Journal of Photochemistry and Photobiology A: Chemistry 156 (2003) 115–119

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Silica gel-supported porphyrinatoantimony(V) complex acting as visible-light driven photocatalyst for dechlorination of chlorophenols in aqueous solution

Tsutomu Shiragami [a,*], Yuichiro Shimizu [a], Kenichi Hinoue [b], Yoshiyuki Fueta [c], Kazunori Nobuhara [c], Izumi Akazaki [d], Masahide Yasuda [a]

[a] *Department of Applied Chemistry, Faculty of Engineering, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-2192, Japan*
[b] *Touyou Kensa Center Co. Ltd., 7-4317 Asahi-machi, Nobeoka, Miyazaki 882-0847, Japan*
[c] *Fuji Silysia Chemical, 16303-3 Kihara, Hichiya, Hyuga, Miyazaki 883-0062, Japan*
[d] *Miyazaki Prefecuture Industrial Technology Center, 16500-2 Higashi-Kaminaka, Sadowara, Miyazaki 880-0303, Japan*

Received 4 March 2002; received in revised form 26 September 2002; accepted 17 October 2002

Abstract

In order to develop the photocatalyst operating under visible-light irradiation, silica gel-supported dihydroxo(tetraphenylporphyrinato)-antimony(V) complex, $[SbTPP(OH)_2]^+/SiO_2$, was prepared. The irradiated $[SbTPP(OH)_2]^+/SiO_2$ particles by fluorescent light induced the dechlorination of chlorophenols in aqueous solution containing $Fe(NO_3)_3$ to give Cl ion, 1,4-benzoquinone (BQ), and Fe^{2+}. The $[SbTPP(OH)_2]^+$ catalyst supported by Fe^{3+}-impregnated SiO_2, $[SbTPP(OH)_2]^+/SiO_2$-Fe^{3+}, was prepared in order to perform the photochemical dechlorination without the $Fe(NO_3)_3$.

Keywords: Dihydroxo(tetraphenylporphyrinato)antimony(V) complex; Dechlorination; 4-Chlorophenol; SiO_2-support; Fe^{3+}-impregnated SiO_2

1. Introduction

Much attention has been paid to photochemical treatments of wastewater containing organochlorides compounds, since harmful organochlorides resist for usual biochemical and chemical treatments. Decomposition of organochloride by TiO_2-semiconductor photocatalysis is a typical photochemical method, where a hydroxy radical generated by UV-light irradiated TiO_2 works as a strong oxidizing reagents [1–8]. In order to develop an efficient visible-light driven photochemical method to decompose organochlorides in water, our attention is focused on the dechlorination photocatalyzed by metalloporphyrins which has a strong absorption in visible region. The photogenerated radical cations of high-valent metalloporphyrins have a high oxidation ability compared with those of low-valent metalloporphyrins [9–13]. Indeed tetraphenylporphrinatoantimony(V) complex (SbTPP) sensitized the photooxidation of simple alkenes with higher oxidation potentials under visible-light irradiation [14,15].

Here, we report visible-light induced dechlorination of chlorophenols in aqueous solution by dihydroxo-coordinated Sb(TPP) complex, $[SbTPP(OH)_2]^+$, supported by silica gel in the presence of ferric nitrate acting as electron acceptor.

2. Experimental

2.1. Analysis

Quantitative analysis of 4-chlorophenol (4-CP), 2-chlorophenol (2-CP), 4-bromophenol (4-BP), and 1,4-benzoquinone (BQ) were performed on a Shimadzu GC-MS QP-5000 spectrometer. Quantitative analysis of Fe^{2+} were determined by absorption method using 1,10-phenanthrorine as color-producing reagent on a Hitachi U-2001 spectrometer. Ion chromatography on a Shimadzu PIA-1000 was used for the quantitative analysis of Cl^-.

