

## Synthesis, Antioxidant Activity and Fluorescence Properties of Novel Europium Complexes with (*E*)-2- or 4-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide Schiff Base

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Two novel Eu(III) complexes with notable properties have been successfully prepared with hydrazone Schiff base ligands, (*E*)-2-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (**3a**) and (*E*)-4-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (**3b**). DFT, FMO energy and Mulliken charge distribution studies of the ligands allowed us to hypothesize that their HC=N, >C=O and -OH (naphthyl) groups were involved in coordinating with the Eu<sup>3+</sup> ion. The eight coordination sites of the Eu<sup>3+</sup> ion were occupied by the three functional groups of the two ligands (**3a** or **3b**) mentioned above and two water molecules. Similar UV, IR and fluorescence spectra indicated the presence of comparable coordination environments for the Eu<sup>3+</sup> ion in both complexes. Both the ligands and their complexes exhibited moderate DPPH radical scavenging activity. Moreover, it was found that the Eu(III) complexes exhibited fluorescence properties.

**Key Words** : Rare earth complexes, Hydrazone Schiff base, Antioxidant activity, Fluorescence

### Introduction

Hydrazones are Schiff bases described by the general formula RR'C=N-NR''R'''. They have received much attention in the fields of chemistry and biology due to their broad spectrum of activities. They have demonstrated antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, anti-tubercular and anti-tumoral activities, among other useful properties. They have been utilized as herbicides, insecticides, nematocides, rodenticides, plant growth regulators and sterilants for houseflies.<sup>1</sup> The hydrazone Schiff base scaffold functions as a building block for synthesizing a variety of useful bioactive compounds. The hydrazides and their hydrazones also possess remarkable anti-tubercular activity.<sup>2</sup> The hydrazone Schiff base forms stable chelate complexes with transition metals as used in many applications.<sup>3,4</sup> In analytical chemistry studies, hydrazones are used as multidentate ligands for transition metals in colorimetric or fluorimetric determinations.<sup>5,6</sup>

During the past few decades, the field of metal-organic coordination compound application has developed rapidly due to their structural diversity and application potential in optical, electronic and magnetic materials, as well as applications in molecular sensing, catalysis, and selective gas adsorption.<sup>7-11</sup> Organic rare earth complexes have garnered growing interest due to their potential application as fluorescent probes, labels in biological immunoassay applications, as optical amplifiers<sup>12,13</sup> and as active central species in photoluminescent materials.<sup>14,15</sup> Due to the unique photophysical and photochemical properties of rare earths complexes which exhibit potential to be harnessed in the development

of new photodynamic therapies, they offer exciting opportunities to elucidate the structural features of nucleotides such as DNA.<sup>16</sup> Rare earth complexes composed of tetracycline, phenanthroline<sup>17</sup>, adriamycin and pyridine<sup>18,19</sup> have been synthesized as probes used to study nucleic acids. More recently, antioxidant and fluorescence properties of La(III) and Eu(III) complexes with hydrazone Schiff base ligands have been reported.<sup>20</sup> In the present study, we report the synthesis of novel europium complexes of (*E*)-2-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide and (*E*)-4-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide, and we evaluated their fluorescent properties. Sun *et al.*<sup>21</sup> and Cui *et al.*,<sup>22</sup> reported the synthesis and crystal structure of (*E*)-2-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (**3a**) and (*E*)-4-hydroxy-*N'*-[(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (**3b**), respectively, but their antioxidant activities have not yet been reported. Here, we report the antioxidant activities of **3a** and **3b** including their Eu(III) complexes. We also performed density functional theory (DFT) studies in order to obtain useful information regarding the coordination properties of the hydrazone Schiff base ligands used in the present study. DFT has received much interest as a reliable, standard tool for the calculation of quantum chemical aspects of molecular structures and properties of biomolecules.

### Experimental

**Synthesis and Characterization.** All reagents used were of commercial grade. Reactions were monitored by TLC using silica gel F<sub>254</sub> plates (Merck, USA) and the compounds

were visualized either by exposure of the gels to UV light or by dipping the gels in an iodine chamber. Melting points were determined on an X-5 melting point apparatus (Yuxiangyiqi Gongyi City Yuxiang Instruments Co., Ltd., China) and the results were reported without correction, *i.e.*, the melting point of the synthesized compounds were not compared with reference compound. Most melting points published in papers nowadays are uncorrected. Electronic absorption spectra were measured on a Varian Cary 4000 spectrophotometer in an EtOH solution, and the fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. IR spectra were obtained using an FTIR-8430S (Shimadzu, Japan) and KBr discs. <sup>1</sup>H NMR spectra was recorded on an AM-400MH (Bruker, USA) in DMSO-*d*<sub>6</sub> using TMS as an internal standard. Elemental analyses (C, H, N) were performed utilizing a Perkin-Elmer 2400 II CHN elemental analyzer. Absorbance for determination of antioxidant activity was measured using an Optizen 2120 UV/VIS Spectrophotometer (Mecasys Co. Ltd., Korea).

