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In situ electrochemically tuned photoluminescence of $[Ru(bpy)_2(dppz)]^{2+}$ aggregates with single-walled carbon nanotubes and DNA monitored by guanine oxidation

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Abstract A classical ruthenium(II) complex $[Ru(bpy)_2(dppz)]^{2+}$ (bpy = 2,2′-bipyridine, dppz = dipyrido[3,2-a:2′,3′-c]phenazine) was combined with guanine and single-walled carbon nanotubes dispersed with DNA (SWCNTs-DNA) to prepare electrochemically tunable photoluminescence materials. These multi-component aggregates were found to show enhanced luminescence by the electrocatalytic oxidation of guanine under the excitation of a continuous wave green laser at a constant anodic potential via an electrode-solution interface. The results from this study provide a significant foundation for better understanding of DNA-based luminescent devices.

Introduction

Since polypyridyl ruthenium complexes possess excellent photoluminescent, electroluminescent and/or electrochemiluminescent properties [1–4], they have been exploited as spectroscopic or redox indicators in DNA-based devices involving non-covalent interactions between the ruthenium complexes and DNA, such as electrostatic attraction, groove-surface binding, and intercalation [5, 6]. The emission properties of Ru(II) complexes possessing ligands with a phenazine unit can provide a means to turn their luminescence on and off. For example, $[Ru(bpy)_2(dppz)]^{2+}$ (bpy = 2,2′-bipyridine, dppz = dipyrido[3,2-a:2′,3′-c]phenazine) shows no photoluminescence in aqueous solution at ambient temperatures, but intense photoluminescence in the presence of double stranded DNA. Hence, this classical Ru(II) complex was dubbed as a molecular light switch compound of DNA [7, 8]. The well-characterized emission properties of Ru(II) complexes, when intercalated strongly between DNA bases, have allowed them to be employed as spectroscopic probes to study DNA-mediated charge transfer kinetics using a modified flash-quench technique [9]. However, this type of photo-induced charge transfer through DNA simultaneously results in the permanent oxidation of guanine, which has the lowest oxidation potential among naturally occurring bases [10, 11]. Hence, there is need for a method to measure the photoluminescence of DNA-based materials associated with guanine oxidation.

To effectively clarify the effects of DNA oxidation on DNA-based luminescent devices, electrochemical methods can be combined with emission spectroscopy under visible light irradiation using Ru(II) complexes as electrocatalytic mediators or photo-oxidants. On the other hand, single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) have been identified as a catalyst of redox reactions [12]. However, poor dispersion of CNTs in both aqueous and non-aqueous solvents has severely limited their effective use and further development. To adequately disperse CNTs in water for the preparation of CNT-based functionalized materials, various surfactants and DNA have been used with the help of ultrasonic agitation [13–15]. Therefore, one would expect

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to be able to electrochemically monitor the luminescence of Ru(II) complexes upon incorporation of DNA-dispersed SWCNTs.

Our laboratory has previously focused on the photoluminescence of DNA-$[Ru(bpy)_2(tatp)]^{2+}$ conjugates (tatp = 1,4,8,9-tetra-aza-triphenylene) on a polyaniline/indium-tin oxide (ITO) electrode tuned by applied potentials under the excitation of a continuous wave (CW) green laser [16]. In the current work, we have studied the photoluminescence of a classical polypyridyl complex $[Ru(bpy)_2(dppz)]^{2+}$ upon incorporation of DNA-dispersed SWCNTs, monitored by the oxidation of guanine. The results from this study should be valuable for better understanding of DNA-based luminescent devices.

