

## Spectroscopic Properties of DNA-Templated Polyaniline Self-Assembled Nanoropes Formed by Photopolymerization

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### ABSTRACT

Herein, we describe the spectroscopic properties of “DNA-templated polyaniline nanoropes” self-assembled from DNA/polyaniline complexes formed by the photo polymerization of aniline dimers in the presence of tris(2,2'-bipyridyl)ruthenium(II) as a photo catalyst. The products of the photo polymerization reaction were pH-dependent however, the progress of the reaction was curtailed in the higher pH region, and only oligomer formation was observed. In the lower pH region (pH 3.0), the photo polymerization reaction yielded an emeraldine salt with a conductive polyaniline structure.

**Key words:** DNA-template, Nanoropes, Photopolymerization, Polyaniline, Self-assembled.

### 1. INTRODUCTION

In the “more Moor” era where the fabrication of devices with several nanometer dimensions is required, a fundamentally different approach from conventional processes using photolithography must be used. An attractive approach for developing interconnected 1-D structures involves utilizing DNA as a template for coating conductive materials [1]. The advantages of DNA templates include their chemical robustness owing to the double-helical structure and length that can be controlled in the order of a few micrometers through elongation reactions. Nanowires coated with conducting polymers and metals including gold, copper, nickel, rhodium, iron, and palladium have been fabricated using this method [2-11]. Templated reactions occur through noncovalent interactions between the conducting reagents and templates and involve two types of binding sites: Anionic phosphate groups and aromatic bases. Upon coating with a conducting polymer, the growing cationic polymer chains bond with the anionic phosphate backbone to generate metal wires on the template. Metal coatings can be deposited through a reaction that reduces the metal ions bound to DNA. Templatation is widely utilized to produce nanoscale fibers and conducting polymer tubes [12-15]. We focused on the formation of polyaniline (PANI) by photopolymerization using aniline dimers as the starting material in an aqueous solution [15,16]. Herein, we describe “DNA-templated polyaniline nanoropes,” in which the DNA/PANI complex self-assembles into rope-like structures. Suitable pH conditions suitable for forming a conductive emeraldine salt from polyaniline structures are investigated.

### 2. EXPERIMENTAL

Salmon sperm DNA, aniline dimers, *N*-phenyl-*p*-phenylenediamine (PPD), tris(2,2'-bipyridyl)ruthenium(II) chloride ([Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>), whose cation acts as a photooxidation catalyst for PPD, were purchased from FUJIFILM Wako Chemicals Co. After adjusting the pH of aqueous solutions containing given concentrations of DNA, 0.59 mM PPD (which corresponds to 1.18 mM aniline monomer) and 60 μM Ru(bpy)<sub>3</sub><sup>2+</sup> in hydrochloric acid were combined and the solution was irradiated using a 300 W xenon lamp (MAX-303, Asahi Spectra

Co.) through a 400–700 nm band-path filter (VIS, Asahi Spectra Co.). The light intensity was adjusted to 55 mW/cm<sup>2</sup> at 405 nm using a laser power meter (LP10; Sanwa Electric Instrument Co.). Ultraviolet-Visible-Near Infrared (UV-vis-NIR) spectra were acquired using a V-780 spectrophotometer (JASCO Co.). The Circular dichroism (CD) spectra were obtained using a J-1700 instrument (JASCO Co.) with high tension ≤500 V and absorbance values ≤1.5 in the measurement wavelength range of 210–320 nm. All measurements were performed at 20–23°C.

### 3. RESULTS AND DISCUSSION

Before investigating the aqueous systems containing mixtures of PPD, Ru(bpy)<sub>3</sub><sup>2+</sup>, and DNA (as described in Section 2), we separately examined PPD and the mixtures (PPD + DNA), and (Ru(bpy)<sub>3</sub><sup>2+</sup> + DNA).

