IRAQI JOURNAL OF MATERIALS
Volume (5) Issue (4) October-December 2022, pp. 157-166

Preparation and Physical Properties of Hydroxyquinoline Complexes in Different Solvents

Atheer A.R. Mahmood [1], Oday A. Hammadi [2], Kais R. Ibraheem [3]

[1] *Department of Chemistry, College of Education, Al-Iraqia University, Baghdad, IRAQ*
[2] *Department of Physics, College of Education, Al-Iraqia University, Baghdad, IRAQ*
[3] *Department of Chemistry, College of Science, University of Anbar, Ramadi, IRAQ*

Abstract

In this work, different organometallic complexes were prepared by linking metallic ions such as aluminum, barium, copper, manganese and zinc to 8-hydroxyquinoline ligand. The physical properties of these complexes in different solvents, mainly DMF and DMSO, were studied. Most complexes showed lower absorbance as well as lower refractive index when compared to those of 8-hydroxyquinoline in DMF or DMSO. Some samples showed comparable values due to the formation of nanoparticles within the prepared structures. As well, the zinc-hydroxyquinoline (Znq2) complex showed that two absorption edges with comparable intensities are formed. These results may encourage to consider these complexes for some spectroscopic applications such as laser dyes and random gain media.

Keywords: Hydroxyquinoline; Spectroscopy; Organometallic complex; Physical properties
Received: 18 March 2022; **Revised:** 21 June 2022; **Accepted:** 28 June; **Published:** 1 September 2022

1. Introduction

The 8-hydroxyquinoline (8-HQ) may be a cyclic compound ensuing from quinolone (1-azanaphthalene) and consists of 2 ring systems [1]. It is one phenolate a part of catecholate and one alkali donor of bipyridyl and is mirrored as a conjugate of 2 coordinating positions. It is thought about as monoanionic species and bridges the gap between the dianionic catecholate and therefore the neutral bipyridine [2].

A fast survey of the structure of 8-HQ reveals that it's -OH cluster and pyridyl N atom gift in 8-hydroxyquinoline that have the flexibility to act as a weak base and a weak acid underneath basic and acidic conditions, severally that is in a position to come with the equilibrium between quinolinate N~O in deprotonated type and quinolinium NH^+~OH within the protonated form [3].

Zinc complexes are particularly vital as a result of the simplicity in synthesis procedures and wide spectral response. In depth analysis work goes on in varied laboratories to synthesize new Zn complexes containing new ligands to supply variety of novel light zinc complexes [4-6].

Many complexes of 8-hydroxyquinoline such as AlQ_3, ZnQ_2, MgQ_2, ZnQ_2, and BeQ_2 have been extensively studied as emitters [7,8].

It is acknowledge that by substitution of a π-donor cluster akin to chemical element atom on the phenolate ring Associate in nursing an electron-withdrawing one on the alkali pyridine ring leads to red and blue shifted emissions [9-11].

8-Hydroxyquinoline is an organic compound with the formula C_9H_7NO. It is a derivative of the heterocycle quinoline by placement of an OH group on carbon number 8. 8-hydroxyquinoline (8-HQ) is a conjugated system and a bi functional hydrogen bonding molecule, in parotic solvents simultaneously acts as an H donor at the O-H group and as an H acceptor at the N atom [12].

The aluminium complex of 8-HQ, known as Alq_3 [13,14] has been applied to solar cells and optoelectronics [15]. Ruthenium complexes of 8-hydroxyquinoline are promising for catalysis in photosynthetic systems for fuel production [16].

It is known that Cr(III) and Al(III) have very similar ionic radii, coordination numbers (typically six) as well as comparable thermodynamic stabilities. In addition, 8-hydroxyquinolinate complexes of Cr(III) and Al(III) also exhibit excellent electronic spectral properties [17-20]. However, to the best of our knowledge, Cr(III) 8-hydroxyquinolates are rarely explored, even though 8-hydroxyquinoline shown excellent coordination ability with various metal ions [21,22].

In this work, organometallic complexes were prepared by direct mixing of 8-hydroxyquinoline ligand with some aqueous precursors to extract metals linked to this ligand and form the required complexes. Some physical properties and spectroscopic characteristics of the prepared complexes were determined. Such study is required to assess the performance of such complexes as fluorescent media in visible region of electromagnetic spectrum.

2. Experimental Part

Table (1) shows the chemicals and precursors used in this work to prepare the organometallic complexes. Table (2) shows the properties of the Dimethyl Formamide (DMF) and Dimethyl sulfoxide (DMSO) solvents used in this work to prepare the final samples for spectroscopic measurements.

