


SYNTHESIS AND OPTICAL PROPERTIES OF THE NOVEL Ho(5-SSA), (5-SSA = 5-SULFOSALICYLIC ACID) CAGE STRUCTURE

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Abstract

In recent years, intensive studies have been made on metal-organic frameworks (MOFs) which is kind of spongy structures having excellent original architectures formed by ligands in organic forms and metal centers classified as binders. The main reason for this condensation is due to the great huge potential for such materials to be used in many technological application areas such as sensors, gas storage, photo-catalysis, organic light emitting diodes (OLEDs), solar cells (SCs) and luminescent emitting devices. The properties of the metal-organic frameworks depend on the selected organic ligands and metal ions. Therefore, new research and technology development (R-T-G) fields can be discovered with these materials that can be originally synthesized. In this work, Ho(III)-based metal-organic framework (Ho-MOF; [Ho(5-SSA)]), 5-SSA = 5-sulfosalicylic acid) was synthesized by hydrothermal method. The structural characterization has been made by powder X-ray diffraction, a room temperature solid-state UV and FT-IR spectroscopy. In addition, the solid-state photoluminescence measurements have been taken at room temperature in the UV-visible and near-infrared region (NIR) and the energy transfer mechanism from 5-SSA ligand to the Ho⁺³ ion is investigated in detail. Under the excitation of UV light (at 349 nm), 5-SSA ligand exhibited a broad navy-blue emission while its Ho-MOF complex exhibited several characteristic emissions of the Ho⁺³ ion in the UV-Visible and NIR region. The excellent luminescent performances make this compound very good candidate for efficient luminescence materials.

Keywords: Luminescence, Metal-Organic Frameworks, Holmium

ÖZGÜN Ho(5-SSA), (5-SSA = 5-SÜLFOSALİSİLİK ASİT) KAFES YAPISININ SENTEZLENMESİ VE OPTİKSEL ÖZELLİKLERİ

Öz

Birleştirici olarak adlandırılan organik yapıdaki ligandlar ile bağlayıcı olarak sınıflandırılan metal merkezlerin oluşturdukları mükemmel özgün mimariye sahip olan süngerimsi yapılar diğer bir deyişle Metal organik çerçeveler (MOÇ) üzerinde son yıllarda oldukça yoğun çalışmalar yapılmaktadır. Bu yoğunlaşmanın başlıca nedeni bu tür malzemelerin sensörler, gaz depolama, foto-katalizörler, organik ışık yayan diyotlar (OLED), güneş hücreleri (SC) ve lüminesans yayabilen aygıtlar gibi birçok teknolojik uygulama alanlarında kullanılabilme potansiyelinin yüksek olmasından ötürüdür. Metal organik çerçevelerin özellikleri, seçilen organik ligandlara ve metal iyonlarına bağlıdır. Dolayısıyla özgün olarak sentezlenebilen bu kristal malzemeler ile yeni araştırma ve teknoloji geliştirme (Ar-Te-Ge) alanları keşfedilebilmektedir. Bu çalışmada, Ho(III)-tabanlı metal-organik çerçevesi (Ho-MOÇ; [Ho(5-SSA)]), 5-SSA = 5-Sülfosalisilik asit) hidrotermal metot ile sentezlenmiştir. Toz kristal X-ışını kırınımı, oda sıcaklığında katı-hal UV ve FT-IR spektroskopisi teknikleri yardımıyla yapısal karakterizasyonu yapılmıştır. Buna ek olarak, oda sıcaklığında görünür ve yakın kızıl ötesi (NIR) bölgede katı hal fotoluminesans ölçümleri alınmış ve 5-SSA ligandından Ho⁺³ iyonuna olan enerji transfer mekanizması detaylı bir şekilde incelenmiştir. UV ışınım altında (349 nm'de), 5-SSA ligandı geniş bir lacivert renginde yayılım sergilerken, Ho-MOÇ kompleksi UV-Görünür ve NIR bölgesinde Ho⁺³ iyonunun çeşitli karakteristik emisyonlarını sergilemiştir. Mükemmel ışıldama performansları, bu bileşiği yüksek verimli ışınım veren malzemeler için çok iyi bir aday haline getirmektedir.

