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Effect of binding mode on the photoluminescence of CTMA–DNA doped with (*E*)-2-(2-(4-(diethylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile

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ABSTRACT

Purified natural DNA extracted from Salmon sperm can only be dissolved in water; it is not soluble in any other organic solvent. Therefore, in this study, the structure of DNA was modified and its solubility was changed. The preparation of organic-soluble DNA was carried out by precipitating the purified DNA in water with the cationic surfactant cetyltrimethylammonium chloride (CTMA). The resulting DNA–lipid complex shows good solubility in alcohol, which allows the fabrication of thin films for studying the photophysical properties of DNA in a solid state. The absorption and photoluminescence (PL) behaviors of CTMA–DNA and polymethylmethacrylate (PMMA) doped with (*E*)-2-(2-(4-(diethylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile (DCM) were investigated. In addition, different PL spectral behaviors with differing concentrations of DCM in two different host materials were observed. These behaviors were explained by a mechanism based on intercalation or groove binding of fluorescent dye into the base pairs or aliphatic side-chain moieties of CTMA–DNA.

1. Introduction

DNAs are among the oldest naturally occurring polymers, with a history that goes back to the time when the first primitive life form came into being [1]. Since that time, DNA science has been not only the center of life science, but also of current biotechnology.

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 [2–4]. Biological polymeric materials have many attractive features: they have unusual optical and electrical properties that are not readily reproduced in man-made materials; they are a widely available resource; and they are biodegradable and environmentally friendly. The most important molecular characteristic of DNA is that it is an important biomacromolecule [5] that offers several binding sites for a variety of functional guest molecules [6–9]. In particular, the design of small complexes that can bind at specific sequences of DNA is of interest, since these complexes have unique base pairs in double-stranded DNA (dsDNA). 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.

Thus, DNA-binding reagents exhibit high potential as chemotherapeutic drugs to suppress gene replication or transcription in tumor cells [10,11]. In addition, such a host–guest interaction may be used for the detection of nucleic acids when the physical properties of the guest molecule change upon binding; these changes may be easily monitored. In general, guest molecules may bind to DNA by (a) minor or major groove binding or (b) intercalation; external binding may occur by attractive electrostatic interactions. When introducing functional dye molecules into dsDNA, the binding mode could help to impose a site isolation effect, thereby preventing dye aggregation at a high concentration. If the dyes are all fluorescent, a very high fluorescence yield could be obtained, even at an unusually high concentration, without severe photoluminescence (PL) quenching.

The most interesting report relates to the fact that DNA is an efficient host for certain luminescent organic and organometallic fluorescent molecules in both solution and solid-state thin films. Grote et al. [12] intercalated the DNA–hexadecyl cetyltrimethylammonium (DNA–CTMA) complex with a fluorescent dye, 4-(4-(dimethylaminol styryl))-1-dodecylpyridinium bromide (DMASDPB). The film containing the least amount of dye

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(DNA–CTMA:dye = 56:1) achieved the maximum fluorescence. Compartmentalization of the dye in the DNA chain should not only reduce the vibronic energy transfer of the dye, but should also reduce the excited-state proton transfer, as in the above case of ethidium bromide intercalation.

The enhancement of photoluminescence (PL) in DNA host materials has been well documented in the literature; however, the mechanism of this enhancement has not been established. In order to study this mechanism, organic-soluble CTMA–DNA was prepared by following the accepted method [12]. Photochemically inactive polymethylmethacrylate (PMMA) was employed as another host and doped (*E*)-2-(2-(4-(diethylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile (DCM) was used as a fluorescent molecule, which is different from the ionic dyes or metal complex dyes used in the previous studies. The concentration of fluorophore was used to measure the absorption and PL spectra of the solid film samples. The PL spectral behaviors were compared with varying concentrations of DCM dye and the effects of mono-intercalation on the PL intensity and quenching behavior were studied.

2. Experimental section

2.1. Synthesis

The starting double-stranded DNA (dsDNA) material used in this study was purchased from Aldrich Co. To change the solubility, a cationic surfactant reaction was used to convert DNA to a DNA–lipid complex. Cetyltrimethylammonium bromide (CTMA) was used to form a DNA–CTMA complex as shown in Fig. 1, which is not soluble in water but can be dissolved in methanol, ethanol and chloroform/EtOH mixtures. The as-received DNA has a molecular weight (MW) of the order of million daltons. Cetylammonium bromide was dissolved in deionized water and this solution was mixed with natural DNA. As soon as the cetylammonium solution was added, white fibrous materials began to precipitate. At the completion of the reaction, the white solid was filtered after washing thoroughly with water. For comparison to DNA, we have also used poly(methyl methacrylate) (PMMA) with a MW of 35,000 (Sigma–Aldrich) as a fluorophore host material. (*E*)-2-(2-(4-(Diethylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile was also synthesized as a fluorescence dopant by following the literature method [13].