**Preparation of 2-Hydroxybenzohydrazide (2a) and 4-Hydroxybenzohydrazide (2b).** 2-Hydroxybenzohydrazide (2a) and 4-hydroxybenzohydrazide (2b) were prepared by refluxing methyl salicylate (15.2 g, 0.1 M) and methyl 4-hydroxybenzoate (15.2 g, 0.1 M) with hydrazine hydrate (12.5 g, 0.25 M) in approximately 100 mL of ethanol for 3 h. The progress of the reaction was monitored by TLC. The precipitated hydroxybenzohydrazide was filtered and then recrystallized in an ethanol-water mixture. As the <sup>1</sup>H NMR spectra of compound 2a and 2b were recorded while they were in a mixture of CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub>, the NH<sub>2</sub> peaks may have merged with water in DMSO and thus, were rendered indistinct.

**2-Hydroxybenzohydrazide (2a).** Yield: 90%. mp 146-147 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>, 400 MHz) δ 9.25 (br, 1H, CONH), 7.48 (d, 1H, Ar-H, *J* = 7.2 Hz), 7.30 (m, 3H, Ar-H).

**4-Hydroxybenzohydrazide (2b).** Yield: 87.5%. mp 266-267 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>, 400 MHz) δ 9.55 (br, 1H, CONH), 7.82 (d, 2H, Ar-H, *J* = 7.2 Hz), 7.64 (d, 2H, Ar-H, *J* = 7.2 Hz).

**Preparation of (E)-2-Hydroxy-*N'*-(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (3a) and (E)-4-Hydroxy-*N'*-(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (3b).** Hydrazone Schiff base ligands (3a and 3b) were prepared in accordance with the following method: 2a and 2b (1.36 g, 10 mM) in 30 mL ethanol were respectively added drop-wise into 20 mL of 2-hydroxynaphthaldehyde (1.72 g, 10 mM) and ethanol solution. The mixture was stirred and refluxed for 2.5 h. The precipitates were collected and recrystallized in a mixture of ethanol and DMF in order to produce pure ligands.

**(E)-2-Hydroxy-*N'*-(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (3a).**<sup>21</sup> Yield: 80%. mp 255-256 °C. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3372 (OH), 3063, 1654 (C=O), 1623 (NH-C=O), 1599 (C=N). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 7.09-8.09 (m, 10H, Ar-H), 8.95 (s, 1H, CH=N), 11.85 (s, 1H, -NH) 11.99 (s, 1H, OH), 12.05 (s, 1H, OH); Anal. Calcd

(%) for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 70.58; H, 4.61; N, 9.15. Found (%): C, 70.49; H, 4.74; N, 9.12.

**(E)-4-Hydroxy-*N'*-(2-hydroxynaphthalen-1-yl)methylene]benzohydrazide (3b).**<sup>22</sup> Yield: 75%. mp 293-294 °C. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3378 (OH), 3053, 1656 (C=O), 1624 (NH-C=O), 1604 (C=N). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 7.12-8.11 (m, 10H Ar-H), 8.89 (s, 1H, CH=N), 10.91 (s, 1H, OH), 11.87 (s, 1H, -NH) 12.05 (s, 1H, OH). Anal. Calcd (%) for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 70.58; H, 4.61; N, 9.15. Found (%): C 70.51; H 4.70; N 9.20.

**Preparation of Eu(III) Complexes (4a and 4b).** To a solution of hydrazone Schiff base ligand (0.306 g, 1 mM) in 50 mL of ethanol-water (1:1) mixture, 2 mL of KOH (1.0 M) was added. The solution was then added to Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.471 g, 1.1 mM) in ethanol-water (1:1) mixture and stirred for 3 h at room temperature. The precipitates were collected and washed with an ethanol-acetone mixture three times, and then dried *in vacuo*.

**K[Eu(3a)<sub>2</sub>]·2H<sub>2</sub>O (4a):** Yield: 85%. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3106 (OH), 1612 (C=O), 1583 (NH-C=O) 1555 (C=N), 475 (Eu-O). Anal. Calcd (%) for KC<sub>36</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>Eu: C, 51.74; H, 3.38; N, 6.70; Eu, 18.18. Found (%): C, 51.85; H, 3.45; N, 6.81.

**K[Eu(3b)<sub>2</sub>]·2H<sub>2</sub>O (4b):** Yield: 89%. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3109 (OH), 2986, 1608 (C=O), 1561 (NH-C=O), 1536 (C=N), 467 (Eu-O). Anal. Calcd (%) for KC<sub>36</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>Eu: C, 51.74; H, 3.38; N, 6.70; Eu, 18.18. Found (%): C, 51.79; H, 3.42; N, 6.80.