#### 3.1. Protonation of PPD

A previously reported mechanism for the photocatalytic polymerization of PPD indicates that in the acidic region, protonated PPD is effectively oxidized by photoexcited Ru(bpy)<sub>3</sub><sup>2+</sup> (with an oxidation power of 1.1 V [vs. SCE]) to generate cation radicals. The formed Ru(bpy)<sub>3</sub><sup>+</sup> is reoxidized to Ru(bpy)<sub>3</sub><sup>2+</sup> by an electron-accepting molecule [15,16]. This process is the rate-limiting step during PANI formation. Polymerization proceeds through the reaction of the protonated form of doubly oxidized PPD with unoxidized PPD, followed by sequential reactions at the chain ends via photoinduced electron transfer, as shown in Figure 1 [17,18].

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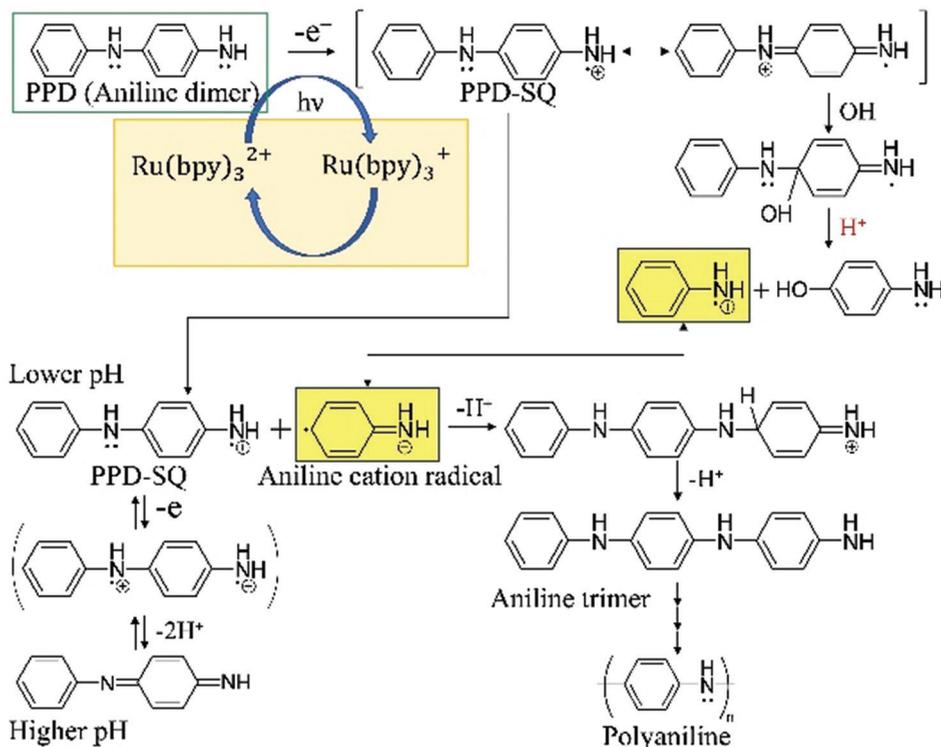
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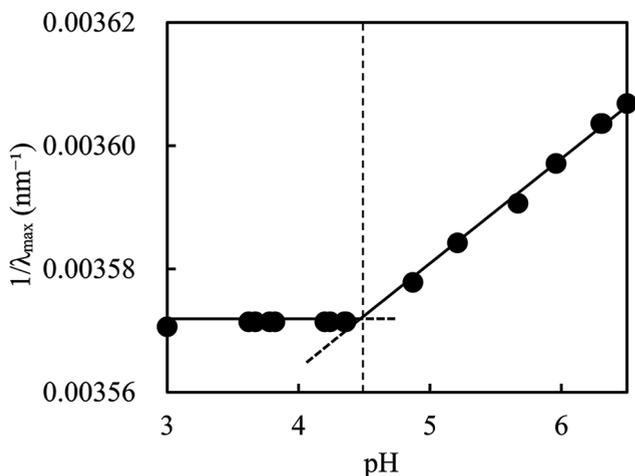
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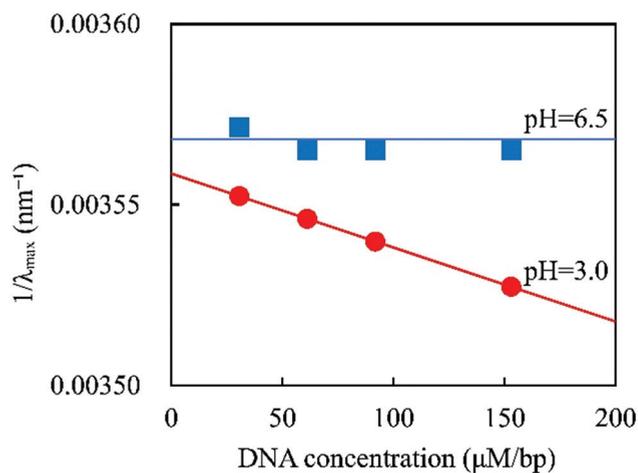