Experimental

Tris-hydroxy methyl amino-methane (Tris) from Sigma was used to prepare electrolyte buffer solutions. Single-walled carbon nanotubes (SWCNTs) with an inside diameter of 2–5 nm and length of 10–30 μm were obtained from Chengdu Organic Chem. Co., China. Herring sperm DNA (Qiyun Co.) and guanine (Shanghai Chem. Co.) were used as received. Unless otherwise noted, the buffer solution was 10 mmol L^{-1} Tris/50 mmol L^{-1} NaCl of pH 7.2, prepared with doubly distilled water. $[Ru(bpy)_2(dppz)]Cl_2$ and $[Ru(bpy)_2tatp]Cl_2$ were synthesized following the reported procedures [7, 17]. The structure of $[Ru(bpy)_2(dppz)]^{2+}$ is shown in Fig. 1. The DNA-stabilized SWCNT suspensions were prepared by adding a desired amount of SWCNTs to 0.25 mmol L^{-1} DNA buffer solutions with the aid of ultrasonic agitation (200 W) for ca. 40 min, and then mixing with guanine and $[Ru(bpy)_2(dppz)]^{2+}$ or $[Ru(bpy)_2(tatp)]^{2+}$. Unless otherwise noted, the suspensions contained 0.2 mmol L^{-1} DNA, 28 mg L^{-1} SWCNTs, 0.1 mmol L^{-1} $[Ru(bpy)_2(dppz)]^{2+}$ or $[Ru(bpy)_2(tatp)]^{2+}$, and/or 0.2 mmol L^{-1} guanine.

Voltammetric measurements were performed on a CHI660a electrochemical system (Shanghai, China). Unless otherwise noted, a regular three-electrode system in 0.4 mL test solution was used. It consisted of an indium-tin oxide (ITO) working electrode (sheet resistance ≈20 Ω cm^{-2}, Shenzhen Nanbo Co., China), a platinum counter electrode and an Ag/AgCl (50 mmol L^{-1} NaCl) reference electrode.

Steady-state emission spectra were recorded at ambient temperature using a RF-2500 spectrofluorimeter with 1-cm cell path length. The samples were excited at 450 nm, and the emission spectra were recorded over a wavelength range of 550–670 nm. Fluorescence images were taken using a Nikon Eclipse TS100 inverted fluorescence microscope (Japan), equipped with a 50 W mercury lamp.

