Photoreactivity of σ-Bonded Metalloporphyrins. 2. Germanium Porphyrin Complexes with σ-Bonded Alkyl, Aryl, or Ferrocenyl Groups. Intramolecular Quenching of Porphyrin Excited Triplet States by Linked Ferrocene

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Continuous visible-light irradiation of $(TPP)Ge(R)_2$, where TPP is the dianion of *meso*-tetraphenylporphyrin and R is either C_6H_5 or $CH_2C_6H_5$, results in a photocleavage of one σ-bonded R group to give a zwitterionic porphyrin that was characterized by UV–visible, ^1H NMR, and ESR techniques. Laser-flash photolysis and ferrocene quenching studies indicate that the triplet states of $(TPP)Ge(R)_2$ are photoreactive. In contrast, $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$, where Fc is σ-bonded ferrocene, are photostable under the same experimental conditions. An energy transfer from the porphyrin triplet state to the axially bound ferrocene in $(TPP)Ge(C_6H_5)(Fc)$ or $(TPP)Ge(Fc)_2$ is postulated to be involved in the photostability of these two complexes.

Introduction

Germanium porphyrins of the type $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$ (where TPP is the dianion of tetraphenylporphyrin and Fc is σ-bonded ferrocene) and their aryl and alkyl analogues $(TPP)Fe(C_6H_5)_2$ and $(TPP)Ge(CH_2C_6H_5)_2$ (see Figure 1) have been synthesized and characterized both spectrally and electrochemically.[2–4] It was shown that the latter two complexes can be converted to $(TPP)Ge(R)Cl$ (where R = C_6H_5 or $CH_2C_6H_5$) by white-light irradiation in chloroform $(CHCl_3)$[2] while $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$ are photostable under similar experimental conditions as are $(OEP)Ge(C_6H_5)(Fc)$ and $(OEP)Ge(Fc)_2$[4] (where OEP is the dianion of octaethylporphyrin). However, no details regarding the mechanism of the observed photochemical reactions or the reason for the photostability of the other complexes have been published.

Studies on the light-induced indium–carbon bond cleavage of $(TPP)In(C_2H_5)$ have established that when ferrocene is added to a benzene solution of $(TPP)In(C_2H_5)$ the excited triplet state of the porphyrin is quenched and the photoreaction quantum yields are reduced.[5] A detailed study of (P)M(R) (where P = TPP or OEP), M = In or Ga, and R = CH_3, C_2H_5, C_4H_9, $CH(CH_3)_2$, or $C(CH_3)_3$) has also shown that ferrocene quenching of these porphyrin triplet states occurs by an energy-transfer mechanism that results in a net reduction of the photoreaction quantum yields.[6]

In this paper, we present data from steady-state and laser-flash photolysis studies on $(TPP)Ge(C_6H_5)_2$, $(TPP)Ge(CH_2C_6H_5)_2$, $(TPP)Ge(C_6H_5)(Fc)$, and $(TPP)Ge(Fc)_2$ in tetrahydrofuran (THF). A mechanism for the photocleavage reactions of $(TPP)Ge(C_6H_5)_2$ and $(TPP)Ge(CH_2C_6H_5)_2$ in THF is presented, and the photostability of $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$ is discussed in light of their photophysical properties. One aim of this study was to see whether an intramolecular energy transfer would occur in a metalloporphyrin that has ferrocene directly σ-bonded to the central metal ion.

