

Chapter 3

Thesis Work Motivations

3.1 Introduction

The first Chapter was a comprehensive view effort, however not exhaustive, on gallium chemistry. The motivation of this approach was to obtain organized knowledge on metal which is attracting a lot of research interest.

One of the motivations was also to have an idea about the gallium *life cycle* starting from the natural source, throughout the applications, to end up to the recovery methods of waste production. Further because of gallium compounds are attractive materials for optoelectronic applications, the overview on OLED technologies was organized in order to explore perspective locations of a possible research study on the synthesis of new gallium compounds.

3.2 General consideration on gallium chemistry

Gallium metal cations show high chemical versatility which can be exploited to synthesis a large variety of molecular structure. The strong affinity towards phenoxides and carboxylates or O,O, O,N, N,N bidentate and polidentate ligands, Lewis bases ligands, allows to synthesis stable tetra-, penta- and hexacoordinated compounds and supramolecular compounds in a bottom-up approach. Gallium compounds display promising perspective in three different application fields as medicine, catalysis and optoelectronic technologies.

Gallium chemistry is characterized by the possibility to synthesis charged compounds; structures of ionic gallium compounds can be obtained using both rigid and flexible ligands, and the counter ions of these complexes can differ from halides to anion gallium compound as $[\text{GaCl}_4]^-$. Their properties and applications are mostly unexplored.

3.3 Focus on quinolate hexacoordinated gallium compound

8-hydroxyquinoline (HQ) and 2-methyl-8-hydroxyquinoline (HQ'), O,N chelating agents, which structures are reported in **Figure 3.1**,

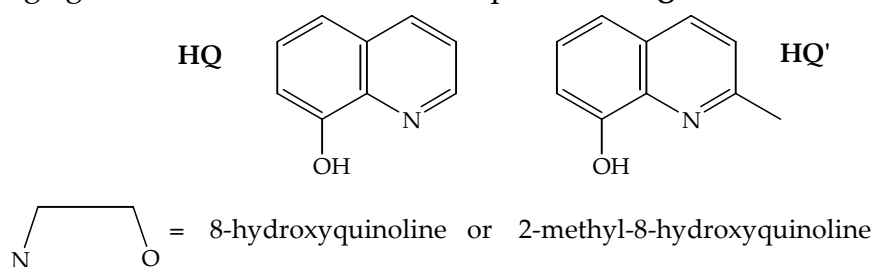


Figure 3.1: 8-hydroxyquinoline (left) and 2-methyl-8-hydroxyquinoline (right).

show very low emission intensities in solution because of the intramolecular or intermolecular hydroxyl proton transfer on the pyridinic nitrogen.¹

Absorption and emission spectra of HQ' show blue-shift respect to HQ, as shown in **Figure 3.2**.

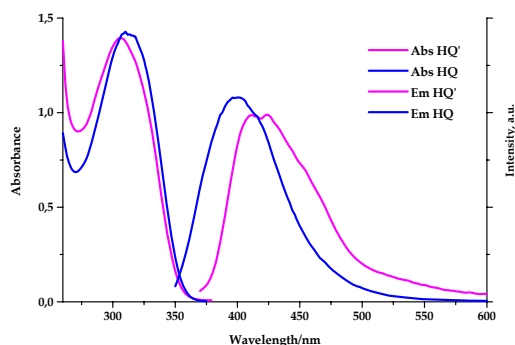


Figure 3.2: HQ and HQ' absorption and emission spectra.

While homoleptic hexacoordinated gallium compounds synthesised with three equivalents of HQ and HQ' show intense fluorescence bands, the emission intensities and energies of the quinolate compounds of the metal of the XIII Group depend on the nature of the metallic centre and of the chemical groups eventually present on the aromatic rings. Chemical, luminescent and charge transport properties of these compounds can be modulated by introducing electro-withdrawing (W) or electro-donating (D) substituents in different positions of the heteroaromatic ring. In **Figure 3.3** are represented the positions on the quinolate ring in which W and D influence the luminescent behaviour of the metal quinolate compounds.²