2.2. Instrumental analysis

Transition metal ions and impurities were determined by the Korea Basic Science Institute (Seoul, Korea) using inductively coupled plasma-mass spectrometry (ICP-MS; ELAN 6000, Perkin-Elmer) and inductively coupled plasma Atomic Emission spectrometry (ICP-AES; Ultima 2C, Jobin Yvon Horiba).

2.3. Absorption and photoluminescence (PL) spectroscopies

In order to study absorption behavior, the films of two polymers doped with DCM were fabricated on quartz substrates as follows. The solution (1.9–2.5 wt.%) of each polymer either in ethanol or chloroform/ethanol mixture was subsequently spin-cast on the quartz glass. The films were dried overnight at 40 °C for 24 h under vacuum.

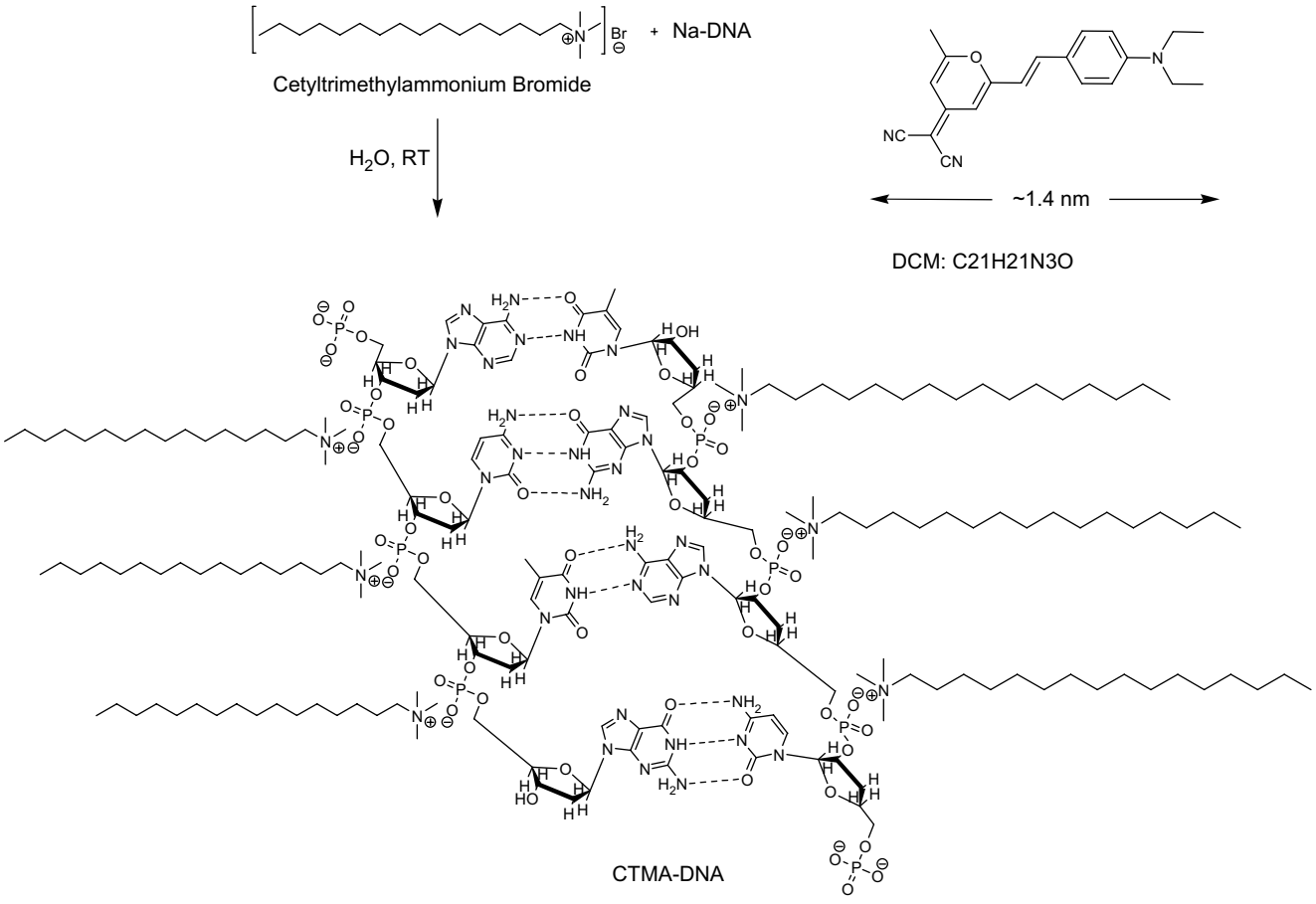

Fig. 1. Synthetic procedure for CTMA–DNA and the structure of the DCM dye used in the present study.

Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10^{-5} mol/L) were obtained 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 behavior, all PL spectra were recorded using the 488 nm line of an Ar ion 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 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.

3. Results and discussion

3.1. Materials

In order to prepare CTMA–DNA, we employed the natural double-stranded (ds) DNA extracted from Salmon sperm. Each strand is composed of an ordered combination of four nucleotides, each nucleotide consisting of a purine or pyrimidine base (adenine, guanine, thymine or cytosine) associated with a deoxyribose sugar molecule and a phosphate group. The %G–C content for DNA from Salmon testes is 41.2%. The molecular weight (MW) is around 1.3×10^6 (approximately 2000 base pairs).

Cetylammonium 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 56,770 ppm; after the reaction with CTMA, the concentration of sodium dropped to less than 10 ppm. Therefore, CTMA was substituted into the phosphate anion up to 99.5% or higher. The resultant DNA–lipid complex is not soluble in water, but is soluble in alcohol or its mixed solvent. After complete drying under a vacuum oven at 40 °C, it was ready for use in the investigation of its photophysical properties as a host polymer. For comparison, polymethylmethacrylate (PMMA, MW = 35,000) was also used as a host material that can bear DCM dyes.

The well-known DCM dye (*E*)-2-(2-(4-(diethylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile was synthesized following the method in the literature [13]. In chloroform solution, the DCM dye has a maximum absorption and fluorescence emission at 479 and 564 nm, respectively. The structure of the DCM dye molecule is shown in Fig. 1. Recently, several studies have addressed the photophysical properties of DNA after doping with fluorescent dyes. The dyes used in those studies were ionic dyes, which can have some ionic interactions with the phosphate anion and usually induce an external binding of the particular dye. In this work, the authors doped purely organic non-ionic dye which is well miscible with organic-soluble CTMA–DNA. Although the authors heavily doped 15 wt.% DCM into CTMA–DNA, no phase separation or crystallization could be observed.

3.2. Absorption and photoluminescence behaviors

The basic optical properties of the host–dye molecule thin films were characterized first, by determining the absorption and PL spectra for CTMA–DNA, DCM, and CTMA–DNA doped with DCM (1 wt.%) (see Fig. 2). CTMA–DNA exhibited the maximum absorption at approximately 260 nm, which is identical to that of water-soluble natural DNA.

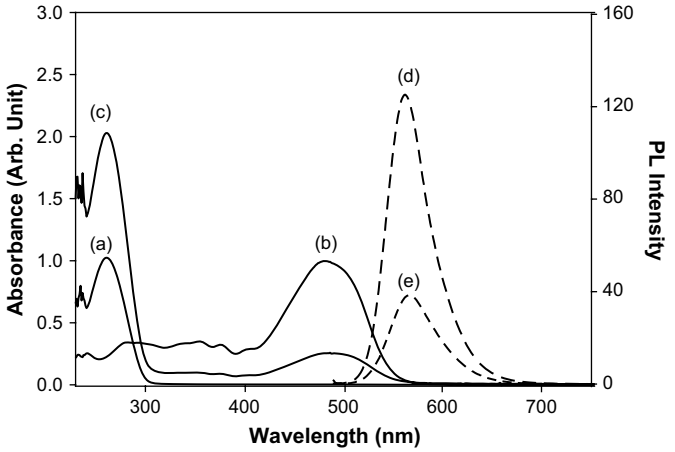

Fig. 2. Absorption (solid lines) and PL spectra (dotted lines) of CTMA–DNA, DCM, and DCM-doped CTMA–DNA in solution states (chloroform, conc. 1×10^{-5} mol/L). (a) Absorption spectrum of CTMA–DNA, (b) absorption spectrum of DCM, (c) absorption spectrum of DCM-doped CTMA–DNA (1 wt.%), (d) PL spectrum of DCM, and (e) PL spectrum of DCM-doped CTMA–DNA (1 wt.%).

