A dysprosium-based metal-organic framework: Synthesis, characterization, crystal structure and interaction with calf thymus-DNA and bovine serum albumin

BIPLAB MONDAL^a, BUDDHADEB SEN^a, ENNIO ZANGRANDO^b and
PABITRA CHATTOPADHYAY^{a,*}

^aDepartment of Chemistry, Burdwan University, Golapbag, Burdwan 713104, India

^bDepartment of Chemical and Pharmaceutical Sciences, Via Licio Giorgieri 1, 34127 Trieste, Italy
e-mail: pabitracc@yahoo.com

MS received 9 November 2013; revised 6 February 2014; accepted 16 February 2014

Abstract. A dysprosium-based metallo-organic framework (MOF) containing calcium ions formulated as $\{Dy(pyda)_3Ca_{1.5}(H_2O)_6\} \cdot 5.5H_2O$ (**1**) (H_2pyda = pyridine-2,6-dicarboxylic acid) was solvothermally synthesized in ethanolic medium and characterized by physico-chemical and spectroscopic tools. A detailed structural analysis of the solid state structure of **1** by single crystal X-ray diffraction study showed a tricapped trigonal prism geometry for lanthanide in the $[Dy(pyda)_3]^{3-}$ fragment. The mode of interaction of **1** with calf thymus-DNA and with protein bovine serum albumin (BSA) was investigated by using absorption and emission spectroscopic tools. The apparent association constant of complex **1** with CT-DNA was deduced from an absorption spectral study ($K_b = 4.08 \times 10^4 M^{-1}$). Spectral and viscosity measurements indicated a groove-binding mode of **1** with CT-DNA, and from spectroscopic study the formation of a metal complex-BSA adduct was assumed to be the result of the interaction of **1** with BSA.

Keywords. Metallorganic framework (MOF); dysprosium complex; crystal structure; DNA binding; BSA binding.

1. Introduction

The current revolutionary increase in the number of synthesized and structurally characterized metal-organic coordination frameworks (MOFs) reflects the demand for new materials with predesigned functionalities.^{1–3} Structures of polymeric networks and their properties are largely determined by a suitable combination of metal ions and polydentate organic linkers. The correct choice of building blocks together with a proper synthetic strategy can lead to networks of different branching, topologies and dimensionality.^{4–6} By virtue of the unique properties originating from their 4f electron configurations,^{7–10} lanthanides are often utilized as MOFs nodes because of their propensity to high coordination numbers and inherent luminescence, which are essential for the formation of unusual network topologies and luminescent material, respectively.^{11–13} Usually lanthanide ions have high affinity for hard donor atoms such as oxygen and chelating ligands containing oxygen–nitrogen donors. There-

fore, such ligands are good sensitizers for lanthanide ions in the construction of lanthanide-based MOFs.

Taking into account the above facts and as part of our continuous interest in the interaction of metal complexes with calf thymus-DNA (CT-DNA),^{14–18} herein we report the synthesis, structural characterization of a newly designed complex, $\{Dy(pyda)_3Ca_{1.5}(H_2O)_6\} \cdot 5.5H_2O$ (**1**) (where H_2pyda = pyridine-2,6-dicarboxylic acid, scheme 1), which was duly characterized by physico-chemical and spectroscopic tools along with its detailed structure using single crystal X-ray crystallography. The study of the interaction of complex **1** with CT-DNA and with bovine serum albumin (BSA) was performed. The interaction with CT-DNA was investigated with the help of absorption and emission spectroscopic tools. In order to establish the association mode of this molecule to DNA, the binding (K_b) and the quenching constant (K_q) of the complex with the double-helix have been determined from UV-Vis study and fluorescence displacement experiments using ethidium bromide as spectral probe. On the other hand, the strong binding propensity of **1** to interact with BSA was examined using absorption-fluorescence spectroscopy, which allowed to detect the fluorescence quenching of

*For correspondence

Pyridine-2,6-dicarboxylic acid

Scheme 1. Schematic structural representation of pyridine-2,6-dicarboxylic acid (H₂pydca).

BSA by complex **1** due to the formation of a metal complex-BSA species.

