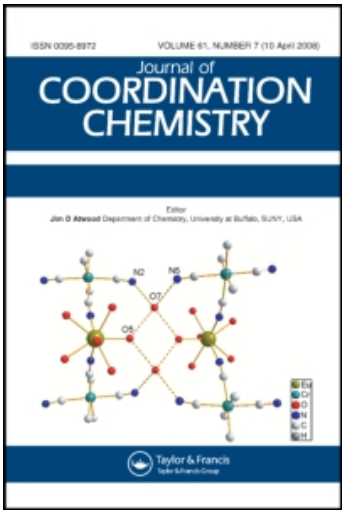

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Synthesis, characterization, and DNA-binding of Ln(III) complexes with 2-hydroxybenzylidene-2-phenylquinoline-4-carbonylhydrazone

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Synthesis, characterization, and DNA-binding of Ln(III) complexes with 2-hydroxybenzylidene-2-phenylquinoline-4-carbonylhydrazone

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2-Hydroxybenzylidene-2-phenylquinoline-4-carbonylhydrazone (H_2L) and five Ln(III) complexes, $[Ln(H_2L)(NO_3)_2]NO_3$ [Ln = La (**1**), Pr (**2**), Sm (**3**), Eu (**4**), and Tb (**5**)], have been synthesized and characterized by ^1H NMR, elemental analysis, conductivity measurements, mass spectra, IR spectra, and UV spectra. The interaction of these complexes with calf thymus DNA was investigated by UV absorption spectroscopy, fluorescence spectroscopy, circular dichroism spectroscopy and viscosity measurements. Results suggest that these complexes bind to DNA via groove binding.

Keywords: 2-Hydroxybenzylidene-2-phenylquinoline-4-carbonylhydrazone; Rare earth complex; DNA binding; Groove binding mode

1. Introduction

Interactions of metal complexes with DNA have been extensively studied as DNA structural probes and DNA-dependent electron transfer probes [1–3]. There are several sites in DNA where binding of metal complexes can occur: (i) between two base pairs (intercalation), (ii) in the minor groove, (iii) in the major groove, and (iv) on the outside of the helix [4]. Numerous biological experiments have demonstrated that DNA is the primary intracellular target of anticancer drugs; interaction between small molecules and DNA can cause damage in cancer cells, blocking the division and resulting in cell death [5–7].

Schiff bases play an important role in bioinorganic chemistry due to their remarkable biological activity. The acid hydrazides R–CO–NH–NH_2 and their corresponding aroylhydrazones R–CO–NH–N = CH–R′, have been examined for their mode of chelation with transition metal ions present in the living systems [8–12]. Coordination compounds of the aroylhydrazones have been reported to act as enzyme inhibitors [13]

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and have significant pharmacological applications [14–16]. 4-Quinolinecarboxylic acid amides and hydrazides, substituted at position 2, exhibit anti-inflammatory and analgesic activity at quite low toxicity [17–21], but no metal complexes of these compounds have been reported. Studies of the metal complexes are important to explore possible new drugs.

To continue our earlier work [22, 23], in the present work, we synthesized and characterized the 2-hydroxybenzylidene-2-phenylquinoline-4-carbonylhydrazone (H_2L) and five rare earth complexes; the DNA-binding properties have been studied to evaluate their pharmaceutical activities.

2. Experimental

All reagents and solvents were purchased commercially and used without purification unless otherwise noted. The Ln(III) nitrates were derived from their oxides (99.9%) acquired from Nong Hua (P.R. China) [24]. Calf thymus DNA (CT-DNA) was obtained from Sigma Chemicals Co. (USA) and was used as received. Solutions of CT-DNA in 50 mM NaCl, 5 mM Tris-HCl (tris(hydroxymethyl)aminomethane hydrochloride) (pH 7.2) gave a ratio of UV-vis absorbance of 1.8–1.9 : 1 at 260 and 280 nm, indicating that the DNA was sufficiently free of protein [25]. The concentration of DNA was determined spectrophotometrically using a molar absorptivity of 6600 $M^{-1}\,cm^{-1}$ (260 nm) [26]. Double-distilled water was used to prepare buffers.