**Quantum Chemical Calculations.** The molecular geometries of the Schiff base ligands were optimized using MM+ molecular modeling and semi-empirical molecular orbital AM1 methods.<sup>23</sup> The density functional theory (DFT) calculations were performed using a hybrid functional B3LYP (Becke's three parameter nonlocal exchange functional theory along with the Lee-Yang-Parr correlation functional theory)<sup>24,25</sup> at a basis set 6-311G and using the GAMESS (version March 25, 2010 R2) software package.<sup>26</sup> No imaginary frequencies were obtained in the vibration calculations, indicating that the structures were stable. After optimization, Mulliken charge and properties of the frontier molecular orbitals (FMOs) of the Schiff base ligands were analyzed using the results calculated at the B3LYP/6-311G level.

**DPPH Radical Scavenging Activity.** The free radical scavenging activities of the synthesized compounds were assayed according to the Blois method with some modification<sup>27</sup> using 1,1-diphenyl-2-picrylhydrazyl (DPPH). Aliquots of 0.1 mL of different concentrations (2.5 to 20 mg/mL) of sample in ethanol were added to 4 mL of a 1.5 × 10<sup>-5</sup> M DPPH solution and mixed thoroughly. The solution was then left to stand at room temperature in the dark. After 30 min of incubation, the absorbance of the solution was measured at 520 nm and the antioxidant activity was calculated using the following equation:

$$\text{DPPH radical scavenging activity \%} = \frac{(\text{Absorbance of the control} - \text{Absorbance of the sample})}{\text{Absorbance of the control}} \times 100$$

