulse width ~ 8 ns, pulse energy ~ 18 mJ, pulse repetition rate 10 Hz). In addition, FT-EPR measurements were carried out at different excitation wavelengths; the third harmonic of a Quanta Ray GCR12 Nd:Yag laser (~ 18 mJ/pulse, 10 Hz) was used for excitation at 355 nm and a Lambda-Physik EMG103 MSC XeCl excimer laser for excitation at 308 nm (~ 18 mJ/pulse, 10 Hz). All measurements were performed at room temperature. The FID produced by a $\pi/2$ (15 ns) microwave pulse was recorded for a series of delay times ($10 \text{ ns} < \tau_d < 180 \mu\text{s}$) between laser excitation and the microwave pulse. The FID was the time average of signals generated by a total of 4000 laser shots (1000 per phase) when porphyrins were present or 400 laser shots (100 per phase) for solutions containing C_{60} only. The amplitudes, phases, and line widths of resonance peaks were derived from the FIDs with a LPSVD analysis routine.¹³

Results and Discussion

MgTPP/ C_{60} in Toluene. FT-EPR spectra obtained upon photoexcitation of a solution of MgTPP (4×10^{-4} M) and C_{60} (2×10^{-4} M) in toluene for a series of delay times between laser excitation and the microwave pulse are depicted in Figure 1a. For comparison, spectra given by a solution containing C_{60}

(2×10^{-4} M) only are also displayed. The spectra show a single resonance peak at $g = 2.0012$ due to C_{60} in the photoexcited triplet state.^{14–18}

The time profiles of the ${}^3\text{C}_{60}$ signal intensity are shown in Figure 1b. As noted previously,^{15–18} triplets formed by direct excitation of C_{60} followed by isc from the singlet excited state are born with spin polarization (P_0) well below that at Boltzmann equilibrium (P_B). As a consequence, in the absence of porphyrin, the development of the absorption signal at early times ($\tau_d < 1 \mu\text{s}$) is determined by P_0/P_B and the triplet spin–lattice relaxation rate (k_{T1C}). Signal decay is governed by a first-order process (k_d) and (second-order) triplet–triplet annihilation (k_{tt}).^{19,20} A least-squares analysis of the data given by C_{60} (2×10^{-4} M) in toluene in the absence of porphyrin gave the following values for these parameters: $k_{\text{T1C}} = 2.2 \times 10^6 \text{ s}^{-1}$, $k_d = 1.7 \times 10^4 \text{ s}^{-1}$, $k_{\text{tt}}[{}^3\text{C}_{60}]_0 = 0.1 \times 10^6 \text{ s}^{-1}$, and $P_0/P_B = 0.11$. These values are in satisfactory agreement with those reported previously.^{15,18} Taking the value of k_{tt} ($5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) reported in the literature for ${}^3\text{C}_{60}$ in toluene,²⁰ the triplet concentration at zero time $[{}^3\text{C}_{60}]_0$ is estimated to be 2×10^{-5} M.

A comparison of the spectra and time profiles presented in Figure 1 shows that the introduction of MgTPP has a significant effect on the time evolution of the ${}^3\text{C}_{60}$ signal. At short delay times ($\tau_d < 200$ ns) the resonance is in emission rather than absorption. In addition, the triplet lifetime is strongly reduced. The effect of MgTPP on the development of the triplet signal is attributed to ${}^3\text{C}_{60}$ formation by energy transfer from ${}^3\text{MgTPP}$ (eq 3). At the C_{60} to MgTPP concentration ratio (1:2) used in this measurement, the porphyrin accounts for $\sim 80\%$ of the absorption of light at 532 nm so that it is excited preferentially. Photoexcitation of MgTPP is followed by spin-selective isc, generating ${}^3\text{MgTPP}$ with excess population in the upper spin

state of the triplet manifold.^{21,22} The emissive ³C₆₀ signal observed at short delay times (<200 ns) provides unequivocal evidence that these triplets are produced by a triplet energy-transfer process from ³MgTTP. A similar triplet–triplet energy-transfer process has been reported for the octaethylporphyrin/C₆₀ system.³