Experimental Section

Materials. Tetrahydrofuran (THF) was purified by distillation, first from CaH_2 and then from sodium/benzophenone. $(TPP)Ge(R)_2$ (where R = Cl⁻, C_6H_5, or $CH_2C_6H_5$), $(TPP)Ge(C_6H_5)(Fc)$, and $(TPP)Ge(Fc)_2$ were synthesized according to reported procedures.[2,3,7]

Methods. UV–visible spectra were taken with an IBM Model 9430 spectrophotometer. A 1000-W xenon arc lamp was used in conjunction with an Oriel Corp. Model 7240 monochromator to irradiate the samples at 595 nm. Water having a temperature of 20 °C was continuously circulated through a metal jacket surrounding the cell holder during the steady-state photolysis experiments. Ferrioxalate actinometry was employed to determine the intensity, I_0. Quantum yields (Φ) were determined from changes in the absorbance of the initial complex as described in the literature.[8] Transient absorption spectral measurements and kinetic analyses of the transient decays were performed at the Center for Fast Kinetics Research (CFKR), Austin, TX. The utilized system has been described in the literature.[9] ESR spectra were recorded with an IBM Model ER 100 D spectrometer. DPPH was used as the g marker (g = 2.0036). ^1H NMR spectra were recorded with a QE-300 spectrometer using tetramethylsilane as the internal standard. Oxygen was rigorously excluded from the samples by continuously bubbling purified N_2 through the solution for at least 15 min prior to performing the experiment.

Results and Discussion

Steady-State Photolysis. Figure 2 illustrates the changes that occur in the UV–visible spectrum of $(TPP)Ge(C_6H_5)_2$ during irradiation at 595 nm in deoxygenated THF. Similar spectral changes are observed when the samples were irradiated over the wavelength range 450–600 nm. $(TPP)Ge(C_6H_5)_2$ has peak maxima at 637, 592, and 548 nm. These peaks disappear upon irradiation, and new peaks appear at 827, 616, 571, and 530 nm. Isosbestic points are observed at 652, 625, 605, and 579 nm. Analogous spectral changes occur for $(TPP)Ge(CH_2C_6H_5)_2$, and the absorption maxima before and after irradiation of both complexes are listed in Table I.

$(TPP)Ge(C_6H_5)Cl$ has Q-bands at 616, 574, and 532 nm in THF[2] while most tetraphenylporphyrin anion radicals exhibit broad UV–vis absorptions between 700 and 900 nm.[10] Thus, an irradiation of $(TPP)Ge(C_6H_5)_2$ results in a species having dual spectral characteristics. The bands of the photoproduct at 612 and 571 nm suggest a Ge(IV) complex of the type $(TPP)Ge(C_6H_5)X$, where X = Cl⁻, Br⁻, F⁻, OH⁻, or ClO_4⁻,[2] while the band at 827 nm suggests formation of a Ge(IV) porphyrin π-anion radical.[7]

The photoproduct obtained upon irradiation of $(TPP)In(C_2H_5)$ in MTHF also has dual spectral characteristics and has been described as a zwitterionic porphyrin[5,11] of the type $(TPP)^-In^+$. This suggests that the photoproducts generated upon irradiation of $(TPP)Ge(C_6H_5)_2$ and $(TPP)Ge(CH_2C_6H_5)_2$ are also zwitterionic porphyrin complexes.

Proton resonances of the bound phenyl groups on $(TPP)Ge(C_6H_5)_2$ in $CDCl_3$ occur at 0.42 (d, 4 H, *o*-H), 4.85 (t, 4 H, *m*-H), and 5.34 ppm (t, 2 H, *p*-H) in the absence of light. However in

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(2) Kadish, K. M.; Xu, Q. Y.; Barbe, J. M.; Anderson, J. E.; Wang, E.; Guilard, R. *J. Am. Chem. Soc.* 1987, *109*, 7705.
(3) Kadish, K. M.; Xu, Q. Y.; Barbe, J.-M. *Inorg. Chem.* 1987, *26*, 2565.
(4) Xu, Q.-Y.; Barbe, J.-M.; Kadish, K. M. *Inorg. Chem.* 1988, *27*, 2373.
(5) Hoshino, M.; Ida, H.; Yasufuku, K.; Tanaka, K. *J. Phys. Chem.* 1986, *90*, 3984.
(6) Kadish, K. M.; Maiya, G. B.; Xu, Q. Y. *Inorg. Chem.*, preceding paper in this issue.
(7) (a) Guilard, R.; Barbe, J.-M.; Boukhris, A.; Lecomte, C.; Anderson, J. E.; Xu, Q. Y.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* 1988, 1109. (b) Kadish, K. M.; Xu, Q. Y.; Barbe, J.-M.; Anderson, J. E.; Wang, E.; Guilard, R. *Inorg. Chem.* 1988, *27*, 691.

