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Author(s)	Koizuka, Toru; Kitagawa, Yuichi; Nakanishi, Takayuki; Fushimi, Koji; Hasegawa, Yasuchika
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**Highly luminescent tetranuclear Eu(III) complex  
with characteristic cavity space**

Toru Koizuka,<sup>1,2</sup> Yuichi Kitagawa,<sup>3</sup> Takayuki Nakanishi,<sup>4</sup> Koji Fushimi,<sup>3</sup> and Yasuchika Hasegawa<sup>3\*</sup>

<sup>1</sup>*Semiconductor Development Division, Nichia Corporation, 1-1 Tatsumi, Anan, Tokushima 774-0001*

<sup>2</sup>*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku,*

*Sapporo, Hokkaido 060-8628*

<sup>3</sup>*Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628*

<sup>4</sup>*Faculty of Industrial Science and Technology, Tokyo University of Science, 6-3-1, Niijuku, Katsushika-ku,*

*Tokyo, 125-8585*

E-mail: hasegaway@eng.hokudai.ac.jp

**Abstract**

Novel luminescent tetranuclear Eu(III) complex  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  (btfa: benzoyltrifluoroacetate, salbn: *N,N'*-bis(salicylidene)-1,4-butanediamine) with characteristic cavity space is reported. The Eu(III) complex excited at 480 nm exhibits the highest photosensitized emission quantum yield (36%) reported for similar previously reported tetranuclear Eu(III) complexes. The Eu(III) complex with salbn and btfa

also showed the spectral change under addition of  $K^+$  and  $Zn^{2+}$  ions. In this study, we demonstrated metal ions sensor ability of a highly luminescent Eu(III) complex.

Keywords:

Tetranuclear; complex; Luminescence; Europium; Sensor

## 1. Introduction.

Metal-organic frameworks and porous coordination polymers (MOFs and PCPs) have been used in many applications including gas adsorption/storage, separation and catalysis based on their porous cavities.<sup>1-4</sup>

Developing effective detection methods for monitoring cavity are therefore highly necessary.<sup>5-7</sup> The

lanthanide metal-organic frameworks have been recognized as excellent materials for the effective

detector because of their strong visible luminescence with narrow bandwidth.<sup>8-10</sup> At the present stage,

tetranuclear Eu(III) complexes as the basic models of PCPs have been attracted attention in soluble micro

cavity. Hamacek and coworkers reported tetrahedral tetranuclear Eu(III) complex with tripodal ligands

shows anion sensor in solution.<sup>11,12</sup> Liu and coworkers achieved the highly selective probes for both

anions and cations using tetranuclear Eu(III) complex with oxazoline-based ligands.<sup>13</sup> Fan and Yang

reported MOF type tetranuclear Eu(III) cluster showed the largest emission quantum yield (27.6%)<sup>14</sup> in

previously reported tetranuclear Eu(III) complexes.<sup>11-16</sup> Their quantum yields are relatively low compared

with the mononuclear Eu(III) complexes and coordination Eu(III) polymers.<sup>7</sup> In particular, Eu(III)

complexes with  $\beta$ -diketonate ligands show highly emission quantum yield ( $> 50\%$ ).<sup>17-19</sup> Recently, we found that Eu(III) complex composed of  $\beta$ -diketonate and Schiff base ligands exhibited strong red luminescence excited by visible light (460 nm).<sup>20</sup> Visible-light sensitized Eu(III) complex is suitable for luminescent sensor because of the demand for less-harmful sensing reagents. Synthesis of tetranuclear Eu(III) complex composed of  $\beta$ -diketonate and Schiff base ligand leads to the development of highly luminescent Eu(III) complexes with sensing ability using visible light. In this study, we report that tetranuclear Eu(III) complex with characteristic porous structure exhibits highly photosensitized emission quantum yield owing to combination of Schiff base (salbn: *N,N'*-bis(salicylidene)-1,4-butanediamine) and  $\beta$ -diketonate ligands (btfa: benzoyltrifluoroacetate).