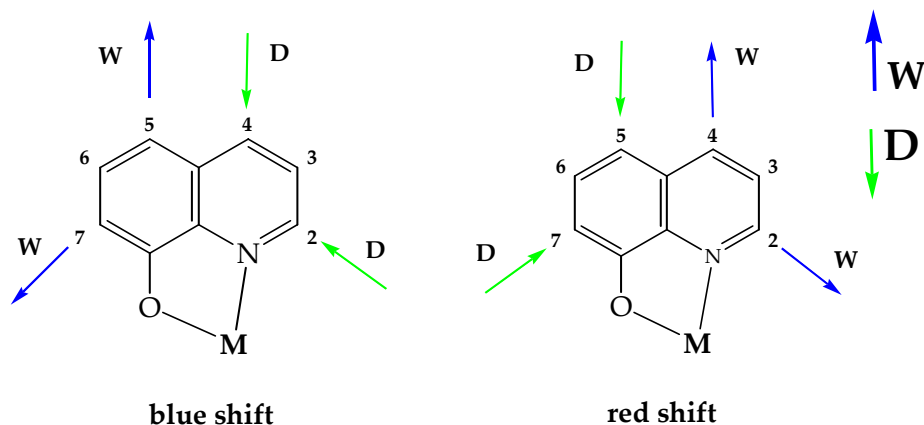


Figure 3.3: relative position of W and D on the quinolate ring.

Electro-donating (D) groups, in the second or fourth position, influence a blue-shift in both absorption and emission bands. Instead, electro-withdrawing (W) groups in the fifth and seventh position induce red-shift.

Metal quinolates of Al^{3+} , Ga^{3+} , In^{3+} metal cations (**Figure 3.4**) are under investigation as key materials to be applied as electroluminescent or charge transport layers in OLEDs. Tris(8-hydroxyquinolate)aluminium(III) is the most well-known molecule of this family and is extensively used.³

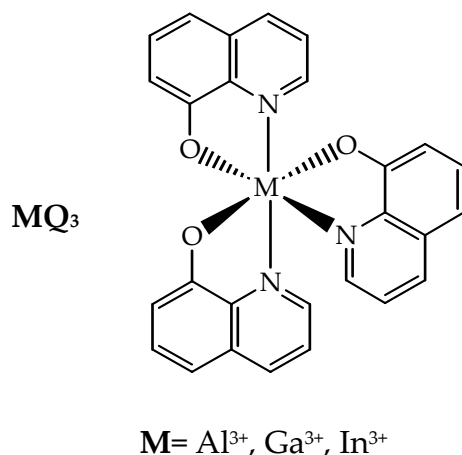


Figure 3.4: tris(8-hydroxyquinolate)M(III) complexes.

The photophysical characterization of AlQ_3 , GaQ_3 and InQ_3 , and organic emitting devices obtained with these materials, show that the emission shift to higher wavelength are correlated to the increasing of the metal atomic number hence to the covalent nature of the metal-ligand bond.

In the course of forming the metal chelates complexes (AlQ_3 , GaQ_3 and InQ_3) the oxygen in 8-quinolinol group uses a $2p$ orbital to form covalent bond and the nitrogen uses $2sp^2$ hybrid orbital to form ligand bond with metals. The central atom Al, Ga and In, use $3sp^3 3d^2$, $4sp^3 4d^2$, and $5sp^3 5d^2$ to form the octahedral chelate complexes, respectively.

As the atomic number increases, the orbital energy of central atoms and ligand becomes larger and the chemical bond becomes weaker. This may affect the luminescence properties (**Table 3.1**) and charge transport capability of these materials.

The photoluminescence quantum yield (Φ_{PL}) and the electroluminescence (EL) efficiencies of devices are in inverse ratio with the atomic dimension while the electron mobility is enhanced.⁴

MQ_3	Absorption λ_{max} / nm	Emission λ_{max} / nm	Φ^*_{PL} in CH_2Cl_2
AlQ ₃	385	510	1.00
GaQ ₃	392	540	0.23
InQ ₃	362	520	0.32

Φ^*_{PL} normalized respect to AlQ₃

Table 3.1: MQ_3 absorption, emission and photoluminescent quantum yields.

