Metal and Lanthanide Ion-Co-doped Synthetic and Salmon DNA Thin Films

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Supporting Information

ABSTRACT: Researchers have begun to use DNA molecules as an efficient template for arrangement of multiple functionalized nanomaterials for specific target applications. In this research, we demonstrated a simple process to co-dope synthetic DNA nanostructures (by a substrate-assisted growth method) and natural salmon DNA thin films (by a drop-casting method) with divalent metal ions (M2+, e.g., Co2+ and Cu2+) and trivalent lanthanide ions (Ln3+, e.g., Tb3+ and Eu3+). To identify the relationship among the DNA and dopant ions, DNA nanostructures were constructed while varying the Ln3+ concentration ([Ln3+]o) at a fixed [M2+] with ion combinations of Co2+−Tb3+, Co2+−Eu3+, Cu2+−Tb3+, and Cu2+−Eu3+. Accordingly, we were able to estimate the critical [Ln3+]o (named the optimum [Ln3+]o) at a given [M2+] in the DNA nanostructures that corresponds to the phase change of the DNA nanostructures from crystalline to amorphous. The phase of the DNA nanostructures stayed crystalline up to [Tb3+]o≡0.4 mM and [Eu3+]o≡0.4 mM for Co2+ ([Tb3+]o≡0.6 mM and [Eu3+]o≡0.6 mM for Cu2+), and then changed to amorphous above 0.4 mM (0.6 mM). Consequently, phase diagrams of the four combinations of dopant ion pairs were created by analyzing the DNA lattice phases at given [M2+] and [Ln3+]o.

Interestingly, we observed extrema values of the measured physical quantities of DNA thin films near [Ln3+]o, where the maximum current, photoluminescence peak intensity, and minimum absorbance were obtained. M2+- and Ln3+-multidoped DNA nanostructures and DNA thin films may be utilized in the development of useful optoelectronic devices or sensors because of enhancement and contribution of multiple functionalities provided by M2+ and Ln3+.

INTRODUCTION

DNA molecules have been widely explored as useful building materials because of their intrinsic characteristics, for example, base sequence design capability, self-assembly predicted by complementary binding, and simple adaptability with various functionalized materials. Various dimensional structures made of synthetic DNA oligonucleotides have been constructed with precise control of size, shape, and pattern.1−9 DNA structures can serve as effective building platforms for arrangement of various nanomaterials to be used in specific target applications such as optoelectronic devices, chemical sensors, drug delivery, and biocomputing.10−14 DNA can be functionalized with various materials such as proteins, drugs, metallic and semiconducting nanoparticles, carbon-based materials, fluorescence dye molecules, and metal and lanthanide ions.15−26 Similarly, natural DNA such as lambda and salmon DNA (SDNA) has also been used in the fields of biology, medicine, and bionanotechnology.27,28 Such DNA can be easily obtained in large quantities at a relatively low cost, and these molecules can be easily incorporated with various functionalized nanomaterials.

DNA structures embedded with individual nanomaterials such as quantum dots, gold nanoparticles, cobalt ions, and doxorubicin were fabricated, and their chemical, physical, and biological properties have been reported. However, there are certain limitations to construction of multiple functionally embedded DNA complexes containing various types of nanomaterials because of difficulties in estimating appropriate amounts of the nanomaterials at a given DNA concentration. Consequently, DNA structures with optimum concentrations of nanomaterials are expected to show drastic enhancements of specific physical characteristics for further applications.29 Among functionalized materials, metal ions (M2+) and lanthanide ions (Ln3+), which have unique physical character-
istics, especially with regard to electromagnetism and photonics, have been considered useful dopants in DNA molecules because of their easy preparation, ion species variety, and efficient functionality enhancement. To construct multifunctional devices or sensors, methodology development of construction techniques and systematic study of characterization of DNA complexes with multiple dopant ions are needed.

