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Activation of a Metal–Axial Ligand Bond in Aluminum Porphyrin by Visible Light

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Abstract: Irradiation with visible light induced a remarkable effect on the reactivity of a metal–carbon bond in (tetraphenylporphinato)aluminum methyl in the nucleophilic substitution reaction with protic compounds such as phenol. A similar photoacceleration effect was also observed in the reversible ligand exchange of (tetraphenylporphinato)aluminum phenoxide with phenol. As for the former reaction, comparable quantum yields were observed upon irradiation at the Soret band and at the Q-band.

Photochemistry of metalloporphyrins is of much interest in connection with the role of chlorophyll in photosynthesis.[1] In thylakoid membranes of chloroplast, the light-absorbing pigments are arranged so that light energy is transmitted with a very high efficiency from light-harvesting chlorophyll molecules to the reaction center chlorophyll where the photochemical act occurs. The vacant fifth and sixth coordination sites of the magnesium atom located at the center of the chlorophyll macrocycle are considered to be occupied by electron-donating groups such as ϵ-amino group of lysine or an imidazole group of histidine in the chlorophyll protein, or water molecules as the axial ligand. Both the effect of the axial ligand on the photoexcitation of the macrocycle and the effect of a photoexcited macrocycle on the coordination of the axial ligand should be closely associated with the efficient transmission of light energy and electron transfer to acceptor.

The photochemistry of metalloporphyrin has been largely studied with respect to the photostimulated electron transfer from metalloporphyrin mainly of a non transition metal, such as zinc[2] or tin,[3] with some examples of transition-metal porphyrins.[4] On the other hand, the effect of light on the metal–axial ligand bond in metalloporphyrins has been investigated on metalloporphyrins and related compounds of transition metals such as iron, cobalt, and ruthenium by steady-light photolysis, flash photolysis, and luminescence measurements,[5] in connection with the mechanism of ligand binding in vitamin B_{12} or heme group compounds.

It has been well documented that the transition metal–carbon bond in macrocycles is subject to homolysis by light, accompanied by the change in valence of the central metal.[6] On the other hand, coordinated ligands, such as dioxygen, carbon monoxide, imidazole, and pyridine, are known to be subject to the reversible dissociation and/or ligand exchange.

As for non transition metals, an indium–carbon bond in the porphyrin macrocycle is subject to homolysis by light,[7] accompanied by the change in valence of the central metal, similar to the transition-metal–carbon bond. On the other hand, aluminum- and zinc–carbon bonds are subject to homolysis slowly in alkyl halides[8,9] to form metal–halogen bonds, but in benzene the metal–carbon bonds are resistant to decomposition. The excited-state exchange of coordinated ligands such as pyridine, piperidene, and triphenylphosphine on indium[7] or zinc[10] porphyrin was also reported.

The quantum yields reported for the photodissociation of the transition-metal–carbon bond,[4,6] transition-metal–nitrogen bond,[11] and nontransition-metal–carbon bond[7,8] range from 10^{-7} to 1.

The non transition metal–ligand bond may not be excited directly by visible light, and the non-transition-metal complexes are considered to be free from the complications introduced by partially filled d orbitals and ambiguities in coordination numbers, spin states, and oxidation states. Hence, the effect of photoexcitation of the porphyrin macrocycle on the reactivity, including exchange, of the central metal–axial ligand bond is expected to be able to be discussed with less complexity.