2.2. Preparation of photocatalyst

2.2.1. Silica gel-supported tetraphenylporphrinatoantimony(V) complex ($[SbTPP(OH)_2]^+/SiO_2$)

According to the literature [14–16], dihydroxo(tetraphenylporphyrinato)antimony(V) bromide, $[SbTPP(OH)_2]Br$,

---

[*] Corresponding author. Tel.: +81-985-58-7313; fax: +81-985-58-7315.
E-mail address: t0g109u@cc.miyazaki-u.ac.jp (T. Shiragami).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00406-9

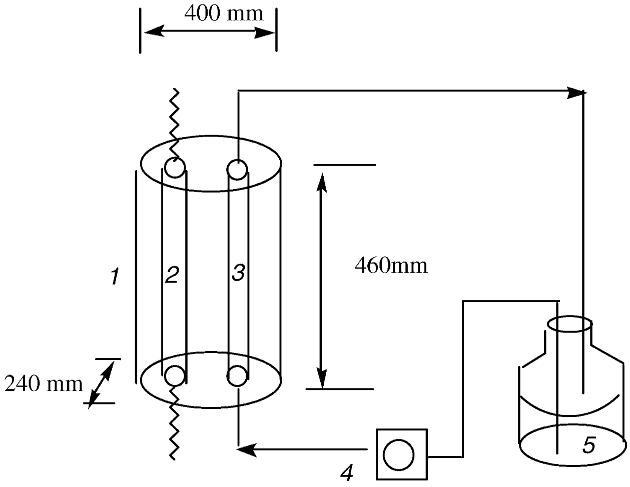
was prepared. Into MeOH-toluene solution (1:4 v/v, 500 ml) of $[SbTPP(OH)_2]Br$ (0.06 g), silica gel (Fuji silysia CARiACT Q-10, 5–10 mesh, 70 g) was added and then stand for 18 h. The MeOH was evaporated from the solution at 40 °C under reduced pressure. The treated silica gel was filtered and then dried under reduced pressure at 40 °C to give the SiO_2-supported $[SbTPP(OH)_2]^+$ photocatalyst ($[SbTPP(OH)_2]^+/SiO_2$), where the content of $[SbTPP(OH)_2]^+$ chromophore was 0.087 wt.%. Similar treatment using 600 and 6 mg of $[SbTPP(OH)_2]Br$ gave the $[SbTPP(OH)_2]^+/SiO_2$ containing 0.87 and 0.0087 wt.% of $[SbTPP(OH)_2]^+$ contents.

2.2.2. *Tetraphenylporphrinatoantimony(V) complex supported by Fe^{3+}-impregnated silica gel ($[SbTPP(OH)_2]^+/SiO_2$-Fe^{3+})*

Into aqueous solution (250 ml) of $Fe(NO_3)_3$ (0.2 mol dm^{-3}), SiO_2 (CARIACT Q-10, 5–10 mesh, 3 mmϕ, 100 g) was added and stand for 1 day. Aqueous ammonia solution (28 wt.%) was added to the solution until the pH reached to 1.5. After the standing for 2 h, the treated SiO_2 were filtered, washed by water, and dried in evaporator under reduced pressure to give the Fe^{3+} ion impregnated silica gel (SiO_2-Fe^{3+}). The impregnation of $[SbTPP(OH)_2]^+$ into the SiO_2-Fe^{3+} was performed as follows. Into a toluene solution (125 ml) of $[SbTPP(OH)_2]Br$ (0.225 g), SiO_2-Fe (30 g) was added and the solution was refluxed for 18 h. Then filtration and dryness under reduced pressure gave the $[SbTPP(OH)_2]^+$ photocatalyst supported by the Fe^{3+}-impregnated SiO_2 ($[SbTPP(OH)_2]^+/SiO_2$-Fe^{3+}), where $[SbTPP(OH)_2]^+$ and Fe^{3+} contents were 0.85 and 2.2 wt.%, respectively.

2.3. *Photocatalyst and apparatus*

As the chromophore absorbing visible-light, $[SbTPP(OH)_2]^+$ complex was selected since the catalytic ability has been known in the photochemical epoxidation of alkenes [15]. $[SbTPP(OH)_2]Br$ was insoluble in aqueous solution in spite of the cationic complex.



Scheme 1. Oval-type photoreaction apparatus: 1, oval-type mirror; 2, fluorescent lamp (18 W); 3, photocatalyst inside the reactor (20 mmϕ × 500 mm, 150 cm^3); 4, pump; 5, sample holder.

The photoreaction was performed on an oval-type apparatus which consisted of a fluorescent lamp (18 W) and reactor (20 mmϕ × 500 mm, 150 cm^3) packed by the photocatalyst (80 g), as shown in Scheme 1. In the oval-type apparatus, the visible-light emitted from fluorescent lamp set on one focus of oval mirror was intended to be concentrated on the reactor set at another focus. Irradiation was performed for the solution which was fed from the holder containing aqueous solution (usually 500 cm^3) of 4-CP (initial concentration was ca. 500 μM) and $Fe(NO_3)$ (initial concentration was ca. 1500 μM) at the rate of 300 ml min^{-1}.