Herein, we developed a methodology to construct M$_{2+}$ (e.g., cobalt ion Co$_{2+}$ and copper ion Cu$_{2+}$ for electrical enhancement) and Ln$_{3+}$ (e.g., terbium ion Tb$_{3+}$ and europium ion Eu$_{3+}$ for optical improvement) co-doped double-crossover DNA (DX-DNA) nanostructures (grown on a given substrate) and SDNA thin films (prepared via drop-casting). In addition, we evaluated their topological (analyzing phase transition), electrical (current–voltage ($I$–$V$) measurements), and optical [absorbance and photoluminescence (PL)] characteristics. To investigate the significances of the physical characteristics, DNA thin films with 4 different combinations of M$_{2+}$ and Ln$_{3+}$ dopants (i.e., Co$_{2+}$–Tb$_{3+}$, Co$_{2+}$–Eu$_{3+}$, Cu$_{2+}$–Tb$_{3+}$, and Cu$_{2+}$–Eu$_{3+}$) were evaluated to determine the optimum Ln$_{3+}$ concentration ([Ln$_{3+}$]$_{O}$) at a given M$_{2+}$ concentration ([M$_{2+}$]$_{O}$) through examination of phase diagrams obtained by theoretical analysis and experiments.

## RESULTS AND DISCUSSION

Figure 1 illustrates the preparation and physical characterization of M$_{2+}$- and Ln$_{3+}$-co-doped DX-DNA nanostructures and SDNA thin films. We used 4 combinations of M$_{2+}$ and Ln$_{3+}$ mixtures, that is, Co$_{2+}$–Tb$_{3+}$, Co$_{2+}$–Eu$_{3+}$, Cu$_{2+}$–Tb$_{3+}$, and Cu$_{2+}$–Eu$_{3+}$. To fabricate co-doped DX-DNA nanostructures, separate DX-DNA oligonucleotides with an O$_2$ plasma-cleaned substrate and appropriate amounts of M$_{2+}$ and Ln$_{3+}$ were mixed in a test tube and annealed from 95 to 25 °C. Similarly, SDNA thin films were formed by drop-casting of a SDNA solution containing M$_{2+}$ and Ln$_{3+}$. Four distinct physical measurements were carried out to evaluate the intrinsic properties of the samples. DX-DNA nanostructures with a combination of M$_{2+}$ and Ln$_{3+}$ grown on a substrate were used for atomic force microscope (AFM) measurements to identify the phase change from crystalline to amorphous. Current measurements of the co-doped SDNA thin films were used to evaluate the electric properties. The absorbance was measured to analyze the optical characteristics, and PL was utilized to determine the luminescence.

DX-DNA nanostructures doped with either M$_{2+}$ or Ln$_{3+}$ were constructed, and their structural behavior was evaluated at various [M$_{2+}$] or [Ln$_{3+}$]. Interestingly, phase changes of the DX-DNA nanostructures from crystalline to amorphous occurred above a certain ion concentration (referred to as the optimum concentration, i.e., [M$_{2+}$]$_{O,S}$ or [Ln$_{3+}$]$_{O,S}$, where S stands for single-ion doping), and extrema values of the physical quantities (e.g., maximum current at [M$_{2+}$]$_{O,S}$ and minimum absorbance at [Ln$_{3+}$]$_{O,S}$) were obtained at [M$_{2+}$]$_{O,S}$ or [Ln$_{3+}$]$_{O,S}$. The measured [Co$_{2+}$]$_{O,S}$, [Cu$_{2+}$]$_{O,S}$, [Tb$_{3+}$]$_{O,S}$, and [Eu$_{3+}$]$_{O,S}$ were 1.0, 6.0, 1.0, and 1.0 mM, respectively (the yellow dots in Figure 2 indicate [Co$_{2+}$]$_{O,S}$, [Cu$_{2+}$]$_{O,S}$, [Tb$_{3+}$]$_{O,S}$, and [Eu$_{3+}$]$_{O,S}$).

