

Research Article

Synthesis, Crystal Structure, and Luminescence Properties of a New Calcium(II) Coordination Polymer Based on L-Malic Acid

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A new calcium coordination polymer $[\text{Ca}(\text{HL-MA})]_n$ ($\text{H}_3\text{L-MA}$ = L-malic acid) has been solvothermally synthesized. The structure of the newly synthesized complex has been determined by single-crystal X-ray diffraction analysis and further characterized by elemental analysis, reflectance UV-Vis & IR spectra, powder X-ray diffraction (PXRD), and thermogravimetric analysis (TGA). The single crystal structure analysis showed that the complex forms three-dimensional framework. The new Ca(II) complex has displayed very high thermal stability which was inferred from TGA and PXRD results. As far as the optical property of the new complex is concerned, the complex emitted its own characteristic sensitized luminescence.

1. Introduction

Multidimensional coordination polymers (CPs) or metal-organic frameworks (MOFs) which are derived from metal ions and organic ligands are emerged in the past two decades as an important family of porous materials with intriguing new structural topologies and potential application as functional materials [1–20]. In this regard, studies on the application aspects of MOFs such as ion exchange [1, 2], separation [3, 4], gas storage [5], catalysis [6–9], sensor [10, 11], magnetism [12, 13], photoluminescence [14, 15], drug delivery [16, 17], and proton conduction [18–20] are slowly developing. So, the synthesis and characterization of infinite one-, two-, and three-dimensional (1D, 2D, and 3D) networks has been an area of rapid growth. Apart from numerous application-oriented studies of CPs, considerable attention has also been devoted to their structures that were shown to change broadly from simple discrete species to complicated supramolecular networks depending on the nature of metal ion, ligand substituents, stoichiometry, and with the presence of additional components [21, 22].

On the other hand, the use of carboxylates can generate a large number of coordination polymeric complexes composed of chains, sheets, and 3D networks with an enormous variety of intriguing structural topologies [23–30]. Such systems have received considerable attention due to their fascinating properties as well as their potential applications in many fields. However, the hydroxyl polycarboxylates (HPCs) such as malate and tartrate have less been studied as building blocks in the construction of MOFs though they can display versatile coordination modes [29, 30]. In contrast to the aliphatic dicarboxylate compounds, the presence of the hydroxyl group in HPCs mostly allows the formation of five- and six-member rings which can stabilize the solid networks [31]. In particular, the naturally existing chiral L-malic acid ($\text{H}_3\text{L-MA}$) ligand, besides two terminal carboxyl groups, contains a hydroxyl group which can potentially provide an additional coordination site. In most of the malate-bridged CPs, the oxygen atoms of the alkoxy or hydroxyl groups participate in coordination along with the α -carboxyl and/or β -carboxyl groups. In addition, being an important biological

ligand, H₃L-MA has been found to have versatile coordination behaviour. Structurally characterized metal complexes of H₃L-MA include monomers [32], dimers [33], and polymeric chain complexes [34], as well as 3D coordination polymers [35].

Moreover, only a little attention has been drawn on the coordination chemistry of metal complexes with H₃L-MA ligand recently. And also, to the best of our knowledge, no attempts were made to synthesize calcium coordination polymers of H₃L-MA. With the previous background in mind, herein, we reported the synthesis, characterization, crystal structure, and photoluminescence properties of a new Ca(II) coordination polymer, [Ca(HL-MA)]_n.

2. Material and Methods

2.1. General. All chemicals were obtained from commercial sources and were used without further purification. Elemental analyses are performed on a PE-2400 CHN Elementar analyzer instrument. Reflectance UV-Vis spectra were recorded by Jasco V-630 spectrophotometer. Emission spectra were measured by Jasco F-4500 spectrofluorometer. Thermogravimetric analyses (TGA) were carried out using a DuPont TA Q50 analyzer on powder samples under flowing nitrogen gas with a heating rate of 10°C/min. Infrared (IR) spectra were recorded in the range of 400–4000 cm⁻¹ on a JASCO FT/IR-4200 spectrophotometer by using KBr disks. Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical PW3040/60 diffractometer. Mercury (version 2.4) software has been used for the simulation of theoretical peaks using single-crystal X-ray diffraction data for PXRD measurement.