3. Results

3.1. *Photochemical dechlorination of 4-chlorophenol*

The electron acceptor was requisite for the present dechlorination. It was found that $Fe(NO_3)_3$ and $FeCl_3$ were better the electron acceptor than the electron acceptor tested (e.g. K_2PtCl_6, $Cu(NO_3)_2$). In order to prevent interfering the quantitative analysis of Cl^-, we used the $Fe(NO_3)_3$ as the electron acceptor. In order to find optimum content of $[SbTPP(OH)_2]$ in the photocatalyst, the photochemical dechlorination of 4-CP was performed using the photocatalysts containing various contents of $[SbTPP(OH)_2]^+$. The rates for the formation of Cl^- were 7.2, 9.1 and 4.3 μM h^{-1} using the content of 0.87, 0.087 and 0.0087 wt.% of $[SbTPP(OH)_2]^+$, respectively. Therefore, we used the 0.087 wt.% content of $[SbTPP(OH)_2]^+$ on SiO_2 throughout the present investigation.

Fig. 1 shows a typical example of time-course plots for the photochemical dechlorination of 4-CP in the presence of $Fe(NO_3)_3$ in aqueous solution on the $[SbTPP(OH)_2]^+/SiO_2$ photocatalyst. Before the irradiation, the aqueous solution of 4-CP (initial concentration was 493 μM) was fed for 3 h under dark conditions and the concentration 4-CP decreased to 400 μM probably due to the adsorption on the SiO_2 carrier. Upon irradiation for 72 h, the concentration of 4-CP decreased to 6 μM along with the formation of Cl^- (233 μM) and BQ (205 μM). Fe^{2+} (811 μM) was produced as the consequence of the reduction of Fe^{3+}. These results are summarized in Table 1. The photocatalytic reaction of $[SbTPP(OH)_2]^+/SiO_2$ was applied to the dehalogenation of 2-CP and 4-BP (Table 1).

In order to develop the photochemical dechlorination without the $Fe(NO_3)_3$, the photochemical dechlorination using $[SbTPP(OH)_2]^+/SiO_2$-Fe^{3+} as photocatalyst was performed. Fig. 2 shows the time-course of the repeated photochemical dechlorination of 4-CP for 20 h using $[SbTPP(OH)_2]^+/SiO_2$-Fe^{3+}. The $[SbTPP(OH)_2]^+/SiO_2$-Fe^{3+} catalyst with high content of $[SbTPP(OH)_2]^+$ (0.87 wt.%) was employed to obtain the efficiently reactivity