In this study, M$_{2+}$- and Ln$_{3+}$-co-doped DX-DNA nanostructures were constructed at a fixed [M$_{2+}$] while varying [Ln$_{3+}$]. Analysis of AFM images provided [Ln$_{3+}$]$_{O}$ for co-doping, succeeded by achievement of the phase diagram (a graphical illustration of the crystalline and amorphous phases of M$_{2+}$- and Ln$_{3+}$-co-doped DX-DNA nanostructures). DX-DNA nanostructures with M$_{2+}$ and Ln$_{3+}$ dopants possess the inherent unique properties of each species of M$_{2+}$ and Ln$_{3+}$. Consequently, DX-DNA nanostructures with multiple func-
tionalities can be achieved easily by embedding combinations of M\textsuperscript{2+} and Ln\textsuperscript{3+}, which is beneficial than single doping.

The crystalline and amorphous domains with specific pairs of M\textsuperscript{2+} and Ln\textsuperscript{3+} co-doped DX-DNA nanostructures followed relationships between [M\textsuperscript{2+}] and [Ln\textsuperscript{3+}], that is, \[\frac{[M\textsuperscript{2+}]}{[M\textsuperscript{2+}]_{0.5}} + \frac{[Ln\textsuperscript{3+}]}{[Ln\textsuperscript{3+}]_{0.5}} \leq 1 \] and \[\frac{[M\textsuperscript{2+}]}{[M\textsuperscript{2+}]_{0.5}} + \frac{[Ln\textsuperscript{3+}]}{[Ln\textsuperscript{3+}]_{0.5}} > 1\], respectively. The analytically obtained expected line (shown as a black solid line) in the phase diagram of co-doped DX-DNA nanostructures separates the crystalline and amorphous phases, as shown in Figure 2. Here, the ratio of [M\textsuperscript{2+}]\textsubscript{0.5} to [Ln\textsuperscript{3+}]\textsubscript{0.5} indicates the numerical value of the slope of the expected (theoretical) line. For instance, the slope of Co\textsuperscript{2+} and Tb\textsuperscript{3+} (Cu\textsuperscript{2+} and Tb\textsuperscript{3+}) co-doped DX-DNA nanostructures was [Co\textsuperscript{2+}]\textsubscript{0.5}/[Tb\textsuperscript{3+}]\textsubscript{0.5} = 1 ([Cu\textsuperscript{2+}]\textsubscript{0.5}/[Tb\textsuperscript{3+}]\textsubscript{0.5} = 6), which indicates identical (different) optimum ion concentrations.

Figure 2 shows the phase diagrams of the 4 combinations of M\textsuperscript{2+} and Ln\textsuperscript{3+} (i.e., Co\textsuperscript{2+}−Tb\textsuperscript{3+}, Co\textsuperscript{2+}−Eu\textsuperscript{3+}, Cu\textsuperscript{2+}−Tb\textsuperscript{3+}, and Cu\textsuperscript{2+}−Eu\textsuperscript{3+})-co-doped DX-DNA nanostructures with typical AFM images. The phases (crystalline and amorphous) of the DX-DNA nanostructures were controlled by varying [Tb\textsuperscript{3+}] and [Eu\textsuperscript{3+}] (from 0.2 to 1.0 mM at an increment of 0.2 mM) at a fixed [Co\textsuperscript{2+}] of 0.5 mM (here, we labeled DX-DNA nanostructures with [Co\textsuperscript{2+}] of X mM and [Tb\textsuperscript{3+}] of Y mM as Co X + Tb Y). The phase transition occurred from crystalline (up to [Tb\textsuperscript{3+}]\textsubscript{0} ≡ 0.4 mM and [Eu\textsuperscript{3+}]\textsubscript{0} ≡ 0.4 mM, the optimum concentrations of Tb\textsuperscript{3+} and Eu\textsuperscript{3+}, respectively) to amorphous (above 0.4 mM). For clarity, the boundary and region of the crystalline phase are indicated by a red solid line and light-blue shaded area, respectively. Similarly, the phase change of DX-DNA nanostructures with varying either [Tb\textsuperscript{3+}] or [Eu\textsuperscript{3+}] at a fixed [Cu\textsuperscript{2+}] of 3.0 mM occurred at 0.6 mM, which correspond to the optimum concentrations of each ion, that is, [Tb\textsuperscript{3+}]\textsubscript{0} and [Eu\textsuperscript{3+}]\textsubscript{0}. Although a small number of sample sets (5 sets of each M\textsuperscript{2+} and Ln\textsuperscript{3+} combination) were analyzed, the experimental values agree well with the expected results. Here, the difference of [Ln\textsuperscript{3+}]\textsubscript{0} between the expected and experimental values (i.e., ([Ln\textsuperscript{3+}]\textsubscript{0,expected} − [Ln\textsuperscript{3+}]\textsubscript{0,experimental})) was only 0.1 mM [Ln\textsuperscript{3+}] in all cases.