2.2. Synthesis of [Ca(HL-MA)]_n. H₃L-MA (0.0804 g, 0.6 mmol), Ca(NO₃)₂·4H₂O (0.2361 g, 1.0 mmol), EtOH (5.0 mL), and H₂O (3.0 mL) were placed in a 23 mL Teflon-lined digestion bombs and stirred for 20 min at room temperature. The reaction mixture turned into homogenous solution with the pH value of 2.32. Then, the solvothermal reaction was carried out by heating the reaction mixture to 180°C for 2 days under autogenous pressure followed by slow cooling at the rate of 6°C h⁻¹ to room temperature. The colorless single crystals were collected in 79.38% (0.082 g) yield on the basis of H₃L-MA. Elemental Analysis: Found (calculated) (%) for C₄H₄CaO₅: C, 27.78 (27.91); H, 2.30 (2.34). Reflectance UV-Vis: λ_{max} (nm): 212, 299, 409. IR: ν_{max} (cm⁻¹): 3604 (w), 3456 (w), 3212 (w), 2982 (w), 2907 (w), 2820 (w), 2704 (w), 1564 (s), 1438 (s), 1398 (s), 1340 (w), 1307 (w), 1201 (m), 1107 (m), 1046 (m), 964 (w), 934 (w), 897 (w), 809 (w), 681 (s), 620 (m), 531 (m), 484 (m), 406 (w).

2.3. Crystal Structure Determination. Single-crystal X-ray diffraction data for the complex was collected on Bruker AXS KAPPA APEX II diffractometer. All data were corrected for Lorentz and polarization effects, and the program SADABS in APEX2 was used for the absorption correction [36, 37]. While the hydrogen atoms bound to carbon were placed in idealized positions, the hydrogen atoms bound to other atoms were

TABLE 1: Crystallographic data for the complex.

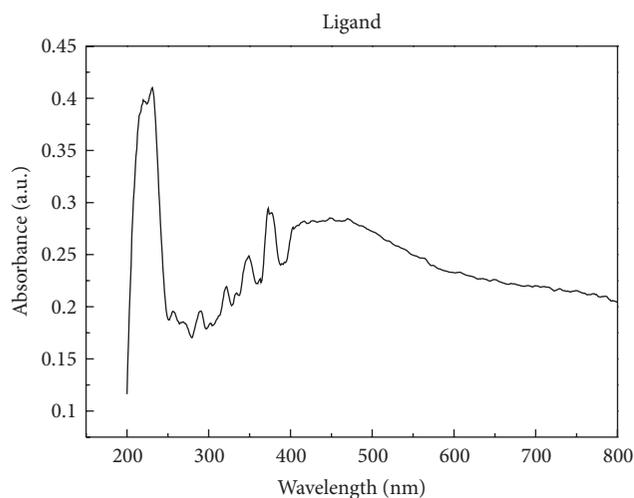
	Complex
Formula	C ₄ H ₄ CaO ₅
Formula weight	172.15
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	6.7256 (4)
<i>b</i> (Å)	7.0259 (5)
<i>c</i> (Å)	10.5577 (7)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	619.75 (2)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.845
μ (mm ⁻¹)	0.969
<i>T</i> (°C)	296 (2)
λ (Å)	0.71073
Reflections collected	4645
Independent reflections	1531
<i>R</i> (int)	0.0215
Flack parameter	0.03(3)
Goodness-of-fit on <i>F</i> ²	1.055
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0228
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0539
<i>R</i> ₁ (all data)	0.0252
<i>wR</i> ₂ (all data)	0.0549
CCDC no.	806001

TABLE 2: Selected bond lengths (Å) for the complex.

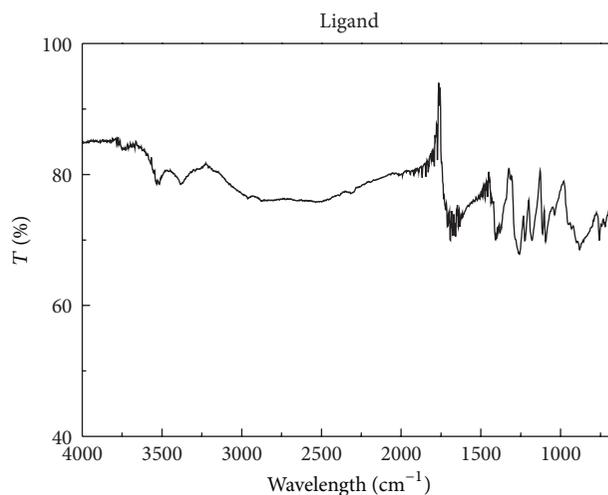
Ca(1)–O(5)	2.2974
Ca(1)–O(1) ^{#1}	2.3452
Ca(1)–O(2) ^{#2}	2.3473
Ca(1)–O(4) ^{#3}	2.3625
Ca(1)–O(3) ^{#3}	2.3851
Ca(1)–O(2) ^{#4}	2.4242
Ca(1)–O(1) ^{#4}	2.6222

