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Photoinduced Electron-Transfer Reaction from the Excited Triplet State of Ethylindium(III) Tetraphenylporphyrin to Tetracyanoquinodimethane. Cleavage of the Carbon-Indium Bond in 2-Methyltetrahydrofuran

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The photochemical reaction of ethylindium(III) tetraphenylporphyrin, $C_2H_5In^{III}TPP$, in the presence of tetracyanoquinodimethane, TCNQ, was studied by means of steady light photolysis as well as laser flash photolysis. The triplet state of $C_2H_5In^{III}TPP$ originating from the porphyrin ligand reacts with TCNQ to give rise to the formation of the anion radical $TCNQ^{\bullet-}$ and indium(III) tetraphenylporphyrin, $(In^{III})^+TPP$, in consequence of electron transfer. The photoinduced cleavage of the carbon-indium bond is interpreted by assuming that the cation radical of $C_2H_5In^{III}TPP$, $C_2H_5In^{III}TPP^{\bullet+}$, is produced as an intermediate responsible for the bond cleavage: $C_2H_5In^{III}TPP^{\bullet+} \rightarrow C_2H_5^{\bullet} + (In^{III})^+TPP$.

Introduction

Metalloporphyrins exhibit a variety of photochemical reactions: photoinduced ligand attachment and detachment,[1-5] photoinduced electron-transfer reactions,[6-9] and photooxidation of organic molecules.[10] In particular, electron transfer from an excited state of porphyrins to electron acceptors has been extensively studied because of their importance for understanding of the detailed mechanisms for electron-transfer phenomena.[11-16]

In recent decades, several alkylmetal porphyrins having a carbon-metal bond have been detected and isolated as stable products.[17] In a previous paper,[18] we have reported that ethylindium(III) tetraphenylporphyrin, $C_2H_5In^{III}TPP$, undergoes photoinduced cleavage of a carbon-indium bond. In benzene solutions, the photocleavage of the bond was confirmed to occur from the triplet state of $C_2H_5In^{III}TPP$ originating from the porphyrin ligand. The quantum yield measurements as well as the laser photolysis studies for the photodecomposition of $C_2H_5In^{III}TPP$ in the presence of 2,4,7-trinitrofluorenone, TNF, have revealed that the triplet state interacts with TNF, resulting in an increase in the quantum yield for the photoinduced cleavage of the carbon-indium bond. The triplet exciplex formed between the triplet $C_2H_5In^{III}TPP$ and TNF was assumed as an intermediate for the photodecomposition assisted by TNF.

Photolysis of $C_2H_5In^{III}TPP$ in 2-methyltetrahydrofuran, MTHF, solutions gives a stable product that shows an ESR signal and an optical absorption spectrum located in the near-infrared region. On the basis of the ESR and optical absorption spectra, the stable product is identified as a zwitterionic porphyrin, $(In^{III})^+TPP^{\bullet-}$, in which an unpaired electron is principally located on the porphyrin ligand.[19] The zwitterionic porphyrin was found to react with TCNQ to yield the anion radical, $TCNQ^{\bullet-}$.

In the present study, we have carried out steady light photolysis and laser flash photolysis of $C_2H_5In^{III}TPP$ in MTHF solutions containing TCNQ. The reaction mechanisms for (1) the formation of $TCNQ^{\bullet-}$ and (2) the cleavage of the carbon-indium bond are discussed.

Experimental Section

Materials. Ethylindium(III) tetraphenylporphyrin was prepared according to the literature by a Grignard reaction.[18] The crude product was chromatographed on alumina columns by using benzene as a developing solvent. The IR, NMR, and UV-vis spectra of purified $C_2H_5In^{III}TPP$ were in good agreement with those reported previously.[20] Reagent grade TCNQ supplied from Wako Pure Chem. Ind. Ltd. was used without further purification. 2-Methyltetrahydrofuran was purified by fractional distillation and stored over Na-K alloy in vacuo to remove traces of water.

