

Red–Green–Blue Emission from Tris(5-aryl-8-quinolinolate)Al(III) Complexes

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Abstract: A simple yet effective strategy for synthesis of 5-aryl-8-quinolinolate-based electroluminophores with tunable emission wavelengths is presented. Two different pathways for the attachment of electron-donating or electron-withdrawing aryl groups to the 5-position of the quinolinolate ligand via Suzuki coupling were developed. A successful tuning in the emission color was achieved: the emission wavelength was found to correlate with the Hammett constant of the respective substituents, providing a powerful strategy for prediction of the optical properties of new electroluminophores.

The availability of full-color displays based on the small-molecule organic light-emitting diode (SMOLED) technology is predicated upon a successful development of red-, green-, and blue-emitting electroluminophores.^{1,2} Organometallic SMOLED materials are valued for their stability and emission-color purity. The major obstacle in the fabrication of SMOLED-based full color displays is the so far limited availability of complexes that span the whole visible spectrum, while possessing similar emissive characteristics, physical properties, and processability.

Here we present a method for tuning the tris(8-quinolinolate)Al(III) (Alq₃) emission from blue-green to yellow and red via attaching electron rich/poor aryl moieties to the 5-position of the quinolinolate ligand. We selected Alq₃ as the most important SMOLED material, which is also the most stable electron-transporting compound currently used.^{2,3} Photophysical properties of Alq₃-type complexes are dominated by ligand-centered excited states⁴ originating from the electronic π - π^* transitions in the quinolinolate ligands.⁵ Because the highest density HOMOs of the quinolinolates are located on the phenoxide oxygen and the C5 (para position to

the oxygen),^{3b} we decided to manipulate the HOMO-LUMO energy gap responsible for the emission energy via attaching electron-withdrawing (EWG) or electron-donating groups (EDG) to the C5-aryl moieties of the quinolinolate.

At first glance, this approach may not seem as entirely new. The literature reports that emission tuning via EWG/EDGs attached to the C5 of 8-quinolinolate was attempted; however, there did not seem to be a clear connection between the electronic properties of the C-5 substituent and the emission of the resulting Al(III) complex.^{3b} For example, attaching the C≡N group did not result in an appreciable blue shift in the emission^{6a} compared to the parent Alq₃ (525 nm). Similarly the introduction of fluoro^{6b} and chloro substituents^{6c} resulted only in a small red-shifted emission, to 535 and 540 nm, respectively. The only example of a successful blue-shifted emission was reported for piperidine-amide of quinolinolate-5-sulfonic acid (emission maximum \approx 480 nm).^{6d}

Recently, we showed that the emission of Alq₃ derivatives with aryl-ethynylene moieties attached to the quinolinolate ligand may allow for tuning of the emission color in the resulting Al(III) complex.⁷ These materials provided an insight into the emission tuning in the Al(III) quinolinolates; however, the thermal stability required for OLED fabrication was less satisfactory. Here we present a series of 5-aryl-quinolinolate Al(III) complexes, in which the electron-withdrawing/-donating nature of the substituent is projected via the C-5 aryl bridge to the quinolinolate chromophore.

Complexes **1a–j** were designed to provide a varying degree of electronic density in the quinolinolate ligand, which is modulated by the aryl moiety.

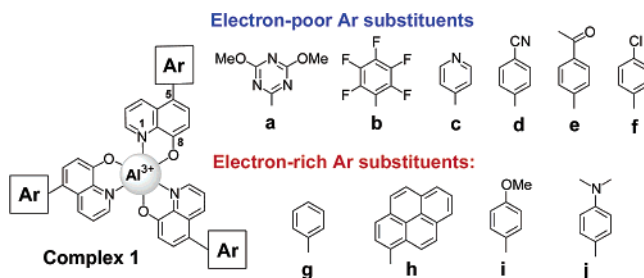


FIGURE 1. Novel 5-aryl Alq₃-type complexes prepared.