**Figure 1:** Mechanism of photopolymerization of *p*-phenylenediamine in the presence of photooxidation catalyst, Ru(bpy)<sub>3</sub><sup>2+</sup>. SQ is semiquinone.



**Figure 2:** Relationship between pH and 1/λ<sub>max</sub> in the presence of 59 μM PPD.

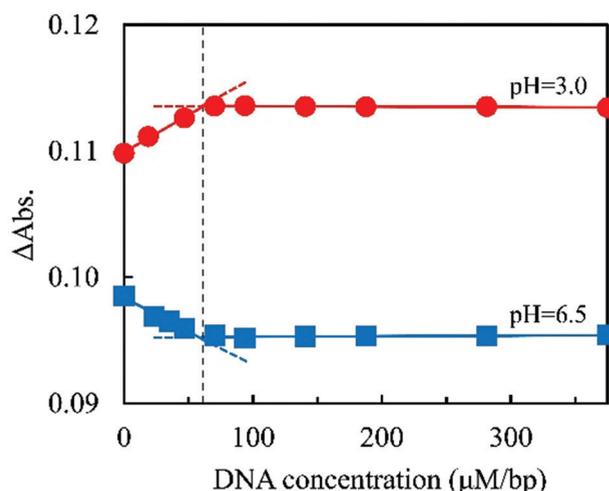
The UV-vis spectra of aqueous PPD solutions were acquired, where the pH was adjusted with hydrochloric acid to determine a suitable pH range for forming protonated PPD. Figure 2 shows the relationship between the pH and 1/λ<sub>max</sub> in the presence of 59 μM PPD. The maximum absorption wavelength, λ<sub>max</sub>, arising from the π-π\* transition of PPD was at approximately 280 nm, and two regions with a boundary at approximately pH 4.5 were observed. The 1/λ<sub>max</sub> value decreased linearly from pH 6.5 to approximately 4.5, but remained constant at pH ≤4.5, indicating that PPD protonation was saturated below pH 4.5. Herein, pH 3.0 and 6.5 were selected for comparison. pH 3 is the lower limit for minimizing the probability of cleavage of the DNA backbone via depurination at room temperature [19].



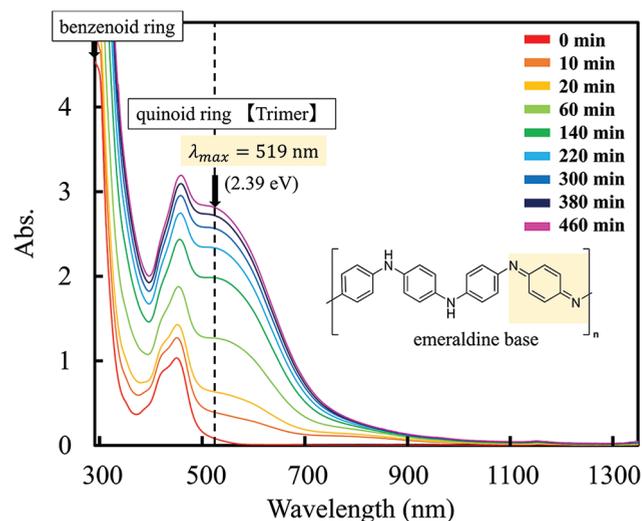
**Figure 3:** Relationship between DNA concentration and 80 μM *p*-phenylenediamine 1/λ<sub>max</sub> at pH 6.5 and 3.0.