(8) Hoshino, M.; Hirai, T. *J. Phys. Chem.* 1987, *91*, 4510.
(9) Foyt, D. C. *Comput. Chem.* 1981, *5*, 49.
(10) Fajer, J.; Borg, C. D.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. of Sci.* 1973, *206*, 349.
(11) Hoshino, M.; Yamaji, M.; Hama, Y. *Chem. Phys. Lett.* 1986, *125*, 369.

Table I. UV–Visible Spectral Data and Photophysical Properties of Germanium Porphyrins in THF

	λ_{max}, nm				
compound	before irradn	after irradn[a]	Φ[b]	$10^{-4}k^{\circ}{}_{T}$,[c] s^{-1}	$10^{-9}k_{q}$,[d] M^{-1} s^{-1}
(TPP)Ge(Cl)$_2$	599, 559, 520	e	e	0.7	2.0
(TPP)Ge(C$_6$H$_5$)$_2$	637, 592, 548	827, 616, 571, 530	0.007	0.4	0.5
(TPP)Ge(CH$_2$C$_6$H$_5$)$_2$	650, 602, 558	863, 650, 617, 553	0.023	6.1	1.0
(TPP)Ge(C$_6$H$_5$)(Fc)	642, 596, 557	641, 596, 557	<0.0002	4.1	
(TPP)Ge(Fc)$_2$	641, 597, 559	641, 597, 557	<0.0002	9.8	

[a] Irradiation carried out at 595 nm. [b] Quantum yield for the photoreaction given by eq 1. Error limit ±15%. [c] Transient absorption decay rate at 480 nm. [d] Rate constant for transient quenching by ferrocene (±10%). [e] Steady-state irradiation experiments were not carried out.

R = R' = C$_6$H$_5$

R = R' = CH$_2$C$_6$H$_5$

R = R' = Fc

R = C$_6$H$_5$, R' = Fc
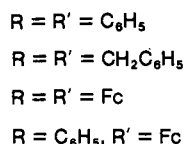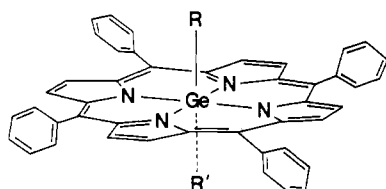
Figure 1. Structures of the investigated σ-bonded germanium porphyrins.
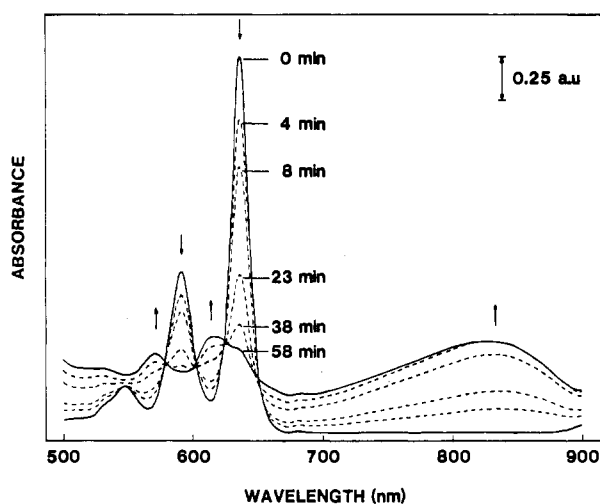
Figure 2. Spectral changes observed during irradiation of (TPP)Ge-(C$_6$H$_5$)$_2$ at 595 nm in THF.

