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Preparation of a $[Ru(bpy)_2(dppz)]^{2+}$-Intercalated DNA Cast Film Using a Self-Standing Method and Its Luminescence Tuning by Cu^{2+} Ions and EDTA

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Supporting Information

ABSTRACT: In this correspondence, we report on the first preparation of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated (bpy = 2,2'-bipyridine; dppz = dipyrido[3,2-*a*:2',3'-*c*]phenazine) DNA films on an indium−tin oxide surface via a solution-based self-standing strategy, carried out by the direct mixing of aqueous solutions of both anionic DNA and cationic metallointercalator at a molar ratio of 5:6. The luminescence of a $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast film is studied and found to show excellent tunable characteristics by Cu^{2+} ions and ethylenediaminetetraacetic acid addition.

DNA is very important either as a source of biological information depending on base sequences[1] or as a molecular material of π-electron-rich base pairs.[2] Because intercalation of $[Ru(bpy)_2(dppz)]^{2+}$ (bpy = 2,2′-bipyridine; dppz = dipyrido-[3,2-*a*:2′,3′-*c*]phenazine) between DNA bases leads to an enhanced emission (structure shown in Figure 1), numerous DNA-light-switch compounds have been reported.[3,4] These systems are of interest because they may have potential applications in sensing and signaling, as well as in data storage and communication.[5,6] To date, the DNA-light-switch behavior of metallointercalators in dilute solutions has been rigorously studied,[7,8] and the energy of $[Ru(bpy)_2dppz]^{2+}$ at the excited state varies with the polarity of the solvents. There are two major approaches to achieving DNA-light-switch mechanisms. (i) Intercalation of the dppz ligand between DNA bases leads to an increase in the energy of nonemissive ^{3}MLCT excited states, thus making the emissive state thermally accessible and turning on the emission.[9] (ii) Protection of the dppz ligand by DNA from its interaction with solvent water molecules results in an enormous increase in the quantum yield.[10]

The enhanced emission of metallointecalators by DNA was recently shown to be "turned off" by coordination of various foreign metal ions to a vacant multidentate ligand.[11,12] These studies probing the chemical modulation of a DNA molecular light switch were typically carried out in aqueous buffer solutions.[13,14] Because DNA or luminescent material could also be present in a condensed or solid state,[15,16] the measurements in dilute solutions may not always be representative of cellular DNAs and solid-state luminescent devices. Therefore, chemical tuning of the photoluminescence of a metallointercalator-based DNA solid film becomes increasingly important. To the best of our knowledge, the result from this study describes the first example of the fabrication of a metallointercalator-based luminescent DNA film and a further study of the light-switch behavior of the cast film through chemical modulation of the solid−liquid interface.

We propose a simple, self-standing preparation of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films as follows (see Figure 1): two aqueous solutions of $[Ru(bpy)_2(dppz)](ClO_4)_2$ (1.0 mM in 0.30 mL) and DNA from sperm herring (5.0 mM in 0.05 mL) were first introduced into a typical cell on an ITO-coated glass plate and then mixed at room temperature for 5 min under vigorous shaking. The resultant solution was kept at a constant temperature of 40 °C for 15 h to evaporate the solvent. To remove unimmobilized $[Ru(bpy)_2(dppz)]^{2+}$ and/or DNA, the cast films were immersed in Tris buffer solutions (10 mM Tris/50 mM NaCl, pH 7.2) for 3 h. After removal from the buffer solution, the cast film was dried at room temperature, leading to a uniform orange-red film on the ITO surface. As shown in Figure 1, two distinct small silver pellets were seen through the film. ***Caution!*** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of the material should be prepared and handled with great care.*

The obtained film shows a broad IR absorption peak at 3200 cm^{-1}, indicating the presence of hydrogen bonds between complement nucleic bases in double-helical structures.[17] The $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films are found to be soluble in aqueous media but only sparingly soluble in Tris buffer solutions and most organic solvents, suggesting that $[Ru(bpy)_2(dppz)]^{2+}$ intercalates completely between base pairs of DNA. The electronic absorption spectra of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films exhibit a ligand-centered (LC) n → π^* transition arising from the dppz ligand in the 350−400 nm region and a Ru (dπ) → ligand (π^*) (metal-to-ligand charge transfer, MLCT) transition in the visible region (curve 1 of Figure 2). These LC and MLCT absorptions are typical features of polypyridylruthenium(II) complexes.[18] The lowest-energy MLCT maximum is observed at 443 nm. Moderate emission from the ^{3}MLCT excited state of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films is observed with λ_{em} = 600.2 nm, similar to that measured for the cast films (λ_{em} = 606.0 nm) or 10 μM $[Ru(bpy)_2(dppz)]^{2+}$/8.3 μM DNA (λ_{em} = 603.4 nm) in buffer solutions (curves 2 and 3 of Figure 2).