The light-blue-shaded and white regions shown in the phase diagram indicate the crystalline and amorphous domains of the M\textsuperscript{2+}- and Ln\textsuperscript{3+}-co-doped DX-DNA nanostructures, respectively. The crystal domains of DX-DNA nanostructures were indicated by the white dotted lines in the AFM images. The insets in the images containing noise-filtered reconstructed images constructed by fast Fourier-transformation (FFT) indicate the periodicities of the DX motifs in the DNA nanostructures (crystalline phase). The periodic arrays of the DX motifs did not appear in the amorphous phase (additional AFM images are shown in Figure S2 in Supporting Information). Because of improper binding of excess Ln\textsuperscript{3+}, deformation of DX-DNA nanostructures (amorphous phase)
occurred in the presence of excess Ln3+ ([Ln3+] > [Ln3+]O) at a fixed [M2+]n.

To enhance the reproducibility of the experimental data and reduce the buffer influence of DNA structures, SDNA thin films were introduced, which are easily fabricated at a low cost. During preparation of a co-doped SDNA thin film, aggregation of the SDNA duplex started to occur above [Ln3+]O at a fixed [M2+] in solution. Although noticeable precipitation was observed at relatively higher [Ln3+] (roughly 3 times higher [Ln3+] than [Ln3+]O) at a fixed [M2+] above) because of the excess of Ln3+ in the presence of M2+, the minute aggregation of SDNA in solution did not influence the experimental measurements (i.e., I−V, absorbance, and PL) because our measurements were performed with M2+- and Ln3+-co-doped SDNA thin films below and near [Ln3+]O at a fixed [M2+]n.

Figure 3 shows the I−V characteristics of SDNA thin films without Ln3+ and at various [Ln3+] at fixed [M2+]n. I, which is one of the most fundamental physical characteristics, can provide the overall electrical behavior of a sample through controlling the applied V. Each sample with a different combination and concentration of dopant ions was evaluated by sweeping the input V from −3 to 3 V. Interestingly, we noticed I offsets at 0 V, which may be caused by charge trapping and the negatively charged nature of DNA molecules.25 The SDNA thin films with different [Ln3+] (either [Tb3+] or [Eu3+]) from 0.2 to 1.0 mM at a fixed [M2+] (either [Co2+] = 0.5 mM or [Cu2+] = 3.0 mM) showed increasing I up to a certain critical [Ln3+] at a fixed [M2+] and then decreased as [Ln3+] was further increased. While varying [Tb3+] ([Eu3+]) with [Co2+] = 0.5 mM, the maximum I occurred at a [Tb3+] of 0.8 mM ([Eu3+] = 0.4 mM) because of the maximum capability of appropriate coordination of Tb3+ ([Eu3+]) and Co2+ on DNA base-pairing sites and negatively charged phosphate backbones at a given [SDNA]. Similarly, for [Tb3+] ([Eu3+]) at [Cu2+] = 3.0 mM, the maximum I occurred at a [Tb3+] of 0.2 mM ([Eu3+] = 0.6 mM). Above such critical concentrations, I tended to decrease because of inappropriate and nondesignated coordination of excess Ln3+ into the DNA molecules. Although [Tb3+] in the SDNA thin films at a fixed [M2+] showing the maximum I differed slightly from the [Tb3+]O obtained from the phase analysis of the co-doped DX-DNA nanostructures, the differences of critical [Eu3+] with the maximum I and [Eu3+]O values are compatible.

