New Photogeneration System of Dihydronicotinamide and Viologen Radical Using $Ru(bpy)_3^{2+}$

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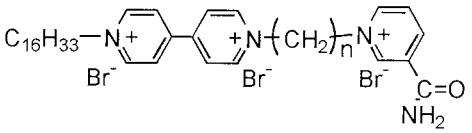
Visible light irradiation ($\lambda > 440$ nm) on a methanol solution containing $Ru(bpy)_3^{2+}$ and nicotinamide covalently bound to viologen produces both dihydronicotinamide and viologen radical.

Nicotinamide adenine dinucleotide (NAD^+) and its reduced compound, dihydronicotinamide adenine dinucleotide (NADH), play an important role in numerous biological reactions such as intermediary metabolism and energy conversion, e.g., electron transfer and oxidative phosphorylation.[1-10] Various aspects of their chemistry and biological mode of action have been investigated with respect to their roles, modes of chemical and enzymatic reductions, structures, activities, and electrochemistry. During numerous biological reactions, the NAD^+ participates in the processes with the reversible redox reaction of the nicotinamide segment. On the other hand, the formation of the NADH through photoreduction of MV^{2+} with the photoexcited $Ru(bpy)_3^{2+}$ has been reported,[11] and rhodium(III) complexes containing porphyrin or polypyridine ligands have been found to be useful catalysts to mediate the reduction of NAD^+ to NADH.[12-15] However, such systems frequently require the sacrificial electron donors Here we describe a new photogeneration system of dihydronicotinamide and a viologen radical using $Ru(bpy)_3^{2+}$ as a photosensitizer and nicotinamide derivatives consisting of nicotinamide linked to alkylviologen through alkylene spacer in methanol.

The nicotinamide derivatives were prepared by heating DMF containing 4-(4'-pyridyl)-1-hexadecyl-pyridinium bromide[16] and 6-nicotinamide-1-bromohexane or 12-nicotinamide-1-bromododecane[17] (Figure 1) and identified by elemental analysis.[18] The sample solutions were adjusted to 2.0×10^{-5} M $Ru(bpy)_3^{2+}$ and various concentrations of $C_{16}VC_6NA^+$ and $C_{16}VC_{12}NA^+$ in methanol. Light irradiation was carried out using a 300 W slide projector equipped with a Toshiba Y-44 cut filter to cut light less than 440 nm.



n = 6 $C_{16}VC_6NA^+$
n = 12 $C_{16}VC_{12}NA^+$

Figure 1. Chemical structure of nicotinamide derivatives

In spite of no addition of sacrificial electron donors, the viologen radical was formed upon irradiation; namely, the photosensitized charge separation was achieved. During light irradiation, the absorbances not only at 605 nm and 398 nm, corresponding to viologen radical, but also at *ca.* 346 nm which is independent of $Ru(bpy)_3^{2+}$ and viologen segment changed.

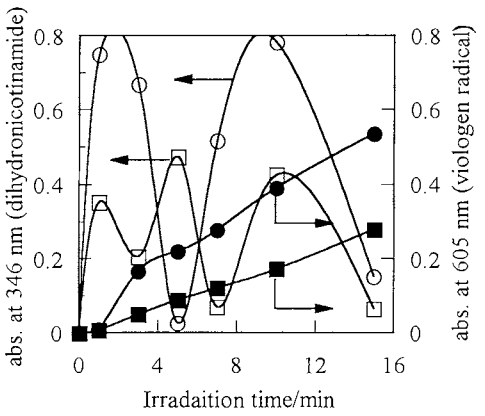


Figure 2. Changes in the absorbances at 346 nm (dihydronicotinamide) and 605 nm (viologen radical) with visible light irradiation at [Ru(II)] = 2.0×10^{-5} M and [C_{16}VCnNA$^+$] = 1.0×10^{-3} M. $C_{16}VC_6NA^+$: (○) and (●). $C_{16}VC_{12}NA^+$: (□) and (■). Open symbols and closed symbols correspond to absorbances of dihydronicotinamide and viologen radical, respectively

Namely, the absorbance at *ca.* 346 nm increased in the initial stage of irradiation (no viologen radical forms), and then it repeatedly decreased and increased with forming viologen radical (Figure 2). It is well-known that NADH has an absorption maxima at *ca.* 350 nm in methanol.[15] Therefore, the dihydronicotinamide species would form in the initial stage through viologen segment.[19] Furthermore, an absorbance at 450 nm, which is an absorption maximum of $Ru(bpy)_3^{2+}$, decreases in the initial stage. Based on these facts, the reaction mechanism can be explained as follows. In the initial stage, electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to the nicotinamide segment occurs *via* the viologen (probably the viologen radical is an intermediate), leading to the accumulation of dihydronicotinamide and the formation of $Ru(bpy)_3^{3+}$. The accumulated dihydronicotinamide then acts as an electron donor; it reduces the ruthenium(III) complex and the absorbance at 346 nm decreases. Because electron transfer from the viologen radical to dihydronicotinamide does not occur, the viologen radical is accumulated (charge separation is achieved). Furthermore, during the visible light irradiation, the Ru(III) species also form and the formation of Ru(III) species is large when the dihydronicotinamide decreases. The dihydronicotinamide acts as the electron donor when it is accumulated, while the formation of dihydronicotinamide and viologen radical involving the formation of Ru(III) species is competitive when the concentration of dihydronicotinamide is small. Therefore, these reactions proceed competitively and repeatedly.