In the course of our studies on the interesting behaviors of aluminum porphyrin,[12] we have observed some examples of the acceleration of nonhomolytic reactions by irradiation with visible light.[13]

This paper describes the photochemical activation of the metal–alkyl and metal–aryloxy bond by visible light in aluminum porphyrin in the irreversible substitution or reversible exchange reactions with phenol.[14]

Results and Discussion

Photochemical Activation of the Metal–Alkyl Bond in Aluminum Porphyrin in the Reaction with Phenol. The reaction between (tetraphenylporphinato)aluminum methyl ((TPP)AlMe, **1**) and an equimolar amount of 2-*tert*-butyl-4-methoxyphenol in C_6D_6 in the dark was examined by ^1H NMR spectroscopy (Figure 1). In the reaction mixture after 2 days, the signals due to 2-*tert*-butyl-4-methoxyphenol (d–i) and the methyl group bound to the aluminum atom in (TPP)AlMe (j) completely disappeared. Instead, the signal due to methane (l) appeared, and a set of new signals assignable to a phenoxide group (D–H) was observed at much higher magnetic field than the signals of the parent phenol, which indicates that the phenoxide group is attached to the central aluminum atom in the porphyrin ring and is affected by the ring current. The shielding effect is particularly remarkable as to the

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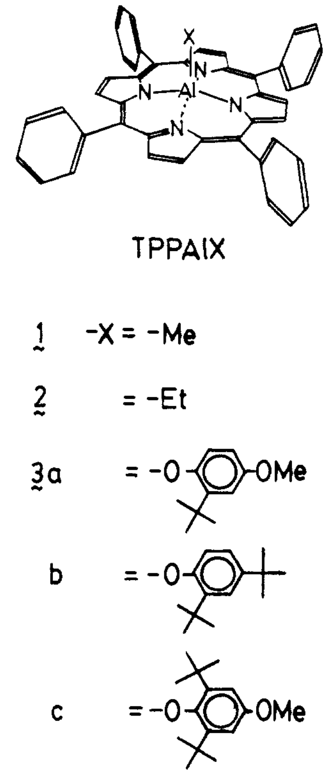
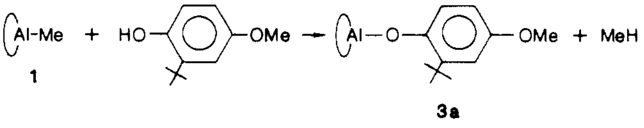


aromatic proton (F) and the *tert*-bütyl protons (D). The intensity ratio of the signals due to the phenoxide group (D, 9 H; E, 3 H; F, 1 H; G, 1 H; H, 1 H) to the porphyrin group (A, 8 H; B, 8 H; C, 12 H) confirms the quantiative formation of **3a**.



The formation of **3b** and **3c** from (TPP)AlMe and the corresponding phenol was also confirmed by ^{1}H NMR analysis (Table I).

Figure 2 shows the absorption spectral changes of the reaction mixture of **1** and a 2-fold amount of 2-*tert*-butyl-4-methoxyphenol under irradiation at 430 nm. Before irradiation, the spectrum of (TPP)AlMe (**1**) exhibits major absorption peaks at 564 and 606 nm in the Q-band region. The intensities of these peaks decrease, and a new remarkable peak of **3a** appears at 547 nm with an increase in the irradiation time.[15]

As shown in Figure 3, the reaction of (TPP)AlMe with 2-*tert*-butyl-4-methoxyphenol was found to proceed slowly in the dark. For example, the conversion of (TPP)AlMe was 28% after 4 h when (TPP)AlMe was allowed to react with 2 equiv of 2-*tert*-butyl-4-methoxyphenol in the dark at room temperature. On the other hand, the substitution reaction was accelerated by irradiation with visible light of the wavelength corresponding to the Soret band (λ = 430 nm) and was completed within 4 h. The quantum yield for the above reaction to form **3a** was found to be (0.93 ± 0.07) × 10^{-2}. The reaction was similarly accelerated under the irradiation with visible light of the wavelength corresponding to the Q-band (λ = 563 nm), where the quantum yield for the formation of **3a** was found to be (1.1 ± 0.1) × 10^{-2}.