2. Experimental

2.1 Materials and physical measurements

Chemicals and reagents used for the synthesis were obtained from commercial sources. Solvents were distilled before use and treated with an appropriate drying agent. Elemental (C, H, N) analyses were performed on a Perkin Elmer–model 2400 elemental analyser. IR spectrum of **1** was recorded on a Perkin–Elmer FTIR model RX1 spectrometer (KBr disc, 4000–300 cm^{−1}). Room temperature magnetic susceptibility was recorded by using a vibrating sample magnetometer PAR 155 model. Thermo-gravimetric analysis (TGA) was performed on a Perkin–Elmer Diamond TG/DTA analyser. Electronic absorption spectra were recorded on a JASCO UV-Vis/NIR spectrophotometer model V-570. Fluorescence spectra complex bound to DNA were obtained at an excitation wavelength of 522 nm with Hitachi-4500 fluorimeter.

2.2 Synthesis of complex **1**

Solvothermal process was carried out to synthesize this complex as it follows. The organic moiety, pyridine-2,6-dicarboxylic acid (H₂pydca, 501 mg, 3.0 mmol) was dissolved in dry ethanol by stirring the mixture for 15 min. A volume of 1.0 mmol of Dy(NO₃)₃·6H₂O (456 mg) was dissolved in a minimum quantity of water and this aqueous solution was added dropwise to the ethanolic H₂pydca solution under stirring condition. Then, the resulting solution mixture was refluxed for 2 h and calcium chloride (CaCl₂·2H₂O, 147 mg, 1.0 mmol) was added under stirring condition. The mixture was kept in teflon reaction chamber for 32 h at a temperature of 130°C and filtered off for collecting clear filtrate. This filtrate was kept aside for slow

evaporation at room temperature. After a few days, a fine microcrystalline compound was separated out and washed thoroughly with water, ethanol and dried *in vacuo* over silica gel desiccator. Single crystals of **1** suitable for X-ray diffraction study were also obtained by slow evaporation of this solution. The dried material was used also for elemental analysis and characterization using physico-chemical and spectroscopic tools.

{[Dy(pyda)₃Ca_{1.5}(H₂O)₆]}·5.5H₂O: Yield: 70% (0.6391 g); C₂₁H₃₂Ca_{1.50}DyN₃O_{22.50}: Anal. Found: C, 27.74; H, 3.55; N, 4.62; Calc.: C, 27.58; H, 3.14; N, 4.60. IR: the 3252 cm^{−1} band was assigned as characteristic peak of water OH bond, ν_{C=N} 1471, ν_{asCOO} 1608, ν_{C=O} 1565 cm^{−1}. Magnetic moment (μ, B.M.): 10.64.

2.3 X-ray crystal structure analysis

Diffraction data for structural characterization of **1** were collected at room temperature (293(2) K) on a Bruker Kappa CCD imaging plate mounted on a Nonius FR591 rotating anode (Cu-Kα radiation, λ = 1.54180 Å). Cell refinement, indexing and scaling of the data set were carried out using Denzo and Scalepack.¹⁹ The structure was solved by Patterson and Fourier analyses²⁰ and refined by the full-matrix least-squares method based on *F*² with all observed reflections.²⁰ Based on Fourier peaks, occupancy of one lattice water molecule was fixed at 0.5, H atoms of all water molecules were not assigned. All the calculations were performed using the WinGX System, Ver 1.80.05.²¹ Crystal data and details of data collection and refinement for **1** are summarized in table 1.

2.4 DNA binding experiments

Tris-HCl buffer solution (pH 7.2) used in all the experiments involving CT-DNA was prepared using deionized and sonicated HPLC grade water (Merck). The CT-DNA used in the experiments was checked to be sufficiently free from protein as the ratio of UV absorbance of DNA solution in Tris-HCl at 260 and 280 nm (A₂₆₀/A₂₈₀) was around 1.9.²² Concentration of DNA was estimated by using the extinction coefficient (6600 M^{−1} cm^{−1}) at 261 nm²³ and stock solution of DNA was always stored at 4°C. Stock solution of the complex was prepared by dissolving it in 2 mL of DMSO and diluted with Tris-HCl buffer to get the required concentration for all the experiments. Absorption spectral titration experiment was performed by maintaining constant the complex concentration and varying the CT-DNA concentration. To eliminate the

Table 1. Crystal data and details of refinement for compound **1**.

