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Synthesis, Characterization and DNA-Binding Studies of Lanthanide(III) Complexes Ln $(H_2L) \cdot (HL) \cdot 0.5(bipy) \cdot nH_2O$ [1]

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Synthesis, Characterization and DNA-Binding Studies of Lanthanide(III) Complexes Ln (H_2L) · (HL) · 0.5(bipy)·nH_2O [1]

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Abstract---A series of lanthanide (III) complexes Ln (H_2L) · (HL) · 0.5(bipy)·nH_2O (where Ln =Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb and H_3L=N-(2-propionic acid)-salicyloyl hydrazone, bipy= 2, 2 '-dipyridine) have been synthesized in ethanol-water mixture and characterized. The DNA-binding properties of these complexes were searched for the interaction with CT-DNA by electronic absorption titration and emission titration. The results showed that the interaction between Nd(III) complex and CT-DNA by surface/electrostatic binding, while all the other complexes can bind to calf thymus DNA mainly by intercalation mode.

Key words: Lanthanide(III) Complexes, DNA-binding, hydrazone

INTRODUCTION

The DNA-binding metal complexes have been extensively studied as DNA structural probes, DNA-dependent electron transfer probes and so on during the past decade [1-4]. DNA-binding small molecules have since long attracted interest because of their interference with important mechanisms in the cell, some inducing mutations and cancer, while others have found use as cancer therapeutics [5]. Small molecules recognizing specific DNA sequences have attracted great interest for gene-targeted drugs, which may alter the local structure of DNA to inhibit access of activators or repressors to regulate ultimate gene expression processes [6]. The interaction of lanthanide complexes, containing multidentate aromatic ligands, with DNA has recently gained much attention following the important biological and medical roles [7, 8].

Aromatic ring stacking between nucleobases is considered to be a major driving force that leads to binding. The size, electron density of the interacting aromatic rings and the combined effect of hydrophobic and hydrophilic interactions determine the extent of binding [9-11]. Thus by using mixed ligand complexes, it is possible to systematically vary parameters of interest hence changing the properties of the intercalating groups without altering the chemical nature of the intercalating moiety [12, 13]. In the previously published works [14], the crystal structure and fluorescence properties of $Dy(H_2L)(HL)(bipy)\cdot 5H_2O$ had been studied. This work is a continuation of our studies on mixed ligand complexes $Ln(H_2L)(HL)(bipy)\cdot nH_2O$ (Ln=Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb). DNA binding properties of these complexes are studied by electronic absorption titration and emission titration.

EXPERIMENTAL

Calf thymus DNA (CT-DNA) was purchased from Sigma (USA). Pyruvic acid was a biochemical reagent. All the other chemicals used were of analytical grade.

The C, H, and N analyses were taken with a Perkin Elmer model 2400 elemental analyzer. The metal ion was determined by titration. Molar conductance measurement was made in DMF using a

1 The article is published in the original.

DDS–11A conductivity meter. TG-DTG curves were measured by TG-209 gravitational thermal analyzer. X-ray powder diffraction was performed using a D/max-III X-ray powder diffraction apparatus. The UV spectra were recorded on a Lambda 40P UV-vis spectrophotometer. Fluorescence measurements were made on a Hitachi F-4500 pectrophotometer.

Synthesis of the complexes. The $Ln(NO_3)_3 \cdot nH_2O$, H_3L and bipy in 1:2:2 molar ratio were dissolved in a mixed solution of water-ethanol, respectively, and then mixed. The resultant solution was refluxed in 80°C in a water bath for 3 h, then cooled to room temperature, filtrated and dried under vacuum.

DNA binding experiments The interaction of the complex with CT-DNA was studied in a doubly distilled water buffer containing of tris(hydroxymethyl)aminomethane (Tris) (5 mmol), 0.4% DMSO, and NaCl (5 mmol). The system was adjusted to pH 7.2 with hydrochloric acid. In order to eliminate the absorbance of nucleic acid itself, an equal amount of CT-DNA was added to the sample and the reference cell, respectively. Spectrometric titrations were performed according to References [16–18].

RESULTS AND DISCUSSION

Composition of the Complexes

The results of element analysis for all the complexes are listed in Table 1 along with their formulae. From the data of table 1, it can be seen that the compositions of the complexes the complexes are very similar except water molecular number. At the same time, the molar conductivity in DMF of the complexes was also measured and the value was around 27.49–43.76 $\Omega^{-1}\cdot cm^{2}\cdot mol^{-1}$, which shows that all the complexes are non-electrolytes in DMF [19].

Infrared Spectra

The important IR frequencies of the ligand and its complexes along with their relative assignments are recorded in Table 2. IR spectra of the complexes and the (H_3L) are identified according to the literature [20, 21]. The bands appearing in the infrared spectra of the free ligand (H_3L) at 3291, 1642, 1756 cm^{-1} are assigned to ν_{N-H}, $\nu_{C=N}$ and ν_{COOH} respectively. All complexes show a strong band in 1522-1538 cm^{-1} assigned to ν(C=N) vibration, which indicates that the C=N (N atom) was coordinated. The absorption band at 1756 cm^{-1} of free ligand $H_3L(\nu_{COOH})$ has been replaced by two new bands around 1598-1612 $cm^{-1}$and 1337-1358 cm^{-1} in all the complexes, which were assigned to $\nu_{as,\,COO}$, and $\nu_{s,\,COO}$ respectively. The $\Delta\nu$ (ν_{as}-ν_{s}) is more than 200 cm^{-1} which indicates that COO^{-} is coordi- nated with the lanthanide ion in the form of one dentate[22]. The bands at 742-765 and 579-587 cm^{-1} in all the complexes are assigned to the in-plane and out-of-plane vibration of water which are associated with the coordinated water.

UV Spectra

UV Spectra of the ligand and the complexes were obtained in DMF solution with DMF as a reference. The data are listed in Table 3. There are two bands at 273 and 313 nm in the ligand, which is the π-π* transition of the salicyloyl group. They red shift to 284-302 and 325-331nm in the complexes show that the coordination of the ligands.