When the porphyrin concentration is reduced to 2 × 10⁻⁴ M, the emissive signal is not observed. In this case, the signal contribution from triplets formed by direct excitation of C₆₀ apparently exceeds that given by triplets formed by the energy-transfer route. The fact that at this porphyrin concentration the rate of signal growth matches the triplet spin–lattice relaxation rate found for ³C₆₀ in toluene (2.2 × 10⁶ s⁻¹) is in agreement with this interpretation. Excitation at 355 nm, where the ratio of laser light absorbed by MgTTP (4 × 10⁻⁴ M) over that absorbed by C₆₀ (2 × 10⁻⁴ M) is less than 0.6, also produces a ³C₆₀ signal that does not show an emissive contribution at early times. Furthermore, the signal intensity is a factor of 2 larger than that found upon excitation at 532 nm. In this case, the signal rise time matches the ³C₆₀ spin–lattice relaxation time as well, so that it can be concluded that triplets generated by direct excitation of the fullerene provide the major signal contribution.

The optical density at 532 nm of the C₆₀ (2 × 10⁻⁴ M)/MgTTP (4 × 10⁻⁴ M) sample is about a factor of 4 higher than that of a solution containing C₆₀ only. Hence, the overall triplet concentration produced by laser excitation is expected to increase by a factor of 4 as well. Even so, the maximum ³C₆₀ (absorptive) signal intensity, corrected for the increased decay rate, is only ~1.6 times larger than that given by C₆₀ in toluene without the porphyrin. The fact that the transfer of triplet energy involves only a fraction of the porphyrin triplets formed is attributed to the near degeneracy of the energy levels²³ involved so that [³C₆₀] is governed by the equilibrium



In agreement with this interpretation, it is found that the concentration of C₆₀ triplets formed upon excitation of MgTTP/C₆₀ samples decreases as the MgTTP concentration is increased from 2 × 10⁻⁴ to 4 × 10⁻⁴ to 8 × 10⁻⁴ M. In a recent study Boyd et al.²⁴ found that fullerenes and porphyrins form complexes in toluene. This can also be a factor that plays a role in the attenuation of ³C₆₀ formation with increasing porphyrin concentration.

As noted above, the overall triplet concentration is estimated to be about 4 times as large as the ³C₆₀ concentration (~2 × 10⁻⁵ M) given by a solution containing no porphyrin. In the MgTTP (4 × 10⁻⁴ M)/C₆₀ (2 × 10⁻⁴ M) solution, the concentration of C₆₀ triplets formed is ~3 × 10⁻⁵ M. According to these estimates of the triplet concentrations, the equilibrium constant of eq 4 is near unity. The experimental results, therefore, point to nearly isoenergetic triplet levels. Given the uncertainty in triplet energy measurements, the literature values of 1.48 and 1.57 eV for ³MgTTP^{23,25} and ³C₆₀,^{8,26} respectively, are consistent with this finding.

It is remarkable that the ³C₆₀ signal carries the signature of spin polarization transfer from ³MgTTP. It signifies that triplet–triplet energy transfer is fast enough to compete with spin–lattice relaxation (T_{1P}) of the porphyrin triplets. Since k_{T1P} is expected to be on the order of 10⁷ s⁻¹^{27,22} and [C₆₀] = 2 × 10⁻⁴ M, the rate constant of energy (spin polarization) transfer must be in the 10⁹ to 10¹⁰ M⁻¹ s⁻¹ range. This is a rather high rate for a triplet–triplet energy-transfer process with near-zero driving force.²⁸ In principle, spin exchange between spin-

polarized ³MgTTP and ³C₆₀ formed by direct excitation can provide an additional route of spin polarization transfer. However, at the triplet concentrations generated in these experiments, this process cannot play a significant role.

As shown in Figure 1b, the decay of the ³C₆₀ signal given by MgTTP/C₆₀ in toluene is an order of magnitude faster than that observed for C₆₀ alone. Measurements as a function of porphyrin concentration gave decay rates of 0.6 × 10⁶, 1.1 × 10⁶, and 2.2 × 10⁶ s⁻¹ for porphyrin concentrations of 2 × 10⁻⁴, 4 × 10⁻⁴, and 8 × 10⁻⁴ M, respectively, corresponding to a rate constant of 2.8 × 10⁹ M⁻¹ s⁻¹. Decay rates of 0.6 × 10⁶ and 1.3 × 10⁶ s⁻¹ were found for porphyrin concentrations of 2 × 10⁻⁴ and 4 × 10⁻⁴ M, respectively, when the samples were excited with 355 nm light instead of 532 nm light. Thus, the triplet lifetime does not depend on whether ³C₆₀ is generated by energy transfer from ³MgTTP or primarily by direct excitation of C₆₀. Furthermore, while increases in excitation light intensity (532 nm) cause increases in ³C₆₀ signal intensity, this also did not affect the kinetics so that the decay is independent of ³MgTTP and ³C₆₀ concentrations as well.