## 2. Experimental

**General Methods.** <sup>1</sup>H-NMR spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub> on a JEOL ECS-400 (400 MHz) spectrometer; CD<sub>2</sub>Cl<sub>2</sub> ( $\delta_{\text{H}} = 5.28$  ppm) was used as the internal reference. Elemental analyses were performed using MICRO CORDER JM10. Thermogravimetric analyses (TGA) were performed using an EXSTAR 6000 TG/DTA 6300 instrument (Seiko Instruments Inc.). Emission spectra were measured using a Horiba FluoroLog<sup>®3</sup> spectrofluorometer. Photosensitized emission quantum yield was measured using a FP-6300 spectrofluorometer with an integration sphere (ILF-533). Infrared spectrum was recorded with a JASCO FTIR-4600 spectrometer.

**Single-Crystal X-ray crystallography.** The orange crystal of the complex was mounted on a MiTeGen micromesh using paraffin oil. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71075 \text{ \AA}$ ) at  $-150^\circ\text{C}$ . Corrections for decay and Lorentz polarization effects were made based on empirical absorption correction. The structure was solved by direct methods using *SHELXS-97*<sup>21</sup> and expanded using Fourier techniques. Structure refinements were performed by the full-matrix least-squares techniques in *SHELXL-2014*.<sup>21</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding model. The *SQUEEZE* program,<sup>22</sup> which is a part of the *PLATON* package of crystallographic software,<sup>23</sup> was used to calculate the solvent-disorder area and remove its contribution to the overall intensity data because solvent molecules in the unit cell were disordered and could not be modeled properly. All calculations were made using *CrystalStructure* (Rigaku Corporation, Tokyo, Japan, **2000-2014**), a crystallographic software package.

**Materials.** Europium chloride hexahydrate was purchased from Kanto Chemical Co., Inc. 4,4,4-trifluoro-1-phenyl-1,3-butanedione was obtained from Aldrich Chemical Company Inc. Salicylaldehyde, bis[2-(diphenylphosphino)phenyl]ether and 1,4-butanediamine were obtained from Tokyo Chemical Industry Co., Ltd. Potassium acetate and zinc acetate were purchased from Wako Pure Chemical Industries Ltd. All other solvents were reagent grade and used without further purification.

**Preparation of *N,N'*-bis(salicylidene)-1,4-butanediamine (salbn).** Salbn was prepared according to the literature.<sup>20</sup>

**Preparation of  $[\text{Eu}(\text{btfa})_3(\text{H}_2\text{O})_2]$  and  $[\text{Eu}(\text{btfa})_3(\text{DPEPO})]$  (DPEPO: bis[2-(diphenylphosphino)phenyl] ether oxide).**  $[\text{Eu}(\text{btfa})_3(\text{H}_2\text{O})_2]$  and  $[\text{Eu}(\text{btfa})_3(\text{DPEPO})]$  were prepared according to the literature.<sup>24</sup>

**Preparation of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$ .** Prepared  $[\text{Eu}(\text{btfa})_3(\text{H}_2\text{O})_2]$  (1.67 g, 2.0 mmol) was dissolved in diethyl ether (40 mL). Salbn (0.59 g, 2.0 mmol) was added to the solution. After stirring at room temperature for 24 h, the precipitates were filtered and dried in vacuo. The yellow powder was obtained. Recrystallization from diethyl ether gave orange block crystals of the title lanthanide complex.

$[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$ . Yield: 1.6 g (18%); Elemental analysis calcd (%) for  $\text{C}_{192}\text{H}_{152}\text{Eu}_4\text{F}_{36}\text{N}_8\text{O}_{32}$ : C, 52.71; H, 3.50; N, 2.56. Found: C, 52.49; H, 3.36; N, 2.50. IR (KBr): 2948-2863, 1647, 1626, 1616, 1536, 1489, 1319, 1287, 1242, 1133  $\text{cm}^{-1}$ .

