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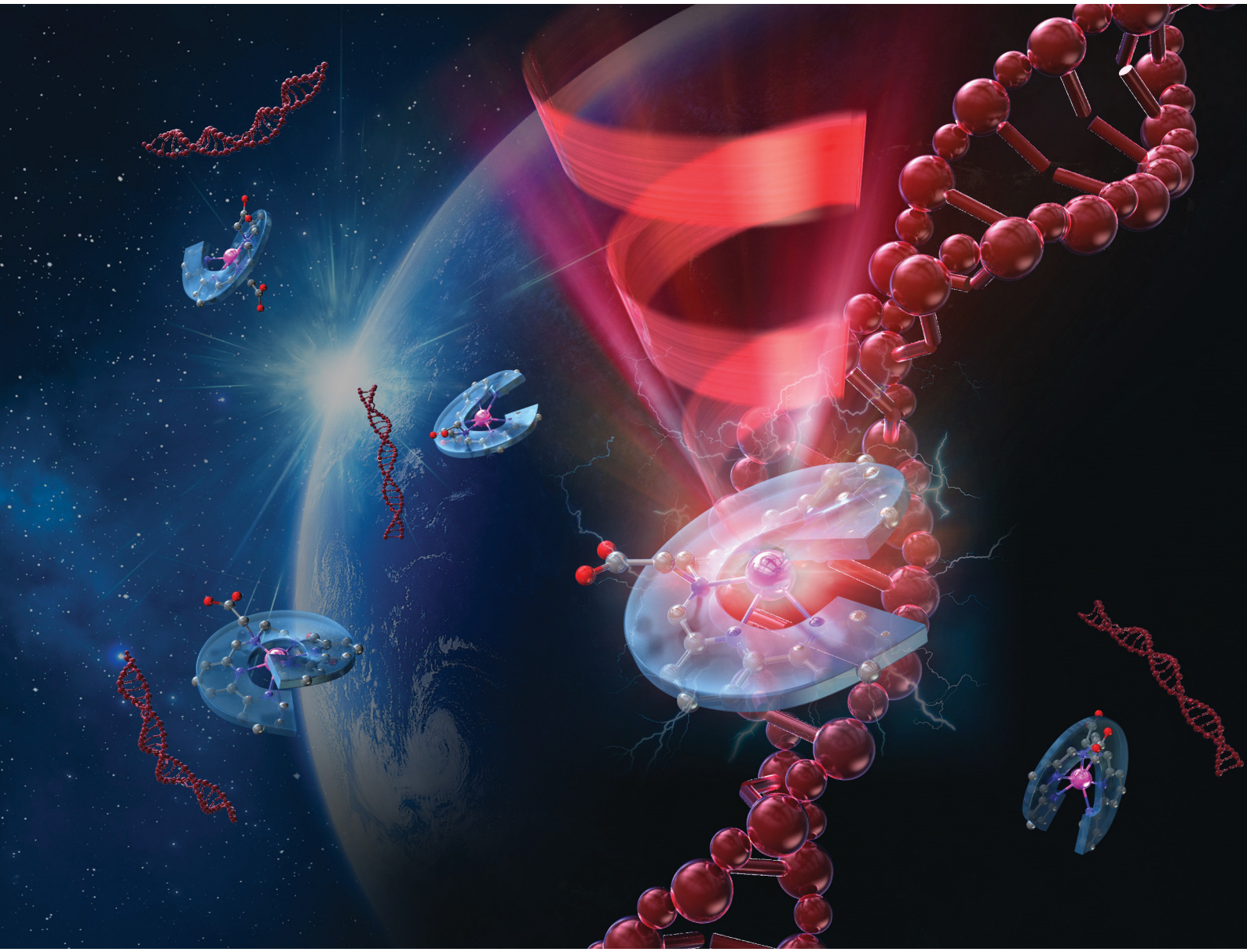

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Induced chiroptical properties of helical Eu(III) complex by electrostatic interaction with DNA†

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Circularly polarized luminescence (CPL) has significantly increased the interest in biological fields. In this research, a water-soluble Eu(III) complex with a helical complex structure, EuL^{COOH}, was incorporated in chiral DNA in aqueous solutions. The photoluminescence performance of this DNA/EuL^{COOH} hybrid system was investigated. Compared to EuL^{COOH} alone, emission intensity and emission lifetime were effectively improved in the presence of DNA. The major binding between EuL^{COOH} and DNA was proven to be the electrostatic interaction. Owing to this interaction, the chiral environment provided by DNA successfully induced CPL from EuL^{COOH}.