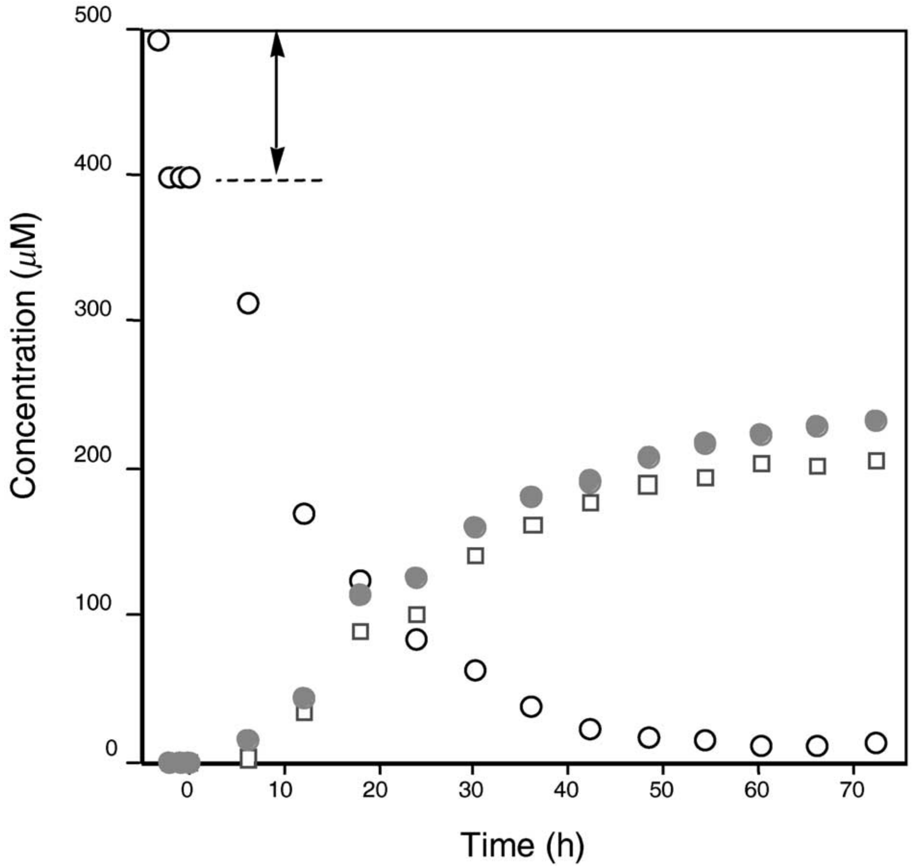


Fig. 1. Time conversion of the dechlorination of 4-CP photocatalyzed by $[SbTPP]^+/SiO_2$: (○) 4-CP; (●) Cl ion; and (□) BQ.

by locating more $[SbTPP(OH)_2]^+$ around the fixed Fe^{3+} ion and showed the similar reactivity to the case of $[SbTPP(OH)_2]^+/SiO_2$ in the presence of $Fe(NO_3)_3$. During the photoreaction, the formation of Fe^{2+} ion by the elution from SiO_2 cage was also slightly observed in the reaction solution until 4 cycles reaction. However, the $[SbTPP(OH)_2]^+/SiO_2\text{-}Fe^{3+}$ catalyst was inactivated and gave no more formation of Fe^{2+} ion in the solution after 4 cycles reactions. The inactivation was attributed to the loss of Fe^{3+} ion around $[SbTPP(OH)_2]^+$ supported on SiO_2 by the reduction to Fe^{2+} ion, but to the decomposition of $[SbTPP(OH)_2]^+$, since the inactivated $[SbTPP(OH)_2]^+/SiO_2\text{-}Fe^{3+}$ recovered the activity for the photochemical dechlorination of 4-CP in the presence of the additional $Fe(NO_3)_3$.

Table 1
Photochemical dehalogenation of chlorophenols and 4-BP using photocalyst[a]

Run number	Substrates[b] (concentration (μM))[c]	Concentration (μM) (yield (%))[d]			
		4-CP	X^-	BQ	Fe(II)
1	4-CP (493)	6	233 (48)	205 (42)	811 (83)
2	4-CP (98)	0.8	50 (51)	44 (45)	173 (89)
3	2-CP (532)	107	51 (12)	–	443 (52)
4	4-BP (411)	62	91 (26)	89 (26)	418 (60)
5[e]	4-CP (509)	274	61 (36)	–	–

[a] Photoreaction in oval-type apparatus using $[SbTPP(OH)_2]^+$ (0.087 wt.%)/SiO_2 (3 mmϕ) photocatalyst under the following conditions: initial concentrations of $Fe(NO_3)_3$ was 1500 μM.

[b] 4-CP, 4-chlorophenol; 2-CP, 2-chlorophenol; 4-BP, 4-bromophenol.

[c] Initial concentration of substrates.

[d] Based on the consumed substrates.

[e] Using $[SbTPP(OH)_2]^+$ (0.87 wt.%)/SiO_2 (3 mmϕ)/$-Fe^{3+}$ (2.0 wt.%).

3.2. Reaction mechanism

Incident light was absorbed exclusively by $[SbTPP(OH)_2]^+/SiO_2$. It is suggested that the electron transfer from the excited triplet state of $[SbTPP(OH)_2]^+/SiO_2$ to Fe^{3+} was responsible for the initiation process of the photodechlorination, since the photodechlorination under oxygen atmosphere was very inefficient and the lifetime for the excited singlet state of $[SbTPP(OH)_2]^+$ was too short to react with 1000 μM order concentrations of Fe^{3+} (Scheme 2). The resulting reactive $[SbTPP(OH)_2]^{2+}/SiO_2$ undergo the hole transfer to 4-CP adsorbed on SiO_2 and/or solved in bulk aqueous solution to give the cation radical of 4-CP, since the oxidation potential ($E^{ox}_{1/2}$) of $[SbTPP(OH)_2]^+$ (e.g. $E^{ox}_{1/2}$ of $[SbTPP(OH)_2]Br$ versus SCE = 1.40 V) was close to that of 4-CP ($E^{ox}_{1/2}$ = 1.40 V) [17]. The cation radical of 4-CP allow the nucleophilic addition of H_2O [18]. The