A possible mechanism of triplet quenching is excited-state electron transfer. Because there is a dynamic equilibrium between ³MgTTP and ³C₆₀ (eq 4), the triplet quenching reactions



and



will contribute to ³C₆₀ signal decay. As indicated in these reaction equations, these processes are not expected to yield redox products because in a nonpolar solvent such as toluene back electron transfer will occur before cage escape of radical ions takes place. ΔG° values for these electron-transfer reactions can be estimated using the Rehm–Weller equation²⁹

$$\Delta G^\circ \approx E^{\text{ox}}(\text{D}) - E^{\text{red}}(\text{A}) - E_{\text{T}} + \frac{e^2}{8\pi\epsilon_0 r_+} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon'} \right) + \frac{e^2}{8\pi\epsilon_0 r_-} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon''} \right) - \frac{e^2}{4\pi\epsilon_0 \epsilon R} \quad (7)$$

For electron-transfer quenching of ³C₆₀, with E_T(³C₆₀) = 1.57 eV,²⁶ E^{red}(C₆₀) = -0.42 V¹⁰ (vs SCE, solvent benzonitrile), E^{ox}-(MgTTP) = 0.54 V³⁰ (vs SCE, solvent butyronitrile), 2r₊ = 0.8 nm, 2r₋ = 0.71 nm, R = 0.75 nm, ε(toluene) = 2.38, ε'(butyronitrile) = 24.83, and ε''(benzonitrile) = 25.9, eq 7 gives ΔG° ≈ 0.04 eV. Since E_T(³C₆₀) ≈ E_T(³MgTTP), the driving force for oxidative quenching of ³MgTTP by C₆₀ will have a similar value. Considering the fact that ΔG° ≥ 0, it appears unlikely that electron transfer can account for the short triplet lifetime. An alternative or competing triplet quenching path is suggested by the finding²⁴ that in toluene porphyrins show unusually strong interactions with fullerenes. This property apparently plays a role in the application of tetraphenylporphyrin-appended silicas for chromatographic separation of fullerenes.³¹ It suggests the possibility of efficient deactivation of porphyrin and/or C₆₀ triplets via an exciplex (³[MgTTP/C₆₀]) formation step.

In principle, the values of all the rate constants governing ³C₆₀ formation and decay can be derived from a quantitative analysis of the time profile of the ³C₆₀ signal intensity.⁴ However, because of the complexity of the systems studied here, such a comprehensive nonlinear least-squares analysis is unlikely

