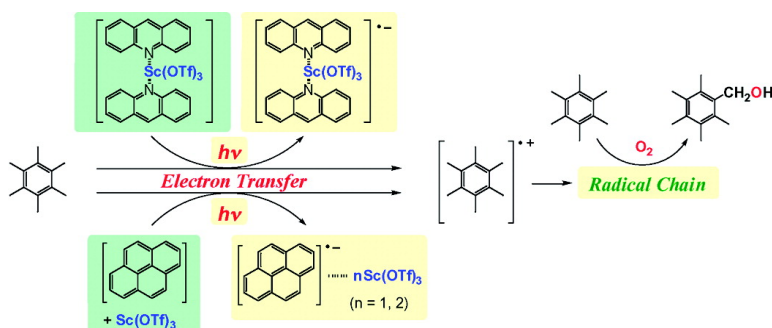


# Scandium Ion-Promoted Photoinduced Electron Transfer from Electron Donors to Acridine and Pyrene. Essential Role of Scandium Ion in Photocatalytic Oxygenation of Hexamethylbenzene

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## Scandium Ion-Promoted Photoinduced Electron Transfer from Electron Donors to Acridine and Pyrene. Essential Role of Scandium Ion in Photocatalytic Oxygenation of Hexamethylbenzene

Shunichi Fukuzumi,\* Junpei Yuasa, Naoya Satoh, and Tomoyoshi Suenobu

Contribution from the Department of Material and Life Science, Graduate School of Engineering, Osaka University, CREST, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan

Received December 11, 2003; E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

**Abstract:** Photoinduced electron transfer from a variety of electron donors including alkylbenzenes to the singlet excited state of acridine and pyrene is accelerated significantly by the presence of scandium triflate [Sc(OTf)<sub>3</sub>] in acetonitrile, whereas no photoinduced electron transfer from alkylbenzenes to the singlet excited state of acridine or pyrene takes place in the absence of Sc(OTf)<sub>3</sub>. The rate constants of the Sc(OTf)<sub>3</sub>-promoted photoinduced electron-transfer reactions ( $k_{\text{et}}$ ) of acridine to afford the complex between acridine radical anion and Sc(OTf)<sub>3</sub> remain constant under the conditions such that all the acridine molecules form the complex with Sc(OTf)<sub>3</sub>. In contrast to the case of acridine, the  $k_{\text{et}}$  value of the Sc(OTf)<sub>3</sub>-promoted photoinduced electron transfer of pyrene increases with an increase in concentration of Sc(OTf)<sub>3</sub> to exhibit first-order dependence on [Sc(OTf)<sub>3</sub>] at low concentrations, changing to second-order dependence at high concentrations. The first-order and second-order dependence of  $k_{\text{et}}$  on [Sc(OTf)<sub>3</sub>] is ascribed to the 1:1 and 1:2 complexes formation between pyrene radical anion and Sc(OTf)<sub>3</sub>. The positive shifts of the one-electron redox potentials for the couple between the singlet excited state and the ground-state radical anion of acridine and pyrene in the presence of Sc(OTf)<sub>3</sub> as compared to those in the absence of Sc(OTf)<sub>3</sub> have been determined by adapting the free energy relationship for the photoinduced electron-transfer reactions. The Sc(OTf)<sub>3</sub>-promoted photoinduced electron transfer from hexamethylbenzene to the singlet excited state of acridine or pyrene leads to efficient oxygenation of hexamethylbenzene to produce pentamethylbenzyl alcohol which is further oxygenated under prolonged photoirradiation of an O<sub>2</sub>-saturated acetonitrile solution of hexamethylbenzene in the presence of acridine or pyrene which acts as a photocatalyst together with Sc(OTf)<sub>3</sub>. The photocatalytic oxygenation mechanism has been proposed based on the studies on the quantum yields, the fluorescence quenching, and direct detection of the reaction intermediates by ESR and laser flash photolysis.

### Introduction

Since photoexcitation induces significant enhancement in the reactivity of electron transfer, photochemical reactions via photoinduced electron transfer have been explored extensively.<sup>1–15</sup> In particular, there have been a number of reports on photoin-

duced electron-transfer reactions of carbonyl compounds.<sup>9–15</sup> Photoexcitation of carbonyl compounds with lowest  $n\text{-}\pi^*$  singlet excited states generally results in formation of the nonfluorescent triplet excited state via the fast intersystem crossing.<sup>16</sup> Thus, the most photochemical reactions of carbonyl compounds are known to undergo via the triplet excited states.<sup>9–19</sup> In the case

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of photoinduced electron transfer reactions, however, the oxidizing power of the triplet excited state is generally lower than that of the singlet excited state because of the lower excitation energy. Accordingly, electron donors which can be employed in the photoinduced electron transfer reactions of carbonyl compounds have been limited to relatively strong reductants such as ketene silyl acetals,<sup>17</sup> allylic stannanes,<sup>11,18</sup> and amines.<sup>19</sup> The promoting effects of metal ions on the photoinduced electron transfer have made it possible to expand the scope of photoinduced electron-transfer reactions of carbonyl compounds.<sup>20–23</sup> However, such promoting effects of metal ions on photoinduced electron transfer have so far been limited to carbonyl compounds which can form the ground-state complexes with metal ions. As such, no photocatalytic system using sensitizers which have no interaction with metal ions at the ground state has ever been reported.

We report herein remarkable promoting effects of scandium triflate, Sc(OTf)<sub>3</sub>, on photoinduced electron transfer from a variety of electron donors to the singlet excited state of not only acridine which can form the ground-state complex with Sc(OTf)<sub>3</sub> but also pyrene which has no interaction with Sc(OTf)<sub>3</sub> in the ground state. Although the oxidizing ability of the singlet excited state of pyrene or acridine is too weak to oxidize alkylbenzenes,<sup>24</sup> the Sc(OTf)<sub>3</sub>-promoted photoinduced electron transfer from hexamethylbenzene to the singlet excited state of pyrene and acridine leads to efficient oxygenation of hexamethylbenzene to produce pentamethylbenzyl alcohol as the primary oxygenated product. Without Sc(OTf)<sub>3</sub>, pyrene or acridine has no ability to photocatalyze the oxygenation of hexamethylbenzene. Thus, the essential role of Sc(OTf)<sub>3</sub> in the photocatalytic reaction found in this study will expand the scope of photocatalytic reactions via photoinduced electron transfer. The photocatalytic mechanism is examined in detail based on the studies on the quantum yields, the fluorescence quenching

experiments, and direct detection of the reaction intermediates by ESR and laser flash photolysis.

## Experimental Section

**Materials.** 10-Methyl-9,10-dihydroacridine (AcrH<sub>2</sub>) was prepared from 10-methyl-acridinium iodide (AcrH<sup>+</sup>I<sup>-</sup>), which was obtained by the reaction of acridine with methyl iodide in acetone, by reduction with NaBH<sub>4</sub> in methanol and purified by recrystallization from ethanol.<sup>25</sup> *p*-MeO-*N,N*-dimethylaniline was prepared according to the literature.<sup>26</sup> The dimeric 1-benzyl-1,4-dihydronicotinamide dimer [(BNA)<sub>2</sub>] was prepared according to the literature.<sup>27</sup> Pyrene (Py), acridine (AcrN), ferrocene, *N,N*-dimethylaniline, 1,4-dimethoxybenzene, 1,3-dimethoxybenzene, 1,2,4-trimethoxybenzene, hexamethylbenzene, pentamethylbenzene, naphthalene, 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, *p*-xylene, *o*-xylene, *m*-xylene, ethylbenzene, toluene, and benzene were obtained commercially and purified by the standard methods.<sup>28</sup> 1,1'-Dimethylferrocene, 1,2,4,5-tetramethyl-1,4-cyclohexadiene, pentamethylbenzyl alcohol and 1,2,4-trimethoxybenzene were obtained from Aldrich. Sodium iodide (NaI) was obtained from Nakalai Tesque, Inc. Scandium trifluoromethanesulfonate, Sc(OTf)<sub>3</sub> (99%, F. W. = 492.16) was obtained from Pacific Metals Co., Ltd. (Taiheiyō Kinzoku). 1,4-Dioxane was obtained commercially from Tokyo Kasei Organic Chemicals. Tetra-*n*-butylammonium hexafluorophosphate used as a supporting electrolyte for the electrochemical measurements also obtained commercially from Tokyo Kasei Organic Chemicals. Acetonitrile (MeCN) and propionitrile (EtCN) used as solvents were purified and dried by the standard procedure.<sup>28</sup> [<sup>2</sup>H<sub>3</sub>]Acetonitrile (CD<sub>3</sub>CN) was obtained from EURI SO-TOP, CEA, France.