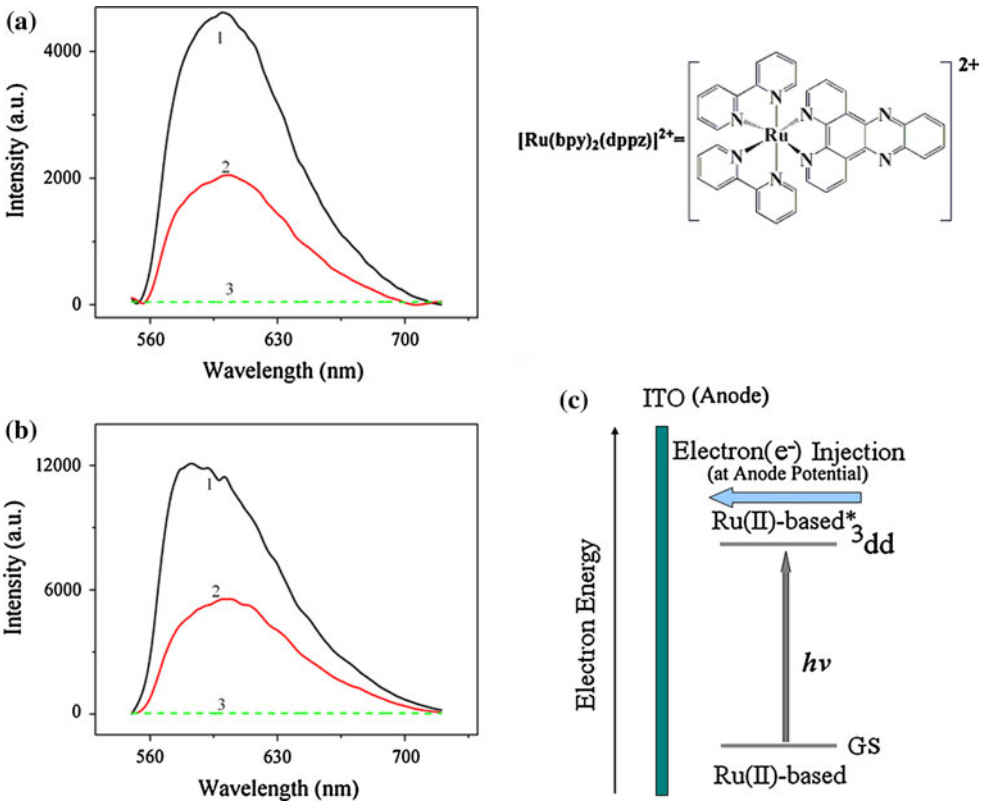

Fig. 1 Emission spectra of (SWCNTs-DNA)-$[Ru(bpy)_2(dppz)]^{2+}$ in the absence (**a**) and presence (**b**) of guanine on the ITO electrode in buffer solution under the excitation of a CW *green* laser at *open* circuit potential (*1*) and 1.2 V (vs. Ag/AgCl) (*2*) for 2 min, respectively. The *dashed line 3* is the emission spectrum in the absence of a CW *green* laser at 1.2 V anodic potential. Diagram **c** shows the luminescence principles of (DNA-SWCNTs)-incorporated $[Ru(bpy)_2(dppz)]^{2+}$ aggregates tuned by external electric field. *Inset* is the structure of the complex

The images were captured with a Nikon E4500 camera with blue light.

The electrochemically tuned emission spectra were recorded using a home-built system similar to that used in our previous report [16]. This system consisted of an optical microscope (Zeiss Axio Observer A1, Germany), a continuous wave (CW) green laser source (532 nm, Coherent Verdi-5, USA), and an electrochemical setup. The full scale was obtained by the modulation of a photo multiplier tube (PMT) and lock-in amplifier, operated at a biased voltage of 400 V. The collected emission intensity was calibrated with fluorescent polystyrene particles [18]. All the experiments were performed at room temperature (23–25 °C).

Results and discussion

Figure 2 shows the steady emission spectra and fluorescence microscopic images of $[Ru(bpy)_2(dppz)]^{2+}$ in the absence and presence of DNA, SWCNTs and guanine on the ITO surface by solution cast method, i.e., placing $[Ru(bpy)_2(dppz)]^{2+}$, DNA, SWCNTs, and/or guanine suspensions dropwise on the ITO surface, followed by solvent evaporation/drying at room temperature. $[Ru(bpy)_2(dppz)]^{2+}$ exhibits a negligible luminescence (curve 1 and image 1). The addition of DNA increases the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ due to intercalation between the DNA bases, involving a $d\pi(Ru) \rightarrow \pi^*(dppz)$ electron transition (curve 2 and image 2) [19]. In general, SWCNTs used in aggregates can serve as a catalyst of redox reactions [20]. In the present case, SWCNTs act as a quencher to decrease the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ intercalated with DNA (curve 3 and image 3). However, addition of guanine is found to enhance the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in the SWCNTs-DNA aggregates (curve 4 and image 4). These results reveal that $[Ru(bpy)_2(dppz)]^{2+}$, DNA, SWCNTs, and guanine can be assembled to form an aggregate on the ITO surface and their photoluminescence is based on the metal-to-ligand charge transfer (MLCT) transition of $[Ru(bpy)_2(dppz)]^{2+}$.

The aggregates immobilized on the ITO electrode surface were then put into buffer solutions using an electrochemical cell [16]. The luminescence of the resulting $[Ru(bpy)_2(dppz)]^{2+}$-based species in the electrode-solution interface, under the excitation of a CW green laser, in the absence and presence of guanine is shown in Fig. 1. In the absence of the biased voltage, i.e., under open-circuit conditions, a broad emission peak was observed at about 601 nm (curve 1). This result is in good agreement with the observations from emission spectra and fluorescence microscopic images shown in Fig. 2, suggesting that the luminescence of the aggregates present at the electrode-solution interface also arises from the MLCT excited state of $[Ru(bpy)_2(dppz)]^{2+}$-based species. Therefore, it is interesting to investigate whether an external electric field and guanine oxidation in the aggregates could influence the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-based aggregates.