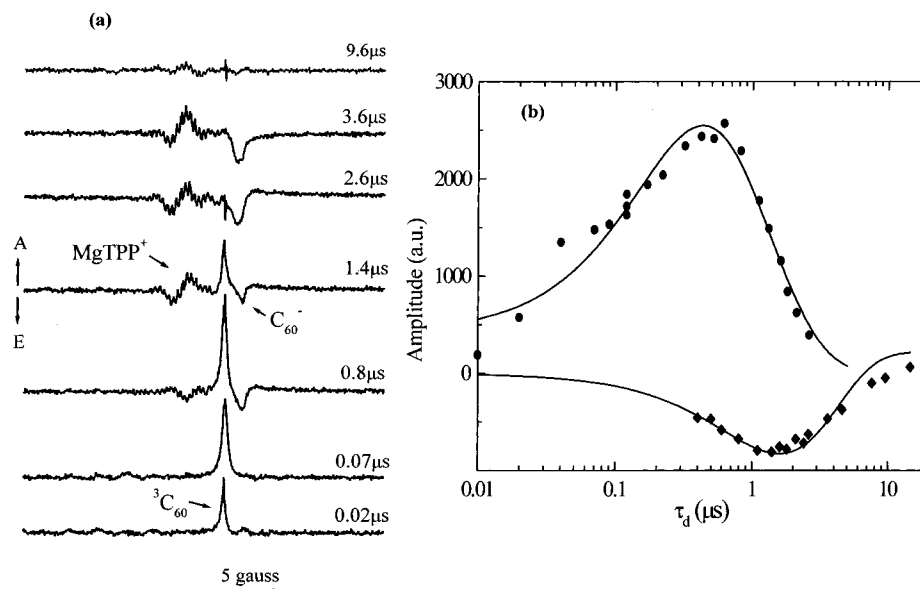


Figure 2. (a) FT-EPR spectra of free radicals produced by excitation of deaerated MgTPP (4×10^{-4} M)/C₆₀ (2×10^{-4} M) in benzonitrile for a series of delay times (τ_d) between laser and microwave pulses. (b) Time profiles of (●) ³C₆₀ and (◆) C₆₀⁻ signal intensities given by MgTPP/C₆₀ in benzonitrile. Solid lines represent least-squares fits based on models described in the text.

to provide a unique solution. For this reason, *semiquantitative* data on rates of ³MgTPP spin–lattice relaxation, ³C₆₀ spin–lattice relaxation, and triplet energy transfer were derived from an analysis of the growing in of the ³C₆₀ signal. It takes into account (1) spin-polarized triplet porphyrin formation at $t = 0$, (2) ³MgTPP spin–lattice relaxation (k_{TIP}), (3) exponential establishment of equilibrium concentrations of ³MgTPP and ³C₆₀ (k_{en}), and (4) ³C₆₀ spin–lattice relaxation (k_{TIC}). A least-squares fit of the data obtained for MgTPP (4×10^{-4} M)/C₆₀ (2×10^{-4} M)/toluene gave the following results: $k_{TIP} = 7.9 \times 10^6$ s⁻¹, $k_{TIC} = 3.4 \times 10^6$ s⁻¹, and $k_{en} = 1.4 \times 10^7$ s⁻¹. The value of k_{TIP} corresponds to a spin–lattice relaxation time $T_1(^3\text{MgTPP})$ of 125 ns. This is the order of magnitude predicted by theory²⁷ and is in line with the value of 230 ns derived for ³MgTPP in ethanol at ~ -30 °C.²²

MgTPP/C₆₀ in Benzonitrile. Figure 2a shows the FT-EPR spectra generated by excitation of a solution containing C₆₀ (2×10^{-4} M) with MgTPP (4×10^{-4} M) in benzonitrile for delay times ranging from 10 ns to 10 μ s. A number of features distinguish the results obtained with this system from those given by MgTPP/C₆₀ in toluene (Figure 1a). First, in addition to the ³C₆₀ resonance peak, an emissive multiline signal (hyperfine splitting, $a_H = 0.29$ G) develops at lower field over a period of about 1 μ s. This is accompanied by the appearance of a broad emissive signal ($g = 2.0000$, $\Delta B_{pp} = 1.29(3)$ G) on the high-field side of the ³C₆₀ resonance. The multiline signal is assigned to the porphyrin radical cation, MgTPP⁺, on the basis of the position and hyperfine splitting (literature values, $g = 2.0028$, $a_H = 0.28$ G, in dichloromethane).³² The high-field line is assigned to the C₆₀⁻ anion since the g value matches the one reported for the electrochemically prepared species ($g = 1.9999$).³³ The line width of the resonance peak attributed to C₆₀⁻ (1.29 G) is considerably larger than the value of 0.103 G reported by Bennati et al.¹⁷ for C₆₀⁻ in toluene, but closely matches the result reported by Stasko et al.³⁴ Second, in contrast to what is found for MgTPP/C₆₀ in toluene at high porphyrin concentrations, the ³C₆₀ signal is in absorption independent of [MgTPP] and for all delay times. Finally, the ³C₆₀ signal is about a factor of 2 weaker than that found when toluene is used as solvent. Figure 2b displays the time profiles of the ³C₆₀ and

C₆₀⁻ signal intensities; identical scales are used for the display of the signal intensities.

The results show that the triplet energy-transfer route of ³C₆₀ formation plays a minor role in benzonitrile. The absorptive ³C₆₀ signal can be attributed entirely to direct photoexcitation of C₆₀. The solid line in Figure 2b represents the least-squares fit based on a model in which ³C₆₀ signal growth is determined by spin–lattice relaxation and signal decay by a pseudo-first-order quenching reaction. In agreement with this interpretation, it is found that the rate of signal growth for all porphyrin concentrations ($\sim 2.1 \times 10^6$ s⁻¹) matches the triplet spin–lattice relaxation rate found for ³C₆₀ in benzonitrile without porphyrin (2.0×10^6 s⁻¹).