DCM dye itself exhibits a longer wavelength absorption in the range of 479 nm, which originates from the π–π^* transition in the dye structure. After doping DCM dye (1 wt.%) into CTMA–DNA, the PL emission was observed at 567 nm, which is identical with that of DCM dye. Therefore, no severe interaction between the DCM and DNA structures occurs. The large Stokes shift between the DCM emission and absorption ($\Delta\lambda = 85$ nm) does not lead to residual self-absorption.

To vary the concentration of DCM in the CTMA–DNA and PMMA thin films, solid CTMA–DNA and DCM were dissolved in chloroform/ethanol (9:1) with different weight ratios. PMMA and DCM dye were dissolved in chloroform. The solid content in mixed solution was controlled to be 1.9–2.5 wt.% in each solution.

First, the absorption spectrum of the DCM dye in chloroform was measured to show that the maximum absorption is at approximately 479 nm. A representative absorption set is shown in Fig. 3. The CTMA–DNA film exhibits its well-known UV absorption peak at 260 nm, owing to the presence of aromatic nitrogenous bases.

However, the film sample of CTMA–DNA with a low concentration of DCM dye exhibited a slight blue-shift from 504 nm to 484 nm ($\Delta\lambda = 20$ nm), and the intensity increased monotonically with the concentration. The case of PMMA doped with DCM dye showed a slight red-shift, which is the opposite of the phenomenon in the CTMA–DNA sample (465 nm → 472 nm; $\Delta\lambda = 7$ nm). When comparing the absorption maxima, the sample comprised of CTMA–DNA and DCM has lower energy absorption than that of the PMMA-doped sample, which is attributed to the polar environment from the amide bonds in the base pairs.

In two samples, no severe aggregation behavior can be found in the spectra, indicating that DCM dyes are mono-intercalated into the base pair, which is supported by the similar interaction of cyanine dyes in the literature [7]. Without the non-ionic character of the DCM dye, another external-binding forward phosphate anion is not feasible in the DNA mixture.

DCM dye is strongly fluorescent in a dilute solution, but is weakly emissive, or not emissive at all in the solid state, because of a great tendency to aggregate. The strong intermolecular dipole–dipole interactions or intermolecular π-stacking, as a result of either the polar or extensively π-conjugated structure of the DCM dye, leads to a high tendency toward aggregation, and therefore,

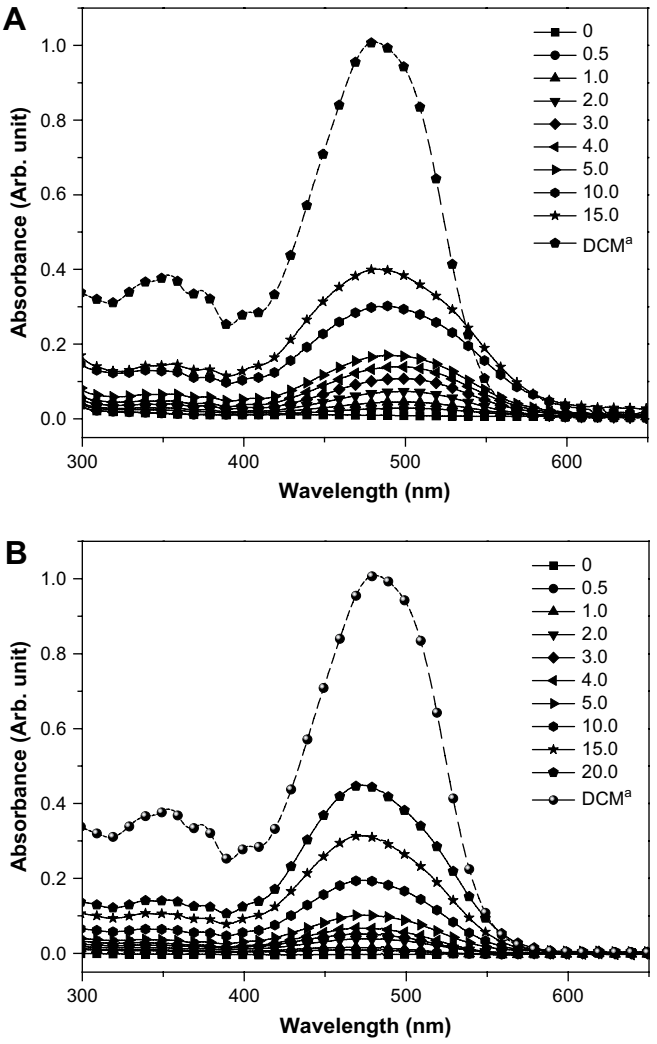

Fig. 3. Absorption spectral behaviors of CTMA–DNA and PMMA doped with DCM dye. Effect of dye concentration (wt.%) on the absorption spectral behaviors. *Sample: thin film with an identical thickness. ($t \sim 100$ nm) (A) CTMA–DNA $\lambda = 504$–484 nm. (B) PMMA $\lambda = 465$-472 nm. [a]Solution in chloroform.

