—Communication—

Structure of DNA-Ru(bpy)₃²⁺ Complex and Its Application to Orange Color Electroluminescence Device

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DNA-Ru(bpy)₃²⁺ complex was prepared to study EL characteristics. Ru(bpy)₃²⁺ was associated with duplex of DNA by the interaction such as intercalation in the pH 3 aqueous solution. It was revealed that the EL device composed of DNA-Ru(bpy)₃²⁺ complex exhibited extremely faster response than the other Ru(bpy)₃²⁺ based EL devices. The emission mechanism was discussed. DNA-Ru(bpy)₃²⁺ complex is expected to be applicable to an optoelectro-functional molecular wire.

Key Words : DNA, Ru(bpy)₃²⁺, EL Device, Orange Color Emission

1 Introduction

DNA, a unique one-dimensional molecule with the sequence of four bases, plays an important role for all livings, and is well known to have information in itself with an address of 0.34 nm base-pair pitch. DNA has been collecting keen interest as a functional material since the stacked aromatic bases of DNA may act as a "π-way" for the efficient electron transfer.¹ This is possibly because of an application to novel electronic devices such as highly integrated circuit with nano-structure. The electron transfer and conductivity of DNA have been extensively reported. However, the actual magnitude of these conductive properties is not clear due to difference in measurement condition and apparatus.²⁻⁵ On the other hand, attempts to improve the conductivity of DNA have been carried out by modifying DNA with other functional materials.⁶⁻⁸ We have already reported that DNA-Polyaniline (PAn) complex including Ru(bpy)₃²⁺ is prepared by the template photopolymerization of aniline dimmer with Ru(bpy)₃²⁺ in the presence of DNA. In this complex, Ru(bpy)₃²⁺ works as a light-emitting molecule as well as a photosensitizer, and PAn should be a *p*-type conductor. If DNA showed electron conduction as extensively debated^{1,2} or Ru(bpy)₃²⁺ showed electron transfer in solid state, the DNA/PAn complex including Ru(bpy)₃²⁺ would be a light-emitting molecular system where electrons and holes were injected from electrodes through (DNA or Ru(bpy)₃²⁺) and PAn respectively and both charges were combined at Ru(bpy)₃²⁺ on the complex to emit light. In fact, we fabricated the orange-light emitting EL device with the complex.⁹ The EL device showed higher light emitting characteristics than the other Ru(bpy)₃²⁺ based EL devices previously reported.

In this communication, we report the structure of DNA-Ru(bpy)₃²⁺ complex without PAn and its application to an EL device. It was revealed that the EL device exhibited much faster response than the other previously-

reported Ru(bpy)₃²⁺ based EL devices despite the absence of *p*-type conductor such as PAn in the complex.

2 Experimental

Ru(bpy)₃Cl₂ was prepared according to the literature and was then purified by recrystallization from water. Sodium salts of DNA from salmon testes were provided by the Nippon Chemical Feed Co., Ltd and were used as received. DNA-Ru(bpy)₃²⁺ complex was prepared by mixing the aqueous solution of DNA and Ru(bpy)₃²⁺. DNA helix melting measurement was carried out for the aqueous solution of the complex at pH 3 with JASCO V-570 spectrophotometer and ETC-505 temperature control unit. The monitor wavelength was 260 nm at pH 6.5 and 270 nm at pH 3, respectively. The EL device was prepared by dipping an ITO electrode in the DNA-Ru(bpy)₃²⁺ (molar ratio of base pair of DNA and Ru(bpy)₃²⁺ is 1/6 to study the effect of DNA) complex aqueous solution. After drying sufficiently *in vacuo*, the top Al electrode was deposited on the complex film. The thickness of DNA-Ru(bpy)₃²⁺ complex film was measured with TENCOR alpha step 200 surface profiler and was estimated to be 240 ± 50 nm. Emitting area was 0.3 × 0.3 cm². Luminance and EL response were measured with an Otsuka Electronics MCPD-7000 system and Shimadzu AT-100 photomultimeter with Iwatsu SG-4105 function generator, respectively. All measurements were carried out under the reduced pressure lower than *ca.* 10³ Pa.

3 Results and Discussion

The interaction between DNA and Ru(bpy)₃²⁺ was analyzed with photoemission behavior of Ru(bpy)₃²⁺ in the solution at pH 6.5. The emission intensity and lifetime increased with DNA concentration. However, any remarkable change was not found in DNA helix melting temperature in the presence and absence of Ru(bpy)₃²⁺.⁶ We concluded that Ru(bpy)₃²⁺ was bound to the outside

Fig. 1 The helix melting curves of 5.0×10^{-6} M DNA aqueous solution in the presence and absence of 6.0×10^{-7} M Ru(bpy)₃²⁺.

Fig. 2 Current-voltage characteristics of the DNA-Ru(bpy)₃²⁺ complex based EL device. Inset is the actual EL output of the device.