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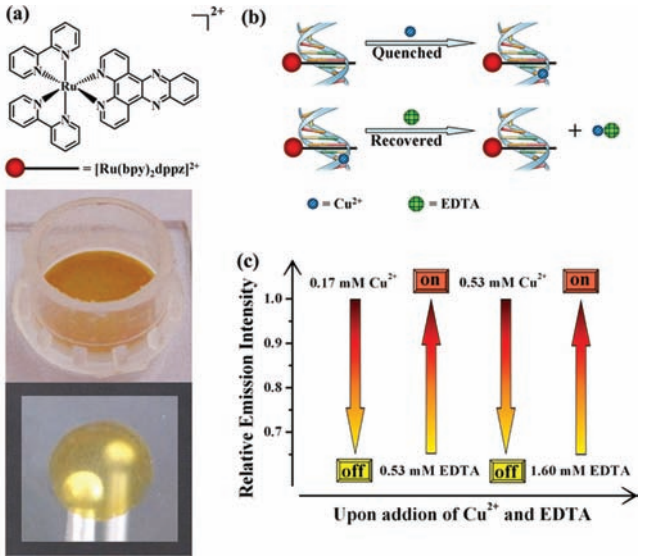

Figure 1. Schematic illustration and a photograph of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films formed on an ITO surface. Insets a and b show the structure of $[Ru(bpy)_2(dppz)]^{2+}$ and the tuning principle of luminescence of self-standing cast films by Cu^{2+} and EDTA, respectively. Inset diagram c represents the relative emission intensity of cast films upon the sequential addition of Cu^{2+} and EDTA in buffer solutions containing 10 mM Tris and 50 mM NaCl for 5 min interval (λ_{ex} = 450 nm; λ_{em} = 606 nm).

To estimate the effect of the solvent on the luminescence efficiency of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films, we concentrate on the changes in the emission and absorption spectra shown in Figure 2. The ratios of emission-integrated areas between 550 and 700 nm to absorption areas ($\Delta\lambda$=100 nm) centered around 450 nm for $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films on the ITO surface and in a buffer solution are found to be 1025 and 389, respectively, suggesting that the luminescence efficiency of the cast films is weakened by water molecules.[19] In addition, the buffer solution containing 10 μM $[Ru(bpy)_2(dppz)]^{2+}$ and 8.3 μM DNA (at a 6:5 molar ratio) shows a 19-fold increase in the ratio between emission and absorption areas compared with $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films in a buffer solution. This finding suggests that strong interactions between $[Ru(bpy)_2(dppz)]^{2+}$-based molecules decrease the luminescence efficiency of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films under excitation of 450 nm light.

With the success of preparing $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films, chemical tuning of the luminescence of the resultant cast films is assessed by the introduction of Cu^{2+} ions and EDTA. As shown in Figure 3a, the emission spectra of 10 μM $[Ru(bpy)_2(dppz)]^{2+}$/50 μM DNA in a buffer solution exhibit intense luminescence (switch on). The addition of 400 μM Cu^{2+} quenches the luminescence intensity by 30%, thus turning the light switch off. The result provides indirect evidence for the association of Cu^{2+} ions with $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA in solution. The electronic absorption spectra of $[Ru(bpy)_2(dppz)]^{2+}$ or DNA with Cu^{2+} addition (Figures S1 and S2 in the Supporting Information) revealed that the binding of Cu^{2+} to the dppz ligand already bound to the Ru^{2+} ion is basically impossible under the conditions used in this experiment. In contrast, Cu^{2+} can bind to the DNA,[20] leading to a decrease in the absorbance intensity of DNA. As a result, the Cu^{2+} ions are attached by electrostatic attraction to a $[Ru(bpy)_2(dppz)]^{2+}$-

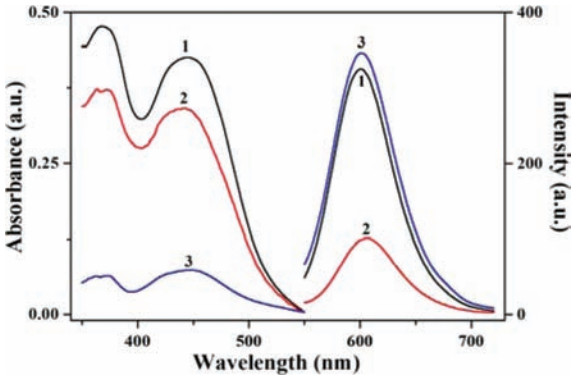

Figure 2. UV−vis absorbance and photoluminescence spectra of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films: (1) cast film on the ITO surface; (2) cast film in a buffer solution; (3) 10 μM $[Ru(bpy)_2(dppz)]^{2+}$ and 8.3 μM DNA in buffer solutions. λ_{ex} = 450 nm.

