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Photoactive Deoxyribonucleic Acid (DNA) Bearing Carbazole Moieties and Its Photoluminescence Behavior With Ir(III) Complex

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*The preparation of organic-soluble DNA bearing carbazole side chain (Cz-DNA) was carried out and the resulting Cz-DNA shows good solubility in alcohol, which allows the fabrication of thin films for studying the photophysical properties of DNA in a solid state. We demonstrated the absorption and photoluminescence behaviors of new soluble Ir(III) complex in two polymer hosts of Cz-DNA and poly(*N*-vinylcarbazole) (PVK). We compared the absorption and photoluminescence (PL) spectra with the concentration of Ir(III) complex. The Ir(Cz-ppy)$_3$ in Cz-DNA was observed to have a larger quantum yield and induce enhancement of green emission of Ir(Cz-ppy)$_3$.*

Keywords Cz-DNA; isolation effect; natural DNA; photoluminescence; PVK

Introduction

Double-stranded (ds) DNA obtained from salmon sperm are interesting biodegradable and environmentally friendly biomacromolecules. Because of the regular sequence of the four base pairs in ds-DNA and the abundance of π electrons, ds-DNA can be used in novel electronic devices as an electroactive material [1–2].

More recently, the unique nanostructure and replication properties of DNA molecules have been investigated by physical scientists and engineers interested in incorporating these properties into new or improved devices [3–4]. In contrast to normal polymeric materials, dsDNA has major and minor grooves at which small molecules can bind and some unique molecules are intercalated through the base pairs. The binding interaction between external guest molecules and nucleic acids often leads to a significant change in both structures, which may have an important effect on physiological functions. The enhancement of photoluminescence (PL) in DNA host

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materials has been well documented in the literature; however, the mechanism of this enhancement has not been established. Among the many different kinds of light-emitting organic materials available, phosphorescent materials are particularly promising because both singlet and triplet excitons can generate unique light emission with a theoretical internal quantum efficiency of 100% [5–6]. As is well known, the known Ir(III) complexes in general are excellent candidates for highly efficient electroluminescent (EL) devices after doping into poly(*N*-vinyl carbazole) (PVK).

In this work, we demonstrated the absorption and photoluminescence behaviors of new soluble Ir(III) complex in Cz-DNA and PVK. Soluble iridium complex of Ir(Cz-ppy)$_3$ was selected to be doped into the matrix. We compared the absorption and PL spectra with the concentration of Ir(III) complex. The PL spectral behaviors were compared with varying concentrations of Ir(III) complex and the effects of Cz-DNA structure on the PL intensity was studied.

Experimental

Cz-DNA and Ir(Cz-ppy)$_3$ were synthesized according to our previous reports [7–8].

In order to study absorption behavior, the films of two polymers doped with Ir(Cz-ppy)$_3$ were fabricated on quartz substrates as follows: the solution (2.5 wt.%) of each polymer either in ethanol or chloroform/ethanol mixture was subsequently spin-cast on the quartz glass followed by drying overnight at 40°C for 24 hours under vacuum.

Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10^{-5} mole/L) were measured by using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm. PL spectra of the solutions at room temperature were acquired on a Hitachi's F-7000 FL Spectrophotometer.

When we investigate the temperature dependence of PL spectral behaviour, all PL spectra were recorded using the 325 nm line of a HeCd laser as the excitation light source. For PL measurements, the specimen was mounted on the cold finger in the vacuum chamber (pressure $< 10^{-5}$ Torr) of a closed cycle refrigerator. Emitted light was collected by a lens and analyzed by using a single monochromator with 1 m focal length and a GaAs cathode photomultiplier. Standard lock-in detection techniques were used to maximize the signal-to-noise ratio. The diameter of incident laser beam was about 0.3 mm.