Introduction

The high prevalence and importance of chirality in biological fields have always been of great interest to scientists. In particular, the chiroptical property of circularly polarized luminescence (CPL) provides a rich resource of information on the chiral environment of molecules. CPL has received significant attraction in a wide range of biological applications such as bio-probes, biosensors and bio-imaging.[1–7] CPL spectroscopy measures the luminescence difference between left and right circularly polarized lights. The degree of CPL is normally evaluated by the emission dissymmetry factor, $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L (I_R) is the intensity of the left (right) CPL. Theoretically, g_{lum} is defined as $g_{lum} = 4(|m|/|\mu|)\cos\tau$, where m and μ are magnetic and electric dipole transition moments, respectively, and τ is the angle between them.[8] Therefore, a higher g_{lum} value prefers luminophores with magnetic dipole allowed and electric dipole forbidden transitions. Thus, lanthanide complexes have become the most potential candidates for CPL activity in the development of emission systems.[3,9–11]

Notably, only the lanthanide ions located in a chiral environment are expected for CPL activity. This is because the dissymmetry in the ligand field of the chiral lanthanide complex guarantees their m and μ transitions are non-orthogonal ($\cos\tau \neq 0$).[11] One method to realize the chiral environment for the lanthanide ions in the complex is to coordinate them with chiral molecules. On the other hand, biopolymer-based materials have long attracted attention due to their highly ordered structure, environmentally friendly nature and potential applications as photo-functional materials.[12–14] Natural chiral molecules such as DNA, which exhibits a characteristic helix structure, has the unique ability to bind various types of functional materials through electrostatic binding, intercalation and groove binding.[15,16] In some DNA-based hybrid systems, DNA molecules were reported to transfer their natural chirality to their coordinated lumiphores and to induce the CPL activity in DNA/lumiphore hybrid systems.[17,18] Moreover, DNA-based hybrid systems have been proven promising in significantly improving the photo-functional properties of metal complexes.[19–21] DNA-based hybrid systems with high structural orders exhibit flexible responsive optical functions and can be applied as a soft crystal.[13]

Recently, some authors in this research have reported a novel water-soluble Eu(III) complex, EuL^{COOH}, in which two carboxyl groups are selected as hydrophilic skeletons and introduced into EuL. The water-solubility and excellent luminescence performances make EuL^{COOH} especially attractive in the biological field.[22] In this study, a DNA/Eu(III) complex hybrid system based on the helical complex structure of EuL^{COOH} was fabricated and investigated in an aqueous solution. Compared with EuL^{COOH} alone, the photoluminescence performance of the Eu(III) compound was effectively improved, and structural chirality was endowed by the presence of DNA. The major binding mode between DNA and EuL^{COOH} was revealed to be electrostatic interaction. Based on this interaction, CPL was successfully induced from the helical Eu(III) complex through the chiral environment provided by DNA.

Experimental section

Materials

EuL^{COOH} was synthesized according to the reported procedure.[22] The sodium salts of DNA (base pairs: *ca.* 10 000) were provided

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by Piotrek Co., Ltd. (Japan). These were marine-based salts that were first isolated from frozen salmon milt through a homogenization process followed by the removal of proteins and impurities.

Preparation of the DNA/EuL^{COOH} hybrid solutions

DNA/EuL^{COOH} hybrid solutions were prepared by mixing EuL^{COOH} and DNA in the aqueous solution. The concentration ratios of DNA and EuL^{COOH} ([DNA]:[EuL^{COOH}]) were 1 : 1, 5 : 1, 10 : 1, 15 : 1, 20 : 1 and 30 : 1. The concentration of EuL^{COOH} was fixed at 0.02 mmol L^{-1}.