2.1. *Physical measurement*

The melting points of the compounds were determined on a Beijing XT4-100x microscopic melting point apparatus (the thermometer was not corrected). The molar conductance values were determined in methanol on a Shanghai No. 2 Instrument Factory DSS-11A conductivity meter. Carbon, hydrogen, and nitrogen were analyzed on an Elemental Vario EL analyzer. An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for Ln(III) determinations. Infrared spectra (4000–400 cm^{-1}) were determined with KBr disks on a Therrno Mattson FTIR spectrometer. The UV-visible spectra were recorded on a Varian Cary 100 UV-vis spectrophotometer. The fluorescence spectra were recorded on a Hitachi RF-4500 spectrofluorophotometer. ^1H NMR spectra were measured on a Varian VR 300 MHz spectrometer, using TMS as a reference in $CDCl_3$ or DMSO-d_6. Mass spectra were performed on a VG ZAB-HS (FAB) instrument and electrospray mass spectra (ESI-MS) were recorded on a LQC system (Finngan MAT, USA) using CH_3OH as mobile phase.

The CD spectra were recorded on an Olos RSM 1000 at increasing complex/DNA ratio ($r = 0.0, 0.5$). Each sample solution was scanned from 220 to 320 nm. A CD spectrum was generated from the average of three scans from which the buffer background had been subtracted. The concentration of DNA was 1.0×10^{-4} M.

Viscosity experiments were conducted on an Ubbelodhe viscometer, immersed in a thermostated water bath maintained at $25 \pm 0.1^{\circ}C$. Titrations were performed for the complexes (1–10 μM) and each compound was introduced into the CT-DNA

solution (10 μM) present in the viscometer. Data were presented as $(\eta/\eta_0)^{1/3}$ *versus* the ratio of the concentration of the compound to CT-DNA, where η is the viscosity of CT-DNA in the presence of the compound and η_0 is the viscosity of CT-DNA alone. Viscosity values were calculated from the observed flow time of CT-DNA containing solutions corrected from the flow time of buffer alone (t_0), $\eta = t - t_0$ [27].

2.2. *Synthesis of the ligand*

The ligand (figure 1) was prepared according to a literature method [22]. 2-Phenylquinoline-4-carboxylic acid (12.49 g, 50 mmol) was esterified to 2-phenylquinoline-4-carboxylate (yield: 12.86 g (93%)). Treatments of the esters with N_2H_4 gave the corresponding hydrazine (10.98 g, 90%), which was mixed with 2-hydroxybenzaldehyde (5.13 g, 42 mmol) and refluxed for 3 h; H_2L was obtained in 86% yield.

Ester: Yellowish solid, m.p. = 51°C. ^{1}H NMR (300 MHz, $CDCl_3$, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet) δ (ppm): 1.49–1.53 (t, 3H, -CH_3), 4.52–4.59 (q, 4H, –CH_2–), 7.49–7.81 (m, 5H, –Ph), 8.20–8.27 (m, 3H, –quinoline), 8.40 (s, 1H, –quinoline), 8.73–8.76 (d, 1H, –quinoline).

Hydrazine: White solid, m.p. = 222°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 4.73 (s, 2H, –NH_2), 7.58–8.31 (m, 10H, –Ar), 10.04 (s, 1H, –NH–).