so-called concentration quenching [14,15]. Consequently, these dyes are frequently applied as dopants in appropriate hosts for optoelectronic applications. Careful control of the dopant concentration is critical in order to avoid both insufficient energy transfer and concentration quenching in these devices. Generally, the optimum dopant concentration is no greater than 2–3 wt.% and the effective doping range is no greater than ±0.5 wt.% of the optimum concentration.

The DCM dye also exhibits remarkably high affinity for association with nucleic acid along a significant change of electronic and photophysical properties upon DNA binding. The size of DCM dye (optimized by using Spartan 6.0) can be defined to be a length from a nitrogen in an amino group to a nitrogen in a cyanine group. It is around ~1.4 nm, which is far smaller than the length of the maximum distance between the single strands.

From the absorption spectral analyses, it was noted that the intercalation-induced spectral shift is only observed in the CTMA–DNA samples. The interaction between the base pairs and the DCM polar dye induced the intercalative arrangement to change the transition behavior (dipole-allowed transition can occur at a higher energy level). As the polar environment from the amide groups in the base pairs enhances the electron delocalization of excited-state DCM dyes, the dipole moment of the DCM dye should be larger in the first excited state as compared with the ground state or the non-polar environment. Therefore, at a high concentration (ca. ~10 wt.%), dipoles in the amide group of the base pair strongly interact with those of the DCM polar dye. It can be conjectured that this interaction is induced by effective intercalation of the DCM dyes into the interior (between base pairs) of duplex DNA.

To determine the optimal doping concentration for PL emission, CTMA–DNA and PMMA thin films containing a range of DCM concentrations were photoexcited at 488 nm and 477 nm, respectively. In Fig. 4, the PL spectra of samples bearing different concentrations of DCM dye were compared. With a 0.5 wt.% concentration of DCM dye, the CTMA–DNA sample exhibited emission at 572 nm, which is shifted bathochromically. With increased concentration, the emission maximum shifted to 601 nm. Hence, the intensity of fluorescence was increased at a 10 wt.% concentration of DCM. The large shift of the emission center indicates that the polar character of the interior base pairs induced the effect, which is similar to solvatochromism in a solution state.

In the case of PMMA doped with DCM, the fluorescence begins to be quenched when the concentration is at 4 wt.%. The red-shift of the PL maximum of DCM-doped PMMA is observed with the increasing DCM concentrations, which can be attributed to the self-polarization of the red dopant. With an increasing dopant