Empirical Formula	C ₂₁ H ₃₂ Ca _{1.50} DyN ₃ O _{22.50}
Formula Weight	909.12
Crystal System	Monoclinic
Space group	<i>P</i> 2/c
<i>a</i> (Å)	16.231(3)
<i>b</i> (Å)	9.431(3)
<i>c</i> (Å)	24.107(3)
β (deg)	108.22(3)
Volume (Å ³)	3505.2(14)
Radiation type	Cu-K α
Wavelength (Å)	1.5418
Measurement temperature	293(2)
<i>Z</i>	4
ρ_{calc} (g/cm ³)	1.723
<i>F</i> (000)	1820
θ range (deg)	4.03–65.45
Goodness-of-fit	1.006
Data/restraints/parameters	5642/0/445
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> < 2 σ (<i>I</i>)]	0.0620, 0.1777
<i>R</i> indices (all data)	0.0828, 0.1888
Residuals e.Å ^{−3}	2.228, ^a −1.448

^aat 1.96 Å from O8w, likely a fraction of disordered water molecule

absorbance of DNA itself, equal amount of CT-DNA was added to the reference solution.

In the ethidium bromide (EB) fluorescence displacement experiment, 5.0 μ L of the EB Tris-HCl solution (1.0 mmol L^{−1}) was added to 1.0 mL of DNA solution (at saturated binding levels),²⁴ stored in the dark for 2.0 h. Then, the solution of complex **1** was titrated into the DNA/EB mixture and diluted with Tris-HCl buffer to 5.0 mL to get the solution with the appropriate complex/CT-DNA mole ratio. Before taking measurements, the mixture was shaken up and incubated at room temperature for 30 min. Fluorescence spectra of EB bound to DNA were obtained in the fluorimeter with λ_{ex} of 522 nm.

To adjudge the binding mode (groove/intercalative) of **1** with DNA, viscosity measurement method was used by employing Ostwald's viscometer. Titrations were carried out in the viscometer by adding complex **1** (0.5–3.5 μ M) to the CT-DNA solution (5.0 μ M). Viscosity values of the solutions were calculated from the observed flow time of CT-DNA-containing solution corrected from the flow time of buffer alone (*t*₀), $\eta = t - t_0$. The obtained data were used to plot the $(\eta/\eta_0)^{1/3}$ versus the ratio of the concentration of **1** and CT-DNA, where η is the viscosity of the CT-DNA solution in presence of **1** and η_0 is the viscosity of the CT-DNA solution only.

2.5 Protein (bovine serum albumin) binding experiments

A similar experiment was performed with BSA, the only difference being the concentration of BSA that was kept constant throughout the experiment. Figure 11 shows the gradual increase of absorbance with increasing concentration of complex **1**. In order to confirm that the observed absorption change in the spectrum was not due to experimental errors, a baseline correction was performed for all the measurements. The results clearly indicate an interaction between complex **1** and BSA.

Fluorescence quenching study of BSA was carried out in similar fashion keeping fixed the concentration of BSA in solution while increasing the concentration of complex **1**. Baseline correction was carried out for all the measurements to get rid of probable scattering effects due to the suspended nature of complex **1** in aqueous medium. This ensures that fluorescence quenching occurs only for the interaction between BSA and complex **1**.

3. Result and discussion

3.1 Synthesis and characterization

The title compound **1** was synthesized and isolated through solvothermal process by using dysprosium nitrate hexahydrate, pyridine-2,6-dicarboxylic acid (H₂pydca) and calcium chloride in a molar ratio of 1:3:1, respectively in a teflon reaction vessel at a temperature of 130°C. Micro-analytical data confirm the composition of the complex. Paramagnetic nature of compound **1** was established by its magnetic moment μ that was measured to be 10.45 B.M. at room temperature.

3.2 Structural analysis of **1**

The X-ray structural analysis of **1** revealed that the independent unit comprises a [Dy(pyda)₃]^{3−} moiety, three calcium(II) ions located at special crystallographic positions (see below), and 11.5 water molecules, of which 5.5 are lattice species. The ORTEP diagram of the lanthanide complex (figure 1) shows that the Dy³⁺ ion is nine-coordinated by three pyridine-2,6-dicarboxylates anions, where Dy–O bond lengths range from 2.397(5) to 2.438(5) Å, while the Dy–N distances are slightly longer (2.469(7)–2.496(6) Å). A selection of bond distances is reported in

Figure 1. ORTEP diagram (35% probability ellipsoid) of the $[\text{Dy}(\text{pyda})_3]^{3-}$ anionic moiety with atom label scheme.

table 2. This tricapped trigonal prism geometry and the relative coordination distances are similar to those found for dysprosium ion in $[\text{Dy}_2(\text{pyda})_3(\text{H}_2\text{O})_4]_n$ ²⁵ and $(\text{ImH})_3[\text{Dy}(\text{pyda})_3]$ ²⁶ (imH = imidazolium ion) frameworks.