As was found for MgTPP/C₆₀ in toluene, ³C₆₀ signal decay is linearly dependent on porphyrin concentration. It increases from 0.4×10^6 to 0.9×10^6 to 2×10^6 s⁻¹ for porphyrin concentrations of 2×10^{-4} , 4×10^{-4} , and 8×10^{-4} M, respectively, giving a value of 2.3×10^9 M⁻¹ s⁻¹ for the rate constant of ³C₆₀ quenching by MgTPP. By comparison, the decay rate found in toluene is 2.8×10^9 M⁻¹ s⁻¹.

From the fact that the doublet radicals (MgTPP⁺, C₆₀⁻) at early times ($\tau_d < 1$ μ s; cf. Figure 2a) give rise to overall emissive EPR signals, it can be concluded that the dominant signal contribution must be electron-transfer quenching of ³MgTPP (eq 2). In this process, the (emissive) spin polarization of the porphyrin triplets is carried over to the doublet radicals (TM CIDEP).³⁵ Electron-transfer quenching of ³C₆₀ (eq 1) is expected to generate C₆₀⁻ as well,² but may make a minor signal contribution because of the low ³C₆₀ concentration and the absence of signal amplification by TM CIDEP. The signal due to reaction 1 is expected to be absorptive and apparently merely attenuates that given by the ³MgTPP quenching process.

According to this interpretation, the time profile of the C₆₀⁻ signal intensity (cf. Figure 2b) depends on the rate of electron-transfer quenching of ³MgTPP (k_{et}), spin–lattice relaxation rates of ³MgTPP (k_{TIP}) and C₆₀⁻ (k_{TID}), and the rate of back electron transfer. In the analysis of the C₆₀⁻ data it was assumed that signal growth primarily reflects electron transfer from spin-polarized ³MgTPP and that signal decay is mainly due to relaxation of the C₆₀⁻ spin system to thermal equilibrium. The

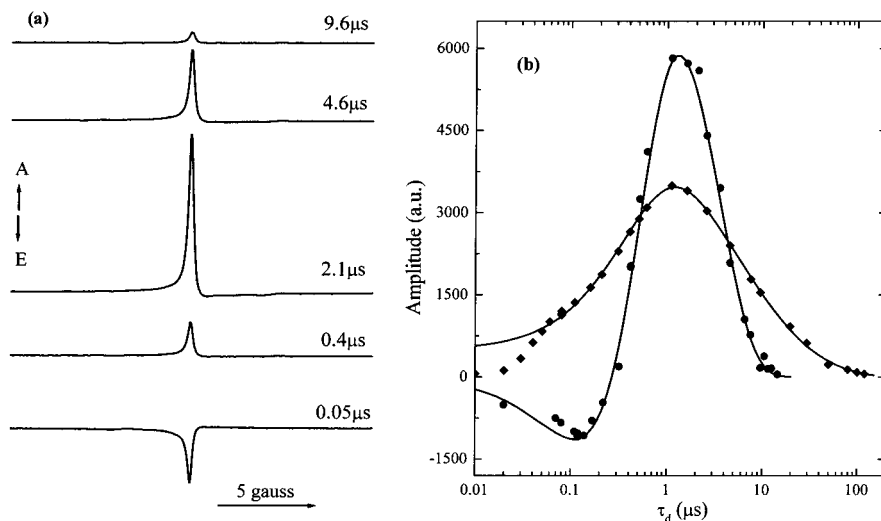


Figure 3. (a) FT-EPR spectra of ${}^3\text{C}_{60}$ produced by excitation of deaerated OEP (4×10^{-4} M)/C₆₀ (2×10^{-4} M) in toluene for a series of delay times (τ_d) between laser and microwave pulses. (b) Time profiles of the ${}^3\text{C}_{60}$ signal intensity given by (●) OEP/C₆₀ and (◆) C₆₀ in toluene. Solid lines represent least-squares fits: see the text for the models used.

solid line in Figure 2b represents the result of the analysis. Rate constants are $k_{\text{et}} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{TID}} = 0.5 \times 10^6 \text{ s}^{-1}$ ($T_{\text{ID}} = 2 \mu\text{s}$), respectively.