Electronic π - π^* transitions in MQ_3 are localized on the quinolate ligands. The filled π orbitals (or HOMOs) are located on the phenoxide side of the quinolate ligand, and the unfilled π^* orbitals (or LUMOs) are on the pyridyl side. The phenoxide π -system is the highest energy filled state and hence should be the most readily oxidized, making it the likely site of the trapped holes. Conversely, the pyridyl system is the lowest energy vacant state, making it the likely site of reduction, and thus of the trapped electrons.^{5,6} It has been reported that OLEDs built with GaQ₃ exhibit higher electroluminescence yields and power efficiency than other equivalent devices based on AlQ₃ or InQ₃.⁵

The crystal packing of GaQ₃ and GaQ'₃ shows close and extended π - π stacking interactions between the quinolate ligands of adjacent molecules. Crystal structural analysis of GaQ₃ revealed that the π - π stacking takes place in a multiple direction fashion.⁷ Good overlap between adjacent molecules, closely packed face to face interactions, facilitates carrier transport ability when an electric field is applied.⁸ Furthermore recent work has focused the attention on the AlQ₃ polymorphism. These studies show that α , β and δ phases influence the optical properties of AlQ₃.^{9,10}

Polymorphism was induced in the solid state structure of GaQ₃ obtaining different polymorphs. The *mer*-isomer shows α , β , and clathrates polymorphs, while δ phase was observed in the *fac*-isomer. These studies correlate the dependence of optical behaviours, such as fluorescence, with the solid state

organization.⁹ The steric hindrance of the methyl substituent in the second position influence the GaQ₃ structural properties; for this reason stable compounds of Al³⁺ with three equivalents of 2-methyl-8-hydroxyquinoline are not reported to be stable.

The average bond length of the Ga–N bond ranging from 2.085(4) Å to 2.214(4) Å because of the surrounding methyl group, while the average Ga–O bond distance decreases from 1.955(3) Å to 1.904(3) Å.

An examination of the solid state packing of AlQ₃, GaQ₃ and GaQ'₃ shows that there are close π - π stacking interactions between the quinolate ligands of adjacent molecules, with ligand stacking distance ranging from 3.29(2) Å to 3.52(2) Å.^{11,12} These results explain the lesser stability of the GaQ'₃ compounds, the Ga–N bond became more reactive to the nucleophilic water attack. Sizeable blue-shift observed in both absorption and emission spectra of GaQ'₃ relative to GaQ₃ are reported in **Table 3.2**.

<i>MQ₃</i>	<i>Absorption</i> λ_{max} / nm	<i>Emission</i> λ_{max} / nm	Φ^*_{PL} <i>in CH₂Cl₂</i>
AlQ₃	385	510	0.15
GaQ₃	392	540	0.40
GaQ'₃	362	520	0.40

Table 3.2: absorption and emission spectra of AQ₃, GaQ₃ and GaQ'₃.

Recently the chemical structure of a series tris(8-hydroxyquinolinolate) chelates (*n*MeQ₃M: *n*= 0, 3, 4, 5; M= Al³⁺, Ga³⁺), bearing methyl (Me) substituents in different positions of the quinolate ring, was related to their photoluminescence (PL), electroluminescence (EL), and thermal properties.

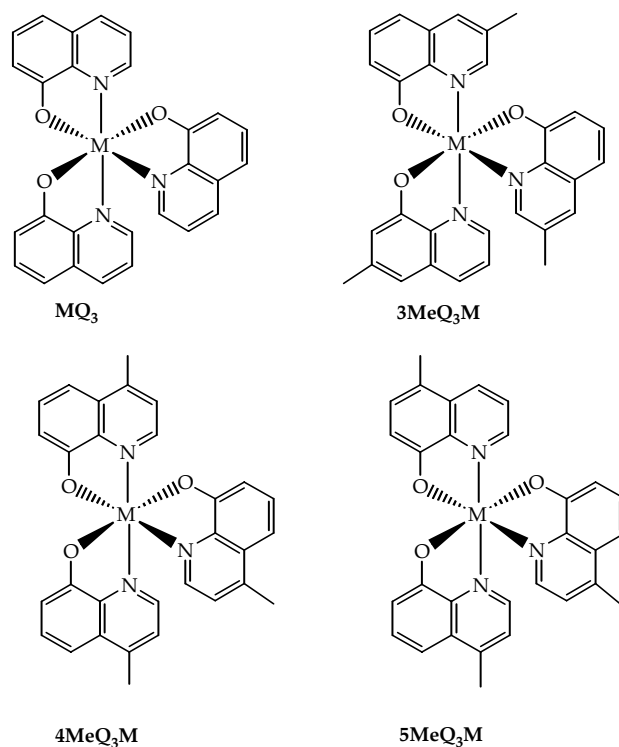


Figure 3.5: tris(8-hydroxyquinolinolate) chelates ($n\text{MeQ}_3\text{M}$: $n=0, 3, 4, 5$; $M=\text{Al}^{3+}, \text{Ga}^{3+}$)