### 3. Results and discussion

Single crystal of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  was obtained by recrystallization from diethyl ether solution. The chemical and crystal structures of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  are shown in Figure 1. The crystallographic data is summarized in Table 1. The coordination site of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  comprises three btfa and two salbn

ligands. Two hydroxy groups in one salbn ligand are bonded with two Eu(III) ions, which bear ring-typed tetranuclear Eu(III) complex. Intermolecular CH/F, CH/ $\pi$  and  $\pi$ - $\pi$  interactions were observed (Figure 2). We also found four trifluoromethyl groups in btfa ligands formed a small cavity in the center of ring-typed tetranuclear Eu(III) complex (Figure 1b). The cavity space (blue circle) is constructed along the c axis with a window size of 3.1 Å (F-F distance), which is relatively small in comparison with previous tetranuclear complex.<sup>11-13,25</sup> The space composed of fluorine atoms is expected to interact with metal ions.

Coordination geometry around Eu(III) ion is related to radiative rate constant and emission quantum efficiency.<sup>18</sup> The continuous shape measure factor  $S$  was calculated to estimate distortion degree of the coordination structure in the first coordination sphere based on the crystal structure data. The  $S$  value is given by following equation.

$$S = \min \frac{\sum_k^N |Q_k - P_k|^2}{\sum_k^N |Q_k - Q_0|^2} \times 100 \quad (1),$$

where  $Q_k$  is the vertices of an actual structure,  $Q_0$  is the center of mass of an actual structure,  $N$  is the number of vertices and  $P_k$  is the vertices of an ideal structure.<sup>26</sup> The 8-coordinated lanthanide complexes exhibit square antiprism (SAP, point group:  $D_{4d}$ ), trigonal dodecahedron (TDH, point group:  $D_{2d}$ ) or biaugmented trigonal prism (BTP, point group:  $C_{2v}$ ) structures, according to evaluation of the  $S$  values. From the calculation,  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  is categorized to be asymmetric coordination geometry of TDH ( $D_{2d}$ ) structure, which is expected to show highly efficient luminescence (Table 2).<sup>18</sup>

Emission spectrum of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  in solid state is shown in Figure 3. The emission bands at 578, 592, 615, 652, and 698 nm were attributed to the 4f–4f transitions of Eu(III) ( $^5\text{D}_0$ - $^7\text{F}_J$ ;  $J = 0-4$ ). The photosensitized emission quantum yields of tetranuclear Eu(III) complex excited at 480 nm was estimated to be 36%, which is the highest photosensitized quantum yields in tetranuclear Eu(III) complexes.<sup>11-16</sup>

In order to evaluate a cation sensor ability of Eu(III) complex, potassium and zinc acetate (10 mM) were added in ethanol solution with  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  (10 mM). The emission spectra of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  with  $\text{K}^+$  and  $\text{Zn}^{2+}$  ions in ethanol are shown in Figure 4. The spectra were normalized with respect to the magnetic dipole transition intensity at 592 nm (Eu:  $^5\text{D}_0$ - $^7\text{F}_1$ ), which is known to be insensitive to the environment surrounding Eu(III) ion.<sup>27, 28</sup> The normalized emission intensity at 615nm ( $^5\text{D}_0$ - $^7\text{F}_2$ ) of Eu(III) complex is decreased under addition of  $\text{K}^+$  or  $\text{Zn}^{2+}$  ion. In general, the emission intensity at  $^5\text{D}_0$ - $^7\text{F}_2$  is depended on coordination geometry around Eu(III) ions. These results indicate that tetranuclear  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  is transformed from asymmetrical to symmetrical coordination structures around Eu(III) ions by addition of inorganic ions.