Spectroscopic Measurements and Laser Photolysis. Optical absorption spectra were measured by a Hitachi 330 spectrophotometer. ESR spectra were recorded on a JEOL JES-FE-3AX X-band spectrometer. Laser photolysis studies were carried out by using a Nd-YAG laser (Model HY 500 from JK Lasers Ltd.) equipped with the second-, third-, and fourth-harmonic generators. The second harmonic (532 nm) was used as light pulses for the photolysis of solutions: the energy and the duration were ca. 100 mJ and 20 ns, respectively. The detection system of the transient spectra has been reported elsewhere.[21]

Quantum Yield Measurements. Monochromatic light used for determination of the quantum yields was obtained from a xenon lamp incorporated in a Hitachi MPF 4 spectrofluorimeter. The photon flux at 310 nm was determined by using methyldiphenylamine in aerated methylcyclohexane as a chemical actinometer: the quantum yield for the formation of *N*-methylcarbazole from methyldiphenylamine has been established as 0.42.[22] Relative light intensity distribution of the xenon lamp between 250 and 600 nm was determined by the measurement of the excitation spectrum of Rhodamine B in ethylene glycol (8 g/L). From light intensity distribution and the photon flux at 310 nm, the photon flux at a given wavelength was readily obtained. Changes in the concentration of $C_2H_5In^{III}TPP$ upon irradiation were monitored at 580 nm. Because of no wavelength dependence of the quantum yield for the photodecomposition of $C_2H_5In^{III}TPP$,[18] steady light photolysis was performed solely at 580 nm; the concentrations of $C_2H_5I^{III}TPP$ in MTHF were ca. 3.8×10^{-5} M throughout this study. The photon flux of incident light at 580 nm was 2.54×10^{-11} mol cm^{-2} s^{-1}. Samples for all measurements were degassed on a vacuum line.

Hydrocarbons produced by steady light photolysis of $C_2H_5In^{III}TPP$ in an MTHF solution containing TCNQ were detected by gas chroma-

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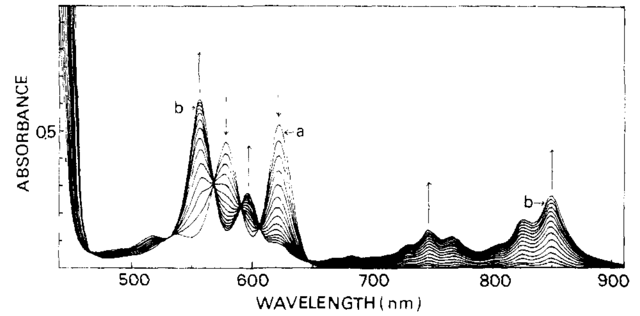

Figure 1. Absorption spectral changes observed for an MTHF solution of $C_2H_5In^{III}TPP$ in the presence of 1.29×10^{-4} M TCNQ upon irradiation at 580 nm. Spectra a and b are measured before and after photolysis for 60 min, respectively.

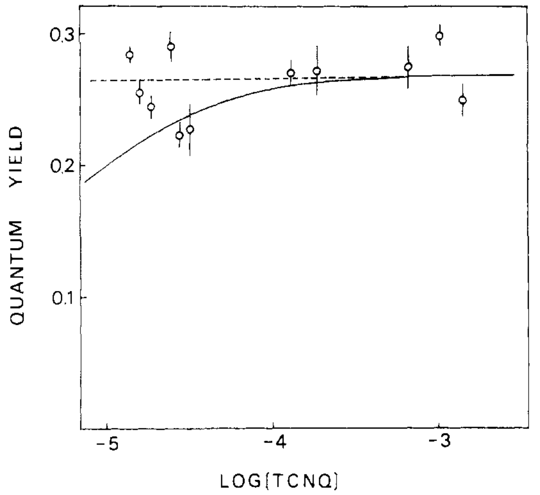

Figure 2. Quantum yields for the photodecomposition of $C_2H_5In^{III}TPP$ in MTHF solutions represented as a function of the logarithmic concentration of TCNQ. The solid curve represents the yields calculated according to the reaction mechanism (see text).

tography. The column, sebaconitrile on Chromosorb W, was used for analysis of hydrocarbons.