The synthesis of complexes **1a–j** (Scheme 1) departs from that of 5-bromo-8-hydroxyquinoline,⁸ which was

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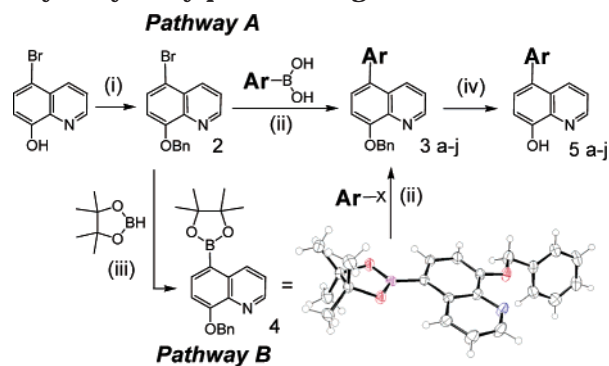
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SCHEME 1. Synthesis of 5-Aryl-8-hydroxyquinoline Ligands^a


^a Conditions: (i) Bn-Cl, K₂CO₃, AcCN, reflux; (ii) Pd(TPP)₄ (5%), 1 M aq K₂CO₃, toluene, TBACl, 90 °C; (iii) Pd(TPP)₄ (3%), TEA/THF, 90 °C; (iv) 1,4-cyclohexadiene, Pd-C (10%), isopropyl alcohol, reflux.

converted to the corresponding benzyl-derivative **2**. Intermediate **2** was coupled by Suzuki reaction with a suitable arylboronic acid bearing electron-donating group (EDG) to yield **3** (Pathway A), followed by hydrogenolytic deprotection.⁹ The introduction of aryl moieties bearing EWGs was performed according to Pathway B: **2** was converted to the pinacolato-boronate ester **4**, then reacted with an appropriate haloaromate to yield protected ligands of a general structure **3**. The final Al(III) complexes were obtained by reacting the ligands **5a–j** with AlCl₃·6H₂O in ethanol.

Successful emission color tuning in complexes **1a–j** mediated by substituents is easily observed by a naked eye examination of the complexes solution-based fluorescence. Complexes **1a–j** show bright photoluminescence upon excitation of dichloromethane solutions with black light (365 nm). As expected, the emission shifts from blue to yellow and red depending on the electronic nature of the aryl group (Figure 2).

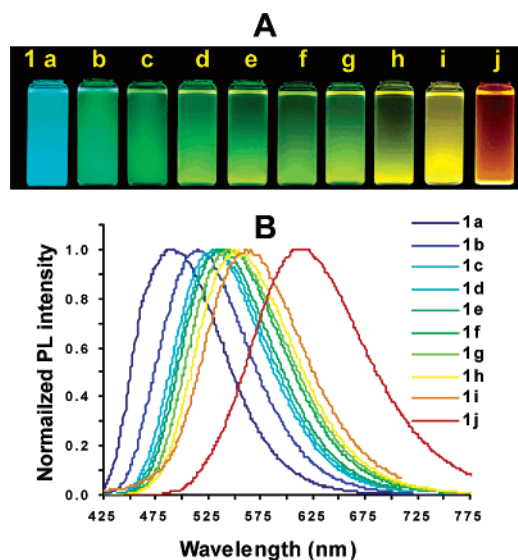


FIGURE 2. Panel A: Emission of complexes **1a–j** upon illumination with black light (365 nm). Panel B: Emission spectra of complexes **1a–j**.

TABLE 1. Photophysical and Electrochemical Properties of Complexes **1a–j^a**

complex	A_{\max} (ϵ [mol ⁻¹ ·cm ⁻¹])	λ_F [nm]	Φ_F^b	τ_F [ns]	HOMO-LUMO gap [eV]
Alq ₃	388 (7.0×10^3)	526	0.171	15.38	2.570
1a	390 (2.7×10^4)	490	0.533	29.50	3.255
1b	388 (1.1×10^4)	516	0.453	20.31	3.266
1c	397 (7.5×10^3)	530	0.301	16.57	3.246
1d	398 (1.4×10^4)	534	0.298	14.53	2.908
1e	394 (1.4×10^4)	537	0.234	12.76	2.752
1f	402 (1.0×10^4)	541	0.201	11.13	2.797
1g	402 (1.0×10^4)	545	0.100	9.72	2.718
1h	385 (2.2×10^4)	551	0.098	6.53	2.801
1i	410 (1.1×10^4)	564	0.057	4.73	2.534
1j	422 (1.0×10^4)	612	0.008	1.49	2.473

