

Figure 1. ^1H NMR assignment of C-allylated carboranyl acetic ester.

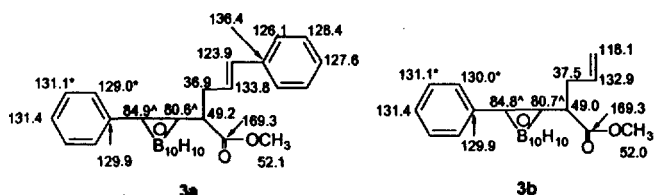


Figure 2. ^{13}C NMR assignment of C-allylated carboranyl acetic ester.

ances (**3a**, **3b**) showed in Figure 1 and Figure 2, respectively.

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The Synthesis of Bis-(2,2'-bipyridine) [4,4'-di-(hexadecyloxy-carbonyl)-2,2'-bipyridine] ruthenium(II) and Its Application for Photolysis of Water

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For the solar energy storage, many studies have been concerned with mimicking the plant photosynthetic system. A vesicle system of water photolysis has been designed by several groups.¹⁻³ For that purpose a photosensitizer, an electron donor and an electron acceptor are needed and must be oriented properly in the vesicle system, just like chlorophyll, O_2 -evolving complex, and ferredoxin in plant membrane. However, few authors have made a vesicle system which generates hydrogen and oxygen from water by visible light.

In this study, we synthesized tris(bipyridine) ruthenium(II) with two long hydrocarbon chains, **6** $[\text{Ru}(\text{bipy})_2(\text{lhcbipy})]^{2+}$, as a photosensitizer to be inserted into the vesicle system. For the first time, a vesicle system prepared with photosensitizer itself was examined for the water photolysis.

We planed to coordinate *cis*-dichloro-bis(bipyridine) ruthenium(II) with 4,4'-di-(hexadecyloxy-carbonyl)-2,2'-bipyridine (**4**) to prepare bis-(2,2'-bipyridine) [4,4'-di-(hexadecyloxy-carbonyl)-2,2'-bipyridine] ruthenium(II) $[\text{Ru}(\text{bipy})_2(\text{lhcbipy})]^{2+}$, **6**. Thus, 4,4'-di-(hexadecyloxy-carbonyl)-2,2'-bipyridine (**4**) was first prepared as follows. A key intermediate, 4,4'-dimethyl-2,2'-bipyridine (**1**, 10 g, yield 6%) was prepared by reacting 4-picoline (175 ml) with palladium (10% charcoal, 9.5 g) as previously described in ref. (4). The oxidation of the methyl groups of bipyridine **1** (8 g) with potassium permanganate (25 g) afforded 4,4'-dicarboxy-2,2'-bipyridine (**2**), (2.7 g, yield 26%), using the reported method.⁵ The carboxylic acid group of the bipyridine **2** was converted to acyl chloride **3** by heating the mixture of 4,4'-dicarboxy-2,2'-bipyridine **2** (700 mg) and thionyl chloride (7 ml) to reflux. The esterification of 4,4'-di-(chlorocarbonyl)-2,2'-bipyridine (**3**) (700 mg) was performed by heating it with cetyl alcohol (1.45 g) in benzene (25 ml) to reflux for 2 hrs. Adding 40 ml of chloroform, the mixture was washed with aqueous sodium bicarbonate. The organic layer was dried with magnesium sulfate. Evaporation of the solvent produced a colorless crystal. The recrystallization from acetone/chloroform afforded 4,4'-di-(hexadecyloxy-carbonyl)-2,2'-bipyridine (**4**), as colorless crystal, (950 mg, yield 48%) with mp. 78 °C.

The esterified bipyridine **4** was confirmed by ^1H NMR, UV, and elemental analysis.⁶ The ultraviolet absorption (λ_{max} 300 nm in CHCl_3) spectra of this compound were found to be very similar to that of 2,2'-bipyridine (λ_{max} 280 nm in MeOH). In the ^1H NMR of compound **4**, the signal for terminal protons appeared as a triplet at 0.89 ppm, middle methylene protons as a multiplet at 1.10-1.60 ppm, homomethoxy protons as a quintet at 1.80 ppm, and methoxy protons as a triplet at 4.40 ppm. Protons (6- and 6'-) on the pyridine