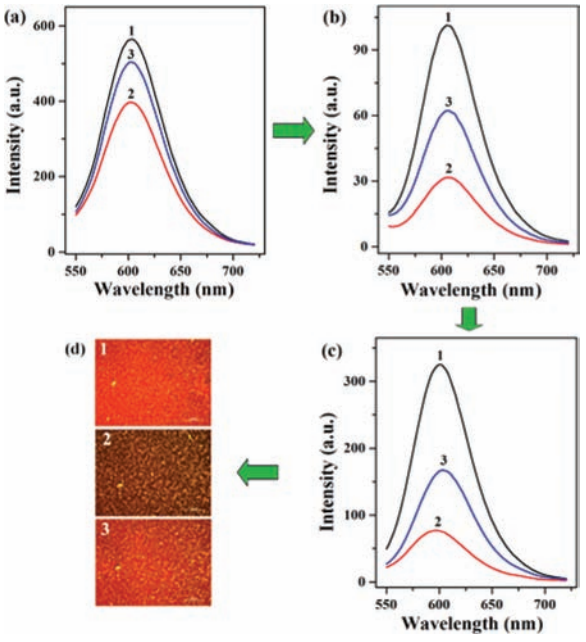

Figure 3. Emission spectra of a 10 μM $[Ru(bpy)_2(dppz)]^{2+}$/50 μM DNA buffer solution (a) and a $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast film (b) in the absence (1) and presence of 0.4 mM Cu^{2+} (2) and 0.4 mM Cu^{2+}/0.4 mM EDTA (3) and emission spectra (c) and fluorescence microscope images (d) of cast films (1) upon the sequential addition of Cu^{2+} (2) and EDTA (3), obtained by immersion of the film in 0.2 mM Cu^{2+} and 0.2 mM EDTA solutions for 15 min, respectively.

intercalated DNA backbone, as depicted in inset b of Figure 1. Moreover, introducing an equimolar amount of EDTA into the turned-off system partially recovered the quenched luminescence (turned back on). The incomplete switch on by equimolar EDTA to quenchers is attributed to the binding of Cu^{2+} with $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA.

When $[Ru(bpy)_2(dppz)]^{2+}$ and DNA in a buffer solution are fabricated on the ITO surface, as shown in Figure 3b, the equimolar Cu^{2+} and EDTA in solution are capable of turning the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films off and on, similar to that measured for the solution system. This finding reveals that association of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA with Cu^{2+} also exists at the solid−liquid

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interface, and subsequently EDTA in solution is capable of binding Cu^{2+} on the ITO surface, leading to the release of the Cu^{2+} bound to $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films and the switching on of the luminescence. As shown in inset c of Figure 1, controlled quenching and complete recovery in the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films can be accomplished by the addition of appropriate amounts of Cu^{2+} and EDTA, respectively. The complete recovery of luminescence suggests that luminescence of the cast film can be switched on and off repetitively with a gradual increase in the concentrations of Cu^{2+} and EDTA.

Furthermore, we found that emission of the cast film decreases linearly with an increase in the Cu^{2+} concentration and recovery by the EDTA addition of quenched emission increases with the EDTA concentration (Figures S3 and S4 in the Supporting Information). In addition, luminescence of a $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast film showed a larger, slower quenching than that in solution because of strong interactions of the cast film with Cu^{2+} ions (Figure S5 in the Supporting Information). Because diffusion is reduced in the cast films, the quenching is likely to be static in nature.[11]

As shown in Figure 3c, the introduction of Cu^{2+} and EDTA in the absence of a buffer solution can also turn the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films off and on, respectively. Under excitation of blue lights, the fluorescence images of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films on an ITO surface in the absence and presence of Cu^{2+} and EDTA confirm the observations from corresponding emission spectra. The fluorescence images of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films in Figure 3d show an intense orange-red appearance, indicating quenching of the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films by Cu^{2+}. However, the presence of Cu^{2+} does not alter the configuration of the cast films, suggesting that coordination of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films to Cu^{2+} does not mangle the backbone structure of the cast films. Also, the addition of EDTA recovers fully the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films quenched by Cu^{2+}.

In summary, a simple solution-based self-standing strategy is effective for the preparation of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films. Spectral studies suggest that the cast film possesses excellent photosensitive and luminescent properties. The introduction of Cu^{2+} and EDTA was found to chemically turn off and on the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-intercalated DNA cast films.

■ ASSOCIATED CONTENT

Supporting Information. Absorption and emission changes of ruthenium(II) complex/DNA upon Cu^{2+} (or EDTA) addition (Figures S1−S4) and emission changes as a function of the interaction time of the introduction of Cu^{2+} (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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