Fluorescence Properties

The emission spectrum of H_3L and Dy(III) complex were measured in the solid state at room temperature. The excitation wavelength of the ligand and Dy(III) complex are 300 nm and 350 nm respectively. The fluorescence spectrum of the ligand and the complex are shown in Fig. 1. The free ligand H_3L shows two broad bands around 407 and 453 nm. Spectra exhibit a broad band around 430 nm, attributed to the ligand and dipy. Three other peaks at 480, 575 and 645 nm can be attributed to $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$ and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ transitions of Dy(III), respectively [24]. The fluorescence enhancement of Dy(III) reflects efficient energy transfer from the conjugated π-electron system of the ligand to the Dy^{3+} ion, as compared to $Dy(NO_3)_3\cdot 5H_2O$ under the same conditions. These observations suggest that the Dy(III) complex could be anticipated as a potential fluorescent material.

X-Ray Powder Diffraction

The results of the X-ray powder diffraction for the salt ($Gd(NO_3)_3\cdot 6H_2O$), ligand (H_3L), and the complexes are shown in Table 4. The X-ray powder diffraction data on the salt were carried out according to standard card no. 30-0553: Quality. From Table 4, it can be seen that X-ray power diffraction of the complexes is obviously different from the ligands and the salt, and the complex is not a simple lap joint of the ligands and the salt either. It can be deduced that a new complex is formed.

Thermal Analysis of the Complexes

The typical TG-DTG analysis and DSC for the three selected samples (Pr(III) complex, Gd(III) complex and Er(III) complex) were performed from 20 to 1000□ at a heating rate of 10□·min^{-1} under N_2 atmosphere and the thermal decomposed procedure are deduced as Scheme

1. Theoretical and experimental mass loss data (%) for the thermal decomposition of the complexes are listed in table 5. Upon heating under nitrogen, the complex undergoes three major stages of weight loss. The first stage(20-280□)is connected with the loss of water from the complexes; the second stage(280-340□) is the loss of bipy ligand, and the last stage is the decomposition of the ligands H_3L

Crystal structure

The structure of Dy(III) complex [14] and Eu(III) complex [15] showed in Fig.2. The coordination environment around Eu and Dy are very similar. The metal atom is nine-coordinated by two tridentate ligands and three water molecules in each complex.

DNA binding studies

Before reacting of the complexes with CT-DNA, their solution behaviors in a buffer solution at room temperature were monitored by UV-vis spectroscopy for 24 h. No liberation of the ligand was observed under these conditions. These suggest that all the complexes are stable under the conditions studied.

Absorption spectral studies

The application of electronic absorption spectroscopy in DNA-binding studies is one of the most useful techniques [24, 25]. The absorption spectra of all the complexes in the absence and presence of DNA are shown in Fig. 3 and the values of the DNA binding are shown in table 6. Upon increasing concentrations of DNA, all of the absorption bands of the complexes displayed hypochromicities. The addition of DNA resulted in hypochromism ΔH% (ΔH%=100 (A_{free}-A_{bound})/A_{free}) for the π-π* absorption at about 280 nm of 64%, 53%, 33%, 61% and 35% for Ce(III) complex, Eu(III) complex, Gd (III)complex, Tb(III)complex and Yb(III) complex,

respectively. As reported previously [26], the hypochromism of 26% was obtained upon the addition of DNA to $[Ru(bpy)_2(pip)]^{2+}$ implied the interaction of the complex with DNA by an intercalative mode. So these five complexes interact with calf thymus DNA quite probably by intercalating the ligand into the base pairs. While for the other complexes, the hypochromism of the absorption bands are all less than 26%, so the interaction modes of these complexes with DNA need to confirm by further experiments.

Emission spectral studies

The emission spectra of the complexes in the absence and presence of DNA are illustrated in Fig. 4. We used [DNA] = 0, 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6} and 50×10^{-6} mol/L. Arrow shows the absorbance changes upon increasing DNA concentration. All of the complexes can emit strong luminescence in Tris buffer. For Ce(III) complex, Eu (III)complex, Gd (III)complex, Tb(III) complex and Yb(III) complex, the emission intensities at maximum wavelength increase about 1.15-1.85 times with increasing concentrations of CT-DNA. The results of the emission titrations also indicate that the complexes are protected from solvent water molecules by the hydrophobic environment inside the DNA helix. This implies that the complexes can insert between DNA base pairs, which also agrees with those observed for the UV. For Er complex, the F/F0=1.40. This phenomenon also implies that the complex is protected by DNA, so the interaction mode between Er complex and DNA may probably be an intercalative mode.

Luminescence Quenching by $K_4[Fe(CN)_6]$

Steady-state emission quenching experiments using $K_4[Fe(CN)_6]$ as the quencher were also used to gauge the DNA binding properties of Pr(III) complex, Nd (III)complex, Sm (III)complex and Dy(III) complex. Anionic quenchers such as $K_4[Fe(CN)_6]$, very efficiently quench the

emission of complexes which are free in solution due to ion pairing [27] but poorly quench the emission of complexes which are closely bound to the DNA polyanion. The emission quenching spectra of the four complexes in the absence and presence of DNA are shown in Fig. 5. Figure 6 shows Stern Volmer plots for the emission quenching of these four complexes by $K_4[Fe(CN)_6]$ in the absence and presence of DNA. For Nd (III)complex, with increasing $K_4[Fe(CN)_6]$ quencher concentrations, the system of the complex and complex-DNA causes obvious reduction in the emission intensity, but the emission intensity of complex in the absence of DNA is higher than that in the presence of DNA under the same $K_4[Fe(CN)_6]$ quencher concentration, indicating that DNA can not protect Nd(III) complex from quenching by $K_4[Fe(CN)_6]$. So the interaction mode between Nd(III) complex and DNA may probably be surface/electrostatic binding. For Pr(III) complex, Sm(III) complex and Dy(III) complex, with increasing $K_4[Fe(CN)_6]$ quencher concentrations, the system of these complexes and complex-DNA causes obvious reduction in the emission intensity, but the emission intensity of complex in the absence of DNA are less than that in the presence of DNA under the same $K_4[Fe(CN)_6]$ quencher concentration, indicating that the complex binds to DNA and is protected from the $K_4[Fe(CN)_6]$ quencher in the presence of DNA..

