Fluorescence Properties and Density Functional Theory Calculation of a Structurally Characterized Heterotetranuclear [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] 4,4′-Bipy-Salamo-Constructed Complex

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Abstract: A new heterotetranuclear complex, [[Zn(L)Sm(NO\textsubscript{3})\textsubscript{3}]	extsubscript{2}(4,4′-bipy)]-2CH\textsubscript{3}OH, was synthesized via an unsymmetrical single salamo-like ligand H\textsubscript{2}L: 6-methoxy-6′-ethoxy-2,2′-[ethylenedioxybis(azinomethyl)]diphenol, with Zn(OAc)\textsubscript{2}-2H\textsubscript{2}O, Sm(NO\textsubscript{3})\textsubscript{3}-6H\textsubscript{2}O, and 4,4′-bipyridine by the one-pot method. The [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] complex was validated via elemental analysis, powder X-ray diffraction (PXRD) analysis, infrared spectroscopy, and ultraviolet–visible (UV–Vis) absorption spectroscopy. The X-ray single crystal diffraction analysis of the [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] complex was carried out via X-ray single-crystal crystallography. The crystal structure and supramolecular features were discussed. In addition, while studying the fluorescence properties of the [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] complex, the density functional theory (DFT) calculation of its structure was also performed.

Keywords: unsymmetrical salamo-like ligand; heterotetranuclear complex; crystal structure; fluorescence property; DFT calculation

1. Introduction

Self-assembly in coordination chemistry refers to the acquisition of a multinuclear complex or polymer by the reaction of a metal ion with an organic ligand [1–8]. The choice of organic ligand tends to be a polynitrogen-containing ligand, a polynitrate carboxylic acid ligand, or a polynitrogen carboxylic acid pyridine ligand. These ligands can be directly self-assembled with transition/rare-earth metal ions to give the corresponding homopolynuclear complexes or polymers. They can also be assembled as auxiliary ligands into a heteropolynuclear complex or polymer in the form of bridges, or even constitute Metal Organic Frameworks (MOFs). Many homopolynuclear or heteropolynuclear complexes have been studied with salen-like or salamo-like complexes [9–17]. In addition to potential applications in the fields of magnetism [18–25], catalysis [26,27], biology [28–32], electrochemical research [33–37], functional [38–40] and nonlinear optical materials [41–47], such complexes also play an important role in the field of supramolecular building [48–51] and sensors [52–56]. The luminescence of rare-earth complexes has been a hot area for researchers due to its excellent application value in lasers, sensing, and fluorescence imaging. Therefore, designing and self-assembling heteropolynuclear salamo-like complexes containing auxiliary ligands with good fluorescence properties is a major challenge for researchers today.

It is not surprising that, in the past few years, rare-earth metal ions have been introduced into the coordination of organic compounds [57–59], and a large number of heterobimetallic 3d-4f salamo-like
complexes have also been reported [60–64]. However, heterobimetallic 3d-4f salamo-like complexes containing auxiliary ligands have rarely been investigated [65]. Here, a polydentate nitrogen-containing ligand was used as an auxiliary ligand in the synthesis of a heterobimetallic 3d-4f salamo-like complex, and a newly designed tetrancular [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] salamo-like complex was successfully assembled by a one-pot reaction of H\textsubscript{2}L, Zn(OAc)\textsubscript{2}·2H\textsubscript{2}O, Sm(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O, and 4,4′-bipyridine. The [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] complex was validated by elemental analysis, powder X-ray diffraction (PXRD) analysis, infrared and UV–Vis absorption spectroscopy. At the same time, fluorescent print imaging and the density functional theory (DFT) calculation were performed.

