A Dimeric Tris(2,2′-bipyridine)ruthenium(II) System: Emission Spectrum and Cyclic Voltammogram

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(Received August 26, 1987)

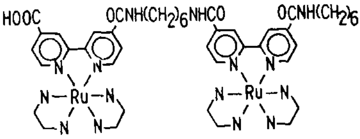
Abstract

A dimeric ruthenium(II) compound in which two Ru(bpy)$_3$ groups are linked by an amide bonding has been prepared as a model compound to study an energy transfer between Ru(bpy)$_3$ chelates. The nature of the solution luminescence spectrum varied with concentration: the emission maximum appeared at 650 nm for dilute solutions and at 670 nm for concentrated solutions. This concentration dependence has been interpreted in terms of excimers that are formed due to an energy transfer between two Ru(bpy)$_3$ groups in a dimer molecule. The cyclic voltammogram for the Ru^{3+}/Ru^{2+} reaction is quasi-reversible: the reaction is governed by a sluggish electron transfer which may be due to an intradimer electronic interaction.

Introduction

The excited state of tris(2,2′-bipyridine)ruthenium(II) cations, [Ru(bpy)$_3$]$^{2+}$, is luminescent and leads to novel redox reactions such as hydrogen generation in an aqueous system under solar irradiation [1]. The energy-transfer processes of the excited state are important in the photoinduced phenomena. For a condensed system in which light-active sites are in proximity, an energy transfer may occur between an electronically excited site and its adjacent ground-state site, resulting in the formation of an excited dimer (*i.e.* excimer). This photoinduced process readily occurs in aromatic polymers such as poly(*N*-vinylcarbazole). The resulting excimers give rise to the photoelectrical conductivity of the polymers [2]: an excimer formed on a pair of aromatic groups successively migrates along the polymer chain, leading to photocurrent. The formation of excimers has been pointed out to be an important factor also in the process of photosynthesis: a chlorophyl involves porphyrine dimers that may function as a photosynthetic reaction center [3].

These findings have prompted us to study a [Ru(bpy)$_3$]-dense system in which the metal chelates are in proximity, because it is expected to exhibit novel photogenic and electrochemical properties. One of the approaches for the preparation of such a system is the metallation of preformed ligand-containing polymers. Poly(vinylpyridine) and copolymers of vinylbipyridine have been used for the preparation of Ru-containing polymers [4]. The metallation of the preformed polymers was, however, difficult to complete for steric and/or electrostatic reasons, although the products showed high catalytic efficiencies in photochemical reactions; the function was due to isolated Ru ions. In our previous work, we synthesized a polyamide that involved bpy groups in the main chain [5]. This polymer, however, had a low capacity of metal ion capture. In the present study, we have prepared the dimeric Ru(bpy)$_3$ chelate **1** as a model compound to study an energy transfer between Ru(bpy)$_3$ chelates. The synthesis has been performed by a condensation reaction between the Ru(bpy)$_3$ derivative **2** and hexamethylenediamine. The obtained PF$_6$ salt of **1** has shown novel emission-spectroscopic properties that differ from those of [Ru(bpy)$_3$]$^{2+}$.



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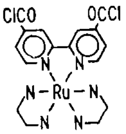

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Experimental

Preparation of the PF$_6$ Salt of 1

[Ru(bpy)$_2$(4,4′-dicarboxy-bpy)](PF$_6$)$_2$ (0.203 g), which was prepared by the same method as reported

0020-1693/88/$3.50

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by Sprintschnik *et al.* [6], was refluxed with excess thionyl chloride in dry benzene (20 ml) for 24 h. The solvent and excess thionyl chloride were removed by distillation and the residue was dried in vacuum for 1 h. To the dark brown product 2 was added hexamethylenediamine (0.0250 g) dissolved in dry benzene (20 ml) involving pyridine (0.5 ml). After the mixture was refluxed for 3 h, the solvent was distilled away. The obtained powder was filtered off and then treated successively with chloroform three times and twice with an aqueous solution saturated with NH_4PF_6. The product was filtered off, washed successively with water and methanol, and dried in vacuum. IR spectrum (KBr): 1730 (COOH), 1620 (amide), and 1545 (amide) cm^{-1}. Electronic absorption spectrum (acetonitrile solution): 476 ($\epsilon = 1.4 \times 10^4$), 287 ($6.7 \times 10^4$), and 244 ($3.3 \times 10^4$) nm. *Anal.* Calc. for $C_{76}H_{74}N_{16}O_5Ru_2P_4F_{24}$: C, 44.02; H, 3.60; N, 10.80. Found: C, 44.01; H, 3.38; N, 10.64%. The compound is soluble in acetonitrile and slightly soluble in water and methanol. The elemental analyses were performed by Huffman Laboratories, Golden, Co. U.S.A.