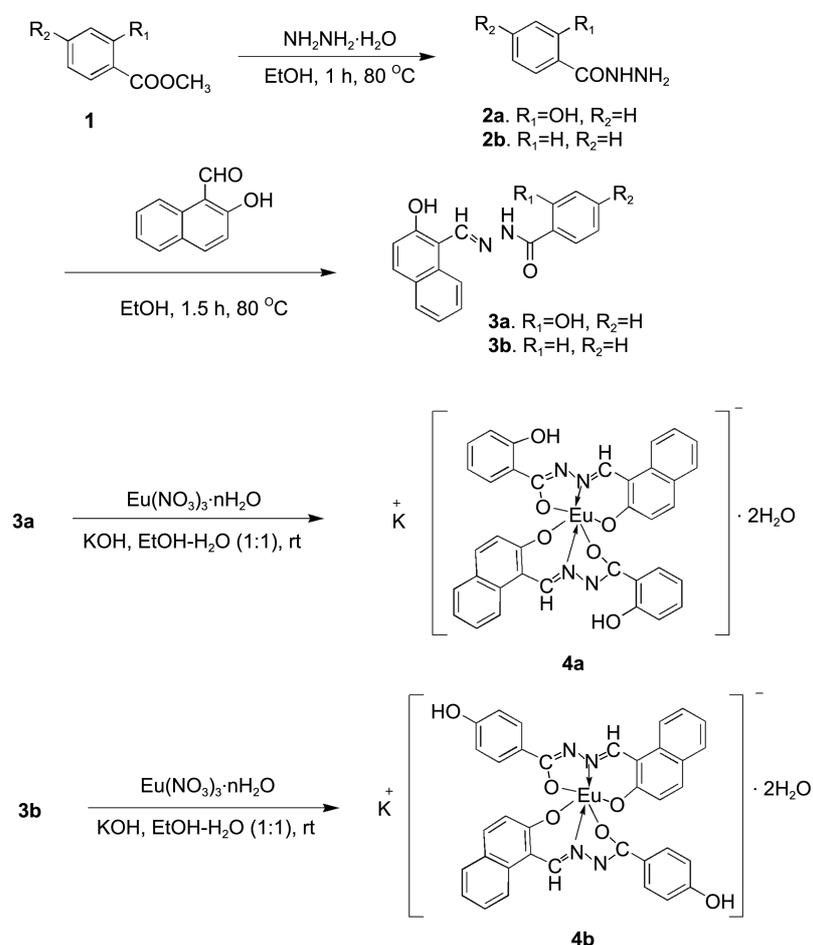
## Results and Discussion

**Synthesis of Hydrazone Schiff Base Ligand and Their Europium Complexes.** The synthetic routes of the hydrazone Schiff base ligands (**3a** and **3b**) and their europium complexes (**4a** and **4b**) are outlined in Scheme 1. Synthesis of the Schiff base ligands was carried out according to a convenient two-step procedure: the reaction of commercially available methyl salicylate and methyl 4-hydroxybenzoate with hydrazine hydrate in ethanol followed by a condensation reaction with 2-hydroxy-naphthaldehyde, a process which provided excellent yields (75-80%). The  $^1\text{H}$  NMR spectra of compounds **3a** and **3b** revealed two singlets characteristic of the azomethine proton ( $-\text{CH}=\text{N}-$ ) and imino proton ( $-\text{NH}-$ ) at 8.89-8.95 and 11.85-11.87 ppm, respectively. The aromatic protons of both ligands were assigned as multiplets at 7.09-8.11 ppm, equivalent to 10 protons. The rare earth complexes (**4a** and **4b**) were synthesized by reacting europium nitrate pentahydrate with the ligands (**3a** and **3b**) in a basic ethanol-water (1:1) mixture. In the FTIR spectrum, the ligands revealed bands at 3372-3378, 1654-1656, 1623-1624 and 1604-1599  $\text{cm}^{-1}$ , which we propose represented  $\nu(\text{OH})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{NH}-\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$ , respectively. On the other hand, in the IR spectra of the complexes, the bands shifted to 3109-3106, 1612-1608,

1583-1561 and 1555-1536  $\text{cm}^{-1}$ . These results indicated that the OH, C=O and C=N (Schiff) groups corresponded to rare earth ions. The band recognized around 467-475  $\text{cm}^{-1}$  may have been due to Eu-O stretch vibration.<sup>28</sup> In addition, a strong and broad band was observed around 3400-3000  $\text{cm}^{-1}$ , indicating there were coordinated  $\text{H}_2\text{O}$  molecules in the complexes, a finding in agreement with the elemental analysis result.

**DFT Calculations, FMO Energy and Mulliken Charge Distribution of the Ligands.** Quantum chemical calculations were carried out using density functional theory (DFT) at the B3LYP/6-311G level to determine the properties of the frontier molecular orbitals and Mulliken charge in order to determine the coordination properties of the Schiff base ligands. The optimized geometric parameters obtained from the DFT-B3LYP/6-311G calculations of the ligands are listed in Table 1. The theoretical geometric structure of the hydrazone Schiff base ligands is shown in Figure 1. Bond lengths and angles of the optimized ligands (**3a** and **3b**) were within normal ranges.<sup>29</sup>

FMO results play a vital role in determining the reactivity of a molecule and its ability to absorb light. FMOs are important indicators of optical and electric properties and molecular reactivity. The single point energies and FMOs were determined according to quantum chemical calculations.



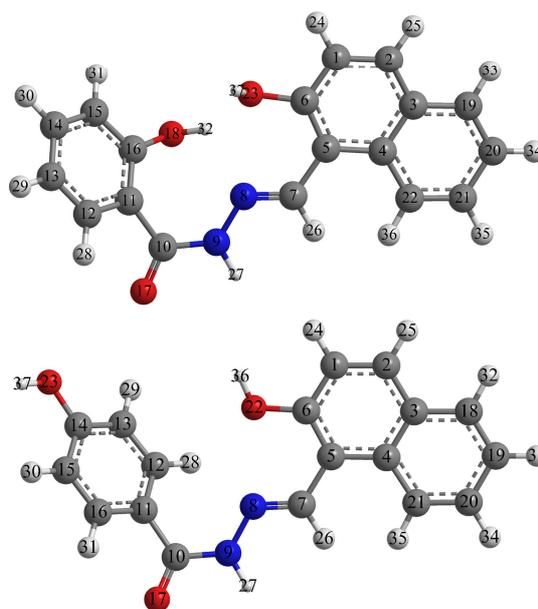
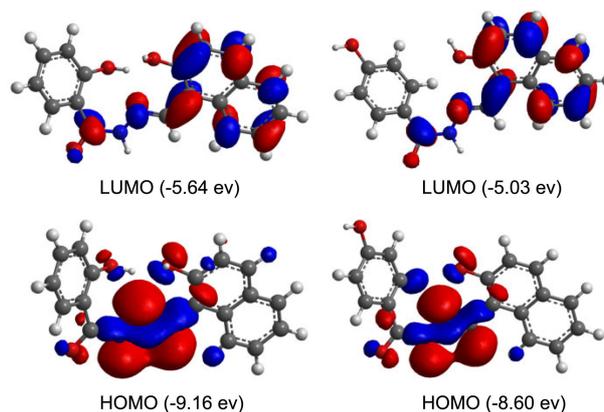
**Scheme 1.** Synthesis of hydrazone Schiff base ligands and their europium complexes.