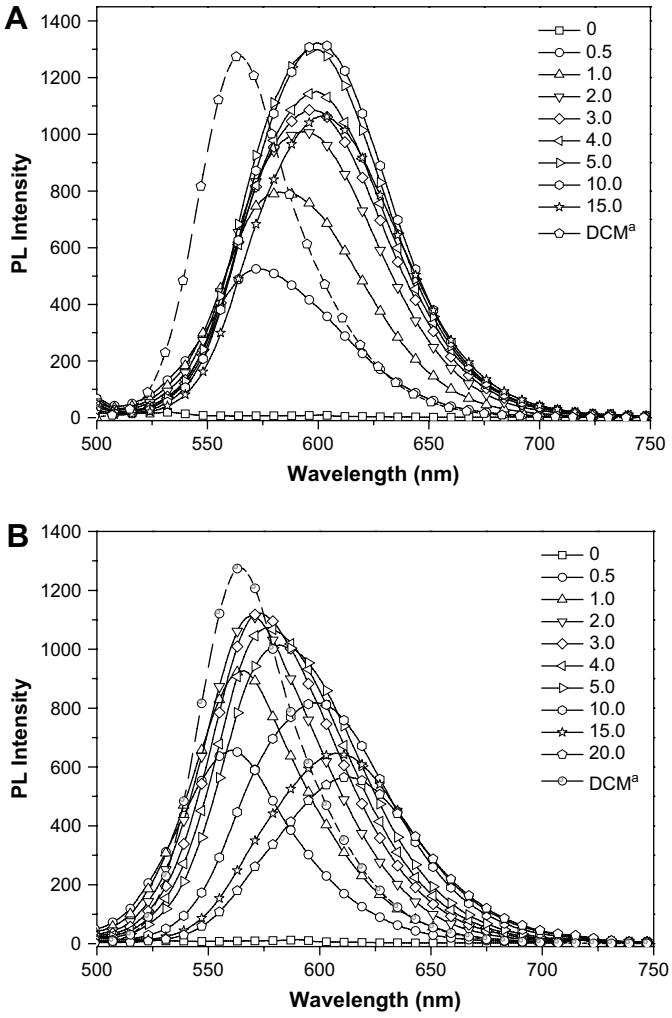

Fig. 4. Photoluminescence spectra of CTMA–DNA and PMMA doped with DCM dye. Effect of dye concentration on the photoluminescence spectral behaviors. *Sample: thin film with an identical thickness. ($t \sim 100$ nm) (A) CTMA–DNA. (B) PMMA. [a]Solution in chloroform.

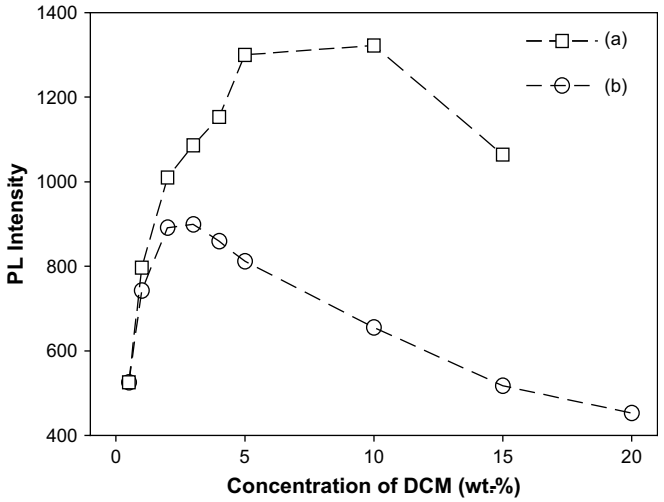

Fig. 5. Integrated DCM photoluminescence vs. concentration in CTMA–DNA and PMMA. (a) CTMA–DNA-based films, (b) PMMA-based films.

concentration, the distance between the DCM molecules decreases and the interaction is enhanced, which causes the red-shift in the PL spectra of the dopant. Under identical concentrations, the same shift behaviors were observed in DCM-doped polystyrene, which implies that the spectral shift is not affected by the polarity of the host matrix, rather by dye aggregation or self-association.

The fluorescence intensity of the CTMA–DNA:DCM sample increased continuously with the concentration of DCM dyes, due to chromophore isolation. Based on many studies [7,9], it can be conjectured that the isolation effect is attributed to groove binding or intercalation of dye through the base pairs. For instance, the intercalation of DCM dyes verifies the site isolation of the dyes when increasing the concentration to 10 wt.%. Almost no dye aggregation occurred at this high concentration, which is quite different from the guest–host system in common amorphous polymers such as PMMA and polystyrene.

In addition, the fluorescent spectra show a significant red-shift in CTMA–DNA at a constant concentration (0.5 wt.%) (ca. $\Delta\lambda =$ 11 nm), which is attributed to the polarity of dsDNA. It is indicative of the charge transfer character of the fluorescent state.

The thickness of the PMMA-doped film is slightly greater than that of the CTMA–DNA films ($t_{\mathrm{CTMA-DNA}} = 0.86\ t_{\mathrm{PMMA}}$). At low concentrations ranging from 0.5 to 1.0 wt.%, two of the samples showed comparable PL intensity. The 3.0 wt.% DCM-doped PMMA showed the highest PL intensity, whereas continuous increments of the PL intensity of doped CTMA–DNA up to 10 wt.%. were observed (see Fig. 5). Generally, the PL intensities of the CTMA–DNA samples were higher than those of the PMMA-doped samples at high concentrations. It is consistent with the results reported in the literature, which describe intercalation-induced fluorescence enhancement [16].

It is interesting to consider the reasons behind the ability of the CTMA–DNA films to emit light more efficiently than other polymers. The intercalation or groove binding of certain fluorophores between the CTMA–DNA base pairs, which is frequently reported as a highly sensitive sign of the presence of CTMA–DNA molecules [17–19] could be the reason for the efficient luminescence. DCM may be more effectively prevented from intermolecular interaction when isolated by the base pairs in the CTMA–DNA structure. Furthermore, the tight spatial fit between DCM molecules and the base pair structure may retard the conformational relaxation of excited fluorophores and thereby enhance the process of radiative relaxation.