In the case of the 3MeQ and 4MeQ ligands, higher EL device operating voltages were observed when metal tris-chelates were used as emitting material in OLEDs. This phenomenon was interpreted as the evidence of a decreased overlap between the π -electron systems in the pyridyl rings of adjacent molecules, which is the site of the lowest unoccupied molecular orbital (LUMO) and, hence, the likely location of injected electrons.

This was the first established link between the electroluminescent and thermal (physical) properties of a series of electroluminescent compounds.

Methylation of the 8-hydroxyquinoline ligand at the 3rd or 4th position (pyridyl ring) results in a factor of 1.4 and 3.0 enhancement of Φ_{PL} respectively, while methylation at the 5th position (phenoxide ring) results in a factor of ~ 3.0 decrease in Φ_{PL} relative to the unsubstituted analogue. The materials were tested also in multilayer devices as electroluminescent layers. Differences in EL

performance of the $n\text{MeQ}_3\text{M}$ chelates in this study can be related to the changes in the chemical molecular structure and thus the material properties in the bulk. The efficiency of charge-transport in organic molecular crystals is enhanced by strong intermolecular interactions of the polarizable π -system and is dependent on the molecular packing in the solid-state. Although vapor-deposited films of AlQ_3 and GaQ_3 are amorphous, crystallographic data of single crystals provides important information about their molecular packing preferences. For example, AlQ_3 and GaQ_3 show strong dipolar π - π stacking interactions (3.5-3.9 Å) of the 8-hydroxyquinoline ligands between adjacent molecules with preferential overlap of the pyridyl rings. Since pyridyl ring is the location of the LUMO, this could explain the higher electron versus hole mobility in AlQ_3 and related metal 8-hydroxyquinolate chelates. Therefore, it is not unexpected that a decrease in π - π stacking (due to steric factors, changes in polarity, as well as loss of hydrogen-bonding interactions of the metal chelates) will be produced by methylation of the 8-quinolinol ligand.

These changes will reduce the cohesive forces between molecules, and thermal analysis of the series of methyl-substituted derivatives reveals these differences. A systematic study of the effect of methylation of aluminium and gallium tris(8-quinolinolate) chelates on the PL, EL, and thermal properties was reported by Saphochak *et al.*⁶ Methylation of the 8-hydroxyquinoline ligand decreases the crystalline melting point of the metal tris-chelates and increases the glass transition temperatures of the amorphous materials compared to the unsubstituted analogues, in both cases indicative of reduced intermolecular interactions.

In order to increase the solubility of the quinolate gallium tris-chelate, the 5-amido-pyridine-8-hydroxyquinolate (**Figure 3.6**) were studied to understand the complementary function that the amido and pyridine groups exert towards H-bond networking. Addition of the $\text{NHCOC}_5\text{H}_4\text{N}$ fragment causes a red-shift

of the PL spectra. Resulting complexes of the tris(5-substituted-8-hydroxyquinoline)gallium(III) with reference to the parent 8-hydroxyquinoline compounds show emission at 590 nm. Thin films of these species applied in optoelectronic devices are usually obtained through vacuum-deposition or solution-based methods. But with the high vacuum-deposition technique isomerisations or oligomerisations occur upon high temperature sublimation. The molecular nature of the active films can be therefore different from that of the starting material.