**Table 1.** Selected bond lengths (Å) and angles (°) determined by B3LYP/6-311G theoretical calculations for compound **3a** and **3b**

<b>3a</b>		<b>3b</b>	
Bonding atoms	Bond lengths /Å	Bonding atoms	Bond lengths /Å
C(4)-C(3)	1.4142	C(2)-C(1)	1.3719
C(2)-C(3)	1.4044	C(3)-C(2)	1.4248
C(1)-C(2)	1.3959	C(4)-C(3)	1.4090
C(5)-C(4)	1.4044	C(18)-C(3)	1.4277
C(19)-C(3)	1.4044	C(5)-C(4)	1.4401
C(6)-C(5)	1.3959	C(21)-C(4)	1.4309
C(20)-C(19)	1.3959	C(6)-C(1)	1.4217
C(22)-C(4)	1.4045	C(7)-C(5)	1.4767
C(7)-C(5)	1.3370	O(22)-C(6)	1.3611
C(21)-C(22)	1.3959	C(19)-C(18)	1.3738
O(23)-C(6)	1.3550	C(20)-C(21)	1.3762
N(8)-C(7)	1.2600	N(8)-C(7)	1.2771
N(9)-N(8)	1.3520	N(9)-N(8)	1.3527
C(10)-N(9)	1.3690	C(10)-N(9)	1.3654
C(11)-C(10)	1.3510	C(11)-C(10)	1.5173
C(12)-C(11)	1.3948	C(12)-C(11)	1.3562
C(16)-C(11)	1.3948	C(16)-C(11)	1.4741
C(13)-C(12)	1.3949	C(13)-C(12)	1.4974
C(14)-C(13)	1.3948	C(14)-C(13)	1.5102
C(15)-C(16)	1.3949	C(15)-C(16)	1.3547
O(18)-C(16)	1.3550	O(23)-C(14)	1.3575
O(17)-C(10)	1.2080	O(17)-C(10)	1.3098

<b>3a</b>		<b>3b</b>	
Bonding atoms	Bond angles/°	Bonding atoms	Bond angles/°
C(2)-C(3)-C(4)	119.2642	C(3)-C(2)-C(1)	119.8310
C(1)-C(2)-C(3)	120.7472	C(4)-C(3)-C(2)	119.5435
C(5)-C(4)-C(3)	119.2703	C(18)-C(3)-C(2)	119.7673
C(19)-C(3)-C(2)	121.4703	C(5)-C(4)-C(3)	119.5589
C(6)-C(5)-C(4)	120.7375	C(21)-C(4)-C(3)	117.3338
C(20)-C(19)-C(3)	120.7459	C(6)-C(1)-C(2)	121.8741
C(22)-C(4)-C(3)	119.2660	C(7)-C(5)-C(4)	120.8568
C(7)-C(5)-C(4)	119.6312	O(22)-C(6)-C(1)	118.0860
C(21)-C(22)-C(4)	120.7406	C(19)-C(18)-C(3)	120.3859
O(23)-C(6)-C(1)	120.0031	C(20)-C(21)-C(4)	121.4284
N(8)-C(7)-C(5)	120.0000	N(8)-C(7)-C(5)	125.3624
N(9)-N(8)-C(7)	120.0000	N(9)-N(8)-C(7)	121.5254
C(10)-N(9)-N(8)	120.0000	C(10)-N(9)-N(8)	123.5551
C(11)-C(10)-N(9)	120.0000	C(11)-C(10)-N(9)	116.2422
C(12)-C(11)-C(10)	119.9986	C(12)-C(11)-C(10)	119.6848
C(16)-C(11)-C(10)	119.9986	C(16)-C(11)-C(10)	118.6284
C(13)-C(12)-C(11)	119.9969	C(13)-C(12)-C(11)	119.0855
C(14)-C(13)-C(12)	120.0013	C(14)-C(13)-C(12)	117.3539
C(15)-C(16)-C(11)	119.9996	C(15)-C(16)-C(11)	121.2223
O(18)-C(16)-C(11)	120.0002	O(23)-C(14)-C(13)	121.2314
O(17)-C(10)-N(9)	120.0000	O(17)-C(10)-N(9)	120.4831

And in these calculations, 37 atoms which involved 235 basis functions, including 80 occupied orbitals, were shown to be involved for both ligands (**3a** and **3b**). According to the molecular orbital theory, the HOMO-LUMO and their vicinal

**Figure 1.** The theoretical geometric structure of compound **3a** (up) and **3b** (below), and their atom-numbering schemes.**Figure 2.** Contour plots and energies of the HOMO and LUMO frontier molecular orbitals of compound **3a** (left) and **3b** (right).

molecular orbitals are involved in the coordination property of a molecule, and its molecular stability depends on the negative energy values of their FMOs.<sup>30</sup> The HOMO and its vicinal orbital play the role of electron donor while the LUMO and its vicinal orbital play the role of electron acceptor. The energy levels of the HOMO and LUMO orbitals computed at the B3LYP/6-311G level for compounds **3a** and **3b** are shown in Figure 2. The energy levels of HOMO and LUMO for compound **3a** were  $-9.16$  and  $-5.64$  eV, and for compound **3b** they were  $-8.60$  and  $-5.03$  eV. The energy differences between HOMO and LUMO for compound **3a** and **3b** were  $3.52$  and  $3.57$  eV, respectively. The total energies of compounds **3a** ( $-1019$  a.u.) and **3b** ( $-1017$  a.u.) were lower, and the energies of HOMO and LUMO and their neighboring orbitals (data not shown) were all negative, a finding which indicated that the ligands were stable.