3.3. Temperature effect of photoluminescence behavior of DCM-doped CTMA–DNA

In order to investigate the origin of PL in DCM-doped CTMA–DNA, three samples with different DCM concentrations were selected (ca. 1, 3, and 10 wt.%). In the PL spectra of DCM-doped

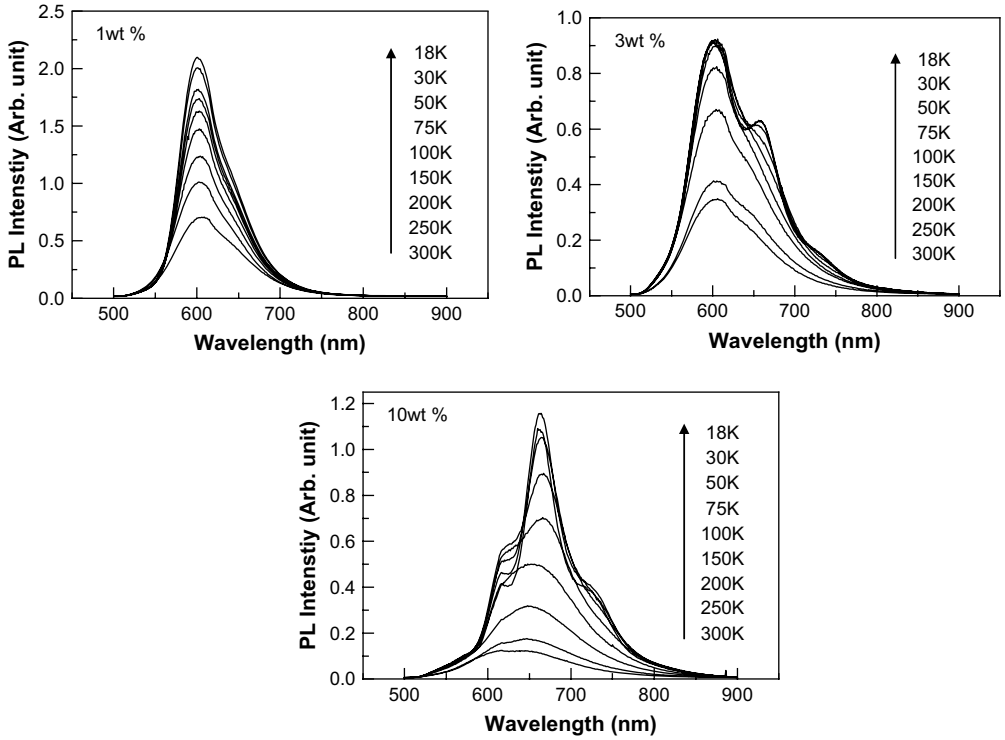

Fig. 6. Temperature dependence of PL behaviors of CTMA–DNA in different concentration of DCM dye.