Table (1) The chemicals and precursors used in this work

Chemical	Description
$AlCl_3.6H_2O$	Potassium alum
$KAl(SO_4)_2.12H_2O$	Aluminium chloride hexahydrate
$BaCl_2.2H_2O$	Barium chloride dihydrate
$CuCl_2.2H_2O$	Copper chloride dihydrate
$MnCl_2.4H_2O$	Manganese chloride tetrahydrate
$ZnCl_2$	Zinc chloride
$Zn(CH_3COO)_2{\cdot}2H_2O$	Zinc acetate dihydrate

Table (2) The properties of the DMF and DMSO solvents used in this work

	Polarity Index	Dipole Moment	Dielectric Constant
DMF	6.4	3.86	36.71
DMSO	7.2	4.1	46.68

A sample of 4.35g of 8-Hydroxyquinoline was dissolved in a mixture of 15 mL methanol and then it was stirred well till orange transparent solution was obtained. Separately, 3.75 g of $AlCl_3.6H_2O$ was dissolved in methanol, and stirred well till crystal transparent solution was obtained. These two solvents were mixed and the resultant suspension was stirred for 20 minutes. The other complex solutions such as Baq_2, Cuq_2, Mnq_2 and Znq_2, were prepared using the same method as used for Alq_3. As well, the mole ratios of 8-quinolinol to $Zn(CH_3COO)_2{\cdot}2H_2O$ was chosen as 2:1. Finally, the products were dried in oven at 60°C.

The absorbance of the prepared complexes was determined using UV-visible spectrophotometer in the spectral range of 200-900 nm. From these measurements, the refractive index of each complex was determined using suitable software.

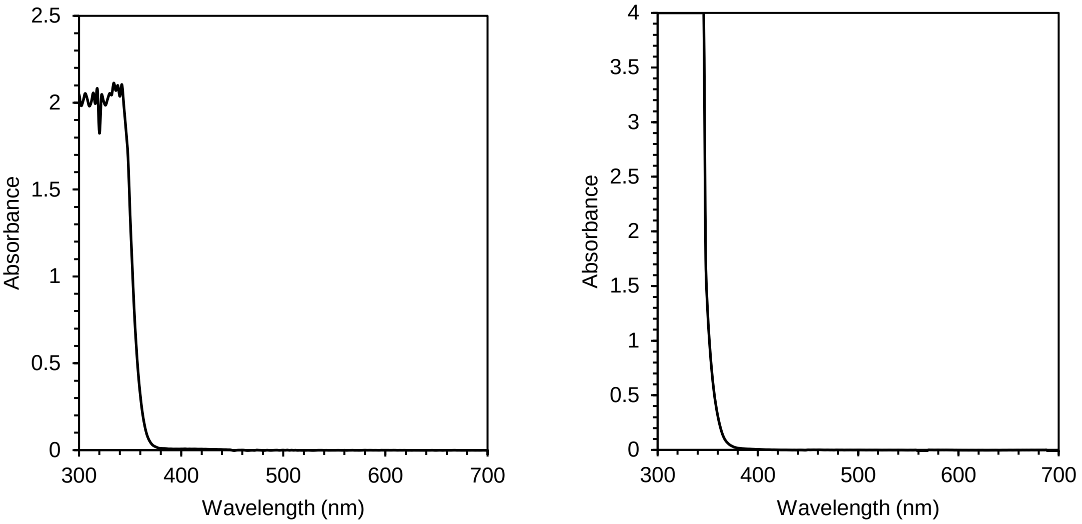
Some samples were tested with the field-effect scanning electron microscopy (FE-SEM) in order to confirm the formation of nanoparticles within these samples. The effect of nanoparticle formation on the physical properties of prepared complexes was introduced.

3. Results and Discussion

Figure (1) shows the absorption spectra of the 8-hydroxyquinoline (8-Hq) ligand dissolved in two different solvents (DMF and DMSO). It is clear that this ligand shows high absorbance in the ultraviolet (UV) wavelengths shorter than 340 nm before a fast decrease to be approximately transparent at 380 nm and longer wavelengths (visible region). However, the 8-Hq dissolved in DMSO shows higher absorbance (>100%) than that in DMF. This may be attributed to the properties of these solvents mainly polarity index, dipole moment, and dielectric constant.

