

Preparation and Photoluminescence Spectra of Organometallic Complexes Containing Nanoparticles as Random Gain Media

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Abstract: This work prepared organometallic complexes from the 8-hydroxyquinoline ligand linked to metal ions such as Ba²⁺, Ca²⁺, and Zn²⁺. The effects of metal ion type and adding nanoparticles to the complex solution on the absorption and photoluminescence characteristics of the prepared complexes were introduced. These nanoparticles were added to the prepared complex solutions to act as scattering centers to form random gain media with emission in the visible region of the electromagnetic spectrum. The random gain media made from the Znq₂ complex with nanoparticles showed the best characteristics with good chemical and spectroscopic stabilities, high reliability, and reproducibility in addition to the low production cost and reasonably simple requirements.

Keywords: photoluminescence; organometallic complex; nanoparticles; random gain medium

■ INTRODUCTION

As of late, different interchanges, natural, biomedical, and space applications have been created by using irregular addition media as laser sources known as "random lasers" [1]. Additionally, the continuous and extraordinary improvements in nanotechnology have prompted uncommon advancements in the plan and manufacture of irregular increase media [2-3]. 8-Hydroxyquinoline zinc has many advantages, such as simple synthesis conditions [4]. In general, the random gain medium can be fabricated by adding nanoparticles to a laser dye solution to play the role of scatters within the dye solution to amplify the generated laser signal [5]. However, the spectroscopic characteristics of both dye solution and nanoparticles must be precisely determined as a requirement for successful gain amplification.

As the power of the random lasing activity is amazingly high, then, at that point, the population inversion is reached so rapidly, bringing about a short peak in the fluorescence spectrum. The population inversion is effectively achieved and consumed with continuous excitation of the added particles, prompting a

progression of peaks in the emission range. The emission range of a random laser is high in intensity and narrow in width.

The host or gain media used to fabricate random laser systems are laser dyes like xanthene and coumarin. These dyes are characterized by high gain, high fluorescence efficiency, and extremely broad energy bands allowing both absorption and emission over a wide range of wavelengths. Also, the emission of laser dye can be controlled by several parameters, mainly dye-solution concentration, and solvent type. Therefore, the search for new organic complexes with featured spectroscopic and chemical characteristics continuously replaces common laser dyes and explores new dye laser physics and technology [6]. Znq₂ has many advantages, such as high luminous efficiency [6]. Many scholars have done in-depth research focused on extending application potential of MQ₂ [7]. At present, liquid-phase method is the main method to synthesize MQ₂ [8].

The 8-hydroxyquinoline (H.Q.) ligand is impressively used in coordination science for the extraction and goal of component particles [9-10].

Chelato-aromaticity can happen in metallo-cyclic rings shaped during metal particle complexation or in rings of the ligand that do not connect straightforwardly with metal particles [11]. The 8-hydroxyquinoline can arrange with different particles as bidentate through nitrogen of quinolone ring and oxygen molecule after deprotonation of hydroxyl group [12]. The 8-hydroxyquinoline (oxine) acts as a bidentate (N, O^-) univalent ligand to frame chelates with a few metal particles [13]. The zinc(II) buildings of amide and urea subbed of 8-hydroxyquinoline have shown superb photoluminescence and fluorescence qualities compared to their friend metalorganic edifices [14].

This work synthesized new organometallic complexes by connecting some metal ions to the 8-hydroxyquinoline ligand. The photoluminescence of the incorporated complexes was estimated before and after adding metal oxide nanoparticles to introduce their effects and form a random gain media to produce a random laser.

■ EXPERIMENTAL SECTION

Materials

Three different solvents, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and ethanol, were used in this work, while the 8-Hydroxyquinoline (8-HQ) was used as a ligand and barium(II) chloride dihydrate, calcium(II) chloride and zinc (II) chloride were used as metal salts to synthesize the required complexes.

Instrumentation

The precursors, ligands, and synthesized complexes were characterized as follows. The Fourier-transform infrared (FTIR) spectra were recorded using the Nicolet Impact 410 spectrophotometer using KBr disk in the range $400\text{--}4000\text{ cm}^{-1}$. The absorption spectra were recorded using a UV-Visible SPEKOL 2000 double-beam spectrophotometer supplied by P.G. Instruments (U.K.), which has a slit width in a spectral range of $190\text{--}1100\text{ nm}$. Both FTIR and UV-visible measurements were performed on the samples in ethanol. The field-effect scanning electron microscopy (FE-SEM) was used to study the effect of nanoparticle size and distribution on the characteristics of the prepared samples.