Fig. 3 Emission-time response of the DNA-Ru(bpy)₃²⁺ complex based EL device by applying 0-10 V rectangular wave at each frequency. (a) 0-10 V rectangular reference wave at 10 Hz, (b) EL emission response of the DNA-Ru(bpy)₃²⁺ device at 7 Hz, (c) EL emission response of the DNA-Ru(bpy)₃²⁺ device at 10 Hz, (d) EL emission response of Alq/TPD device at 10 Hz.

of main chain of DNA by electrostatic interaction of phosphoric groups of DNA. On the other hand, the measurement at pH 3 gave us different results. It was difficult for us to determine clear helix melting point of the DNA at pH 6.5, possibly because of purity and lower molar mass of the provided sample. For the measurement at pH 3, DNA helix melting point was observed at 67°C as shown in Fig. 1. Further, symmetric CD band assignable to π - π^* transition of the base pair at pH 6.5 was somewhat changed by decreasing pH to 3. This CD spectral change may be explained by the conformational change of DNA from B-form to A-form because of the CD spectral resemblance between A-form⁽¹⁰⁾ and the result at pH 3. However, alternative explanation is also considered as follows; The hydrogen bonding at the base pair of DNA is weakened by decreasing pH of the solution. Duplex DNA is unwound partly (not completely) at pH 3, leading to the CD spectral change. The remaining stronger interacted part is unwound at 67°C. Further analysis is being carried out to clarify this behavior. The helix melting temperature of the DNA increased to 74°C in the presence of Ru(bpy)₃²⁺ (the molar ratio of Ru(bpy)₃²⁺ and the base pair of DNA is 6/50) as shown in Fig. 1. The photoemission intensity of Ru(bpy)₃²⁺ also increased in the presence of DNA at pH 3, indicating the interaction between DNA and Ru(bpy)₃²⁺. pH-Titration measurements indicated that the *pK_a* of the present DNA was *ca.* 4-4.5. This suggests that electrostatic interaction between Ru(bpy)₃²⁺ and DNA hardly takes place at pH 3. Ru(bpy)₃²⁺ is, therefore, associated with duplex of DNA by the interaction such as intercalation at pH 3.

EL device was fabricated with DNA-Ru(bpy)₃²⁺ complex, and EL properties were studied. The solution at pH 6.5 was employed for the preparation of the complex film in order to study the EL device with common DNA duplex structure. The current (I)-voltage (V) curve of the device was plotted in Fig. 2. Inset is the actual EL output of the device. The current abruptly increased above the bias voltage of 3 V. On reflection of I-V characteristics, light was emitted from the device above the bias voltage of 3 V, and the luminance of the device increased with the bias voltage. The maximum luminance of 50 cd m⁻² was observed at 15 V. No EL output was found from a fresh device under the continuous application of bias voltage lower than 3 V for more than an hour. The dura-

bility of the EL output was not good at present. The EL output intensity at 15 V decreased to one-half its initial value within a few minute. This may be due to Joule's heat by low conversion efficiency from current to EL output.

It was reported that the emission mechanism of Ru complex based device was believed to obey electrochemistry.⁽¹¹⁾ Namely, oxidized and reduced Ru complexes were generated from the anode and cathode by applying bias voltage respectively, and moved toward the counter electrode to form the interface. Consequently the emission was obtained from the interface between oxidized and reduced Ru complexes. This has advantages such as low driving voltage and better electrode variation, but has disadvantages such as slow response. In order to characterize the emission mechanism of the present device, the emission-time response was studied with photomultimeter. Fresh device was prepared in each measurement to avoid the formation of the history of the electrochemical reaction, if any, before actual measurement. Figure 3 depicts the emission-time response of the device by applying 0-10 V rectangular wave at 7 and 10 Hz. The response of the EL device with Alquinolinium com-

plex and triphenylamine derivative (Alq/TPD) was also shown in Fig. 3(d) as a reference. The Alq/TPD device showed fast response, and the luminance reached steady state within 4 msec after turning-on. On the other hand, the present DNA-Ru(bpy)₃²⁺ based EL device showed slower response than that of Alq/TPD device, but much faster than previously reported Ru complex based EL device.^{11,12)} From the results of 7 and 10 Hz as shown in Fig. 3(b and c), the luminance increased rapidly for *ca.* 10 msec and reached steady state within *ca.* 70 msec. The maximum EL output intensity reached in 5-10 Hz measurement was not changed in each cycle. If the emission followed electrochemical mechanism, the maximum intensity should increase with cycle. Further, EL output was not observed by applying the reverse bias voltage and for the measurement in air. In fact, the current flow under applying reverse bias voltage was lower than that applying forward bias voltage. These observations indicate that the contribution of electrochemical mechanism for the EL output of DNA-Ru(bpy)₃²⁺ device is small and the mechanism probably follows that commonly observed for Alq/TPD EL device.

We cannot reject the contribution of electrochemical mechanism completely. We found 2 msec of delay in the emission response at 10 and 30 Hz, but this delay time was not changed with cycle. This may be due to Ru(bpy)₃²⁺ which is not associated with DNA. We do not have sufficient explanation on the role of DNA and of the interaction between DNA and Ru(bpy)₃²⁺ for the EL output. Further analysis on effects of Ru(bpy)₃²⁺ content, DNA-Ru(bpy)₃²⁺ structure and its detail pH dependence must be done to clarify the EL output mechanism of DNA-Ru(bpy)₃²⁺ EL device and further to realize an optoelectro-functional molecular wire.

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