Results and Discussion

In order to prepare Cz-DNA, we employed the natural double stranded (ds) DNA extracted from Salmon sperm. Carbazolyl ammonium bromide was employed to replace the sodium ions associated with a phosphate anion. In order to confirm the reaction completeness, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was performed to measure the concentration of the sodium ion tethering to the phosphate anion. Prior to the reaction, the concentration of sodium was 56770 ppm, while after the reaction with carbazolyl ammonium bromide, the concentration of sodium decreased to less than 62 ppm. Therefore, carbazole (Cz) was substituted into the phosphate anion up to 99.8 or higher. The resultant Cz-DNA is not soluble in water, but is soluble in alcohol or its mixed solvent. For comparison, PVK ($M_w \sim 90{,}000$, ACROS Co.) was also used as a host material that can bear Ir(III) dyes.

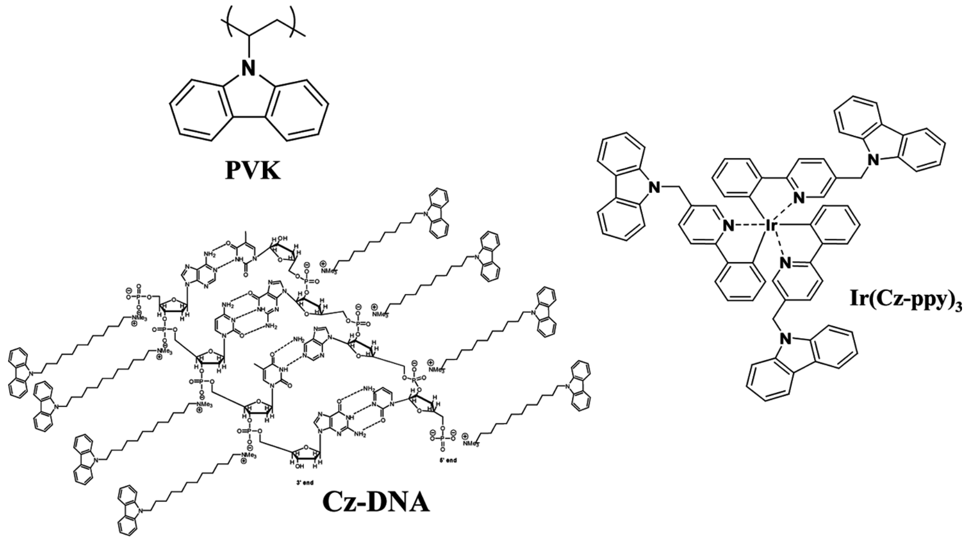


Figure 1. Structures of Ir(Cz-ppy)$_3$, Cz-DNA, and PVK used in this study.

UV-Vis Absorption and Photoluminescent Properties

The absorption and photoluminescent (PL) spectra of the film samples of Cz-DNA and PVK are shown in Figure 2. The absorption spectrum of CzDNA and PVK films are quite similar showing two representative characteristic absorption peaks of carbazole between 333 and 347 nm. In emission spectra of Cz-DNA and PVK, significant difference can be observed; the spectrum of PVK is completely featureless and the spectrum of Cz-DNA exhibits well resolved emission behaviors. It indicates that the carbazole units are well isolated in the solid state compared to those in PVK.

The absorption and PL spectra of the solution sample of Ir(Cz-ppy)$_3$ are also shown in Figure 2. The absorption bands of the spectra of two Ir(Cz-ppy)$_3$ below 320 nm are ascribed to the intra-ligand $\pi-\pi^*$ transitions originating from the Ir-complex, while the absorption at around 343 nm is due to the carbazole moieties. In a lower energy region spanning from 380 to 500 nm, we could observe weak and broad absorption band with shoulders, which can be attributed to spin-allowed and spin-forbidden metal-to-ligand charge transfer (MLCT) transitions of the Ir(III) complexes. The PL spectrum of the Ir(Cz-ppy)$_3$ in $CHCl_3$ solutions is shown in Figure 2 (as a dotted line). The emission maxima of Ir(Cz-ppy)$_3$ was observed at 517 nm in the solution state.