H_2L: White solid, ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 6.94 (d, 1H, –2-hydroxyl-Ph–), 6.99 (d, 1H, –2-hydroxyl-Ph–), 7.34 (t, 1H, –2-hydroxyl-Ph), 7.52–7.69 (m, 5H, –quinoline), 7.87 (t, 1H, –2-hydroxyl-Ph), 8.19 (d, 1H, –Ph), 8.27 (d, 1H, –Ph), 8.33–8.42 (m, 3H, –Ph), 8.62 (s, 1H, –CH), 11.08 (s, 1H, –NH–), 12.47 (s, 1H, –OH). IR (KBr) (cm^{-1}): ν_{O-H} 3436, ν_{N-N} 3144, $\nu_{C=O}$ 1676, $\nu_{C=N}$ 1619, $\nu_{C=N-N}$ 1564, δ_{N-H} 1492, ν_{C-N} 1357. UV: λ_{max} (nm): 220, 261, 329. FAB-MS: $m/z = 368$ $[M + H]^+$.

2.3. *Synthesis of the complexes [Ln(H_2L)(NO_3)$_2$]NO_3*

H_2L (0.1837 g, 0.5 mmol) was added to 20 mL acetonitrile and stirred at 80°C. $La(NO_3)_3 \cdot 6H_2O$ (0.2165 g, 0.5 mmol) was added to the suspension; the solution turned red immediately and yellow precipitate formed in a few minutes. The solution was further stirred 3 h and **1** was isolated by filtration, washed by hot acetonitrile and then dried under vacuum. Yield: 36%. (Found: C, 40.02; H, 2.54; N, 12.06; La, 19.89.

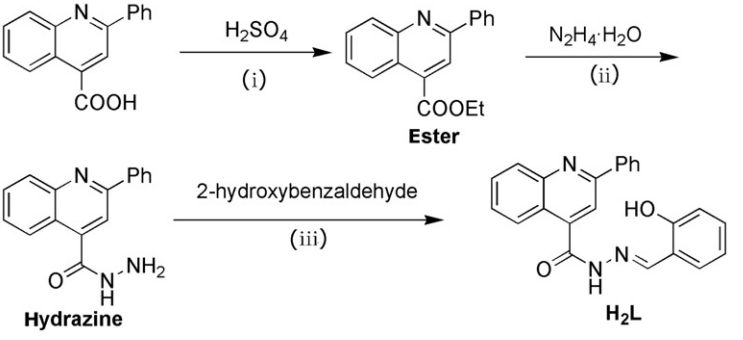

Figure 1. The synthetic route of the ligand. (i) C_2H_5OH, reflux, 20 h; (ii) C_2H_5OH, reflux, 4 h; and (iii) CH_3OH, reflux, 3 h.

Calcd for $LaC_{23}H_{17}N_6O_{11}$: C, 39.90; H, 2.47; N, 12.14; La, 20.06%). IR (KBr) (cm^{-1}): ν_{O-H} 3392, $\nu_{C=O}$ 1614, $\nu_{C=N}$ 1549, ν_{NO_3}: 1474, 1385, 1304, 1155, 862, ν_{Ln-O} 585, ν_{Ln-N} 464. UV: λ_{max} (nm): 205, 254, 342. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 6.90–8.37 (m, 14H, –Ar), 8.60 (s, 1H, –CH–), 11.05 (s, 1H, –NH–), 12.43 (s, 1H, –OH). ES–MS [CH_3OH, m/z]: $\{[La(H_2L)\cdot 2(NO_3)]\cdot NO_3 + H\}^+$ 693.

Compounds **2**–**5** were prepared in a similar way to that of **1** except for $Pr(NO_3)_3\cdot 6H_2O$, $Sm(NO_3)_3\cdot 6H_2O$, $Eu(NO_3)_3\cdot 6H_2O$, and $Tb(NO_3)_3\cdot 6H_2O$ instead of $La(NO_3)_3\cdot 6H_2O$. Yield: 38, 42, 33, and 40%, respectively. (Found: C, 40.08; H, 2.31; N, 12.24; Pr, 20.01. Calcd for $PrC_{23}H_{17}N_6O_{11}$: C, 39.79; H, 2.47; N, 12.10; Pr, 20.29%). (Found: C, 39.31; H, 2.34; N, 11.82; Sm, 21.14. Calcd for $SmC_{23}H_{17}N_6O_{11}$: C, 39.25; H, 2.43; N, 11.94; Sm, 21.36%). (Found: C, 39.08; H, 2.60; N, 11.80; Eu, 21.12 Calcd for $EuC_{23}H_{17}N_6O_{11}$: C, 39.16; H, 2.43; N, 11.91; Eu, 21.54%). (Found: C, 38.82; H, 2.48; N, 11.92; Tb, 22.04. Calcd for $TbC_{23}H_{17}N_6O_{11}$: C, 38.78; H, 2.41; N, 11.80; Tb, 22.31%). The IR, UV spectra, and ^{1}H NMR of these complexes are similar to **1**.