Results

The optical absorption spectrum of $C_2H_5In^{III}TPP$ in MTHF has peak maxima at 536, 578, and 621 nm in the Q-band region. The molar absorption coefficient is determined as 1.27×10^4 M^{-1} cm^{-1} at 578 nm. Since no spectral changes are observed by addition of 10^{-5}–10^{-3} M TCNQ, it is concluded that the ground-state complex is not formed between $C_2H_5In^{III}TPP$ and TCNQ concentration range studied.

Figure 1 shows the absorption spectral changes observed for an MTHF solution of $C_2H_5In^{III}TPP$ containing 1.29×10^{-4} M TCNQ upon 580-nm irradiation. The absorption peak intensities of $C_2H_5In^{III}TPP$ decrease with irradiation time, and new bands appear at 519, 557, 597, 746, and 850 nm. The first three bands are very similar to those of chloroindium(III) tetraphenylporphyrin,[12] and the last two are identical with the absorption bands of $TCNQ^{\bullet -}$ in MTHF produced by chemical reduction with *sec*-butylamine. The formation of $TCNQ^{\bullet -}$ was further confirmed by ESR measurements. The irradiated solution gave the ESR signal identical with that of $TCNQ^{\bullet -}$ reported in a previous paper.[23] These results indicate that photoinduced electron transfer occurs from $C_2H_5In^{III}TPP$ to TCNQ, resulting in the formation of $TCNQ^{\bullet -}$ and indium(III) tetraphenylporphyrin, $(In^{III})^+TPP$.

Figure 2 shows the quantum yields for the photodecomposition of $C_2H_5In^{III}TPP$ represented as a function of the TCNQ concentration. The yield, 0.27 ± 0.04, is fairly constant in the concentration range 10^{-5}–10^{-3} M TCNQ. The absorption spectral changes of $C_2H_5In^{III}TPP$ in an MTHF solution upon irradiation were examined in order to determine the quantum yield for the photodecomposition in the absence of TCNQ. However, no isosbestic point was observed for the spectral changes, indicating that the photoreaction is complicated by further photochemical and/or thermal reactions of the photoproducts.[19] The yield in the absence of TCNQ could not be determined experimentally. As mentioned later, the solid curve in Figure 2 represents the quantum yields calculated according to the reaction scheme for the photodecomposition of $C_2H_5In^{III}TPP$ in the presence of TCNQ.

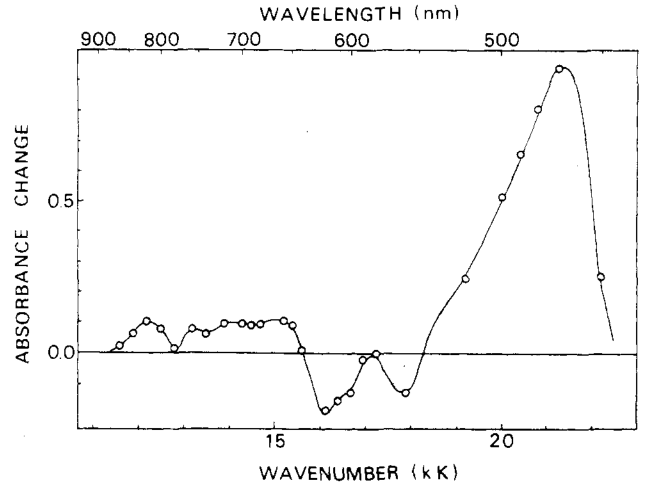

Figure 3. Transient absorption spectrum observed for an MTHF solution of $C_2H_5In^{III}TPP$ without TCNQ at 50 ns after 532-nm laser pulsing.