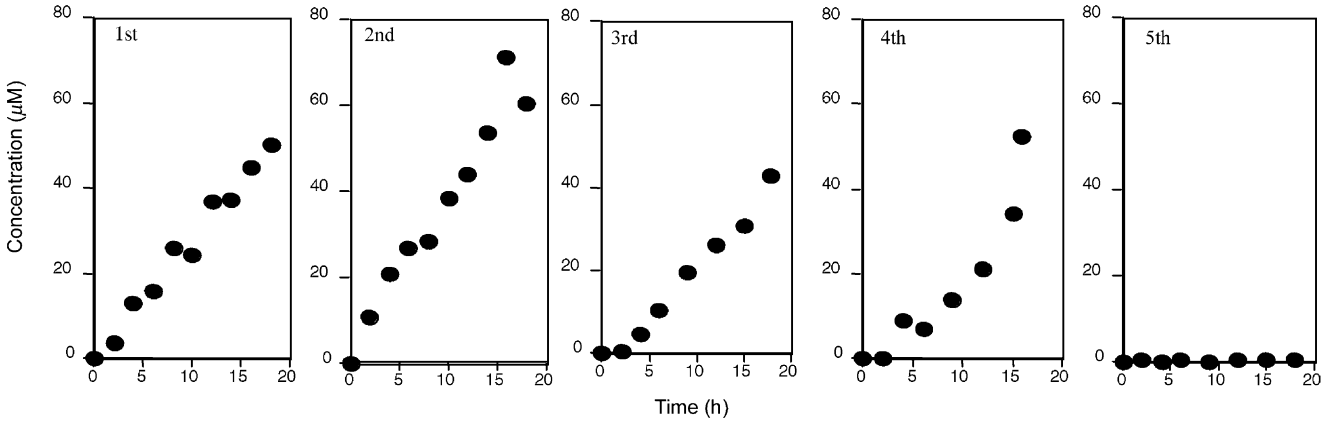
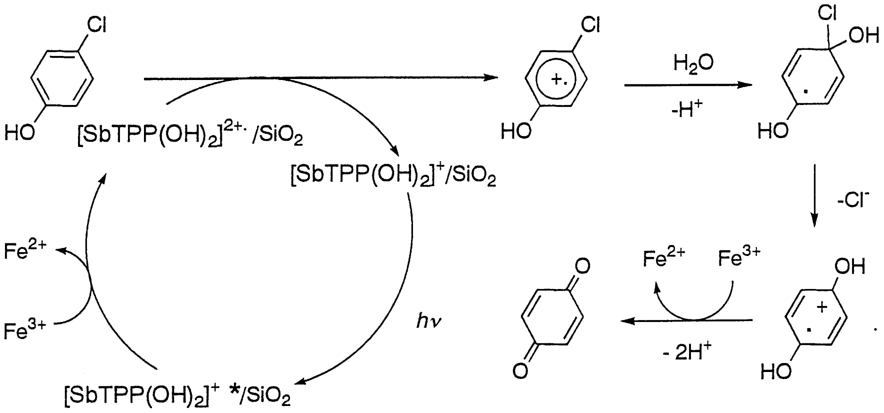


Fig. 2. Time-course plots for the repeated dechlorination of 4-CP for 20 h: (●) Cl ion.



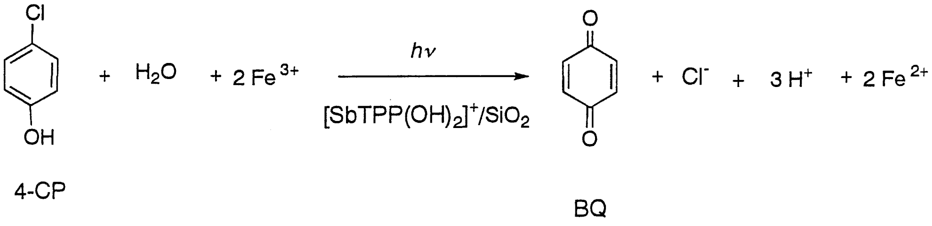
Scheme 2.

substitution of Cl with OH via the hydroxy-adduct followed by the oxidation by Fe^{3+} gave BQ. Therefore, the formation of 1 mol of BQ required the 2 mol of Fe^{3+} (Scheme 3).