### 3.2. Electrostatic Interaction between PPD and DNA

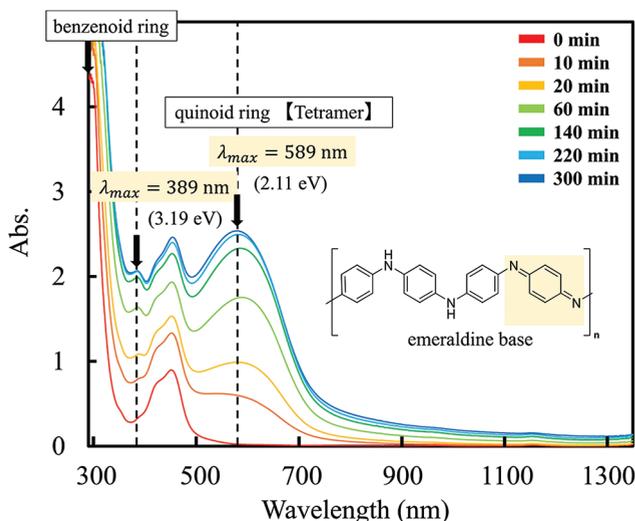
The effect of the DNA concentration on the spectroscopic properties of PPD was evaluated by monitoring λ<sub>max</sub> due to the π-π\* transition in a mixture of 80 μM PPD and given concentrations of DNA at pH 6.5 and 3.0. Figure 3 shows the relationship between the DNA concentration and PPD 1/λ<sub>max</sub>. With increasing DNA concentration, PPD 1/λ<sub>max</sub> was almost constant at pH 6.5, but decreased linearly at pH 3.0. This indicates that at pH 6.5, there is no electrostatic interaction between DNA and PPD. However, at pH 3.0 the interactions are operative and become stronger with increasing DNA concentration, suggesting that a similar electrostatic interaction with PPD would also be present with PANI.



**Figure 4:** Difference in absorbance of aqueous mixtures of 6.0  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and given concentrations of DNA versus that of aqueous solutions of DNA of the corresponding concentrations at pH 6.5 and 3.0.



**Figure 6:** Absorption spectra of 0.59 mM *p*-phenylenediamine and 60  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  mixture in the presence of 0.94 mM/bp DNA at pH 6.5.



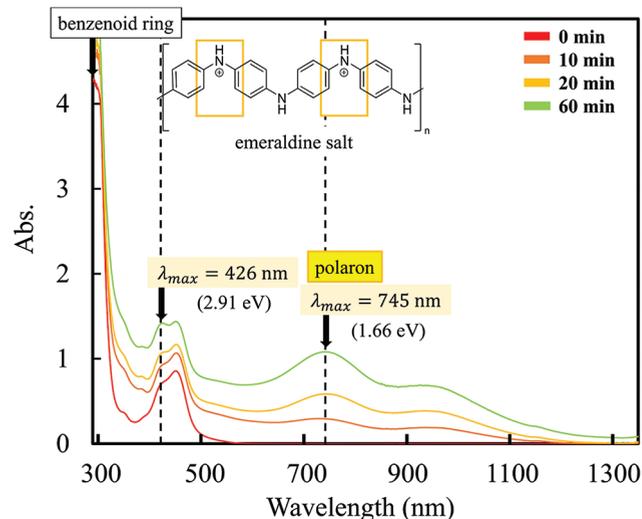
**Figure 5:** Absorption spectra of the mixture of 0.59 mM *p*-phenylenediamine and 60  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  at pH 6.5.