The quantum yields for the formation of $TCNQ^{\bullet -}$ were determined as 0.07 ± 0.01 in the TCNQ concentration range studied. For determination of the quantum yield, we assumed that the molar absorption coefficient of $TCNQ^{\bullet -}$ in MTHF is nearly identical with that in acetonitrile: 4.7×10^4 M^{-1} cm^{-1} at 850 nm.[24]

Gas chromatographic studies have confirmed that the hydrocarbons produced by photolysis of $C_2H_5In^{III}TPP$ in MTHF in the presence of TCNQ are composed of 97% *n*-butane and <3% ethane. Further, photodecomposition of 1 mol of $C_2H_5In^{III}TPP$ was found to give ca. 0.1 mol of *n*-butane. These results indicate that ca. 20% of the ethyl radicals produced by reaction 4 undergo dimerization to give *n*-butane. As mentioned later, it is suggested that ca. 80% of the ethyl radicals react with $TCNQ^{\bullet -}$ to give unidentifed addition products.

Laser photolysis of $C_2H_5In^{III}TPP$ was carried out to elucidate the primary processes of the photochemical reaction. Figure 3 shows the transient absorption spectrum observed for an MTHF solution of $C_2H_5In^{III}TPP$ at 50 ns after 532-nm laser pulsing. The spectrum exhibits a strong absorption band at 470 nm similar to the triplet–triplet (T–T) absorption of $C_2H_5In^{III}TPP$ in benzene.[18] We, therefore, consider that the transient is ascribed to the triplet state of $C_2H_5In^{III}TPP$ originating from the porphyrin ligand. The T–T absorption spectrum of $C_2H_5In^{III}TPP$ in MTHF is found to be rather broad in comparison with that in benzene.

The triplet state of $C_2H_6In^{III}TPP$ in MTHF decays according to first-order kinetics with a rate constant of 6.6×10^4 s^{-1}. It is noteworthy that the decay rate constant, 6.6×10^4 s^{-1}, is 4.6 times larger than that in benzene, 1.43×10^4 s^{-1}. The triplet state is found to be efficiently quenched by TCNQ. Figure 4 shows plots of the decay rate constant, k_t, vs. TCNQ concentration, [TCNQ]. The rate constant increases with an increase in [TCNQ]. From the slope of the line, the quenching rate constant is obtained as 6.5×10^9 M^{-1} s^{-1}:

$$k_t = 6.6 \times 10^4 + 6.5 \times 10^9[\mathrm{TCNQ}]\ \mathrm{s}^{-1}$$

The value of the quenching rate constant is close to that of the diffusion-controlled process.

Figure 5 shows the transient absorption spectra observed for an MTHF solution of $C_2H_5In^{III}TPP$ containing 1.24×10^{-4} M

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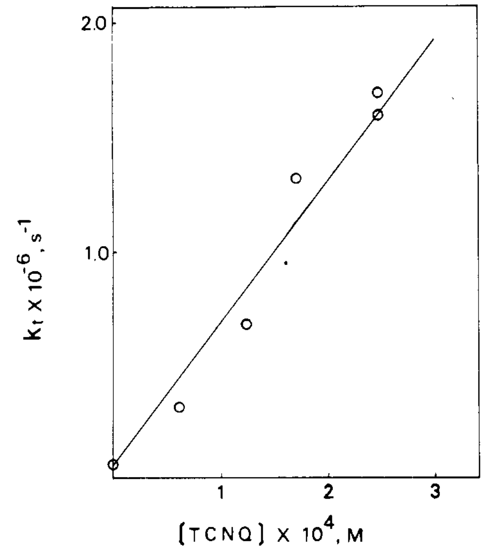

Figure 4. Rate constants for the decay of the triplet $C_2H_5In^{III}TPP$ represented as a function of TCNQ concentration.