2. Experimental

2.1. General Details

2-Hydroxy-3-Methoxybenzaldehyde (99%) was purchased from Meryer Chemical Technology Co., Ltd., 3-Ethoxysalicylaldehyde (>97%) was purchased from Tokyo Chemical Industry Co., Ltd., and other reagents and solvents were purchased from the Tianjin Chemical Reagent Factory and used as received without further purification. X-ray single-crystal diffraction data of the [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] complex were measured and recorded using a Bruker APEX-II CCD surface inspection diffractometer (Bruker, Germany). The PXRD experiment with the [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] complex was recorded in the range of 2θ = 5–50° using a D/max-2400 powder X-ray diffractometer (Rigaku, Japan). The fluorescence lifetime of H\textsubscript{2}L and the [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] complex were measured using a FLS920 time-resolved fluorescence spectrometer (Edinburgh, United Kingdom). DFT calculations were performed on H\textsubscript{2}L and the [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] complex using the Gaussian 09 software package [33,35,47,54]. The test methods of other instruments used in this paper are the same as those in the previous literature [27,66].

2.2. Synthesis of H\textsubscript{2}L

As depicted in Scheme 1, 1,2-bis(aminooxy)ethane was obtained according to a previously reported method [66]. 2-Hydroxy-3-Methoxybenzaldehyde (304.3 mg, 2.0 mmol) in an ethanol solution (50 mL) was slowly added to an ethanol solution (15 mL) of 1,2-bis(aminooxy)ethane (368.4 mg, 4.0 mmol). The mixed solution was stirred at 45–55 °C for 4 hours and distilled under reduced pressure. The residue was purified by column chromatography (dichloromethane:ethyl acetate = 15:1) to acquire a white crystalline solid of 2-[O-(1-ethoxyamide)]oxime-6-methoxyphenol [67]. Yield: 69.7%. m.p: 93–94 °C. Anal. Calcd for C\textsubscript{18}H\textsubscript{14}N\textsubscript{2}O\textsubscript{4} (%): C, 53.09; H, 6.24; N, 12.38. Found: C, 53.22; H, 6.11; N, 12.32.

Scheme 1. Synthetic routes to H\textsubscript{2}L and its [Zn\textsuperscript{II}\textsubscript{2}–Sm\textsuperscript{III}\textsubscript{2}] complex.
An ethanol solution (50 mL) of the obtained 2-[O-(1-ethoxyamide)]oxime-6-methoxyphenol (452.4 mg, 2.0 mmol) was added to an ethanol solution (30 mL) of 3-Ethoxysalicylaldehyde (332.3 mg, 2.0 mmol). The mixed solution was stirred at ca. 55 °C for about six hours, concentrated under reduced pressure, and a white crystalline powder H$_2$L was obtained. Yield: 83%. m.p: 100−101 °C. Anal. Calcd for C$_{19}$H$_{22}$N$_2$O$_6$ (%): C, 60.95; H, 5.92; N, 7.48. Found: C, 61.02; H, 5.89; N, 7.41.

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.73 (s, 1H, –OH), 9.69 (s, 1H, –OH), 8.26 (s, 2H, –N=CH), 6.91 (d, $J = 7.2$, 2.8Hz, 2H, –ArH), 6.88–6.80 (m, 4H, –ArH), 4.47 (t, $J = 4.2$ Hz, 4H, –CH$_2$), 4.11 (q, $J = 8.4$ Hz, 2H, –OCH$_2$), 3.91 (s, 3H, –OCH$_3$), 1.48 (t, $J = 5.6$ Hz, 3H, –CH$_3$). IR (KBr, cm$^{-1}$): 3427 (vs), 2978 (w), 2930 (m), 2876 (w), 2835 (w), 2073 (m), 1613 (vs), 1468 (s), 1420 (w), 1386 (w), 1352 (m), 1250 (vs), 1059 (vs), 985 (m), 733 (m), 638 (s), and 488 (m). UV–Vis (CH$_3$CH$_2$OH), $\lambda_{max}$ (nm) [($\epsilon_{max}$): (dm$^3$ mol$^{-1}$ cm$^{-1}$)]: 270 and 319 nm (1.0 × 10$^{-5}$ M).