Based on the optimized structure of **3a** and **3b**, the Mulliken charge distribution for all the atoms was calculated and the

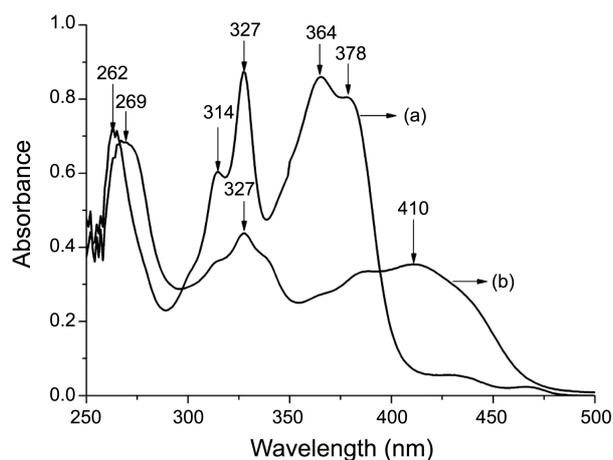
**Table 2.** Mulliken charges ( $e$ ) for compounds **3a** and **3b**

<b>3a</b>		<b>3b</b>	
Atom	Charge/ $e$	Atom	Charge/ $e$
C(1)	-0.230	C(1)	-0.264
C(2)	-0.184	C(2)	-0.177
C(3)	-0.097	C(3)	-0.106
C(4)	-0.077	C(4)	-0.068
C(5)	-0.156	C(5)	-0.173
C(6)	0.390	C(6)	0.448
C(7)	0.248	C(7)	0.235
N(8)	-0.734	N(8)	-0.738
N(9)	-0.371	N(9)	-0.331
C(10)	0.964	C(10)	0.954
C(11)	-0.218	C(11)	-0.240
C(12)	-0.172	C(12)	-0.141
C(13)	-0.260	C(13)	-0.277
C(14)	-0.223	C(14)	0.394
C(15)	-0.259	C(15)	-0.298
C(16)	0.390	C(16)	-0.163
O(17)	-0.788	O(17)	-0.747
O(18)	-0.623	C(18)	-0.180
C(19)	-0.182	C(19)	-0.249
C(20)	-0.242	C(20)	-0.221
C(21)	-0.223	C(21)	-0.219
C(22)	-0.216	O(22)	-0.733
O(23)	-0.755	O(23)	-0.637
H(24)	0.264	H(24)	0.242
H(25)	0.257	H(25)	0.255
H(26)	0.237	H(26)	0.226
H(27)	0.368	H(27)	0.360
H(28)	0.277	H(28)	0.291
H(29)	0.240	H(29)	0.257
H(30)	0.244	H(30)	0.234
H(31)	0.260	H(31)	0.286
H(32)	0.457	H(32)	0.244
H(33)	0.248	H(33)	0.246
H(34)	0.250	H(34)	0.247
H(35)	0.251	H(35)	0.245
H(36)	0.248	H(36)	0.400
H(37)	0.414	H(37)	0.395

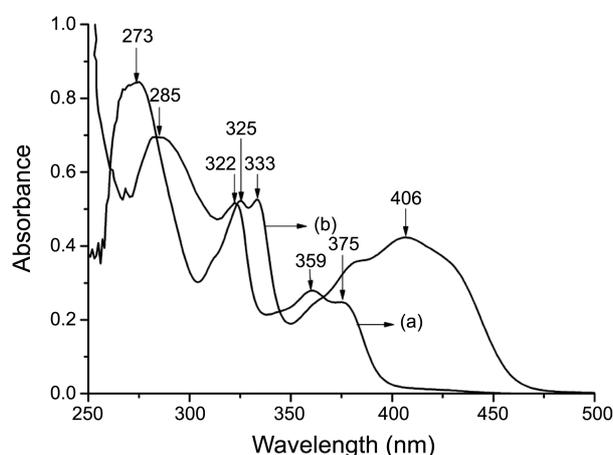
results are provided in Table 2. The analysis indicated that the electronegativity of the atoms played an important role in the Mulliken charge distribution, *i.e.*, between the two connecting atoms with the atom having a higher electronegativity carrying negative charges and the atom having a lower electronegativity carrying positive charges.<sup>31</sup> Therefore, for compounds **3a** and **3b**, H and C (bonding with O and N atoms) were all positive while N (from azomethine and imine), O (bonding with C) and C (bonding with H) were all negative. Therefore, the hetero atoms N8, N9, O17, O18 and O23 for **3a**, and N8, N9, O17, O22 and O23 for **3b**, which bear the negative charges, may act as electron donors when coordinating with metals. According to the Mulliken charge distribution result, atom N9 ( $-0.371$  &  $-0.331$ ) had a