Measurement and characterization

Oxygen dissolved in the DNA/EuL^{COOH} hybrid solutions was removed by bubbling nitrogen gas through the solution prior to carrying out the optical measurements. The absorption and CD (circular dichroism) spectra were obtained using a circular dichroism spectrometer (J-1100, JASCO Corporation, Japan). The photoluminescence spectra were acquired using a spectrofluorometer (FP-8500, JASCO Corporation, Japan). The emission lifetimes were determined using a time-resolved fluorescence spectrometer (Quantaurus-Tau C11367-21, Hamamatsu Photonics K. K., Japan). The CPL (circularly polarized luminescence) measurements were conducted using a previously reported system.[23] This system consists of the following components: a 300 nm LED (M300L4, Thorlabs Japan Inc., Japan), an LED driver (DC2100, Thorlabs Japan Inc., Japan), a photoelastic modulator (PEM-90, Hinds Instruments Inc., United States), a photomultiplier tube (H7732-10, Hamamatsu Photonics K. K., Japan), a linearly polarized cubic prism (200 000 : 1), a photomultiplier tube (H7732-10, Hamamatsu Photonics K. K., Japan), and a dual-phase DSP (digital signal processing) lock-in amplifier (7265, Signal Recovery Ltd., United Kingdom). The appropriate detection wavelengths of the monochromator and the PEM (photoelastic modulator) were controlled using a PC (Dell D11M). The molecular structure and coordination environment of EuL^{COOH} were reported to be extremely stable at pH = 4.0–9.7.[22] In this research, all the experiments are carried out under solution conditions with a pH range of 5.0–8.0.

Results and discussion

Photoluminescence performance of EuL^{COOH} in the presence of DNA

Circular dichroism (CD) spectroscopy originates from the interactions of chiral molecules with circularly polarized electromagnetic rays and exhibits high sensitivity and efficiency over the other conformational analysis. It suggests the difference between the absorption of right- and left-handed circularly polarized light and is quantified by ellipticity. Notably, CD spectroscopy is a highly sensitive diagnostic tool for determining the absolute configuration of chiral systems and monitoring their intermolecular interactions.[24,25]

Fig. 1(a) shows the absorption and CD spectra of the EuL^{COOH} alone and the DNA/EuL^{COOH} hybrid solutions at various concentration ratios of DNA and EuL^{COOH}. DNA has a well-known axisymmetric helical structure and shows a characteristic absorption band near 260 nm, which is attributed to its nucleic acid bases, as illustrated in Fig. S1 (ESI†). For all solutions that DNA involved, the absorbance of DNA bases appeared and increased with the increasing DNA concentration. Moreover, an absorption band assigned to the π–π* transition of the ligands of EuL^{COOH} was observed around 305 nm.[26] The unchanged absorption band from ligands of Eu(III) complex in all solutions indicates that the electronic transition of the ligands was not perturbed even when adding DNA. On the other hand, the CD behaviors of EuL^{COOH} obviously differed in the absence or presence of DNA. No CD signal was detected for EuL^{COOH} alone. The split Cotton effect with the first positive (275 nm) and second negative (250 nm) signals centered at the absorption peak of DNA was observed upon the addition of DNA because of its chiral structure. Furthermore, as the expanded CD spectra in Fig. 1(b) show, a negative ellipticity near 305 nm was induced, corresponding to the absorption of the Eu(III) complex. This suggests that DNA interacts with the Eu(III) complex and thus induces the chirality in its coordination structure without affecting the electronic transitions of the ligands. The ellipticity generated from the interaction between DNA and EuL^{COOH} was further amplified when additional DNA was added. Presumably, this phenomenon can be ascribed to