### 3.3. Electrostatic Interactions between $\text{Ru}(\text{bpy})_3^{2+}$ and DNA

The spectroscopic behavior of  $\text{Ru}(\text{bpy})_3^{2+}$  in the presence of DNA was evaluated by monitoring the absorbance band at 451 nm due to the MLCT, at pH 6.5 and 3.0 [20]. Figure 4 shows the difference in the absorbance of mixed aqueous systems of 6.0  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and given concentrations of DNA versus that of aqueous solutions of DNA of the corresponding concentrations at pH 6.5 and 3.0.

There were two regions with a boundary around the DNA concentration of approximately 63  $\mu\text{M}/\text{bp}$ . When the DNA concentration was increased to approximately 63  $\mu\text{M}/\text{bp}$ , the absorbance decreased at pH 6.5 but increased at 3.0, and remained constant above approximately 63  $\mu\text{M}/\text{bp}$  at both pH values. This indicates that  $\text{Ru}(\text{bpy})_3^{2+}$  interacts with the DNA phosphate groups through 10.5 pairs of nucleotides, that is, one turn of the DNA.

Double helix per  $\text{Ru}(\text{bpy})_3^{2+}$ . Based on this relationship, the DNA concentration (per base pair) was adjusted to exceed 10.5 times that of the photocatalyst.



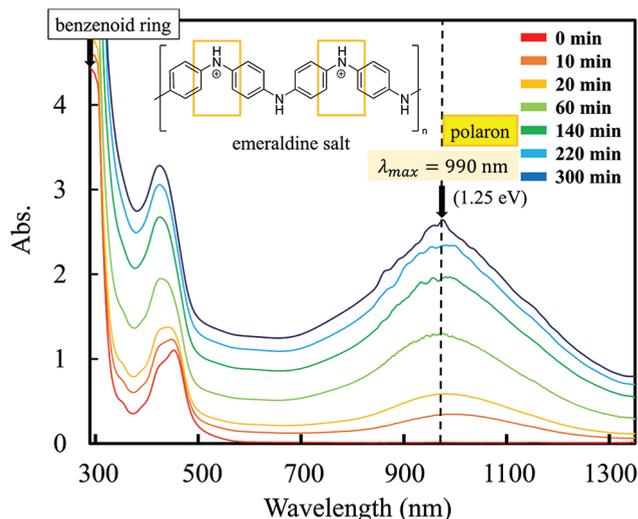
**Figure 7:** Absorption spectra of 0.59 mM *p*-phenylenediamine and 60  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  mixture at pH 3.0.

### 3.4. UV-vis-NIR Absorption Spectra of PPD and $\text{Ru}(\text{bpy})_3^{2+}$ Mixture with and Without DNA

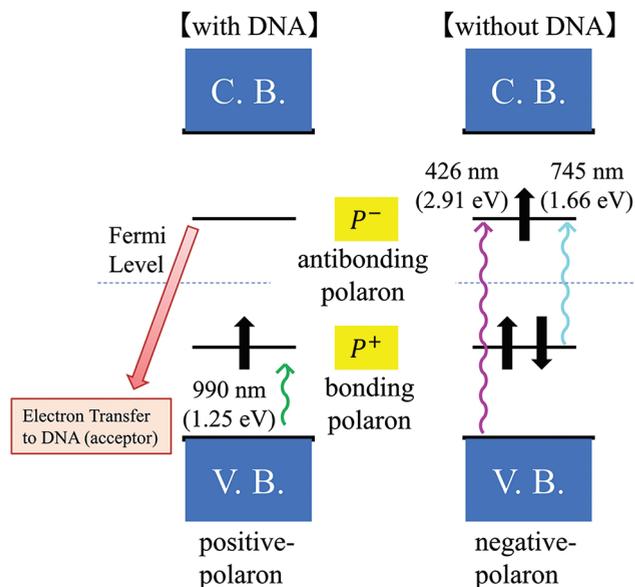
UV-vis-NIR absorption spectra were acquired in aqueous systems containing a mixture of PPD and  $\text{Ru}(\text{bpy})_3^{2+}$  with and without the addition of DNA, at pH 6.5 and 3.0 (adjusted with hydrochloric acid).