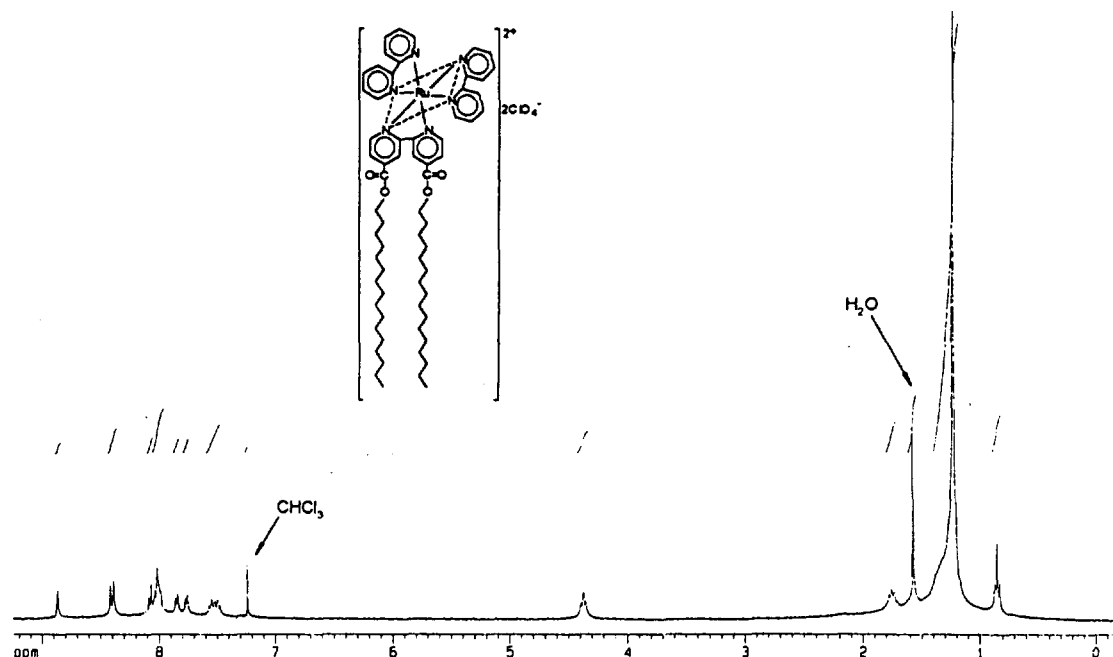
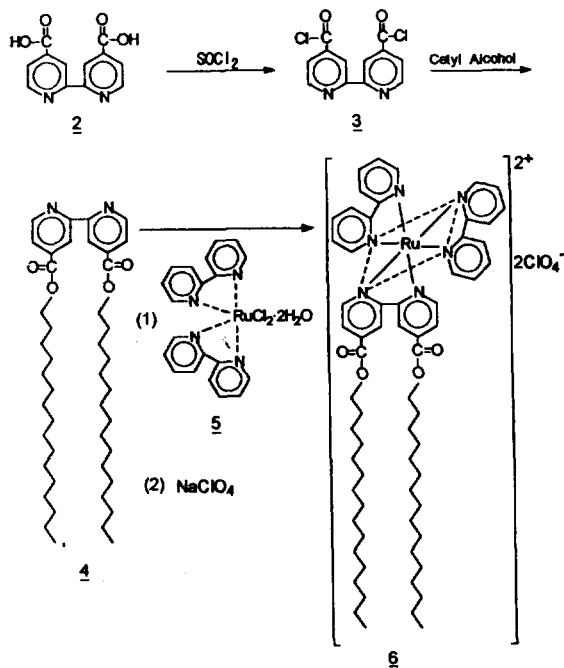


Figure 1. The ^1H NMR spectrum of $\text{Ru}(\text{bipy})_2(\text{lhcbipy})^{2+}$ **6**.



Scheme 1.

rings appeared as a doublet at 7.90, 5- and 5'-protons as a doublet at 8.90, and 3- and 3'-protons as a singlet at 9.01 ppm.⁶

The complexation of bipyridine **4** (375 mg) and [*cis*-dichlorobis(bipyridine)ruthenium(II)], **5** (270 mg), under nitrogen in boiling ethanol (50 ml), followed by treatment of sodium perchlorate gave a brown complex **6** (yield 49%, scheme). This complex was recrystallized in ethyl alcohol and was identified with ^1H NMR, UV and elemental analysis.⁷ The maximum absorption (478 nm, in CHCl_3) appeared at rather longer wavelength than tris(2,2'-bipyridine) ruthenium(II) ch-

loride ($\lambda_{\text{max}}=450$ nm in CHCl_3).

The photosensitizer which absorbs visible light is better in the storage system of solar energy because of the visible light portion of the sun spectrum on the earth.