${}^3\text{C}_{60}$ signal decay ($2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is attributed to excited-state electron transfer (eq 1), but as noted above, this triplet quenching process does not contribute significantly to the intensity of doublet radical signals. That the rate constant of ${}^3\text{C}_{60}$ signal decay closely matches that of C₆₀⁻ signal generation ($2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) by electron-transfer quenching of ${}^3\text{MgTPP}$ (eq 2) is consistent with the fact that the triplet energies are virtually degenerate. It is of interest to note that the flash photolysis study of ZnTPP/C₆₀ in benzonitrile by Nojiri et al.² gave quite distinct values for the rate constants of electron-transfer quenching of ${}^3\text{C}_{60}$ ($1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and ${}^3\text{ZnTPP}$ ($0.48 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The large difference between these rate constants is remarkable in view of the fact that the literature value of the triplet energy of ZnTPP (1.59 eV²³) is virtually identical to that of ${}^3\text{C}_{60}$.

The rate constants for electron-transfer quenching of ${}^3\text{MgTPP}$ and ${}^3\text{C}_{60}$ in benzonitrile are close to the diffusion-controlled limit, which is consistent¹⁰ with the thermodynamic driving force of ~ -0.6 eV given by the Rehm–Weller equation.²⁹ Triplet C₆₀ decay in toluene occurs at a rate ($2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) very similar to the rate found in benzonitrile ($2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Since the driving force for electron transfer in toluene is ~ 0.6 eV less than in benzonitrile, it is unlikely that this process can be the major route of triplet quenching. Instead, the result provides indirect support for the conclusion that, in a nonpolar solvent, triplet quenching via an excimer formation step route may play an important role.

OEP/C₆₀ in Toluene and Benzonitrile. In many respects the results obtained with the OEP/C₆₀ system mirror those obtained with MgTPP/C₆₀. As shown in Figure 3a, for OEP (4×10^{-4} M)/C₆₀ (2×10^{-4} M) in toluene only the ${}^3\text{C}_{60}$ peak is observed. The signal is initially ($\tau_d < 200$ ns) in emission and subsequently turns into absorption, becoming stronger (cf. Figure 3b) than the signal given by C₆₀ in the absence of OEP even though the triplet lifetime is considerably reduced by the addition of porphyrin. From this fact, it can be deduced that triplet energy transfer (eq 3) gives a major signal contribution. Similar time profiles are found as well at other OEP concentrations (8×10^{-4} and 2×10^{-4} M).

A comparison with the results obtained with MgTPP/C₆₀ in toluene shows that, at similar concentrations, more ${}^3\text{C}_{60}$ is formed by energy transfer from ${}^3\text{OEP}$ than from ${}^3\text{MgTPP}$. This reflects the fact that OEP absorbs more light than MgTPP at 532 nm and also may be due to the fact that the driving force for triplet–triplet energy transfer is somewhat higher (the triplet energy of OEP is given as 1.61 eV).²³ Even so, the maximum ${}^3\text{C}_{60}$ signal, corrected for variations in decay time, shows a gradual decrease as [OEP] is increased from 2×10^{-4} to 4×10^{-4} to 8×10^{-4} M, possibly reflecting a shift of the ${}^3\text{OEP} + \text{C}_{60} \leftrightarrow \text{OEP} + {}^3\text{C}_{60}$ equilibrium to the ${}^3\text{OEP}$ side.

The time evolution of ${}^3\text{C}_{60}$ signal growth was analyzed with the same model as the one used for MgTPP/C₆₀. Estimates of the rate constants of ${}^3\text{OEP}$ spin–lattice relaxation, ${}^3\text{C}_{60}$ spin–lattice relaxation, and triplet energy transfer derived from the analysis of the data given by C₆₀ (2×10^{-4} M)/OEP (2×10^{-4} M) in toluene are 4.5×10^6 , 2.5×10^6 , and $1.0 \times 10^7 \text{ s}^{-1}$, respectively. The ${}^3\text{OEP}$ spin–lattice relaxation time given by the data analysis, ~ 220 ns, is in reasonable agreement with the value of 208 ns cited in the study of Fujisawa et al.³