Of calcium ions, Ca(1) is located on a two-fold axis and is eight-coordinated by four water molecules and four oxygen donors from different pyda ligands, resulting in a square antiprismatic geometry (figure 2). On the other hand, Ca(2) and Ca(3) ions are located on an inversion centre and both are six-coordinated by four water molecules and two oxygen donors from *pyda* ligands in *trans* position so that they assume, octahedral geometry (figure 3). It is noteworthy that Ca(1)-O bond distances are 0.1–0.2 Å longer than the Ca(2)-O and

Figure 2. Coordination geometry of calcium ion Ca(1); symmetry codes (i) $-x, y, -z+1/2$; (ii) $-x, y-1, -z+1/2$; (iii) $x, y-1, z$.

Ca(3)-O ones due to larger coordination number for Ca(1). Moreover, for each independent calcium ion, Ca-OH₂ bond distances appear slightly longer than the Ca-O(carboxylate) ones (table 2), likely due to hydrogen bonds involving the aqua ligands, although H atoms of water molecules cannot be located on the Fourier map.

The described coordinative interactions give rise to a 3D porous framework. The crystal packing evidences the lanthanide $[\text{Dy}(\text{pyda})_3]^{3-}$ complexes (located on *ac* plane) that sandwich the calcium ions and water molecules (figure 4). Thus, calcium ions are trapped between the lanthanide moieties completing their coordination sphere with water molecules. The crystal packing viewed down axis-*b* (figure 5) shows the formation of a 3D framework of 48-atom rings comprising six $[\text{Dy}(\text{pyda})_3]^{3-}$ units and six hydrated Ca ions. The channels are filled by lattice water molecules and correspond to a void volume of 884.7 Å³, (ca. 25% of the unit cell), as calculated by program Platon²⁶ by removing the solvent molecules. The present architecture is isostructural to that of the Tb derivative reported few years ago;²⁷ although in the present case, based on the Fourier peak height, a half occupancy was assigned to a lattice molecule.

Table 2. Coordination bond distances (Å) of **1**^a.

Dy-O(1)	2.438(5)	Dy-O(11)	2.408(5)
Dy-O(3)	2.409(5)	Dy-N(1)	2.488(7)
Dy-O(5)	2.401(5)	Dy-N(2)	2.469(7)
Dy-O(9)	2.397(5)	Dy-N(3)	2.496(6)
Dy-O(7)	2.419(5)		
Ca(1)-O(6')	2.446(5)	Ca(2)-O(3w)	2.323(8)
Ca(1)-O(10)	2.410(5)	Ca(2)-O(4w)	2.323(5)
Ca(1)-O(1w)	2.514(5)	Ca(3)-O(12)	2.266(5)
Ca(1)-O(2w)	2.459(5)	Ca(3)-O(5w)	2.321(5)
Ca(2)-O(4)	2.299(5)	Ca(3)-O(6w)	2.373(6)

^a Only crystallographic independent values reported. Symmetry code for O(6') = $-x, y-1, -z+1/2$

Figure 3. Coordination geometry of calcium ions Ca(2) and Ca(3); symmetry codes (i) are $-x+1, -y+1, -z+1$; and $-x, -y+1, -z+1$, respectively.

3.3 Thermal analysis of **1**

Thermogravimetric analysis of the complex indicates that the guest and coordinated water molecules are removed in the range from room temperature to 430.37°C as shown in figure S1. Weight loss of 21.03% is only slightly smaller than the theoretical value (21.67 %), corresponding to the displacement of 11 water molecules. Then, the sample begins to rapidly decompose resulting in Dy₂O₃ as final product (table 3).