Anahtar Kelimeler: Lüminesans, Metal-Organik Çerçeveler, Holmiyum

Cite

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1. Introduction

Metal-organic frameworks (MOFs) which are Nano-dimensional materials have porous structures [1-5].

Research interest in metal-organic frameworks (MOFs) is a relatively young and dynamic research field from the beginning of the 21st century, when compared to other scientific fields, is one of the most important candidates

for the interdisciplinary research [6–10]. MOFs which consist of the rare earth elements have some interesting magnetic and luminescence properties [11–17]. These materials also have high hydrogen storage, gas adsorption, and separation, photo-catalysis, and sensor properties [2,18,19]. The materials designed with organic ligands and lanthanide ions which have a porous structure are called lanthanide metal-organic frameworks (Ln-MOFs). The design and synthesis of the 1D, 2D or 3D Ln-MOFs can be accomplished by intelligently choosing the appropriate combination of the binder lanthanide ions and organic ligands [20–24]. Ln-MOFs gain high absorption capacities through organic based chromophores.

One of the most commonly used methods of synthesis of Ln-MOFs is the hydrothermal technique, which is less harmful to the environment. This technique is an ideal method for the synthesis of solid-state compounds such as on organic hybrid, inorganic hybrid, supramolecular and so on. The hydrothermal technique is defined as a heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature to dissolve and crystallize insoluble materials under normal conditions [25–27]. Nowadays, hydrothermal technique is used extensively in the synthesis of the metal complexes, polymers and ceramics with increasing demands on the Nano-structures.

Recent advances in Nano-technology have attracted considerable interest in the Holmium-based metal-organic frameworks (Ho-MOFs) which have interesting structural and luminescent properties [28,29]. Ho-MOFs which are frequently used in luminescent-based material designs is one of the prominent candidates in the development of the multifunctional materials. Holmium complexes find the usage in telecommunication, photonics and biological applications as infrared radiation emitting materials [30–33].

In this work, new Ho-MOF complex was synthesized by hydrothermal method. The structural characterization has been made by powder X-ray diffraction, a room temperature solid-state UV and FT-IR and photoluminescence spectroscopy.

2. Material and Method

The chemical reagents and solvents used in this study were obtained commercially from Sigma-Aldrich and Merck and used without any purification. Powder XRD pattern of the organic ligand (5-SSA) and the complex (Ho-MOF) were measured using Philips X'Pert Pro powder diffractometer with the Cu-K α radiation. The IR and UV spectra of these materials were measured at room temperature in solid state condition using Perkin-Elmer Spectrum 65 FT-IR spectrometer and Ocean Optics Maya 2000Pro spectrometer, respectively. Photoluminescence measurements were made at room temperature with a Perkin Elmer LS 55 molecular fluorimeters and Andor Solis SR 500i-BL model spectrometer equipped with a triple grating and used an air-cooled CCD camera as a detector. Spectra-Physics

model Nd-YLF (349 nm) laser was used as an excitation source for emission spectra. Each laser pulse has a pulse width of 5 ns and 1.33 mJ of energy per pulse.

2.1. Preparation of the Ho-MOF: Ho(5-SSA)], 5-SSA = 5-Sulfosalicylic Acid

The hydrothermal technique has been used for the synthesis of the Ho-MOF. In this technique, the organic ligand 5-sulfosalicylic acid (0.1 mmol, 0.0254 g) which is indicated in Fig. 1. was dissolved in 10 mL distilled water by heating to the boiling point. Then the Ho(NO₃)₃·5H₂O (0.1 mmol, 0.0441 g) was added to the former solution and stirred for 30 minutes with the magnetic stirrer. During the whole process, the pH values of this solution have been observed. The final pH value of this reaction media are around 4.0. This mixture was sealed into the acid reactor equipped with a Teflon liner which has a 45 mL volume and heated 140 °C for 5 days. After 5 days, the reactant mixture was slowly cooled to the room temperature. The obtained crystals were separated by filtration paper and washed with distilled water.