the presence of UV–visible light, these resonances shift to 0.49, 5.07, and 5.54 ppm, and there is a 50% decrease in the peak intensities.[2] Similar light-dependent changes occur in the case of (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ in CDCl$_3$. A ^{1}H NMR and UV–visible characterization of the product shows a loss of one σ-bonded R group from (TPP)Ge(R)$_2$ (where R = C$_6$H$_5$ or CH$_2$C$_6$H$_5$) and a photochemical generation of (TPP)Ge(R)Cl.[2] In contrast, the ^{1}H NMR spectra taken after photolysis of (TPP)Ge(C$_6$H$_5$)$_2$ or (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ in THF-d_8 show broad resonances which are consistent with a π anion radical but do not provide evidence for the exact structure of the photoproduct.

The ESR spectrum taken after a 20-s irradiation of 10^{-4} M (TPP)Ge(C$_6$H$_5$)$_2$ in THF at 595 nm is shown in Figure 3. The signal has a g = 2.005 and a peak-to-peak separation, $\Delta H_{p,p}$, of 6 G. An almost identical spectrum is obtained after irradiation of (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ in THF. The ESR spectra of metal(II) tetraphenylporphyrin anion radicals that are generated in nonaqueous solvents by either chemical or electrochemical methods have g values between 2.002 and 2.005 and have $\Delta H_{p,p}$ values between 4 and 7 G.[12] Furthermore, the ESR signal of singly
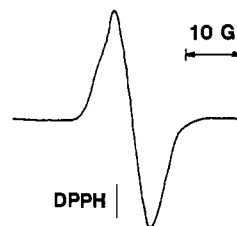
Figure 3. Room-temperature ESR spectrum obtained after a 20-s irradiation of (TPP)Ge(C$_6$H$_5$)$_2$ at 595 nm in THF.

reduced (TPP)Ge(F)$_2$ in CH$_2$Cl$_2$ containing 0.1 M TBAP has a g value of 2.001 ± 0.005 and a total width of 8.06 G at 115 K.[7] Thus, the ESR spectra obtained after irradiation of either (TPP)Ge(C$_6$H$_5$)$_2$ or (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ are similar to ESR spectra of other metalloporphyrin anion radicals generated by chemical or electrochemical methods and provide evidence for an anion radical character of the photoproducts.

On the basis of the UV–visible, ^{1}H NMR, and ESR data, a light-initiated cleavage of one metal–carbon bond in (TPP)Ge(R)$_2$ (where R = C$_6$H$_5$ or CH$_2$C$_6$H$_5$) is postulated to occur. It should be noted that a cleavage of both metal–carbon bonds in (TPP)-Ge(R)$_2$ would produce a porphyrin dianion whose UV–visible spectrum would be quite different from the one shown in Figure 2.[10] A porphyrin dianion would also be diamagnetic and hence would not have an ESR spectrum.[12] Thus, the photoreaction of (TPP)Ge(R)$_2$ can only be formulated as shown in eq 1, where

$$(TPP)Ge(R)_2 \xrightarrow{h\nu} (TPP)^-Ge(R)^+ + R^{\bullet} \qquad (1)$$
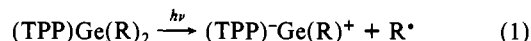
R = C$_6$H$_5$ or CH$_2$C$_6$H$_5$. The fate of the generated R$^{\bullet}$ in eq 1 was not investigated. Also, THF is a potential coordinating solvent and can bind to reduced metalloporphyrins.[13] However, the results presented here do not suggest a ligation by THF to these zwitterionic photoproducts.

Quantum yields for the photoreactions that occur during irradiation of (TPP)Ge(C$_6$H$_5$)$_2$ and (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ in THF at 595 nm are 0.007 and 0.023, respectively. The lower quantum yield of (TPP)Ge(C$_6$H$_5$)$_2$ is consistent with the stronger electron-withdrawing power of the axial C$_6$H$_5$ ligand compared to CH$_2$C$_6$H$_5$.

