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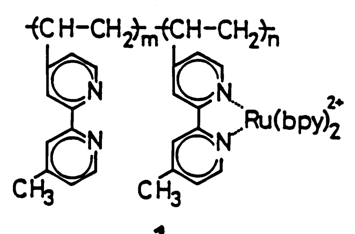
Synthesis and Luminescence Properties of Di- and Tri-methylene Linked Tris(2,2'-bipyridine)ruthenium(II) Complex Dimers. Ground-Excited State Interaction

Masaoki FURUE, Noritaka KURODA, and Shun-ichi NOZAKURA
Department of Macromolecular Science, Faculty of Science,
Osaka University, Toyonaka, Osaka 560

Di- and tri-methylene-linked Ru(bpy)$_3^{2+}$ complexes **2** were synthesized. The luminescence properties of **2** were compared with those of its component monomer. In the excited **2** systems, the intramolecular interaction leading to the enhanced quenching or the formation of a new triplet excimer was not observed.



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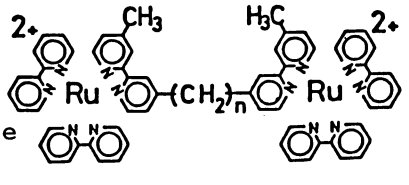


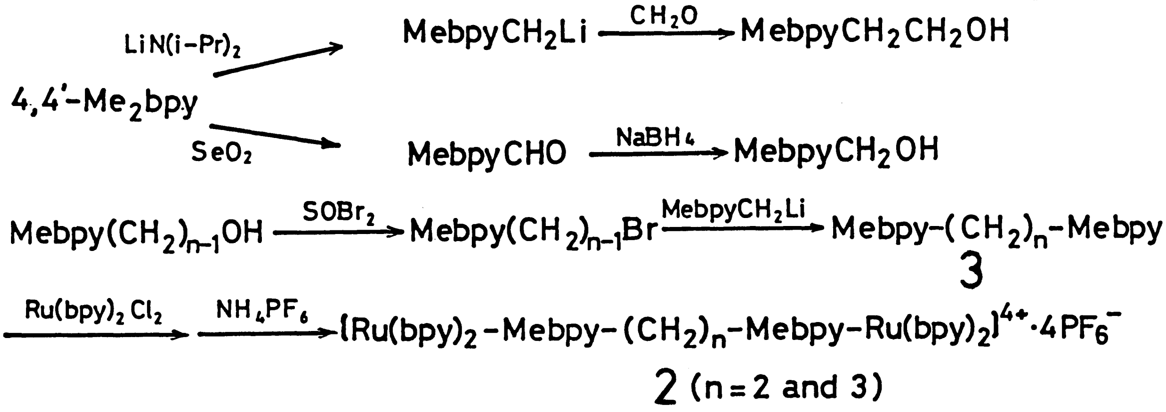
2 (n = 2, 3)

Polymeric metal complexes and polyvinylaromatics are of interest in view of mutual interaction, energy transfer, or electron transfer among chromophores.[1-2] A possible use of these materials is to control photochemical processes in which optical excitation is followed by a spatially directed energy or electron migration along the polymer chain. We have studied photochemical and photophysical properties of Ru(bpy)$_3^{2+}$ complexes which were covalently incorporated into the vinyl polymer **1**.[1,3-5] The luminescence properties of **1** showed a close resemblance to Ru(bpy)$_3^{2+}$. In contrast to polyvinylaromatics,[6] there was no marked evidence for the energy migration and electron exchange between ruthenium complexes on the polymer chain of **1**.[1,5] These findings suggest us the interaction between adjacent Ru(bpy)$_3^{2+}$ complexes of **1** was not present in the excited state under the steady state illumination. To ascertain the events which take place in the polymer, we worked on a covalently linked dimer of Ru(bpy)$_3^{2+}$ complex. To our knowledge, there has been no report on such a ruthenium dimer.

Here we wish to communicate the synthesis of di- and tri-methylene-linked tris(bipyridine)ruthenium(II) [Ru(bpy)$_3^{2+}$] complex dimers **2** and their luminescence properties. Starting from synthesis of new dimeric ligands **3**,[6] 2 were prepared according to Scheme 1. 4,4'-Dimethyl-2,2'-bipyridine was lithiated by an equimolar amount of lithium diisopropylamide in tetrahydrofuran and then was treated with the respective bromides at room temperature to yield **3** [**3**(n=2); Mp 198 °C, **3**(n=3); Mp 128 °C]. 4-Bromoalkyl-4'-methyl-2,2'-bipyridines were prepared by bromination of the corresponding 4-hydroxyalkyl derivatives with thionyl bromide in methylene chloride. **2** were obtained by treatment with Ru(bpy)$_2$Cl$_2$ in ethanol. **2** were purified by chromatography on Sephadex LH-20 with an ethanol eluent and was recrystallized from water as a hexafluorophosphate salt. In ^{1}H-NMR spectra of **2**(n=2 and 3), we observed two kinds of chemical shift of methyl groups which were derived from the 1:1 stereoisomeric mixture of (Δ-Δ, Λ-Λ) and (Δ-Λ) of ruthenium complex. The possibility of rotational isomers can be ruled out by the inspection of the temperature dependency of NMR spectrum. With increasing from 35 to 95 °C, there has not been observed any significant change in both the chemical shifts and the linewidth of two methyl signals.