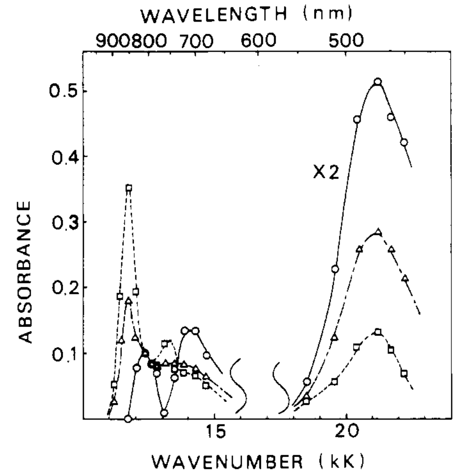

Figure 5. Transient absorption spectra observed for an MTHF solution of $C_2H_5In^{III}TPP$ in the presence of 1.24×10^{-4} M TCNQ at 20 ns (○), 1 μs (△), and 3 μs (□) after laser pulsing.

TCNQ. The spectrum measured at 20 ns after pulsing is identical with the T–T absorption spectrum of $C_2H_5In^{III}TPP$ in the MTHF solution without TCNQ. An absorption band at 470 nm due to the triplet state decreases with time, and a new band appears at 850 nm. The absorption bands in the near-infrared region, 650–900 nm, detected at 3 μs after pulsing are in good agreement with those of $TCNQ^{\bullet-}$ in MTHF.

Figure 6 shows the oscilloscope traces after laser pulsing observed for the MTHF solution of $C_2H_5In^{III}TPP$ containing 1.24×10^{-4} M TCNQ. The decay profile of the triplet $C_2H_5In^{III}TPP$ is represented as an oscilloscope trace monitored at 470 nm (part A in Figure 6). The rate constant for the triplet decay is determined as 6.9×10^5 s^{-1}. The rise in the curve for $TNCQ^-$ is also represented as an oscilloscope trace monitored at 850 nm (part B in Figure 6). The rate for the formation of $TCNQ^{\bullet-}$ is obtained as 7.2×10^5 s^{-1}. Since the rate constant for the formation of $TCNQ^{\bullet-}$ is in fairly good agreement with the decay rate constant of the triplet state, it is concluded that electron transfer occurs from the triplet $C_2H_5In^{III}TPP$ to TCNQ, resulting in the formation of $TCNQ^{\bullet-}$. Part C in Figure 6 shows an oscilloscope trace monitored at 850 nm, exhibiting the rise and decay profile of $TCNQ^{\bullet-}$ after laser pulsing. The TCNQ anion radial initially produced by electron transfer partly decays, leaving residual absorption after laser pulsing. Neither first-order nor second-order kinetics is fitted for the decay of $TCNQ^{\bullet-}$. The half-life of $TCNQ^{\bullet-}$ is obtained as ca. 35 μs. The ratio of the maximum absorbance at 850 nm measured at 6 μs after pulsing to the residual absorbance was calculated to be 0.28. This result indicates that the residual $TCNQ^{\bullet-}$ can be detected as a final product formed by steady light photolysis of the MTHF solution of $C_2H_5In^{III}TPP$ in the presence of TCNQ.

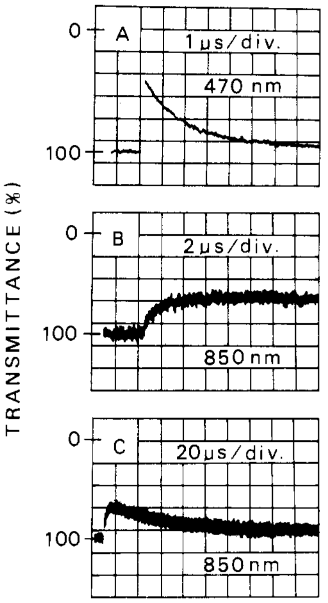

Figure 6. Oscilloscope traces observed for an MTHF solution of $C_2H_5In^{III}TPP$ in the presence of 1.24×10^{-4} M TCNQ after 532-nm laser pulsing: (A) monitored at 470 nm; (B, C) monitored at 850 nm.