We also found broad emission band at around 450 nm of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  with  $\text{Zn}^{2+}$  ion. Yuko Hasegawa has reported Schiff-based Eu complex with  $\text{Zn}^{2+}$  ion in  $\text{CHCl}_3$  shows blue emission.<sup>28</sup> In our experiment,  $\text{Zn}^{2+}$  ion is captured by salbn parts. Mononuclear  $[\text{Eu}(\text{btfa})_3(\text{DPEPO})]$  (DPEPO: bis[2-(diphenylphosphino)phenyl] ether oxide) does not show the spectral change under addition of  $\text{K}^+$  ion (Figure 5). To clarify the sensing mechanism, we performed  $^{19}\text{F}$ -NMR measurements of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  (ethanol-d<sub>6</sub>, 10 mM),  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  (ethanol-d<sub>6</sub>, 10 mM) with  $\text{K}^+$  (0.2 eq), and



[Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub> (ethanol-d<sub>6</sub>, 10 mM) with Zn<sup>2+</sup> (0.2 eq) (Figure S1). The NMR signal of [Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub> with Zn<sup>2+</sup> is similar with that of [Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub> (-80.1 ppm), indicating that Zn<sup>2+</sup> ions is not fixed in cavity space of tetranuclear [Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub>. On the other hand, the NMR signal of [Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub> with K<sup>+</sup> is slightly shifted to low magnetic field side (-79.8 ppm) and significantly broadened, which originates from exchange interaction between fluorine atoms and K<sup>+</sup>. The characteristic cavity space in [Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub> is considered to provide the sensing ability of K<sup>+</sup> ions.

#### **4. Conclusion**

In this study, we successfully synthesized tetranuclear Eu(III) complex with characteristic cavity space. The characteristic cavity space provided the sensing ability of potassium ion based on visible light absorption. The tetranuclear Eu(III) complex is expected to be useful for novel luminescent metal ion sensor.

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## Notes

The Cambridge Crystallographic Data Centre provides the supplementary crystallographic data for

[Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub> (CCDC-No. 1836246). This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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### Figure caption

**Figure 1.** (a) Chemical structure of tetranuclear  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$ , (b) ORTEP view of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$  (blue circle is small cavity) and (c) packing structure of  $[\text{Eu}(\text{btfa})_3(\text{salbn})]_4$ .

**Figure 2.** Intermolecular (a) CH/F interactions (red line), (b) CH/ $\pi$  interactions (blue line) and (c)  $\pi$ - $\pi$  interactions (green line) of the tetranuclear Eu(III) complex.

**Figure 3.** Emission (right) and excitation (left) spectra of Eu(III) complex excited at 480 nm in solid state at room temperature.

**Figure 4.** Emission spectra of a) Eu(III) complex in ethanol (10 mM), b) Eu(III) complex in ethanol (10 mM) with potassium acetate (0.2 eq), and c) Eu(III) complex in ethanol (10 mM) with zinc acetate (0.2 eq) excited at 380 nm at room temperature.

**Figure 5.** Emission spectra of a) [Eu(btfa)<sub>3</sub>(DPEPO)] in ethanol (0.2 mM, black line) and b) [Eu(btfa)<sub>3</sub>(DPEPO)] in ethanol (0.2 mM with potassium acetate, 0.2 eq, red broken line) excited at 380 nm at room temperature.

Table 1. X-ray crystal data of the Eu(III) complex

	<b>[Eu(btfa)<sub>3</sub>(salbn)]<sub>4</sub></b>
<b>chemical formula</b>	C <sub>192</sub> H <sub>152</sub> Eu <sub>4</sub> F <sub>36</sub> N <sub>8</sub> O <sub>32</sub>
<b>fw</b>	4375.13
<b>crystal system</b>	tetragonal
<b>space group</b>	<i>P</i> 4̄ (no. 81)
<b><i>a</i> (Å)</b>	28.5364(6)
<b><i>c</i> (Å)</b>	11.7218(3)
<b>vol. (Å<sup>3</sup>)</b>	9545.4(4)