3.4 Spectral properties

Electronic spectrum of complex **1** recorded in DMF solution showed two absorption bands at 270 (sh) and

319 nm (br) (figure 6). Photoluminescent properties of the Dy³⁺ complex were investigated at room temperature (figure 7). Emission spectra of the complex display good photoluminescence exhibiting two narrow, sharp and well-separated emission bands. Excitation spectra of the complex reveal that the effective energy absorption occurred in the ultraviolet region (270–350 nm). Emission spectrum exhibits two intense emission bands at 479 and 573 nm under excitation wavelength of 321 nm. Dysprosium(III) ion usually shows several emission bands around 480 and 571 nm, which are generally originated from $^4F_{9/2} \rightarrow ^6H_J$ transitions.^{28–30} Therefore, the two intense emission bands at *ca.* 479 and 573 nm can be attributable to these transitions ($J = 13/2$ and $15/2$). This implies that effective energy

Figure 4. Packing viewed down axis *a*. Lattice water molecules not shown.

Figure 5. 3D framework viewed down axis *b* with lattice water molecules (indicated by large spheres).

transfer occurs and the conjugated system between the pyridine-2,6-dicarboxylate and Dy^{3+} metal ion was formed.

3.5 DNA binding experiments

Binding phenomenon of metal complexes with DNA was investigated by electronic absorption spectral technique. Thus, absorption and emission spectra were applied to investigate the interaction of complex **1** with calf thymus DNA (CT-DNA). In general, an intercalative interaction of the aromatic chromophore of the complex and the base pairs of DNA helix is reflected by hypochromism and red shift of charge transfer band.³¹ Absorption spectra of complex **1** in the absence and presence of CT-DNA (depicted in figure 8) showed a significant hyperchromism in the charge transfer band at 261 nm, which suggests that there is a strong non-intercalative interaction. Spectral changes of complex **1** observed in the presence of CT-DNA can be exemplified in terms of groove binding.²² It is reported that aromatic ring of the molecule closely matches with the helical turn of the CT-DNA groove and the aromatic ring of ligand interacts with DNA in Tris-HCl buffer through the formation of vander Waal's contacts or hydrogen bonds in DNA grooves.

Binding strength in addition to the type of binding of complex **1** with CT-DNA were examined by evaluating

Figure 6. UV spectra of complex **1** in DMF solution with λ_{max} at 270 nm ($\log \epsilon = 4.20$) and 319 nm ($\log \epsilon = 3.54$).

the apparent association constant, K_b from the spectral titration data using the following equation:³¹

$$\frac{[\text{DNA}]}{(\epsilon_a - \epsilon_f)} = \frac{[\text{DNA}]}{(\epsilon_b - \epsilon_f)} + \frac{1}{[K_b (\epsilon_b - \epsilon_f)]}, \quad (1)$$

where [DNA] is the concentration of DNA, ϵ_f , ϵ_a and ϵ_b correspond to the extinction coefficient for the free complex **1**, for each addition of DNA to the complex **1** and for complex **1** in the fully bound form, respectively. The apparent association constant K_b for complex **1** was estimated to be $4.08 \times 10^4 \text{ M}^{-1}$ ($R^2 = 0.99586$ for five points) from $[\text{DNA}]/(\epsilon_a - \epsilon_f)$ versus [DNA] plot (figure 9). This also establishes the presence of groove-binding interaction of complex **1** with CT-DNA being the behaviour comparable with the well-established binding agent spermine.³²

From the viscosity measurements, it was found that there was hardly any effect on the relative viscosity of the DNA solution. This experiment suggests that the interaction mode is groove binding, which gives support to the above results obtained via spectroscopic study. On the other hand, an intercalative interaction would induce a change in the relative viscosity of DNA, since intercalation leads to an increase in the DNA viscosity by lengthening the DNA helix, or non-classical intercalation could bend (or kink) the DNA helix by reducing its effective length and, concomitantly, its viscosity.^{33,34}

Table 3. Thermal analysis.

Temperature (°C)	Weight loss (%)	Weight loss (g)	Inference
0–97.95	5.879	53.709	3 water molecules
97.95–167.47	7.24	70.565	4 water molecules
167.47–430.37	7.907	72.237	4 water molecules
430.37–651.27	39.432	360.24	After 430°C thermal decomposition leads to Dy_2O_3 .