The electronic and redox properties of **2** in the ground state were compared with those of its compornent monomer, that is, 4,4'-dimethyl-2,2'-bipyridine-bis(2,2'-bipyridine)ruthenium(II) complex, **4**. Redox potentials in acetonitrile were measured by cyclic voltammetry using a platinum electrode and tetrabutylammonium perchlorate as a supporting electrolyte. There have been no substantial differences between **2** and **4** in values of the redox potentials and the peak separation at various stages as shown in Table 1. Electronic absorption spectra of **2** in water showed the same maxima and double the molar absorptivity at 455 nm in comparison with that of **4**(Table 2). These results indicated that ruthenium complexes of **2** did not interact with each other in the ground state.

The luminescence spectra of **2** were recorded with deaerated aqueous solutions at 293 K and showed maxima at 614 nm for **2**(n=2) and 616 nm for **2**(n=3). The luminescence intensities of **2** were slightly larger than that of **4** as shown in Table 2. Luminescence lifetime of **2** in a dearated aqueous



Scheme 1. Synthesis of Tris(bipyridine)ruthenium(II) Complex Dimers.

Table 1. Redox potentials[a)] for ruthenium(II) complexes

Ruthenium Complex	Oxidation 1st $E_{1/2}$	ΔE_p[b)]	Reduction 1st $E_{1/2}$	ΔE_p	2nd $E_{1/2}$	ΔE_p	3rd $E_{1/2}$	ΔE_p
2 (n=2)	+1.21	64	-1.38	64	-1.57	nwd[c)]	-1.81	nwd
2 (n=3)	+1.21	66	-1.38	72	-1.56	nwd	-1.82	nwd
4	+1.20	64	-1.38	56	-1.57	62	-1.82	84

a) V vs. SCE in CH_3CN/0.1 M $n\text{-}Bu_4NClO_4$.
b) Separation(mV) between anodic and cathodic peaks.
c) Anodic peaks are not well-defined.

solution was measured by the single photon counting method (the excitation wavelength at 514.5 nm and the pulse width of 300 ps). Both **2**(n=2) and **2**(n=3) exhibited a single exponential decay as illustrated in Fig. 1. Careful examination on the fast decay process has been carried out by the observation of the decay at a short time range of 50 ns. There was no indication of the fast decay processes. It is often observable as the concentration quenching in the concentrated solution of aromatic chromophors that the quantum yield and lifetime of emission decrease in comparison with those in a dilute solution.[8)] When two aromatic chromophores were linked with a trimethylene chain, the intramolecular interaction leading to the excimer formation or other annihilation processes takes place in the excited state in a dilute solution.[9)] Thomas and a coworker reported that the decay of $^*Ru(bpy)_3^{2+}$ in water was dependent on the concentration of $Ru(bpy)_3^{2+}$ in the higher concentration range (0.01-0.1 mol dm^{-3}).[10)] The rate constant constant for quenching was estimated to be 5.1×10^7 $mol^{-1}dm^3s^{-1}$. The quenching mechanism was not clear. But it was suggested that very close contact between $^*Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ is necessary to promote the ground-state quenching. In the excited **2** systems, we can expect intramolecular quenching caused by the high local concentration of Ru(II) complex in the ground state around *Ru(II) complex. However, we could not observe the enhanced

Table 2. Absorption and luminescence properties of ruthenium(II) complexes in water

Ruthenium Complex	Absorption λ_{max}/nm	ε/$mol^{-1}dm^3cm^{-1}$	Luminescence λ_{max}/nm	Relative[a)] intensity	Lifetime[b)]/μs
2 (n=2)	455	27100	614	1.34	0.63
2 (n=3)	455	27800	616	1.10	0.52
4	455	13000	618	1.00	0.49

a) Excitation at 455 nm and at the same optical density.
b) Single photon counting method. Excitation at 514.5 nm at 20 °C.

quenching or the formation of a new triplet excimer. The MLCT(metal-to-ligand charge transfer) excited state of $Ru(bpy)_3^{2+}$ has been suggested to be ligand-lccalized by resonance Raman spectroscopy.[11] Therefore, we conclude that the localized formation of the excited state of **2** prevented the intra-molecular interaction leading to the ground-state quenching and even energy transfer. This is also the case for the ruthenium polymer **1**.

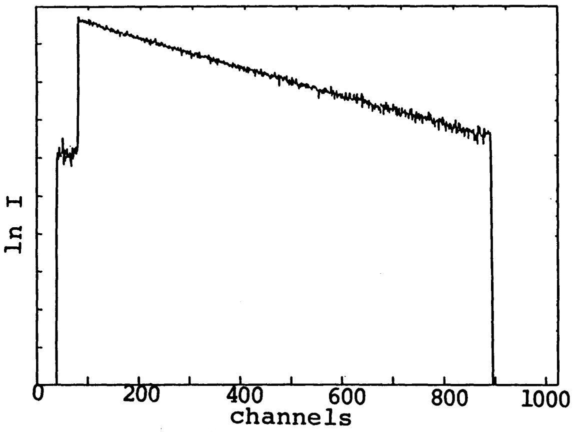


Fig. 1. Luminescence decay for **2**(n=3) measured by the single-photon counting method at 20 °C: 1.637 ns/channel, [**2** (n=3)] = 1.25×10^{-5} mol dm^{-3} in H_2O.

In the case of polyvinylaromatics and their dimer models, the interaction in the excited state are in general resulted from the cofacial alignment of planar aromatic rings. $Ru(bpy)_3^{2+}$ is a spherical molecule and is charged positively. From the geometric and electrostatic grounds the ground state-excited state interaction may hardly take place in **1** and **2** systems.

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