First, photopolymerization with and without DNA was performed at pH 6.5. Figure 5 shows the absorption spectra of the mixed 0.59 mM PPD and 60  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$ . No absorption peaks of the  $\pi-\pi^*$  transitions of the benzenoid and quinoid rings of the aniline-derived oligomers ( $n \approx 4$ ) were observed at 389 and 589 nm in the absence of visible-light irradiation. However, as the irradiation time increased, the peaks gradually became more intense and converged after approximately 5 h [21]. Figure 5 shows the absorption spectra of the mixture of 0.59 mM PPD and 60  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$ .

In contrast, when DNA was added to the system at 0.94 mM/bp, no absorption peak was observed at 519 nm without photo-irradiation, but



**Figure 8:** Absorption spectra of 0.59 mM *p*-phenylenediamine and 60  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  mixture in the presence of 0.94 mM/bp DNA at pH 3.0.

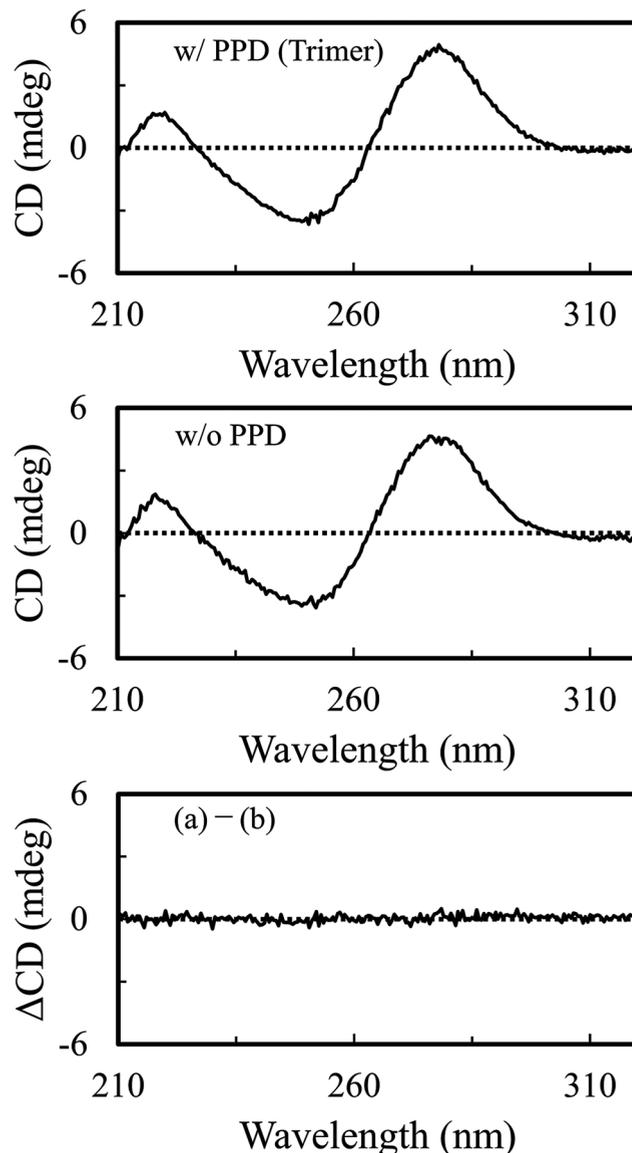


**Figure 9:** Band diagram of polaron generated during photopolymerization of DNA/PANI complex.

the intensity of the shoulder peak gradually increased with increasing irradiation time, as shown in Figure 6.