Discussion

Photolysis of $C_2H_5In^{III}TPP$ in MTHF has been demonstrated to give rise to the homolytic cleavage of the carbon–indium bond:[19]

$$C_2H_5In^{III}TPP \xrightarrow{h\nu} C_2H_5^{\bullet} + (In^{III})^{+}TPP^{\bullet-}$$

Here $(In^{III})^{+}TPP^{\bullet-}$ is a zwitterionic porphyrin in which an unpaired electron is located in the tetraphenylporphyrin ligand. When TCNQ was added to the solution after photolysis, $TCNQ^{\bullet-}$ was found to be produced:

$$(In^{III})^{+}TPP^{\bullet-} + TCNQ \rightarrow (In^{III})^{+}TPP + TCNQ^{\bullet-}$$

Steady light photolysis of $C_2H_5In^{III}TPP$ in MTHF without TCNQ was complicated. In the presence of TCNQ, the absorption spectral changes observed upon irradiation give isosbestic points, showing that the photoreaction is simplified by addition of TCNQ. Photolysis of $C_2H_5In^{III}TPP$ in MTHF in the presence of TCNQ gives rise to the formation of $(In^{III})^{+}TPP$ and $TCNQ^{\bullet-}$. The formation of $TCNQ^{\bullet-}$ is interpreted in terms of electron transfer from the triplet state of $C_2H_5In^{III}TPP$ to TCNQ. The quantum yields for (1) the photodecomposition of $C_2H_5In^{III}TPP$ and (2) the formation of $TCNQ^{\bullet-}$ are determined as 0.27 ± 0.04 and 0.07 ± 0.01, respectively, by steady light photolysis. This result implies that the photodecomposition of 1 mol of $C_2H_5In^{III}TPP$ gives rise to the formation of ca. 0.26 mol of $TCNQ^{\bullet-}$.

The laser photolysis studies have revealed that $TCNQ^{\bullet-}$ initially produced by photoinduced electron transfer partly decays, leaving residual $TCNQ^{\bullet-}$ as a final product. The ratio of an amount of the residual $TCNQ^{\bullet-}$ to that of initially produced $TCNQ^{\bullet-}$ is obtained as 0.28. This fact indicates that 1 mol of $TCNQ^{\bullet-}$ produced by photoinduced electron transfer gives only 0.28 mol of $TCNQ^{\bullet-}$ as a residual product because of the thermal reaction as mentioned later. On the basis of the quantum yield measurements and laser photolysis studies, it is suggested that 1 mol of $C_2H_5In^{III}TPP$ reacts with 1 mol of TCNQ upon irradiation to yield 1 mol of $TCNQ^{\bullet-}$, which decays partly to leave only 0.26–0.28 mol of $TCNQ^{\bullet-}$ as a final product.

Laser spectroscopic studies of the transient species have shown that the excited triplet state of $C_2H_5In^{III}TPP$ originating from the porphyrin ligand transfers an electron to TCNQ to yield $TCNQ^{\bullet-}$. The triplet $C_2H_5In^{III}TPP$ is considered to be transformed to the cation radical, $[C_2H_5In^{III}TPP]^{\bullet+}$, after electron transfer. It has been frequently observed that metalloporphyrins undergo photoinduced electron transfer toward suitable electron acceptors, A, to give the cation radical of metalloporphyrin and the anion radical of A, $A^{\bullet -}$.[25]

The quenching rate constant of the triplet $C_2H_5In^{III}TPP$ by TCNQ is determined as 6.5×10^9 M^{-1} s^{-1}. Since the rate constant for the decay of the triplet does not exhibit a leveling off even at higher concentrations of TCNQ, no formation of the long-lived triplet exciplex is concluded. Presumably, a short-lived triplet exciplex is responsible for the charge-transfer reaction from the triplet $C_2H_5In^{III}TPP$ to TCNQ.