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REFERENCES

1. Wu, B.Y., Gao, L.H., Duan, Z.M., and Wang, K.Z., J. Inorg. Biochem., **2005**, *99*, 1685.

2. Erkkila, K.E., Odom, D.T., and Barton, J.K., Chem. Rev., **1999**, *99*, 2777.

3. Metcalfe, C. and Thomas, J.A., Chem. Soc. Rev., **2003**, *32*, 215.

4. Arturo S., Giampaolo B., Giuseppe R., Maria L.G. and Salvatore T., *J. Inorg. Biochem.,* **2004**. *98*, 589.

5. Wilhelmsson L. M., Westerlund,F., Lincoln P., and Norden B. , *J. Am. Chem. Soc.,* **2002**, *124*, 12092.

6. Denison C., Kodadek T., *Chem. Biol.* **1998**, *5*, 129.

7 Yang Z. Y., Wang B. D. and Li Y. H, *J. Organomet. Chem.*, **2006**, *691*, 4159.

8. Wang B. D., Yang Z. Y.and Li T. R. *Bioorg. Med. Chem.* **2006**, *14*, 6012.

9. Barton J. K., Science **1986**, *233*, 727.

10 Delaney S., Pascaly M., Bhattacharya P.K., Han K., Barton J. K., *Inorg. Chem*. **2002**, *41*, 1966.

11 Pyle M., Barton J. K., *Prog. Inorg. Chem.* **1990**, *38* 413..

12. Rupesh K.R., Deepalatha S., Krishnaveni M., Venkatesan R., Jayachandran S., Eur. *J. Med. Chem.* **2006**, *41* 1494.

13 Liu F., Zhang W. P., and He S. Y., *Russ. J. Coord. Chem*. **2010**, *36*, 105.

14 Wu W. T., He S. Y., Hu H. M., *et.al. J. Coord. Chem.* **2007**, *60*,125.

15 Wu W. T., He S. Y., Hu H. M., *et.al. Acta Chim. Sinica*, **2005**, 63,.2032.

16 Satyanarayana, S., Dabrowiak, J. C., and Chaires, J. B., *Biochemistry*, **1992**, *31*,9319.

17. Wang, Y. and Yang, Z.Y., *Transition Met. Chem.*, **2005**, *30*, 902.

18. Li, H. B., Wang, X. P., Liu, H. P., *et al*., *Chin. J. Inorg. Chem.,* **2006**, *22*, 9.

19 Geary, W.J. *Coord. Chem. Rev.*, **1971**, *7*, 81.

20 Kazuo, N. Infrared and Raman Spectra of Inorgnic and Coordination Compounds; Huang, D.R., Wang, R.Q., Eds.; Chemical Industry Press: 1986.

21 Deacon, G. B., and Philips, R.J. *Coord. Chem. Rev.*, **1980**, *33*, 227.

22 Gao. S., Shi. Z., Hua J., Feng, S.H.; Xu, R.R.; Liu, S.X.; Huo, L.H.; Chen, P.G. *Chem. J. Chin. Univer*, **2000**, *21*, .177

23Sardar D. K., Bradley W. M., Yow R.M., Gruber J.B., Zandi Z.. *J. Lumin.*, **2004**, *195*, 106.

24 Barton J. K., Raphael A. L., *J. Am. Chem. Soc*. **1984**,*106*,.2172.

25 T. M. Kelly, A.B. Tossi, D.J. McConnell, T.C. Strekas, *Nucleic Acids Res.* **1985**□*13*, 6017.

26 Tysoe S A, Morgan R J, Baker A D, Strekas T C, *J. Phys. Chem*, **1993**, *.97*, 1707.

27 Barton, J. K.; Goldberg, J. M.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc*. **1986**, *.108*, 2081.

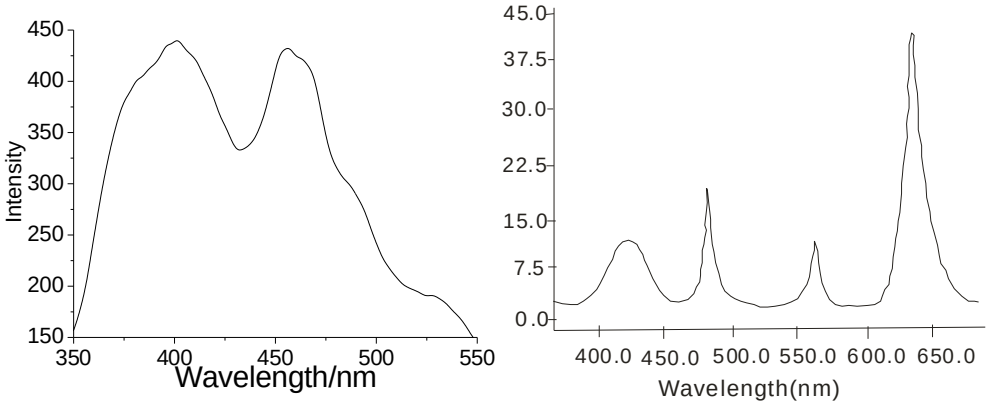


Fig.1 Fluorescence spectra of H_3L (left) and Dy(III) complex (right) in the solid state.