Figure 3b shows that the ${}^3\text{C}_{60}$ lifetime is shortened substantially by the introduction of the porphyrin. It was found that the decay of the ${}^3\text{C}_{60}$ resonance peak is exponential with $k_d = 0.2 \times 10^6$, 0.4×10^6 , and $0.7 \times 10^6 \text{ s}^{-1}$ for OEP concentrations of 2×10^{-4} , 4×10^{-4} , and 8×10^{-4} M, respectively, corresponding to a rate constant of $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. As was found for MgTPP/C₆₀ in toluene, this rate constant is not affected by changes in excitation light intensity or wavelength. With $E^{\text{ox}}(\text{OEP}) = 0.81$ V (vs SCE, solvent butyronitrile)³⁰ the Rehm–Weller equation gives $\Delta G^\circ \approx 0.31$ eV for reductive quenching of ${}^3\text{C}_{60}$ by OEP in toluene (eq 1). Therefore, it is unlikely that the reduction in triplet lifetime is due to electron transfer. As in the case of MgTPP/C₆₀ in toluene, there must be an alternative channel of triplet decay. A possible explanation is triplet quenching via an excimer formation step.²⁴

Using benzonitrile as solvent, the FT-EPR spectra show resonance peaks due to ${}^3\text{C}_{60}$ and C₆₀⁻ (Figure 4a). In this system no resonance peaks due to the cation radical OEP⁺ could be detected at any OEP concentration. The ${}^3\text{C}_{60}$ signal is in absorption for all delay times, whereas the anion radical signal is initially in emission. As was found in the case of the MgTPP/C₆₀ system, in benzonitrile the formation of free radicals is

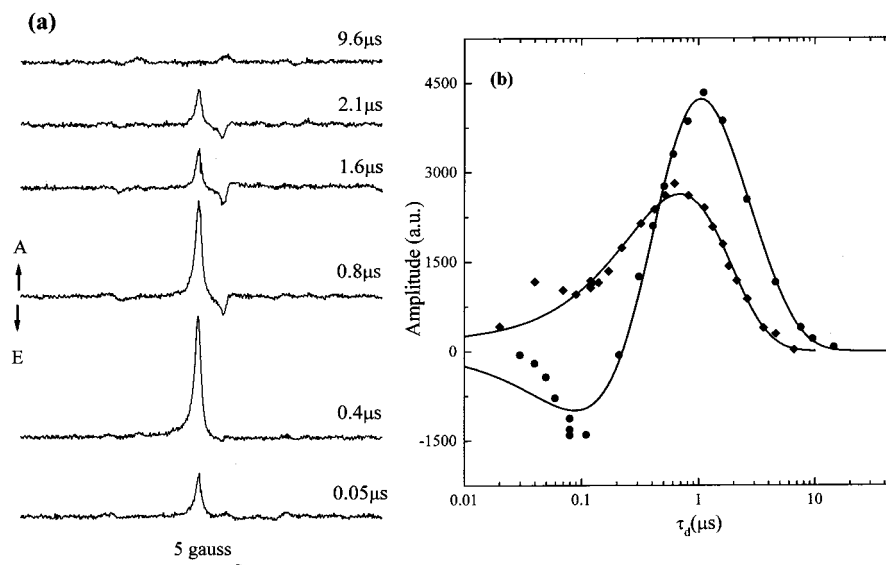


Figure 4. (a) FT-EPR spectra of free radicals produced by excitation of deaerated OEP (4×10^{-4} M)/C₆₀ (2×10^{-4} M) in benzonitrile for a series of delay times (τ_D) between laser and microwave pulses. (b) Time profiles of the ³C₆₀ signal intensity given by (●) OEP/C₆₀ in toluene and (◆) C₆₀ (2×10^{-4} M)/OEP (4×10^{-4} M) in benzonitrile. Solid lines represent least-squares fits; see the text for the models used.

promoted and the oxidative quenching of ³OEP by C₆₀ (eq 2) is the major route of porphyrin triplet decay. Evidence for this is the fact that the relatively weak ³C₆₀ signal is in absorption at all times and apparently stems from direct excitation of C₆₀. It also accounts for the observation of the emissive C₆₀⁻ resonance peak (cf. Figure 4a).

Assuming that ³C₆₀ signal decay is governed by electron-transfer quenching by OEP (eq 1), a least-squares analysis of the data given by C₆₀ (2×10^{-4} M)/OEP (4×10^{-4} M) gives a value of 2.1×10^9 M⁻¹ s⁻¹ for the electron-transfer rate constant.

