

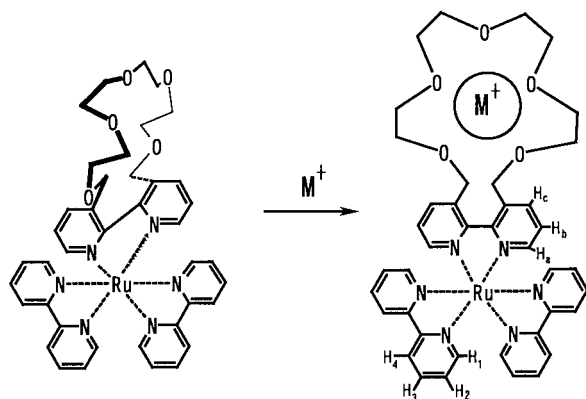
Ruthenium(II) Complex Having Crown-Ether Moiety at 3,3'-Positions on 2,2'-Bipyridine Ligand: Spectroscopic Responses upon Ion Recognition

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$\text{Ru}(\text{bpy})_2(\text{CE-bpy})^{2+}$ was prepared where bpy and CE-bpy were 2,2'-bipyridine and bpy having a crown-ether moiety at the 3,3' positions, respectively. Although the Ru(II) complex showed only very weak emission in acetonitrile, recognition of Na^+ or Li^+ by the crown-ether moiety in CE-bpy resulted in an increase in the emission intensity of the complex.

Photochemistry of polypyridine ruthenium(II) complexes (Ru(II)) has been studied extensively in the past decades.¹ However, the most of the studies have been directed to Ru(II) with bpy or 4,4'-disubstituted-bpy and, those with 3,3'-disubstituted-2,2'-bipyridine (3,3'-R₂-bpy) have been rarely reported.²⁻⁵ In free 3,3'-R₂-bpy, R orients to *trans* with respect to one another owing to steric hindrance between Rs. When 3,3'-R₂-bpy coordinates to a ruthenium ion, its structure would be distorted more or less from an octahedral symmetry because of steric repulsion between Rs.^{2,3} Such a circumstance in the complex brings about a non- or weakly-emissive property. In practice, Ru(II) having 3,3'-R₂-bpy ligands (R = $-\text{CH}_3$, $-\text{COOCH}_3$, $-\text{COOC}_2\text{H}_5$, or $-\text{COOCH}(\text{CH}_3)_2$) has been demonstrated to be a very weak emitter at room temperature.² When steric hindrance between Rs in Ru(II) is tuned by an external signal or stimulus, photophysical and spectroscopic properties of the complex would be varied. Actually, Rebek et al. reported 3,3'-R₂-bpy having a polyether ring as R and, demonstrated structural changes of the compound upon ion (Hg^{2+} or Pd^{2+}) binding by the ether ring.⁶ Therefore, Ru(II) having a ligand shown in Scheme (CE-bpy) is a very interesting target as a photochemical ion receptor. Furthermore, effects of structural changes of CE-bpy and/or Ru(II) on the spectroscopic and excited-state properties of the complex are worth studying for further advances in photochemistry and photophysics of polypyridine ruthenium(II) complexes. In this letter, we report here structural changes and relevant spectroscopic responses of



Scheme

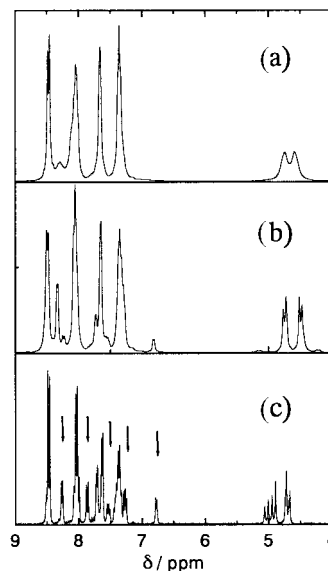


Figure 1. ^1H NMR (270 MHz, in acetone- d_6) spectra of $\text{Ru}(\text{bpy})_2(\text{CE-bpy})^{2+}$ in the absence of ((a) 303 K and (b) 238 K) and presence of NaClO_4 ((c) $\text{Ru(II)}:\text{Na}^+ = 1:90$ at 303 K).