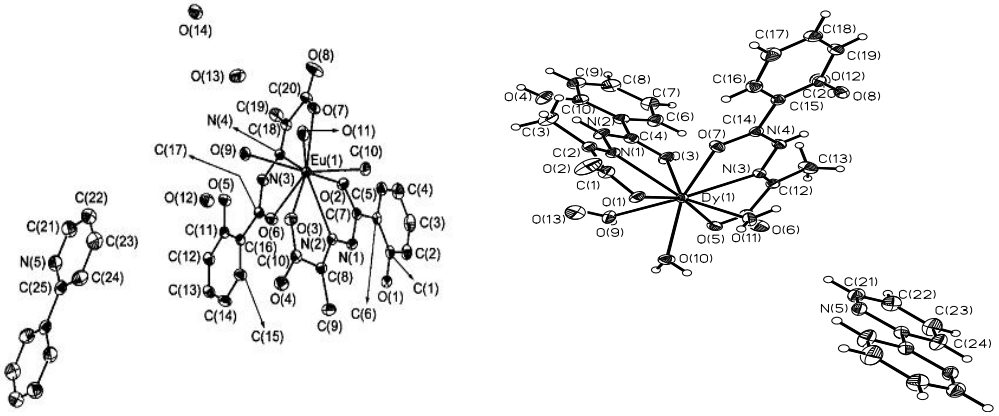
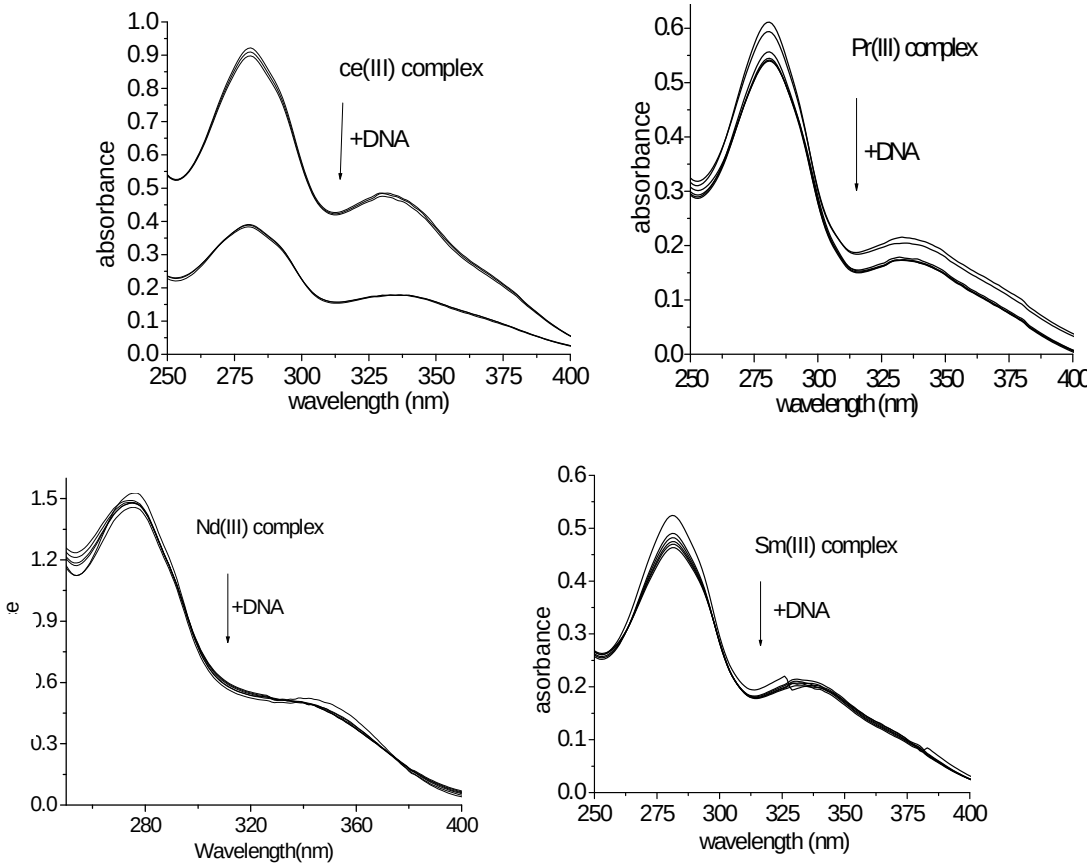


Fig. 2. Perspective view of coordination for Eu(III) complex (left) and Dy(III) complex (right), where H atom are omitted for clarity