The resistances (R, obtained by Ohm’s law) of M2+- and Ln3+-co-doped SDNA thin films as a function of [Ln3+]1 based on observed I−V data are shown in the insets in Figure 3. As expected, R decreased until a critical [Ln3+] and then increased as [Ln3+] was further increased (opposite trend as I). A noticeable reduction of R at a critical [Ln3+] in the SDNA thin film was observed for most of the samples at a fixed [M2+] compared to pristine SDNA. Interestingly, R of M2+- and Ln3+-co-doped SDNA thin films revealed significantly lower R of ~ΩΩ range than those from single M2+- or Ln3+-doping, whose R was within the GΩ range.23,30 The minimum R obtained at a [Eu3+] of 0.4 mM and a [Eu3+] of 0.6 mM at fixed [Co2+] and [Cu2+] were roughly 2.0 and 14 MΩ at a V of 3 V, respectively. These critical concentrations were matched to [Eu3+]O, resulting in the phase diagrams shown in Figure 2.
The critical concentrations acquired from R for [Tb³⁺] at a fixed [M²⁺] and at different [Ln³⁺] at a fixed [M²⁺] were 0.8 and 0.2 mM, respectively. These critical concentrations were slightly different from [Tb³⁺]O (0.4 mM at a fixed [Co²⁺] and 0.6 mM at a fixed [Cu²⁺]) obtained from the phase diagrams.

Figure 4 shows the absorbance spectra used to reveal the interactions between DNA molecules and dopant ions of M²⁺- and Ln³⁺-co-doped SDNA thin films. Figure S3 in Supporting Information shows representative PLE spectra of Co²⁺−Tb³⁺ and Co²⁺−Eu³⁺ co-doped SDNA thin films at fixed λ_em values of 545 and 615 nm, respectively. DNA molecules absorbed photon energy through excitation of electrons from the ground state to the single state. Energy transfer then occurred within the singlet state through the process of internal conversion. After internal conversion, electrons from the singlet state in SDNA are relaxed to the triplet state in co-doped SDNA by intersystem crossing, followed by relaxation from the emissive state to the ground state, resulting in PL emission.

The PL emission and PL excitation (PLE) spectra (Figure 5a,c) and Gaussian-fitted PL intensities and areas (Figure 5b,d) of Co²⁺- and Tb³⁺ (Eu³⁺)-co-doped SDNA thin films are shown in Figure 5 (PL spectra of Cu²⁺- and Ln³⁺-co-doped SDNA are shown in Figure S4). PL and PLE spectra were obtained to study energy transfer among SDNA and dopant ions. As shown in the insets in Figure 5, both Co²⁺−Tb³⁺ and Co²⁺−Eu³⁺ co-doped SDNA thin films showed the same excitation wavelength (λ_ex) of 290 nm at fixed emission wavelengths (λ_em) of 545 and 615 nm, respectively. Figure S3 in Supporting Information shows representative PLE spectra of Co²⁺−Tb³⁺ and Co²⁺−Eu³⁺ co-doped SDNA thin films at fixed λ_em values of 545 and 615 nm, respectively. DNA molecules absorbed photon energy through excitation of electrons from the ground state to the single state. Energy transfer then occurred within the singlet state through the process of internal conversion. After internal conversion, electrons from the singlet state in SDNA are relaxed to the triplet state in co-doped SDNA by intersystem crossing, followed by relaxation from the emissive state to the ground state, resulting in PL emission.