2.3. Synthesis of the [Zn$^{II}_2$–Sm$^{III}_2$] Complex

A solution of H$_2$L (7.5 mg, 0.02 mmol) in dichloromethane (2 mL) was added to Zn(OAc)$_2$·2H$_2$O (4.50 mg, 0.02 mmol) and Sm(NO$_3$)$_3$·6H$_2$O (9.0 mg, 0.02 mmol) in methanol (4 mL). After the mixture was stirred for about 10 minutes, a solution of 4,4′-bipyridine (3.50 mg, 0.02 mmol) in methanol (2 mL) was added and continued to be stirred for an additional 10 minutes. The mixture was filtered off and the filtrate was sealed with a foil paper. It was placed in an undisturbed environment for about two weeks, and transparent white block-like single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calcd for [{Zn(L)Sm(NO$_3$)$_3$}$_2$ (4,4′-bipy)]·2CH$_3$OH (C$_{50}$H$_{56}$N$_{12}$O$_{32}$Sm$_2$Zn$_2$) (%): C, 33.96; H, 3.19; N, 9.50; Sm, 17.00; Zn, 7.43. Found: C, 33.99; H, 3.05; N, 9.44; Sm, 17.32; Zn, 7.43. IR (cm$^{-1}$, KBr): 3400 (vs), 2984 (m), 2937 (w), 2359 (w), 2076 (m), 1604 (vs), 1461 (w), 1372 (m), 1284 (w), 1273 (w), 1216 (m), 1063 (s), 788 (m), 723 (s), 624 (s), and 478 (m). UV–Vis (CH$_3$CH$_2$OH), $\lambda_{max}$ (nm) [$\epsilon_{max}$]: (dm$^3$ mol$^{-1}$ cm$^{-1}$): 273 and 343 nm (1.0 × 10$^{-5}$ M).

2.4. X-ray Crystallography Analysis

The description of X-ray crystallography is presented in the Supplementary Information (SI). Crystallographic data of the [Zn$^{II}_2$–Sm$^{III}_2$] complex and the refinement parameters are presented in Table 1. CCDC: 1959376.

Table 1. Crystal data and refinement parameters for the [Zn$^{II}_2$–Sm$^{III}_2$] complex.

| Compound | [Zn$^{II}_2$–Sm$^{III}_2$] Complex |
|----------|----------------------------------|
| Formula  | C$_{50}$H$_{56}$N$_{12}$O$_{32}$Sm$_2$Zn$_2$ |
| Formula weight | 1768.50 |
| Temperature (K) | 273.15 |
| Wavelength (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | C 2/c |
| a (Å) | 36.6271(14) |
| b (Å) | 8.8968(3) |
| c (Å) | 21.485(8) |
| α (°) | 90.00 |
| β (°) | 112.6490(10) |
| γ (°) | 90.00 |
| V (Å$^3$) | 6448.2(4) |
| Z | 4 |
| $D_{calc}$ (g·cm$^{-3}$) | 2.631 |
| μ (mm$^{-1}$) | 3.325 |
| F (000) | 3520.0 |
| Crystal size (mm) | 0.15 × 0.11 × 0.09 |
| θ Range (°) | 2.5–26.0 |
3. Results and Discussion

3.1. PXRD Analysis

The PXRD experiment with the [ZnII2–SmIII2] complex was performed with an X-ray diffractometer using Cu-Kα radiation (λ = 0.154 nm) in the range of 2θ = 5–50°. A comparison of the simulated and experimental PXRD patterns of the [ZnII2–SmIII2] complex is shown in Figure 1. The experimental pattern was in good agreement with the simulated pattern, which confirmed the phase purity and isomorphism of the [ZnII2–SmIII2] complex. It further illustrated that the [ZnII2–SmIII2] complex had sufficient purity to be used to study its spectral characteristics and fluorescence properties.

![Simulated and Experimental PXRD Patterns](image)

Figure 1. Comparison of the simulated and experimental powder X-ray diffraction (PXRD) patterns of the [ZnII2–SmIII2] complex.