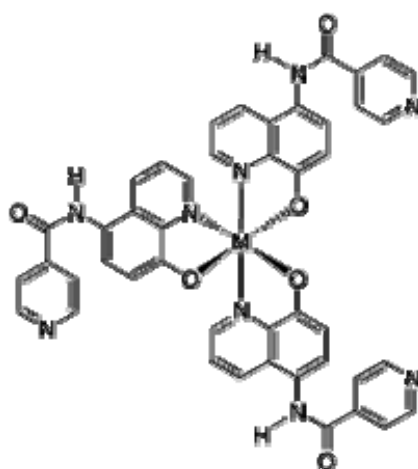


Figure 3.6: $Ga(Q'NHCOC_3H_4N)_3$

Introduction of a substituent on the aromatic ligand reflects on solubility. The aim is to obtain soluble materials in different solvents to improve practical applications based on solution methods for the production of amorphous thin solid films for optoelectronic devices.¹³

3.4 Focus on quinolate pentacoordinated gallium compound

Pentacoordinated compounds with the general formula Q'_2GaL were synthesised using gallium(III), 2-methyl-8-hydroxyquinoline, and a

monodentate ligands, in 1:2:1 molar ratio. Such complexes are promising materials to be applied as electroluminescent or charge transport layer. Pentacoordination is achieved using an halide, or with mono- and bifunctional carboxylates. The monometallic and bimetallic compounds reported in literature are illustrated in **Figure 3.7** and **3.8**.

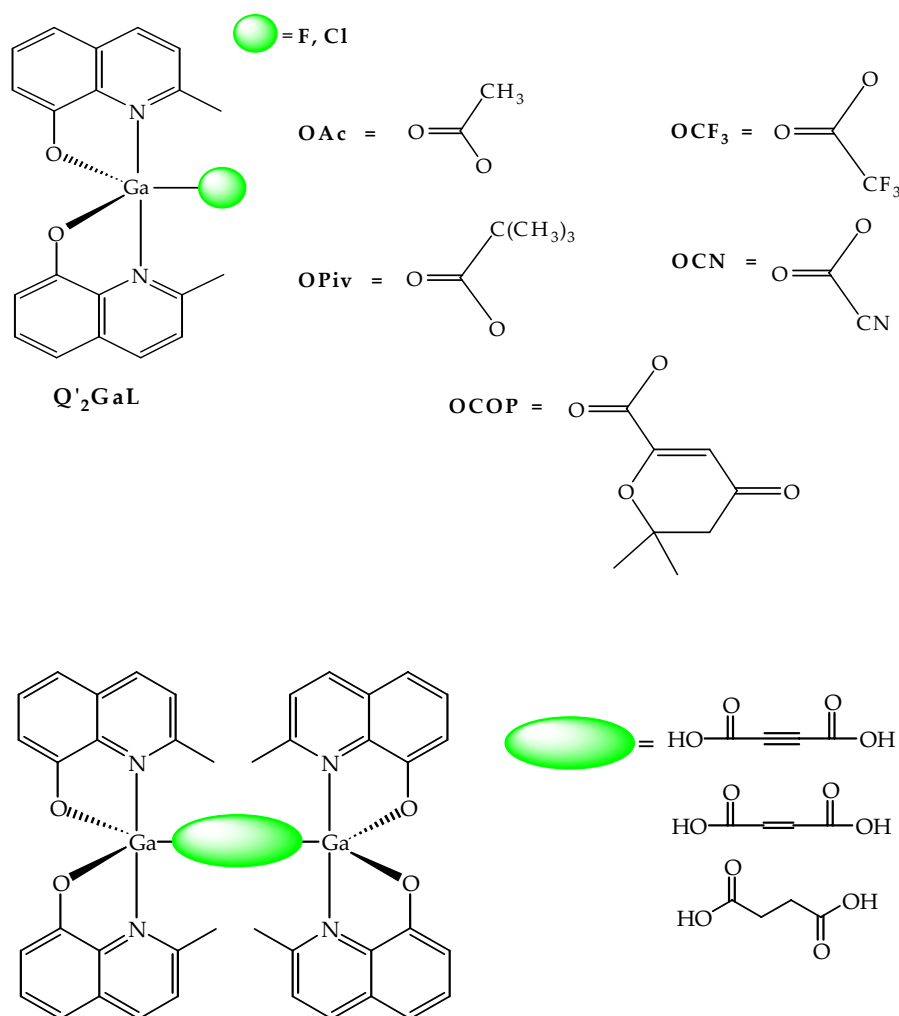


Figure 3.7: monometallic and bimetallic pentacoordinated compounds.

