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SYNTHESIS AND LUMINESCENCE PROPERTIES OF TRIS(BIPYRIDINE)RUTHENIUM(II)-CONTAINING VINYL POLYMERS

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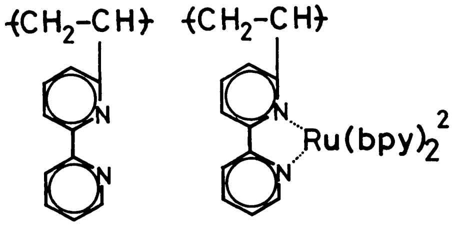
The luminescence properties of poly[Ru(bpy)$_2$(6-vinyl-bpy)-co-6-vinyl-bpy],(I) were compared with those of Ru(bpy)$_3^{2+}$ at 77-298 K. A larger depletion of luminescence intensity and lifetime was observed in I in fluid solution. The dynamic quenching processes were suggested to be the dominant factor for the energy dissipation in I.

The extensive work directed toward photochemical energy storage has generated intense interest in the luminescence properties of transition-metal complexes.[1,2] The tris(bipyridine)ruthenium(II) complex ion, Ru(bpy)$_3^{2+}$, has found widespread use as a photosensitizer for splitting of water.[3-7] In order to pursue the role of polymer playing in such photosensitized reaction sites, we have synthesized poly(6-vinyl-2,2'-bipyridine) [poly(6-vinyl-bpy)] which was photochemically stable and could anchor various transition metal salts.[8]

In this communication, we wish to report the preparation of poly[Ru(bpy)$_2$(6-vinyl-bpy)-co-6-vinyl-bpy] (I), and its luminescence properties. Poly(6-vinyl-bpy) was prepared as described in the previous paper.[8] I was obtained by the following polymer reaction. In a mixture of 1-propanol and dioxane (5:3 v/v, 80 ml), poly(6-vinyl-bpy) (130 mg, 0.71 mmol unit) and Ru(bpy)$_2$Cl$_2$·2H$_2$O[9] (375 mg, 0.72 mmol) were dissolved and refluxed for 15 h under nitrogen pressure. Keeping the reaction system homogeneous and distilling away the organic solvent, 80 ml of water was added by 16 ml portions with a period of 1 h and was refluxed for another hour. The resulting aqueous solution was dialysed through a cellophane tubing (Union Carbide Co.) to remove unreacted Ru(bpy)$_2$Cl$_2$. The aqueous dialysate was freezed-dried to give I as an orange-red powder (280 mg). The extent of reaction



(I)

was estimated to be 25% (molar unit) by using molar extinction coefficient at 452 nm of Ru(II)(bpy)$_3$Cl$_2$. This polymer complex was denoted by I-25. Treatment with less amount of Ru(bpy)$_2$Cl$_2$ (78 mg, 0.15 mmol) by the same procedure afforded I-10. I-10 and I-25 were soluble in water, alcohol, dimethylformamide, and dimethylsulfoxide and insoluble in benzene, chloroform, and acetonitrile.

Infrared absorption spectrum of I-25 was observed to be the superposition of those of Ru(bpy)$_3^{2+}$ and poly(6-vinyl-bpy). At 1599, 1310, 1258, and 1230 cm^{-1}, there exsisted several characteristic bands for metal complexes of the tris-bipyridine type.[10)] The visible absorption spectrum of I-25 in Fig. 1 has a maximum at 452 nm, which can be a spin-allowed charge-transfer band as in Ru(bpy)$_3^{2+}$.[11)] There was no indication of the existence of Ru(bpy)$_2^{2+}$ in the polymer complex. These spectra clearly suggest that Ru(bpy)$_3^{2+}$ complexes incorporated into poly(6-vinyl-bpy) are quite similar to a model complex, Ru(bpy)$_3^{2+}$, at the ground state.

The luminescence spectra of I-25 and I-10 were recorded with deaerated ethanol solutions at 298 and 77 K and are compared with that of Ru(bpy)$_3^{2+}$ in Fig. 2. Like Ru(bpy)$_3^{2+}$ I exhibited a broad band at 610 nm at 298 K. However, compared with Ru(bpy)$_3^{2+}$, the luminescence

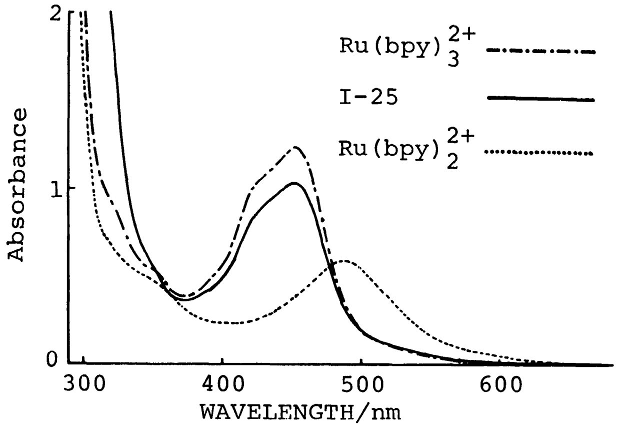


Fig. 1 Absorption Spectra of I-25, and Ru(bpy)$_3^{2+}$ (1.00 x 10^{-4} mol dm^{-3}) and Ru(bpy)$_2^{2+}$ (1.30 x 10^{-4} mol dm^{-3}) in H$_2$O at r.t.