3.2. IR Spectra

The infrared spectra of H2L and the [ZnII2–SmIII2] complex are shown in Figure S1 (Supplementary Materials) and Table 2. The O–H stretching vibration of the phenolic hydroxyl group of the ligand H2L exhibited a strong band at about 3427 cm⁻¹, and at the same time, the [ZnII2–SmIII2] complex exhibited a strong absorption band at about 3400 cm⁻¹ due to the O–H stretching vibration band on the crystalline methanol molecules, which was consistent with the results of the element analysis. A stretching vibration band of the free ligand H2L was observed at 1613 cm⁻¹, which corresponds to the stretching vibration band of the C=N double bond. That of the [ZnII2–SmIII2] complex was observed at

| Compound | The [ZnII2–SmIII2] Complex |
|----------|-----------------------------|
| Index ranges | -44 ≤ h ≤ 44, -10 ≤ k ≤ 10, -26 ≤ l ≤ 26 |
| Reflections collected | 25,740 |
| Independent reflections | 6310 |
| Rint | 0.0291 |
| Completeness to θ | 99.7% (θ = 26.0°) |
| Data/restraints/parameters | 6310/100/473 |
| GOF | 1.036 |
| R [I > 2σ(I)] | R1 = 0.0333, wR2 = 0.0747 |
| Largest differences peak and hole (e Å⁻³) | 0.92/−0.64 |

R₁ = Σ||Fo|−|Fc||ΣFo|, wR₂ = [Σw(Fo²−Fc²)²/Σw(Fo²)²]¹/², w = [σ²(Fo²)+(0.0289)Fo²+31.396P]⁻¹, where P = (Fo² + 2FoFc + Fc²)/3, GOF = [Σw(Fo²−Fc²)²/|Foobs−Foparam|]¹/².
1604 cm\(^{-1}\) because the N atom provided a lone pair of electrons to the Zn\(^{II}\) ions, thereby reducing the bond intensity of the C=N double bond and causing a red shift, indicating that the nitrogen atoms of the C=N double bond in H\(_2\)L were coordinated with the Zn\(^{II}\) ions. In addition, a typical Ar–O stretching vibration band was observed at 1250 cm\(^{-1}\) in the spectrum of the free ligand H\(_2\)L. The Ar–O stretching band shifted to a lower frequency of about 1216 cm\(^{-1}\) in the spectrum of the [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex, indicating that M–O bonds were formed between the phenolic oxygen atoms and the metal (II/III) ions.

Table 2. Main infrared data (cm\(^{-1}\)) for H\(_2\)L and the [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex.

| Compound                      | \(\nu\)(O-H) | \(\nu\)(C=N) | \(\nu\)(Ar-O) | \(\nu\)(C=C) |
|-------------------------------|---------------|---------------|---------------|---------------|
| H\(_2\)L                      | 3427          | 1613          | 1250          | 1468          |
| The [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex | 3400          | 1607          | 1216          | 1461          |

3.3. UV–Vis Spectra

The UV–Vis absorption spectra of H\(_2\)L and the [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex were measured at room temperature in concentrations of 1.0 \(\times\) 10\(^{-5}\) M, respectively. As depicted in Figure 2, the absorption spectrum of H\(_2\)L mainly exhibited two relatively strong absorption peaks, which appeared at approximately 270 and 319 nm. The former absorption peak at 270 nm was part of the \(\pi-\pi^*\) transition of the benzene ring conjugate system, while the latter absorption peak at 319 nm was part of the \(\pi-\pi^*\) transition of the chromophore C=N groups. In the [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex, the absorption peak formed by the \(\pi-\pi^*\) transition of the benzene ring conjugate system still existed, but only moved to a high wave number at 3 nm. The absorption peak at 319 nm disappeared, and a new absorption peak appearing at approximately 343 nm was found in the [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex. This peak may be part of the L→M charge-transfer transition [68], which is characteristic absorption peak of an N\(_2\)O\(_2\)-donor metal complex.