3. Results and discussion

The complexes are stable in atmospheric conditions and soluble in ethanol, methanol, DMF, and DMSO. The Λ_M values of the complexes in methanol are 110, 106, 100, 104, and 102 $Scm^2\,mol^{-1}$, respectively, and in accord with 1 : 1 electrolytes [28]. In the ^{1}H NMR, the –OH of the complex shifts downfield compared to the free ligand due to coordination of the oxygen.

3.1. *IR spectra*

The IR spectra of these complexes are very similar. The ν_{O-H} of the free ligand is at 3436 cm^{-1}, while for **2**, **3**, **4**, and **5** this peak shifted to 3385, 3378, 3384, and 3397 cm^{-1}. The $\nu_{C=O}$ of the free ligand is at 1676 cm^{-1}, while for the complexes this peak shifted to 1614, 1609, 1605, 1606, and 1607 cm^{-1}; ν(ligand–complexes) is equal to 63, 73, 69, 70, and 71 cm^{-1}, respectively. The band at 586 for **1**, **2**, **3**, **4**, and **5** is assigned to ν_{M-O} [29]. These data strongly indicate that oxygen of the carbonyl bonds with the metal ions. The band at 1564 cm^{-1} for the free ligand, assigned to the $\nu_{C=N}$ stretch, shifts to 1548, 1550, 1551, 1550, and 1549 cm^{-1} for **1**, **2**, **3**, **4**, and **5**. Weak bands at 465 cm^{-1} for these complexes are assigned to ν_{M-N} [30]. These observations confirm that nitrogen of the imino bonds to the metal ions. The absorption bands of the coordinated nitrates were observed at 1474 (ν_{as}) and 862 (ν_s) cm^{-1}. The ν_3 (E′) of the free nitrate appears at 1384 cm^{-1} in spectra of the complexes. The separation of the two highest frequency bands $|\nu_4-\nu_1|$ is approximately 170 cm^{-1}, strongly indicating that the coordinated nitrates are bidentate [31].

3.2. *UV spectra*

The electronic spectra in buffer solution of ligand had a strong band at $\lambda_{max} = 220$ nm, a medium band at $\lambda_{max} = 261$ nm, and a weak band at $\lambda_{max} = 329$ nm. The complexes have these bands, but shifted to 206, 254, and 342 nm, indicating complex formation.

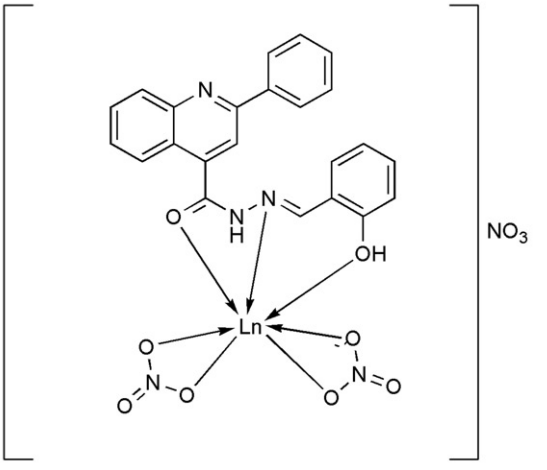

Figure 2. The suggested structure of the complexes. Ln = La, Pr, Sm, Eu, and Tb.