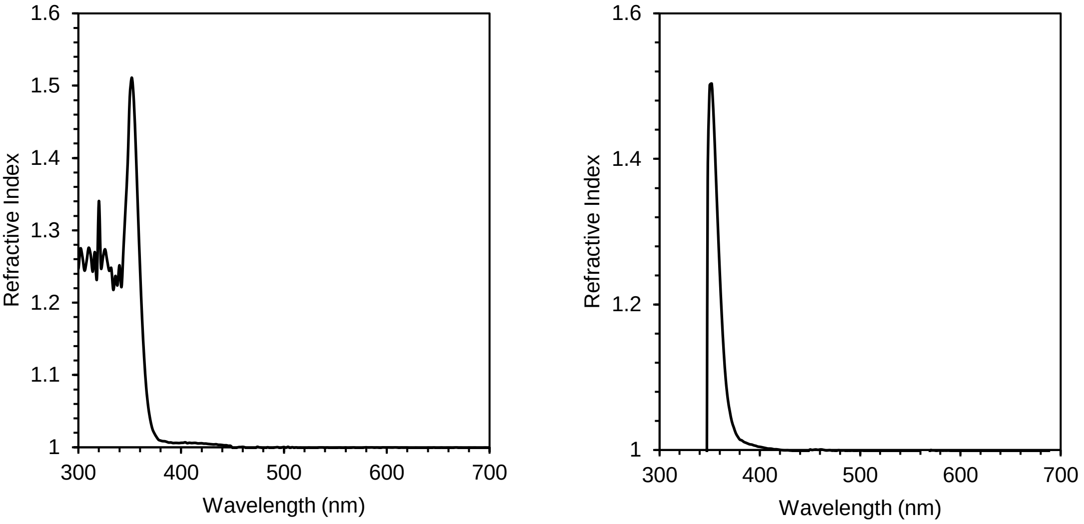
In similar way, the values of refractive index of the 8-Hq ligand in two different solvents (DMF and DMSO) were determined and compared as shown in Fig. (2). At wavelengths shorter than 345 nm, the 8-Hq in DMF shows higher value of refractive index than that in DMSO. However, the maximum value of refractive index about 1.5 was determined at 352 nm for both cases. Also, both samples show identical behavior in the visible region (380-700 nm). Accordingly, the effect of solvent was clearly observed in the UV region.

The absorption spectra of organometallic complexes (Alq_3, Baq_2, Cuq_2, Mnq_2 and Znq_2) in DMF are presented in Fig. (3). Table (3) shows the absorption edges of the 8-Hq ligand and prepared complexes in DMF. Similarly, the absorption spectra of organometallic complexes (Alq_3, Baq_2, Cuq_2, Mnq_2 and Znq_2) in DMSO are presented in Fig. (4). Table (4) shows the absorption edges of the 8-Hq ligand and prepared complexes in DMSO. The summary of these results are shown in Fig. (5).



(a) (b)

Fig. (1) Absorbance of 8-hydroxyquinoline ligand in different solvents (a) DMF and (b) DMSO



(a) (b)

Fig. (2) Variation of refractive index of 8-hydroxyquinoline ligand in different solvents (a) DMF and (b) DMSO

It is clear that the type of solvent has no effect on the absorption edge of the Alq_3 complex, has slight effect on the absorption edge of the Cuq_2 and Mnq_2 complexes, and reasonable effect on the absorption edge of the Baq_2 complex. The Znq_2 shows two comparable absorption edges at 340 and 400 nm in DMF and at 338 and 400 nm in DMSO. Also, in general, the organometallic complexes show shift in absorption edge towards longer wavelengths. However, the Baq_2 in DMF shows irregular behavior as the absorption edge was simply decreased by ~100% (at 318nm) when compared to the absorption edge of the 8-Hq in DMF (at 334nm).

It is clear that the type of solvent has no effect on the absorption edge of the Alq_3 complex, has slight effect on the absorption edge of the Cuq_2 and Mnq_2 complexes, and reasonable effect on the absorption edge of the Baq_2 complex. The Znq_2 shows two comparable absorption edges at 340 and 400 nm in DMF and at 338 and 400 nm in DMSO. Also, in general, the organometallic complexes show shift in absorption edge towards longer wavelengths. However, the Baq_2 in DMF shows irregular behavior as the absorption edge was simply decreased by ~100% (at 318nm) when compared to the absorption edge of the 8-Hq in DMF (at 334nm).