![Figure 2. The UV–Vis spectra of H\(_2\)L and the [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] complex.](image)

3.4. Crystal Structure and Supramolecular Interactions

As depicted in Figure 3a, two chemically and crystallographically identical dinuclear [Zn(L)Sm] units and one 4,4′-bipyridine linker were self-assembled to obtain a heterotetranuclear [Zn\(^{II}\)\(_2\)-Sm\(^{III}\)\(_2\)] salamo-like complex ([Zn(L)Sm(NO\(_3\))\(_3\)](4,4′-bipy))\(_2\)CH\(_3\)OH. The coordination polyhedrons are depicted in Figure 3b. The coordination environments of the two Zn\(^{II}\) and Sm\(^{III}\) ions were the same in each heterobinuclear [Zn(L)Sm(NO\(_3\))\(_3\)] unit. Compared with the previously reported Salamo-type Zn–La complex [65], the coordination environments of Zn\(^{II}\) ions are similar, while the coordination
environments of Sm\textsuperscript{III} ions are different. The penta-coordinated Zn\textsuperscript{II} ion (Zn1) was located at the N\textsubscript{2}O\textsubscript{2} coordination cavity (N1, N2, O2, and O5) of the (L)\textsuperscript{2-} unit, and the axial position was occupied by the nitrogen atom (N6) of 4,4′-bipyridine, bearing a slightly twisted square pyramidal coordination geometry with \( \tau = 0.1845 \)\textsuperscript{[27,69]}. The four atoms (N1, N2, O2, and O5) in the N\textsubscript{2}O\textsubscript{2} cavity of the ligand formed an equatorial plane of the square pyramid, and the nitrogen atom (N6) on the pyridine ring occupied the apex of the square pyramid. The deca-coordinated Sm\textsuperscript{III} ion (Sm1) was coordinated to the O\textsubscript{4} coordination environment (O2, O5, O1, and O6) of the (L)\textsuperscript{2-} unit, and the six oxygen atoms (O7, O8, O10, O11, O13, and O14) from the three bidentate nitrates. Therefore, the Sm\textsuperscript{III} ion (Sm1) bore a twisted double-capped tetragonal anti-prism geometry. The 4,4′-bipyridine was located in the inversion center of two heterobinuclear [Zn\textsubscript{II}(L)Sm(NO\textsubscript{3})\textsubscript{3}] units. Referring to Figure S2, the dihedral angle of the two pyridine rings (N6–C20–C21–C22–C23–C24 and N6\textsuperscript{#1}–C20\textsuperscript{#1}–C21\textsuperscript{#1}–C22\textsuperscript{#1}–C23\textsuperscript{#1}–C24\textsuperscript{#1}) of 4,4′-bipyridine was about 36.33(5)°, exhibiting that the two pyridine rings were non-planar. This result was different from the coplanarity of the two pyridine rings in the Zn–La complex, which indirectly indicated that the formation process of the [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] complex was more prone to torsion and had a better chance of forming a novel structure complex. Symmetry transformations were used to generate equivalent atoms: \#1 = 1 – x, \( + \) y, \( 1/2 – z \). The essential bond lengths and angles of the [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] complex are summarized in Table S1.

Figure 3. (a) Crystal structure diagram of the [Zn\textsuperscript{II}_2–Sm\textsuperscript{III}_2] complex (30% probability displacement ellipsoids, a hydrogen atom, and two free methanol molecules are omitted for clarity), (b) Coordination pattern diagram of Zn\textsuperscript{II}/Sm\textsuperscript{III} ions and 4,4′-bipyridine.
For the supramolecular structure of the [Zn$_{II}^2$–Sm$_{III}^2$] complex, the relevant data are summarized in Table 3. There were two pairs of intramolecular hydrogen-bonding interactions (C20–H9B···O13 and C24–H24···O4) in the [Zn$_{II}^2$–Sm$_{III}^2$] complex, as depicted in Figure 4a,b. The [Zn$_{II}^2$–Sm$_{III}^2$] complex included four pairs of intermolecular hydrogen-bondings (C12–H12···O9, C23–H23···O11, C23–H23···O14, and C24–H24···O11), with C23–H23 and C24–H24 of the pyridine ring and C12–H12 on the C=N group acting as donors for the hydrogen-bondings, and the oxygen atoms on the bidentate nitrate groups serving as hydrogen-bonding acceptors [70]. A structurally stable two-dimensional (2-D) supramolecular structure was formed along the alternating current (ac) direction via intermolecular hydrogen-bonding interactions. As depicted in Figure 4c, finally, a three-dimensional (3-D) central perspective structure was formed.