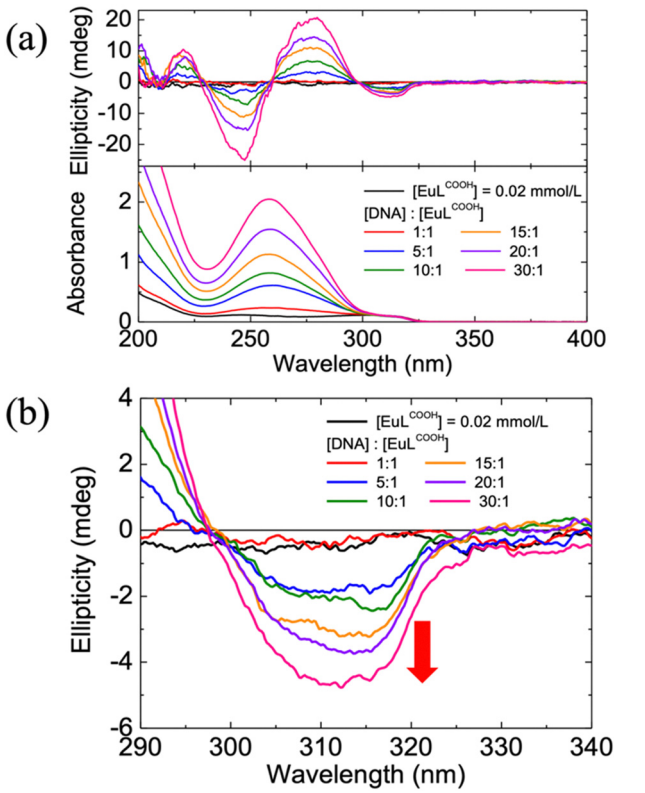

Fig. 1 (a) Absorption (bottom) and CD (top) spectra of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions. [DNA]:[EuL^{COOH}] were varied from 1 : 1 to 30 : 1. (b) Expand CD spectra of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions at 290–340 nm.

the exciton coupling between multiple chromophores of the ligands of the Eu(III) complex upon interaction with DNA.[27]

According to the induced chirality of EuL^{COOH}, the DNA in the second coordination sphere may have significantly distorted the first coordination sphere of EuL^{COOH}. High-resolution emission spectroscopy can well reflect even minor changes in the coordination sphere of the Eu(III) complex. Subsequently, emission measurements of EuL^{COOH} alone and the DNA/EuL^{COOH} hybrid solutions at various concentration ratios of DNA and EuL^{COOH} were shown in Fig. 2(a). Characteristic intense emission bands due to the $^5D_0 \rightarrow {}^7F_J$ transition of the Eu(III) complex were observed at approximately 580 nm ($J = 0$), 590 nm ($J = 1$), 614 nm ($J = 2$), and 650 nm ($J = 3$). With the addition of DNA, the total emission intensity of EuL^{COOH} exhibits obvious enhancement. This can be explained by that the luminescence quenching caused by the vibration and rotation of the Eu(III) molecule is significantly suppressed. It is likely that the -OH oscillators of the water molecule are inhibited to some extent in DNA/EuL^{COOH} hybrid solutions. Therefore, the luminescence of EuL^{COOH} was effectively improved in the presence of DNA.

Fig. 2(b) shows the amplified spectra of the emission peaks corresponding to $^5D_0 \rightarrow {}^7F_2$ (left) and $^5D_0 \rightarrow {}^7F_4$ (right) transitions, respectively. These two transitions are known for their sensitivity to the structure of the matter around Eu^{3+} ions,[28] and notable changes in their spectra patterns were observed in the presence of DNA. This indicates a perturbed ligand field of EuL^{COOH} owing to the interaction between DNA and EuL^{COOH}.

Combining the CD and luminescence spectroscopy results, it was concluded that DNA interacts with EuL^{COOH} and changes its coordination structure in aqueous solutions. On the other hand, the $^5D_0 \rightarrow {}^7F_1$ transition is essentially independent of the chemical environment and acts as a reference for all transitions originating from the $^5D_0$ excited state.[29] The ratio (I_{rel}) of the integrated intensity of insensitive $^5D_0 \rightarrow {}^7F_1$ to hypersensitive $^5D_0 \rightarrow {}^7F_2$ transitional probabilities is normally used to evaluate the site symmetry around the Eu^{3+} ions. A larger value of I_{rel} indicates a lower symmetry occupied by the Eu^{3+} sites.[30] For all EuL^{COOH} solutions, the values of I_{rel} were almost constant at 2.25 with and without DNA (Fig. S2, ESI†). Although some variations in the coordination environment of EuL^{COOH} occurred reflected by changed luminescence and CD spectra, EuL^{COOH} maintained the site symmetry around the Eu^{3+} ions, even with the addition of DNA.