Aniline-derived oligomers were formed when aniline dimers (as the starting material) were irradiated with visible light, even when DNA was added. With the addition of DNA, the absorption peak was blue-shifted by 70 nm compared to the peak of the quinoid ring at 589 nm in the absence of DNA. Thus, it is proposed that energy transfer from PPD to DNA results in insufficient PPD excitation energy, which suppresses the photopolymerization reaction and results in the formation of oligomers with relatively short bond conjugation lengths ( $n \approx 3$ ). Therefore, the data confirmed that the photopolymerization reaction in the higher pH region (pH 6.5), starting from the aniline dimer, did not progress to PANI and stopped at the formation of oligomers, regardless of the presence or absence of DNA.

Photopolymerization in the absence of DNA was evaluated at pH 3.0. With increasing proton concentration, the peak derived from the quinoid

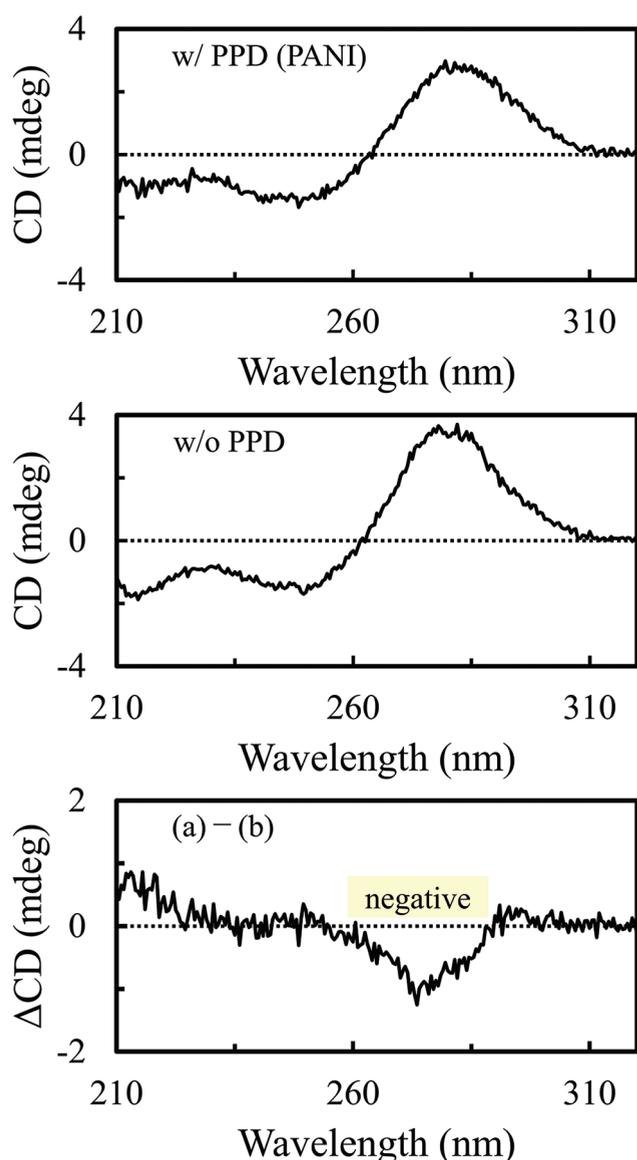


**Figure 10:** CD spectra of 38  $\mu\text{M}$ /bp DNA and 2.4  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  mixture (a) with and (b) w/o 24  $\mu\text{M}$  *p*-phenylenediamine at pH 6.5. (c) Differential CD spectrum of (a) versus (b).

ring at approximately 589 nm was attenuated; instead, new peaks appeared near 426 and 745 nm (2.91 and 1.66 eV), as shown in Figure 7.

Previous studies have shown that this peak originates from “polaron” bands of PANI and that the electron-accepting molecule responsible for polaron formation is oxygen in the aqueous medium. It is proposed that increasing the acidity of the system promotes PPD protonation. This increases the degrees of polymerization in the reaction system, where the process was terminated by oligomerization, and promotes polaron formation. Based on these facts and the green color of the solution after irradiation, it is deduced that the emeraldine salt, known to exhibit electrical conductivity owing to its polaron structure, was obtained by photopolymerization at lower pH. This is consistent with previously reported mechanisms for the photocatalytic polymerization of PPD [15,16].