Symmetry transformations used to generate equivalent atoms: for complex, no. 1: *x* – 1/2, –*y* + 1/2, –*z* + 1; no. 2: *x* + 1/2, –*y* + 1/2, –*z* + 1; no. 3: –*x* + 1/2, –*y* + 1, *z* – 1/2; no. 4: *x*, *y* + 1, *z*.

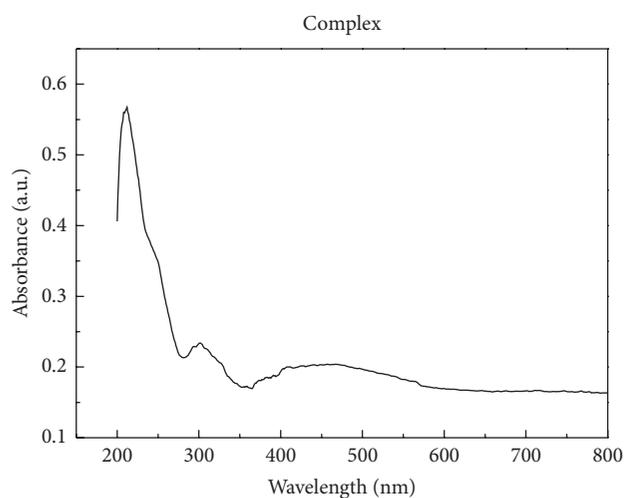
located from the difference Fourier map and were set riding on the parent atom with idealized distances. All nonhydrogen



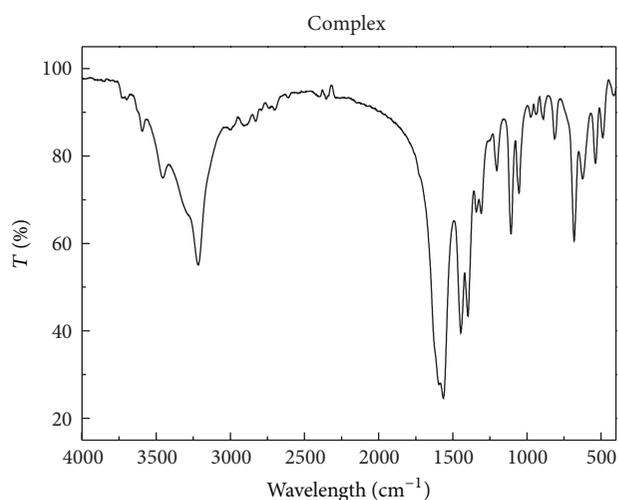
(a)



(a)



(b)



(b)

FIGURE 1: UV-Vis absorption spectra for the ligand and the complex.

FIGURE 2: FT-IR spectra of H₃L-MA and complex.

atoms were refined with anisotropic thermal parameters. All the structures were refined (weighted least squares refinement on F^2) to convergence [38]. Relevant data concerning data collection and details of the structure refinements are summarized in Table 1. Selected Ca–O bond lengths are listed in Table 2.

3. Results and Discussion

3.1. Synthesis and Characterization. The complex has been synthesized as described in the experimental section using solvothermal reaction condition. A particular (3 : 5) H₃L-MA and metal salt molar ratio has been used to prepare the complex. The complex is stable in air and insoluble in common organic solvents such as acetone, methanol, ethanol, dichloromethane, acetonitrile, chloroform, DMF, and DMSO. The elemental analysis results of the complex are in accord with

the theoretical values. The diffuse reflectance UV-Vis spectra at room temperature have been recorded for the ligand and the complex (Figure 1). On comparing the ligand spectra with the complex, the observed peaks for the complex are mainly due to the intraligand charge transfer transitions. The IR spectra of the ligand and the complex have been given in Figure 2. The IR peak shifts of the ligand in the complex gave an idea about its coordination behaviour. The exact polymeric structure of the new complex was finally confirmed by single crystal X-ray crystallographic studies.