Time-resolved emission decay profiles were then obtained to further investigate the luminescence behaviour of the DNA/EuL^{COOH} hybrid solutions. Fig. 3 shows the emission decay profiles of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions at various concentration ratios of DNA and EuL^{COOH}. The emission lifetime of the DNA/EuL^{COOH} hybrid solution became longer than that of EuL^{COOH} alone and further increased with increasing DNA concentration. Table 1 lists the values of the average emission lifetime (τ_{ave}) and the contribution (%) of each exponential component (τ_1 and τ_2). The emission lifetime of EuL^{COOH} had only one exponential component (0.53 ms). This mono-exponential emission decay was attributed to the stable monolithic structure of EuL^{COOH}. Conversely, the DNA/EuL^{COOH} hybrid solutions exhibited multi-exponential emission decay with two components: τ_1 and τ_2. The short τ_1 component (0.5 ms) was similar to that of the single component of EuL^{COOH} alone (0.53 ms). The longer τ_2 component (1.1 ms) was derived from EuL^{COOH} with coordinating DNA. Therefore, the τ_1 and τ_2 components represent EuL^{COOH} without and with interacting DNA, respectively. With increasing concentrations of DNA, the contributions of the short lifetime τ_1 component decreased and those of the long lifetime τ_2 component increased. This indicates that more interaction between EuL^{COOH} and DNA occurred.

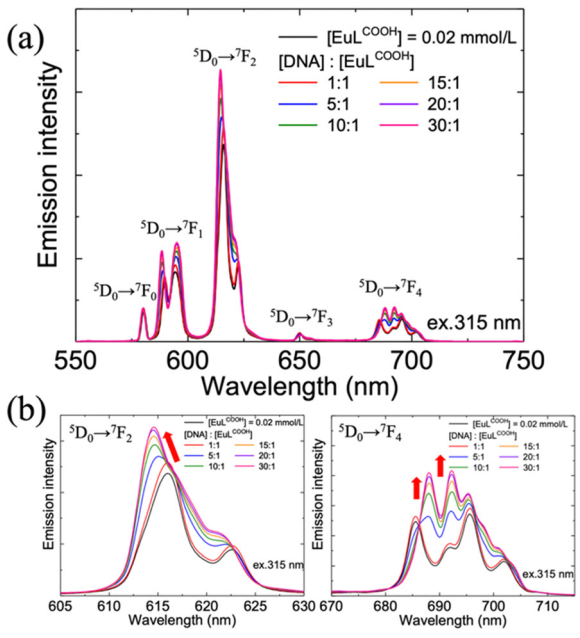

Fig. 2 (a) Emission spectra of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions. (b) Expand emission spectra of the DNA/EuL^{COOH} hybrid solutions for $^5D_0 \rightarrow {}^7F_2$ (left) and $^5D_0 \rightarrow {}^7F_4$ (right) transitions. [DNA] : [EuL^{COOH}] were varied from 1 : 1 to 30 : 1. The excitation wavelength was 315 nm.

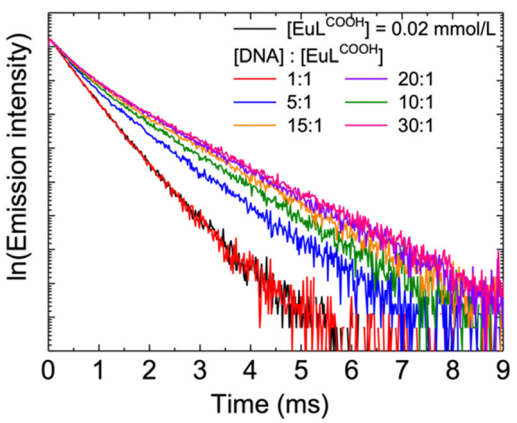

Fig. 3 Emission decay profiles of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions. [DNA]:[EuL^{COOH}] were varied from 1 : 1 to 30 : 1.