**Reaction Procedure.** Typically, hexamethylbenzene (2.0 × 10<sup>-3</sup> M) was added to an NMR tube that contained a CD<sub>3</sub>CN solution (600 μL) of Py (2.0 × 10<sup>-5</sup> M) or AcrN (2.0 × 10<sup>-5</sup> M) in the presence of Sc(OTf)<sub>3</sub> (4.0 × 10<sup>-2</sup> M) under atmospheric pressure of oxygen. The solution was flushed with oxygen gas for 8 min, and the NMR tube was sealed with a rubber septum. Then, the solution was irradiated with UV-visible light from a xenon lamp (Ushio Model V1-501C) through a cut-off filter (Toshiba UV-31) transmitting λ > 300 nm at 298 K for 5 h. The reaction solution was analyzed by <sup>1</sup>H NMR spectroscopy. The product from photooxygenation of hexamethylbenzene with O<sub>2</sub> in the presence of Sc(OTf)<sub>3</sub> was identified by comparing the <sup>1</sup>H NMR spectra with that of a CD<sub>3</sub>CN solution of pentamethylbenzyl alcohol in the presence of Sc(OTf)<sub>3</sub>. The yield of the reaction was determined based on the concentration of the internal standard, 1,4-dioxane (5.0 × 10<sup>-3</sup> M). <sup>1</sup>H NMR measurements were performed with a Japan Electron Optics JNM-GSX-400 (400 MHz) NMR spectrometer at 298 K. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 298 K); δ (Me<sub>3</sub>Si, ppm): 4.60 (d, J = 4.0 Hz, 2H), 2.23 (s, 6H), 2.21 (s, 9H). The isolation of the preparative scale photocatalytic oxygenation product of hexamethylbenzene was performed as follows. Typically, an MeCN solution of hexamethylbenzene (1.0 × 10<sup>-2</sup> M, 50 mL) was added to the reaction vessel containing an MeCN solution (50 mL) of AcrN (4.0 × 10<sup>-5</sup> M) in the presence of Sc(OTf)<sub>3</sub> (2.0 × 10<sup>-2</sup> M). The solution was flushed with oxygen gas for 20 min. Then, the solution was irradiated with UV-visible light from a xenon lamp (Ushio Model V1-501C) through a cut-off filter (Toshiba UV-31) transmitting λ > 300 nm at 298 K for 7 h. Deionized water (100 mL) was added to the resulting solution containing the products, and the MeCN was removed by vacuum evaporation. The resulting suspension was washed with chloroform. The organic layer was separated and the solvent was removed from

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the reaction mixture by distillation at 313 K under vacuum. The residue was purified by silica gel column chromatography (chloroform as an eluent) to afford pentamethylbenzyl alcohol as a white solid. The isolated yield of pentamethylbenzyl alcohol was determined to be 30%.

**Quantum Yield Determination.** A standard actinometer (potassium ferrioxalate)<sup>29</sup> was used for the quantum yield determination of the photooxygenation of hexamethylbenzene by O<sub>2</sub> in the presence of Sc(OTf)<sub>3</sub> and Py. A square quartz cuvette (10 mm i.d.) which contained an O<sub>2</sub>-saturated MeCN (3.0 cm<sup>3</sup>) of hexamethylbenzene (2.0 × 10<sup>-2</sup> – 5.0 × 10<sup>-2</sup> M), Py (1.0 × 10<sup>-4</sup> M), and Sc(OTf)<sub>3</sub> (4.0 × 10<sup>-2</sup> M) was irradiated by monochromatized light of λ = 335 nm from a Shimadzu spectrofluorophotometer (RF-5000). Under the condition of actinometry experiments, both the actinometer and Py absorbed essentially all the incident light of λ = 335 nm. The light intensity of monochromatized light of λ = 335 nm was determined as 9.3 × 10<sup>-7</sup> einstein dm<sup>-3</sup> s<sup>-1</sup>, 1.8 × 10<sup>-6</sup> einstein dm<sup>-3</sup> s<sup>-1</sup> and 5.7 × 10<sup>-6</sup> einstein dm<sup>-3</sup> s<sup>-1</sup> with the slit width of 10, 15, and 20 nm. The photochemical reaction was monitored using a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 mass spectrometer. The quantum yields were determined from the decrease in the amount of hexamethylbenzene.

**Fluorescence Quenching.** Quenching experiments of the fluorescence of AcrN and Py were carried out on a Shimadzu spectrofluorophotometer (RF-5000). The excitation wavelength of AcrN and (AcrN)<sub>2</sub>-Sc(OTf)<sub>3</sub> complex was λ = 355 nm. The monitoring wavelengths were those corresponding to the maxima of the emission band at λ<sub>max</sub> = 397 nm (AcrN) and λ<sub>max</sub> = 480 nm [(AcrN)<sub>2</sub>-Sc(OTf)<sub>3</sub>]. The excitation wavelength of Py was λ = 335 nm in MeCN. The monitoring wavelength was that corresponding to the maximum of the emission band at λ<sub>max</sub> = 390 nm. Typically, an MeCN solution of AcrN or Py was deaerated by argon purging for 8 min prior to the measurements. Relative fluorescence intensities were measured for MeCN solutions containing Py (1.3 × 10<sup>-6</sup> M) with various electron donors (6.5 × 10<sup>-5</sup> – 4.0 × 10<sup>-1</sup> M) in the presence of Sc(OTf)<sub>3</sub> (0–1.5 × 10<sup>-1</sup> M). Relative fluorescence intensities were also measured for MeCN solutions containing AcrN (1.0 × 10<sup>-4</sup> M) with various electron donors (2.5 × 10<sup>-3</sup> – 1.5 M) in the presence of Sc(OTf)<sub>3</sub> (4.0 × 10<sup>-2</sup> M). There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of a quencher (D). The Stern–Volmer relationship (eq 1) was obtained for

$$I_0/I = 1 + K_{SV}[D] \quad (1)$$

the ratio of the emission intensities in the absence and presence of Sc(OTf)<sub>3</sub> and concentrations of various electron donors (D) used as quenchers. The fluorescence lifetimes of AcrN<sup>30</sup> and (AcrN)<sub>2</sub>-Sc(OTf)<sub>3</sub> complex were determined as τ = 31.0 and 32.2 ns, respectively in deaerated MeCN solution at 298 K by single photon counting using a Horiba NAES-1100 time-resolved spectrofluorophotometer. The fluorescence lifetimes of Py in the absence<sup>31</sup> and in the presence of Sc(OTf)<sub>3</sub> (4.0 × 10<sup>-2</sup>, 8.0 × 10<sup>-2</sup>, 1.2 × 10<sup>-1</sup>, and 1.5 × 10<sup>-1</sup> M) were determined as τ = 295, 256, 171, 163, and 104 ns, respectively, in a deaerated MeCN solution at 298 K. The fluorescence lifetime of Py in the presence of Sc(OTf)<sub>3</sub> (4.0 × 10<sup>-2</sup> M) was also determined as τ = 4.1 ns in O<sub>2</sub>-saturated MeCN at 298 K. The observed quenching rate constants k<sub>q</sub> (K<sub>SV</sub>τ<sup>-1</sup>) were obtained from the Stern–Volmer constants (K<sub>SV</sub>) and the fluorescence lifetime τ.

**Electrochemical Measurements.** The second harmonic ac voltammetry (SHACV) measurements of Py and AcrN in the absence and

presence of Sc(OTf)<sub>3</sub> were carried out with a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M *n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (TBAPF<sub>6</sub>) as a supporting electrolyte at 298 K. The gold working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgNO<sub>3</sub> (0.01 M) reference electrode. The E<sub>red</sub><sup>0</sup> values (vs Ag/AgNO<sub>3</sub>) are converted into those vs SCE by addition of 0.29 V.<sup>32</sup>

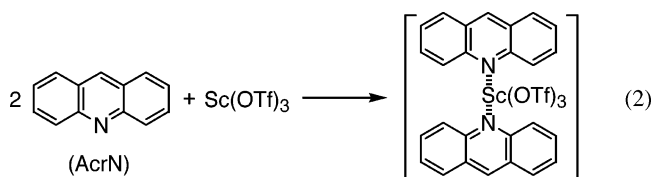
**Laser Flash Photolysis.** A deaerated MeCN solution containing AcrN and hexamethylbenzene was excited by a Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at λ = 355 nm with the power of 20 mJ per pulse. The transient absorption spectra in the photoinduced electron-transfer reactions were measured by using a continuous Xe-lamp (150 W) and a photomultiplier tube (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation at 298 K.

**ESR Measurements.** The ESR spectra of the scandium complexes of acridine radical anion (AcrN<sup>•-</sup>) and pyrene radical anion (Py<sup>•-</sup>) were recorded on a JEOL JES-FA100 spectrometer under irradiation of a high-pressure mercury lamp (USH-1005D) which is focused at the sample cell containing a deaerated EtCN solution of AcrN or Py, (BNA)<sub>2</sub>, and Sc(OTf)<sub>3</sub> (400 μL) in the ESR cavity at 203 K. ESR spectra of electrochemically generated Py<sup>•-</sup> were taken on a JEOL JES-FA100 by using an electrolysis cell designed for ESR measurements.<sup>33</sup> The ESR cell is composed of a helical gold wire with large surface area (12 cm<sup>2</sup>) as the working electrode, which can generate enough Py<sup>•-</sup> to detect the ESR spectra, a platinum wire as a counter electrode, and a silver wire as a reference electrode. The controlled potential electrolysis of Py was carried out in anhydrous deaerated EtCN containing 0.20 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte in the ESR cavity. The ESR spectrum of the Sc(OTf)<sub>3</sub> complex of superoxide radical anion (O<sub>2</sub><sup>•-</sup>) was measured at 203 K by using a JEOL TES-FA100 with low-temperature cooling apparatus. The mixed solution of hexamethylbenzene (6.2 × 10<sup>-2</sup> M), Py (1.0 × 10<sup>-1</sup> M), and Sc(OTf)<sub>3</sub> (5.0 × 10<sup>-2</sup> M) in O<sub>2</sub>-saturated EtCN at 203 K was irradiated by using a high-pressure mercury lamp (USH-1005D) focusing at the sample cell in the ESR cavity. All the ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra. The *g* values and hyperfine splitting constants (hfs) were calibrated by using an Mn<sup>2+</sup> marker. Computer simulation of the ESR spectra was carried out by using ESR<sup>4</sup>II Version 1.2 (Calleo Scientific Software Publisher) on a Macintosh personal computer.