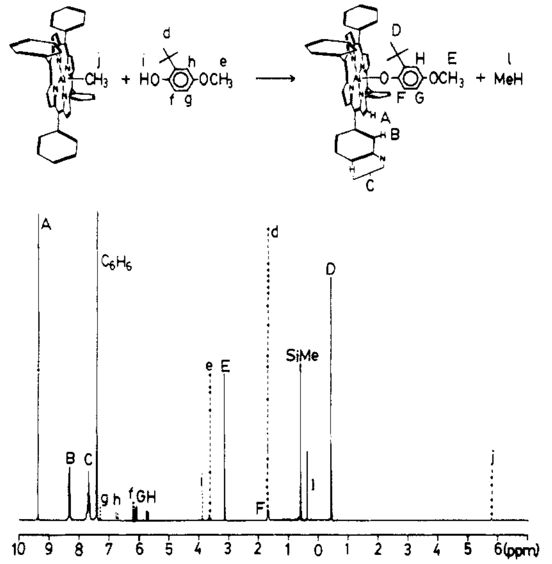


Figure 1. 270-MHz ^{1}H NMR spectrum in C_6D_6 of the reaction mixture between (TPP)AlMe (1.0 × 10^{-2} mol·dm^{-3}) and 2-*tert*-butyl-4-methoxyphenol (1.0 × 10^{-2} mol·dm^{-3}) in the dark after 2 days. Broken lines represent the mixture in the initial stage of the reaction.

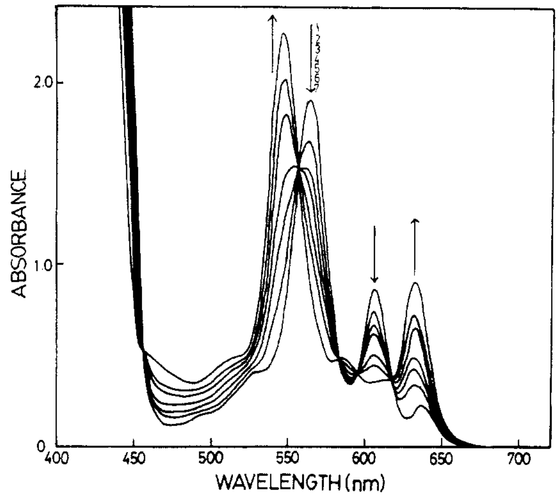
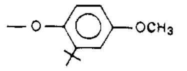
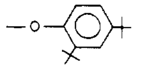
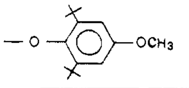


Figure 2. Absorption spectral changes of the reaction mixture of (TPP)AlMe (1.0 × 10^{-2} mol·dm^{-3}) with 2-*tert*-butyl-4-methoxyphenol (2.0 × 10^{-2} mol·dm^{-3}) in C_6H_6 upon irradiation at 430 nm: (1) before irradiation; (2) after irradiation for 15 min; (3) 30 min; (4) 60 min; (5) 90 min; (6) 120 min; (7) 240 min.

Table I. ^{1}H NMR Data of (TPP)AlOAr[a]

(TPP)AlOAr: –OAr	chemical shifts of protons of OAr: δ (intensity, multiplicity)
	6.13 (1 H, d), 5.76 (1 H, m), 3.17 (3 H, s), 1.68 (1 H, d), –0.40 (9 H, s)
	6.48 (1 H, d), 6.21 (1 H, m), 1.70 (1 H, d), 1.04 (9 H, s), –0.35 (9 H, s)
	6.18 (2 H, s), 3.42 (3 H, s), –0.30 (18 H, s)

[a] Measured in C_6D_6 at room temperature. Concentration: 1.0 × 10^{-2}–2.0 × 10^{-2} mol·dm^{-3}.

The accelerating effect of the irradiation with visible light was also observed in the reaction of (TPP)AlR (R = alkyl) with hindered phenols. For example, irradiations with visible light (λ > 420 nm) brought about an acceleration effect on the reactions of (TPP)AlEt (**2**) with 2-*tert*-butyl-4-methoxyphenol, 2,4-di-*tert*-butylphenol, and 2,6-di-*tert*-butyl-4-methoxyphenol. In particular, a remarkable accelerating effect of visible light was observed on the reaction of (TPP)AlEt (**2**) with 2,6-di-*tert*-bu-

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[15] The absorption at 632 nm is considered to be due to the formation of a chlorin, but the amount was less than 5% with respect to the porphyrin.