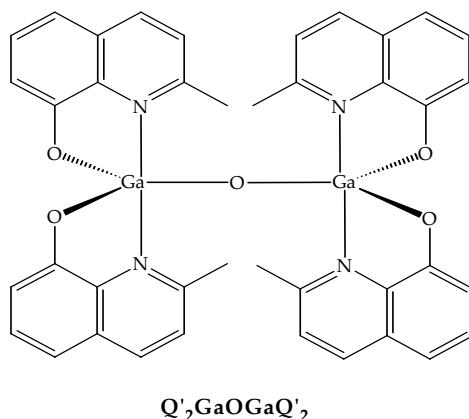


Figure 3.8: monometallic and bimetallic quinolate compounds.

These materials show green electroluminescence and their electron transport abilities were used as electron transport layers or electron injection layers in different kind of device architectures; in other cases they were tested as electroluminescent layers blended with different chromophores.¹⁴⁻¹⁸

All complexes show blu-shifted emission and in some cases more interesting photoluminescent quantum yields than the ones reported for AlQ₃ (Table 3.3)¹⁸.

Compounds	Absorption λ_{max}, nm	Emission λ_{max}, nm	Φ_{PL}
AlQ ₃	385	510	0.15
Q' ₂ GaOAc	366	504	0.13
Q' ₂ GaOPiv	366	501	0.13
Q' ₂ GaF	359	499	0.25
Q' ₂ GaCl	361	499	0.24
Q' ₂ GaOCN	366	499	0.18
Q' ₂ GaOCOP	365	501	0.03
Q' ₂ GaOCF ₃	360	500	0.21
Q' ₂ GaOGaQ' ₂	363	501	0.18

Table 3.3: absorption, emission and photoluminescence quantum yields of Q'₂GaL compounds.

3.5 Experimental study

The possibility to carry out functionalities simultaneously or to switch between them, for instance to accomplish both luminescence and/or charge transport properties in a single system, means that these compounds can act as multifunctional materials. As showed with the previously illustrated coordination gallium compounds, multifunctional materials can be small and relatively simple chemical systems and not necessarily bulky chemical structures.

These considerations suggest us to look further into the systems based on the luminescent Q'_2Ga^- fragment.

3.5.1 New charged hexacoordinated gallium(III) compounds

Charge gallium compounds reported in literature, and described in Chapter 1, are often studied only from the structural point of view. Another consideration is the almost total absence of photophysical characterization in most of the reported neutral and charged gallium compounds. In particular, charged gallium bis-(2-methyl-8-hydroxyquinolate) are unknown. Furthermore, no study was conducted on the possible role of the counter ions in technological applications.¹⁹

The target of the present work is to study the reactivity of gallium(III) towards N,N bidentate ligands in the presence of the strong chelating agent 2-methyl-8-hydroxyquinoline, avoiding the competitive formation of the neutral homoleptic trischelate GaQ'_3 . The purpose is to obtain an hexacoordinated ionic structure keeping contemporaneously the Q'_2Ga^- fragment, with general formula $[Q'_2Ga(N,N)][X]$, in which the hexacoordination is achieved using a

N,N as 2,2'-bipyridine and 1,10-phenantroline. The studies on this kind of systems and the perspective application will be discussed.

3.5.2 New pentacoordinated gallium(III) compounds

In the present experimental study synthetic protocols were planned to synthesis new pentacoordinated gallium compound.

For this purpose phenol (HL^n) and benzoic acids (HL'^n) derivatives were chosen as monodentate ligands in order to obtain two series of Q'_2GaL^n and $Q'_2GaL'^n$ monometallic pentacoordinated compounds. The ligands differentiate each other by the chemical nature of substituents in the *para* position on the aromatic ring, and in the case of trisubstituted benzoic acids also by the further presence of substituents in the *meta* positions. The possible influence of these ligands on both the chemical and the physical properties of the bis(2-methyl-8-hydroxyquinolate) gallium compounds was discussed.

Bidentate and polydentate ligands of this class of compounds were chosen for the synthesis of molecules in which more chromophores are covalently linked on the same chemical structure. The properties of these molecules were studied. Once characterised the synthesised Q'_2GaL^n compounds, the final step was to fabricate a single layer device structure to verify the collected data on the chemical and physical behaviour of the synthesised materials.

The studies of these gallium complexes may give a contribution to the synthesis of new interesting electro-optical materials to be exploited not only in OLEDs technologies.

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