$\text{Ru}(\text{bpy})_2(\text{CE-bpy})^{2+}$ upon ion recognition.⁷

Figure 1 shows ^1H -NMR spectra of the complex. At 303 K (before ion recognition, (a)), the peaks at $\delta = 4.4\text{--}4.9$ (4H) and 8.3 ppm (2H) are responsible for the benzyl and H_a protons of CE-bpy, respectively (see Scheme for numbering of the protons). The peaks at $\delta = 7.4$, 8.0, and 8.5 ppm are assigned as the H_2/H_b (6H), H_3/H_c (6H), and H_1 (4H) protons of bpy and CE-bpy (not resolved), respectively, and that at $\delta = 7.7$ ppm (2H) is attributed to the H_4 protons in bpy. At 238 K (b), the spectrum became relatively sharp and was well resolved compared to that at 303 K. In particular, the ambiguous benzyl and H_a proton signals observed at 303 K split into well-resolved peaks (4.3–4.8 and 8.3 ppm, respectively). Furthermore, the H_c protons shifted to an up-field direction and recognized as the peak at $\delta = 6.8$ ppm (2H), while the proton signals of bpy were almost unchanged. These characteristics indicate conformational and structural fluctuations of the crown-ether moiety and CE-bpy. Since the rate of thermal fluctuation or interconversion between different conformers decreases upon cooling, the spectrum becomes sharper and is well resolved at a lower temperature. In the presence of Na^+ (at 303 K, (c)), on the other hand, the benzyl protons split into a more complicated pattern (4.6–5.1 ppm) and other protons of the pyridine rings in CE-bpy were separated from the relevant protons in bpy as indicated by the arrows in Figure 1c. The results demonstrate that the conformations of CE-bpy change upon ion recognition. The changes in the chemical shift of the benzyl protons by an addi-

tion of Na^+ also suggest a variation of the dihedral angle between the two pyridine rings in CE-bpy. Our preliminary experiments on X-ray crystallography of the complex indicate (data are not shown here) that both crown-ether moiety and CE-bpy are structurally distorted from a planarity, though detailed structural parameters have not been determined yet. In a solution phase, the structure of the complex would vary upon ion recognition.

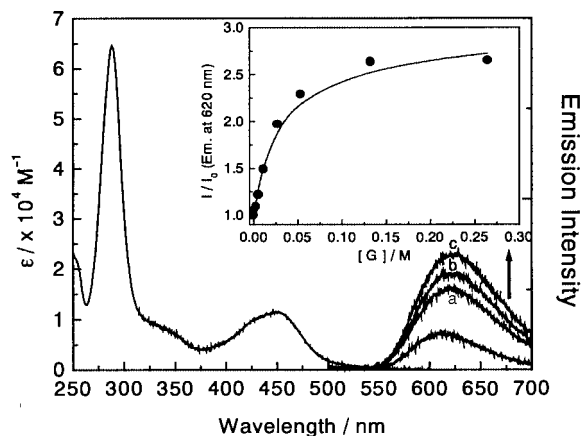


Figure 2. Absorption and emission spectra of $\text{Ru}(\text{bpy})_2(\text{CE-bpy})^{2+}$ ($4.36 \times 10^{-5} \text{ M}$) in the absence of NaClO_4 (in acetonitrile at 298 K) and the emission response upon ion recognition: $[\text{NaClO}_4] = 2.67 \times 10^{-2} \text{ (a)}$, 0.059 (b) , and 0.264 M (c) . The inset represents a NaClO_4 concentration dependence of the I/I_0 ratio (determined at 620 nm).