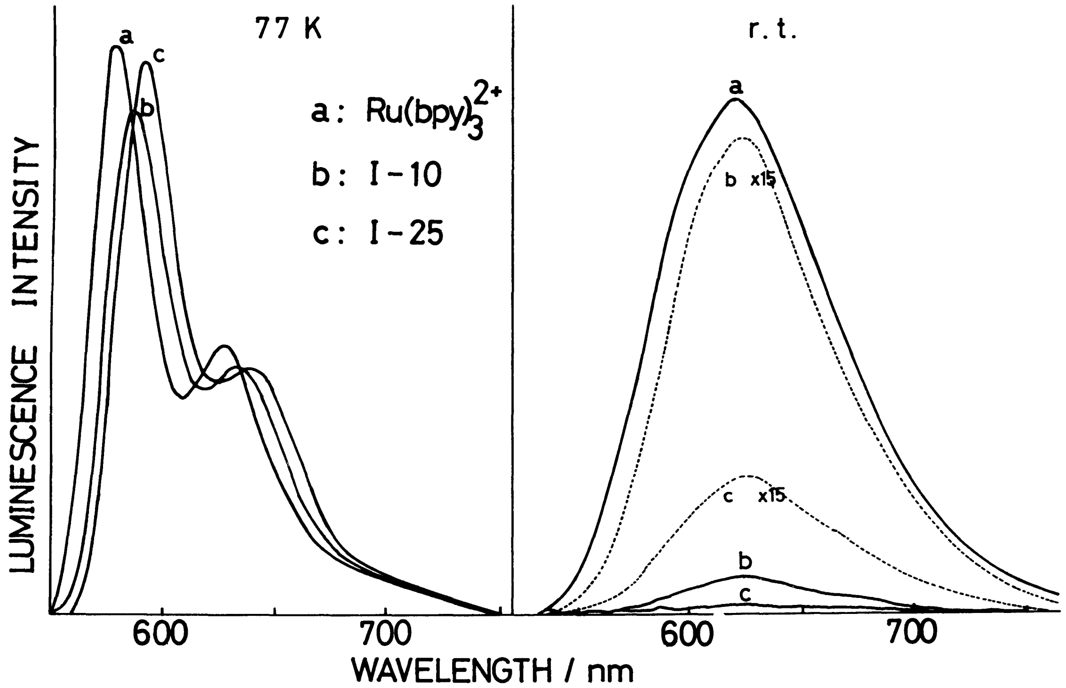


Fig. 2 Luminescence Spectra of I-10, I-25, and Ru(bpy)$_3^{2+}$ in ethanol at 77 and 298 K. [Ru^{2+}] = 5.56 x 10^{-5} mol dm^{-3}.

intensity of I was very weak, i.e. 1/70 for I-25 and 1/15 for I-10. At 77 K, the luminescence of I showed a slight red shift but was similarly structured to $Ru(bpy)_3^{2+}$.[11)] There was no substantial difference in luminescence intensity among them in a rigid alcoholic glass at 77 K.

In order to utilize these polymer complexes as a photosensitizer, it is very important to clearify the reason for the depletion of luminescence which is found in the polymer complexes at ambient temperature. Uncomplexed bpy units might act as a quencher. The luminescence of $Ru(bpy)_3^{2+}$, however, was not quenched with a large amount of 2,2'-bipyridine, and moreover an increase of bpy-units in the polymer complexes from I-25 to I-10 resulted in increase of luminescence intensity. Therefore, it is clear that bpy-units in the polymer complexes are not concerned with the quenching processes.

Both the luminescence quantum yield and lifetime of $Ru(bpy)_3^{2+}$ are known to be strongly temperature dependent.[12-14)] Figure 3 and 4 show the relative luminescence intensity and the lifetime of I and $Ru(bpy)_3^{2+}$ as function of temperature, respectively. For the lifetime measurement, deaerated solutions of ruthenium(II) complexes in ethanol were subjected to the irradiation at 337.1 nm with a pulsed nitrogen laser (pulse width ∿2 ns). Lifetime at 590 nm was calculated from the slope of a plot of ln(intensity) vs. time taken from