Procedure

Synthesis of bis(8-hydroxyquinolato) zinc (Znq_2) complex

A sample of 1.83 g (10 mmol) $Zn(CH_3COO)_2$ was dissolved in 10 mL of distilled water. Then this solution was added as drops to another solution of 2.9 g (2 mmol) 8-hydroxyquinoline ligand dissolved in a mixture of 0.11 g potassium hydroxide (KOH) in 6 mL of distilled water. The first solution prepared in the first step was added to the second solution, and then the reaction mixture was stirred as the complex was prepared by filtration, washed by absolute ethanol, dried at room temperature for 24 h. The result is a white-green solid with a yield of 3.26 g (92.35%).

Synthesis of bis(8-hydroxyquinolato) barium (Baq_2) complex

A 2.44 g (10 mmol) of $BaCl_2 \cdot 2H_2O$ was dissolved in 10 mL distilled water, then the prepared solution was added to a solution of 2.9 g (2 mmol) 8-HQ dissolved in a solution of 0.11g KOH in 6 mL of distilled water. The first solution was added to the second solution, and the mixture was stirred until the complex was prepared by filtration, washed by absolute ethanol, dried at room temperature for 24 h to get a white green solid with a yield of 4.08 g (81.6%).

Synthesis of bis(8-hydroxyquinolato) calcium (Caq_2) complex

A solution was prepared by dissolving 1.11g (10 mmol) $CaCl_2$ in 10 mL distilled water, then added to a solution of 2.9 g (2 mmol) 8-HQ ligand dissolved in the same mixture (0.11g KOH in 6 mL of distilled water). The first solution was added to the second one, and the produced mixture was stirred until the complex was prepared by filtration, washed by absolute ethanol, dried at room temperature for 24 h. The final sample was a white-yellow solid with a yield of 1.82 g (98.7 %).

Adding nanoparticles

In order to form the random gain media, highly-pure titanium dioxide nanoparticles with an average particle size of 25 nm were added to the complex solution, and the absorption and photoluminescence spectra were recorded and compared before and after

adding these nanoparticles. The minimum amount of added nanoparticles was 0.5 mg for 5 mL of a complex solution of 10^{-5} M concentration. Many experiments were carried out to determine these preparation conditions.

■ RESULTS AND DISCUSSION

To affirm the arrangement of organometallic linkage, the FTIR spectra of the free 8-hydroxyquinoline ligand and all edifices arranged in this work were recorded in the wavenumber scope of $400\text{--}4000\text{ cm}^{-1}$ as displayed in Fig. 1. The range of the 8-Hq ligand shows two groups at 3161 cm^{-1} because of the O–H extending group and at 3049 cm^{-1} to C–H_{st}, group aromatic vibration. The main band was not found in the FTIR spectra of the three complexes, which affirms the coordination through the oxygen atom of the hydroxyl group. The subsequent band was seen inside the reach $3040\text{--}3055\text{ cm}^{-1}$.

One more band at 1576 cm^{-1} attributed to the C=N group was marginally moved to various positions, which affirms the coordination through the nitrogen iota of the C=N group [15]. The groups were seen at 1500 and 1466 cm^{-1} are ascribed to the vibrations of the benzene ring. These bands were seen in all spectra of the prepared complexes with a slight shift, as shown in Table 1. The bands are seen within the range $1366\text{--}1386\text{ cm}^{-1}$ are ascribed to the vibration of C=N. The bands seen in the range $1274\text{--}1281\text{ cm}^{-1}$ are attributed to O–H's bend vibrations [16-17]. The bands observed at 1217 and

1203 cm^{-1} are ascribed to the stretch vibration modes of C–O.

Nonetheless, these groups were seen in the FTIR spectra of the Baq₂ complex and disappeared in the Caq₂ and Znq₂. Therefore, the new groups have seen inside $570\text{--}591\text{ cm}^{-1}$ and $475\text{--}504\text{ cm}^{-1}$ are ascribed to the arrangement of metal-nitrogen (M–N) metal-oxygen (M–O) bonds, separately, because of the coordination with metal particles in the buildings (Baq₂, Caq₂, and Znq₂) [18-20].