The higher the electron-withdrawing power of the axially bound ligand, the stronger the metal–carbon bond and the less reactive the compound. For example, indium and gallium porphyrins with highly electron-withdrawing σ-bonded groups such as CH=CH-C$_6$H$_5$ or C≡CC$_6$H$_5$ do not show any perceptible photoreactivity even after about 2 h of irradiation.[6]

Germanium porphyrins with σ-bonded ferrocene groups are also photostable.[4] The irradiation of (TPP)Ge(C$_6$H$_5$)(Fc) or (TPP)Ge(Fc)$_2$ in THF for 3–4 h results in only small changes in the UV–visible spectra (see Table I) and estimated quantum yields based on these absorption changes are <0.0002. The increased electron-withdrawing power of the axially bonded ferrocene moiety[3,4] might explain the photostability of the germanium–ferrocene bond in both investigated complexes, but it does not explain why no cleavage of the germanium–phenyl bond occurs in (TPP)Ge(C$_6$H$_5$)(Fc). In order to understand this phenomenon

(12) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, Part B.; Chapter 4.

(13) Kadish, K. M.; Xu, Q. Y.; Barbe, J.-M.; Maiya, G. B.; Guilard, R. *J. Chem. Soc., Dalton Trans.*, in press.
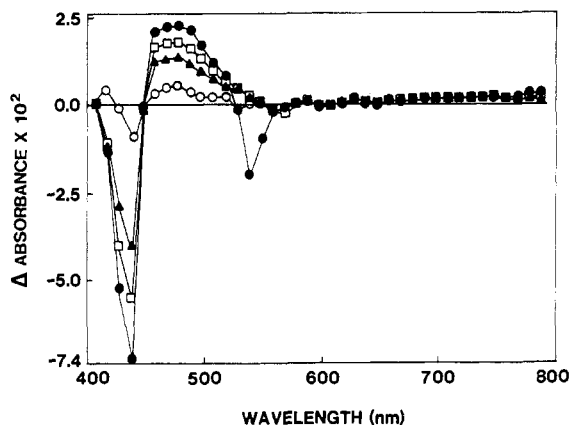
Figure 4. Transient absorption spectra of (TPP)Ge(Fc)$_2$ at (●) 2, (□) 64, (▲) 134, and (O) 269 μs after the laser flash.
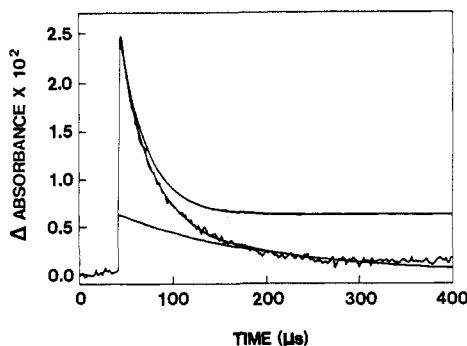

Figure 6. Transient absorption spectrum of (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ in THF 269 μs after the laser flash.

Figure 5. Transient decay of 1 × 10^{-4} M (TPP)Ge(C$_6$H$_5$)$_2$ in THF.

Figure 7. Transient decay rate (k_T) for the quenching of (TPP)Ge(C$_6$-H$_5$)$_2$ in THF as a function of ferrocene concentration.

it is necessary to examine the photophysical properties of the σ-bonded alkyl, aryl, or ferrocenyl germanium porphyrins. This is presented in the following section.

Laser-Flash Photolysis. Data obtained from laser-flash photolysis studies are given in Table I, and the transient absorption spectra of (TPP)Ge(Fc)$_2$ in THF at different time periods after the laser flash are shown in Figure 4.

The spectrum taken after 2 μs shows absorptions at 700, 490, and 450 nm that later decay to the base line without any complications. The initial spectrum is similar to the triplet state spectrum of several other metalloporphyrins.[5,6,14] The similarity of this spectrum to spectra in the literature and the fact that O$_2$ quenches the lifetime of the transient suggest that the spectrum in Figure 4 is the triplet–triplet absorption spectrum of (TPP)-Ge(Fc)$_2$.