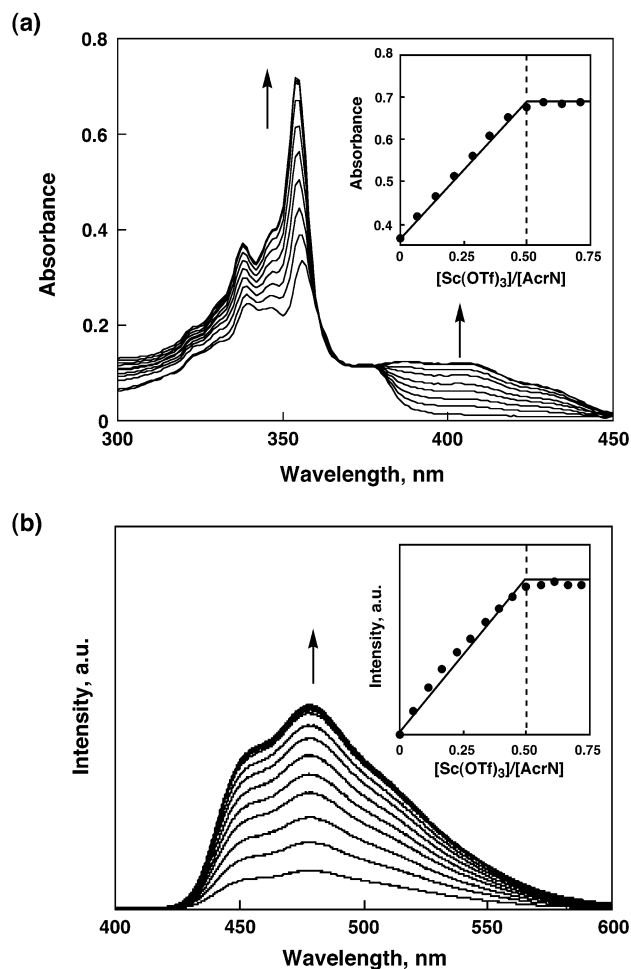
**Spectral Measurements.** The amount of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was determined by titration with iodide ion.<sup>34</sup> The aliquots of the product mixture in MeCN was treated with excess NaI and the amount of I<sub>3</sub><sup>-</sup> formed was determined by the UV–visible spectrum (λ<sub>max</sub> = 365 nm, ε<sub>max</sub> = 28 000 M<sup>-1</sup> cm<sup>-1</sup>)<sup>22</sup> using a Hewlett-Packard 8453 diode array spectrophotometer with a quartz cuvette (path length = 2 mm) at 298 K.

## Results and Discussion

**Sc(OTf)<sub>3</sub>-Promoted Photoinduced Electron Transfer.** Acridine (AcrN) forms a 2:1 complex with Sc(OTf)<sub>3</sub> (eq 2) as indicated by the spectral titration in MeCN (Figure 1a).



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**Figure 1.** (a) UV–visible absorption spectral changes and (b) fluorescence spectral changes observed upon addition of  $\text{Sc}(\text{OTf})_3$  to an MeCN solution of AcrN ( $3.5 \times 10^{-5}$  M) at 298 K. Inset: (a) absorption changes at  $\lambda = 356$  nm and (b) fluorescence changes at  $\lambda = 479$  nm.

There is weak fluorescence of AcrN at 380 nm (Supporting Information S1). When AcrN forms a complex with  $\text{Sc}(\text{OTf})_3$ ,  $(\text{AcrN})_2\text{-Sc}(\text{OTf})_3$ , strong fluorescence of the  $\text{Sc}(\text{OTf})_3$  complex of AcrN appears at 480 nm (Figure 1b). The formation of a 2:1 complex is confirmed by the titration of the fluorescence spectra (inset of Figure 1b).

In contrast to the case of AcrN, there was no change in the absorption and fluorescence spectra of pyrene (Py) in the presence of  $\text{Sc}(\text{OTf})_3$ . This indicates that there is no interaction of  $\text{Sc}(\text{OTf})_3$  with Py and the singlet excited state ( $^1\text{Py}^*$ ).<sup>35</sup>

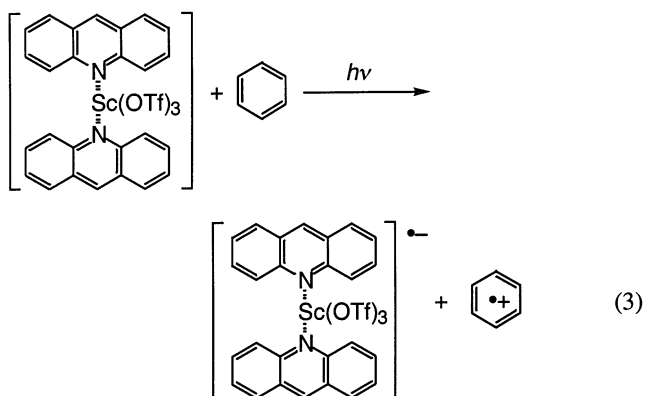
No fluorescence quenching of AcrN by benzene is observed in MeCN. When AcrN forms the complex with  $\text{Sc}(\text{OTf})_3$ , the fluorescence maximum is shifted to  $\lambda = 480$  nm (Figure 1b) and the fluorescence lifetime of the  $(\text{AcrN})_2\text{-Sc}(\text{OTf})_3$  complex (32.2 ns) becomes slightly longer as compared to that of the singlet excited-state AcrN ( $^1\text{AcrN}^*$ ) (31.0 ns) (see Experimental Section). In contrast to the case in the absence of  $\text{Sc}(\text{OTf})_3$ , the fluorescence of the  $(\text{AcrN})_2\text{-Sc}(\text{OTf})_3$  complex is efficiently

**Table 1.** Oxidation Potentials ( $E^0_{\text{ox}}$ ) of Various Electron Donors and Fluorescence Quenching Rate Constants ( $k_q$ ) of AcrN ( $1.0 \times 10^{-4}$  M) by Various Electron Donors in the Absence and Presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) in Deaerated MeCN at 298 K

no.	electron donor	$E^0_{\text{ox}}$ , V vs SCE	in the absence of $\text{Sc}(\text{OTf})_3$ , $k_q$ , $\text{M}^{-1} \text{s}^{-1}$	in the presence of $\text{Sc}(\text{OTf})_3$ , $k_q$ , $\text{M}^{-1} \text{s}^{-1}$
1	1,1'-dimethylferrocene	0.26	$1.2 \times 10^{10}$	$2.6 \times 10^{10}$
2	ferrocene	0.37	$1.2 \times 10^{10}$	$2.9 \times 10^{10}$
3	10-methyl-9,10-dihydroacridine	0.81	$1.0 \times 10^{10}$	$1.5 \times 10^{10}$
4	1,2,4-trimethoxybenzene	1.12	$7.7 \times 10^8$	<sup>a</sup>
5	1,4-dimethoxybenzene	1.34	$4.6 \times 10^7$	<sup>a</sup>
6	hexamethylbenzene	1.49		$1.5 \times 10^{10}$
7	1,2,3,4-tetramethylbenzene	1.71		$1.4 \times 10^{10}$
8	1,2,4-trimethylbenzene	1.79		$1.3 \times 10^{10}$
9	1,2,3-trimethylbenzene	1.88		$1.3 \times 10^{10}$
10	<i>p</i> -xylene	1.93		$1.4 \times 10^{10}$
11	<i>o</i> -xylene	1.98		$1.2 \times 10^{10}$
12	<i>m</i> -xylene	2.02		$9.6 \times 10^9$
13	ethylbenzene	2.14		$7.0 \times 10^8$
14	toluene	2.20		$6.0 \times 10^8$
15	benzene	2.35		$7.4 \times 10^6$

<sup>a</sup> Not determined due to complex formation between electron donors and  $\text{Sc}^{3+}$ .

quenched by benzene and other alkylbenzene derivatives (see Supporting Information S2). The fluorescence quenching occurs by photoinduced electron transfer from benzene to singlet excited state of the  $(\text{AcrN})_2\text{-Sc}(\text{OTf})_3$  complex (eq 3) as discussed below.



The fluorescence quenching rate constants ( $k_q$ ) in the absence and presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) are summarized in Table 1, together with the one-electron oxidation potentials of the electron donors ( $E^0_{\text{ox}}$ ) employed in this study. A plot of  $\log k_q$  vs  $E^0_{\text{ox}}$  is shown in Figure 2, where the  $k_q$  value increases with decreasing the  $E^0_{\text{ox}}$  value to reach a diffusion-limited value ( $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>24</sup> This indicates that the fluorescence quenching proceeds via electron transfer from the electron donors to  $^1\text{AcrN}^*$  and  $^1[(\text{AcrN})_2\text{-Sc}(\text{OTf})_3]^*$  in the absence and presence of  $\text{Sc}(\text{OTf})_3$ , respectively.

The dependence of the activation Gibbs energy of photoinduced electron transfer ( $\Delta G^\ddagger$ ) on the Gibbs energy change of electron transfer ( $\Delta G^0_{\text{et}}$ ) has well been established as given by the Gibbs energy relationship (eq 4),<sup>24</sup> where  $\Delta G^\ddagger_0$  is the

$$\Delta G^\ddagger = (\Delta G^0_{\text{et}}/2) + [(\Delta G^0_{\text{et}}/2)^2 + (\Delta G^\ddagger_0)^2]^{1/2} \quad (4)$$

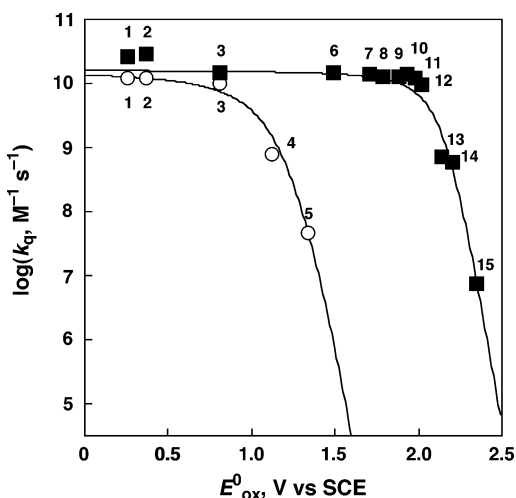
intrinsic barrier that represents the activation Gibbs energy when the driving force of electron transfer is zero, i.e.,  $\Delta G^\ddagger = \Delta G^\ddagger_0$

(32) Mann, C. K.; Barnes, K. K. In *Electrochemical Reaction in Nonaqueous Systems*; Marcel Dekker: New York, 1970.