Fig. 2 shows the absorption spectra of the three complexes prepared in this work before and after adding

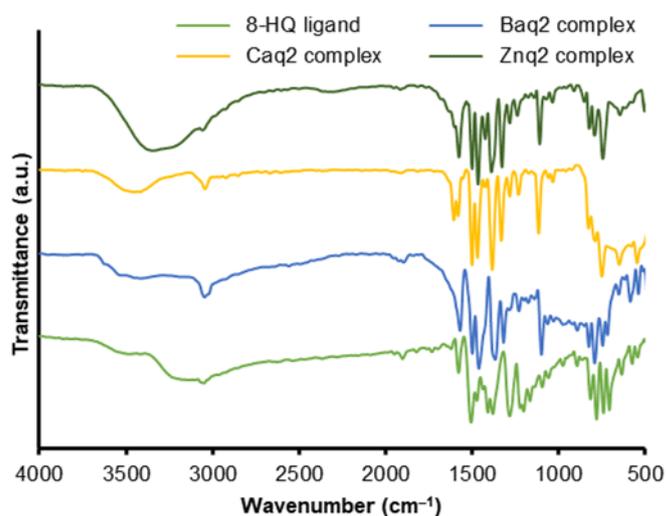


Fig 1. FTIR spectra of free 8-Hq ligand, Baq₂, Caq₂, and Znq₂ complexes prepared in this work

Table 1. Vibration modes of the free ligand and complexes prepared in this work

Vibration mode	8-Hq (cm ⁻¹)	Baq ₂ (cm ⁻¹)	Caq ₂ (cm ⁻¹)	Znq ₂ (cm ⁻¹)
M–O vibration	475	478	492	504
M–N vibration	577	584	591	570
In-plane ring deformation	642	645	648	644
In-plane deformation	743	740	748	742
C–O stretching	1203	1198	1171	1175
O–H bending	1281	1281	1274	1280
C=N vibration	1375	1366	1375	1386
Phenyl group	1466	1460	1459	1466
Pyridyl group	1500	1497	1497	1500
C=N coordination	1576	1567	1569	1577
C–H _{st} , aromatic vibration	3049	3044	3040	3054
OH stretching	3161	-	-	-