The calculation by Rehm–Weller equation [19] predicted that free energy change (ΔG) for the electron transfer from the excited triplet state of $[SbTPP(OH)_2]^+$ ($E^{ox}_{1/2} = 1.40$ V versus SCE, the triplet energy = 1.63 eV) to Fe^{3+} ion ($E^{red}_{1/2} = -0.08$ V versus SCE) was −0.15 V, supporting the above mechanism. When Cu^{2+} ($E^{red}_{1/2} = -0.70$ V versus SCE) was used as the electron acceptor, ΔG was calculated to be +0.47 eV, suggesting that the photoinduced electron transfer from $[SbTPP(OH)_2]^{2+}$ to Cu^{2+} was unfavorable.

Alternative quenching process of the excited triplet state of $[SbTPP(OH)_2]^+/SiO_2$ by 4-CP to generate the cation radical of 4-CP was excluded, since ΔG for the electron transfer process from 4-CP ($E^{ox}_{1/2} = 1.40$ V versus SCE) to the excited triplet state of $[SbTPP(OH)_2]^+$ ($E^{red}_{1/2} = -0.51$ V) was positive (+0.28 eV).

The present mechanism is different from the mechanism proposed for the TiO_2-photocatalytic dechlorination of 4-CP which proceeded by the reaction with OH radical [2]. Indeed, the TiO_2-photocatalytic dechlorination of 4-CP (570 μM) by the oval-type apparatus under UV-irradiation by black light gave the Cl ion (532 μM) but not BQ.



Scheme 3.

Acknowledgements

This work was supported by a Cooperative Project for New Technology from Miyazaki Prefecture.

References

[1] A.L. Pruden, D.F. Ollis, J. Catal. 82 (1983) 404.
[2] T. Hisanaga, K. Harada, T. Tanaka, J. Photochem. Photobiol. A: Chem. 54 (1990) 113.
[3] E. Pelizzetti, M. Borgarello, N. Serpone, Chemophere 17 (1988) 499.
[4] E. Pelizzetti, C. Carlin, C. Minero, M. Gratzel, New J. Chem. 15 (1991) 351.
[5] G. Al-Sayyed, J.C. D'Oliveria, P. Pichat, J. Photochem. Photobiol. A: Chem. 58 (1991) 99.
[6] K. Vinodgopal, U. Stafford, K.A. Gray, P.V. Kamat, J. Phys. Chem. 98 (1994) 6797.
[7] J. Theurich, M. Lindner, D.W. Bahnemann, Langmuir 12 (1996) 6368.
[8] J.C. D'Oliveria, G. Al-Sayyed, P. Pichat, Environ. Sci. Technol. 23 (1990) 990.
[9] A. Harriman, P. Neta, M.C. Richoux, in: E. Pelizzetti, N. Serpone (Eds.), Homogeneous and Heterogeneous Photocatalysis, Reidel, Dordrecht, 1986, p. 123 and references cited therein.
[10] H. Inoue, M. Sumitani, A. Sekita, M. Hida, J. Chem. Soc. Chem. Commun. (1987) 1681.
[11] H. Inoue, T. Okamoto, Y. Kameo, M. Sumitani, A. Fujiwara, D. Ishibashi, M. Hida, J. Chem. Soc., Perkin Trans. 1 (1994) 105.
[12] S. Takagi, T. Okamoto, T. Shiragami, H. Inoue, J. Org. Chem. 59 (1994) 7373.
[13] T. Okamoto, S. Takagi, T. Shiragami, H. Inoue, Chem. Lett. (1993) 687.
[14] T. Shiragami, K. Kubomura, D. Ishibashi, H. Inoue, J. Am. Chem. Soc. 118 (1996) 6311.
[15] S. Takagi, M. Suzuki, T. Shiragami, H. Inoue, J. Am. Chem. Soc. 119 (1997) 8712.
[16] Y. Andou, T. Shiragami, K. Shima, M. Yasuda, J. Photochem. Photobiol. A: Chem. 147 (2002) 191.
[17] A.J. Bard, H. Lund, M. Dekker (Eds.), Encyclopedia of Electrochemistry of the Elements, vol. 11, New York, 1978, p. 189.
[18] X.L. Jerry, W. Cubbage, W.S. Jenks, J. Org. Chem. 64 (1999) 8525.
[19] D. Rehm, A. Weller, Israel J. Chem. 8 (1970) 259.