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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 electroluminesophores 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 electroluminesophores.

The availability of full-color displays based on small-molecule organic light-emitting diode (SMOLED) technology is predicated upon a successful development of red-, green-, and blue-emitting electroluminesophores. Organometallic SMOLED materials are valued for their high photostability 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 material,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),6b we decided to manipulate the HOMOLUMO 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 C5 substituent and the emission of the resulting Al(III) complex.3 For example, attaching the C≡N group did not result in an appreciable blue shift in the emission6a compared to the parent Alq3 (525 nm). Similarly the introduction of fluoro6b and chloro substituents6c 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 ≈ 480 nm).5d

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.](image)

The synthesis of complexes 1a–j (Scheme 1) departs from that of 5-bromo-8-hydroxyquinoline,9 which was

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1 Bowing Green State University.
2 Iowa State University.
EWGs was performed according to Pathway B: 2
converted to the pinacolato-boronate ester
AlCl₃
plexes were obtained by reacting the ligands
5a
ligands of a general structure
with an appropriate haloaromate to yield protected
rescence. Complexes
eye examination of the complexes solution-based fluo-
mediated by substituents is easily observed by a naked
nature of the aryl group (Figure 2).

Successful emission color tuning in complexes 1a–j
mediated by substituents is easily observed by a naked
eye examination of the complexes solution-based fluo-
rescence. Complexes 1a–j show bright photolumines-
cence 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).

Table 1 summarizes the properties of complexes 1a–j
summarized in the Supporting
information.

### Table 1. Photophysical and Electrochemical
Properties of Complexes 1a–j

<table>
<thead>
<tr>
<th>complex</th>
<th>$A_{\text{max}}$ (e mol⁻¹cm⁻¹)</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\Phi_F$</th>
<th>$\tau$ [ns]</th>
<th>HOMO-LUMO gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq₃</td>
<td>388 (7.0 × 10⁻³)</td>
<td>526</td>
<td>0.171</td>
<td>15.38</td>
<td>2.570</td>
</tr>
<tr>
<td>1a</td>
<td>390 (2.7 × 10⁻³)</td>
<td>490</td>
<td>0.533</td>
<td>29.50</td>
<td>3.255</td>
</tr>
<tr>
<td>1b</td>
<td>388 (1.1 × 10⁻³)</td>
<td>516</td>
<td>0.453</td>
<td>20.31</td>
<td>3.266</td>
</tr>
<tr>
<td>1c</td>
<td>397 (7.5 × 10⁻³)</td>
<td>530</td>
<td>0.301</td>
<td>16.57</td>
<td>3.246</td>
</tr>
<tr>
<td>1d</td>
<td>398 (1.4 × 10⁻³)</td>
<td>534</td>
<td>0.298</td>
<td>14.53</td>
<td>2.908</td>
</tr>
<tr>
<td>1e</td>
<td>394 (1.4 × 10⁻³)</td>
<td>537</td>
<td>0.234</td>
<td>12.76</td>
<td>2.752</td>
</tr>
<tr>
<td>1f</td>
<td>402 (1.0 × 10⁻³)</td>
<td>542</td>
<td>0.201</td>
<td>11.13</td>
<td>2.797</td>
</tr>
<tr>
<td>1g</td>
<td>402 (1.0 × 10⁻³)</td>
<td>545</td>
<td>0.100</td>
<td>9.72</td>
<td>2.718</td>
</tr>
<tr>
<td>1h</td>
<td>385 (2.2 × 10⁻³)</td>
<td>551</td>
<td>0.098</td>
<td>6.53</td>
<td>2.801</td>
</tr>
<tr>
<td>1i</td>
<td>410 (1.1 × 10⁻³)</td>
<td>564</td>
<td>0.057</td>
<td>4.73</td>
<td>2.534</td>
</tr>
<tr>
<td>1j</td>
<td>422 (1.0 × 10⁻³)</td>
<td>612</td>
<td>0.008</td>
<td>1.49</td>
<td>2.473</td>
</tr>
</tbody>
</table>

*Absorption maximum ($A_{\text{max}}$), emission maximum ($\lambda_{\text{max}}$), fluo-
rescence quantum yield ($\Phi_F$), and lifetime ($\tau$) 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. Determined
with use of quinine sulfate (30 μM in 0.05 M H₂SO₄) as a standard.

Table 1 shows that the characteristics of the emissive excited state
remain comparable across the series.

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

(10) Values for $k_{\text{rad}}$ and $k_{\text{nr}}$ were obtained by using data in Table 1
and the following equations: $k_{\text{rad}} = \Phi_F$ and $k_{\text{nr}} = 1/\tau - k_{\text{rad}}$. The
table of actual $k_{\text{rad}}$ and $k_{\text{nr}}$ values is included in the Supporting
Information.
Because we were interested in developing a method for predicting emissive properties in Alq3-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 (σp) 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 the photophysical properties of the complexes 1a–j was correct.

Additionally, the electrochemical HOMO-LUMO gap for the complexes was estimated by cyclic voltametry. 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 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.

While the electrochemical HOMO-LUMO gap for the complexes was estimated by cyclic voltametry, 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 (σp). 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 devices 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 Alq3, 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 Alq3, 1c, and 1i.

In conclusion, a new class of electroluminescent compounds with tunable emission based on tris(8-quinolinolato)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 kν and kνν, 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.