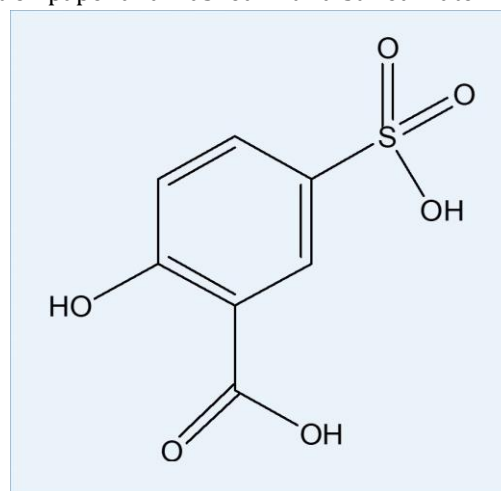


Figure 1. Schematic representation of the 5-SSA organic ligand.

3. Research Findings

3.1. The Powder X-ray Diffraction of the Ho-MOF

Before taking into consideration about some spectroscopic and luminescence analyses, the intensity data of the Ho-MOF obtained from powder X-ray measurement (PXRD) was compared with a similar single crystal structure synthesized with the same ligand in the literature using the Mercury software [34]. The data obtained from the powder X-ray measurement is called “measured” and the data obtained from the literature by using Mercury program is called “calculated” as shown in Fig. 2. The PXRD results showed that the peak positions match well with those from the simulated PXRD patterns on the basis of single-crystal structure data, indicating reasonable crystalline phase purity (Fig. 2).

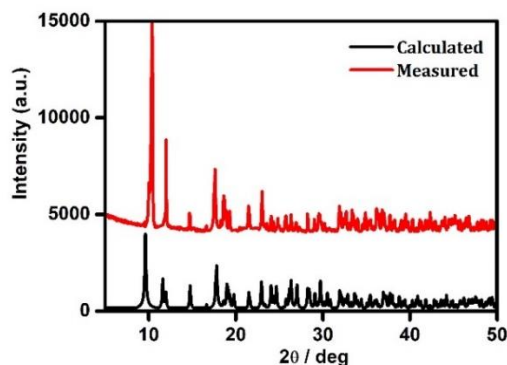


Figure 2. X-ray powder diffraction patterns from the Ho-MOF complex.

3.2. The FT-IR Spectra of the Ho-MOF

To be able to find out bond vibration process of the structures, the IR spectra of Ho-MOF and its free ligand (5-SSA) have been measured and their spectra have been compared with each other. As can be seen in Fig. 3., the peaks observed in the IR spectra of the Ho-MOF and 5-SSA are in almost similar regions except a few of them. It has been overserved that there is a strong broad vibration peak which may be due to the $\nu(\text{O-H})$ stretching vibration of the water molecules at 3353 cm^{-1} for the Ho-MOF complex [28,29,34,35]. The absence of strong vibration peak in the complex, while it has been observing in the $3067\text{--}1662\text{ cm}^{-1}$ region for 5-SSA organic ligand, can be interpreted as the depletion of the protons of the SO_3H and COOH groups [28,29,34]. The strong vibration peaks are originated from carboxylate groups of $\nu_{\text{as}}(\text{COO})$ at 1608 cm^{-1} and $\nu_{\text{s}}(\text{COO})$ at $1506\text{--}1330\text{ cm}^{-1}$ region in the Ho-MOF complex. This case may suggest that the carboxylate groups are coordinated with the holmium ions in the chelating mode [36–38]. In addition, there are some characteristic peaks in the region of $1255\text{--}1048\text{ cm}^{-1}$. The sulfonate groups which are $\nu(\text{S-O})$ and $\nu(\text{C-S})$ may be responsible for these observed peaks [29,39,40]. All of these observed peaks shift towards the lower wave number values with very little difference in the IR spectrum of the 5-SSA ligand. The peaks in the band of $917\text{--}670\text{ cm}^{-1}$ are caused by O-Ho-O and Ho-O stretching vibrations [41].