Figure 7. Excitation ($\lambda_{\text{ex}} = 321$ nm) and emission ($\lambda_{\text{em}} = 479$ and 573 nm) spectra of **1** in solution at room temperature.

Fluorescence intensity of EB bound to CT-DNA at excitation wavelength of 522 nm decreases by increasing the concentration of complex **1** (figure 10). Binding of the complex **1** with CT-DNA causes the replacement of EB and at the same time induces a decrease of fluorescence intensity of DNA-EB system. Quenching of EB bound to DNA by complex **1** is in agreement with the linear Stern–Volmer equation:³⁵

$$I_0/I = 1 + K_{\text{SV}} [Q], \dots \dots \dots (2)$$

where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. K_{SV} is a linear Stern–Volmer quenching constant, Q is the concentration of quencher. The K_{SV} value calculated from the plot of I_0/I versus [complex] (figure 11) was

Figure 8. Electronic spectral titration of complex **1** with CT-DNA at 271 nm in Tris-HCl buffer; $[\mathbf{1}] = 2.56 \times 10^{-5}$; $[\text{DNA}]$: (a) 0.0 , (b) 2.50×10^{-6} , (c) 5.00×10^{-6} , (d) 7.50×10^{-6} , (e) 10.0×10^{-6} , (f) 12.5×10^{-6} mol L^{-1} . The arrow denotes gradual increase in DNA concentration.

Figure 9. Plot of $[\text{DNA}]/(\varepsilon_a - \varepsilon_f)$ ($\text{M}^2.\text{cm}$) vs $[\text{DNA}]$ (μM) for the absorption titration of CT-DNA with complex **1** in Tris-HCl buffer. Association constant $K_b = 4.04 \times 10^4 \text{ M}^{-1}$ ($R = 0.99586$, $n = 5$ points).

found to be 9.1×10^3 ($R^2 = 0.98905$ for five points), suggesting a significant affinity of **1** towards CT-DNA.

3.6 Protein (bovine serum albumin) binding experiments

A similar type of experiment was performed with BSA and complex **1**, the only difference being the concentration of BSA that was kept constant throughout the experiment. Figure 12 shows gradual increase in absorbance with increasing concentration of **1**. In order

Figure 10. Emission spectra of the CT-DNA-EB system in Tris-HCl buffer upon titration with complex **1**. $\lambda_{\text{ex}} = 522$ nm; $[\text{EB}] = 9.6 \times 10^{-5}$, $[\text{DNA}] = 1.58 \times 10^{-5}$; $[\mathbf{1}]$: (a) 0.0 , (b) 1.28×10^{-5} , (c) 2.56×10^{-5} , (d) 3.84×10^{-5} , (e) 5.12×10^{-5} , (f) 6.40×10^{-5} mol L^{-1} . The arrow denotes gradual increase in complex concentration.

Figure 11. Plot of I_0/I vs. [complex] for the titration of CT-DNA-EB system with complex **1**; $k = 9.1 \times 10^3$ ($R = 0.989$, $n = 5$ points).

to confirm that the observed absorption change in the spectrum was not due to experimental errors, a baseline correction was performed for all the measurements. The results clearly indicate that an interaction occurs between complex **1** and BSA³⁶ and the apparent binding constant (K_{ap}) can be determined by using equation (3):³⁷

$$\frac{1}{[A_{obs} - A_0]} = \frac{1}{[A_c - A_0]} + \frac{1}{K_{ap}(A_c - A_0)} \times [\text{complex}], \dots \dots \dots (3)$$

where A_{obs} is the observed absorbance of the solution containing different concentrations of complex **1**, A_0

Figure 12. UV-Vis titration of BSA by increasing the concentration of **1** at 278 nm; [complex **1**] = (a) 0.0, (b) 1.27×10^{-5} , (c) 2.54×10^{-5} , (d) 3.82×10^{-5} , (e) 5.09×10^{-5} , (f) 6.36×10^{-5} and (g) 7.64×10^{-5} M.

Figure 13. Plot of $1/[A - A_0]$ vs $1/[\text{complex}]$ for the titration of BSA with complex **1** in aqueous medium.

and A_c are the absorbances at 280 nm of BSA and of the complex, respectively. From the plot of $1/[A_0 - A]/A$ vs. $1/[\text{complex } \mathbf{1}]$ (figure 13), K_{ap} was determined to be 3.49×10^3 ($R^2 = 0.94287$ for four points). The value of the binding constant K_{ap} indicates a considerably strong affinity of **1** to BSA.