3.2. Structural Description of $[Ca(HL-MA)]_n$. Single-crystal X-ray diffraction result shows that the structure of the complex possesses a 3D framework and crystallizes in the space group of $P2_12_12_1$. The asymmetric unit of the complex consists of one independent Ca²⁺ ion and one HL-MA ligand unit. The independent Ca²⁺ ion center is seven-coordinated

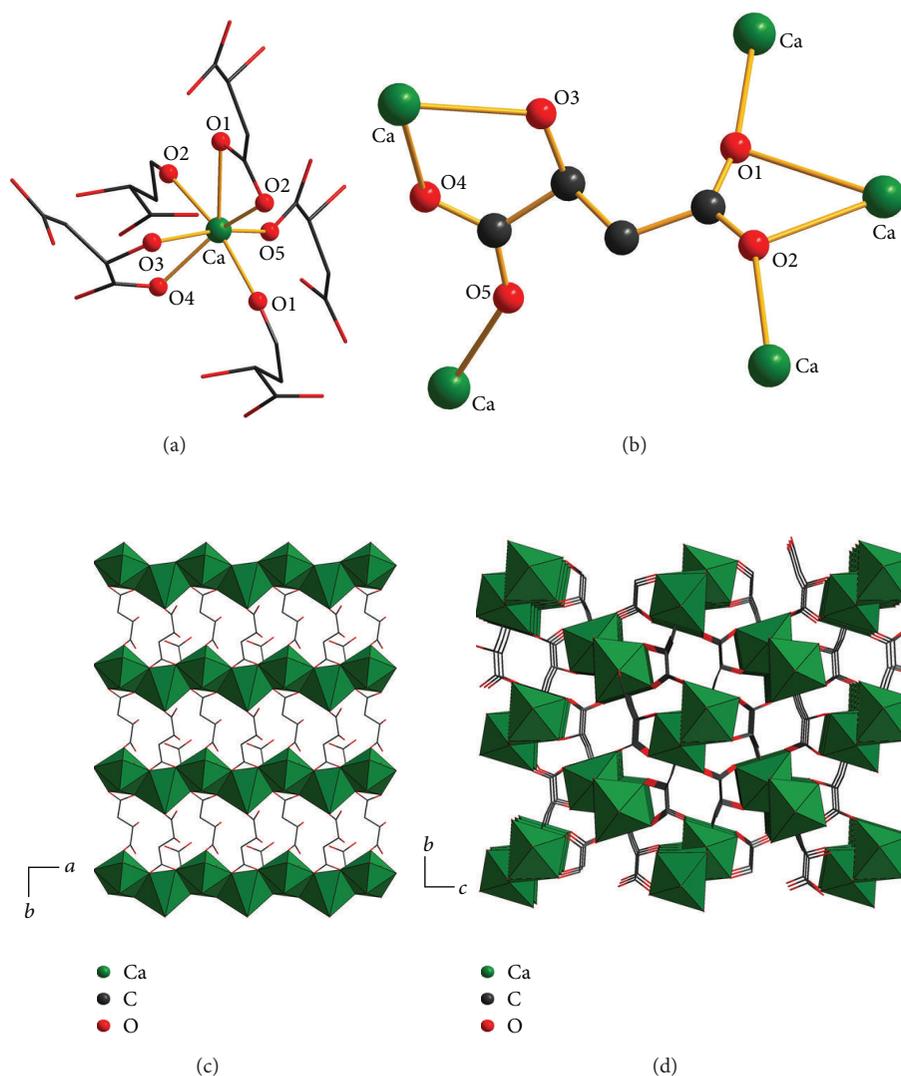


FIGURE 3: (a) The coordination spheres of calcium atom in the complex. (b) The coordination mode of the ligand in the complex. (c) The edge-sharing 2D layer in the complex. (d) The 3D network viewed along the a -axis (H atoms were omitted for clarity).

and exhibits a distorted pentagonal bipyramidal geometry; Ca^{2+} is coordinated by two α -carboxylate O atoms (O4 and O5) belonging to two HL-MA ligands, four β -carboxylate O atoms (O1, O1, O2, and O2) belonging to three HL-MA ligands, and one alkoxy O atom (O3) belonging to a similar HL-MA ligand mentioned for one of the two α -carboxylate O atoms (Figure 3(a)). The ligand in the asymmetric unit has acted as dianionic heptadentate and coordinated to five Ca^{2+} ions (Figure 3(b)). The two of the coordinated β -carboxylate O atoms (O1 and O2) form bridge between two Ca centers. The typical Ca–O bond distances range from 2.2974 (13) to 2.6222 (12) Å (Table 2). The participation of O atom (O3) of hydroxyl group (as neutral donor) in coordination along with the one α -carboxyl group O atom (O4) of the ligand forms five-member chelation ring consisting of Ca1, O4, C4, C3, and O3 atoms in the complex. As shown in Figure 3(c), the CaO_7 pentagonal bipyramidal motifs which are connected

by coordinated β -carboxylate O atoms (O1 and O2) display a 1D zigzag chain in the complex. These 1D chains which are linked together by HL-MA ligands generate the 3D structure (Figure 3(d)).