Physical Measurements

The electronic absorption spectra were recorded on acetonitrile solutions with a Varian DMS-80 VL-UV spectrophotometer. The emission spectra were obtained with the aid of a Perkin-Elmer MPF 66 spectrofluorimeter with a 150 W xenon lamp for the acetonitrile solutions. The wavelength of the excitation light was set to that corresponding to the absorption maximum of the metal–ligand charge-transfer (MLCT) band. The slit width was 5 nm. Cyclic voltammetry experiments were performed with the aid of an EG & G Princeton Applied Research 362 scanning potentiostat equipped with a Hewlett Packard 7015 XY recorder. The ohm compensation was not made. A silver electrode in an acetonitrile solution containing $AgNO_3$ (0.01 M) and $LiBF_4$ (0.1 M) was used as a reference. The supporting electrolyte was 0.1 M $LiBF_4$ solution of acetonitrile (spectroscopic grade). The sample concentration was 1 mM per Ru unit for all experiments. The IR and proton NMR spectra were recorded with a Perkin-Elmer 1420 spectrophotometer and a JEOL JNM PMX60SI spectrometer, respectively.

Results and Discussion

Characterization of Material

The dimer compound **1** showed IR bands that can be assigned to amide bands at 1620 and 1545 cm^{-1}. In addition, a broad band was observed in the NH stretch region, and a sharp peak due to a COOH group was located at 1730 cm^{-1}. These IR data showed that a polyamide was formed and the chain was terminated with COOH and NH_2 groups. The proton NMR spectrum showed signals attributable to NH_2 (chemical shift = 1.4 ppm; relative intensity = 0.09, broad), $-CH_2-$ (3.5; 1), bpy protons (7.2–8.9; 1.5), and COOH (9.8; 0.05). The relative signal intensities indicated that NH_2, $(CH_2)_6$, $[Ru(bpy)_2(bpy\text{-}X_2)]$, and COOH groups were involved in the ratio 1:2:2:1. This supported the formula **1** in which two $Ru(bpy)_3$ units are linked by a hexamethylenediamine unit.

Absorption and Emission Spectra

Figure 1 shows the MLCT band observed for the dimer compound in acetonitrile. The position (476 nm) of the maximum absorbance is red-shifted by 25 nm from that of $Ru(bpy)_3Cl_2$; the molar absorptivities per Ru unit of the compounds are practically identical. The luminescence spectrum excited by the 476 nm light is shown in Fig. 2 for acetonitrile solutions with different concentrations. The nature of the spectrum was significantly dependent on the concentration. At the lowest concentration investigated, the emission peak was centered at

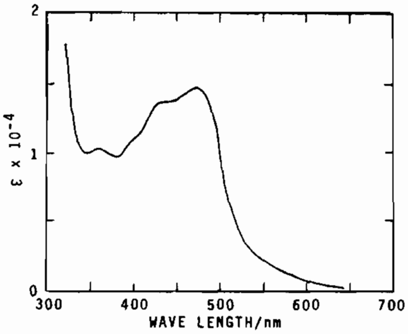

Fig. 1. Absorption spectrum of the dimer compound **1** in acetonitrile. The molar absorptivity is given for each Ru unit.

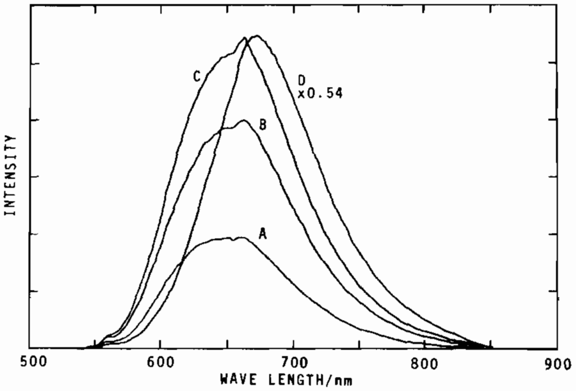

Fig. 2. Emission spectra of the dimer compound **1** in acetonitrile solutions with different concentrations: A, 1.09×10^{-6} M (per Ru unit); B, 2.19×10^{-6} M; C, 2.92×10^{-6} M; D, 8.20×10^{-6} M. The intensity is given in an arbitrary scale.