3.3. *Structure of the complexes*

Since the crystal structure of the metal complexes has not been obtained, we characterized the complexes and determined its possible structure by elemental analyses, molar conductivity, mass spectra, IR data, and UV-vis measurements. The likely structure of the complexes is shown in figure 2.

3.4. *DNA-binding studies*

3.4.1. Electronic absorption titration. The application of electronic absorption spectroscopy in DNA-binding studies is very useful [32]. The absorption spectra of **1**–**5** in the absence and presence of CT-DNA (at a constant concentration of complexes) are similar (figures 3 for **4**). In the presence of DNA, the absorption bands of these complexes at 206 nm exhibit hypochromism of about 42.0, 69.4, 56.2, 50.3, and 50.6% and bathochromism of about 0, 5, 5, 4, and 5 nm, respectively. The spectroscopic changes suggest that the complexes have strong interaction with DNA.

In order to compare quantitatively the binding affinity of the five complexes, the intrinsic binding constants K_b of the five complexes with DNA were obtained by monitoring the changes in absorbance at 220 nm with increasing concentration of DNA using the following equation [33]:

$$[\mathrm{DNA}]/(\varepsilon_a - \varepsilon_f) = [\mathrm{DNA}]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f),$$

where [DNA] is the concentration of DNA in base pairs and the apparent absorption coefficient ε_a, ε_f, and ε_b correspond to $A_{obsd}/[M]$, the extinction coefficient of the free compound and the extinction coefficient of the compound when fully bound to DNA, respectively. In plots of $[\mathrm{DNA}]/(\varepsilon_a - \varepsilon_f)$ *versus* [DNA], K_b is given by the ratio of slope to the intercept. The intrinsic binding constants K_b of the complexes were 0.52×10^5, 3.92×10^5, 4.84×10^5, 3.86×10^5, and $1.12 \times 10^6\ \mathrm{M}^{-1}$, respectively. The results indicate

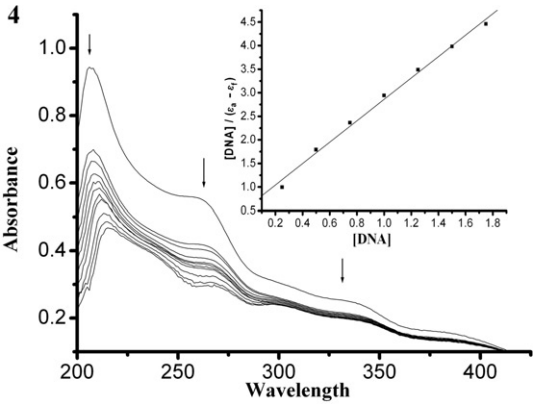

Figure 3. Absorption spectra of **4** in Tris-HCl buffer upon addition of calf-thymus DNA. [complex] = 1×10^{-5} M, [DNA] = (0–5) $\times 10^{-5}$ M. The arrow shows the absorbance change upon increasing DNA concentrations. Inset: plots of [DNA]/($\varepsilon_a - \varepsilon_f$) *vs.* [DNA] for the titration of DNA with the complex.

that the binding strength of the complexes follow the order: **5** > **3** > **2** > **4** > **1**. Such a small change in λ_{max} is more in keeping with groove binding, leading to small perturbations. The K_b value obtained here is lower than that reported for classical intercalators (for ethidium bromide and [Ru(phen)DPPZ] whose binding constants have been found to be in the order of 10^6–10^7 M) [34, 35]. The observed binding constant is in accord with groove binding with DNA as observed in the literature [36].