^a Absorption maximum (A_{\max}), emission maximum (λ_F), fluorescence quantum yield (Φ_F), and lifetime (τ_F) in dichloromethane at room temperature. HOMO-LUMO energy gap was estimated by using cyclic voltammetry of 1.0 mM solutions in acetonitrile containing 0.1 M tetrabutylammonium perchlorate; ^b Determined with use of quinine sulfate (30 μ M in 0.05 M H₂SO₄) as a standard.

Table 1 summarizes the properties of complexes **1a–j** determined from UV–vis, fluorescence, and electrochemical measurements.

The emission maxima of complexes **1a–j** span over 120 nm between 490 and 612 nm, and the emission profiles cover almost the entire visible light spectrum. Examination of the data in Table 1 shows decreasing fluorescence quantum yield and lifetime with decreasing emission energy. This dependence was investigated in terms of the optical energy gap law,¹⁰ which describes the exponential dependence of the nonradiative decay rate constant (k_{nr}) on the energy gap between singlet and ground states for the chromophores (Figure 3).^{11a,b}

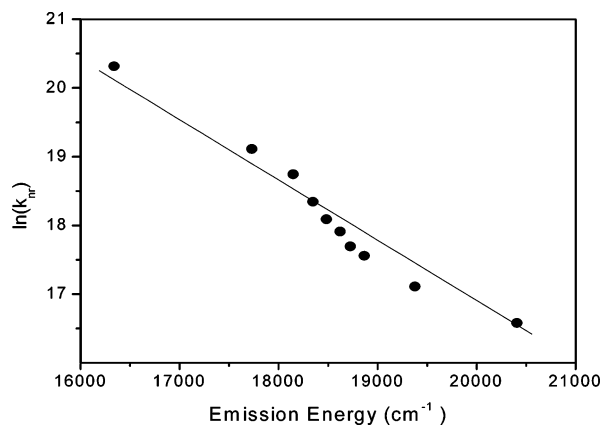


FIGURE 3. Plot of $\ln k_{nr}$ vs emission energy for the complexes **1a–j**.

The graph in Figure 3 showed an excellent linear relationship between $\ln k_{nr}$ and the relevant optical energy gap (correlation coefficient = 0.97), demonstrating that the characteristics of the emissive excited state remain comparable across the series.

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(10) Values for k_{rad} and k_{nr} were obtained by using data in Table 1 and the following equations: $k_{rad} = \Phi/\tau_F$ and $k_{nr} = 1/\tau_F - k_{rad}$. The table of actual k_{rad} and k_{nr} values is included in the Supporting Information.

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Because we were interested in developing a method for predicting emissive properties in Alq_3 -type complexes, we decided to investigate also the relationship between the photophysical properties of complexes **1** and the Hammett constant values of the substituents (Figure 4A,B). Although the pool of complexes **1a–j** bearing substituents with a known Hammett constant (σ_p)¹² is limited, one can clearly see that the photophysical properties, namely the fluorescence quantum yield and lifetime, show excellent correlation (coefficients = 0.97). The results of these correlations provide unambiguous proof that our initial notion that the C-5 aromatic substituents would provide an effective tool for tuning of the photophysical properties of the complexes **1a–j** was correct.