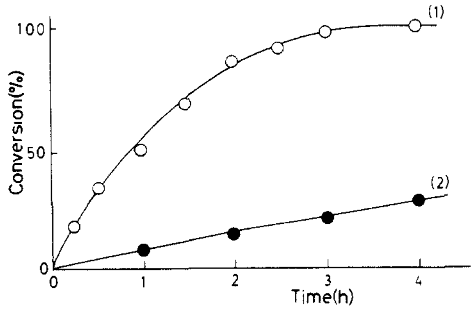


Figure 3. Reaction of (TPP)AlMe (1.0×10^{-2} mol·dm^{-3}) with 2-*tert*-butyl-4-methoxyphenol (2.0×10^{-2} mol·dm^{-3}) in C_6H_6. Conversion as estimated by the intensities of peaks at 547 and 564 nm in the absorption spectra (Figure 2): (1) upon irradiation at 430 nm; (2) in the dark.

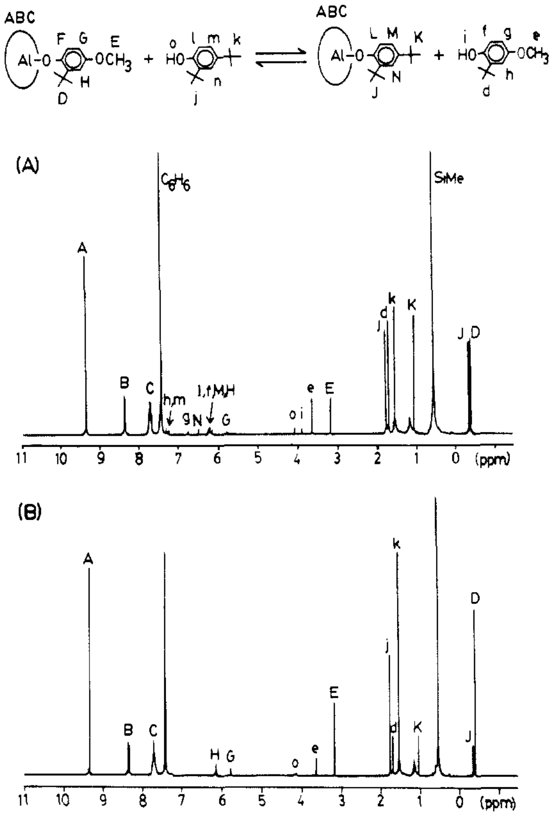


Figure 4. 400-MHz ^{1}H NMR spectra in C_6D_6 of the reaction mixture between **3a** (5.0×10^{-3} mol·dm^{-3}) and 2,4-di-*tert*-butylphenol (5.0×10^{-3} mol·dm^{-3}): (A) after 75 min irradiation at 420 nm; (B) after 95 min in the dark.

tyl-4-methoxyphenol to give **3c**.[14] The reaction scarcely took place even after 148 h in the dark. In contrast, the reaction completed within about 20 h upon irradiation with visible light (λ > 420 nm).

Photochemical Activation of the Metal–Aryloxy Bond in Aluminum Porphyrin in Exchange Reaction with Phenol. An ensuing interest is whether the photoactivation of the aluminum–axial ligand bond is limited to the irreversible substitution reaction involving an aluminum–alkyl bond or it is general for other bonds such as an aluminum–oxygen bond and in reversible ligand exchange reactions. In the system consisting of a hindered phenol and an aluminum porphyrin with hindered phenoxide group, the photoacceleration effect was observed in the reversible exchange reaction between the phenol and the phenoxide group.

