



# Synthesis, characterization and electronic effects investigations of new 5,7-disubstituted tris(8-quinolinolate)Al(III) complexes



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## ABSTRACT

Eight 5,7-diaryl-8-hydroxyquinoline ligands were synthesized and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy and mass spectrometry. The electron-donating and electron-withdrawing aryl groups were attached to the 5- and 7-positions of the quinolinolate ring via Suzuki coupling reaction. The aluminum complexes of these ligands exhibited successful tuning in the emission color, covering a large segment of the visible spectrum.

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## 1. Introduction

8-Hydroxyquinoline (8-HQ), one of the most popular and versatile organic reagents, and its derivatives have found a great variety of applications ranging from pharmacological and pharmaceutical agents [1] to electron carriers in organic light-emitting diodes (OLEDs) [2] and fluorescent chemosensors for metal ions [3]. 8-hydroxyquinoline has bactericidal activity of comparable potency against non-replicating and replicating *Mycobacterium tuberculosis* (Mtb) [4], and *Staphylococcus aureus* [5]. Moreover, many substituted 8-HQ exhibit greater activity against bacterial strains and fungal strains than do the parent compounds, but moderate activity compared with standard drugs [6,7].

It has been almost more than two decades since tris(8-hydroxyquinoline)aluminum (III) [ $\text{AlQ}_3$ ] was introduced as an electron-transporting material in organic light-emitting diodes (OLEDs) [8]. Nowadays, OLEDs are gradually replacing liquid crystal displays (LCD) as the most important full-color flat panel display technology. In order to improve the efficiency of  $\text{MQ}_3$  ( $\text{M}$  = metal ion) complexes, researchers have centered their efforts on two major aspects: changing the chelated metal ion and modifying the structure of the chelating ligands [9–12]. Concerning the chelating ligands, it has been predicted that electron-donating substituents

in the C-5 or C-7 positions of the quinoline skeleton cause a red-shift of the complex emission, while a blue-shift is expected when electron-withdrawing groups are attached in the same positions. In this regard, blue-shifted absorbance/luminescence bands were recorded for 8-hydroxy-5-piperidinylquinolinesulfonamide complexes of aluminum [9]. A successful tuning in the emission color of  $\text{AlQ}_3$  was achieved by attachment of electron-donating (EDG) or electron-withdrawing (EWG) aryl groups to the 5-position of the quinolinolate ligand [13].

Sensing metal ions by fluorescent chemosensors is highly applicable to a wide range of technologies and has currently been studied intensively [14]. A chemosensor having a bipodal thio-carbamate scaffold attached to histidine moieties senses  $\text{Hg}^{2+}$  with a remarkable selectivity [15]. Azathia crown ethers carrying pyrene pendant as receptor molecules showed promising results as metal sensor systems for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  [16]. Aluminum (III) ion exists widely in the environment due to acid rain and human activities. Its toxicity to the environment and to humans is well documented [17]. Therefore, detection of  $\text{Al}^{3+}$  is crucial to control its concentration levels in the biosphere, hence its impact on human health. In this regard, 2-hydroxy-1-naphthaldehyde was used as a highly sensitive and selective fluorescent sensor for  $\text{Al}^{3+}$  in  $\text{EtOH-H}_2\text{O}$  solution [18]. The fluorescent reagent sodium 4-(2,5-diphenyl-1H-pyrrol-1-yl)benzoate (TriPP-COONa) showed good detection limit ( $27 \mu\text{g L}^{-1}$ ) for detecting aluminum ion in water samples [19]. An efficient fluorescent  $\text{Al}^{3+}$  receptor, 1-[[[(2-

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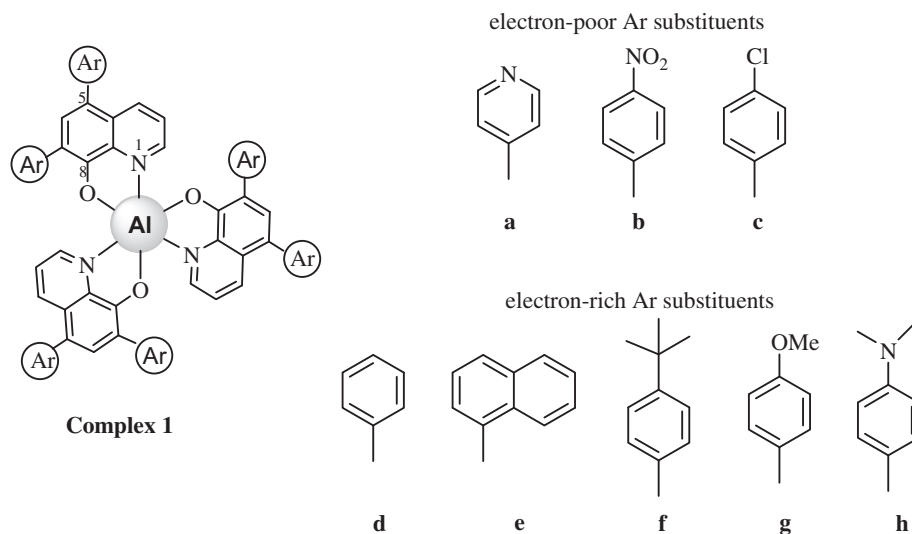


Fig. 1. Structure of  $\text{AlQ}_3$  complexes **1a–h** with electron-rich and electron-poor aromatic moieties.