Absorption spectroscopic measurement of the photolysis products in the MTHF solution of $C_2H_5In^{III}TPP$ have shown that the products are identified as $(In^{III})^+TPP$ and $TCNQ^{\bullet -}$. No other decomposition products were detected in the wavelength range studied. Therefore, the photoreaction is considered to be represented as

$$^3C_2H_5In^{III}TPP^* + TCNQ \rightarrow {}^3[\text{exciplex}]^* \quad (1)$$

$$^3[\text{exciplex}]^* \rightarrow [C_2H_5In^{III}TPP]^{\bullet +} + TCNQ^{\bullet -} \quad (2)$$

$$^3[\text{exciplex}]^* \rightarrow C_2H_5In^{III}TPP + TCNQ \quad (3)$$

$$[C_2H_5In^{III}TPP]^{\bullet +} \rightarrow C_2H_5^{\bullet} + (In^{III})^+TPP \quad (4)$$

Here $^3C_2H_5In^{III}TPP^*$, $^3[\text{exciplex}]^*$, and $[C_2H_5In^{III}TPP]^{\bullet +}$ denote respectively the triplet state of $C_2H_5In^{III}TPP$, the triplet exciplex between $C_2H_5In^{III}TPP$ and TCNQ, and the cation radical of $C_2H_5In^{III}TPP$.

Kadish and his co-workers have carried out the optical and ESR studies of one-electron-oxidation products of alkylindium(III) porphyrins generated by electrochemcal oxidation.[26] However, they could not detect spectroscopically the oxidation products owing to the facile decomposition shown by reaction 4. In the present study, we also could not detect $[C_2H_5In^{III}TPP]^{\bullet +}$ by laser photolysis. It is suggested that the lifetime of $[C_2H_5In^{III}TPP]^{\bullet +}$ is very short because of the facile cleavage of the carbon–indium bond.

Photochemical studies of $C_2H_5In^{III}TPP$ in benzene solutions revealed that (1) the cleavage of the carbon–indium bond occurs via the excited triplet state of $C_2H_5In^{III}TPP$ originating from the TPP ligand and (2) the yield for the photocleavage of the carbon–indium bond increases remarkably by addition of TNF as an electron acceptor.[18] No formation of the anion radicals of TNF was detected after photolysis of the benzene solution of $C_2H_5In^{III}TPP$ in the presence of TNF. It is supposed that the photoinduced electron-transfer reaction is suppressed owing to the low dielectric constant of benzene. The increase in the quantum yield by addition of TNF is interpreted by assuming the triplet exciplex formation between TNF and the triplet $C_2H_5In^{III}TPP$: the carbon–indium bond in the triplet exciplex is dissociated more readily than that in the triplet $C_2H_5In^{III}TPP$.

As described above, both $[C_2H_5In^{III}TPP]^{\bullet +}$ and the triplet exciplex formed between the triplet $C_2H_5In^{III}TPP$ and a strong electron acceptor undergo facile cleavage of the carbon–indium bond. The TPP ligands of both $[C_2H_5In^{III}TPP]^{\bullet +}$ and the triplet exciplex are predicted to be electron-deficient. It is likely that the carbon–metal bond in an alkylmetal porphyrin becomes weak when the porphyrin ligand is electron-deficient.

The quantum yield, Φ, for the photodecomposition of $C_2H_5In^{III}TPP$ in the presence of TCNQ is expressed as a function of the TCNQ concentration, [TCNQ]:[18]

$$\Phi = (\Phi_0 k_R{}^0 + \Phi_\infty k_q[TCNQ])(k_R{}^0 + k_q[TCNQ])^{-1}$$

where Φ_0 and Φ_∞ are the quantum yields in the absence and in the presence of an infinite concentration of TCNQ, respectively, and $k_R{}^0$ and k_q are the rate constant for the decay of the triplet $C_2H_5In^{III}TPP$ and the quenching rate constant of the triplet $C_2H_5In^{III}TPP$ by TCNQ, respectively. On the basis of the quantum yield measurements and laser flash photolysis studies, we obtain $\Phi_\infty = 0.27$, $k_R{}^0 = 6.6 \times 10^4$ s^{-1}, and $k_q = 6.5 \times 10^9$ M^{-1} s^{-1}. Only the value of Φ_0 could not be determined experimentally. In Figure 2, Φ is represented as a solid curve that is calculated on the assumption $\Phi_0 = 0.1$. Taking account of the experimental errors in the quantum yield measurements, we consider that the yield ranges from 0.1 to 0.27: $0.1 \ll \Phi_0 \leq 0.27$.