Figure 4 shows the ^{1}H NMR spectra of the equimolar mixture of **3a** and 2,4-di-*tert*-butylphenol in C_6D_6 at room temperature under irradiation and in the dark. The signals due to **3a** and 2,4-di-*tert*-butylphenol (such as D, E, and j, k, respectively) decreased with time, while two sets of new signals d–i and J–N appeared and increased. Among these, signals d–i are due to 2-*tert*-butyl-4-methoxyphenol liberated from **3a**. Signals appearing at δ −0.35 (J) and 1.04 (K) are identical with those of the *tert*-butyl groups of **3b** separately prepared from (TPP)AlMe (**1**) and 2,4-di-*tert*-butylphenol. The amount of **3a** as estimated by the NMR signal intensity was in good agreement with that of 2,4-di-*tert*-butylphenol, and the amount of **3b** was also in good agreement with that of 2-*tert*-butyl-4-methoxyphenol throughout the reaction. Thus, the axial phenoxide group bound to (porphinato)aluminum was confirmed to exchange with phenol under the conditions examined.

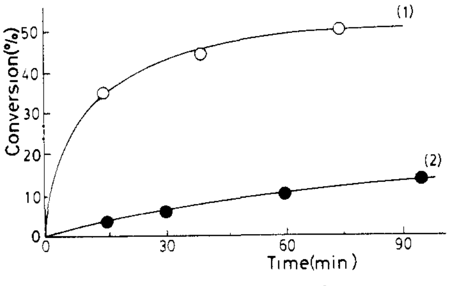
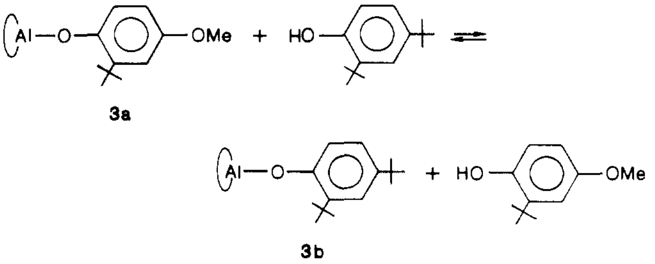


Figure 5. Reaction of **3a** (5.0×10^{-3} mol·dm^{-3}) with 2,4-di-*tert*-butylphenol (5.0×10^{-3} mol·dm^{-3}) in C_6D_6. Conversion as estimated by ^{1}H NMR: (1) upon irradiation at 420 nm; (2) in the dark.



As shown in Figure 5, this ligand exchange reaction attained the equilibrium within about 1.5 h upon irradiation with visible light at 420 nm, where the two types of aluminum porphyrins **3a** and **3b** were present in about an equimolar ratio. On the contrary, the reaction in the dark attained the equilibrium in more than 35 h to furnish the same mole ratio of **3a** and **3b** as observed upon irradiation.

The quantum yield for the ligand exchange reaction between **3a** and 2,4-di-*tert*-butylphenol was found to be $(5.5 \pm 0.5) \times 10^{-1}$ upon irradiation with visible light of the wavelength of 420 nm at room temperature.

The exchange between **3a** and the corresponding phenol, one of the products of the above reaction, is of course taking place. The exchange of phenoxy groups between the molecules of **3a**, for example, is considered to also take place.[16] These exchanges should also be accelerated by the effect of light, although not directly observed in the present experiment.

Related Reactions of Aluminum and Zinc Porphyrins. The effect of visible light was also observed in other reactions of (TPP)AlR (R = methyl, ethyl). Irradiation with visible light brought about an acceleration effect on the reaction of (TPP)AlEt (**2**) with thiol such as ethanethiol, 1-propanethiol, and 2-methyl-2-propanethiol to form the corresponding aluminum thiolate complex. For example, the reaction between (TPP)AlEt (**2**) and a large excess (ca. 5-fold) of 1-propanethiol was completed within 1 h upon irradiation, while it took 2 weeks to be completed in the dark. The reaction of (TPP)AlEt (**2**) with alcohol to give (porphinato)aluminum alkoxide was similarly accelerated upon irradiation with visible light. The effect of irradiation with visible light was also observed in the conjugate addition reaction of (TPP)AlEt (**2**) with vinyl ketone[13b] and in the addition of (TPP)AlEt (**2**) to carbon dioxide in the presence of 1-methylimidazole.[13a]