Luminescence of the aggregates tuned by external electric field

When an external electric field was applied to the luminescent system of $[Ru(bpy)_2(dppz)]^{2+}$-based aggregates under the excitation of a CW green laser, some interesting phenomena were observed. As shown in Fig. 1, when an anodic potential of 1.2 V was added to the $[Ru(bpy)_2(dppz)]^{2+}$-based aggregate-modified ITO electrode, the position of the emission peak was not altered compared with the open-circuit conditions, implying that the emission at two electrode potentials is based on the excited state of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in SWCNTs-DNA aggregates. However, the luminescence intensity at an applied electrode potential of 1.2 V above the open circuit potential was significantly weakened by 55.5%. In the presence of guanine, as depicted in Fig. 1b, the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-based aggregates was enhanced compared with the case without guanine under open-circuit conditions or at 1.2 V anodic

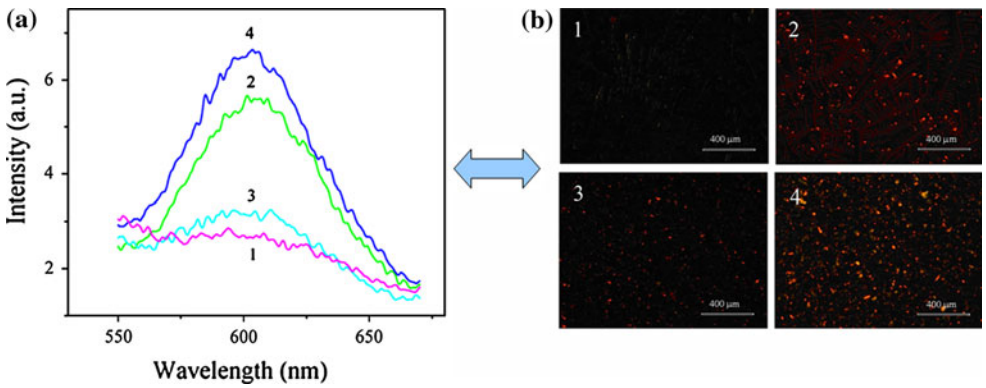

Fig. 2 Emission spectra (**a**) and fluorescence microscope images (**b**) of $[Ru(bpy)_2(dppz)]^{2+}$/ITO (*1*), DNA-$[Ru(bpy)_2(dppz)]^{2+}$/ITO (*2*), (SWCNTs-DNA)-$[Ru(bpy)_2(dppz)]^{2+}$/ITO (*3*) and guanine-(SWCNTs-DNA)-$Ru(bpy)_2(dppz)]^{2+}$/ITO (4) obtained by placing the mixed solution (50 μL) dropwise onto the ITO surface, followed by solvent evaporation/drying at room temperature

potential. In addition, when the green laser was turned off, the application of 1.2 V anodic potential did not lead to a detectable luminescence on the ITO electrode under our experimental conditions, as shown by the dashed line in Fig. 1. Hence, the luminescence change is dependent on the contribution of external electric field to the excited state of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in the aggregates, as shown in Fig. 1c. If the excited level of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in the aggregates is not easily accessible [21], the binding energy between released electrons and injected holes may not be sufficient to overcome the external electric field, leading to the quenching of the $[Ru(bpy)_2(dppz)]^{2+}$ excited state by the external electric field.

Luminescence of the aggregates at constant anodic potential

We wished to know if it is the guanine or DNA in the aggregates that is oxidized at 1.2 V anodic potential. Figure 3 shows the cyclic voltammograms of SWCNTs-DNA and $[Ru(bpy)_2(dppz)]^{2+}$ aggregates in the absence and presence of guanine. There are three oxidative waves, named as peaks I, II, and III. On the basis of our previous report [22, 23], peaks I and III represent the Ru(III)/Ru(II) reactions controlled by diffusion process and surface adsorption process, respectively. Peak II is mainly ascribed to the oxidation of guanine (in SWCNTs-DNA) mediated by the Ru(II) complex. This result reveals that the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ in the aggregates at a constant 1.2 V anodic potential is associated with the oxidation of DNA. To support this conclusion, Fig. 4 gives the emission spectra of (SWCNTs-DNA)-incorporated $[Ru(bpy)_2(dppz)]^{2+}$ aggregates in the absence and presence of guanine upon increasing hold time at 1.2 V. A gradually increasing emission intensity is observed, suggesting that the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in the aggregates at 1.2 V anodic potential is enhanced by the oxidation of guanine. As shown Fig. 4c, the ITO electrode at an anode potential extracts the electrons from Ru(II)-based excited states. The resulting Ru(III) species then oxidize guanine to regenerate the Ru(II) species. As a result, the photoluminescence of $[Ru(bpy)_2(dppz)]^{2+}$-based aggregates under laser irradiation at an anodic potential of 1.2 V is enhanced by the oxidation of guanine. According to this analysis, when the guanine is present in the aggregates, the peak II current values and the increasing emission intensity with increasing hold time at 1.2 V should be larger than those without added guanine. The results from Figs. 3 and 4 (slope of regression lines) prove this proposition, illustrating that the oxidation of guanine may increase the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in aggregates at a constant anodic potential under the excitation of CW green laser.