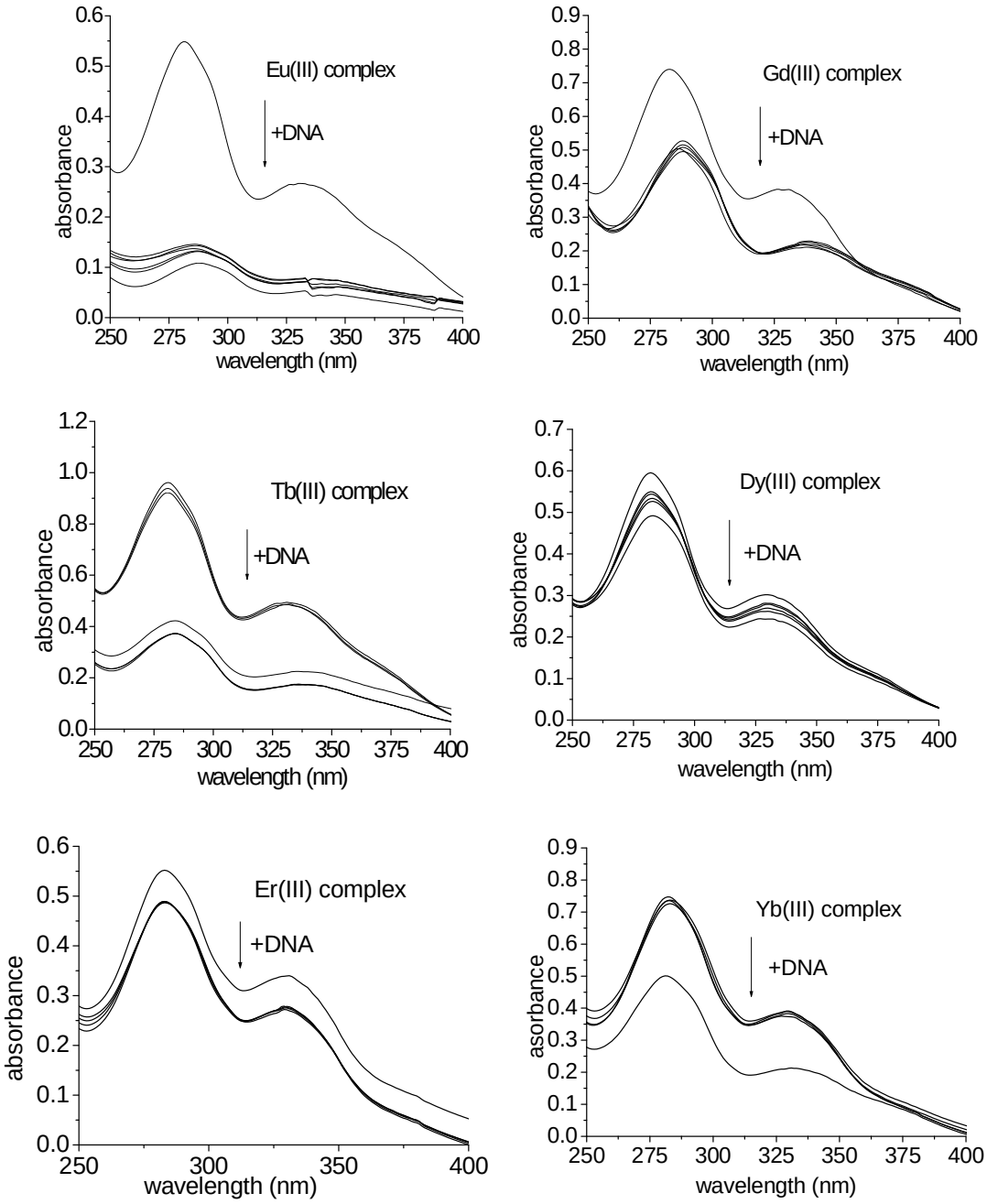
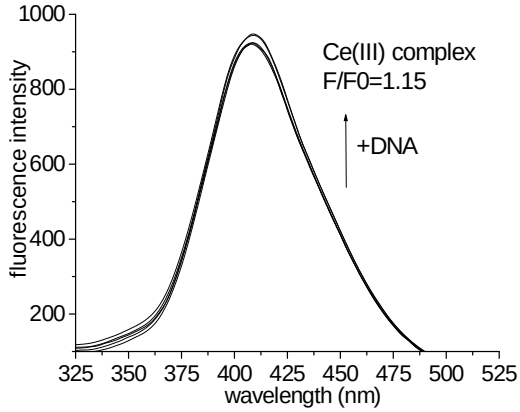
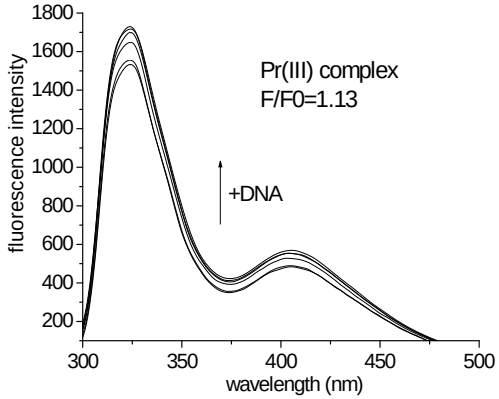
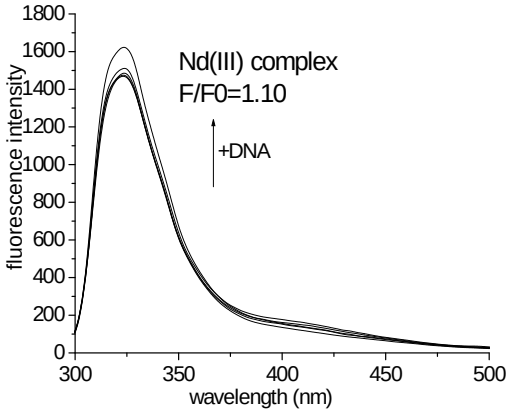
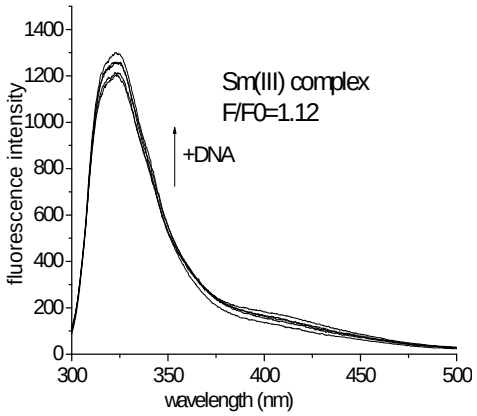