We monitored the absorption spectra of Cz-DNA and PVK films with the concentration of Ir(Cz-ppy)$_3$. No significant variation of absorbance could be observed in two spectra sets due to small concentration. However, most of the characteristic bands were identical with that of Ir(Cz-ppy)$_3$. Shortly, in the comparison of two spectral behaviors, Cz-DNA and PVK doped system did not show any significant interactive absorption bands in the ground state.

In Figure 4, the samples we took the absorption spectra were employed to obtain the emission spectra. As was expected, when increasing the concentration of Ir(Cz-ppy)$_3$ the emission intensity increases monotonically upto 10 wt% of Ir(Cz-ppy)$_3$. At the concentration around 8 wt%, we could not observe the serious

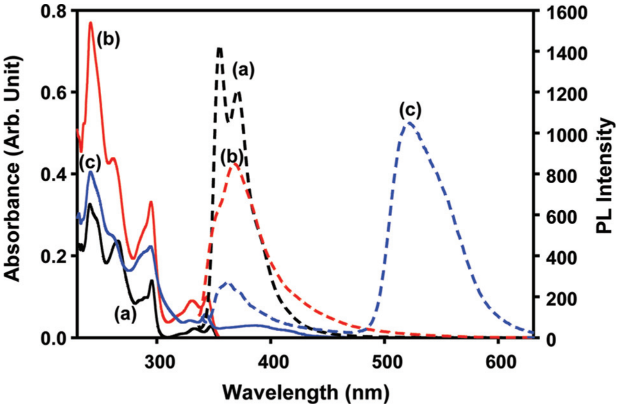
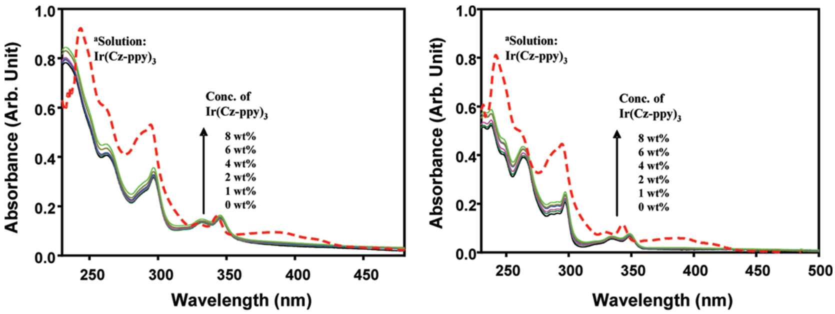
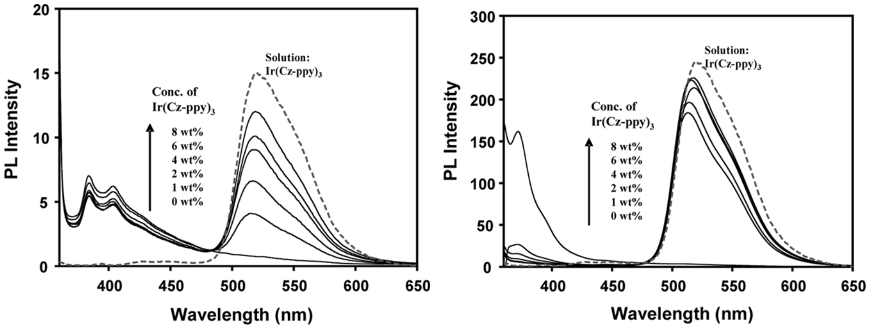


Figure 2. UV-vis absorption and PL spectra of Ir(Cz-ppy)$_3$, Cz-DNA and PVK in the film state. *Sample: (a) Cz-DNA (b) PVK and (c) Ir(Cz-ppy)$_3$ (conc: 1×10^{-5} M in CHCl$_3$).