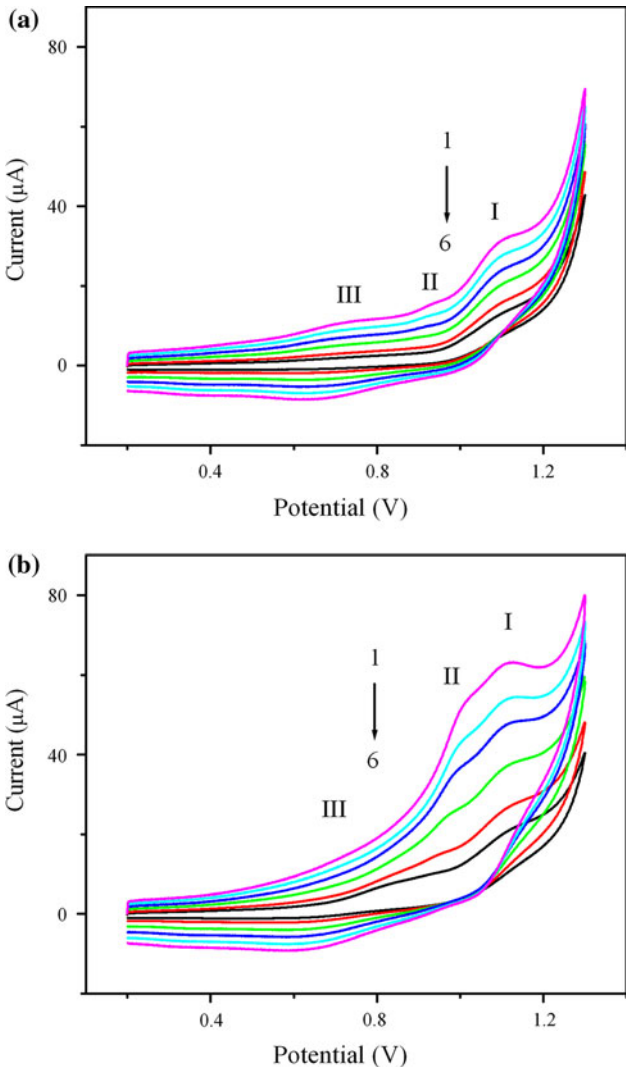

Fig. 3 Cyclic voltammograms of 0.2 mmol L^{-1} DNA/28 mg L^{-1} SWCNTs/0.1 mmol L^{-1} $[Ru(bpy)_2(dppz)]^{2+}$ in the absence (**a**) and presence of 0.2 mmol L^{-1} guanine (**b**). Scan rate (V s^{-1}): (*1*) 0.5, (*2*) 0.4, (*3*) 0.3, (*4*) 0.2, (*5*) 0.1, (*6*) 0.05

To extend this analysis further, we also used a related Ru(II) complex $[Ru(bpy)_2(tatp)]^{2+}$ (tatp = 1,4,8,9-tetraaza-triphenylene) for luminescence measurements at a constant anodic potential under laser irradiation. As shown in Fig. 5, a very interesting result was observed. In the absence of guanine, the emission spectra of $[Ru(bpy)_2(tatp)]^{2+}$ incorporated in SWCNTs-DNA aggregates under green laser excitation showed a decrease in the intensity with increasing hold time at 1.2 V for 5 min, before reaching a constant value. According to the results from the consistent cyclic voltammograms in the absence and presence of SWCNTs-DNA (Fig. 5 inset), the DNA incorporated in SWCNTs and $[Ru(bpy)_2(tatp)]^{2+}$ aggregates (curve 2) is hardly oxidized under our experimental conditions and hence the photoluminescence of $[Ru(bpy)_2(tatp)]^{2+}$ incorporated in SWCNTs-