Fluorescence intensity of BSA at excitation wavelength of 282 nm shows a decrease with increase in concentration of complex **1** (figure 14). Quenching of BSA by complex **1** also follows the linear Stern-Volmer equation (2). The K_{sv} value estimated from the plot of I_0/I vs. [complex] (figure 15) is considerably high and it was calculated to be 3.01×10^5 ($R^2 = 0.9913$ for

Figure 14. Fluorescence quenching titration of BSA by increasing the concentration of **1**. [complex] = (a) 0.0, (b) 1.27×10^{-5} , (c) 2.54×10^{-5} , (d) 3.82×10^{-5} , (e) 5.09×10^{-5} and (f) 7.64×10^{-5} M.

Figure 15. Stern–Volmer plot of I_0/I vs. concentration of complex **1** in the titration of BSA. [complex] = 0.0, 1.27×10^{-5} , 2.54×10^{-5} , 3.82×10^{-5} , 5.09×10^{-5} , 6.36×10^{-5} and 7.64×10^{-5} M.

five points), indicating a strong affinity of complex **1** to BSA with formation of a complex-BSA adduct.

4. Conclusion

Several hydrothermally synthesized lanthanide complexes and coordination polymers have been reported so far highlighting different functionalities and properties.^{38–45} Physical and chemical properties of the lanthanide ions and their chelates have provided a source to investigate various biological systems employing their luminescence. In this article, we have described a newly designed dysprosium-based metal-organic coordination framework comprising calcium ions that proved to be a good groove binding agent by studying its interaction with calf thymus DNA (CT-DNA). In addition, spectroscopic study proved the interaction of dysprosium complex with BSA indicating the formation of a complex-BSA adduct. Although some complexes have been postulated to selectively bind to DNA, with contributions from electrostatic attraction, groove and intercalative binding,^{42–45} the concurrent properties manifested by the present lanthanide complex to interact with CT-DNA and BSA^{46,47} have been less frequently encountered in the literature.

Supplementary Information

Crystallographic data of complex **1** has been deposited with the Cambridge Crystallographic Data Centre with

CCDC no. 873072. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). TGA diagram and FTIR spectrum (figures s1 and s2) are available as supporting information (see www.ias.ac.in/chemsci).

Acknowledgements

Financial support from the University Grants Commission-Department of Atomic Energy-Consortium for Scientific Research (UGC-DAE-CSR), Kolkata Centre, India is acknowledged. We thank (EPSRC) and the University of Reading for providing funds for the Oxford X-Calibur system. E Zangrando thanks MIUR-Rome (PRIN 2007HMTJWP_002) for financial support.

References

- Ockwig N W, Delgado-Friedrichs O, O'Keeffe M and Yaghi M O 2005 *Acc. Chem. Res.* **38** 176
- Gao H, Yi L, Zhao B, Zhao X, Cheng P, Liao D and Yan S 2006 *Inorg. Chem.* **45** 5980
- Champness N R 2006 *Dalton Trans.* 877
- Moulton B and Zaworotko J M 2001 *Chem. Rev.* **101** 1629
- Kitagawa S, Kitaura R and Noro S 2004 *Angew. Chem. Int. Ed.* **43** 2334
- Janiak C 2003 *Dalton Trans.* 2781
- Parker D 2000 *Coord. Chem. Rev.* **205** 109
- Spichal Z, Hegrova B, Moravec Z, Pinkas J and Necas M 2011 *Polyhedron* **30** 1620
- Guo X, Zhu G, Li Z, Sun F, Yang Z and Qiu S 2006 *Chem. Commun.* 3172
- Liu W, Jiao T, Li Y, Liu Q, Tan M, Wang H and Wang L 2004 *J. Am. Chem. Soc.* **126** 2280
- Binnemans K 2009 *Chem. Rev.* **109** 4283
- Bunzli J C G and Piguet C 2005 *Chem Soc Rev.* **34** 1048
- Ghosh K S and Bharadwaj P K 2005 *Inorg. Chem.* **44** 3156
- Patra A, Sen B, Sarkar S, Pandey A, Zangrando E and Chattopadhyay P 2013 *Polyhedron* **31** 156
- Chakraborty R, Chatterjee S, Sarkar S and Chattopadhyay P 2012 *J. Biomater. Nanobiotech.* **3** 462
- Dey S, Sarkar S, Evans H S and Chattopadhyay P 2011 *Trans. Met. Chem.* **36** 631
- Patra A, Sarkar S, Mukherjee T, Zangrando E and Chattopadhyay P 2011 *Polyhedron* **30** 2783
- Sarkar S, Sen S, Dey S, Zangrando E and Chattopadhyay P 2010 *Polyhedron* **29** 3157
- Otwinowski Z and Minor W 1997 *Processing of X-ray diffraction data collected in Oscillation Mode, Methods in enzymology*, Vol. **276**, Macromolecular Crystallography, part A, 307–326, Carter, Jr. CW and Sweet RM Eds. (New York: Academic Press)
- Sheldrick G M 2008 *Acta Cryst. A* **64** 112
- Farrugia L J 1999 *J. Appl. Crystallogr.* **32** 837