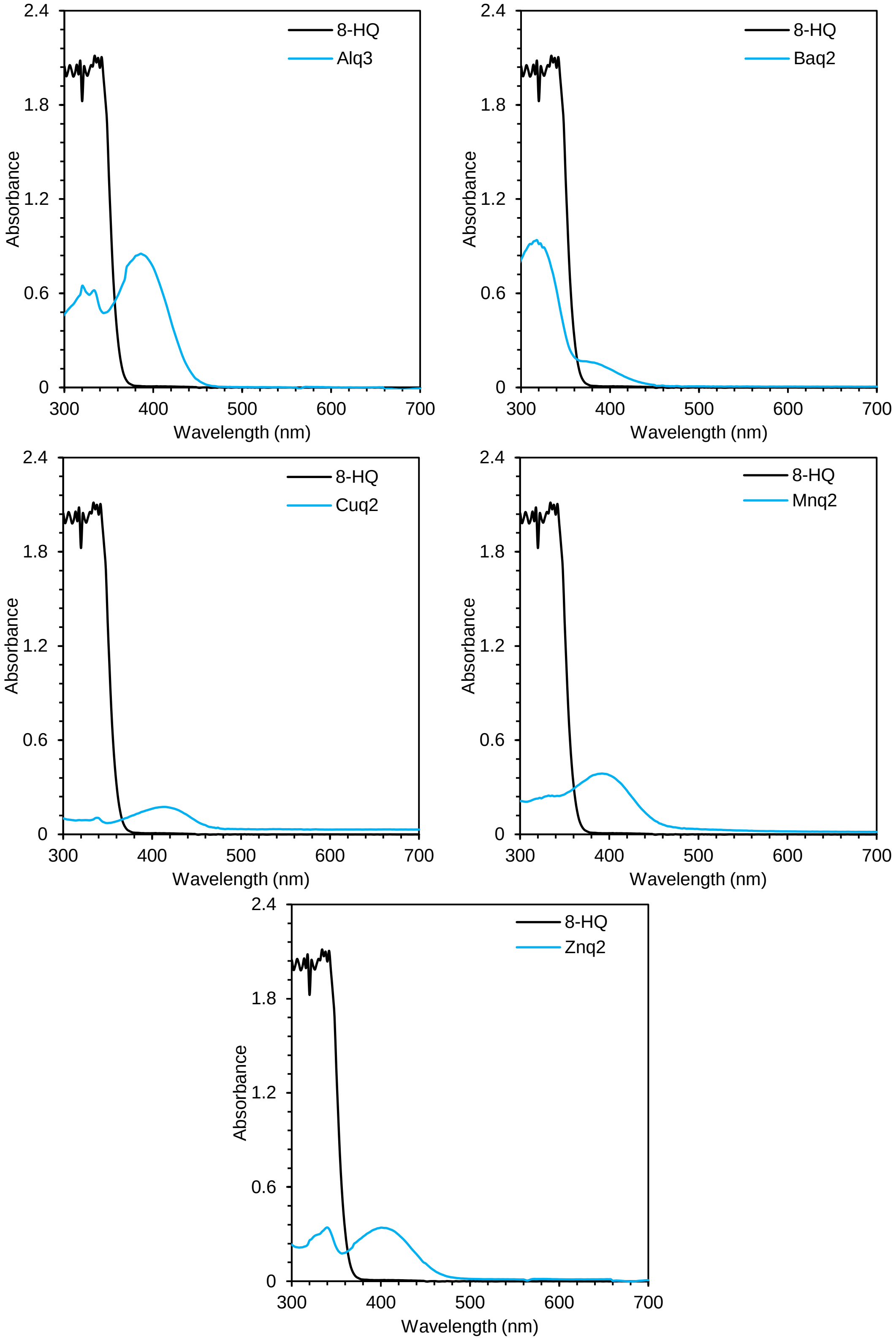


Fig. (3) Absorbance of the M-8-hydroxyquinoline complexes prepared in this work in DMF