relatively low negative value as compared to N8 ( $-0.734$  &  $-0.738$ ) in both of the ligands (**3a** and **3b**), and the former atom might not be involved in the coordination with europium ion in the complexes **4a** and **4b**. The order of the Mulliken charge distribution of the O atoms in both compounds were as follows: O17 ( $-0.788$ ) > O23 ( $0.755$ ) > O18 ( $-0.623$ ) for **3a** and O17 ( $-0.747$ ) > O22 ( $0.733$ ) > O23 ( $-0.637$ ) for **3b**. As shown in Figure 1, O23 of **3a** was equivalent to O22 of **3b**. There was only one structural difference present between these two ligands, an *ortho*-hydroxyl group (O18) present in the phenyl ring of **3a** versus a *para*-hydroxyl group (O23) in the phenyl ring of **3b**. Even though there was a structural difference present in ligands **3a** and **3b**, the complexes **4a** and **4b** provided similar UV, IR and fluorescence spectra, a result indicating a comparable coordination environment may be present in both complexes. The HOMO contour plot (Figure 2) of **3a** shows that the electron density surrounding the O18 atom (*ortho*-hydroxyl group in the phenyl ring) was much lower than that of the O23 atom (*ortho*-hydroxyl group in the naphthyl ring), a finding which justified the lack of electron donor capacity of the former oxygen atom. Whereas the HOMO contour plot (Figure 2) of **3b** shows that there was a lack of electron density surrounding the O23 atom (*para*-hydroxyl group of the phenyl ring) which rendered this atom incompetent in its ability to coordinate with the  $\text{Eu}^{3+}$  ion, even this atom bore an adequate negative charge. Qin *et al.*,<sup>20</sup> reported that the crystal structure of rare earth complexes possessing 7-methoxychromone-3-carbaldehyde benzoyl hydrazone (hydrazone Schiff base) where the N atom of azomethine, the O atom of the benzoyl carbonyl group, and the O atom of the carbonyl group of the chromone ring, were involved in coordinating with an  $\text{La}^{3+}$  ion. The spatial arrangement of these three atoms was identical to N8, O17 and O23 of **3a**, and N8, O17 and O22 of **3b**. From the findings described in the above discussion, we speculate that N8, O17 and O23 of **3a** or N8, O17 and O22 of **3b** were involved in coordination with the  $\text{Eu}^{3+}$  ion in both complexes, **4a** and **4b**.

**UV-Absorption and Fluorescence Spectra.** UV-absorption spectra of the hydrazone Schiff base ligands **3a** and **3b**, and their corresponding complexes in ethanol solution are provided in Figures 3 and 4, respectively. The electronic absorption spectra of the ligands (**3a** and **3b**) used in the present study mainly exhibited three kinds of bands. The higher energy bands within the 262–273 nm range were due to excitation of  $\pi$  electrons ( $\pi \rightarrow \pi^*$  transitions) in the aromatic chromophore. The second kind of band, within the 314–327 nm range, was assigned to the  $\pi \rightarrow \pi^*$  transition within the C=N group, while the longer wavelength band in the 359–378 nm range was due to an intramolecular charge transfer (CT transition) involving the whole molecule.<sup>32,33</sup> DFT calculations performed on ligands **3a** and **3b** showed that HOMO and LUMO were mainly located at the methine donor and naphthyl acceptor parts of the molecule, respectively (Figure 2). The lowest energy electronic transition between the HOMO and the LUMO levels for **3a** were  $-9.16$  and  $-5.64$  eV, and  $-8.60$  and  $-5.03$  eV for **3b**, a result



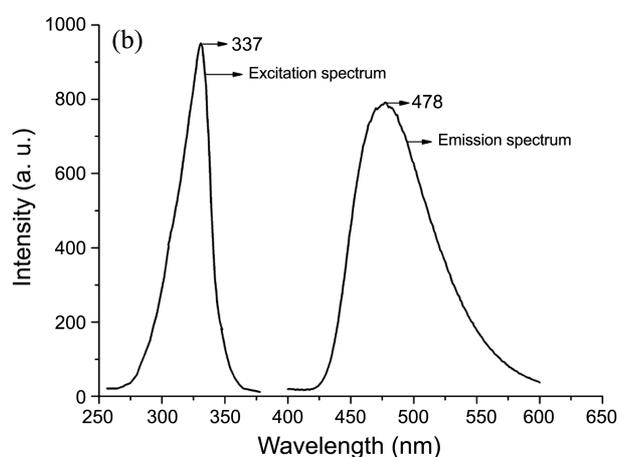
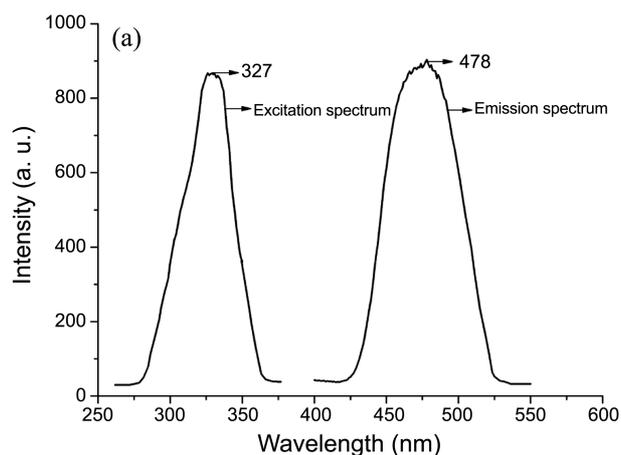
**Figure 3.** UV-absorption spectra of free ligand **3a** (a) and its complex **4a** (b) in ethanol at room temperature.