22. Marmur J 1961 *J. Mol. Biol.* **3** 208
23. Reichmann M E, Rice S A, Thomas C A and Doty P 1954 *J. Am. Chem. Soc.* **76** 3047
24. Barton J K, Goldberg J M, Kumar C V and Turro N J 1986 *J. Am. Chem. Soc.* **108** 2081
25. Huang Y G, Yuan D Q, Gong Y Q, Jiang F L and Hong M C 2008 *J. Mol. Struct.* **872** 99
26. Spek A L 1990 *Acta Crystallogr. Sect A.* **46** 34
27. Song Y S, Yan B and Chen Z X 2004 *J. Solid State Chem.* **177** 3805
28. Li M, Yuan L, Li H and Sun J 2007 *Inorg. Chem. Commun.* **10** 1281
29. Yan B, Zhou B and Wang Q M 2006 *Appl. Organomet. Chem.* **20** 835
30. An Y, Liu S D, Deng S Y, Ji L N and Mao Z W 2006 *J. Inorg. Biochem.* **100** 1586
31. Pyle A M, Rehmann J P, Meshoyrer R, Kumar C V, Turro N J and Barton J K 1989 *J. Am. Chem. Soc.* **111** 3051
32. Strekowski L, Harden D B, Wydra R L, Stewart K D and Wilson W D 1989 *J. Mol. Recognit.* **2** 158
33. Satyanarayana S, Dabrowiak J C and Chaires J B 1992 *Biochemistry* **31** 9319
34. Satyanarayana S, Dabrowiak J C and Chaires J B 1993 *Biochemistry* **32** 2573
35. Stern O and Volmer M 1919 *Phys. Z.* **20** 183
36. Chen C, Qi X and Zhou B 1997 *J. Photochem. Photobiol. A: Chem.* **109** 155
37. Kathiravan A and Renganathan R 2009 *Polyhedron* **28** 1374
38. Kapoor P, Singh R V and Fahmi N 2012 *J. Coord. Chem.* **65** 262
39. Sharif S, Sahin O, Khan I U and Buyukgungo O 2012 *J. Coord. Chem.* **65** 1892
40. Liu Y, Zhang K, Lei R, Liu J, Zhou T and Yang Y Z 2012 *J. Coord. Chem.* **65** 2041
41. Wang J J, Zhang L P, Huang L and Chen J 2012 *J. Coord. Chem.* **65** 3274
42. Yunma D, Guo H F, Qin L, Pan Y, Lu K and Liu J Q 2012 *J. Coord. Chem.* **65** 3424
43. Chowdhury S R, Selim M, Chatterjee S, Igarashi S, Yukawa Y and Mukherjee K K 2012 *J. Coord. Chem.* **65** 3469
44. Wang M F, Yang Z Y, Liu Z C, Li Y, Li T R, Yan M H and Cheng X Y 2012 *J. Coord. Chem.* **65** 3805
45. Che G, Wang X, Liu C, Chen J, Wang S and Li X 2012 *J. Coord. Chem.* **65** 4185
46. Chen W, Chen Y, Liu W, Lei T, Gao Q, Kim D, Su D, Li W and Li Y 2012 *J. Coord. Chem.* **65** 4430
47. Xu J and Chen M D 2013 *J. Coord. Chem.* **66** 509