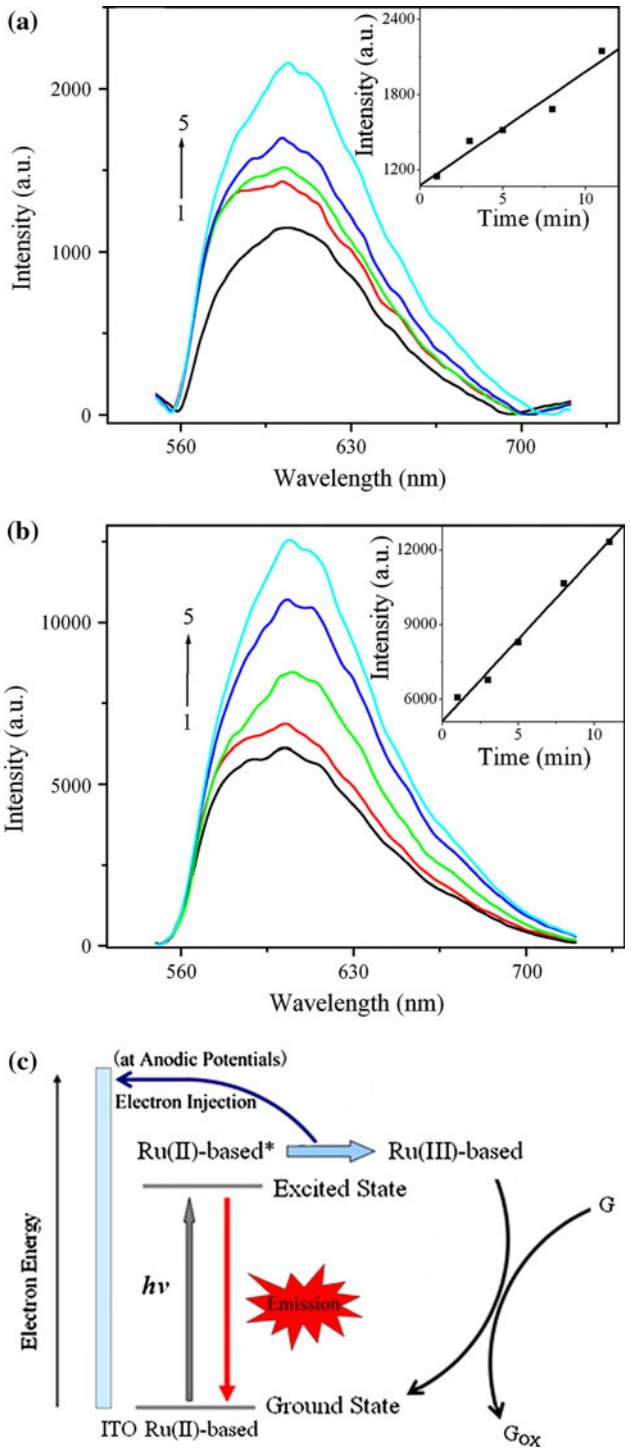

Fig. 4 Emission spectra of (SWCNTs-DNA)-$[Ru(bpy)_2(dppz)]^{2+}$ in the absence (**a**) and presence (**b**) of guanine on the ITO electrode in buffer solution under the excitation of a CW *green* laser on the ITO electrode at 1.2 V anodic potential for different holding times (min): (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 8 and (*5*) 11. Diagram **c** shows the luminescence principles of (DNA-SWCNTs)-incorporated $[Ru(bpy)_2(dppz)]^{2+}$ aggregates at a constant anodic potential monitored by the oxidation of guanine. The *inset* shows the emission intensity as a function of holding time at 1.2 V