The acceleration effect of irradiation with visible light was also observed in the reaction of (*N*-methyltetraphenylporphinato)zinc ethyl ((NMTPP)ZnEt). For example, the reaction of (NMTPP)ZnEt with hindered phenols such as 2,6-di-*tert*-bu-

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[16] For the related exchange of alkoxyl and carboxyl groups on aluminum porphyrin, see: Asano, S.; Aida, T.; Inoue, S. *Macromolecules* **1985**, *18*, 2057.

tyl-4-methoxyphenol and 2,6-di-*tert*-butyl-4-methylphenol[14] or with thiol with a bulky group such as 2-methyl-2-propanethiol[17] proceeded upon irradiation with visible light, whereas the reaction hardly took place in the dark. In the reaction of (NMTPP)ZnEt with the mixture of a secondary amine and carbon dioxide (=dialkylcarbamic acid) to give an (*N*-methyltetraphenylporphinato)zinc dialkylcarbamate, irradiation with visible light also brought about an acceleration of the reaction.[18]

Conclusion. All the observations presented above clearly demonstrate that the central metal–axial ligand bond, not only aluminum-alkyl and zinc-alkyl bonds but also an aluminum-aryloxy bond, is activated via the excitation of the porphyrin macrocycle, although these bonds may not be directly excited by visible light. Indirect photoactivation of the metal–ligand bond of aluminum (and zinc) porphyrins results in a remarkable rate enhancement in the irreversible and reversible ligand exchange reactions.

It has been known that the photoactivation of a transition-metal–axial ligand bond in metalloporphyrins and related complexes brings about the free-radical dissociation, leading to the change in the valence of the central metal,[6,19] ion dissociation,[20] or dissociation and/or exchange of a coordinating ligand such as carbon monoxide.[21] Although the metal–carbon bond in (TPP)AlMe, (TPP)AlEt, and (NMTPP)ZnEt may be homolytically cleaved slowly in the absence of protic compounds,[8,9] the possible homolytic mechanism may be excluded in the present reaction systems of aluminum and zinc porphyrin with protic compounds by the fact, for example, that, in the ESR spectroscopic studies of the reaction mixture between (NMTPP)ZnEt (2.5×10^{-2} mol·dm^{-3}) and 2,6-di-*tert*-butyl-4-methylphenol (1.25×10^{-1} mol·dm^{-3}) upon concurrent irradiation, no phenoxy radical was detected even in the presence of a large excess of α-phenyl *N*-*tert*-butylnitrone as a trapping agent. The ion dissociation mechanism is unlikely in nonpolar solvents employed here such as benzene.

Therefore, these ligand exchanges are considered to proceed probably by the nucleophilic attack of the metal–carbon or –oxygen group toward a protic compound such as phenol, alcohol, thiol, or carbamic acid. In fact, the rate of the reaction of (TPP)AlEt, for example, with a protic compound in the dark increased with decreasing the pK_a value: ROH < ArOH < RCO_2H and RSH < ArSH < RCOSH. The rate-enhancing effect of the axial ligation with 1-methylimidazole, an electron-donating ligand, observed in the reaction of (TPP)AlEt with phenol or methyl vinyl ketone also indicates the nucleophilic attack of an aluminum–ethyl group. Thus, the electron density on the metal–carbon or –oxygen bond is considered to be affected by the photoexcitation of the peripheral porphyrin macrocycle upon irradiation with visible light. Taking into account the fact that the reaction of (TPP)AlMe with 2-*tert*-butyl-4-methoxyphenol is accelerated upon irradiation at either the Soret band (430 nm) or Q-band (563 nm) of (TPP)AlMe with the quantum yields comparable to each other, the S_1 excited state is considered to be responsible for the enhancement of the nucleophilic reactivity of the axial ligand of aluminum porphyrin in the reaction with protic compounds.