3.3. Powder X-Ray Diffraction Analysis of the Complex. The purity and homogeneity of the bulk products of the complex has been determined by the comparison of simulated and experimental X-ray powder diffraction patterns. The peak positions of the experimental patterns for the complex nearly matched with the simulated one generated from single-crystal X-ray diffraction data, as depicted in Figure 4. The differences in intensity may be due to the preferred orientation of the powder samples.

3.4. Thermal Stability. The thermal stability of the complex has been studied using thermogravimetry analysis (TGA),

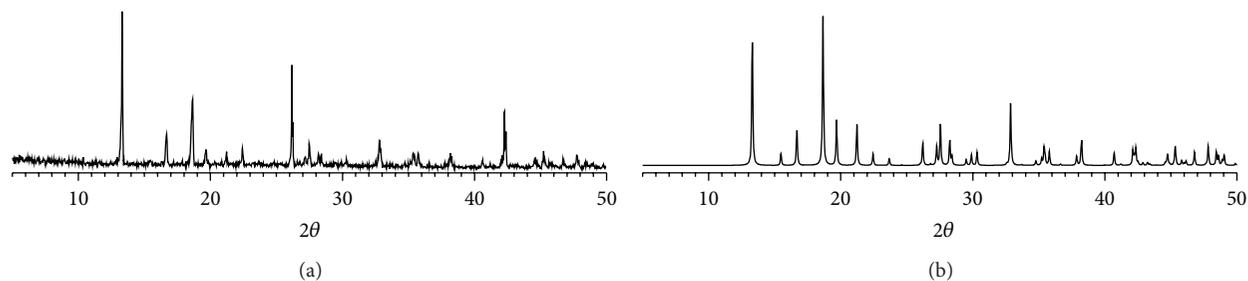


FIGURE 4: Powder XRD patterns of the complex (measured, (a); calculated, (b)).

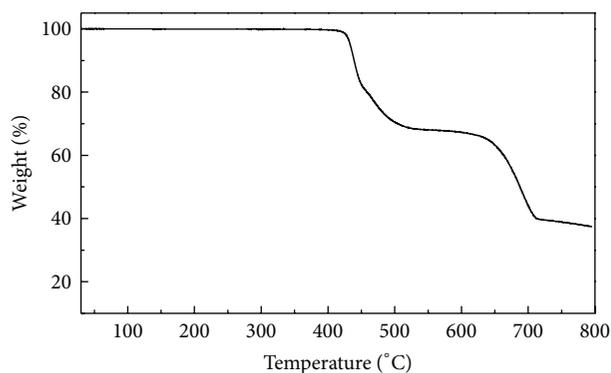


FIGURE 5: The TGA curve of the complex.

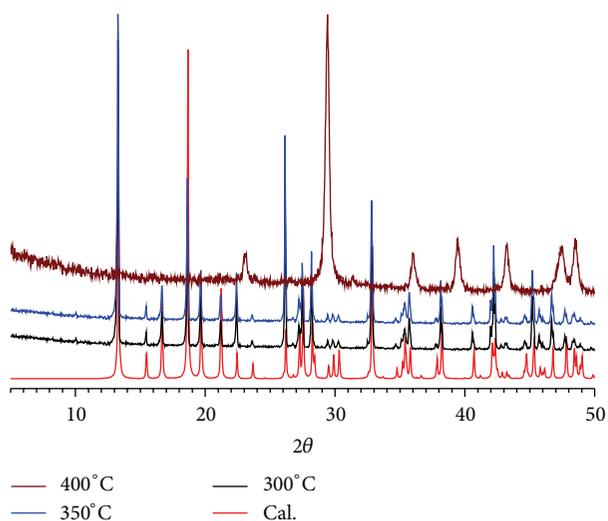


FIGURE 6: Powder XRD patterns of the complex at various temperatures.