(33) Ohya-Nishiguchi, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2064.

(34) Mair, R. D.; Graupner, A. *J. Anal. Chem.* **1964**, *36*, 194.

(35)  $\text{Sc}^{3+}$  probably promotes intersystem crossing process of  $^1\text{Py}^*$  and diminishes the fluorescence lifetime of the Py. However such interaction is not so strong to form a complex.



**Figure 2.** Plots of  $\log k_q$  vs  $E^0_{\text{ox}}$  for the fluorescence quenching of AcrN ( $1.0 \times 10^{-4}$  M) by various electron donors in the absence (○) and presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M, ■) in deaerated MeCN at 298 K. Numbers at each point correspond to those in Table 1.

at  $\Delta G^0_{\text{et}} = 0$ . On the otherhand  $\Delta G^{\ddagger}$  values are related to the rate constant of electron transfer ( $k_{\text{et}}$ ) as given by eq 5, where

$$\Delta G^{\ddagger} = (2.3RT/F) \log[Z(k_{\text{et}}^{-1} - k_{\text{diff}}^{-1})] \quad (5)$$

$Z$  is the collision frequency that is taken as  $1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ,  $F$  is the Faraday constant, and  $k_{\text{diff}}$  is the diffusion rate constant in MeCN ( $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>24</sup> The  $\Delta G^0_{\text{et}}$  value is obtained from the one-electron oxidation potentials of electron donors ( $E^0_{\text{ox}}$ ) and the one-electron reduction potential of  $^1\text{AcrN}^*$  in the absence and presence of  $\text{Sc}(\text{OTf})_3$  ( $E^0_{\text{red}}^*$ ). The plot of Figure 2 is fitted using eqs 4 and 5 as shown by the solid line, which agrees with the experimental results. The best fit lines shown in Figure 2 give the  $E^0_{\text{red}}^*$  values (1.29 V vs SCE in the absence of  $\text{Sc}(\text{OTf})_3$  and 2.23 V vs SCE in the presence of  $\text{Sc}(\text{OTf})_3$ ) and  $\Delta G^{\ddagger}_0$  value (3.94 kcal mol<sup>-1</sup> in the absence of  $\text{Sc}(\text{OTf})_3$  and 2.64 kcal mol<sup>-1</sup> in the presence of  $\text{Sc}(\text{OTf})_3$ ). As compared to the one-electron reduction potential of  $^1\text{AcrN}^*$  in the absence of  $\text{Sc}(\text{OTf})_3$ , the  $E^0_{\text{red}}^*$  value of  $^1[(\text{AcrN})_2-\text{Sc}(\text{OTf})_3]^*$  is significantly shifted to the positive direction (0.94 V). Such a large positive shift in the one-electron reduction potential indicates that the electron acceptor ability of  $^1\text{AcrN}^*$  is drastically enhanced by the complex formation with  $\text{Sc}(\text{OTf})_3$ .

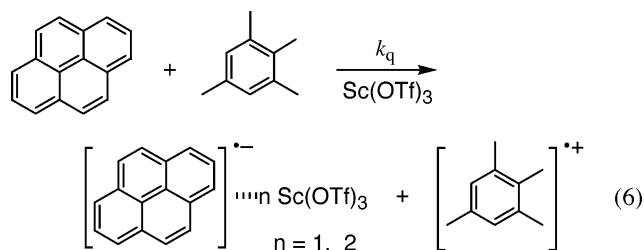
Such a large positive shift in the one-electron reduction potential of  $^1\text{AcrN}^*$  in the presence of  $\text{Sc}(\text{OTf})_3$  is also observed in the case of  $^1\text{Py}^*$ . Irradiation of the absorption band of Py results in fluorescence at  $\lambda = 391$  nm in MeCN. The fluorescence of Py is quenched efficiently by relatively strong electron donors such as methoxybenzenes, *N,N*-dimethylanilines and ferrocenes (see typical Stern–Volmer plots in Supporting Information S3). When relatively weak electron donors such as 1,2,3,5-tetramethylbenzene are employed, no fluorescence quenching is observed. When  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) is added to this system, however, the Py fluorescence is quenched

**Table 2.** Oxidation Potentials ( $E^0_{\text{ox}}$ ) of Various Electron Donors and Fluorescence Quenching Rate Constants ( $k_q$ ) of Py ( $1.3 \times 10^{-6}$  M) by Various Electron Donors in the Absence and Presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) in Deaerated MeCN at 298 K

no.	electron donor	$E^0_{\text{ox}}$ , V vs SCE	in the absence of $\text{Sc}(\text{OTf})_3$ , $k_q$ , $\text{M}^{-1} \text{ s}^{-1}$	in the presence of $\text{Sc}(\text{OTf})_3$ , $k_q$ , $\text{M}^{-1} \text{ s}^{-1}$
1	1,1'-dimethylferrocene	0.26	$2.0 \times 10^{10}$	$1.9 \times 10^{10}$
2	ferrocene	0.37	$1.9 \times 10^{10}$	$1.9 \times 10^{10}$
3	<i>N,N</i> -dimethylaniline	0.71	$1.7 \times 10^{10}$	<sup>a</sup>
4	10-methyl-9,10-dihydroacridine	0.81	$1.3 \times 10^{10}$	$6.8 \times 10^9$
5	1,2,4-trimethoxybenzene	1.12	$6.4 \times 10^9$	<sup>a</sup>
6	1,4-dimethoxybenzene	1.34	$1.6 \times 10^8$	<sup>a</sup>
7	1,2,4,5-tetramethyl-1,4-cyclohexadiene	1.38	$2.2 \times 10^7$	<sup>b</sup>
8	1,2-dimethoxybenzene	1.45	$3.7 \times 10^6$	<sup>a</sup>
9	1,3-dimethoxybenzene	1.49	$2.0 \times 10^6$	<sup>a</sup>
10	hexamethylbenzene	1.49		$7.3 \times 10^7$
11	pentamethylbenzene	1.58		$2.7 \times 10^7$
12	naphthalene	1.60		$2.6 \times 10^7$
13	1,2,4,5-tetramethylbenzene	1.63		$2.1 \times 10^7$
14	1,2,3,5-tetramethylbenzene	1.71		$5.9 \times 10^6$

<sup>a</sup> Not determined due to complex formation between electron donors and  $\text{Sc}^{3+}$ . <sup>b</sup> Not determined.

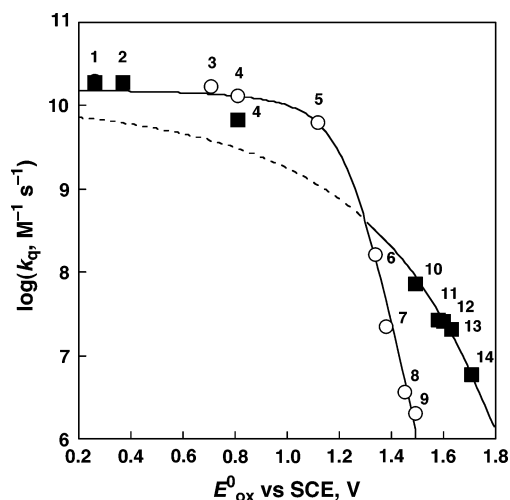
efficiently by 1,2,3,5-tetramethylbenzene in the presence of  $\text{Sc}(\text{OTf})_3$  (eq 6).



Other weak electron donors can also quench the Py fluorescence in the presence of  $\text{Sc}(\text{OTf})_3$  (see Supporting Information S3). The  $k_q$  values in the absence and presence of a constant concentration of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) are summarized in Table 2, where the one-electron oxidation potentials of the electron donors ( $E^0_{\text{ox}}$ ) employed in this study are also listed.

The plots of  $\log k_q$  vs  $E^0_{\text{ox}}$  are shown in Figure 3, where the  $k_q$  value increases with decreasing the  $E^0_{\text{ox}}$  value to reach a diffusion-limited value ( $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>24</sup> Such dependence of  $k_q$  on  $E^0_{\text{ox}}$  is typical for photoinduced electron-transfer reactions,<sup>24</sup> and thus, the fluorescence quenching may proceed via electron transfer from the electron donors to the  $^1\text{Py}^*$  in the absence and presence of  $\text{Sc}(\text{OTf})_3$ .