<b>Z</b>	2
<b>d<sub>calcd</sub> (g cm<sup>-3</sup>)</b>	1.522
<b>temp (°C)</b>	-150
<b>μ<sub>Mo Kα</sub> (cm<sup>-1</sup>)</b>	13.998
<b>max 2θ (deg)</b>	55.0
<b>no. of reflns collected</b>	84669
<b>no. of independent reflns</b>	21790
<b>R<sub>int</sub></b>	0.0764
<b>R<sub>1</sub></b>	0.0495
<b>wR<sub>2</sub></b>	0.1063
<b>Goodness of Fit</b>	1.020

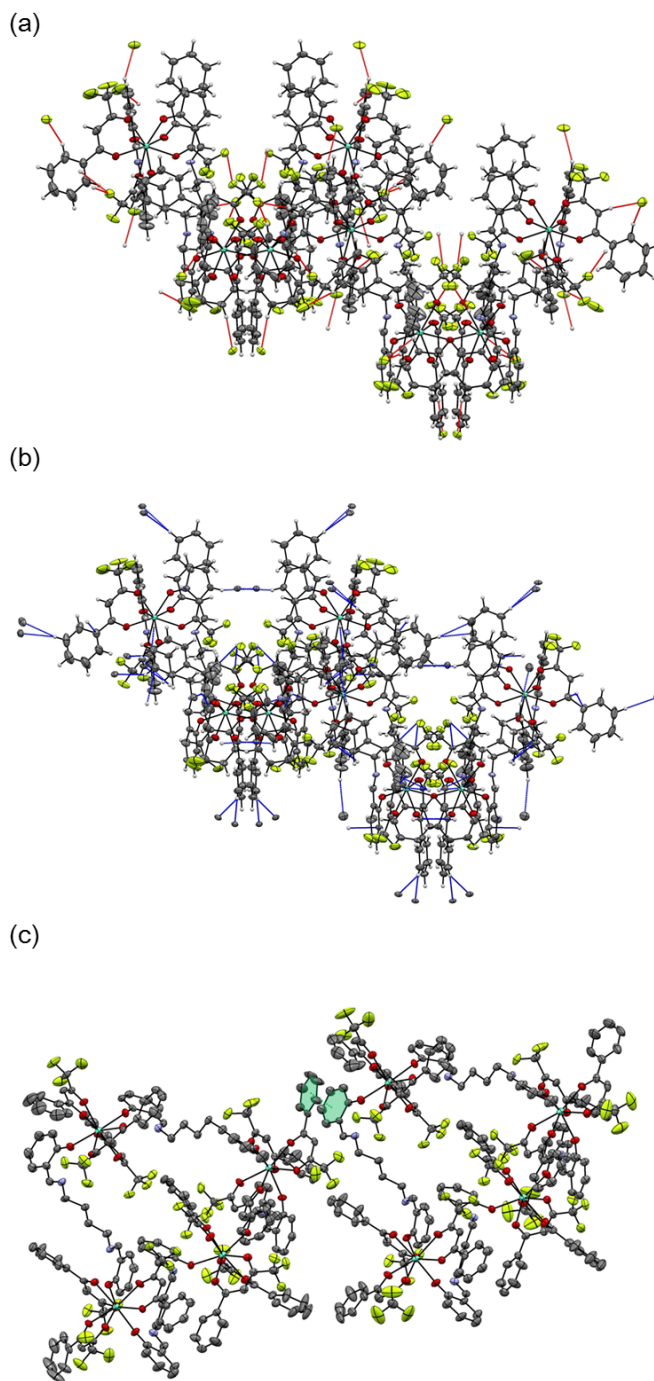
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Table 2. S-factors of the tetranuclear Eu(III) complex

Eu	SAP(D <sub>4d</sub> )	TDH(D <sub>2d</sub> )	BTP(C <sub>2v</sub> )
1	1.872	1.209	1.249
2	1.872	1.209	1.249
3	1.872	1.209	1.249
4	1.872	1.209	1.249