and the TGA curves are given in Figure 5. TGA curve of the complex showed that the weight loss is observed only after 410°C which clearly indicated that the complex is very much stable up to 410°C. The thermal stability of the complex has further been studied with aid of PXRD technique. The PXRD pattern of the complex at various

temperatures confirmed once again the high thermal stability of the complex framework (Figure 6). That is, the PXRD pattern of the complex revealed that the complex is stable up to 350°C. So, it is a rare example that one coordination polymeric complex has retained its original structure up to very high temperature like 350°C. It is also to be noted that the TGA curve of the complex and the two weight losses (62.5%) observed after 410°C suggested that the coordinated ligand started to decompose step by step upon increasing the temperature to 800°C.

3.5. Photoluminescence Properties. The solid-state excitation-emission spectra of the ligand and its alkaline earth metal complexes have been studied at room temperature, and their corresponding spectra are shown in Figure 7. The strongest emission peak for the free H_3L-MA is at 416 nm with the excitation peak at 337 nm. It is attributed to the $\pi^* \rightarrow n$ transitions [39]. Compared with the free ligand, the strongest emission peak for the complex is at 418 nm, and its excitation spectrum mainly showed strong peak at 342 nm. The emission spectrum of the new complex is much similar to that of the free ligand transitions and it may be ligand-centered electronic transition perturbed by the coordination to metal ions rather than to protons. These observations suggest that the new Ca(II) coordination polymer will be a candidate for potential photoactive material.

4. Conclusion

The present investigation demonstrated the structure and properties of a new calcium coordination polymer based on chiral L-malic acid ligand via solvothermal reaction. It is interesting to note that the complex exhibits 3D framework. The TGA and PXRD results revealed that the complex can retain its original framework structure up to 350°C. It is also to be noted that the complex exhibited promising photoluminescence properties. The observed results are very much comparable with our previous report [40].

Conflict of Interests

The authors have declared that there is no conflict of interests.

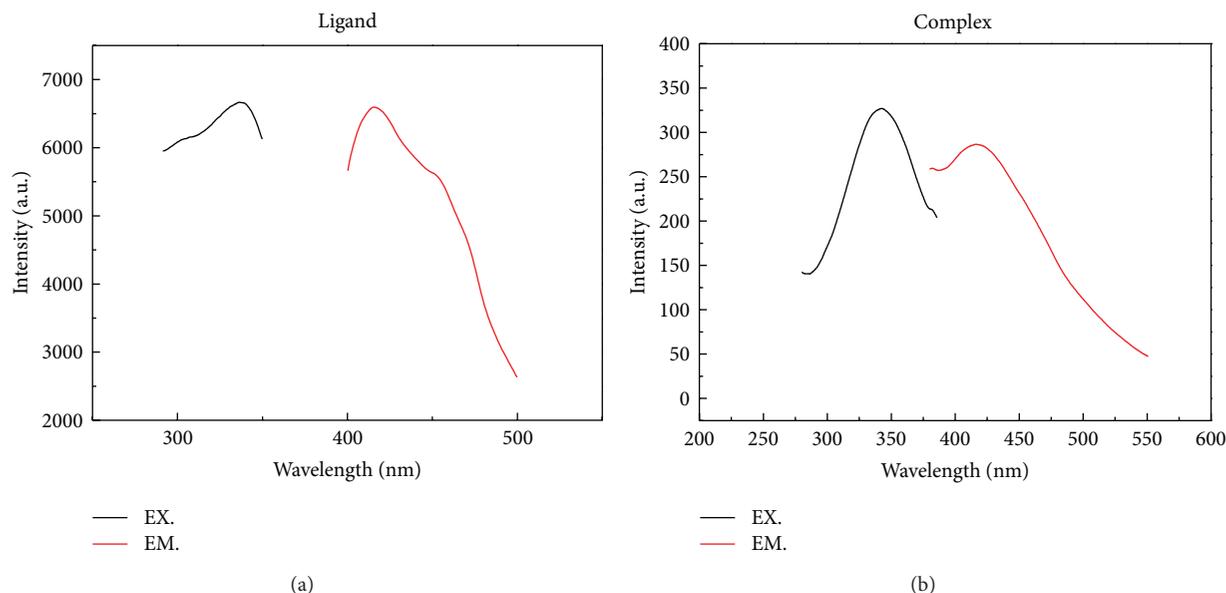


FIGURE 7: Photoluminescence emission spectra of the ligand and the complex.

Acknowledgments

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