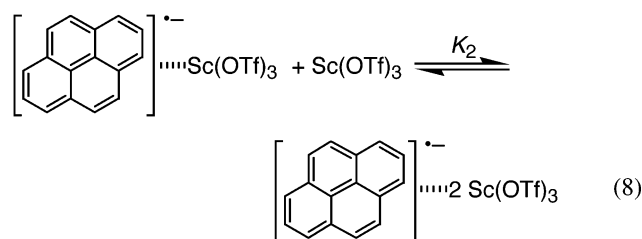
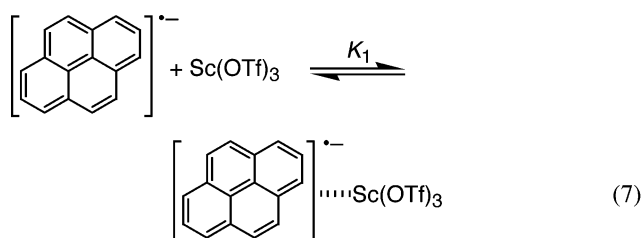
The plots of Figure 3 can also be fitted using eqs 4 and 5 as shown by the solid line, which agrees with the experimental results. The best fit lines shown in Figure 3 give the  $E^0_{\text{red}}^*$  values (1.24 V vs SCE in the absence of  $\text{Sc}(\text{OTf})_3$  and 1.83 V vs SCE in the presence of  $\text{Sc}(\text{OTf})_3$ ) and  $\Delta G^{\ddagger}_0$  (2.46 kcal mol<sup>-1</sup> in the absence of  $\text{Sc}(\text{OTf})_3$  and 7.08 kcal mol<sup>-1</sup> in the presence of  $\text{Sc}(\text{OTf})_3$ ). As compared with the one-electron reduction potential of  $^1\text{Py}^*$  (1.24 V), the  $E^0_{\text{red}}^*$  in the presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) is significantly shifted to the positive direction (0.59 V). Such a large positive shift in the one-electron reduction potential indicates that the electron acceptor ability of  $^1\text{Py}^*$  as



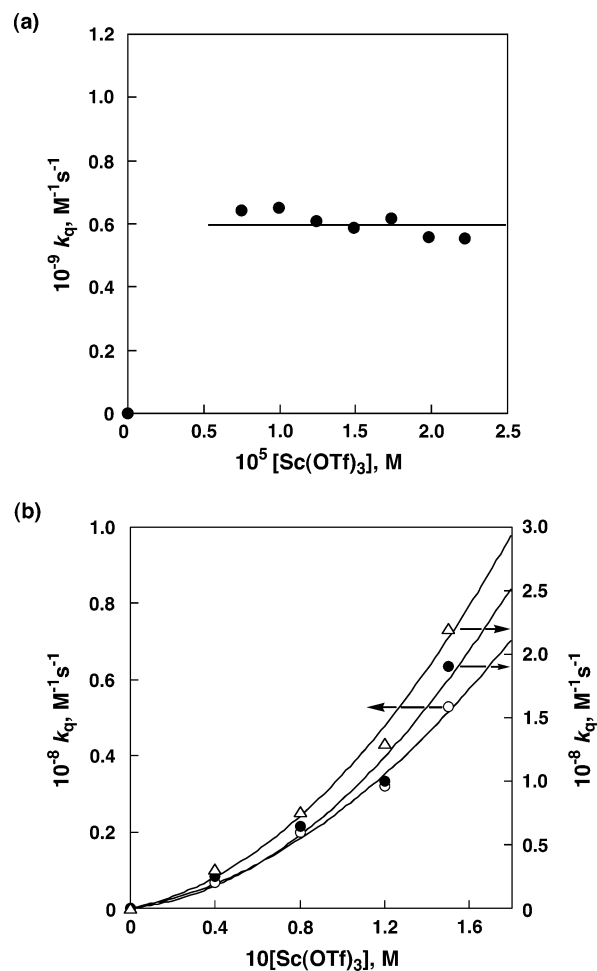
**Figure 3.** Plots of  $\log k_q$  vs  $E^0_{\text{ox}}$  for the fluorescence quenching of Py ( $1.3 \times 10^{-6}$  M) by various electron donors in the absence (○) and presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M, ■) in deaerated MeCN at 298 K. Numbers correspond to those in Table 2.

well as  $^1[(\text{AcrN})_2-\text{Sc}(\text{OTf})_3]^*$  is significantly enhanced as compared to that in the absence of  $\text{Sc}(\text{OTf})_3$ .<sup>36</sup>

The  $k_q$  value for photoinduced electron transfer from ethylbenzene to  $^1\text{AcrN}^*$  in the presence of excess  $\text{Sc}(\text{OTf})_3$  relative to  $\text{AcrN}$  remains constant independent of  $[\text{Sc}(\text{OTf})_3]$  as shown in Figure 4a. This indicates the photoinduced electron transfer occurs from the singlet excited state of the 2:1 complex with  $\text{Sc}^{3+}$  ( $(\text{AcrN})_2-\text{Sc}(\text{OTf})_3$ ). In the case of photoinduced electron transfer from 1,2,3,5-tetramethylbenzene and the other electron donors to  $^1\text{Py}^*$ , the dependence of  $k_q$  on  $[\text{Sc}^{3+}]$  are quite different from the case of  $^1\text{AcrN}^*$ . The  $k_q$  value for photoinduced electron transfer from 1,2,3,5-tetramethylbenzene and the other electron donors to  $^1\text{Py}^*$  increases with an increase in  $[\text{Sc}(\text{OTf})_3]$  to exhibit first-order dependence on  $[\text{Sc}(\text{OTf})_3]$  at low concentration changing to second-order dependence on  $[\text{Sc}(\text{OTf})_3]$  as shown in Figure 4b. Such first-order and second-order dependence of  $k_q$  on  $[\text{Sc}(\text{OTf})_3]$  can be explained by the 1:1 and 1:2 complex formation between  $\text{Py}^{*-}$  and  $\text{Sc}(\text{OTf})_3$  as shown in eqs 7 and 8, respectively. In such a case, the one-electron reduction



(36) A large positive shift in the one-electron reduction potentials of the ground-state  $\text{AcrN}$  and  $\text{Py}$  in the presence of  $\text{Sc}(\text{OTf})_3$  is also observed by the electrochemical study.



**Figure 4.** (a) Dependence of  $k_q$  on  $[\text{Sc}(\text{OTf})_3]$  for the fluorescence quenching of  $\text{AcrN}$  ( $3.5 \times 10^{-5}$  M) by ethylbenzene in the presence of  $\text{Sc}(\text{OTf})_3$  in deaerated MeCN at 298 K. (b) Dependence of  $k_q$  on  $[\text{Sc}(\text{OTf})_3]$  for the fluorescence quenching of  $\text{Py}$  ( $1.3 \times 10^{-6}$  M) by 1,2,3,5-tetramethylbenzene (○), 1,2,4,5-tetramethylbenzene (●), and pentamethylbenzene (△) in the presence of  $\text{Sc}(\text{OTf})_3$  in deaerated MeCN at 298 K.

potential of  $\text{Py}$  in the presence of  $\text{Sc}(\text{OTf})_3$  ( $E_{\text{red}}^*$ ) is shifted to positive direction according to the Nernst equation (eq 9), where  $E_{\text{red}}^0$  is the one-electron reduction potential of  $^1\text{Py}^*$  in the absence of  $\text{Sc}(\text{OTf})_3$ ,  $K_1$  and  $K_2$  are the formation constants of 1:1 and 1:2 complexes of  $\text{Py}^{*-}$  and  $\text{Sc}(\text{OTf})_3$ , respectively. If such a change in the energetics of electron transfer (eq 9)

$$E_{\text{red}}^* = E_{\text{red}}^0 + (2.3RT/F) \log \{ K_1 [\text{Sc}(\text{OTf})_3] (1 + K_2 [\text{Sc}(\text{OTf})_3]) \} \quad (9)$$

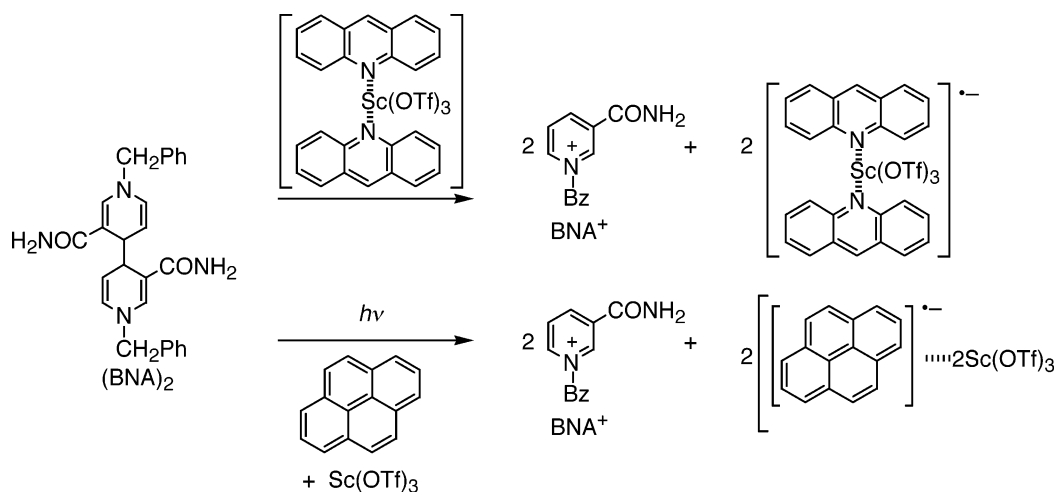
is directly reflected in the transition state of electron transfer, the dependence of the fluorescence quenching rate constant of  $\text{Sc}(\text{OTf})_3$ -promoted electron transfer ( $k_q$ ) on  $[\text{Sc}(\text{OTf})_3]$  may be given by eq 10, where  $k_0$  is the rate constant in the absence of  $\text{Sc}(\text{OTf})_3$ .

$$k_q - k_0 = k_0 K_1 [\text{Sc}(\text{OTf})_3] (1 + K_2 [\text{Sc}(\text{OTf})_3]) \quad (10)$$

From the slopes and intercepts of linear plots of  $(k_q - k_0)/[\text{Sc}(\text{OTf})_3]$  vs  $[\text{Sc}(\text{OTf})_3]$  (Supporting Information S4) are obtained the  $K_2$  values which are listed in Table 3.