(a) (b)

Figure 3. UV-vis absorption spectra of Ir(Cz-ppy)$_3$ doped Cz-DNA (a) and PVK (b) in the film state. ^{a}Solution of Ir(Cz-ppy)$_3$ in chloroform.



(a) (b)

Figure 4. Photoluminescence spectra of Cz-DNA and PVK doped with various concentrations of Ir(Cz-ppy)$_3$ dye; *Sample: Thin films with an identical thickness (t:~150 nm). (a) PVK, (b) Cz-DNA; *solution of Ir(Cz-ppy)$_3$ in chloroform.

molecular aggregation in the blend system. Very unusual phenomenon could be found comparing two sets of spectra. We observed the residual emission of carbazole moiety at a higher energy range (~400 nm) in Figure 4a. The energy transfer efficiency at an identical concentration can be compared between two samples. In Cz-DNA, Ir(III) dye can be excited more efficiently with singlet and triplet energy transfer from carbazole moieties. At the same concentration of Ir(III) dye, Cz-DNA exhibited relatively very high intensity of PL emission at 515–518 nm . Therefore, we made a separate figure with 6 and 8 wt% of Ir(III) dye in Cz-DNA and PVK and monitored PL emission along the wavelength. (See Figure 5)

The inset figures display the difference of green emission from two samples. The PL intensity of 6 wt% doped Cz-DNA exhibited 15 ~ 18 times higher emission intensity in comparison with the sample of PVK blend sample.

The Ir(III) dye can exhibit remarkably high affinity for association with nucleic acid along a significant change of electronic and photophysical properties upon DNA binding. Based on many studies [9–10], it can be conjectured that the isolation effect is attributed to groove binding or intercalation of Ir(III) dye through the base pairs. In order to confirm our hypothesis, we measured the PL quantum yield (PLQY) of two cabazole-based polymers using diphenylanthracene in a solution state (*solvent: Chloroform:ethanol = 9:1). From the experiment, we could determine the PLQYs of Cz-DNA and PVK system to be around 0.09 and 0.02. The Cz-DNA showed more than four time higher PLQY than that of the latter. Therefore, the energy transfer efficiency can be expected to be much higher yielding the enhancement of emission intensity from Ir(III) complex. It is interesting to consider the reasons behind the ability of the Cz-DNA films to emit light more efficiently than other polymers.

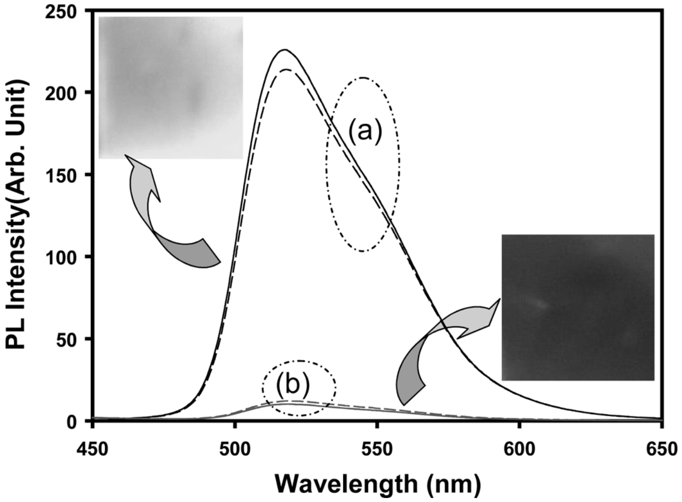
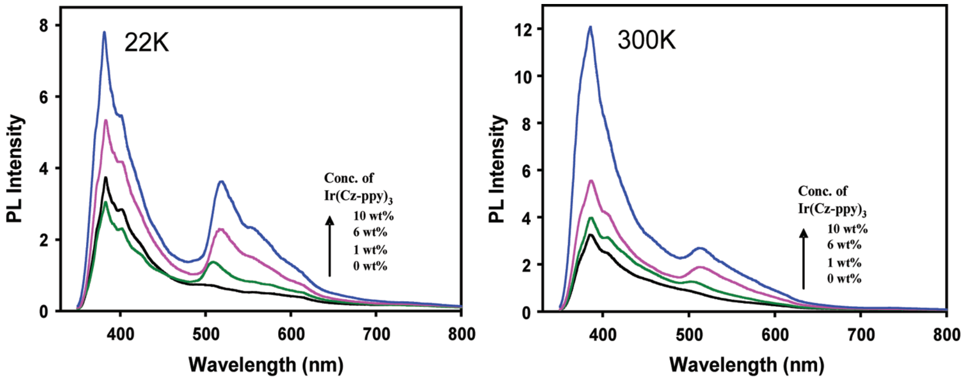