Table 1 Average emission lifetime (τ_{ave}) and contribution (%) of τ_1, τ_2 components of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions

		τ_1 (ms)	
$[EuL^{COOH}]$	τ_{ave} (ms)	0.53	τ_2 (ms)
$[DNA]:[EuL^{COOH}]$	0.53	0.50 (%)	1.10 (%)
1 : 1	0.54	94.2	5.8
5 : 1	0.77	54.5	45.5
10 : 1	0.88	36.7	63.3
15 : 1	0.94	27.1	72.9
20 : 1	0.97	22.4	77.6
30 : 1	0.99	17.8	82.3

Water molecules coordinated with Eu^{3+} ions are of great importance for understanding the surrounding environment and coordination sphere of Eu(III) complex in an aqueous solution. According to Horrocks' equation, the coordinating water of the Eu(III) complex in aqueous solutions can be evaluated using its emission lifetime in H_2O and D_2O.[31,32] The number of coordinating water molecules q is calculated as follows:

$$q = 1.11[\tau_{H_2O}{}^{-1} - \tau_{D_2O}{}^{-1} - 0.31]$$

where τ_{H_2O} and τ_{D_2O} are the emission lifetimes of Eu(III) complexes in H_2O and D_2O, respectively. According to the previous report on the coordination structure and photoluminescence properties of EuL^{COOH}, the q of EuL^{COOH} alone is one, which implies that one water molecule binds to each Eu^{3+} ion in EuL^{COOH}.[22] In the case of the DNA/EuL^{COOH} hybrid solution with a 5 : 1 concentration ratio of DNA to EuL^{COOH}, the measured emission lifetimes in H_2O and D_2O were 0.77 ms and 2.04 ms, respectively. The value of q was thus calculated to be 0.55. This is similar to the contribution of the τ_1 component (54.5%) for the same DNA/EuL^{COOH} hybrid solution ([DNA]:[EuL^{COOH}]= 5 : 1). In this case, the value of q may be explained by the interaction ratio with DNA. The difference in q between EuL^{COOH} alone and the DNA/EuL^{COOH} hybrid solutions occurs because DNA competes for a portion of the complex coordination of Eu^{3+} ions from the water molecule. Water molecules in the second coordination sphere can shorten the emission lifetime of the $^5D_0$ excited state, thereby extending the emission lifetime of the DNA/EuL^{COOH} hybrid solutions by being partially replaced to some extent by DNA.

Interaction mode between EuL^{COOH} and DNA

DNA is well known to be a negatively charged biological helical polymer. The electrostatic properties of its phosphate group and well-defined sites provided by its helical structure contributed to its characteristic counterion binding ability. Additionally, the Eu^{3+} ion possesses a high positive charge character owing to its high Lewis acidity from the well-shielded 4f orbitals.[28,33,34] EuL^{COOH} complex acts as a stable cationic component with 2+ valence in an aqueous solution.[22] Therefore, it is presumed that DNA interacts with EuL^{COOH} by mode of electrostatic binding.[35,36] To clarify this hypothesis, an excess of Na^+ ions (NaCl) was added to a DNA/EuL^{COOH} hybrid solution. The non-

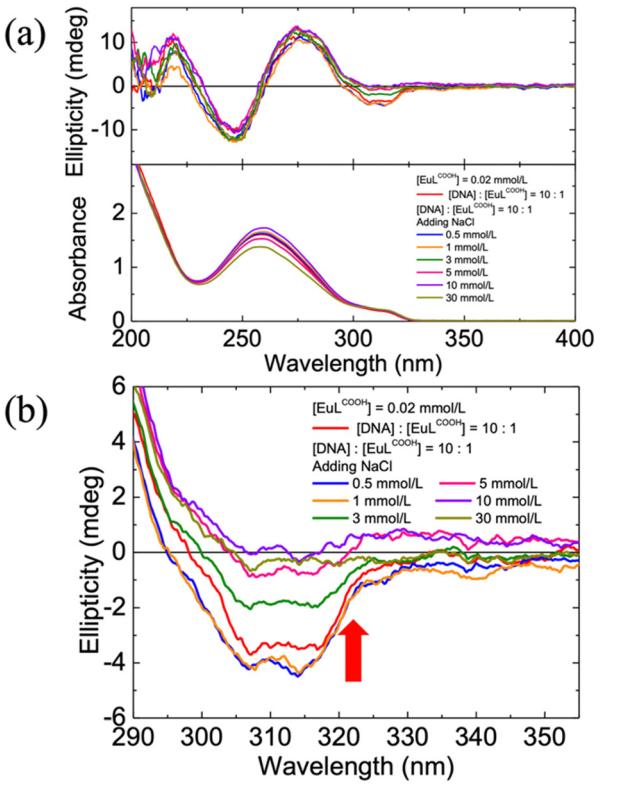

Fig. 4 (a) Absorption (bottom) and CD (top) spectra of EuL^{COOH}, and the DNA/EuL^{COOH} hybrid solution without and with the addition of NaCl at 200–400 nm. (b) Expand CD spectra of EuL^{COOH}, and the DNA/EuL^{COOH} hybrid solution without and with the addition of NaCl at 290–355 nm.