**Direct Detection of  $\text{Sc}(\text{OTf})_3$  Complexes with  $\text{AcrN}^{*-}$  and  $\text{Py}^{*-}$ .** The  $\text{Sc}(\text{OTf})_3$ -promoted electron transfer from electron donors to  $\text{AcrN}$  is expected to produce the  $\text{Sc}(\text{OTf})_3$  complex

Scheme 1



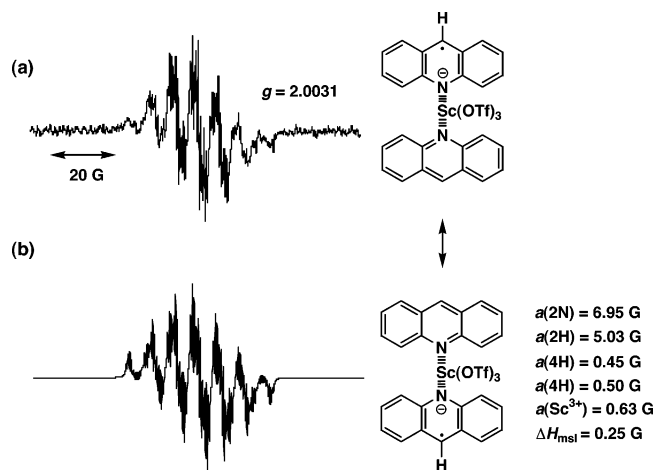
**Table 3.** Fluorescence Quenching Rate Constants ( $k_q$ ) of Py ( $1.3 \times 10^{-6}$  M) by 1,2,3,5-Tetramethylbenzene, 1,2,4,5-Tetramethylbenzene, and Pentamethylbenzene in the Presence of  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M), the Rate Constants ( $k_0K_1$ ), and the Formation Constants of  $\text{Py}^{\bullet-}-2\text{Sc}(\text{OTf})_3$  ( $K_2$ ) in Deaerated MeCN at 298 K

electron donor	$k_q, \text{M}^{-1} \text{s}^{-1}$	$k_0K_1, \text{M}^{-2} \text{s}^{-1a}$	$K_2, \text{M}^{-1a}$
1,2,3,5-tetramethylbenzene	$5.9 \times 10^6$	$1.1 \times 10^8$	13.3
1,2,4,5-tetramethylbenzene	$2.1 \times 10^7$	$3.7 \times 10^8$	14.8
pentamethylbenzene	$2.7 \times 10^7$	$5.0 \times 10^8$	11.6

<sup>a</sup> Determined from the dependence of  $k_q$  on  $[\text{Sc}(\text{OTf})_3]$ .

with  $\text{AcrN}^{\bullet-}$ , that is  $(\text{AcrN})_2^{\bullet-}-\text{Sc}(\text{OTf})_3$  (eq 3). The ESR detection of  $(\text{AcrN})_2^{\bullet-}-\text{Sc}(\text{OTf})_3$  would provide valuable information of the binding of  $\text{Sc}(\text{OTf})_3$  with  $\text{AcrN}$ . The  $(\text{AcrN})_2^{\bullet-}-\text{Sc}(\text{OTf})_3$  complex was produced by electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide  $[(\text{BNA})_2]^{37}$  to  $\text{AcrN}$  in EtCN in the presence of  $\text{Sc}(\text{OTf})_3$  at 203 K (Scheme 1). The  $(\text{BNA})_2$  is known to act as a unique electron donor to produce the radical anions of electron acceptors.<sup>38</sup> The addition of  $\text{Sc}(\text{OTf})_3$  ( $4.4 \times 10^{-2}$  M) to the  $(\text{BNA})_2-\text{AcrN}$  system results in a drastic change in the hyperfine splitting pattern of  $\text{AcrN}^{\bullet-}$  due to the complexation with  $\text{Sc}^{3+}$  (Scheme 1) as shown in Figure 5a.<sup>39</sup> The ESR spectrum is well reproduced by the computer simulation spectrum with the hfc values of  $a(2\text{N}) = 6.95$  G,  $a(2\text{H}) = 5.03$  G,  $a(4\text{H}) = 0.45$  G,  $a(4\text{H}) = 0.50$  G, and  $a(\text{Sc}^{3+}) = 0.63$  G (Figure 5b).<sup>40</sup> The complete agreement of the observed ESR spectrum (Figure 5a) with the computer simulation spectrum (Figure 5b) indicates that  $\text{AcrN}^{\bullet-}$  forms a 2:1 complex with  $\text{Sc}^{3+}$ , which is bridged by  $\text{Sc}(\text{OTf})_3$ .

The 1:2 complex formation between  $\text{Py}^{\bullet-}$  and  $\text{Sc}^{3+}$  ( $\text{Py}^{\bullet-}-2\text{Sc}(\text{OTf})_3$ ) can also be confirmed by ESR in the  $(\text{BNA})_2-\text{Py}$  system. The ESR spectrum of  $\text{Py}^{\bullet-}$  produced by the electrochemical reduction of Py was measured using the electrolysis cell designed for ESR measurements (see Experimental Section) as shown in Figure 6a. The hyperfine structures of the radical anion species are well reproduced by the computer simulation



**Figure 5.** (a) ESR spectrum of a propionitrile solution containing  $(\text{BNA})_2$  ( $1.6 \times 10^{-2}$  M) and  $\text{AcrN}$  ( $5.1 \times 10^{-3}$  M) in the presence of  $\text{Sc}(\text{OTf})_3$  ( $1.6 \times 10^{-1}$  M) at 203 K. (b) Computer simulation spectrum.

with the hyperfine splitting (hfs) values:  $a(4\text{H}) = 4.9$  G,  $a(4\text{H}) = 2.0$  G, and  $a(2\text{H}) = 1.1$  G (Figure 6b), which agree with the literature values.<sup>41</sup> In the presence of  $\text{Sc}^{3+}$ , a drastic change in the hyperfine pattern of  $\text{Py}^{\bullet-}$  due to the complexation with  $\text{Sc}^{3+}$  is observed as shown in Figure 6c. The broad triplet signal indicates that two equivalent protons have a large hfs value of 9.4 G. The ESR spectrum is well reproduced by the computer simulation spectrum with the hfc values of  $a(2\text{H}) = 9.4$  G (Figure 6d). This indicates that the unpaired electron is localized largely on the C2 and C7 positions and that the negative charges are located on the C5 and C10 positions, where two  $\text{Sc}^{3+}$  ions can bind as shown in Figure 6c. Thus, carbon atoms which exhibit the smallest spin density in  $\text{Py}^{\bullet-}$  accommodate the largest spin density in the  $\text{Py}^{\bullet-}-2\text{Sc}(\text{OTf})_3$  complex.<sup>42</sup>

The formation of  $(\text{AcrN})_2^{\bullet-}-\text{Sc}(\text{OTf})_3$  in the  $\text{Sc}(\text{OTf})_3$ -promoted electron transfer from an electron donor to  $\text{AcrN}$  is also confirmed by the laser flash photolysis (vide infra). The transient absorption spectrum obtained after the laser pulse excitation of the  $\text{AcrN}$ -hexamethylbenzene (HMB) system in

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(38) (a) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060. (b) Fukuzumi, S.; Yuasa, J.; Suenobu, T. *J. Am. Chem. Soc.* **2002**, *124*, 12566. (c) Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147.

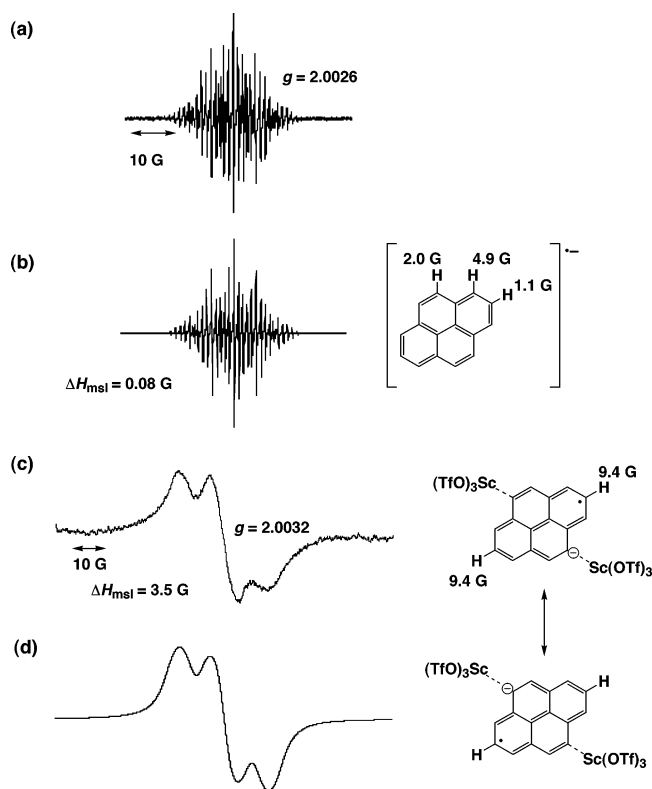
(39) In the presence of  $\text{Sc}(\text{OTf})_3$ , electron transfer from  $(\text{BNA})_2$  to  $\text{AcrN}$  occurs under dark via the  $\text{Sc}(\text{OTf})_3$ -promoted thermal electron-transfer process.

(40) The ESR spectrum of  $\text{AcrN}^{\bullet-}$  was reported previously, see: Chaudhuri, J.; Kume, S.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1968**, *90*, 6421.