Analogous spectral changes occur for (TPP)Ge(C$_6$H$_5$)(Fc) after the laser flash. Transient absorptions for both (TPP)Ge-(C$_6$H$_5$)(Fc) and (TPP)Ge(Fc)$_2$ at 480 nm follow a first order decay with rate constants (k^o_T) of 4.1 × 10^4 s^{-1} and 9.8 × 10^4 s^{-1}, respectively (see Table I). It is interesting to note that the rate constant for the bis(ferrocene) complex is nearly double that of the mono(ferrocene) complex.

Figure 5 illustrates the transient absorption decay for 1 × 10^{-4} M (TPP)Ge(C$_6$H$_5$)$_2$ in THF. A similar profile is obtained for (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$. The faster component in Figure 5 (k^o_T = 0.40 × 10^4 s^{-1}; see Table I) is assigned to a decay of the porphyrin triplet, and the slower component corresponds to a complicated decay of the photoproduct that does not reach the base line at times up to ca. 10 ms. A similar profile is also observed at laser energies lower than those used ($\sim$10 mJ) for obtaining the profile in Figure 5.

An assignment of the residual absorption in Figure 5 to the (TPP)Ge(C$_6$H$_5$)$_2$ photoproduct is convincingly established by the transient absorption spectrum taken after 269 μs. A similar transient spectrum is observed for (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$. This spectrum is shown in Figure 6 and has peak maxima at 430, 480,
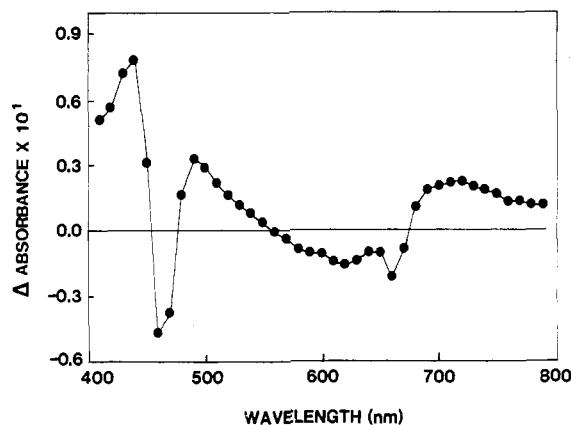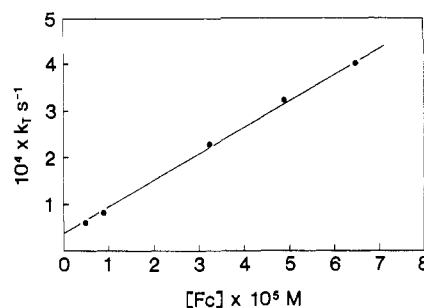
580, 650, and 720 nm. Although, there may be a contribution from the absorption of the pure triplet, this spectrum is nearly identical to the spectrum of the photoproduct obtained after steady-state photolysis of (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ (see Table I).

Analysis of both the transient decay and the transient spectra indicate that the triplet states of (TPP)Ge(C$_6$H$_5$)$_2$ and (TPP)-Ge(CH$_2$C$_6$H$_5$)$_2$ are responsible for their photoreactions. A similar conclusion has been reached from flash photolysis studies of (P)M(R), where P = TPP or OEP, M = In or Ga, and R = CH$_3$, C$_2$H$_5$, C$_4$H$_9$, CH(CH$_3$)$_2$, or C(CH$_3$)$_3$.[5,6]