650 nm with a fwhm (full width at half maximum) of 110 nm. With increasing the concentration, the position of the maximum intensity was red-shifted, and a shoulder appeared on the short wavelength side. At the highest concentration investigated, the peak was located at 670 nm with fwhm = 96 nm, and the shoulder disappeared (spectrum D in Fig. 2). This concentration dependence was markedly different from that of $[Ru(bpy)_3]^{2+}$, whose spectrum nature was independent of the concentration of solution. The spectra of the dimer compound **1** in the dilute solutions consist of two component signals: one at *ca.* 650 nm and the other at *ca.* 670 nm. The former is annihilated in the concentrated solutions. Resembling phenomena have been found for some aromatic compounds (such as pyrene and phenanthrene) in solution and for photoelectrically conducting polymers [2,7]. Pyrene in benzene solution exhibits a luminescence peak due to an excited molecule $^*M$ at *ca.* 384 nm in concentration less than 10^{-4} M. With increasing concentration, the luminescence from $^*M$ becomes weak and a new emission peak appears at *ca.* 478 nm. In concentrated solutions, only the latter emission is observed [7]. The 478 nm emission has been interpreted on the basis of excimer $^*(M\text{--}M)$ formation. The luminescence of pyrene occurs through two processes:

$$^*M \longrightarrow M + h\nu_M \tag{1}$$

$$^*M + M \rightleftarrows {}^*(M\text{--}M) \longrightarrow 2M + h\nu_D \tag{2}$$

The direct process given by eqn. (1) governs the luminescence in dilute solutions, and the excimer process given by eqn. (2) is dominant in concentrated solutions. The emission frequency ν_D is smaller than ν_M. In aromatic polymers, an excimer is readily formed at a site of aromatic groups that are in proximity. The number of potential sites for excimer formation (*i.e.* excimer-forming site) depends on the conformation of the polymer chains. In the dimeric compound **1** also, an excited species $^*Ru\text{--}Ru$ may form an excimer $^*(Ru\text{--}Ru)$, when the molecule has a conformation that facilitates an energy transfer between the Ru chelates. The luminescence peak at 670 nm is attributable to $^*(Ru\text{--}Ru)$ excimers and the 650 nm peak is due to a direct emission process of $^*Ru\text{--}Ru$ to Ru--Ru. In dilute solutions, two $[Ru(bpy)_3]^{2+}$ groups in a dimer molecule are far apart in such a way that an electrostatic repulsion is minimized between the Ru^{2+} chelates: the molecules are 'stretched'. In this conformation, the energy of an excited $^*Ru$ chelate in $^*Ru\text{--}Ru$ is hardly transferred to the other Ru that belongs to the same molecule, because the two Ru chelates are linked by the aliphatic chain system. The $^*Ru\text{--}Ru$ state in a stretched molecule is, therefore, deactivated through the direct process, emitting the 650 nm luminescence. In concentrated solutions, however, electrostatic repulsion and/or collision between dimer molecules become effective. Consequently, the molecules are 'shrinked' so as to minimize the intermolecular interaction energy. In this conformation, two $[Ru(bpy)_3]^{2+}$ groups in a molecule can be so accessible to each other that the molecule is a potential site for excimer formation: excited $^*Ru\text{--}Ru$ molecules are deactivated through $^*(Ru\text{--}Ru)$ excimers to the ground state, in addition to the direct deactivation process. Since the shrinked conformation is more feasible in more concentrated solution, the excimer process is expected to become dominant with increasing concentration. In fact, the 650 nm emission from $^*Ru\text{--}Ru$ became weak and the 670 nm band due to $^*(Ru\text{--}Ru)$ became strong with increasing concentration. In the highest concentration investigated, only the 670 nm emission was observed. Figure 3 shows the concentration dependence of the emission intensity. For the dimer compound is plotted the peak height of the maximum emission whose position is varied with concentration. $Ru(bpy)_3Cl_2$ exhibited a proportional relation of the intensity against concentration throughout the concentration range investigated. By contrast, the dimer compound showed a negative deviation from a proportional relation. For compounds having a large molar absorptivity ϵ, the emission intensity is influenced by the inner filter effect, and is given by [7, 8]:

$$I = K(1 - 10^{-\epsilon bc}) \tag{3}$$

where K is a constant, b the path length, and c the concentration. The broken line in Fig. 3 was calculated with eqn. (3); it disagreed with the observed data. The observed nonproportionality arises probably from the presence of two luminescence processes that are competing with one another.

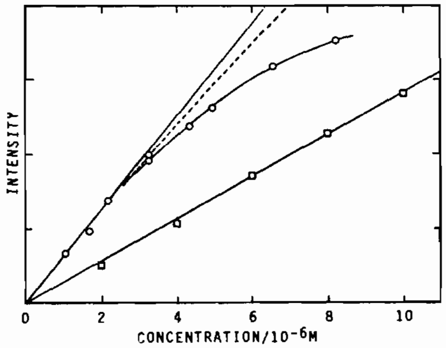

Fig. 3. Plot of luminescence intensity (in an arbitrary scale) against concentration (per Ru unit) for the dimer compound **1** (○) and $Ru(bpy)_3Cl_3$ (□). The maximum peak height of the dimer compound was shifted with concentration. The broken line was calculated by $I = K(1 - 10^{-\epsilon bc})$ with $\epsilon = 1.4 \times 10^{-4}\ M\ cm^{-1}$.

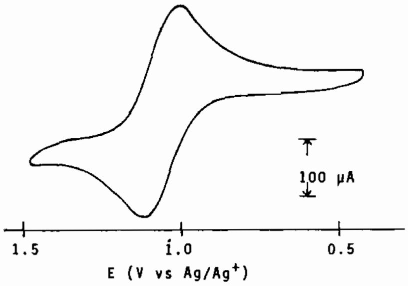

Fig. 4. Cyclic voltammogram of the dimer compound 1. Electrolyte: 0.1 M $LiBF_4$ acetonitrile solution; scan rate: 200 mV s^{-1}; temperature: 25 °C.

Cyclic Voltammogram

Figure 4 shows the cyclic voltammogram in the Ru^{3+}/Ru^{2+} range. The nature of the observed voltammogram was unchanged with the scan cycle. The mid point of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, $(E_{pa} + E_{pc})/2 = 1.06_5$ V, was practically independent of the scan rate in the range investigated, 10–500 mV s^{-1}. On the other hand, the potential difference, $\Delta E_p = E_{pa} - E_{pc}$, was significantly dependent on the scan rate: 0.13_7 V at 500 mV s^{-1}, 0.11_7 V at 200 mV s^{-1}, 0.10_7 V at 50 mV s^{-1}, and 0.10_3 V at 10 mV s^{-1}. These values, even at the lowest scan rate, are much larger than 0.057 V predicted for a reversible one-electron reaction [9]. The ΔE_p values of the dimer compound suggest that the reaction is governed by a sluggish electron process. The solution concentration was 1 mM for the voltammetry experiments. Since it was very high when compared with that for the luminescence experiments, the dimer molecules are shrinked. An intradimer electron transfer occurs in a shrinked molecule, probably leading to a $(Ru\text{--}Ru)^{5+}/(Ru\text{--}Ru)^{4+}$ reaction rather than a Ru^{3+}/Ru^{2+} reaction. The former redox process may be accompanied by a sluggish electron diffusion process.

Conclusions

The novel luminescence spectrum observed for the dimeric $[Ru(bpy)_3]^{2+}$ system can be reasonably explained by assuming the excimer formation. The presence of an intradimer electron transfer is also suggested by the cyclic voltammetry results. These observations show that a polymeric $Ru(bpy)_3$ system will provide a new material with novel photochemical and electrochemical properties.

Acknowledgements

The authors thank the Centro de Investigación en Física, Universidad de Sonora for providing the facility to use the spectrofluorimeter. This work was supported by the Dirección General de Investigación Científica y Superacíon Académica, SEP (Grant C86-01-0219-4).

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