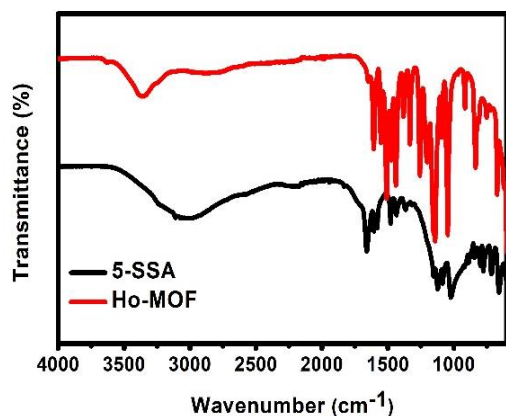


Figure 3. The IR spectra of the Ho-MOF complex and 5-SSA organic ligand.

3.3. The Solid-State UV-Vis spectra of the Ho-MOF

The UV-Vis spectroscopy method is a more powerful technique which could give an idea about the electronic transition of the molecular structures. The solid-state UV-Vis spectra of Ho-MOF complex and 5-SSA ligand have been taken individually at room temperature and the obtained results were compared by each other as shown in Fig. 4.

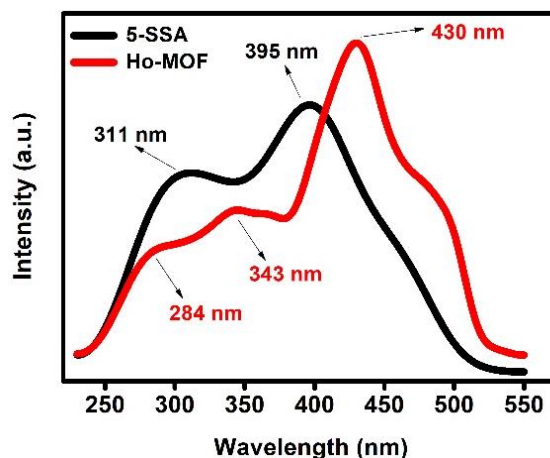


Figure 4. The Solid-state UV-Vis spectra of the Ho-MOF complex and 5-SSA organic ligand.

The first noticeable aspect from UV-Vis spectra is that both spectra have different broad absorption peaks. The maximum values of these absorption peaks are at 311 nm and 395 nm for the ligand 5-SSA and 284 nm, 343 nm and 430 nm for the Ho-MOF complex. The dominant absorption bands might be assigned to $\pi\text{--}\pi^*$ or $n\text{--}\pi^*$ transition of the 5-SSA ligand. It can be concluded that the red shifting of the absorption band in the UV-Vis spectra of Ho-MOF complex reminds the Holmium ion coordination with the 5-SSA ligand [28,41,42].

3.4. The Solid State Photoluminescence Properties of the Ho-MOF

One of the best spectroscopy technique for uncovering the energy transfer mechanism of the metal-organic frameworks is the photoluminescence measurement method. The solid-state photoluminescence measurements were taken for the 5-SSA ligand and the Ho-MOF complex in the visible and near-infrared region at room temperature under the excitation at 349 nm. The PL spectrum of the 5-SSA ligand has a broad navy-blue emission peak upon the excitation at $\lambda_{\text{max}} = 349\text{ nm}$ as indicated in Fig. 5. The maxima of this emission spectrum are located at 466 nm. One can interpret that the $n\text{--}\pi^*$ or $\pi\text{--}\pi^*$ electronic transition (ILCT) causes of this emission band [41,43].

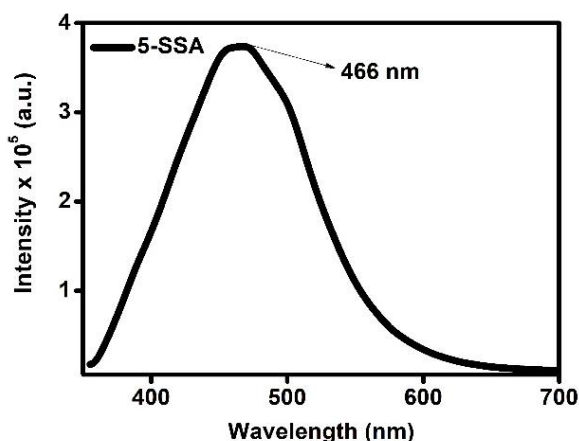


Figure 5. PL spectrum of the 5-SSA free ligand under the excitation at 349 nm at room temperature.