interference of Na^+ ions with EuL^{COOH} alone in an aqueous solution was demonstrated by the unchanged emission spectra (Fig. S3(a), ESI†) and emission decay profiles (Fig. S3(b), ESI†) of EuL^{COOH} alone with and without a large amount of NaCl. Then, various concentrations of NaCl (0.5–30 mmol) were added sequentially to a DNA/EuL^{COOH} hybrid aqueous solution. The CD spectra, emission spectra, and emission lifetimes of these solutions were recorded to investigate the changes in the possible electrostatic interactions between DNA and EuL^{COOH}. As shown in Fig. 4, in addition to the excess Na^+ ions, the induced negative CD signal derived from the Eu(III) complex interacting with DNA at approximately 310 nm, gradually tended towards zero. This phenomenon is caused by the cation exchange of Na^+ and indicates the disassociation of the electrostatic interaction between the Eu^{3+} ion and DNA. Correspondingly, the changes that occurred in the emission spectra (Fig. S4, ESI†) and emission decay profiles (Fig. S5, ESI†) of the DNA/EuL^{COOH} hybrid solution due to the interaction with DNA also gradually disappeared and were finally approximated highly to EuL^{COOH} alone after adding excess Na^+. As the emission lifetimes components analysis shows in Table S6 (ESI†), the contribution of τ_1 component (0.5 ms) from EuL^{COOH} alone increases, and the contribution of τ_2 component (1.1 ms) from EuL^{COOH} with coordinating DNA decrease with the gradual addition of Na^+. This variation occurred in the ratio of the two emission exponential components, which revealed the process of disassociation of the

electrostatic interaction between Eu^{3+} and DNA. These results do reinforce our hypothesis that EuL^{COOH} is mainly with the anionic DNA through electrostatic interaction.

DNA melting is known as the process of heating DNA solutions to cause the tightly intertwined strands to cooperatively unravelling into single strands. This is an important biological process that can be applied to certain aspects of DNA.[37–39] The effect of the DNA melting transition on the DNA/EuL^{COOH} hybrid solutions was investigated by evaluating the photoluminescence performance of the DNA/EuL^{COOH} hybrid solutions at temperatures from room temperature (25 °C) to 80 °C. Thermal quenching of the excited states of the Eu(III) complex sequentially occurred with the increasing temperature.[28] Fig. S7 (ESI†) shows the emission spectra of the DNA/EuL^{COOH} hybrid solution ([DNA]: [EuL^{COOH}] = 1 : 30) at various temperatures. The total emission intensity gradually decreased during the heating treatment. On the other hand, the shapes of the emission peaks from sensitive $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions of EuL^{COOH} were retained over the entire temperature range. Therefore, the unaffected emission spectra suggest that the interaction between EuL^{COOH} and bases in DNA possess excellent thermal stability and this interaction is well kept at even under 80 °C. In the case of the emission lifetime of the DNA/EuL^{COOH} hybrid solution ([DNA]: [EuL^{COOH}] = 1 : 30) through the heating process (Fig. S8, ESI†), the lifetime of EuL^{COOH} became progressively shorter owing to the thermal quenching. Interestingly, the emission lifetime of the DNA/EuL^{COOH} hybrid solution at 80 °C (0.60 ms) was still longer than that of EuL^{COOH} alone at room temperature of 25 °C (0.53 ms). Stable interactions, even at high temperatures, contribute to this excellent emission lifetime performance. Heating a DNA solution can result in the separation of strands, and the melting temperature of the DNA is normally lower than 80 °C, which was the highest temperature in this investigation. The melting process of a DNA solution is normally evaluated using absorption measurement.[37] It is because the amount of UV light absorbed by DNA increases as the ratio of non-bonded base pairs increases during the melting process. Double helix stacking and a reduction in base parity are indicated by the changed electronic configuration of the bases during the melting process. Fig. S9 (ESI†) shows the absorption and CD spectra of the DNA/EuL^{COOH} hybrid solution ([DNA]: [EuL^{COOH}] = 1 : 30) over the investigated temperature range. Absorbance peaks at approximately 257 nm were attributed to the electronic transition of DNA, and its relationship with temperature was shown in the insert of Fig. S9 (ESI†). The absorbance increased with the increasing temperature, suggesting the melting process of DNA in the DNA/EuL^{COOH} hybrid solution. Correspondingly, in the case of CD measurements, the second negative (250 nm) Cotton effect weakened with increasing temperature. Inside the DNA, bases gradually unstacked from neighbouring bases during heating, resulting in these variations including increased absorbance and changed CD signals.[37] Moreover, the negative CD signal at approximately 315 nm from the EuL^{COOH} coordinating with DNA decreased and finally disappeared during heating. This indicates that EuL^{COOH} lost chirality which was obtained from its interaction with DNA at high temperatures owing to the denaturation of DNA. Although the interaction with DNA was not broken, as reflected in the emission spectra, EuL^{COOH} changed from binding to double-stranded DNA to single-stranded DNA binding in the case of high temperature.