These structural changes of CE-bpy and the complex upon ion recognition should lead to variation of the spectroscopic properties of the complex. Absorption and emission spectra of the complex in acetonitrile are shown in Figure 2. The spectra without Na^+ were analogous to those observed for $\text{Ru}(\text{bpy})_3$,¹ showing metal-to-ligand charge transfer absorption and emission at around 452 and 615 nm, respectively. However, the emission quantum yield of the complex was very low (4.3×10^{-4}) compared to that of $\text{Ru}(\text{bpy})_3$ (0.061).¹ On the other hand, an addition of Na^+ brought about an increase in the emission intensity and a slight red shift of the spectrum. The emission properties of the complex certainly sense Na^+ ion and, therefore, $\text{Ru}(\text{bpy})_2(\text{CE-bpy})^{2+}$ can act as an ion sensor. By plotting I/I_0 (I and I_0 are the emission intensities in the presence and absence of a guest ion (G), respectively) against the guest concentration ($[G]$, Figure 2), we determined the association constant of the $\text{Ru}(\text{II}) - \text{Na}^+$ or $\text{Ru}(\text{II}) - \text{Li}^+$ (1:1) complex (K) to be 40 or 20 M^{-1} ($\text{M} = \text{mol/dm}^3$), respectively.⁸ The ion selectivity of the complex agreed with that of a structurally-analogous crown ether derivative: 15-crown-5, $\log K = 3.60$ (Li^+) and 5.28 (Na^+).⁹ This also supports that present ion recognition is based essentially on size-selective binding of a guest ion by the CE-bpy ligand.

In the absence of G, the emission decayed almost single exponentially with the time constant of $\tau_s \sim 4 \text{ ns}$,¹⁰ while the decay was fitted by $\tau_l \sim 20 \text{ ns}$ in the presence of a large excess amount of G ($\text{Ru}(\text{II}) : \text{Na}^+ = 1:2500$). In the medium $[G]$ range, the decay was best analyzed by a double exponential function

($\tau \sim 4$ and 20 ns) with the relevant pre-exponential factor (A_s and A_l , respectively) being varied with $[G]$. These results indicate that τ_s and τ_l are responsible for the free and G-bound $\text{Ru}(\text{II})$ complexes, respectively. The $A_l\tau_l$ value is a measure of the contribution of the G-bound $\text{Ru}(\text{II})$ to the overall complex and, therefore, an analysis of a $[G]$ dependence of the $A_l\tau_l$ value can afford K of the $\text{Ru}(\text{II}) - \text{ion}$ complex. On the basis of the emission decay data, we determined K to be 40 or 20 M^{-1} for Na^+ or Li^+ , respectively, which agreed very well with those obtained by emission titration in Figure 2.

The I/I_0 value in the presence of Na^+ was about 2.7 times larger than that in the absence of the ion, while the τ value increased by 5-fold upon recognition (from 4 to 20 ns). This indicates that the nonradiative decay rate constant (k_{nr}) of the complex varies upon ion recognition: emission intensity $\sim k_{nr}\tau$. Although further systematic studies (X-ray crystallography and photodynamics) on a series of $\text{Ru}(\text{II})$ complexes having various 3,3'- R_2 -bpy are needed, we think that structural changes of both CE-bpy and the $\text{Ru}(\text{II})$ complex upon ion recognition lead to the change in the nonradiative decay rate constant of the complex.

Beside photochemical sensing, we recently showed for the first time that the $\text{Ru}(\text{bpy})_2(\text{CE-bpy})$ complex was also applicable to ECL (electrochemically generated luminescence) detection of an alkali metal ion.¹¹ Therefore, we conclude that the present $\text{Ru}(\text{bpy})_2(\text{CE-bpy})$ complex provides a new opportunity as an ion receptor.

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References and Notes.

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- 7 CE-bpy was synthesized according to the literature.⁶ The $\text{Ru}(\text{II})$ complex was obtained by refluxing the ligand and $\text{cis-Ru}(\text{bpy})_2\text{Cl}_2$ (1:1) in ethanol. $\text{RuC}_{40}\text{H}_{42}\text{N}_6\text{O}_5$ ($(\text{PF}_6)_2$), found (calc): C, 44.32(44.58); H, 4.01(3.93); N, 7.99(7.80).
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- 10 Emission decay measurements (monitored at 610 nm) were conducted by using a Ti:sapphire laser (Coherent, pulse width = 150 fs, excitation wavelength = 400 nm) and a single photon counting module (Hamamatsu Photonics, SPC-300) as an excitation light source and a photodetector, respectively.
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