**Table 3.** Hydrogen-bonding interactions (Å, °) of the [Zn$_{II}^2$–Sm$_{III}^2$] complex.

| D–H···A | d(D–H) | d(H···A) | d(D···A) | d(∠D–H···A)| Symmetry Code |
|---------|--------|---------|---------|------------|---------------|
| C20–H9B···O13 | 0.93   | 2.38    | 2.996(6)| 123       |               |
| C24–H24···O4    | 0.93   | 2.49    | 3.298(6)| 146       |               |
| C12–H12···O9    | 0.93   | 0.93    | 3.291(6)| 167, 1/2   | −x, −1/2, −y, 1/2+z |
| C23–H23···O11   | 0.93   | 2.59    | 2.53    | 120, x, 1−y, −1/2 + z |
| C23–H23···O14   | 0.93   | 2.53    | 2.47    | 127, x, 1−y, −1/2 + z |
| C24–H24···O11   | 0.93   | 2.47    | 2.47    | 127, x, 1−y, −1/2 + z |

**Figure 4.** (a) Intramolecular hydrogen-bonding interactions of the [Zn$_{II}^2$–Sm$_{III}^2$] complex, (b) two-dimensional (2-D) supramolecular structure of the [Zn$_{II}^2$–Sm$_{III}^2$] complex, (c) three-dimensional (3-D) central perspective structure of the [Zn$_{II}^2$–Sm$_{III}^2$] complex.
3.5. Fluorescent Properties

The solid fluorescence spectrum of the [Zn\(^{II}\)\_2–Sm\(^{III}\)\_2] complex is shown in Figure 5. This emission spectrum showed that the [L\_Zn\(^{2+}\)] units and rare-earth ions (Sm\(^{III}\)) exhibited co-luminescence in the solid state.

![Figure 5. The solid fluorescence spectrum of the [Zn\(^{II}\)\_2–Sm\(^{III}\)\_2] complex.](image)

The ethanol solutions of H\(_2\)L and the [Zn\(^{II}\)\_2–Sm\(^{III}\)\_2] complex were prepared in concentrations of 1.0 × 10\(^{-5}\) M, respectively, and the fluorescence spectra were measured at an excitation wavelength of 320 nm at room temperature (Figure 6a). When the excitation wavelength was 320 nm, the emission spectrum of the ligand H\(_2\)L exhibited a broad emission band at 397 nm, which can be assigned to the \(\pi–\pi^*\) transitions in the ligand H\(_2\)L. For the [Zn\(^{II}\)\_2–Sm\(^{III}\)\_2] complex, in addition to a large broad peak at 401 nm, several visible emission bands of Sm\(^{III}\) ions as the lanthanide ions were observed at 564, 598, and 644 nm. These peaks correspond to the energy level transitions of \(^4G_{\frac{5}{2}}–^6H_{\frac{5}{2}, \frac{7}{2}, \frac{9}{2}}\), respectively. The appearance of characteristic emission peaks indicated that the ligand H\(_2\)L can act as an antenna group, sensitizing the emission of Sm\(^{III}\) ions through the [L\_Zn\(^{2+}\)] units, thereby making the luminescence of Sm\(^{III}\) ions sensitive [27].