Figure 5a shows the PL spectra of SDNA thin films with varying [Tb³⁺] at a fixed [Co²⁺] of 0.5 mM. Major peaks were revealed around 486, 545, 586, and 621 nm, which result from the bound state of 5D4 to ground states of 7F6, 7F5, 7F4, and 7F3, respectively. The intensity of the Tb³⁺ characteristic peak at 545 nm increased noticeably as [Tb³⁺] increased to the critical concentration of 0.6 mM. When [Tb³⁺] was higher than the critical concentration, cross-relaxation occurred because of the excess amount of Tb³⁺, resulting in quenching of the emission.
intensity. Similarly, the Gaussian-fitted areas as a function of \([\text{Tb}^{3+}]\) showed similar behavior to the emission peak intensity measured at 545 nm (Figure 5b). Figure 5c displays the PL spectra of Co\(^{2+}\)- and Eu\(^{3+}\)-co-doped SDNA thin films. Major peaks are observed at 590, 615, and 700 nm, which correspond to energy transfer from the bound state of \(5D_{0}\) to the ground states of \(7F_{1}\), \(7F_{2}\), and \(7F_{3}\), respectively. The Co\(^{2+}\)- and Eu\(^{3+}\)-co-doped SDNA thin films also showed a similar trend in which the intensity of the major peak at 615 nm increased as \([\text{Eu}^{3+}]\) increased to the critical concentration of 0.8 mM. As expected, the area of the peak at 615 nm obtained from Gaussian fitting showed the same trend as the PL intensities (Figure 5d).

**CONCLUSIONS**

In conclusion, we synthesized a M\(^{2+}\)- and Ln\(^{3+}\)-co-doped DX-DNA nanostructures via a substrate-assisted growth (SAG) method and SDNA thin films on substrates by a drop-casting method while varying the combination and concentrations of dopant ions. Phase transition from 2D DX nanostructures to amorphous structures occurred at critical concentrations. M\(^{2+}\)- and Ln\(^{3+}\)-co-doped SDNA thin films showed increasing current up to the critical concentration and decreased as the dopant ion concentration was further increased. The same trend was observed for PL, whereas absorbance showed the opposite behavior. The critical concentration for each combination of dopant ions in SDNA thin films was well matched with the critical concentration of DX-DNA nanostructures obtained from phase diagrams. Tunable physical properties of M\(^{2+}\)- and Ln\(^{3+}\)-co-doped DNA structures by simply changing the concentrations of dopant ions are crucial for further applications. By combining the advantages of DNA structures serving as a template and dopant ions possessing intrinsic characteristics, M\(^{2+}\)- and Ln\(^{3+}\)-multiple-doped DNA structures can be used in particular devices and sensors such as transistors, flexible displays, organic light-emitting diodes, and gas sensors.

**Experimental Methods.** To improve the binding affinity among charged DNA molecules and a substrate through electrostatic interaction, a substrate (glass for the phase analysis and fused silica for current, absorbance, and PL measurements) was treated with oxygen (O\(_2\)) plasma. An O\(_2\) plasma treatment (CUTE-1MP/R Plasma processing system, Femto Science, Gyeonggi, Korea) was used to introduce a silanol group on a given substrate. This functional group changes the surface of a substrate from hydrophobic to hydrophilic, which helps to achieve stable growth of DX-DNA nanostructures and the formation of SDNA thin films with uniform thickness (Figure 1).

DX-DNA nanostructures with metallic ion (M\(^{2+}\)) and lanthanide ion (Ln\(^{3+}\)) on a glass substrate (5 mm × 5 mm) were synthesized by a SAG method. DX-DNA nanostructures are composed of two repeating DX motifs each containing 4 strands with dimensions of 4.0 nm × 12.6 nm. A 50 nM amount of individual DX strands is guaranteed to attain full growth on a given substrate. Consequently, 8 different DX strands (Bioneer, Daejeon, Korea) were mixed with specific ions (CoCl\(_2\), Cu(NO\(_3\))\(_2\) for M\(^{2+}\) and Tb(NO\(_3\))\(_3\)-6H\(_2\)O, Eu(NO\(_3\))\(_3\)-5H\(_2\)O for Ln\(^{3+}\), Sigma-Aldrich, USA) at the