The absence of a steady-state photoreaction and the faster triplet decay rates for (TPP)Ge(C$_6$H$_5$)(Fc) and (TPP)Ge(Fc)$_2$ compared to (TPP)Ge(R)$_2$ (see Table I) indicate that another process competes with the photoreaction and originates from the triplet states of these ferrocene-linked porphyrins. In order to test this hypothesis, the intermolecular quenching of (TPP)Ge(R)$_2$ (where R = Cl$^-$, C$_6$H$_5$, or CH$_2$C$_6$H$_5$) triplets by ferrocene was examined. The addition of ferrocene to each of the three complexes quenches the triplet lifetimes, and the observed transient decay rates (k_T) for the quenching of (TPP)Ge(C$_6$H$_5$)$_2$ are given in Figure 7 as a function of ferrocene concentration. Similar plots of k_T vs [Fc] are obtained for the quenching of (TPP)Ge(CH$_2$C$_6$H$_5$)$_2$ and (TPP)Ge(Cl)$_2$ by ferrocene and the intermolecular quenching rate constants (k_q) calculated from the slopes of these plots are listed in Table I.

The magnitudes of k_q ($\sim$10^9 M^{-1} s^{-1}) in Table I suggest an efficient quenching of the porphyrin triplet by ferrocene. Rate constants with a similar order of magnitude have been obtained for the energy-transfer quenching of several organic triplets by ferrocene and related metallocenes.[5,15–18] Since the triplet energy level of metalloporphyrins[19] ranges from 12.5 × 10^3 to 13 × 10^3

(14) Pekkarinen, L.; Linschitz, J. *J. Am. Chem. Soc.* **1960**, *82*, 2407.

(15) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161.

(16) Farmilo, A.; Wilkinson, F. *Chem. Phys. Lett.* **1975**, *34*, 575.

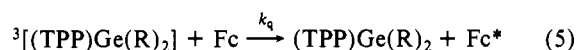(17) Chapple, A. P.; Vikesland, J. P.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *50*, 81.

(18) Rajadurai, S.; Bhattachavya, K.; Das, P. K. *Chem. Phys. Lett.* **1986**, *129*, 244.

(19) Hopf, F. R.; Whitten, D. G. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 667.

cm^{-1} and that of ferrocene[15] is ca. 15×10^3 cm^{-1}, there is a possibility of energy transfer from a metalloporphyrin triplet to ferrocene. In fact, the triplet quenching of $(TPP)H_2$ or $(TPP)Zn$ by nickelocene[18] and of $(P)M(R)$, where $P = TPP$ or OEP, M = In or Ga and R = CH_3, C_2H_5, C_4H_9, $CH(CH_3)_2$, or $C(CH_3)_3$, by ferrocene have been interpreted in terms of an energy-transfer mechanism.[5,6] The same mechanism is suggested for an intermolecular quenching of the three investigated germanium porphyrins by ferrocene.

In summary, the overall photoreaction mechanism for $(TPP)Ge(R)_2$ ($R = C_6H_5$ or $CH_2C_6H_5$) complexes can be written as shown in Scheme I. In the Scheme I, $^3[(TPP)Ge(R)_2]$ represents the triplet state of $(TPP)Ge(R)_2$ and k_b, k_r, and k_q are the rate constants for processes 3, 4, and 5, respectively. Only reactions 2–4 occur in the absence of ferrocene. However, in the presence of ferrocene, a competing quenching reaction (eq 5) also occurs and this influences the overall observed rate constant as well as the photoreaction quantum yield.

Scheme I

$$(TPP)Ge(R)_2 \xrightarrow{h\nu} {}^3[(TPP)Ge(R)_2] \qquad (2)$$

$$^3[(TPP)Ge(R)_2] \xrightarrow{k_b} (TPP)Ge(R)_2 \qquad (3)$$

$$^3[(TPP)Ge(R)_2] \xrightarrow{k_r} (TPP)^-Ge(R)^+ + R^\bullet \qquad (4)$$

$$^3[(TPP)Ge(R)_2] + Fc \xrightarrow{k_q} (TPP)Ge(R)_2 + Fc^* \qquad (5)$$

Equation 6 can be derived from eq 2–5, where k°_T and k_T are the observed transient decay rate constants in the absence and

$$k_T/k^\circ_T = \Phi^\circ/\Phi = 1 + (k_q/k^\circ_T)[Fc] \qquad (6)$$

presence of ferrocene, respectively, and Φ° and Φ represent the corresponding photoreaction quantum yields.[5,6] It then follows that plots of k_T/k°_T vs [Fc] or Φ°/Φ vs [Fc] should give straight lines having identical slopes.