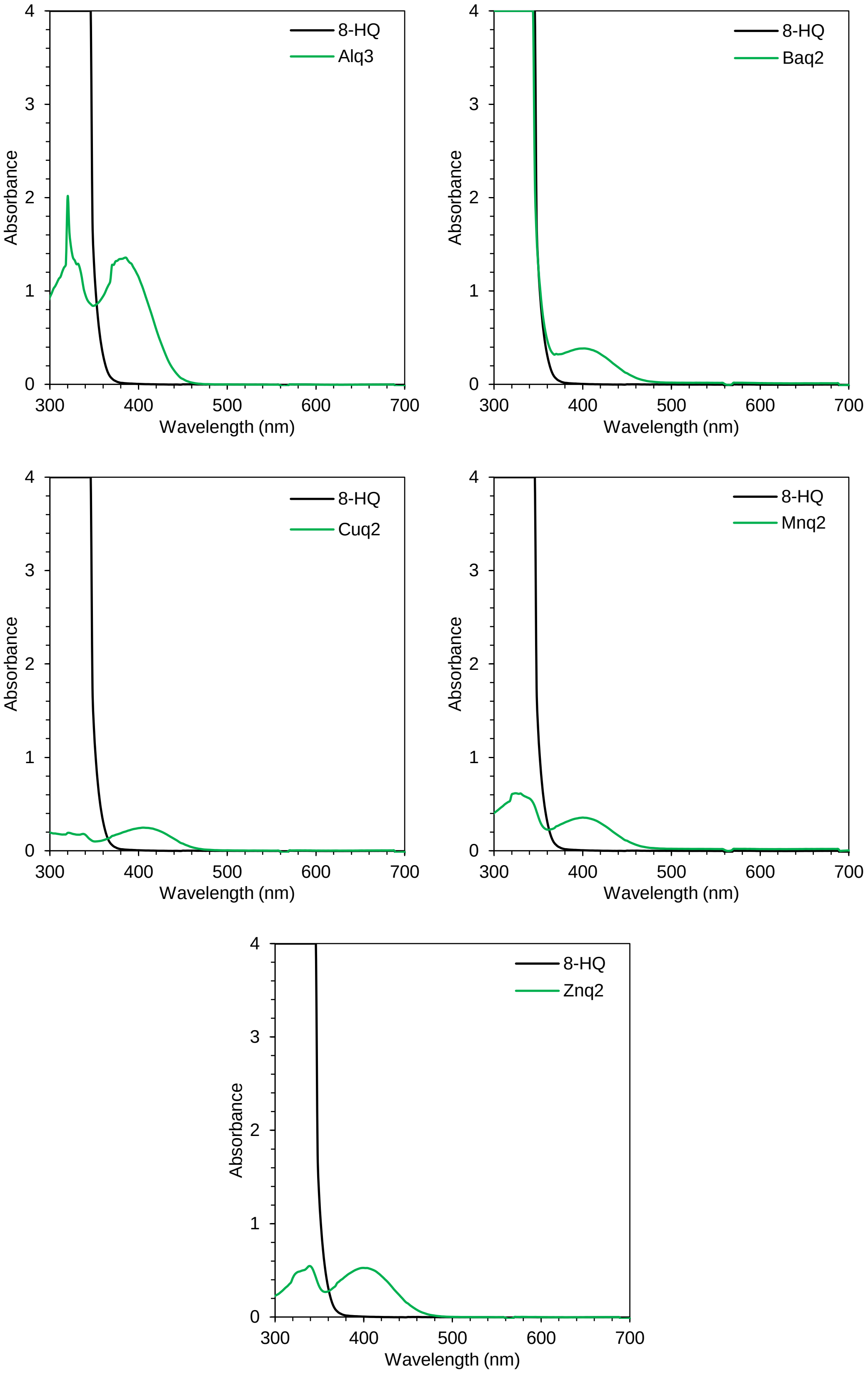


Fig. (4) Absorbance of the M-8-hydroxyquinoline complexes prepared in this work in DMSO

Table (4) Absorption peaks of the prepared complexes compared to that of 8-Hq in DMSO

Complex	Absorption Peak	Absorption Edge (nm)
8-Hq in DMSO	4	346
Alq_3	1.356	386
Baq_2	0.385	402
Cuq_2	0.247	406
Mnq_2	0.354	400
Znq_2	0.544	338
	0.526	400

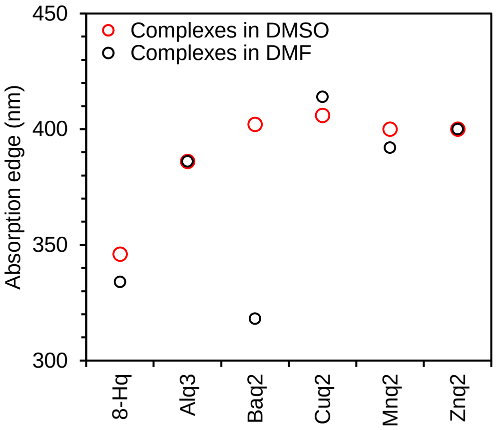
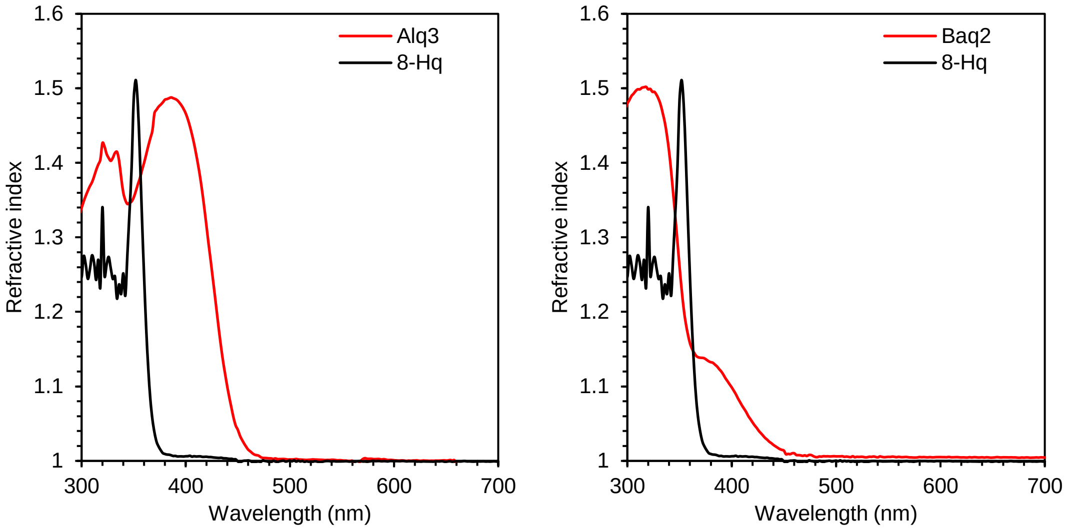


Fig. (5) Summary of absorption edges of the 8-Hq and prepared complexes in two different solvents (DMF and DMSO)

In similar manner, the refractive index of each complex prepared in this work was compared to that of 8-Hq in two different solvents (DMF and DMSO). These results are shown in figures (6) and (7) and the summary is shown in tables (5) and (6).