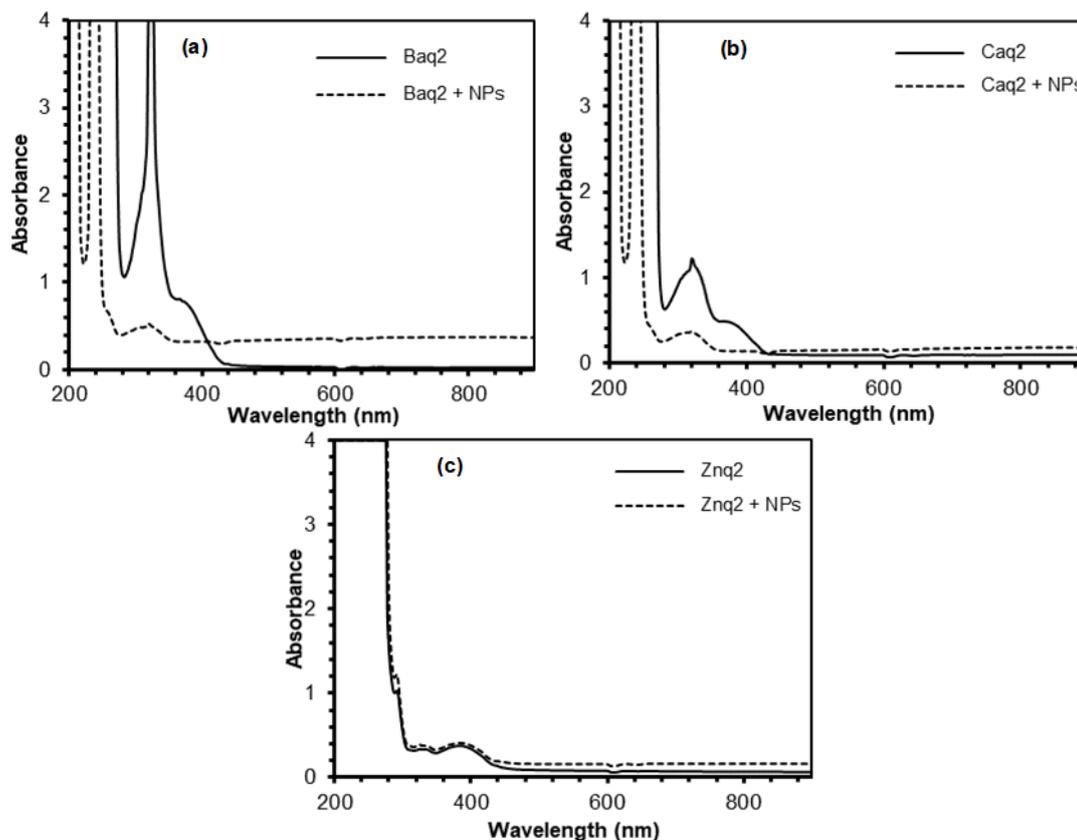


Fig 2. Absorption spectra of Baq₂ complex (a), Caq₂ complex (b), and Znq₂ complex (c) prepared in this work before and after adding nanoparticles

nanoparticles to the complex solution in ethanol solvent. It is clear that the absorption peak for Baq₂ and Caq₂ complexes at 326 and 330 nm, respectively, was suppressed after adding the nanoparticles, while no similar effect was observed for the Znq₂ complex. However, after adding the nanoparticles, all complexes showed high absorbance in the ultraviolet region (< 300 nm). As well, the Baq₂ complex showed higher absorbance in the spectral range 500–800 nm after adding the nanoparticles, while the difference in absorbance for both Caq₂ and Znq₂ complexes was very small.

As the aimed application of the organometallic complexes prepared in this work is the random gain media, then the photoluminescence intensities were compared before and after adding the nanoparticles, as shown in Fig. 3. All complexes showed two distinct peaks; the first in the blue region (450–470 nm) and the second in the green region (510–515 nm). In the Baq₂ and Caq₂ complexes, the intensity of the first peak was higher than

that of the second one. In contrast, the second peak of the Znq₂ was higher than that of the first one.

After adding the nanoparticles, the Caq₂ complex showed a slight decrease in the photoluminescence intensity, whereas both Baq₂ and Znq₂ complexes showed higher photoluminescence intensities. The increase for the Znq₂ complex was 25% and 20% for both peaks, while it was more than 2% and 9% for the Baq₂ complex.

The FE-SEMs (Fig. 4) for both samples before nanoparticles addition were measured to attribute the different increases in photoluminescence for Baq₂ and Znq₂ complexes. The SEM was not performed on the synthesized samples after adding TiO₂ nanoparticles as no reaction is expected between the complex and nanoparticles. Instead, the SEM result of TiO₂ nanoparticles was inserted to confirm their formation. As a result, it was confirmed that the metal ions linked to the ligand form nanoparticles. As shown, the Baq₂ sample