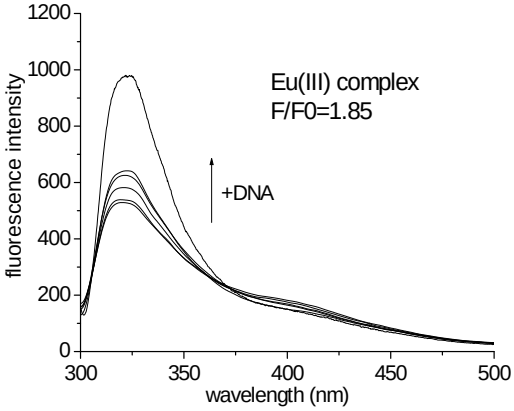
Fig. 3. Electronic spectra of Ln (H_2L) · (HL) · 0.5(bipy)·nH_2O (1.0×10^{-4} mol/L) in the presence of increasing amounts of CT-DNA, [DNA] = 0, 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6} and 50×10^{-6} mol/L.

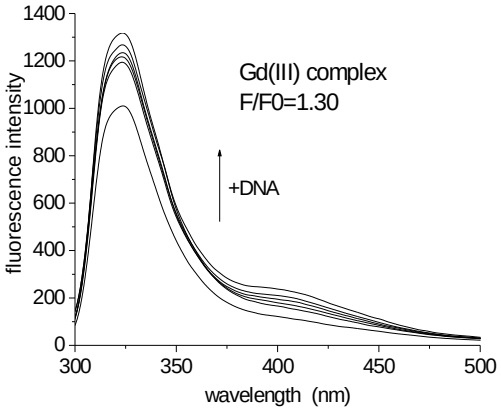












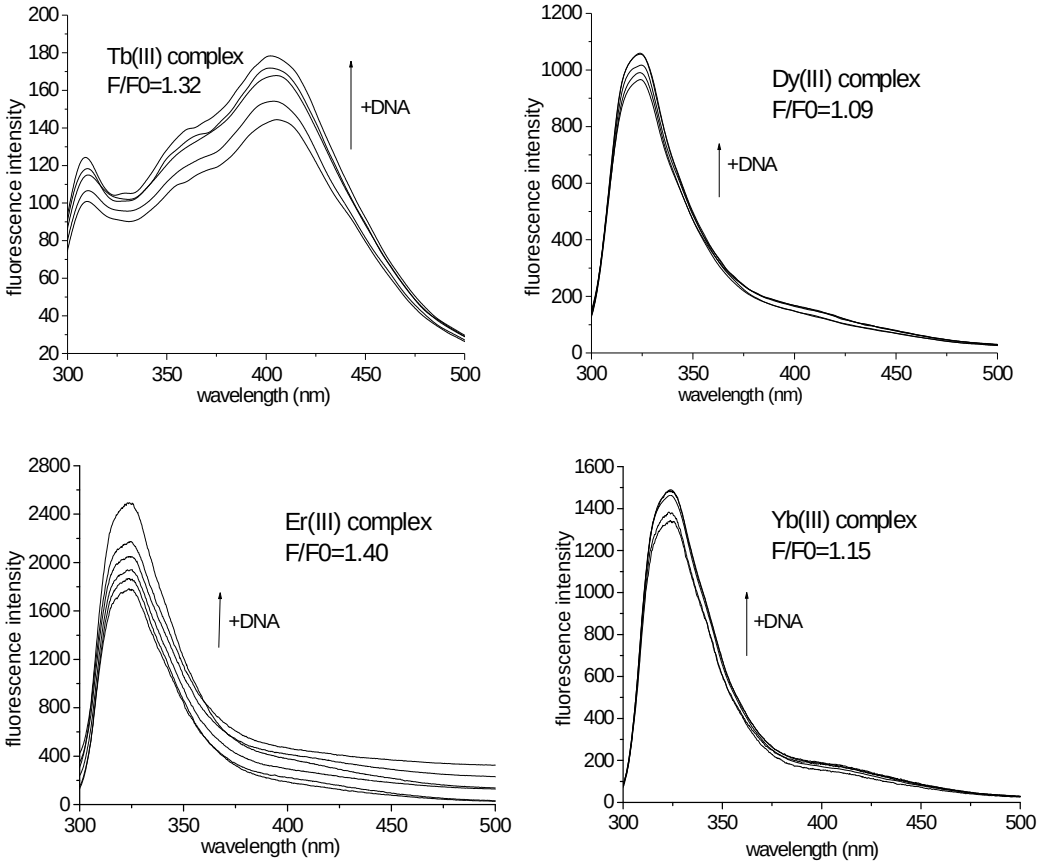
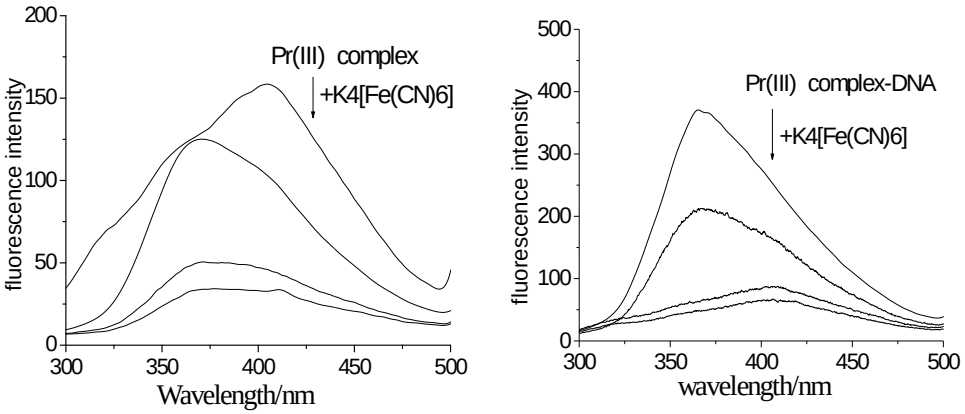


Fig. 4. The emission enhancement spectra of the complexes (1.0×10^{-4} mol/L) in the presence of 0, 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6} and 50×10^{-6} mol/L



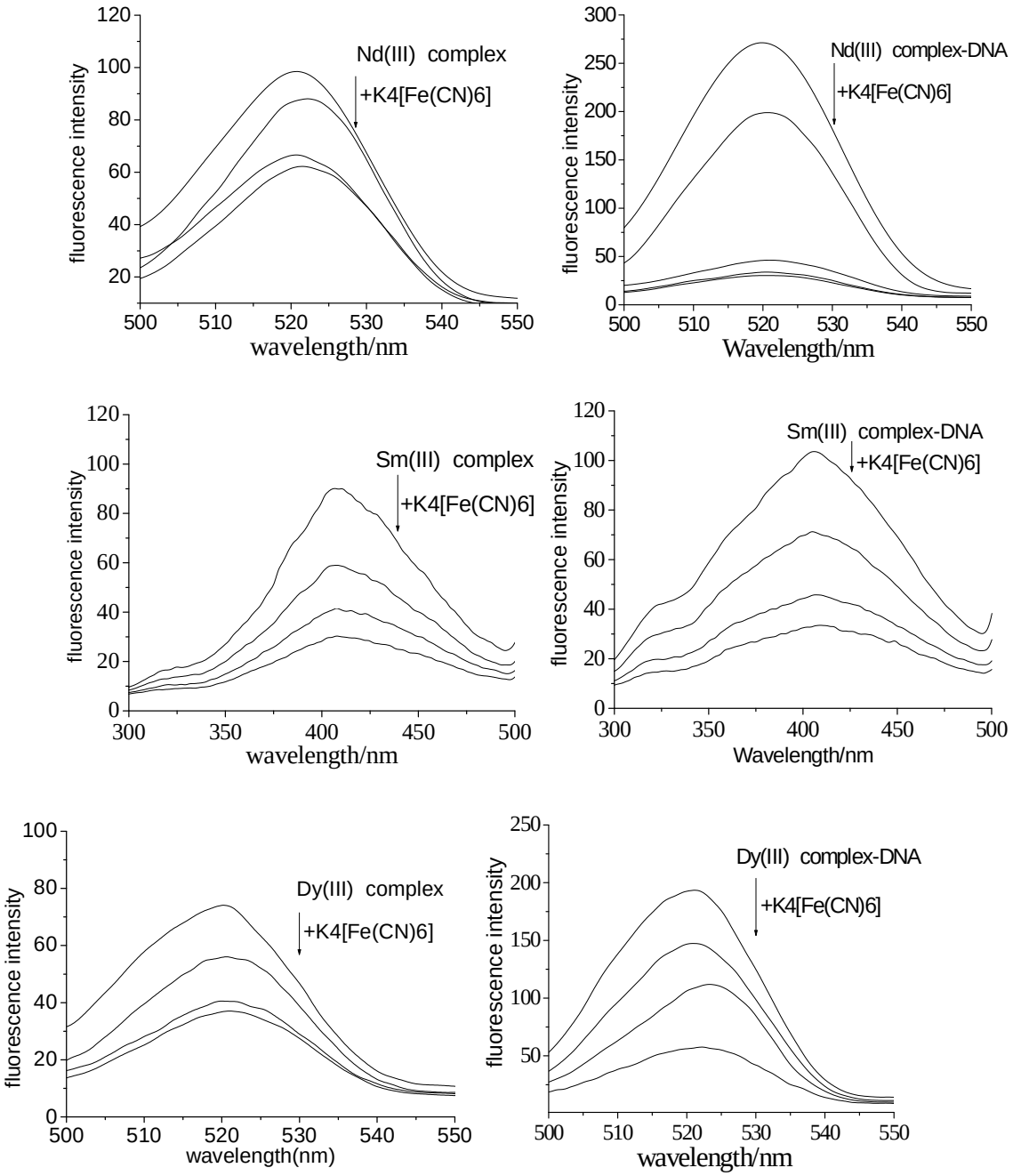


Fig.5. Emission quenching spectra of complexes and complex-DNA (b) with increasing of concentration of the $K_4[Fe(CN)_6]$ quencher. $c_{complex}$= 1.0 × 10^{-4} mol/L, $c_{K4[Fe(CN)6]}$ = 0, 1× 10^{-3}, 2× 10^{-3} and 3× 10^{-3} mol/L, and c_{DNA} = 40 × 10^{-6} mol/L.