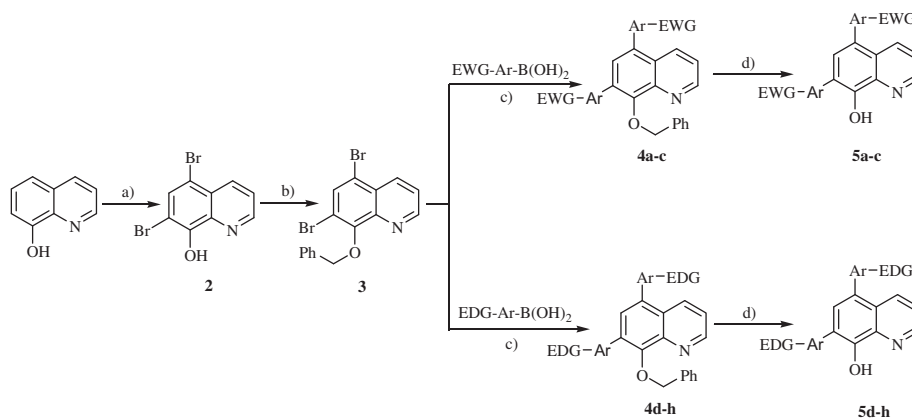
furanylmethyl)imino]methyl]-2-naphthol exhibited high selectivity and affinity towards  $\text{Al}^{3+}$  [20]. Owing to their chelating ability toward a great number of metal ions, 8-HQ and its derivatives have found many applications in the chemosensing field [21]. 8-Hydroxyquinoline was used to detect  $\text{Al}^{3+}$  in soil extracts with fluorometric detection limit of  $\sim 1 \times 10^{-8} \text{ M}$  (0.3 ppb) Al [22]. Moderate selectivity for  $\text{Al}^{3+}$  over other metal ions with detection limit reaching  $< 10^{-7} \text{ M}$  under weak acidic conditions was reported for 8-hydroxyquinoline-carbaldehyde Schiff-base [23].

Nevertheless, there is a need for more research to achieve higher selectivity and sensitivity to detect  $\text{Al}^{3+}$  over other metal ions. Our approach concentrates on increasing the chelating properties of 8-HQ derivative ligands to enhance the fluorescent output of the produced  $\text{AlQ}_3$  complexes and consequently increase the quantum yield and shifting the color to red regions by introducing electron-withdrawing and electron-donating phenyl moieties at the C5 and C7 positions of 8-HQ [24]. In this paper, we report the synthesis, spectroscopic identification, and photo-physical behavior of eight  $\text{AlQ}_3$  complexes **1a–h** in which the phenyl groups at C5 and C7 of the ligands are substituted either with electron-withdrawing groups **a–c** or with electron-donating groups **d–h** (Fig. 1).

## 2. Results and discussion

### 2.1. Synthesis

The eight ligands were prepared starting from 8-hydroxyquinoline following previously published method [25]. Dibromination of 8-HQ at C-5 and C-7 was performed satisfactorily using the published method with some modifications in which the concentrated sulfuric acid was replaced with acetic acid and the reaction was performed at room temperature to give compound **2** in 75.4% yield. The hydroxyl group in **2** was protected smoothly by the stable benzyl (Bn) group prior to the Pd-catalyzed coupling reactions to yield intermediate **3** in 54.0%. Compounds **4a–h** were prepared by coupling intermediate **3** with a suitable arylboronic acid using Suzuki cross-coupling reaction. Hence, the electron-rich EDG arenes and electron-poor EWG arenes were, respectively, attached to 8-benzyloxy-5,7-dibromoquinoline **3** in 50–89% yield. Deprotection of the benzyl group was achieved by catalytic transfer hydrogenation (CTH) using cyclohexa-1,4-diene and Pd/C catalyst in absolute ethanol to give ligands **5a–h** in 50–90% yield (Scheme 1). The final  $\text{AlQ}_3$  complexes **1a–h** were prepared by reacting the ligands **5a–h** with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in methanol. All the



Scheme 1. Synthesis of compounds **5a–h**; reaction conditions: a)  $\text{Br}_2$ ,  $\text{AcOH}$ , RT, 20 min; b) Bn-Cl,  $\text{K}_2\text{CO}_3$ , KI, acetone, reflux, 16 h; c)  $[\text{Pd}(\text{pPh}_3)_4]$  (6%),  $\text{Na}_2\text{CO}_3$ , benzene,  $\text{H}_2\text{O}$ , EtOH, reflux, 24 h; d) 1,4-cyclohexadiene, Pd-C (10%), EtOH, reflux, 5 h.

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