3.4.2. CD spectral studies. Circular dichroic spectral techniques give information on how the conformation of DNA is influenced by binding with the metal complex. The observed CD spectrum of calf thymus DNA exhibit a positive band at 277 nm due to base stacking and a negative band at 245 nm due to helicity, characteristic of DNA in the right-handed B form. While intercalation interaction with DNA enhances the intensities on the base stacking and helicity, stabilizing the right-handed B conformation of CT-DNA, groove binding and electrostatic interactions show little or no perturbations of the bands. The CD spectra of DNA obtained after incubation of the complexes with CT DNA are shown in figure 4. In all five cases, the intensities of both the negative and positive bands decrease significantly. This suggests that the DNA-binding of the complexes induces conformational changes, such as conversion from a more B-like to a more C-like structure within the DNA [37]. These changes are indicative of a nonintercalative mode of binding of these complexes and support their groove binding nature [38].

3.4.3. Fluorescence studies. These complexes emit fluorescence in Tris buffer at ambient temperature, with a maximum appearing at 396 nm for **1**, 397 nm for **2**, 401 nm for **3**, 409 nm for **4**, and 405 nm for **5**. Fluorescence quenchings of theses complexes are similar. As shown in figure 5 (e.g. **3**), the fluorescence intensities are quenched steadily with increasing concentration of CT-DNA. The Stern–Volmer quenching plot from the fluorescence titration data is shown in figure 6. The fluorescence quenching constant (K_{sv}) evaluated using the Stern–Volmer equation is 2.09×10^4, 5.08×10^4, 4.87×10^4,

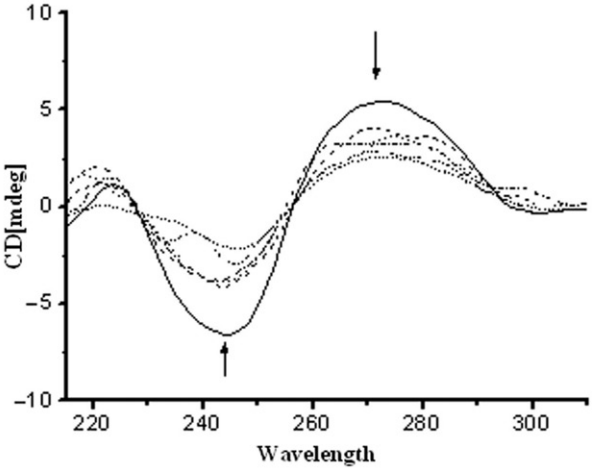

Figure 4. CD spectra of CT-DNA (100 mM) in the absence (Solid line) and presence of **1** (Dash line), **2** (Dot line), **3** (Dash Dot line), **4** (Dash Dot Dot line), and **5** (Short Dash line) (50 mM).

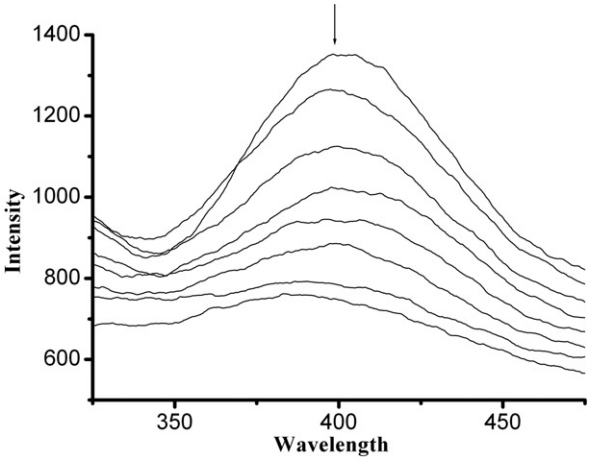

Figure 5. Emission spectra of **3** in Tris-HCl buffer upon addition of calf-thymus DNA. [complex] = 1×10^{-5} M, [DNA] = $(0–5) \times 10^{-5}$ M. The arrow shows the intensity change upon increasing DNA concentrations.

3.18×10^4, and $2.62 \times 10^4\,M^{-1}$. The Stern–Volmer plot is linear, indicating that only one type of quenching process occurs.

The quenching of luminescence of the complex by DNA may be attributed to photoelectron transfer from the guanine base of DNA to the excited MLCT state of the complex [33, 36, 39–43].