Concluding Remarks

The FT-EPR study establishes that encounters of porphyrin triplets with C₆₀ can lead to triplet energy transfer (eq 3) or electron transfer (eq 2). The competition between these two processes shows a strong solvent dependence. For the porphyrins MgTPP and OEP in nonpolar solvents, the energy-transfer path makes a significant contribution to porphyrin triplet quenching as evident from the characteristic spin polarization signature it imposes on the ³C₆₀ resonance. In the case of OEP (4×10^{-4} M)/C₆₀ in toluene, the ³C₆₀ signal intensity, corrected for the increased decay rate, is a factor of 2 stronger than that given by direct excitation of C₆₀ in the absence of porphyrin. Even for MgTPP (4×10^{-4} M)/C₆₀ in toluene, where the triplet energies are virtually isoenergetic, the ³C₆₀ signal corrected for the fast decay rate is 1.5 times larger than that found when C₆₀ is directly excited. From the relative magnitudes of the ³C₆₀ signal generated by triplet energy transfer, it can be deduced that (in toluene) $E_T(\text{C}_{60}) \approx E_T(\text{MgTPP}) < E_T(\text{OEP})$.

A change in solvent from nonpolar (toluene) to polar (benzonitrile) results in a strong reduction of the ³C₆₀ yield. This effect is attributed to an increase in the relative importance of the electron-transfer quenching path (eq 2). Similar solvent effects have been found in studies of quenching of triplet 1-nitronaphthalene by carotenoids,³⁶ sodium nitrite, and *trans*-stilbene,³⁷ and aromatic ketone triplets by organic dyes.³⁸ In the case of the nitronaphthalene/carotenoid systems, triplet quenching by electron transfer is strongly exergonic in both polar and nonpolar solvents. Even so, only triplet energy transfer is

observed when cyclohexane is used as solvent, whereas in methanol the electron-transfer quenching reaction makes a strong contribution.³⁶

In the porphyrin/C₆₀ systems the change in solvent is not expected to affect the energy difference between the triplets significantly. By contrast, the ΔG° values of the triplet porphyrin electron-transfer quenching reactions estimated with the Rehm–Weller equation²⁹ show a pronounced change upon going from toluene to benzonitrile. For MgTPP (OEP)/C₆₀, the thermodynamic driving force for the porphyrin electron-transfer quenching drops from 0.04 (0.31) eV in toluene to -0.69 (-0.42) eV in benzonitrile. This suggests that the solvent-induced shift in relative importance of the two ³P quenching processes is due to a change in thermodynamic driving force of the electron-transfer reaction. Support for this interpretation is provided by the flash photolysis study of triplet C₆₀ quenching by tritolylamine by Biczòk et al.¹¹ These authors found rate constants of 8.5×10^7 and 3.5×10^9 M⁻¹ s⁻¹ in toluene and benzonitrile, respectively.

A remarkable feature is that the ³C₆₀ lifetime in the presence of the porphyrins is strongly reduced even in toluene where electron-transfer quenching is not expected to play a role. In an NMR study of fullerene/porphyrin systems in toluene, Boyd et al.²⁴ found evidence of complex formation apparently driven by strong π - π interactions between the molecules. This could provide for a near-diffusion-controlled triplet quenching mechanism.

In some earlier EPR studies of reductive quenching of ³C₆₀, no signal from the anion radical was detected.^{4,15} In the present study a resonance peak due to the C₆₀⁻ anion generated by electron transfer from ³MgTPP and ³OEP to C₆₀ in benzonitrile has been identified. While there is general agreement with regard to the *g* value of the EPR signal from C₆₀⁻ (2.000),^{17,33,34} reported values of the line width of the resonance peak vary widely. The line width of the signal (~1 G) found in the present study is the same, within experimental error, as that listed for the signal attributed to the anion radical in the study of Stasko et al.³⁴ However, in an FT-EPR study of reductive quenching of ³C₆₀ in toluene, Bennati et al.¹⁷ gave a value that is about an order of magnitude smaller. On the other hand, cw EPR measurements on electrochemically generated C₆₀⁻ carried out

by Schell-Sorokin et al.³⁹ gave much broader signals than those reported here.

The reason for the remarkable variation in results obtained in EPR studies of the anion radical of C₆₀ is not understood at this time. It may be related to the orbital degeneracy of the electronic state of C₆₀⁻ and the formation of aggregates at higher concentrations. It is known that organic free radicals with orbitally degenerate ground states can have unusually short spin–lattice relaxation times as a result of the dynamic Jahn–Teller effect.⁴⁰ Because of the degeneracy of the electronic state of C₆₀⁻, the T₁ of the radical may be strongly affected by perturbations introduced by aggregate formation.

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