The lanthanide-based materials may have very strong sharp emission bands due to the f-f transitions of the lanthanide ions. When the Ho-MOF complex is excited at 349 nm, several characteristic emission bands of the Ho⁺³ ion have popped out in the visible and NIR region regions as seen in Fig. 6. and Fig. 7.

The sharp emission bands at 410 nm (⁵G₄ → ⁵I₈), 428 nm (⁵G₅ → ⁵I₈) and 648 nm (⁵F₅ → ⁵I₈) are much more intense than the others. The other emission peaks which are weaker as an intensively might be attributed to the ⁵G₆ → ⁵I₈ and ⁵F₃ → ⁵I₈ transitions for 463 nm and 536 nm in the visible region. In the NIR region, three weak emission bands at 792 nm, 1139 nm, and 1470 nm are attributed to the f-f transition ⁵S₂ + ⁵F₄ → ⁵I₇, ⁵I₆ → ⁵I₈ and ⁵I₇ → ⁵I₈, respectively [29,35,44–46]. Among all the emission bands, the most intense sharpest emission band is at 648 nm which is due to the ⁵F₅ → ⁵I₈ transition so that the Ho-MOF complex structure emits strong red light.

3.4.1. Energy Transfer Mechanism

The direct excitation of lanthanide ions is nearly impossible. The reason for this phenomena is that the f-f transitions are prohibited due to parity selection rules. Therefore, the lanthanide complexes containing organic ligands absorbs the light in the UV region can transfer the energy through the ligand to the lanthanide ions via antenna effect [35,46,47].

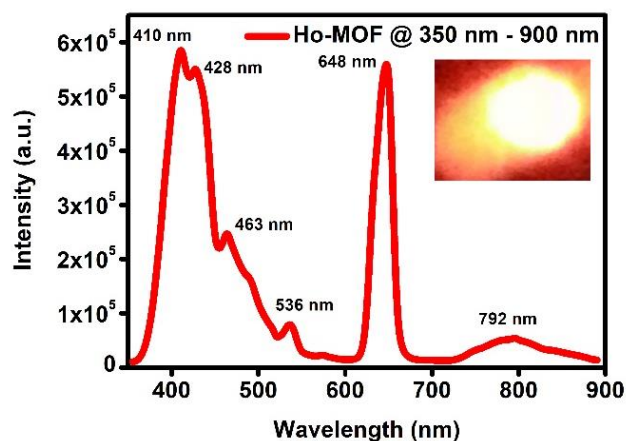


Figure 6. PL spectrum of the Ho-MOF complex in the 350-900 nm region under the excitation at 349 nm at room temperature. The upper right picture in the figure is a photoluminescent image of Ho-MOF while excited at 349 nm

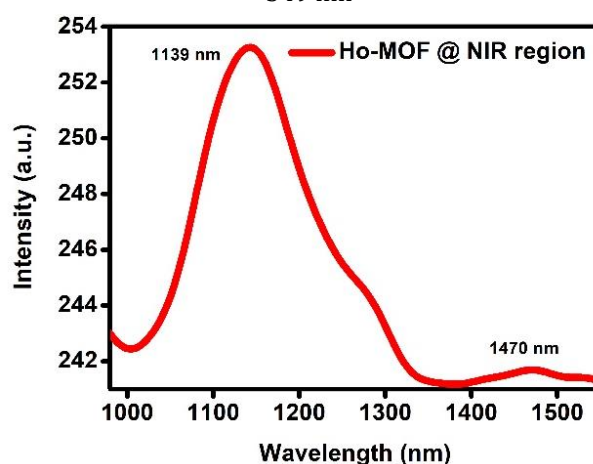


Figure 7. PL spectrum of the Ho-MOF complex in the NIR under the excitation at 349 nm at room temperature.

