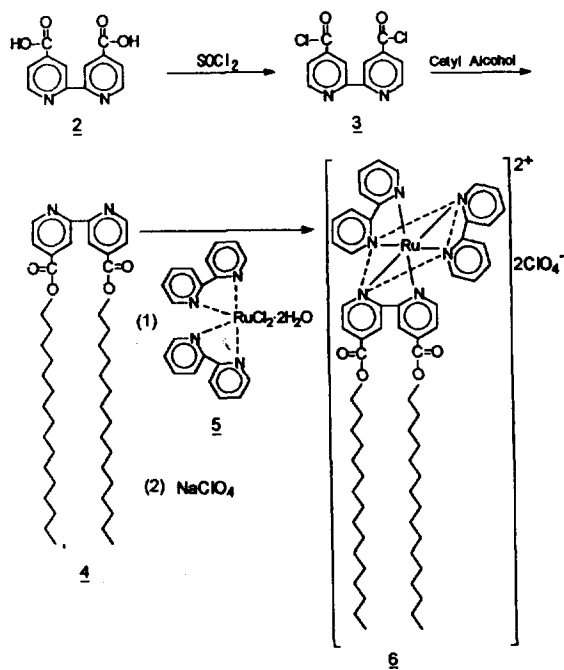


Figure 1. The  $^1\text{H}$  NMR spectrum of  $\text{Ru}(\text{bipy})_2(\text{lhcbipy})^{2+}$  6.



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.<sup>6</sup>

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  $^1\text{H}$  NMR, UV and elemental analysis.<sup>7</sup> The maximum absorption (478 nm, in  $\text{CHCl}_3$ ) appeared at rather longer wavelength than tris(2,2'-bipyridine) ruthenium(II) ch-

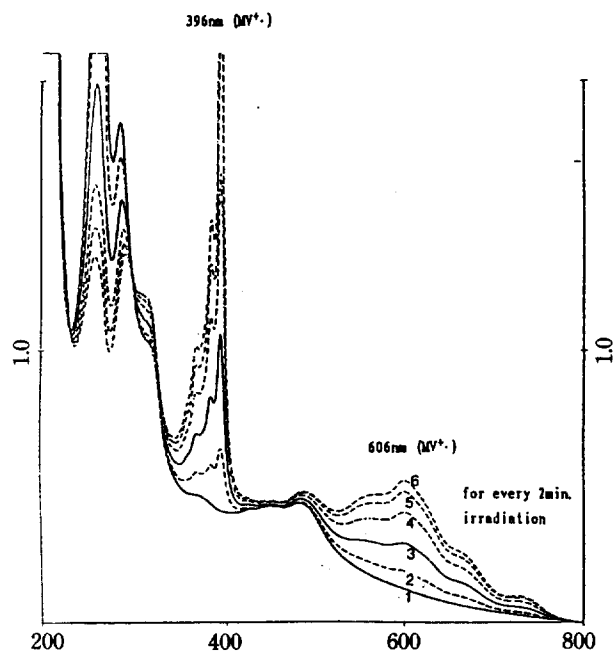
loride ( $\lambda_{\text{max}}=450$  nm in  $\text{CHCl}_3$ ).

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.<sup>7</sup>

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.<sup>8</sup>

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  $2.9 \times 10^{-6}$  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  $0.58 \times 10^{-5}$  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  $\text{Ru}(\text{bipy})_2$  ( $\text{lhcbipy})^{2+}$ , EDTA, and methyl viologen upon irradiation.

(Dioctadecyl dimethyl ammonium bromide) containing  $\text{Ru}(\text{bipy})_2$  ( $\text{lhcbipy})^{2+}$ , EDTA, and methyl viologen (System C).<sup>9</sup>

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6. This compound had mp. 78 °C; UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  300 nm;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J=7.0$  Hz, 6H,  $\text{CH}_3$ ), 1.10-1.60 (m, 52H,  $-(\text{CH}_2)_{13}-$ ), 1.80 (q,  $J=7.0$  Hz, 4H, O- $\text{CH}_2$ - $\text{CH}_2$ -), 4.40 (t,  $J=7.0$  Hz, 4H,  $\text{OCH}_2$ ), 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 ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  478 nm;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $1.0 \times 10^{-4}$  M, 4 ml) of  $\text{Ru}(\text{bipy})_2$  ( $\text{lhcbipy})^{2+}$  **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  $\mu\text{l}$  of  $\text{MV}^{2+}$  ( $1.0 \times 10^{-2}$  M) and 10  $\mu\text{l}$  of EDTA ( $5.0 \times 10^{-2}$  M) were added and then deaerated with argon for 20 min.

## System B

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

## System C

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

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

Nam Sook Cho\* and Chan Hean Park

Department of Chemistry,  
Chungnam National University, Taejeon 305-764, Korea

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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,<sup>1-6</sup> diols,<sup>7</sup> hydroxide ion,<sup>8</sup> phosphines,<sup>9</sup> phenols,<sup>9</sup> amines,<sup>3,8-11</sup> enolizable ketones,<sup>3,9</sup> and indoles.<sup>12</sup> N-Oxoammonium salts have been used as oxidants in three different modes. First, they have been applied as pure compounds.<sup>1-12</sup> 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*.<sup>13-19</sup> The third mode is connected with the formation of oxoammonium salts from acid catalyzed disproportionation of piperidine-1-oxyl radicals.<sup>20</sup> However, it has been only known that N-oxoammonium salts oxidatively cleave benzyl ethers to benzaldehydes and the corresponding alkyl halides.<sup>21</sup> 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,