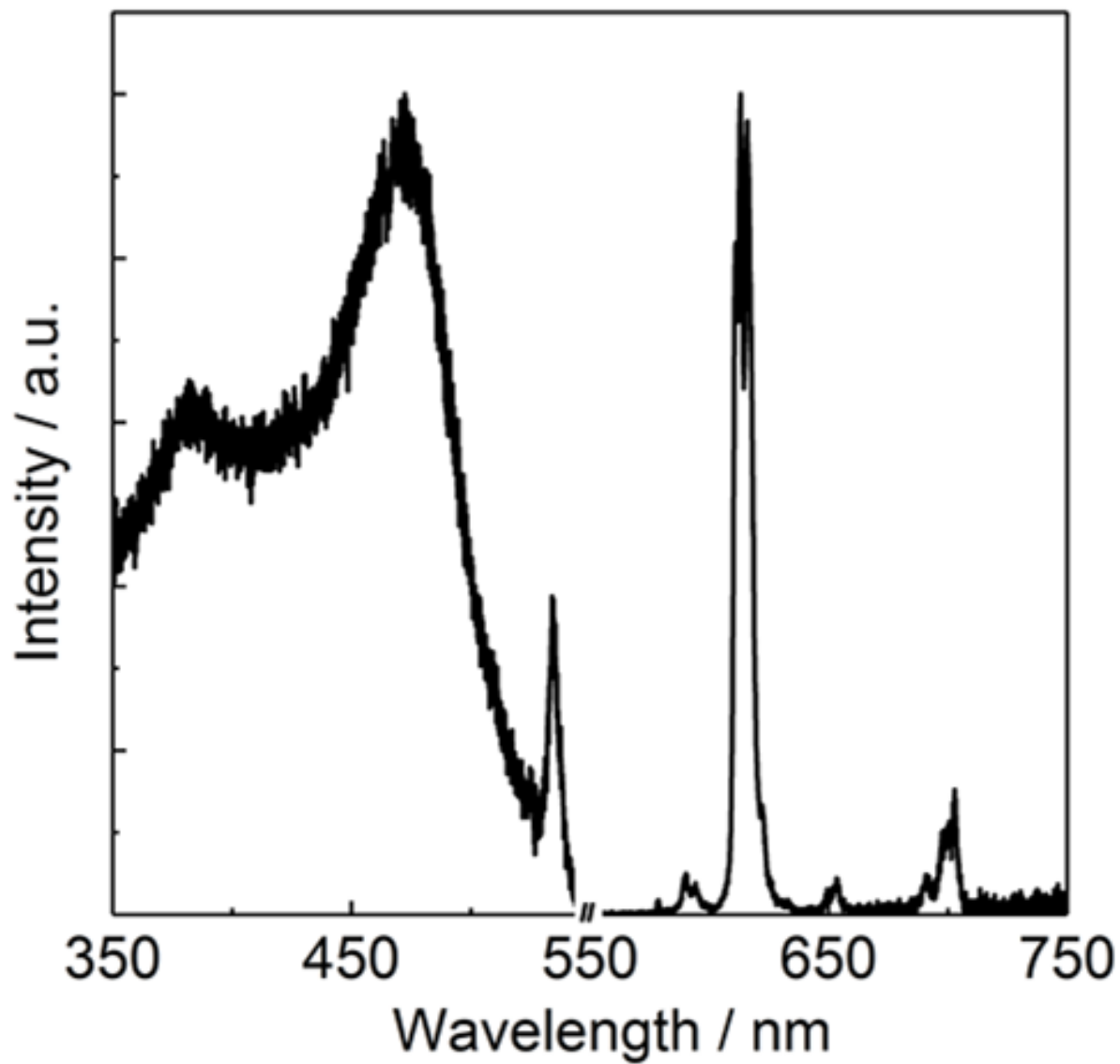


**Figure 2.**