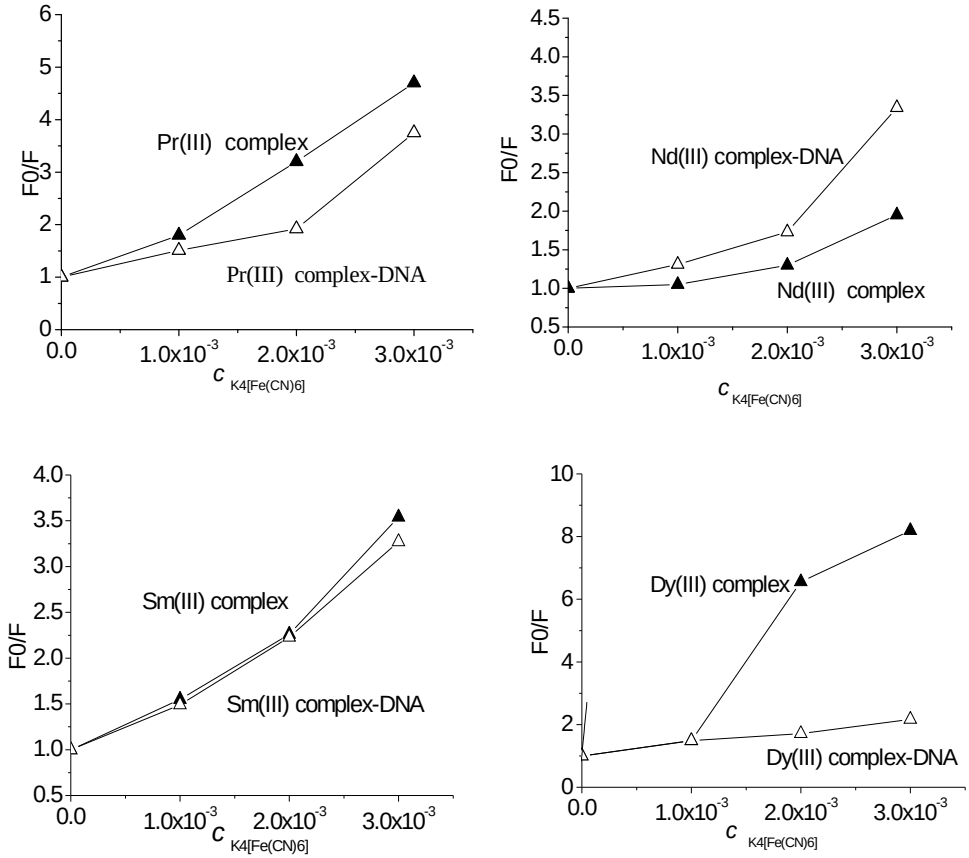


Fig.6. Stern–Volmer plot of complexes for the steady-state emission quenching by $K_4[Fe(CN)_6]$.

Scheme 1.

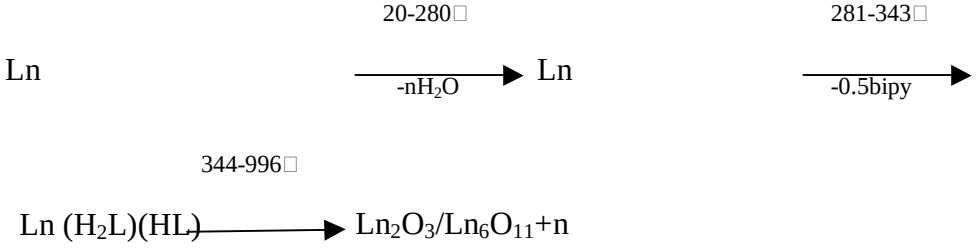


Table 1 Element analysis data and molar conductance for the complexes

complexes	C%	H%	N%	Ln%	$\Lambda_m/\Omega^{-1}\cdot cm^2\cdot mol^{-1}$
$Ce(H_2L)(HL)\cdot 0.5(bipy)\cdot 8$	37.33(37.	4.66(4.	8.55(8.7	17.66(17.	29.34

H_2O	36)	64)	1)	43)	
$Pr(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 4H_2O$	40.95(40. 99)	3.89(3. 99)	10.06(9. 56)	19.53(19. 24)	32.56
$Nd(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 6H_2O$	38.85(38. 91)	3.94(3. 99)	9.59(9.5 6)	19.55(19. 24)	34.29
$Sm(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 6H_2O$	38.41(38. 60)	3.99(4. 28)	9.00(9.0 0)	19.58(l9. 33)	35.67
$Eu(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 6H_2O$	38.45(38. 52)	4.20(4. 27)	8·75(8.9 8)	19.15(19. 49)	37.09
$Gd(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 5H_2O$	39.33(39. 16)	4.27(4. 07)	9.06(9.1 3)	20.33(20. 51)	43.76
$Tb(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 7H_2O$	37.66((37 .32)	4.31(4. 39)	8.52(8.7 1)	20.00(19. 75)	30.59
$Dy(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 5H_2O$	38.90(38. 89)	4.36(4. 05)	9.34(9.0 7)	21.03(21. 05)	36.02
$Er(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 7H_2O$	36.81(36. 94)	4.35(4. 34)	8.62(8.6 2)	20·26(20. 58)	36.47
$Yb(H_2L)(HL)\cdot 0.5$ (bipy)$\cdot 8H_2O$	35.99(35. 89)	4.29(4. 46)	8.37(8.3 7)	20.48(20. 68)	27.49