The quantum yield for the photodecomposition of $C_2H_5In^{III}TPP$ in MTHF is larger than that obtained in benzene solutions (0.043).[18] The photoreaction in benzene is expressed as

$$C_2H_5In^{III}TPP \xrightarrow{h\nu} C_2H_5^{\bullet} + [In^{II}TPP]$$

Here $[In^{II}TPP]$ is considered to be an initial product after photolysis of $C_2H_5In^{III}TPP$. Since benzene is a noncoordinating solvent having a low dielectric constant (2.28),[27] $[In^{II}TPP]$ cannot be transformed to the zwitterionic structure, $(In^{III})^+TPP^{\bullet -}$, as is observed for the MTHF solution. Thus, an unpaired electron in $[In^{II}TPP]$ is expected to be located in the 5s orbital of the central indium atom. From this point of view, $C_2H_5^{\bullet}$ and $[In^{II}TPP]$ initially produced by photolysis in a solvent cage can recombine together to regenerate $C_2H_5In^{III}TPP$, resulting in the decrease in the quantum yield for the photodecomposition. On the other hand, MTHF is a coordinating solvent having a dielectric constant of ca. 7.6.[28] The zwitterionic structure, therefore, is considered to be more stable in MTHF than in benzene with the aid of coordination of an MTHF molecule to the central indium atom as well as the solvation of the zwitterionic porphyrin by surrounding MTHF molecules. Since the zwitterionic porphyrin has an unpaired electron in the porphyrin plane, no regeneration of $C_2H_5In^{III}TPP$ by recombination between $C_2H_5^{\bullet}$ and the zwitterionic porphyrin in a solvent cage is expected. On the basis of these considerations, it is concluded that the inefficient recombination reaction between $C_2H_5^{\bullet}$ and the zwitterionic porphyrin results in an increase in the quantum yield for the photodecomposition of $C_2H_5In^{III}TPP$ in MTHF in comparison with that in benzene.

The stoichiometric studies on steady-state photolysis of $C_2H_5In^{III}TPP$ in an MTHF solution containing TCNQ have shown that photodecomposition of 1.0 mol of $C_2H_5In^{III}TPP$ gives 1.0 mol of $(In^{III})^+TPP$ and 0.26 mol of $TCNQ^{\bullet -}$. On the basis of charge balance, it is suggested that 0.75 mol of anionic species other than $TCNQ^{\bullet -}$ should be produced in the solution after photolysis. The laser photolysis studies demonstrate that $TCNQ^{\bullet -}$ initially produced after laser pulsing disappears, leaving 28% of the $TCNQ^{\bullet -}$ as a residual product. This result indicates that 72% of the $TCNQ^{\bullet -}$ is transformed to unidentified anionic species that act as counterions of $(In^{III})^+TPP$. Although the reaction of $TCNQ^{\bullet -}$ leading to the formation of unidentified anionic species is not clear, it seems likely that, as mentioned earlier, $TCNQ^{\bullet -}$ reacts with an ethyl radical to give the anionic species X^-:

$$2C_2H_5 \rightarrow C_4H_{10}$$

$$C_2H_5 + TCNQ^{\bullet -} \rightarrow X^-$$

A trace amount of ethane was detected by gas chromatographic analysis of the hydrocarbons in the irradiated MTHF solution of $C_2H_5In^{III}TPP$ containing TCNQ. Presumably, the hydrogen abstraction of an ethyl radical from MTHF occurs very inefficiently.

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Registry No. TCNQ, 1518-16-7; $TCNQ^{\bullet -}$, 34507-61-4; $C_2H_5In^{III}TPP$, 63036-65-7; $In^{III}TPP$, 56551-52-1; *n*-butane, 106-97-8; ethane, 74-84-0.

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