**Figure 4.** UV-absorption spectra of free ligand **3b** (a) and its complex **4b** (b) in ethanol at room temperature.

corresponding to a CT electronic transition equaling 3.52 and 3.57 eV, respectively. The calculated wavelengths of this transition were 352 nm (**3a**) and 347 nm (**3b**), a result in satisfactory agreement with the experimental values (364 for **3a** and 359 nm for **3b**). The UV spectra of complex **4a** (Figure 3) and **4b** (Figure 4) showed red shift due to the perturbation induced by the metal coordination,<sup>34</sup> *i.e.*, the charge transfer from the HOMO of the ligand to the vacant **4f** orbital of the metal ion. The electron transition from the HOMO of the ligand to the metal ion requires less energy which resulted push the peak to the longer wavelength.

Figure 5 presents the emission and excitation spectra of **4a** and **4b** in ethanol at room temperature (concentration:  $1 \times 10^{-4}$  mL<sup>-1</sup>, slit 5 nm). Both complexes were excited at broad bandwidth, between 275-375 nm, with a maximum around 327 nm corresponding to transitions populating a ligand-centered excitation state. However, they did not exhibit the characteristic emissions of the Eu<sup>3+</sup> ion. The broad emission band at 478 nm may have been attributed to fluorescence from the singlet state of the ligand, a result which indicated that no effective energy transfer occurred between the ligand



**Figure 5.** Fluorescence spectra of europium complexes **4a** (a) and **4b** (b) in ethanol at room temperature.

and Eu<sup>3+</sup> ions in either complex.<sup>35</sup> Nevertheless, a strong emission broad band was observed between 425-525 nm with main emission peaks located at 478 nm for both europium complexes.

**Antioxidant Activity.** We investigated the free radical scavenging ability of the newly synthesized europium complexes (**4a** and **4b**) including the hydrazone Schiff base ligands (**3a** and **3b**) using DPPH. The DPPH radical scavenging ability of the ligands and their complexes are shown in Table 3. The result revealed that the two complexes displayed IC<sub>50</sub> values of 4.10 μM for **4a** and 11.96 μM for **4b**, indicating they possessed stronger antioxidant activity than their corresponding ligands **3a** (IC<sub>50</sub> value of 13.79 μM)

**Table 3.** DPPH free radical scavenging activity of hydrazone Schiff base ligands (**3a** and **3b**) and their europium complexes (**4a** and **4b**)

Compound	IC <sub>50</sub> (μM)
<b>3a</b>	13.79
<b>3b</b>	23.52
<b>4a</b>	4.10
<b>4b</b>	11.96
Ascorbic acid	0.037

and **3b** (IC<sub>50</sub> value of 23.52 μM). Ascorbic acid, a phenolic antioxidant, used as a positive control, showed stronger antioxidant activity (IC<sub>50</sub> value of 0.41 μM) than that of any of the other synthesized compounds.

### Conclusions

We synthesized novel Eu(III) complexes based on 2-hydroxynaphthaldehyde benzoyl hydrazone ligands. The results of DFT, FMO energy and Mulliken charge distribution studies led us to speculate that the N atom of azomethine, the O atom of the benzoyl carbonyl group, and the O atom of the 2-hydroxyl group of the naphthyl ring of ligands **3a** and **3b** were involved in coordinating with the Eu<sup>3+</sup> ion. The novel Eu(III) complexes demonstrated strong emission spectra indicating they possessed fluorescence properties. Their similar UV, IR and fluorescence spectra indicated comparable coordination environments for the Eu<sup>3+</sup> ion in both complexes. Moreover, the complexes and the ligands demonstrated excellent antioxidant properties and could be useful in combating the free radicals which exist in close relationship with cancerous cells. It was notable that the two complexes exhibited stronger antioxidant effects than their corresponding ligands. It is clear that the novel Eu(III) complexes are good candidates for use in a variety of applications.

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