In the system to which DNA was added at 0.94 mM/bp, the peak derived from the quinoid ring at approximately 589 nm was attenuated and new peaks appeared near 426 and 990 nm (1.25 eV), as shown in Figure 8. Two bands were observed between the valence and conduction bands, corresponding to bonding and antibonding polarons, as shown in Figure 9.



**Figure 11:** CD spectra of 38  $\mu\text{M}$ /bp DNA and 2.4  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  mixture (a) with and (b) w/o 24  $\mu\text{M}$  *p*-phenylenediamine at pH 3.0. (c) Differential CD spectrum of (a) versus (b).

The peak at 426 nm was weak and that at 745 nm was almost absent for the DNA-added system because of the efficient electron transfer from the antibonding polaron bands to the DNA. The peak at 990 nm, that is, the polaron peak, was strong in the spectrum of the DNA-added system, suggesting that more polarons were present when DNA was present, but only a small number of polarons was present when DNA was absent. This suggests that DNA plays a role (acceptor herein) in effectively promoting the formation of polarons, resulting in the formation of a DNA/PANI complex owing to stronger electrostatic interactions between PANI and DNA. Furthermore, the addition of DNA induced a peak shift to the long-wavelength side (by 245 nm) compared with that in the absence of DNA. This long-wavelength shift also supports the stronger electrostatic interaction between PANI and the added DNA, which is consistent with the expectations in Section 3.2. Plausibly, the conformation of the p-orbital perpendicular to the main chain of PANI changed from a non-overlapping state (random structure) to an overlapping state upon adding DNA, resulting in a red-shift of the peak due to extension of the conjugation length.

### 3.5. CD and Differential CD Spectra

To examine the electrostatic interaction between PANI (including oligomers) and DNA from a structural perspective, CD spectra were acquired after photo-irradiation of a DNA and  $\text{Ru}(\text{bpy})_3^{2+}$  mixture that was diluted 25-fold, with and without the addition of PPD. Both spectra showed a “positive Cotton effect” (Figure 10a and b), where the band near 285 nm was positive and the band near 245 nm was negative. This difference was unclear at pH 6.5. Hence, for more detailed analysis, differential CD spectra were obtained with and without PPD. As shown in (Figure 10c), both the negative band at approximately 245 nm, derived from the helicity of B-DNA [22], and the band near 285 nm (attributed to the  $\pi$ - $\pi^*$  transition of PANI) disappeared. This means that there were no electrostatic interactions between the DNA and PANI (oligomers) at pH 6.5.

Subsequently, CD spectra were acquired at pH 3.0. As shown in Figure 11, almost no difference was observed in the CD spectra with and without PPD, similar to that at pH 6.5. Thus, a “differential CD spectrum” was obtained. Because the negative band at approximately 245 nm disappeared, it was concluded that no structural change in the DNA occurred with PANI formation.

In contrast, the band near 285 nm was negative, indicating that the electrostatic interaction of DNA with PANI was activated. In other words, PANI was regularly wound in the direction of the main chain of the DNA to such an extent that it did not change the DNA structure owing to electrostatic interactions at pH 3.0, whereas PANI did not interact with DNA and existed independently at pH 6.5.

## 4. CONCLUSION

PANI prepared by irradiating PPD (an aniline dimer, as a starting material) with visible light at a pH 3.0 in the presence of a photooxidation catalyst,  $\text{Ru}(\text{bpy})_3^{2+}$ , yielded an emeraldine salt structure with polarons, confirming the possibility of imparting conductivity for use in next-generation devices. Adding DNA to this system converted the structure of the main chain of PANI, enabling p-orbital overlap. The DNA/PANI complex prepared under acidic conditions (pH 3.0) exhibited a self-assembled nanorope-like structure, in which DNA acted as a template for PANI.

## 5. ACKNOWLEDGMENTS

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