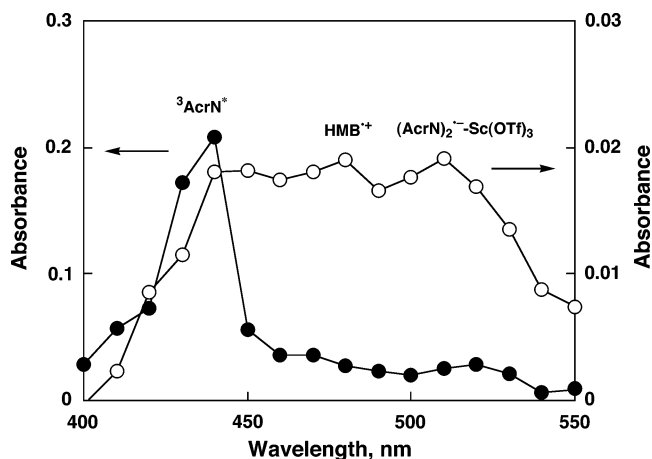
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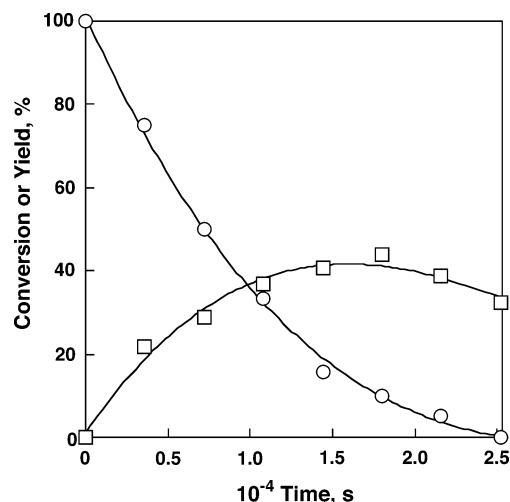
**Figure 6.** (a) ESR spectrum of a propionitrile solution containing Py ( $3.3 \times 10^{-3}$  M) in the presence of  $n\text{-Bu}_4\text{NPF}_6$  (0.2 M) at 203 K. (c) ESR spectrum of a propionitrile solution containing  $(\text{BNA})_2$  ( $2.0 \times 10^{-2}$  M) and Py ( $6.6 \times 10^{-2}$  M) in the presence of  $\text{Sc}(\text{OTf})_3$  (0.5 M) irradiated with a high-pressure mercury lamp at 203 K. The computer simulation spectra are shown in (b) and (d).



**Figure 7.** Transient absorption spectra in the photoreduction of AcrN ( $6.0 \times 10^{-5}$  M) by HMB ( $5.6 \times 10^{-2}$  M) in the absence (●) and presence (○) of  $\text{Sc}(\text{OTf})_3$  ( $9.6 \times 10^{-3}$  M) at  $2.0 \mu\text{s}$  (●) and  $8.0 \mu\text{s}$  (○) after laser excitation at  $\lambda = 355$  nm in deaerated MeCN at 298 K.

the absence and presence of  $\text{Sc}(\text{OTf})_3$  is shown in Figure 7. The transient absorption band at  $\lambda_{\text{max}} = 438$  nm is observed in the absence of  $\text{Sc}(\text{OTf})_3$  (closed circles). This is assigned to the triplet excited state of AcrN.<sup>43</sup> Thus, it is confirmed that no photoinduced electron transfer occurs from HMB to  $^1\text{AcrN}^*$  in the absence of  $\text{Sc}(\text{OTf})_3$ . In the presence of  $\text{Sc}(\text{OTf})_3$ , however, the transient absorption bands are observed at  $\lambda = 485$  and  $\lambda = 510$  nm, which are assignable to HMB radical cation<sup>44,45</sup> and

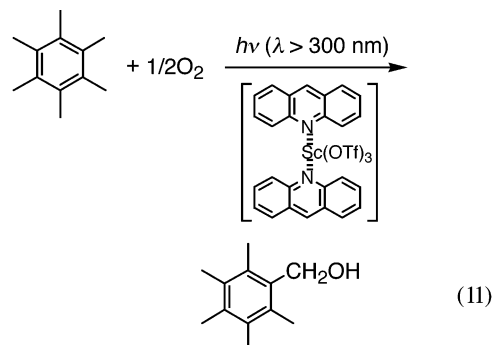
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**Figure 8.** Plots of the conversion of HMB (○) and the yield of pentamethylbenzyl alcohol (□) vs time determined based on the  $^1\text{H}$  NMR spectral change observed in the photosensitized oxygenation of HMB ( $2.0 \times 10^{-3}$  M) in the presence of AcrN ( $2.0 \times 10^{-3}$  M) and  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) under irradiation of UV-visible light ( $\lambda > 300$  nm) in  $\text{O}_2$ -saturated MeCN at 298 K.

(AcrN) $_2^{\bullet-}$ - $\text{Sc}(\text{OTf})_3$ , respectively (Figure 7). The transient spectrum of the (AcrN) $_2^{\bullet-}$ - $\text{Sc}(\text{OTf})_3$  complex is independently detected in the photoinduced electron transfer from ferrocene to AcrN in the presence of  $\text{Sc}(\text{OTf})_3$  (see Supporting Information, S5).

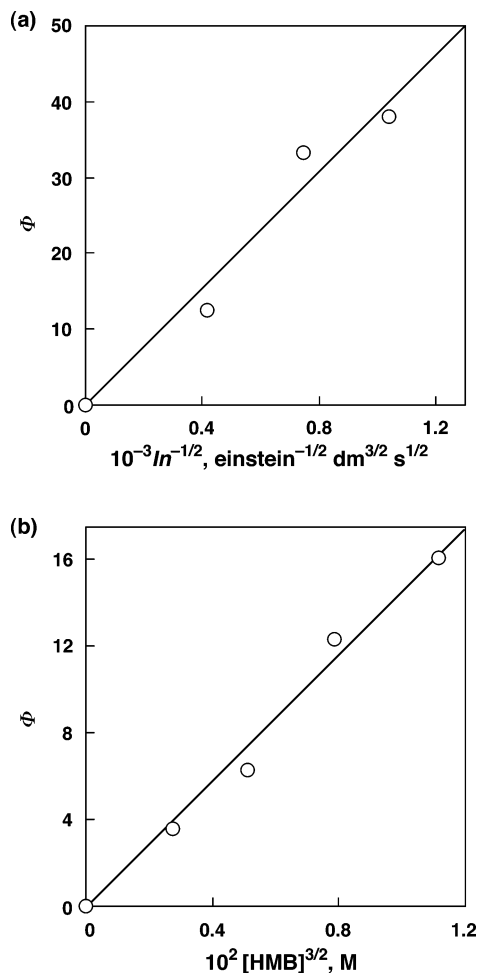
**Photocatalytic Oxygenation of Hexamethylbenzene via  $\text{Sc}(\text{OTf})_3$ -Promoted Photoinduced Electron Transfer.** The  $\text{Sc}(\text{OTf})_3$ -promoted photoinduced electron transfer from HMB to AcrN and Py (vide supra) has led us to develop a new photocatalytic system using AcrN or Py as a photocatalyst in the presence of  $\text{Sc}(\text{OTf})_3$ . Irradiation of the absorption band with UV-visible light ( $\lambda > 300$  nm) of AcrN in an  $\text{O}_2$ -saturated  $\text{CD}_3\text{CN}$  solution containing hexamethylbenzene (HMB) and AcrN results in no change in the  $^1\text{H}$  NMR spectrum. When  $\text{Sc}(\text{OTf})_3$  is added to an  $\text{O}_2$ -saturated  $\text{CD}_3\text{CN}$  solution of HMB and AcrN, however, the  $^1\text{H}$  NMR signals due to HMB decreased and new  $^1\text{H}$  NMR signals due to the oxygenated product, i.e., pentamethylbenzyl alcohol appear during the photoirradiation (eq 11).<sup>46</sup> The time course of the photochemical reaction is



shown in Figure 8, where the disappearance of HMB is accompanied by the formation of pentamethylbenzyl alcohol which is further converted to the more oxygenated products

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**Figure 9.** (a) Dependence of the quantum yields ( $\Phi$ ) on the light intensity ( $I n^{-1/2}$ ) for the photosensitized oxygenation of HMB ( $4.0 \times 10^{-2}$  M) in the presence of Py ( $1.0 \times 10^{-4}$  M) and  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) in  $\text{O}_2$ -saturated MeCN at 298 K. (b) Dependence of the quantum yields ( $\Phi$ ) on  $[\text{HMB}]^{3/2}$  for the photosensitized oxygenation of HMB in the presence of Py ( $1.0 \times 10^{-4}$  M) and  $\text{Sc}(\text{OTf})_3$  ( $4.0 \times 10^{-2}$  M) in  $\text{O}_2$ -saturated MeCN at 298 K.

which were not analyzed here. The preparative scale photocatalytic oxygenation of HMB afforded pentamethylbenzyl alcohol (isolated yield: 30%, see Experimental Section).<sup>47</sup> In the case of Py, virtually the same results are obtained (see Supporting Information S6).

The quantum yields ( $\Phi$ ) of the photocatalytic oxygenation of HMB using Py as a photocatalyst in the presence of  $\text{Sc}(\text{OTf})_3$  were determined from a decrease in the HMB concentration by using GC–MS (see Experimental Section). The  $\Phi$  value for the photooxygenation of HMB is found to vary depending on the light intensity at fixed HMB concentration as shown in Figure 9a, where the  $\Phi$  value is proportional to the reciprocal of the square root of light intensity ( $I n^{-1/2}$ ). The dependence of  $\Phi$  on the HMB concentration was also examined and the  $\Phi$  value increases with increasing  $[\text{HMB}]$  exhibiting the 3/2-order dependence on  $[\text{HMB}]$  as shown in Figure 9b, where a linear correlation is seen between  $\Phi$  and  $[\text{HMB}]^{3/2}$ . The  $\Phi$  value much larger than unity and unusual dependence of  $\Phi$  on  $I n$  and  $[\text{HMB}]$

in Figure 9 can only be explained by the radical chain reactions initiated by the  $\text{Sc}(\text{OTf})_3$ -promoted photoinduced electron transfer from HMB to  $^1\text{Py}^*$  (Scheme 2).