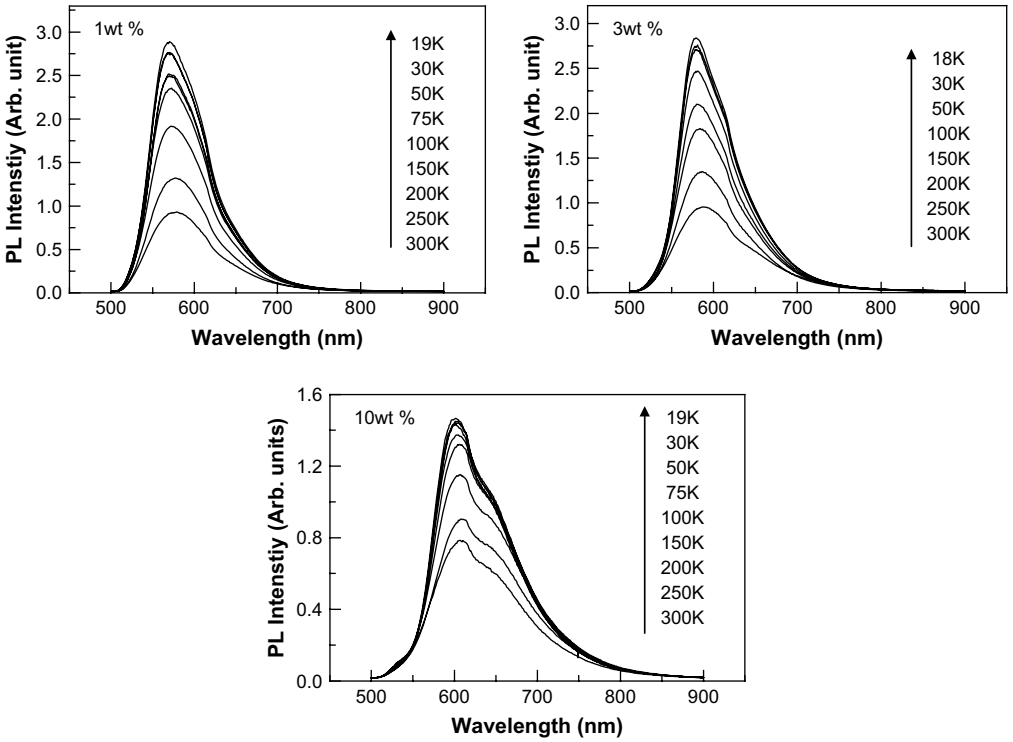

Fig. 7. Temperature dependence of PL behaviors of PMMA in different concentrations of DCM dye.

CTMA–DNA taken at room temperature, the PL intensity has maximum value at the 10 wt.% DCM-doped film. When the PL spectra of DCM-doped CTMA–DNA (3 wt.% or 10 wt.%) were observed, three different binding modes of DCM dyes were expected: intercalation, groove binding, and external binding.

At the lowest temperature (18 K), clearer vibronic transitions were observed; emission peaks of DCM-doped CTMA–DNA (10 wt.%) can be assigned to be 610, 667, and 715 nm. It should be noted that there is a significant difference in emission spectra between 300 K and 18 K. With an increase in the DCM dye concentration, the emission spectrum was transformed from the high energy to the low energy absorption region (Fig. 6). Finally, at 10 wt.%, the doped DNA sample showed a clear shift of the maximum emission peak from 600 to 667 nm. In contrast, when observing the same spectral behaviors of PMMA samples bearing DCM dye, the only difference in a heavily doped (10 wt.%) sample was the appearance of the PL emission at 640 nm as a shoulder; this is commonly understood to be due to the presence of intermolecular interactive species in the blend matrix (Fig. 7).

The peaks at around 600–610 nm are commonly observed in the sample of DCM-doped CTMA–DNA and PMMA, which is attributed to the external binding of DCM dye around the polymer backbone. Below 100 K of the CTMA–DNA sample, the gradual appearance of PL at 667 nm becomes evident as the PL emission at 610 nm gradually disappears. It was found that the DCM molecules in CTMA–DNA along with the base pairs undergo a different excited state under a polar environment. Such a large shift of the maximum emission wavelength can be attributed to the isolation effect of dyes in the CTMA–DNA matrix. The environment around the polar dye was significantly changed compared with that in the PMMA system, which implies that the DCM dyes were intercalated through the base pairs. The polar environment, which bears a high hydrogen-bond density, affects the transition dipole moment by changing the oscillating strength of the dye molecules. Then, the behavior is likely to mimic the solvatochromism in the solution state. At 18 K, the dye molecules in CTMA–DNA become planar, which increases the conjugative effect. In the first-order excited state, the electrons are more highly delocalized, which induces the higher dipole moment than that of the ground state. Therefore, it facilitates the intercalation through the base pairs and shows a larger bathochromic shift of the spectrum. However, the possibility of binding a dimeric or trimeric DCM dyes into the grooves or intercalation cavities cannot be excluded in CTMA–DNA when high concentration of DCM is used.

4. Conclusion

Most DNA studies have been conducted using natural DNA in an aqueous-solution state; its unique properties have been intensely investigated for gene chemistry. CTMA–DNA is well soluble in organic solvents such as alcohol and an alcohol/halogenated solvent mixture. Organic-soluble non-ionic fluorescent dyes could easily be doped into CTMA–DNA without severe phase separation and crystallization. The photoluminescent behaviors of the two different dye-doped polymeric systems were investigated to understand the effect of dye concentration on the spectral shift behavior. In particular, at a low concentration of DCM dye (~3 wt.%) embedded in PMMA, PL quenching behavior was observed to clarify the external binding effect or self-aggregation. However, DCM-doped CTMA–DNA samples do not show any PL quenching behaviors, even with a 10 wt.% concentration. No report has been made about the retardation of PL quenching at such a high concentration of polar fluorescent dye in the polymer matrix. Intercalation-induced 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 and the analytical evaluation of this binding mode are not present, a number of studies support the presented explanation.

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