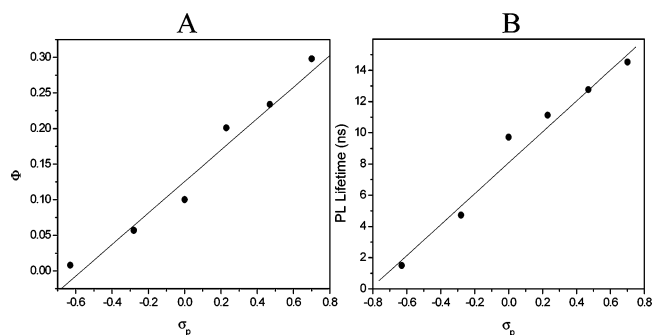


FIGURE 4. Correlation of fluorescence quantum yield (Panel A) and lifetime (Panel B) with the Hammett constant for complexes **1d,e,f,g,i,j**, respectively.

Additionally, the electrochemical HOMO-LUMO gap for the complexes was estimated by cyclic voltametry.¹³ Figure 5 shows the correlation between the magnitude of the electrochemical HOMO-LUMO gap in complexes **1d–g,i,j** and the electronic nature of aryl substituents as described by Hammett constants (σ_p).¹² As expected, the magnitude of the HOMO-LUMO gap directly correlates with electronic properties of the aryl moieties attached to the quinolinolate ligand expressed by Hammett constants.

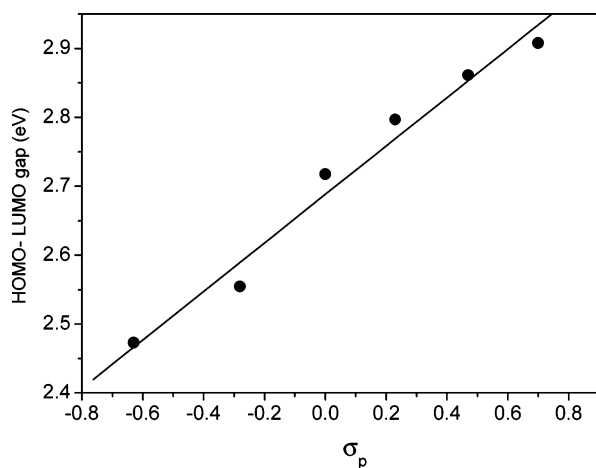


FIGURE 5. HOMO-LUMO gap correlation with the Hammett constants for complexes **1d–g,i,j**.

Last but not least, the preliminary experiments with fabrication of OLED devices¹⁴ utilizing complexes **1c** and

1i indicate that complexes **1a–j** are electroluminescent and, most importantly, that they can be processed via vapor deposition. Figure 6 shows three OLEDs made with Alq_3 , **1c**, and **1i** used as electroluminophores. The emission maxima of the OLEDs are very close to the maxima recorded in solution suggesting that also the OLEDs of the complexes **1a–j** may span the visible spectrum from blue to red.

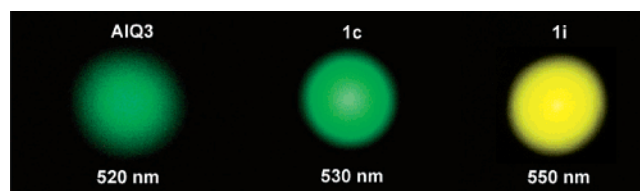


FIGURE 6. Vapor-deposited OLEDs based on Alq_3 , **1c**, and **1i**.

In conclusion, a new class of electroluminescent compounds with tunable emission based on tris(8-quinolinolate)Al(III) with substituted aryl moieties in the 5-position was prepared. We have shown that the electronic nature of the aryl substituent affects the emission color and fluorescence quantum yield of the resulting complex presumably via effective modification of the levels of HOMO located on C5 of the quinolinolate ligand. The optical properties of the resulting Al(III) complexes correlate with the values of the Hammett constant of the respective substituents. This strategy offers a powerful tool for the preparation of EL materials with predictable photophysical properties. Complexes **1a–h** also display reasonably high fluorescence and electroluminescence intensity, which makes them potentially useful as OLED materials. Efforts focused on optimization and evaluation of OLEDs utilizing compounds **1a–j** are currently in progress.

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Supporting Information Available: Experimental procedures for the preparation and characterization of compounds, their UV-vis and fluorescence spectra, numeric values for k_f and k_{nr} used to construct energy gap law correlation, and the crystallographic data for **4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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