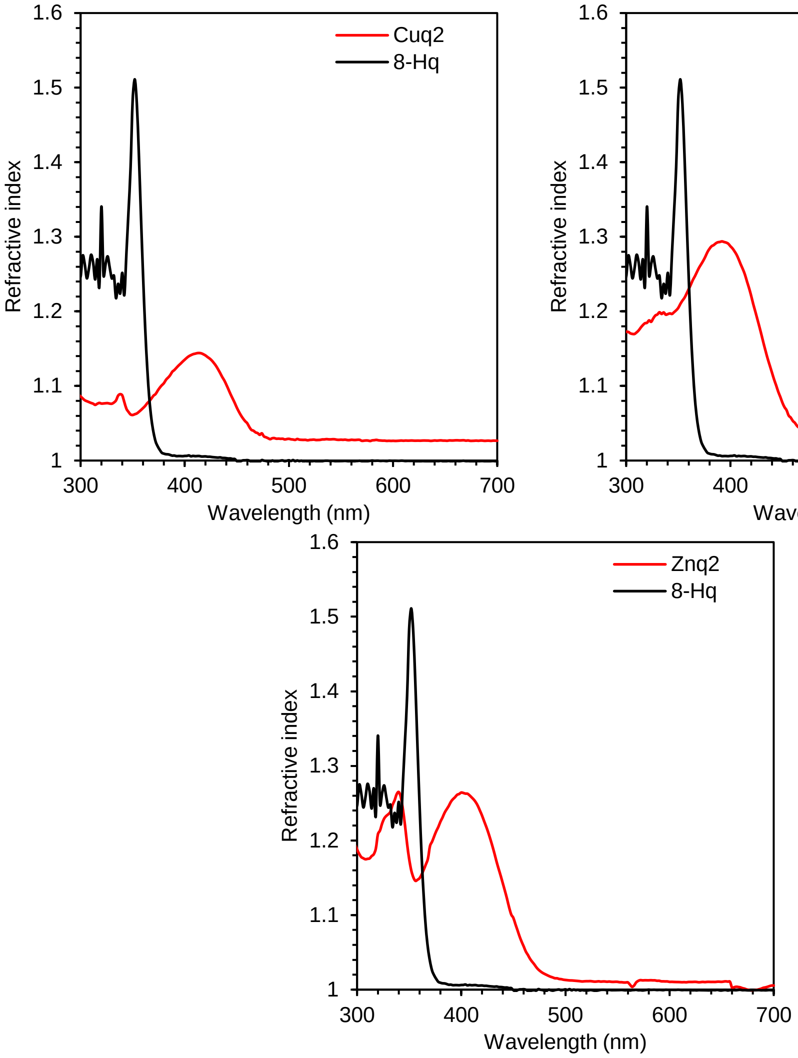
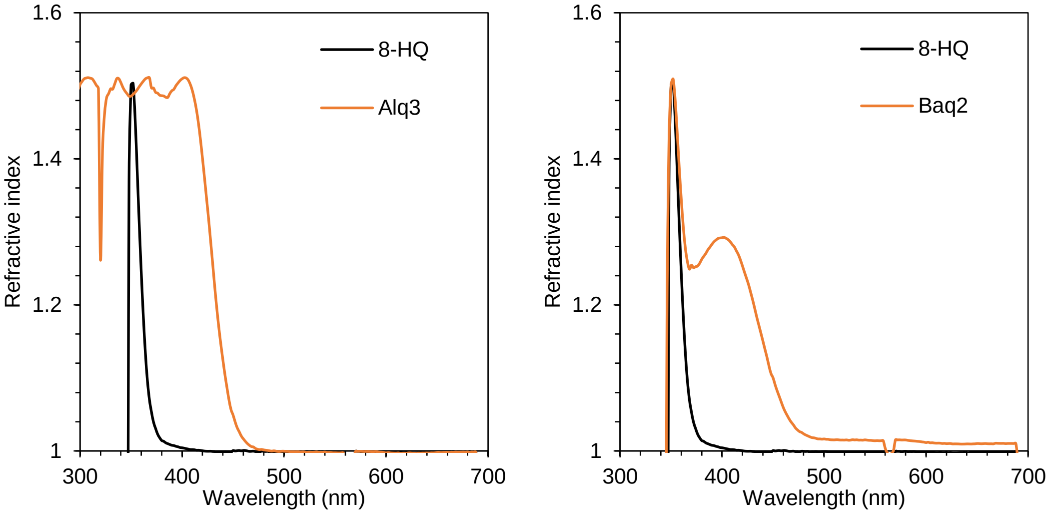


Fig. (6) Variation of refractive index of the M-8-hydroxyquinoline complexes prepared in this work in DMF