The fluorescence titration spectra of H\(_2\)L and the [Zn\(^{II}\)\_2–Sm\(^{III}\)\_2] complex in ethanol solution are depicted in Figure 6b,c. In the fluorescence titration experiment with the [Zn\(^{II}\)\_2–Sm\(^{III}\)\_2] complex, the fluorescence emission peak intensity decreased gradually during the addition of Zn\(^{II}\) ions (1.0 × 10\(^{-3}\) M) to the free ligand H\(_2\)L (1.0 × 10\(^{-5}\) M). When Zn\(^{II}\) ions started from 5 \(\mu\)L and gradually increased to 55 \(\mu\)L in increments of 5 \(\mu\)L, the fluorescence intensity began to stabilize and the titration reached the end point, indicating that the coordination of Zn\(^{II}\) ions with H\(_2\)L was completed and the stoichiometric ratio was 1:1. Immediately thereafter, when the amount of Sm\(^{III}\) ions added reached the equivalent of 1.0 equivalent, the fluorescence intensity was no longer lowered, indicating the coordination of the Sm\(^{III}\) ions with the [L\_Zn\(^{2+}\)] units. This titration curve also clearly indicated that the stoichiometric ratio of H\(_2\)L:Zn\(^{II}\):Sm\(^{III}\) was 1:1:1. This result also corresponds to the coordination of the actually obtained crystal structure.
Figure 6. (a) Fluorescence spectra of H$_2$L and the [Zn$^{II}$_2–Sm$^{III}$_2] complex in ethanol solution (1.0 × 10$^{-5}$ M), (b) Fluorescence spectra of H$_2$L changes after the addition of Zn(OAc)$_2$·2H$_2$O, (c) Fluorescence spectra of the changes in [L–Zn$^{2+}$] upon addition of Sm(NO$_3$)$_3$·6H$_2$O.
3.6. Fluorescence Print Imaging

From the fluorescence spectra, Sm^{III} ions were effectively sensitized, and exhibited characteristic excitation and emission spectra, so the [Zn^{II2}–Sm^{III2}] complex had the pink light that is characteristic emission of Sm^{III} ions. Therefore, we attempted to refer this special property to fluorescent print imaging. As shown in Figure 7, the fluorescence lifetime was measured to further investigate the luminescent properties of H_2L and the [Zn^{II2}–Sm^{III2}] complex. It was determined from the correlation data of the spectra that the fluorescence lifetime of H_2L was 1.5222 ns, and for the [Zn^{II2}–Sm^{III2}] complex, the decay of the excited state became shorter (1.5048 ns). Two bottles with the same concentrations (2.5 × 10^{-5} M) and volumes of the ligand H_2L and the [Zn^{II2}–Sm^{III2}] complex were selected as research objects. Under natural light, both the ligand H_2L and the [Zn^{II2}–Sm^{III2}] complex exhibited a colorless and transparent state (Figure 8a). Under 365 nm ultraviolet (UV) light, the ligand H_2L showed a pale light, at which time the [Zn^{II2}–Sm^{III2}] complex showed a pink light distinctly from the ligand, as depicted in Figure 8b. These excellent optical properties could easily allow for the [Zn^{II2}–Sm^{III2}] complex to be used in fluorescent print imaging under specific conditions. Compared to many other nanoparticle inks, the [Zn^{II2}–Sm^{III2}] complex had a lower concentration (0.44 mg/mL) [71–73], which also reflects the environmental friendliness and economy of selecting such a complex.

![Graph showing fluorescence lifetime of H_2L and the [Zn^{II2}–Sm^{III2}] complex.](image)

**Figure 7.** The Fluorescence lifetime of H_2L and the [Zn^{II2}–Sm^{III2}] complex.

![Color contrast of H_2L and its [Zn^{II2}–Sm^{III2}] complex in ethanol solution under natural light (a), Under 365 nm UV light (b), Fluorescent imaging with H_2L labeling (c), Fluorescent imaging of the [Zn^{II2}–Sm^{III2}] complex (d).](image)

**Figure 8.** Color contrast of H_2L and its [Zn^{II2}–Sm^{III2}] complex in ethanol solution under natural light (a), Under 365 nm UV light (b), Fluorescent imaging with H_2L labeling (c), Fluorescent imaging of the [Zn^{II2}–Sm^{III2}] complex (d).
In order to reduce the interference from background UV fluorescence, a non-fluorescent filter paper was used as the printing paper. The fluorescent imaging of H$_2$L and the [Zn$^{II}$_2–Sm$^{III}$_2] complex solutions as the ink are shown in Figure 8c,d. The word “Crystals” was marked with each of the H$_2$L and the [Zn$^{II}$_2–Sm$^{III}$_2] complex on the same filter paper and dried in an oven. When observed under 365 nm UV light, there was almost no pattern at the mark with the ligand solution, and a pink image of “Crystals” was displayed at the mark with the [Zn$^{II}$_2–Sm$^{III}$_2] complex. This further confirmed that the [Zn$^{II}$_2–Sm$^{III}$_2] complex can be used to create a fluorescent print imaging.