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**Figure 5.** PL spectra of M\(^{2+}\)- and Ln\(^{3+}\)-co-doped SDNA thin films. (a) PL spectra of SDNA thin films at given [Tb\(^{3+}\)] and [Co\(^{2+}\)]. The PLE spectrum at a characteristic emission wavelength (\(\lambda_{em}\)) of 545 nm is shown in the inset. (b) Gaussian-fitted PL intensities and areas with different [Tb\(^{3+}\)] at a fixed [Co\(^{2+}\)] of 0.5 mM and a fixed \(\lambda_{em}\) of 545 nm. (c) Emission of SDNA thin films at given [Eu\(^{3+}\)] and [Co\(^{2+}\)]. The PLE spectrum at a \(\lambda_{em}\) of 615 nm is shown in the inset. (d) Gaussian-fitted PL intensities and areas with different [Eu\(^{3+}\)] at fixed [Co\(^{2+}\)] and \(\lambda_{em}\).
designated concentrations in the presence of a 1× TAE/Mg2+ (40 mM Tris, 20 mM acetic acid, 1 mM ethylenediaminetetraacetic acid (pH 8.0), and 12.5 mM magnesium acetate) buffer solution. The M2+ concentration ([M2+]) was fixed (0.5 mM for Co2+ and 3 mM for Cu2+), whereas [Ln3+] was controlled from 0.2 to 1.0 mM with an increment of 0.2 mM. An O2 plasma-treated substrate was placed in a test tube containing DX-DNA strands with an appropriate concentration of ions (total volume of 250 μL). A sample test tube was then placed in a Styrofoam box containing 2 L of boiled water and slowly cooled from 95 to 25 °C for hybridization (Figures 1, 2, and S1, Tables S1, and S2 in Supporting Information).

Next, 0.1 g of SDNA (Marine Salmon P/no. DPO 1405787, GEM Corporation, Shiga, Japan) dissolved in 10 mL of deionized water was prepared for construction of the SDNA thin film. The SDNA solution was kept on a magnetic stirrer at 800 rpm for 10 h at room temperature to achieve a homogeneous 1 wt % SDNA solution. To fabricate the M2+ and Ln3+-co-doped SDNA thin film, a 0.5 wt % SDNA solution was mixed with the four different sets of [M2+] and [Ln3+]. The 20 μL of SDNA solution with appropriate [M2+] and [Ln3+] was drop-cast on a given substrate and left overnight. The final thickness and the average root mean square displacement of the ion co-doped SDNA thin film was ∼2 μm and ∼4 nm, respectively (Figure 1).

Glass with DX-DNA nanostructures was attached on a metal puck for AFM imaging. Then, 30 and 20 μL of 1× TAE/Mg2+ buffer was added onto the substrate and silicon nitride AFM tip (NP-S10, Veeco Inc., USA), respectively. AFM measurements were carried out by a multimode nanoscope (Veeco Inc., USA) in fluid-tapping mode (Figures 1, 2, and S2 in Supporting Information).

To evaluate the electrical characteristics, two-probe measurements (silver contacts with a channel gap of ∼1 mm) through the M2+ and Ln3+-co-doped SDNA thin film were conducted using a semiconductor parameter analyzer (4200-SCS, Keithley Instruments Inc., USA) (Figures 1 and 3). UV-visible optical absorption of the co-doped SDNA thin film was examined to understand the interaction between the DNA and ions. The spectrophotometer (Cary 5G, Varian, CA, USA) is composed of light sources and detectors (Figures 1 and 4).

The PL and PLE spectra of the co-doped SDNA thin film were performed under an ambient condition using a Xe-arc lamp equipped fluorometer (FS-2, Scinco, Seoul, Korea) with a power of 25 W. The PLE (PL) spectra were attained at fixed wavelengths λex (λem) of 545 and 615 nm (297 nm) (Figures 1, 5, S3, and S4 in Supporting Information).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00319. Schematic diagram, base sequences, and sticky-ends of the DX tiles; additional AFM images of M2+- and Ln3+-co-doped DX DNA nanostructures; and PL and PLE spectra of co-doped SDNA thin films (PDF)

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**Notes**

The authors declare no competing financial interest.

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