3.4.4. Viscometric titration. Hydrodynamic methods that are sensitive to length are regarded as one of the least ambiguous and most critical tests of a binding mode in solution in the absence of crystallographic structural data. Intercalating agents are

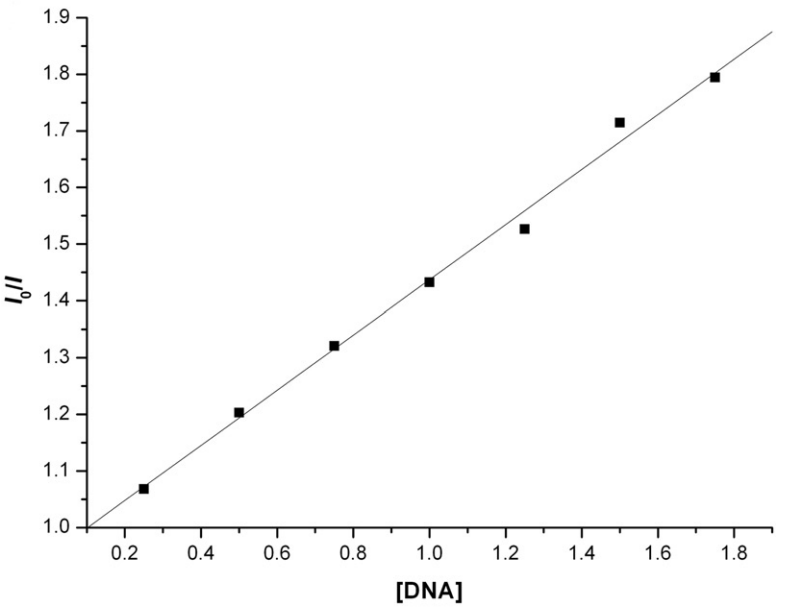

Figure 6. A Stern–Volmer quenching plot of **3** with increasing concentrations of CT-DNA. Other conditions as in figure 5.

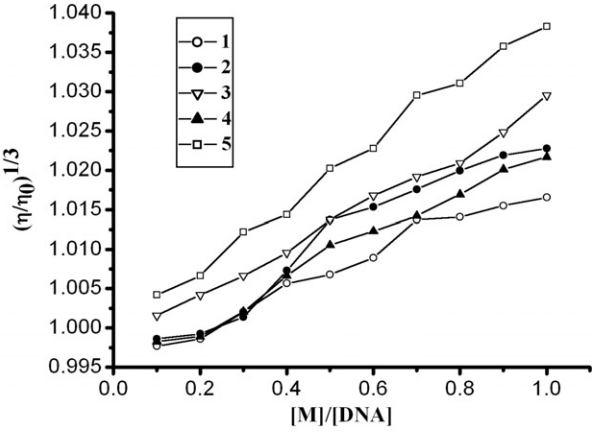

Figure 7. Effect of increasing amounts of the rare earth complex on the relative viscosity of calf thymus DNA at 25.0°C.

expected to elongate the double helix to accommodate the ligands, leading to viscosity increase; under the same conditions, complexes that bind exclusively in the DNA grooves by partial and/or nonclassical intercalation typically cause less obvious or no change in DNA solution viscosity [44]. The values of $(\eta/\eta_0)^{1/3}$ were plotted against [complex]/[DNA] (figure 7). The results reveal that these complexes affect small increase in DNA viscosity, which is consistent with DNA groove binding [45]. The increased degree of viscosity, which may depend on its affinity to DNA, follows the order of **5** > **3** > **2** > **4** > **1**, consistent with our binding constants.

4. Conclusion

Five rare earth complexes have been synthesized and characterized. The DNA-binding properties of these complexes were examined by absorption, fluorescence and CD spectra, and viscosity measurements. Results indicate that the complexes bond to CT-DNA by groove binding, with binding affinity in the order **5** > **3** > **2** > **4** > **1**.

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