The triplet at 0.85 ($J=7.0$ Hz) and multiplet at 1.22 ppm in Figure 1 are assigned to two terminal methyl and 52 methylene protons. The ratio of the line intensities is 3:26. The triplet at 4.37 ($J=6.0$ Hz) and quintet at 1.76 ($J=6.5$ Hz) ppm are assigned to the methoxy and homomethoxy protons. The ratio of the line intensities is 1:1. A singlet at 8.87 and two doublets at 7.75 ($J=4.8$ Hz) and 7.84 ($J=4.8$ Hz) are easily assigned to the 3 and 3'-protons, 6 and 6'-protons, and 5 and 5'-protons, respectively, on pyridines with two long hydrocarbon chains. Two doublets at 8.39 ($J=8.0$ Hz) and 8.06 ($J=8.0$ Hz) ppm are assigned to 3,3'- and 6,6'-protons on bipyridine rings and two multiplets at 8.01 and 7.50, 4,4'- and 5,5'-protons on bipyridine rings.⁷

A vesicle system (System A) was prepared with ruthenium complex **6** as photosensitizer and surfactant itself, in addition EDTA as electron donor, and methyl viologen as electron acceptor.⁸

Transmission electron microscope (TEM) of a system containing $\text{Ru}(\text{bipy})_2(\text{lhcbipy})^{2+}$ **6** in water shows that a ball-shaped vesicle system is formed and the diameter of the vesicle is around 1000 Å. After being deaerated with argon gas, the irradiation of the vesicle system with 500 W Xe-lamp produced reduced methyl viologen [$\lambda_{\text{max}}=396$ nm ($\epsilon=42,100 \pm 800$), $\lambda_{\text{max}}=606$ nm ($\epsilon=13,700 \pm 300$)] which is able to produce hydrogen from water. Upon irradiation for every 2 min, the concentration changes of the reduced methyl viologen are 5.2 , 7.2 , 8.7 , 5.8 and 2.9×10^{-6} M, respectively (Figure 2). Upon 4 min irradiation, the concentration changes of the reduced methyl viologen of systems A, B and C are 1.26 , 1.07 and 0.58×10^{-5} M, respectively. This system is superior to the aqueous system containing $\text{Ru}(\text{bipy})_3^{2+}$, EDTA, and methyl viologen (System B) or a vesicle system of DODAB

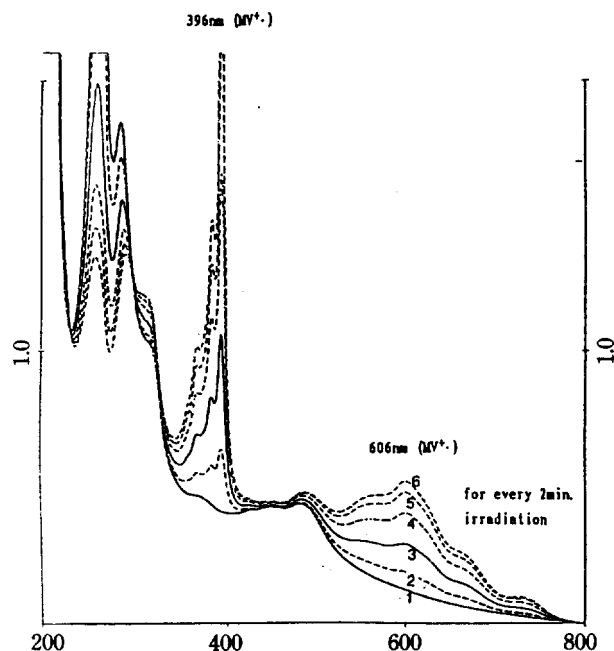


Figure 2. The change of ultraviolet absorption spectra of the vesicle system which contained $\text{Ru}(\text{bipy})_2$ (lhc**6**), EDTA, and methyl viologen upon irradiation.