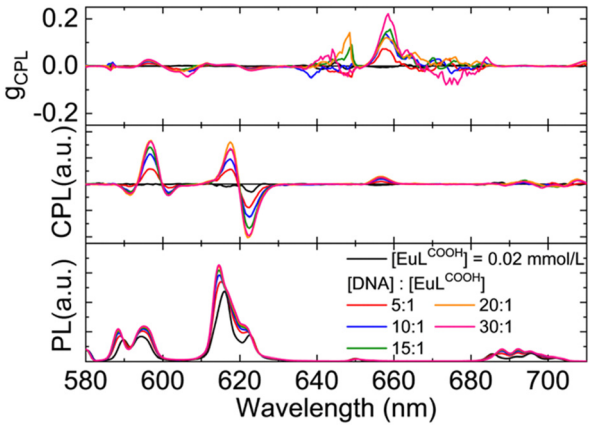

Fig. 5 CPL spectra of EuL^{COOH} and the DNA/EuL^{COOH} hybrid solutions in various concentration ratios in water. The excitation wavelength was 300 nm.

Induced CPL of EuL^{COOH} by interaction with DNA

As discussed in the CD measurement, the optical chirality of the helical EuL^{COOH} complex was due to electrostatic interactions with DNA. In general, CPL is considered a complementary tool for CD to investigate the optical chirality of a material. CPL measurements of EuL^{COOH} alone and the DNA/EuL^{COOH} hybrid solutions at various concentration ratios of DNA and EuL^{COOH} were performed, and their CPL spectra were shown in Fig. 5. As expected, no CPL signal was observed for EuL^{COOH} alone. In contrast, CPL signals appeared with the addition of DNA to the EuL^{COOH} solution and increased with an increasing concentration of DNA. A clear CPL signal assigned to the $^5D_0 \rightarrow {}^7F_4$ transition was observed at approximately 655 nm. The luminescence dissymmetry, g_{lum}, was calculated to +0.22 when the concentration ratio of DNA to EuL^{COOH} was 30 : 1. This induced CPL performance of the helical Eu(III) complex can be attributed to the induced structural chirality, as reflected by CD measurement.

Conclusions

In this study, a water-soluble Eu(III) complex with helical ligands (EuL^{COOH}) was hybridized with DNA in an aqueous solution. The optical chirality of EuL^{COOH} was induced by its interaction with DNA. The photoluminescence performances of the DNA/EuL^{COOH} hybrid solutions were investigated using luminescence and luminescence lifetime measurements. It was found that EuL^{COOH} exhibited more brilliant luminescence with a longer lifetime in the addition of DNA. When an excess amount of Na^+ ions was added to the DNA/EuL^{COOH} hybrid solution, the changes in the emission spectra and CD spectra resulting from the interaction between EuL^{COOH} and DNA

disappeared. This result indicates that the major binding between DNA and EuL^{COOH} is an electrostatic interaction. Furthermore, this interaction contributes to the induced CPL signal of EuL^{COOH} due to the chirality of the DNA. This water-soluble Eu(III) material with excellent photo-luminescence performance and chiroptical properties is highly expected to be an effective bioanalytical tool in practical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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