A plot of k_T/k°_T vs [Fc] for $(TPP)Ge(C_6H_5)_2$ is linear and has a slope of 1.06×10^5 M^{-1} while the Φ°/Φ vs [Fc] is also linear and has a slope of 0.96×10^5 M^{-1}. The similarity of these two values to each other indicates that the triplet state of $(TPP)Ge(C_6H_5)_2$ is the reactive state and that ferrocene efficiently retards the photoreaction rate by quenching the reactive triplet.

The above results on the inter- and intramolecular quenching of the germanium porphyrin triplets by ferrocene establish that the faster transient decays of $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$ are due to an energy transfer from the porphyrin triplet to the linked ferrocene moiety. This process, in turn can compete with the photocleavage reaction originating from the triplet and will explain the photostability of the above ferrocene-linked porphyrins.

In addition to an energy-transfer mechanism, electron-transfer quenching and/or spin–orbit interactions can also contribute to the faster decay rates of $(TPP)Ge(Fc)_2$ and $(TPP)Ge(C_6H_5)(Fc)$. Although an electron transfer from the ferrocene moiety to the porphyrin triplet excited state is thermodynamically favorable (ΔG

$\simeq -0.2$ eV) in these systems,[4] there is no spectral or kinetic evidence for the presence of redox products. The linking of ferrocene, which contains a heavy iron atom, to the germanium porphyrin certainly provides another quenching pathway that can proceed through a spin–orbit-coupling process. However, the data presented does not indicate to what extent the above process contributes to the overall decay rate constants. In any case, triplet-energy transfer is possible and is probably the dominant quenching process in these σ-bonded ferrocene porphyrins.

Two linked porphyrin–metallocene complexes are known in the literature.[20,21] One is (*meso*-tetrakis(ferrocenylphenyl)porphinato)zinc(II) whose phosphorescence spectrum is reported to be indistinguishable from that of nonlinked (*meso*-tetraphenylporphinato)zinc(II).[21] A second compound, tetraferrocenylporphyrin, synthesized by Wolmann and Hendrickson,[20] has never been investigated with respect to its photophysical properties. Thus, this work provides the only example of an intramolecular process that originates from the triplet state of a porphyrin linked to a metallocene moiety.

(*meso*-Tetrakis(ferrocenylphenyl)porphinato)zinc(II)[21] has the metallocene linked to an equatorial position of the macrocycle. This contrasts with $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$, which have axially linked ferrocene moieties. Triplet-energy transfer normally takes place via exchange coupling, which only occurs over short distances.[22] It is also necessary that the relevant donor–acceptor orbitals significantly overlap for an efficient exchange.[23] The structural and spectroscopic properties of $(TPP)Ge(C_6H_5)(Fc)$ and $(TPP)Ge(Fc)_2$[3,4] suggest that both of the above conditions are met in these complexes, which is not the case for the tetraferrocenyl-[20] or tetrakis(ferrocenylphenyl)-porphyrins.[21] The distance and orientation effects on the triplet-energy-transfer efficiencies are not well-known in porphyrin chemistry and have only been indicated in a few cases.[24-26]

(20) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 3079.
(21) Schmidt, E. S.; Calderwood, T. S.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 3718.
(22) Parson, W. W. *Biochim. Biophys. Acta* **1969**, *189*, 384.
(23) Brookfield, R. L.; Ellul, H.; Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 219.
(24) Schwartz, F. P.; Gouterman, M.; Muljiani, Z.; Dolphin, D. *Bioinorg. Chem.* **1972**, *2*, 1.
(25) Brookfield, R. L.; Ellul, H.; Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1837.
(26) Mialocq, J. L.; Giannotti, C.; Maillard, P.; Momenteau, M. *Chem. Phys. Lett.* **1984**, 87.