(Dioctadecyl dimethyl ammonium bromide) containing $\text{Ru}(\text{bipy})_2$ (lhc**6**), EDTA, and methyl viologen (System C).⁹

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6. This compound had mp. 78 °C; UV (CHCl_3) λ_{max} 300 nm; ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, $J=7.0$ Hz, 6H, CH_3), 1.10-1.60 (m, 52H, $-(\text{CH}_2)_{13}-$), 1.80 (q, $J=7.0$ Hz, 4H, $\text{O}-\text{CH}_2-\text{CH}_2-$), 4.40 (t, $J=7.0$ Hz, 4H, OCH_2), 7.90 (d, $J=6.0$ Hz, 2H, pyridine 6-H, 6'-H), 8.90 (d, $J=6.0$ Hz, 2H, pyridines-5-H, 5'-H), and 9.00 (s, 2H, pyridine 3-H, 3'-H). Anal. Calcd for $\text{C}_{44}\text{H}_{72}\text{N}_2\text{O}_4$: C, 76.25; H, 10.47; N, 4.04. Found.: 77.00; H, 10.77; N, 3.83.
7. This compound had mp. 242-244 °C; UV (CHCl_3) λ_{max} 478 nm; ^1H NMR (300 MHz, CDCl_3) δ 0.85 (t, $J=7.0$ Hz, 6H, terminal methyl), 1.22 (m, 52H, methylene), 1.76 (q, $J=7.0$ Hz, 4H, homomethoxy), 4.37 (t, $J=6.0$ Hz, 4H, methoxy), 7.50 (m, 4H, 5,5'-protons on bipyridine rings), 7.75 (d, $J=4.8$ Hz, 2H, 6,6'-protons on bipyridine with two substituents), 7.84 (d, $J=4.8$ Hz, 2H, 5,5'-protons on bipyridine with two substituents), 8.01 (t, $J=8.0$ Hz, 4H, 4,4'-protons on

bipyridine rings), 8.06 (d, $J=5.8$ Hz, 4H, 6,6'-protons on bipyridine rings), 8.39 (d, $J=8.0$ Hz, 3,3'-protons on bipyridine rings), 8.87 (s, 2H, 3,3'-protons on bipyridine with two substituents). Anal. Calcd for $\text{C}_{64}\text{H}_{88}\text{N}_6\text{O}_{12}\text{Cl}_2\text{Ru}$: C, 58.88; H, 6.79; N, 6.43. Found.: C, 59.05; H, 7.09; N, 6.28.

8. System A

An aqueous solution (1.0×10^{-4} M, 4 ml) of $\text{Ru}(\text{bipy})_2$ (lhc**6**) was placed in test tube and sonicated at 70 °C for 20 min to prepare a vesicle solution. The vesicle solution (4 ml) was placed into UV cuvette (1 cm path, 4 ml). To the above solution, 20 μl of MV^{2+} (1.0×10^{-2} M) and 10 μl of EDTA (5.0×10^{-2} M) were added and then deaerated with argon for 20 min.

System B

An aqueous solution of $\text{Ru}(\text{bipy})_3^{2+}$ (1.0×10^{-4} M, 4 ml) was placed into UV cuvette (1 cm path, 4 ml). To the above solution, 20 μl of MV^{2+} (1.0×10^{-2} M) and 10 μl of EDTA (5.0×10^{-2} M) were added and then deaerated with argon for 20 min.

System C

A mixture of $\text{Ru}(\text{bipy})_2$ (lhc**6**) (1.0×10^{-4} M, 4 ml) and DODAB (5×10^{-5} M) was sonicated at 70 °C for 20 min. To above solution, 20 μl of MV^{2+} (1.0×10^{-2} M) and 10 μl of EDTA (5.0×10^{-2} M) were added and then deaerated with argon for 20 min.

9. Park, Y.-T.; Noh, S.-G. *Int. J. Hydrogen Energy* **1994** to be published.

Oxidation of Benzyl Ethers with Sodium Hypochlorite Mediated by N-Oxoammonium Salt

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N-Oxoammonium salts (2,2,6,6-tetramethyl-1-oxopiperidinium salts) have been utilized as very reactive and selective oxidizing agents for alcohols,¹⁻⁶ diols,⁷ hydroxide ion,⁸ phosphines,⁹ phenols,⁹ amines,^{3,8-11} enolizable ketones,^{3,9} and indoles.¹² N-Oxoammonium salts have been used as oxidants in three different modes. First, they have been applied as pure compounds.¹⁻¹² Second, N-oxoammonium salts have been used as mediators. They have been reproduced from piperidine-1-oxyl radicals or their amines by a second oxidant *in situ*.¹³⁻¹⁹ The third mode is connected with the formation of oxoammonium salts from acid catalyzed disproportionation of piperidine-1-oxyl radicals.²⁰ However, it has been only known that N-oxoammonium salts oxidatively cleave benzyl ethers to benzaldehydes and the corresponding alkyl halides.²¹ Thus, we promptly decided to study on the oxidation of benzyl ethers with continuous generation of oxoammonium salt in the presence of catalytic amounts of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-MeO-TEMPO,