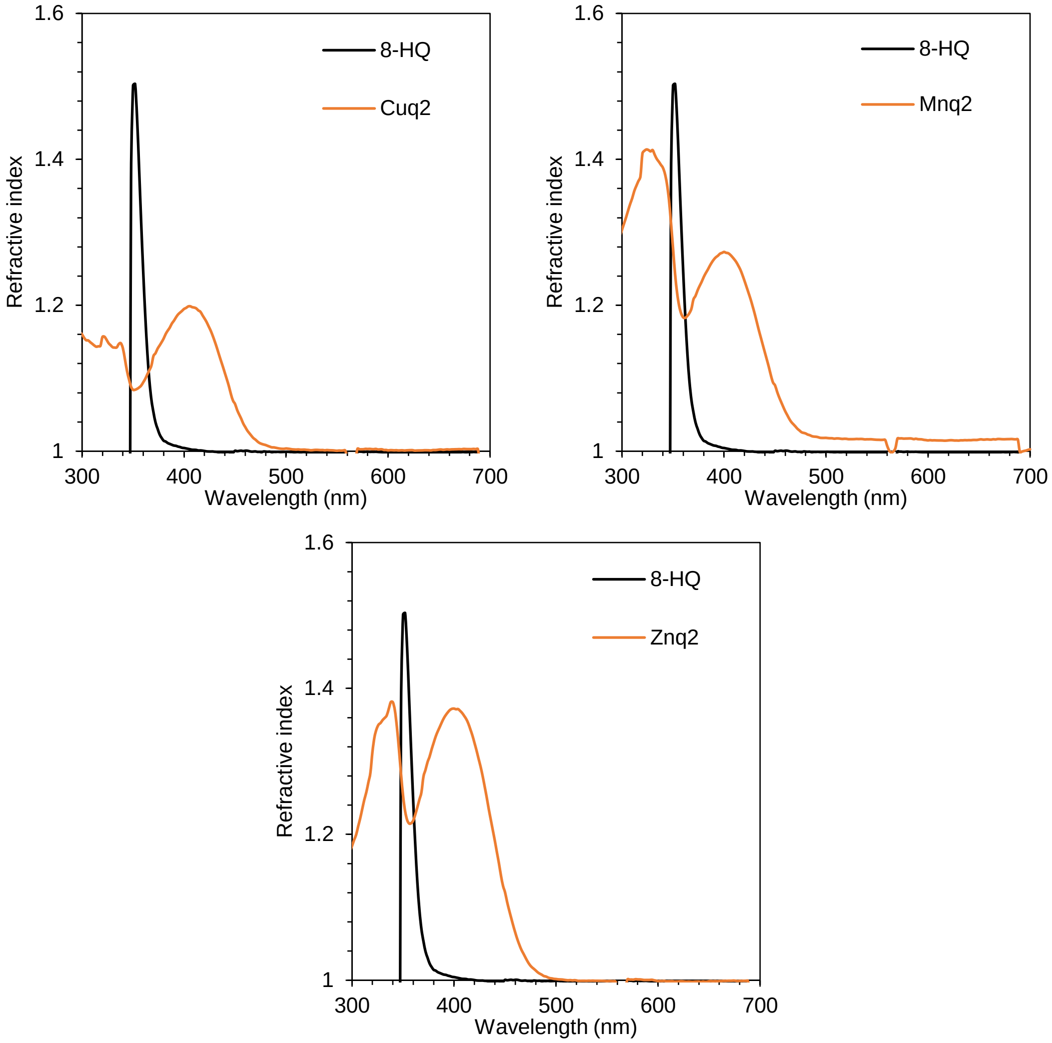


Fig. (7) Variation of refractive index of the M-8-hydroxyquinoline complexes prepared in this work in DMSO

In general, all prepared complexes have lower values of refractive index when compared to the 8-Hq in DMF or DMSO. This is attributed to the linkage of metallic ions to the ligand. However, the Baq_2 in DMF and Alq_3 in DMSO have refractive indices comparable to that of 8-Hq in either DMF or DMSO. This result agrees to that of absorption shown before.

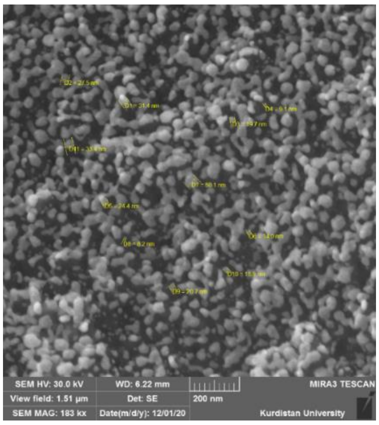
In order to interprete the different behaviors of Alq_3 and Baq_2 complexes, the FE-SEM has confirmed the formation of nanoparticles in these samples with minimum particle size of 8.2 and 49.4 nm for Alq_3 and Baq_2, respectively, while other complexes, such as Znq_2, shows reasonably larger particles. These nanoparticles are highly expected to play a key role in the spectroscopic properties of the prepared complexes due to the quantum size effect.