Table 2 Important Infrared Spectra Data of the Complexes(cm^{-1})

samples	ν_{COOH}	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	$\nu_{C=N}$	$\nu_{C=N}$ (bipy)	ρ_{O-H} (H_2O)	ω_{O-H} (H_2O)	ν_{N-H}
H_3L	1756	—	—	1642	—	—	—	3291
bipy	—	—	—	—	1458	—	—	—
$Ce(H_2L)(HL)\cdot0.5(bipy)\cdot8H_2O$	—	1612	1342	1530	1453	754	579	3235
$Pr(H_2L)(HL)\cdot0.5(bipy)\cdot4H_2O$	—	1616	1357	1531	,1454	765	582	3277
$Nd(H_2L)(HL)\cdot0.5(bipy)\cdot6H_2O$	—	1602	1358	1522	1454	758	581	3268
$Sm(H_2L)(HL)\cdot0.5(bipy)\cdot6H_2O$	—	1600	1341	1538	1456	750	583	3253
$Eu(H_2L)(HL)\cdot0.5(bipy)\cdot6H_2O$	—	1611	1344	1530	1454	761	583	3254
$Gd(H_2L)(HL)\cdot0.5(bipy)\cdot5H_2O$	—	1608	1337	1536	1454	753	585	3284
$Tb(H_2L)(HL)\cdot0.5(bipy)\cdot7H_2O$	—	1598	1338	1526	1455	763	587	3248
$Dy(H_2L)(HL)\cdot0.5(bipy)\cdot5H_2O$	—	1608	1339	1533	1454	742	583	3252
$Er(H_2L)(HL)\cdot0.5$	—	1610	1341	1537	1454	762	586	323

(bipy)·7H_2O								5
Yb(H_2L)(HL)·0.5 (bipy)·8H_2O	—	1610	1341	1536	1453	761	586	324 5

Table 3 Ultraviolet Spectral Data for the Ligand and Complexes

□□	c×10^5(mol·l^{-1})	λ (π-π*) (nm)	
H_3L	9.01	313	273
Ce (H_2L)(HL) ·0.5bipy·8H_2O	1.81	325	302
Pr (H_2L)(HL) ·0.5bipy·4H_2O	2.13	326	301
Nd (H_2L)(HL) ·0.5bipy·6H_2O	1.55	331	284
Sm (H_2L)(HL) ·0.5bipy·6H_2O	1.59	327	289
Eu (H_2L)(HL) ·0.5bipy·6H_2O	1.00	327	287
Gd (H_2L)(HL) ·0.5bipy·5H_2O	1.41	326	288
Tb (H_2L)(HL) ·0.5bipy·7H_2O	1.54	327	302
Dy (H_2L)(HL)	1.65	328	289

·0.5bipy·5H_2O			
Er (H_2L)(HL)	1.80	326	301
·0.5bipy·7H_2O			
Yb (H_2L)(HL)	1.79	329	302
·0.5bipy·8H_2O			

Table 4 Data of X-ray for the ligand, salt, and complex

sample		X-ray powder diffraction data							
$Gd(NO_3)·4H_2O$	I/I_0	100	70	40	40	25	25	25	20
	d/nm	0.792	0.540	0.547	0.260	0.614	0.515	0.387	0.377
H_3L	I/I_0	100	82	73	61	55	46	40	I/I_0
	d/nm	0.3601	0.3286	0.3684	0.5611	0.5764	0.6021	0.4691	d/nm
Gd(III) complex	I/I_0	100	85	67	59	50	40	35	34
	d/nm	1.4430	1.2405	0.5933	0.6146	0.5528	0.5181	0.4721	0.8434

Table 5 Theoretical and experimental mass loss data (%) for the thermal decomposition of the three complexes

sample	fragment	loss%	fragment	loss%	fragment	loss%	residue	residue%
Pr(III) complex	$1H_2O$ $3H_2O$ 30~280 0□	2.92(2.46) 8.03(7.37)	bipy 280~340 0□	11.02 (10.66)	$2C_6H_5O$ + 4CO 340~392□	41.12 (40.68)	Pr_6O_{11} +3C 995.1	27.30 (27.07)

Gd(III) complex	$2H_2O$ $3H_2O$ 30~280□	4.96(4.69) 7.13(7.04)	bipy 280~343□	10.98 (10.18)	$2C_6H_5O$ 343~525□	24.26 (24.26)	□ Gd_2O_3 +C 896.2 □	25.79 (25.17)
Er(III) complex	$4H_2O$ $3H_2O$ 32~228□	8.06(8.86) 7.02(6.64)	bipy 228~342□	9.61 (10.81)	$2C_6H_5O$ 342~545□	22.88 (23.26)	Er_2O_3 +2C 994.5 □	27.03 (26.48)

Table 6 Absorption spectroscopic properties of Ln(III) complexes on binding to CT-DNA

compound	λmax (nm)		Change in absorbance	Red shift (nm)	ΔH(%)
	free	bound			
$Ce(H_2L)(HL)·0.5bipy·8H_2O$	281, 330	281, 330	Hypochromism	1, -3	58, 64
$Pr(H_2L)(HL)·0.5bipy·4H_2O$	280, 331	280, 334	Hypochromism	0, 3	13, 23
$Nd(H_2L)(HL)·0.5bipy·6H_2O$	281, 332	281, 333	Hypochromism	0, 1	5, 0
$Sm(H_2L)(HL)$	281, 325	281, 330	Hypochromism	0, 5	7, 4

·0.5bipy·6H_2O					
Eu(H_2L)(HL) ·0.5bipy·6H_2O	281, 330	285, 335	Hypochromism	4, 5	53, 30
Gd(H_2L)(HL) ·0.5bipy·5H_2O	283, 326	286, 335	Hypochromism	3, 9	33, 47
Tb(H_2L)(HL) ·0.5bipy·7H_2O	281, 331	284, 336	Hypochromism	3, 5	61, 65
Dy(H_2L)(HL) ·0.5bipy·5H_2O	282, 329	283, 326	Hypochromism	1, -3	17, 20
Er (H_2L)(HL) ·0.5bipy·7H_2O	283, 331	283, 329	Hypochromism	0, -2	13, 21
Yb(H_2L)(HL) ·0.5bipy·8H_2O	282, 331	283, 330	Hypochromism	1, -1	35, 48