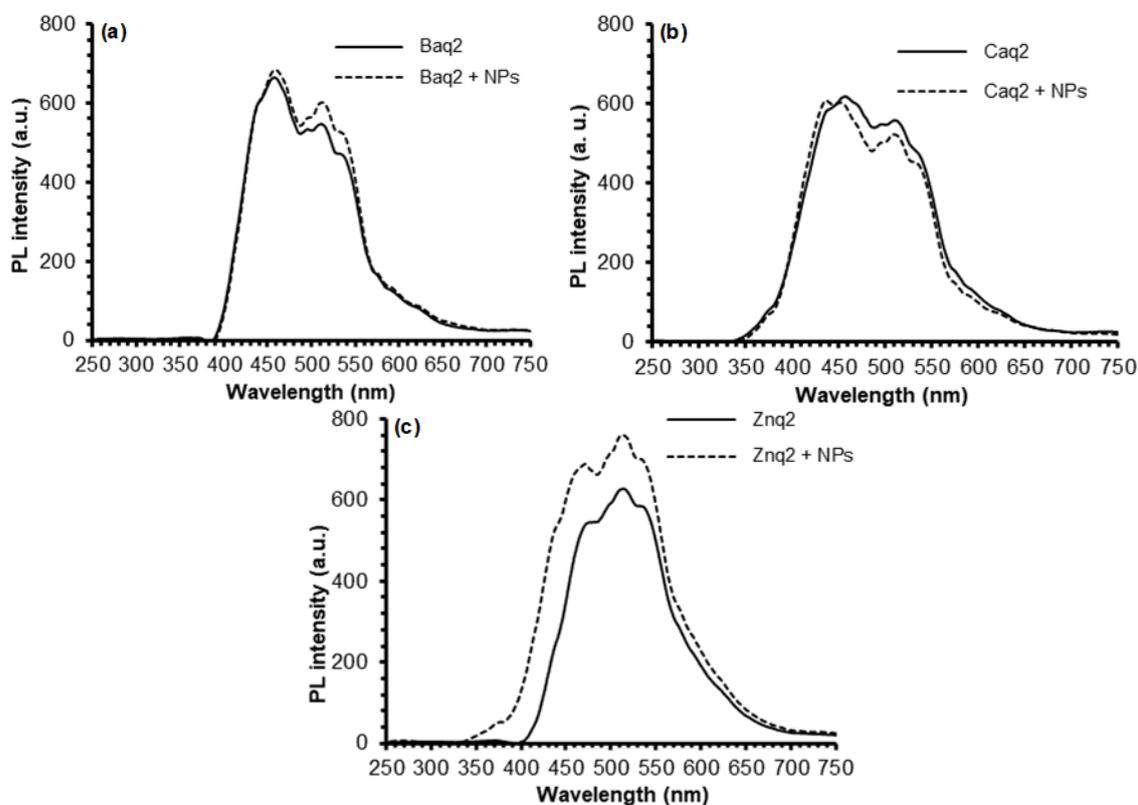


Fig 3. Photoluminescence spectra of Baq₂ complex (a), Caq₂ complex (b), and Znq₂ complex (c) prepared in this work before and after adding nanoparticles

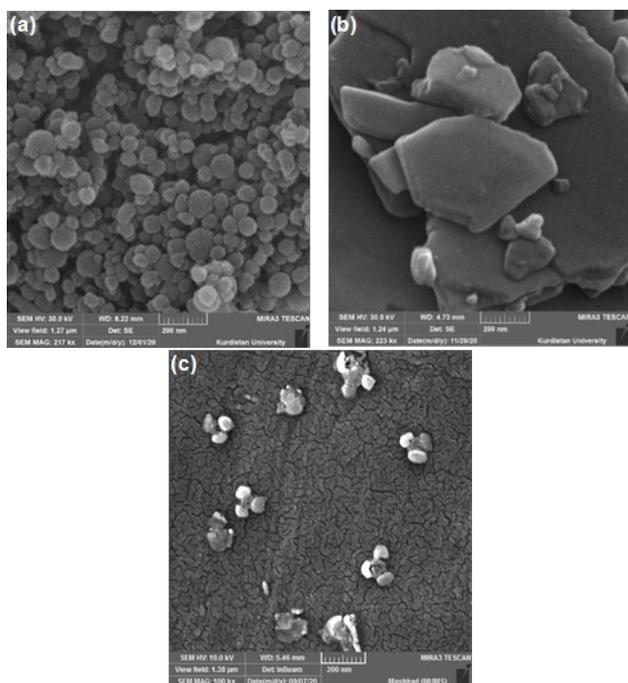


Fig 4. FE-SEM results of Baq₂ complex (a) and Znq₂ complex (b) prepared in this work before adding nanoparticles (c) SEM result of TiO₂ nanoparticles

exhibited a highly uniform distribution, spherical-shaped, and smaller particles when compared to the Znq₂ sample, which exhibited larger sizes and reasonable aggregation. The homogeneous distribution of nanoparticles may cause a homogeneous response to the incident radiation, and hence the average increase is smaller than that in the case of the inhomogeneous distribution of the Znq₂ sample.

Accordingly, the Znq₂ complex can be a good candidate for a random gain medium to produce a random laser. Furthermore, with further optimization of preparation conditions, mainly the concentrations of complex solution and nanoparticles added to the complex solution, the photoluminescence characteristics can be sufficiently enhanced to fabricate the final sample as a solid rod by embedding the sample in a transparent host.

■ CONCLUSION

In concluding remarks, organometallic complexes containing nanoparticles were prepared from the 8-

hydroxyquinoline ligand linked to metal ions such as Ba²⁺, Ca²⁺, and Zn²⁺. The Znq₂ complex showed constant absorbance after adding the nanoparticles but higher photoluminescence intensity in the visible region. The random gain media made from the Znq₂ complex with nanoparticles showed the best characteristics with good chemical and spectroscopic stabilities, high reliability, and reproducibility in addition to the low production cost and reasonably simple requirements.

■ AUTHOR CONTRIBUTIONS

All authors agreed to the final version of this manuscript.

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