Table (5) Refractive indices of the prepared complexes compared to that of 8-Hq in DMF

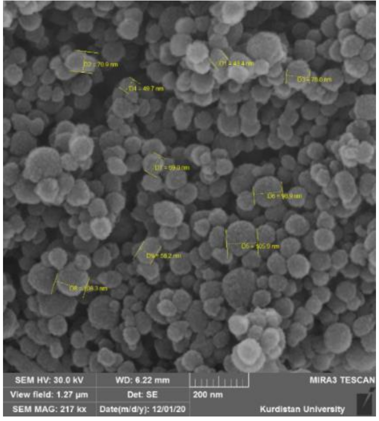
Complex	Maximum Refractive index	@ nm
8-Hq in DMF	1.488	382
Alq_3	1.487	386
Baq_2	1.502	318
Cuq_2	1.144	414
Mnq_2	1.293	392
Znq_2	1.265	340
	1.264	400

Table (6) Refractive indices of the prepared complexes compared to that of 8-Hq in DMSO

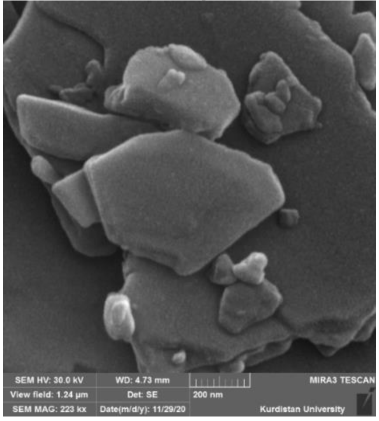
Complex	Maximum Refractive index	@ nm
8-Hq in DMSO	1.503	352
Alq_3	1.511	402
Baq_2	1.292	402
Cuq_2	1.198	406
Mnq_2	1.273	400
Znq_2	1.381	338
	1.371	404



Alq_3



Baq2



Znq2

Fig. (8) FE-SEM images of some M-8-hydroxyquinoline complexes prepared in this work

4. Conclusion

In concluding remarks, the properties of solvent, such as polarity index, dipole moment and dielectric constant, have affected the physical properties of organometallic complexes, especially absorption and refractive index in the spectral range 300-800 nm. Linkage of metal ions to the ligand structure has lead in general to decrease the absorbance as well as the refractive index of the prepared complex. The formation of nanoparticles within the complex structure was found to have reasonable effect on these properties due to the quantum size effect.

References

[1] A. Godard, Y. Robin and G. Queguiner, J. Organomet. Chem., 336 (1987) 1-12.
[2] D.J. Berg, S.J. Rettig and C. Orvig, J. Am. Chem. Soc., 113 (1991) 2528-2532.
[3] Y. Mei, P.A. Bentley and W. Wang, Tetrahedron Lett., 47 (2006) 2447-2449.
[4] S.F. Liu et al., J. Am. Chem. Soc., 122 (2000) 3671-3678.
[5] Q. Wu, J.A. Lavigne and S. Wang, Inorg. Chem., 39 (2000) 5248-5254.
[6] Y.K. Jang et al., J. Korean Phys. Soc., 49 (2006) 1057-1061.
[7] Y. Hamada et al., Jpn. J. Appl. Phys., 32 (1993) L514-L515.
[8] C.H. Cheng and S. Jianmin, Coord. Chem. Rev., 171 (1998) 161-174.
[9] R. Pohl et al., J. Org. Chem., 69 (2004) 1723-1725.
[10] R. Pohl and P. Anzenbacher Jr., Org. Lett., 5 (2003) 2769-2772.
[11] Y. Fazaeli et al., J. Colloid. Interface Sci., 346 (2010) 384-390.
[12] A. Bach et al., J. Chem. Phys., 112(3) (2000) 1192-1198.
[13] C.W. Tang and S.A. van Slyke, Appl. Phys. Lett., 51 (1987) 913-915.
[14] M. Colle, R.E. Dinnebier and W. Brutting, Chem. Commun., (2002) 2908-2909.
[15] L.G.C. Rego et al., J. Phys. Chem. C, 114(2) (2010) 1317-1325.
[16] L. Duan et al., Acc. Chem. Res., 48(7) (2015) 2084-2096.
[17] P.S. Wagenknecht and P.C. Ford, Coordin. Chem. Rev., 255 (2011) 591-616.
[18] L.S. Forster, Coordin. Chem. Rev., 248 (2004) 261-272.
[19] W.A.E. Omar and O.E.O. Hormi, Tetrahedron, 65 (2009) 4422-4428.
[20] V.P. Barberis and J.A. Mikroyannidis, Synth. Met., 156 (2006) 865-871.
[21] B. Li et al., Inorg. Chim. Acta, 366 (2011) 241-246.
[22] C. Lima et al., Phys. Chem. Chem. Phys., 18 (2016) 16555-16565.