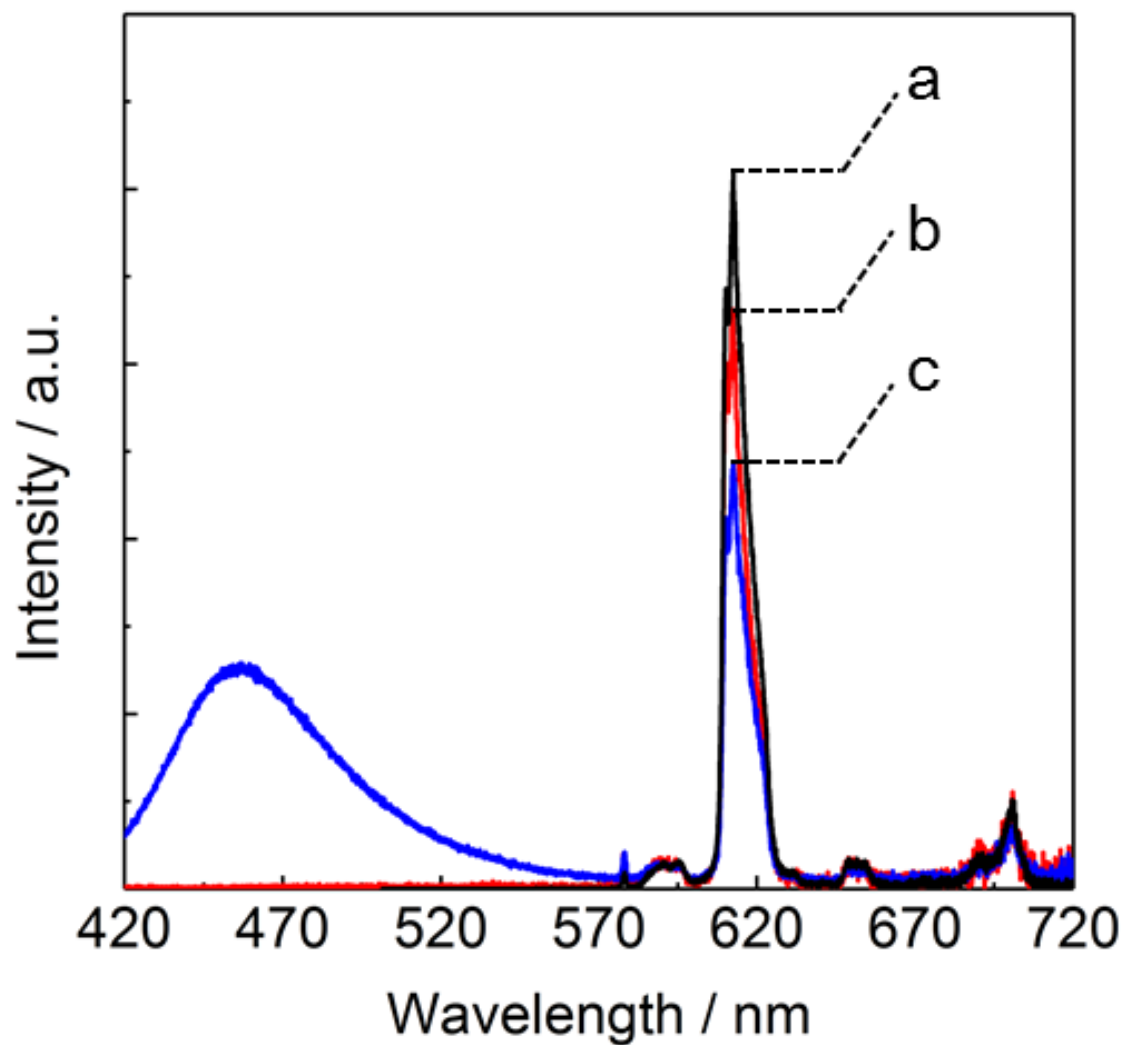




**Figure 3.**



**Figure 4.**



**Figure 5.**