Figure 5. PL spectra of Cz-DNA (a) and PVK (b) doped with Ir(Cz-ppy)$_3$. The concentrations are 6 wt% (dashed line) and 8 wt% (solid line). *Sample: Thin films with an identical thickness. (t:~150 nm).



(a) (b)

Figure 6. Temperature dependence of PL behaviors of Cz-DNA with different concentration of Ir(Cz-ppy)$_3$ dye.

Temperature Effect of PL Behavior of Ir(Cz-ppy)$_3$-doped Cz-DNA

In order to investigate the origin of PL in Ir(Cz-ppy)$_3$-doped Cz-DNA, three samples with different Ir(Cz-ppy)$_3$ concentrations were selected (ca. 1, 6, and 10 wt.%). At the concentration range, no significant dye aggregation behaviors were observed. Both at room temperature and 22 K, we took the PL spectra of the film samples. At a low temperature, there are some resolved vibronic peaks or a shoulder. At 385 nm, the typical carbazole emission was observed in both spectra sets. In Figure 6a, with the concentration, the decrement of emission intensity at 385 nm looks monotonically; however, at 300 K, compared to the emission intensity at 385 nm, 1 wt% doped sample showed significant decrement of the intensity, which implies that the energy transfer efficiency was proved to be higher. Although the decrement of emission intensity at 385 nm is larger, the emission intensity at 515 nm was not comparable to that of the sample at 22 K. Even though the energy transfer efficiency from carbazole to Ir(III) dye is relatively small, the emission at 515 nm was highly developed at low temperature. This might be attributed to the higher quantum efficiency of phosphorescence in singlet-singlet and triplet-triplet levels.

It should be noted that there is a significant difference in emission spectra between 300 K and 22 K in particular at 515 nm. With an increase in the Ir(Cz-ppy)$_3$ dye concentration, the emission spectrum was transformed from the high energy to the low energy absorption region. Shortly, the spectral shapes and emission wavelengths are almost identical, which indicates that the Ir(III) dyes were well isolated via one of the possible binding modes occurring in the guest-DNA host system. However, the possibility of binding a dimeric or trimeric Ir(III) dyes into the grooves or intercalation cavities cannot be excluded in Cz-DNA when high concentration of Ir(Cz-ppy)$_3$ dye is used.

Conclusion

New Cz-DNA is well-soluble in organic solvents such as alcohol and an alcohol/halogenated solvents mixture. It shows highly resolved PL spectrum due to isolation of the carbazole units in a film state. Organic-soluble Ir(Cz-ppy)$_3$ dyes could easily be doped into Cz-DNA and PVK without severe phase separation and crystallization. The PL behaviors of the two different dye-doped polymeric systems were investigated and the intensities of emission in each sample were compared. In particular, at two concentrations of Ir(Cz-ppy)$_3$ dye, Cz-DNA blend matrix showed significant enhancement due to higher PL quantum yield of Cz-DNA. PL enhancement and the isolation effect of dye molecules are quite unique in organic-soluble double-stranded DNA in a solid state. Although direct evidence resulting from general features of intercalation or grove binding and the analytical evaluation of this binding mode are not present, a number of studies support the presented explanation.

Acknowledgment

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