Fig. 8. represents the energy level diagram and energy transfer mechanism for Ho³⁺. Three step takes place for the sensitization. The first one is the ligands absorb the energy and are excited to the singlet (S₁) excited state. The second step is that the energy of this level is transferred to its triplet (T₁) level via intersystem crossing (ISC) as indicated in Fig. 8. The last step for this whole sensitization process is that the energy is transferred to the 4f levels of the Ln⁺³ ions.

According to Dexter's theory, the energy difference between the excited energy levels of the ligand and the triplet state of the Ln⁺³ ions play a key role in efficient energy transfer [46,48]. If the energy difference between these two states is too high, the overlapping of the triplet energy state of the ligand and Ln⁺³ ions will decrease and the energy transfer will drop sharply. If the difference between the triplet energy state is too small, then the transfer process of the ligand from lanthanide ions will starts. As a result, in our work, the energy transfers from the ligand to Ho⁺³ has been done effectively.

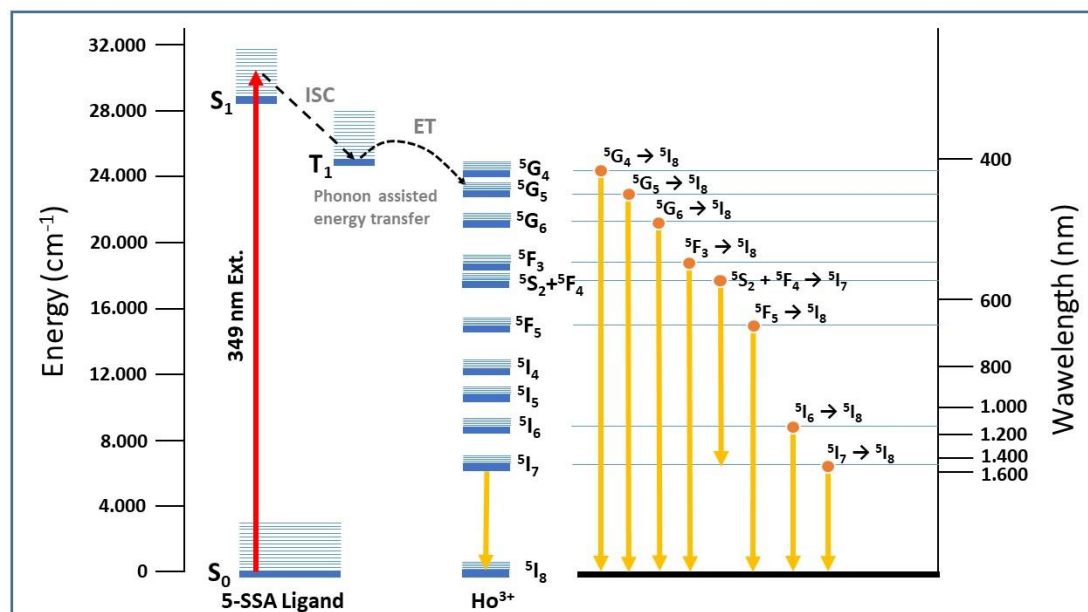


Figure 8. The schematic diagram of the sensitization of Ho³⁺ via intra-4f transition by the 5-SSA organic ligand

4. Conclusion

The new Ho³⁺ based metal-organic frameworks has been synthesized using 5-SSA organic linker by hydrothermal method. Powder XRD, FT-IR, UV-Vis Spectra has been done for the structural characterization of the Ho-MOF complex. The whole analyses show that PXRD, FT-IR and UV-Vis spectra of the Ho-MOF complex are in good agreement with the literature. Besides those analyses, the luminescence properties of the 5-SSA ligand and the Ho-MOF complex have been investigated under the excitation 349 nm at room temperature in the UV visible and NIR region and the energy transfer mechanism from 5-SSA ligand to the Ho³⁺ ion is investigated in detail. The PL measurements show that Ho-MOF complex exhibited several characteristic emissions of the Ho³⁺ ion in the UV-Visible and NIR region and emits strong red light which is attributed to the f-f electronic transitions. We may conclude that the energy transfers from the 5-SSA ligand to the Ho³⁺ ion have been done more effectively a *via* antenna effect. The excellent luminescent performances make this compound very good candidate for efficient luminescence materials.

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