Experimental Section

Materials. Trialkylaluminums (Me_3Al, Et_3Al) were purified by distillation under reduced pressure in nitrogen. Benzene and benzene-d_6 were dried by refluxing over sodium wire and distilled in nitrogen atmosphere. Phenols were recrystallized from hexane.

(5,10,15,20-Tetraphenylporphinato)aluminum methyl ((TPP)AlMe, **1**) was prepared similarly to (TPP)AlEt[13a] by the reaction of the free-base porphyrin (0.3 mmol)[22] and $AlMe_3$ (0.5 mmol) in benzene (20 mL) under nitrogen atmosphere, followed by evaporation to dryness to remove excess $AlMe_3$. **3a**–**3c** were prepared by the equimolar reactions of **1** with the corresponding phenols in benzene at room temperature under nitrogen atmosphere, followed by evaporation to dryness. Anal. Calcd for **3a** ($C_{55}H_{43}O_2Al$): C, 80.66; H, 5.29; N, 6.84; Al, 3.29. Found: C, 80.48; H, 5.53; N, 6.65; Al, 3.50.

Procedures. (i) Reaction of (TPP)AlMe (1) with Phenol. To a benzene solution (2 mL) of **1** (0.03 mmol) in a nitrogen-purged 10-mL flask equipped with a three-way stopcock and wrapped in aluminum foil was added a benzene solution (1 mL) of 2-*tert*-butyl-4-methoxyphenol (0.06 mmol) in a nitrogen stream at room temperature. For the dark reaction, a portion of the reaction mixture was immediately transferred into a nitrogen-purged quartz cell (optical path length 0.01 cm) fitted with a three-way stopcock and wrapped in aluminum foil and allowed to stand at room temperature. The reaction under irradiation was carried out similarly by illuminating the quartz cell containing the reaction mixture with a 500-W Xe lamp (Ushio UXL-500D) placed apart from the cell by about 35 cm, where the light is monochromatized with a band-pass filter (λ = 430 or 563 nm, bandwidth 10 nm) attached to a Pyrex round cell (optical path length 1 cm) filled with water. In both cases, the yield of **3a** was determined by the absorption spectra of the reaction mixture.

(ii) Reaction of 3a with Phenol. In a 50-mL flask equipped with a three-way stopcock and wrapped in aluminum foil, benzene-d_6 solutions, respectively, of **3a** (1.0×10^{-2} mol·dm^{-3}) and 2,4-di-*tert*-butylphenol (1.0×10^{-2} mol·dm^{-3}) were mixed in an equal volume ratio (2 mL) under nitrogen atmosphere at room temperature. For the dark reaction, a portion of the above mixture was transferred in a nitrogen stream into an NMR tube (Φ = 5 mm) wrapped in aluminum foil and allowed to stand at room temperature. For the reaction under irradiation, a portion of the above mixture was transferred into a quartz cell (optical path length 1 cm) equipped with a three-way stopcock and irradiated similarly to the procedures described in i. In both cases, the yield of the product **3b** was determined by ^1H NMR analysis of the reaction mixture.

(iii) Determination of Quantum Yield. Quantum yields were determined from the difference between the yields of the product in the reactions upon irradiation and in the dark (Figures 3 or 5), taking into account the transmitted light intensity, which was constantly monitored by an Anritsu ML96B optical power meter.

Measurements. Absorption spectra were recorded on Hitachi Type-340 and Jasco Ubest-50 spectrophotometers. ^1H NMR spectra were measured with JEOL Type GSX-270 and GX-400 spectrometers and the chemical shifts determined with respect to C_6H_6 (δ 7.40) as internal standard.

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