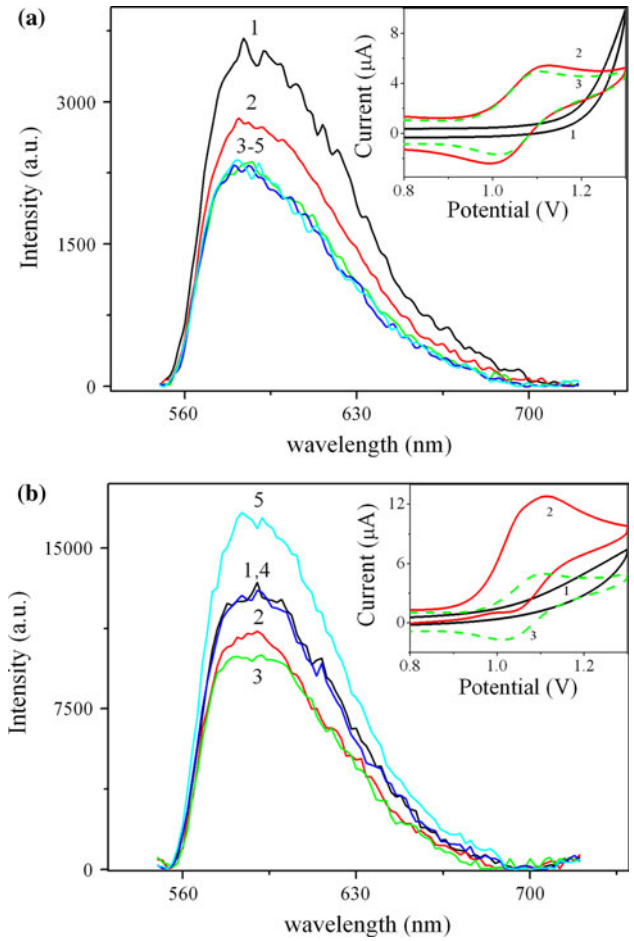

Fig. 5 Emission spectra of (SWCNTs-DNA)-$[Ru(bpy)_2(tatp)]^{2+}$ in the absence (**a**) and presence (**b**) of guanine on the ITO electrode in buffer solution under the excitation of a CW *green* laser on the ITO electrode at 1.2 V anodic potential for different holding times (min): (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 8 and (*5*) 11. The inset shows cyclic voltammograms of 0.2 mmol L^{-1} DNA/28 mg L^{-1} SWCNTs or 0.2 mmol L^{-1} guanine in the absence (*1*) and presence of 0.1 mmol L^{-1} $[Ru(bpy)_2(tatp)]^{2+}$ (*2*) in contrast to 0.1 mmol L^{-1} $[Ru(bpy)_2(tatp)]^{2+}$ alone (*3*) at 0.1 V s^{-1} scan rate

DNA aggregates shows the luminescence changes as illustrated in Fig. 5. However, $[Ru(bpy)_2(tatp)]^{2+}$ has the ability to electrochemically catalyze the oxidation of guanine, as indicated by the larger oxidative currents of $[Ru(bpy)_2(tatp)]^{2+}$ in the presence of guanine in contrast to either $[Ru(bpy)_2(tatp)]^{2+}$ or guanine alone (Fig. 5). As a result, the luminescence intensity of $[Ru(bpy)_2(tatp)]^{2+}$ incorporated in guanine and SWCNTs-DNA aggregates decreases with increasing hold time at 1.2 V over 5 min and then increases for further increasing hold times. This finding indicates that the luminescence of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in SWCNTs-DNA aggregates under green laser excitation at a constant electrode potential can be enhanced by the electrocatalytic oxidation of guanine, as shown in Fig. 4c. Since

the guanine in the aggregates is not continuously replenished, when the holding time at 1.2 V anodic potential becomes longer, the increased luminescence intensity of $[Ru(bpy)_2(dppz)]^{2+}$ incorporated in the aggregates may be changed.

Conclusion

In summary, $[Ru(bpy)_2(dppz)]^{2+}$, DNA, SWCNTs, and guanine can be assembled into a multi-component aggregate. The application of an anodic electrode potential of 1.2 V (versus Ag/AgCl) leads to a tunable luminescence of $[Ru(bpy)_2(dppz)]^{2+}$-based aggregates under laser excitation, as well as the electrocatalytic oxidation of guanine by $[Ru(bpy)_2(dppz)]^{2+}$ upon incorporation into SWCNTs-DNA. The results from this study provide a significant foundation for better understanding of the DNA-based luminescent devices.

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