3.7. DFT Calculation

Molecular orbital calculations were performed by density functional theory. The DFT method used was the gradient-corrected functional proposed by B3LYP, and basis sets with SDD were used to expand the Kohn–Sham orbitals. Surface plots of some selected molecular orbitals of H$_2$L and the [Zn$^{II}$_2–Sm$^{III}$_2] complex are shown in Figure 9. It is worth noting that the HOMO and LUMO of the [Zn$^{II}$_2–Sm$^{III}$_2] complex were detected in both ligands; while the HOMO−1 was mainly concentrated in one of the two ligands, the LOMO+1 was mainly distributed in the orbit of 4,4′-bipyridine. Compared with the ligand H$_2$L, the molecular orbital energies occupied by the [Zn$^{II}$_2–Sm$^{III}$_2] complex are all negative, indicating that it is more chemically stable. The frontier molecular orbital energies of the ligand H$_2$L are $E_{\text{HOMO}}$ = −2.6563 eV and $E_{\text{LUMO}}$ = −0.4351 eV. The frontier molecular orbital energies of the [Zn$^{II}$_2–Sm$^{III}$_2] complex are $E_{\text{HOMO}}$ = −5.3891 eV and $E_{\text{LUMO}}$ = −5.2017 eV. The energy gap ($\Delta E = E_{\text{LUMO}} − E_{\text{HOMO}}$) between the HOMO and LUMO of the [Zn$^{II}$_2–Sm$^{III}$_2] complex was 0.1874 eV, which was lower than that of the ligand H$_2$L (2.2212 eV). Based on these results, electrons are more likely to transition during the formation of the [Zn$^{II}$_2–Sm$^{III}$_2] complex, resulting in a more active complex.

![Surface plots of selected molecular orbitals of H$_2$L and the [Zn$^{II}$_2–Sm$^{III}$_2] complex.](image-url)

Figure 9. Surface plots of selected molecular orbitals of H$_2$L and the [Zn$^{II}$_2–Sm$^{III}$_2] complex.
4. Conclusions

A heterotetranuclear 3d-4f complex was prepared and characterized structurally. In the \([\text{Zn}^{\text{II}}_2\text{Sm}^{\text{III}}_2]\) complex, the auxiliary ligand 4,4'-bipyridine acted as a bidentate connecting rod, introducing its pyridine nitrogen atoms, which tended to coordinate with the axial position of the Zn\text{II} ions, further linking the two [Zn(L)Sm] units. The Zn\text{II} ion (Zn1) was located in the coordination environment of the N\text{2}O2 donor and considered to have a twisted square pyramidal geometry (\(\tau = 0.1845\)). In addition, sensitizing the emission of Sm\text{III} ions through the [L–Zn\text{II}] units, the [Zn\text{II}2–Sm\text{III}2] complex exhibited a pink characteristic fluorescence that can be applied to fluorescent print imaging under specific conditions. The molecular orbital energy levels of the ligand H2L and the [Zn\text{II}2–Sm\text{III}2] complex were discussed by DFT calculation. The calculated results further indicated that the lower the energy gap, the more active and the easier it is to develop in a stable direction.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/9/11/602/s1, Figure S1: Infrared Spectra of H2L and its [Zn\text{II}2–Sm\text{III}2] complex, Figure S2: The dihedral angle between the planes of the two pyridine rings of the [Zn\text{II}2–Sm\text{III}2] complex, Table S1: Essential bond lengths (Å) and angles (°) of the [Zn\text{II}2–Sm\text{III}2] complex.

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