The luminescence data and the concentration of the viologen radical formed after irradiation for 15 min are summarized in Table 1. With increasing initial concentration of the viologen derivatives, the quenching efficiency increased for $C_{16}VC_6NA^+$

Table 1. Luminescence data using excitation wavelength of 485 nm and concentration of viologen radical formed after irradiation for 15 min

	$C_{16}VC_6NA^+$			$C_{16}VC_{12}NA^+$		
Conc./10^{-3} mol dm^{-3}	QE[a]	λ_{max} /nm	$[V^{\bullet+}]/10^{-5}$ mol dm^{-3}	QE[a]	λ_{max} /nm	$[V^{\bullet+}]/10^{-5}$ mol dm^{-3}
0	0	608	0	0	608	0
2	0.12	608	5.68	0.10	605	1.09
4	0.52	608	5.43	0.27	602	1.98
6	0.67	608	4.50	0.35	599	1.91
8	0.76	607	4.28	0.38	594	1.83
10	0.82	607	3.97	0.39	590	1.74
12	0.85	607	3.67	0.39	587	1.34
14	0.87	606	2.50	0.34	585	0.24[b]

[a] Quenching efficiency calculated from $[(I_0 - I)/I_0]$[20]. [b] Irradiation time for 30 min.

system, while it was constant at EQ = 0.34 for $C_{16}VC_{12}NA^+$ system and the luminescence maxima were shifted to shorter wavelength. This indicates that the $C_{16}VC_{12}NA^+$ form some molecular assembly in which incorporates $Ru(bpy)_3^{2+}$ molecules. The formation of the viologen radical for $C_{16}VC_{12}NA^+$ system showed the same behavior as the quenching efficiency, while that for $C_{16}VC_6NA^+$ system decreased with increasing initial concentration of the viologen derivatives. Compared with the $C_{16}VC_{12}NA^+$ system, the generated viologen radical and dihydronicotinamide species are large for a $C_{16}VC_6NA^+$ system. As mentioned above, the $C_{16}VC_{12}NA^+$ forms a molecular assembly, and the $Ru(bpy)_3^{2+}$ is restricted into it, leading to a decrease in the quenching efficiency. Furthermore, in the initial stage, two reactions competitively proceed: the electron transfer from viologen radical to nicotinamide segment and back electron transfer to $Ru(bpy)_3^{3+}$. Since the $C_{16}VC_{12}NA^+$ has a long distance between the viologen and nicotinamide segments due to a long alkylene spacer, the electron transfer to the nicotinamide segment is less effective than that for $C_{16}VC_6NA^+$ system. Consequently, the back reaction is apparently effective. In particular, for $Ru(bpy)_3^{2+}/C_{16}VC_{12}NA^+$ system, the formation of viologen radical is significantly restricted at $[C_{16}VC_{12}NA^+]$ = 14 mM.

In summary, the photosensitized charge separation for the present systems proceeds in two stages: the dihydronicotinamide is formed by electron transfer via viologenand $Ru(bpy)_3^{3+}$ are formed via, and the viologen radical is then accumulated because the dihydronicotinamide acts as an electron donor for the ruthenium(III) complex. The detailed study is now under progress in our laboratory.

References and Notes

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17 These compounds were prepared by refluxing of a mixture of DMF and acetonitrile (1:10, v/v) containing nicotinamide and corresponded dibromoalkanes.

18 Elemental analysis data: for $C_{38}H_{59}N_4OBr_3$ ($C_{16}VC_6NA^+$): Found: C: 55.31; H: 7.32; N: 6.55 %. Calcd.: C: 55.14; H: 7.20; N: 6.77 %. For $C_{44}H_{71}N_4OBr_3$ ($C_{16}VC_{12}NA^+$): Found: C: 58.12; H: 7.98; N: 6.21 %. Calcd.: C: 57.95; H: 7.86; N: 6.14 %.

19 The luminescence of the photoexcited $Ru(bpy)_3^{2+}$ was hardly varied in methanol containing N-alkylnicotinamide, indicating that the $Ru(bpy)_3^{2+}$ did not react directly with the nicotinamide.

20 Quenching efficiency was defined as $[(I_0 - I)/I_0]$, where I and I_0 represented the luminescence intensities of $Ru(bpy)_3^{2+}$ at maximum wavelengths in the presence and in the absence of viologen derivatives, respectively.