The dramatically enhanced electron acceptor ability of  $^1\text{Py}^*$  in the presence of  $\text{Sc}(\text{OTf})_3$  as compared to  $^1\text{Py}^*$  in the absence of  $\text{Sc}(\text{OTf})_3$  (vide supra) makes it possible that electron transfer from HMB to  $^1\text{Py}^*$  occurs efficiently to produce the radical ion pair  $[\text{HMB}^{\bullet+} \text{Py}^{\bullet-} - n \text{Sc}(\text{OTf})_3$  ( $n = 1, 2$ )]. In the presence of  $\text{O}_2$ , the  $\text{Py}^{\bullet-} - n \text{Sc}(\text{OTf})_3$  complex may be rapidly oxidized by  $\text{O}_2$  to produce the  $\text{O}_2^{\bullet-} - \text{Sc}(\text{OTf})_3$  complex which has been reported to be relatively stable.<sup>48</sup> In fact, the ESR signal due to the  $\text{O}_2^{\bullet-} - \text{Sc}(\text{OTf})_3$  complex is observed during the photoirradiation of an  $\text{O}_2$ -saturated EtCN solution of HMB and Py in the presence of  $\text{Sc}(\text{OTf})_3$  as shown in Figure 10. The  $\text{O}_2^{\bullet-} - \text{Sc}(\text{OTf})_3$  complex generates  $\text{H}_2\text{O}_2$  via disproportionation reaction (Supporting Information S7). Pentamethylbenzyl radical produced by the deprotonation of  $\text{HMB}^{\bullet+}$  may also be rapidly trapped by  $\text{O}_2$  to give pentamethylbenzylperoxyl radical which abstracts a hydrogen from HMB to produce pentamethylbenzyl hydroperoxide, accompanied by regeneration of pentamethylbenzyl radical. The bimolecular reaction of pentamethylbenzylperoxyl radicals affords penta-methylbenzyl radicals, accompanied by generation of  $\text{O}_2$ .<sup>49</sup> The pentamethylbenzylperoxyl radical can abstract a hydrogen atom from HMB to yield pentamethylbenzyl alcohol, accompanied by regeneration of pentamethylbenzyl radical to constitute the radical chain cycle (Scheme 2). The bimolecular reaction of pentamethylbenzylperoxyl radicals may also produce pentamethylbenzyl alcohol, pentamethylbenzaldehyde, and oxygen, which is the termination step in the radical chain reaction in Scheme 2.<sup>50,51</sup> Since the aldehyde has hardly been detected, the termination step is negligible as compared with the efficient radical chain process in Scheme 2.

By applying the steady-state approximation to the radical species (pentamethylbenzyl radical cation,  $\text{Py}^{\bullet-} - n \text{Sc}(\text{OTf})_3$ , pentamethylbenzylperoxyl radical, etc.) in Scheme 2, the dependence of  $\Phi$  on  $[\text{HMB}]$  can be derived as given by eq 12.

$$\Phi = k_p [(\Phi_0 k_q \tau [\text{HMB}]) / 2k_t I n (1 + k_q \tau [\text{HMB}])]^{1/2} [\text{HMB}] \quad (12)$$

Under the experimental conditions such that  $k_q \tau [\text{HMB}] \ll 1$  ( $k_q \tau = 3.0 \times 10^{-1} \text{ M}^{-1}$ ,  $[\text{HMB}] = 5.0 \times 10^{-2} \text{ M}$ ), eq 12 is reduced to eq 13

$$\Phi = C [\text{HMB}]^{3/2} I n^{-1/2} \quad (13)$$

where  $C = k_p (\Phi_0 k_q \tau / 2k_t)^{1/2}$ . The dependence of the  $\Phi$  on  $[\text{HMB}]$  and in Figure 9 agrees with eq 13. Such agreement confirms the validity of Scheme 2.

Virtually the same radical chain mechanism can be applied to the photocatalytic oxygenation of HMB via  $\text{Sc}(\text{OTf})_3$ -

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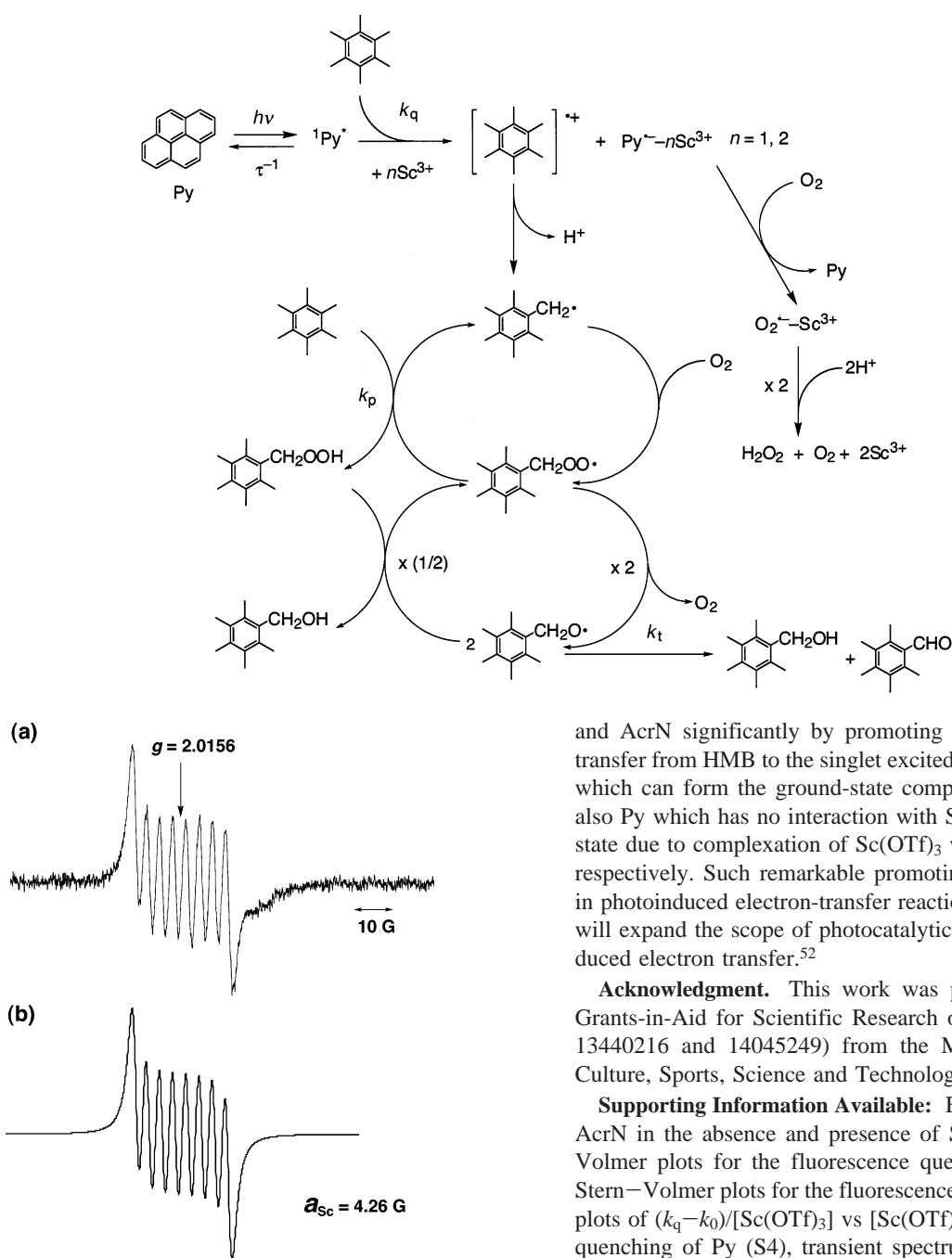
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(50) (a) Howard, J. A. *Adv. Free-Radical Chem.* **1972**, *4*, 49. (b) Howard, J. A. In *Peroxy Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, 1997; pp 283–334.

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Scheme 2



**Figure 10.** ESR spectrum of (a)  $\text{O}_2^{\cdot-}-\text{Sc}(\text{OTf})_3$  complex produced in photosensitized oxygenation of HMB ( $6.2 \times 10^{-2} \text{ M}$ ) in the presence of Py ( $1.0 \times 10^{-1} \text{ M}$ ) and  $\text{Sc}(\text{OTf})_3$  ( $5.0 \times 10^{-2} \text{ M}$ ) in  $\text{O}_2$ -saturated EtCN at 203 K and (b) the computer simulation spectrum.

promoted photoinduced electron transfer from HMB to the  $(\text{AcrN})_2-\text{Sc}(\text{OTf})_3$  complex. It should be emphasized that without  $\text{Sc}(\text{OTf})_3$  no photocatalytic oxygenation of HMB has occurred using Py or AcrN as a photosensitizer. Thus,  $\text{Sc}(\text{OTf})_3$  plays an essential role to improve the photocatalytic activity of Py

and AcrN significantly by promoting photoinduced electron transfer from HMB to the singlet excited state of not only AcrN which can form the ground-state complex with  $\text{Sc}(\text{OTf})_3$  but also Py which has no interaction with  $\text{Sc}(\text{OTf})_3$  in the ground state due to complexation of  $\text{Sc}(\text{OTf})_3$  with  $\text{Py}^{\cdot-}$  and  $\text{AcrN}^{\cdot-}$ , respectively. Such remarkable promoting effects of  $\text{Sc}(\text{OTf})_3$  in photoinduced electron-transfer reactions of photosensitizers will expand the scope of photocatalytic reactions via photoinduced electron transfer.<sup>52</sup>

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**Supporting Information Available:** Fluorescence spectra of AcrN in the absence and presence of  $\text{Sc}(\text{OTf})_3$  (S1), Stern–Volmer plots for the fluorescence quenching of AcrN (S2), Stern–Volmer plots for the fluorescence quenching of Py (S3), plots of  $(k_q - k_0)/[\text{Sc}(\text{OTf})_3]$  vs  $[\text{Sc}(\text{OTf})_3]$  for the fluorescence quenching of Py (S4), transient spectrum of the  $(\text{AcrN})_2^{\cdot-}-\text{Sc}(\text{OTf})_3$  complex (S5), conversion of HMB and the yield of pentamethylbenzyl alcohol in the photosensitized oxygenation of HMB in the presence of Py and  $\text{Sc}(\text{OTf})_3$  (S6), determination of the concentration of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (S7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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