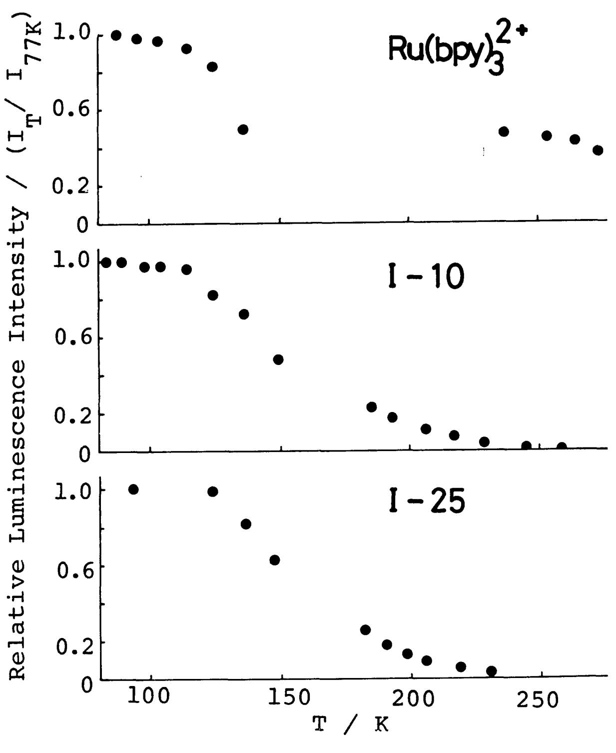


Fig. 3 Temperature Dependence of the Relative Luminescence Intensity $[Ru(bpy)_3^{2+}] = 5.5 \times 10^{-5}$ mol dm^{-3} Solvent: ethanol.

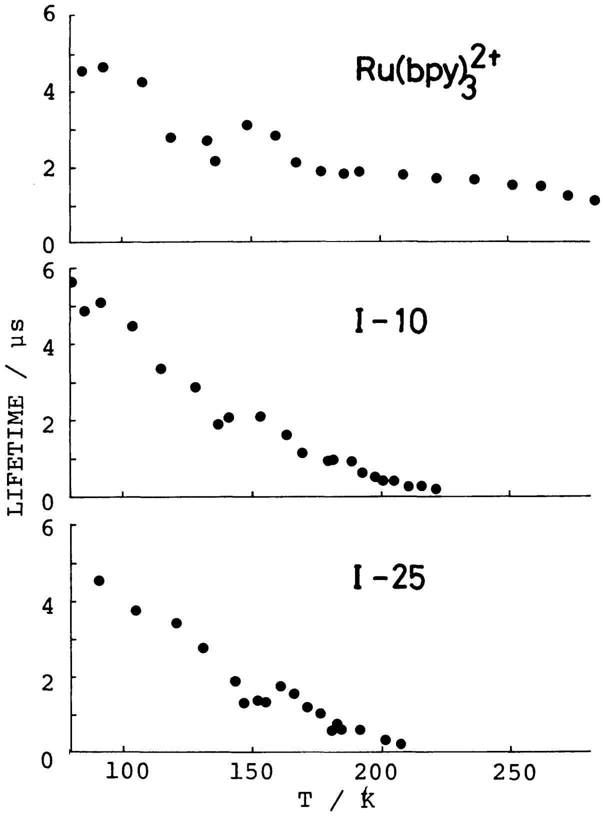


Fig. 4 Temperature Dependence of the Radiative Lifetime $[Ru(bpy)_3^{2+}] = 1.0 \times 10^{-4}$mol dm^{-3}. Solvent : ethanol.

oscilloscope tracings of the decay. At 77 K where a rigid alcoholic glass is formed, there was no marked differences in luminescence intensity and lifetimes between I and $Ru(bpy)_3^{2+}$, while a slight red shift of λ_{max} was observed in I. The $Ru(bpy)_3^{2+}$ unit in I can be assumed to have the same electronic energy levels with $Ru(bpy)_3^{2+}$ itself which are responsible for the luminescence.14) Above the melting point of ethanol (∿150 K), a larger depletion of luminescence intensity and lifetimes was observed in I in comparison with those of $Ru(bpy)_3^{2+}$. The energy dissipation processes characteristic for the polymer do occur in the fluid solution, but not in the rigid state. T-T annihilation processes have been observed when $Ru(bpy)_3^{2+}$ was concentrated in the potential field of sodium lauryl sulfate (SDS) micelles at ambient temperature.15)

In the case of I, the high local concentration of $Ru(bpy)_3^{2+}$ unit is attained. Larger decrease of luminescence intensity and of lifetime were observed in the polymer complex I-25 having higher local concentration of the $Ru(bpy)_3^{2+}$ unit than I-10. The above facts suggest that the dynamic processes between $Ru(bpy)_3^{2+}$ units on the polymer complex are dominant to lead to the energy dissipation rather than the static ones. However, it is difficult to differentiate whether the T-T annihilation or a simple self-quenching with $Ru(bpy)_3^{2+}$ unit in the ground state is operative in the polymer system. It may be possible, at any rate, to avoid a dynamic collision by the use of cross-linked polymer complexes and utilize such a polymer as a photosensitizer. Such an attempt is currently under way.

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