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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 the 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 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. Photophysical properties of Alq3-type complexes are dominated by ligand-centered excited states originating from the electronic π–π* transitions in the quinolinolate ligands. Because the highest density HOMOs of the quinolinolates are located on the phenoxide oxygen and the C5 (para position to the oxygen), 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. For example, attaching the C≡N group did not result in an appreciable blue shift in the emission compared to the parent Alq3 (525 nm). Similarly the introduction of fluoro and chloro substituents 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 piperidino-amide of quinolinolate-5-sulfonic acid (emission maximum ≈ 480 nm).

Recently, we showed that the emission of Alq derivatives with aryl-ethynylene moieties attached to the quinolinolate ligand may allow for tuning of the emission color in the resulting Al(III) complex. 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-arylquinolinolate 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.

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

FIGURE 1. Novel 5-aryl Alq3-type complexes prepared.
converted to the corresponding benzyl-derivative 2. Intermediate 2 was coupled by Suzuki reaction with a suitable arylboronic acid bearing electron-donating group (Pathway A), followed by hydrogenolytic deprotection. The introduction of aryl moieties bearing EDG to yield 3 (Pathway B), 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 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).


**SCHEME 1.** Synthesis of 5-Aryl-8-hydroxyquinoline Ligands

**Pathway A**

Intermediate 2 was coupled by Suzuki reaction with a suitable arylboronic acid bearing electron-donating group (Pathway A), followed by hydrogenolytic deprotection. The introduction of aryl moieties bearing EDG to yield 3 (Pathway B), 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.

**Pathway B**


table 1

<table>
<thead>
<tr>
<th>complex</th>
<th>Amax ((\text{mol}^{-1} \cdot \text{cm}^{-1}))</th>
<th>(\lambda_{max}) [nm]</th>
<th>(\Phi_F^a)</th>
<th>(\tau_F^a) [ns]</th>
<th>HOMO-LUMO gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq₃</td>
<td>388 ((7.0 \times 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 \times 10^4))</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 \times 10^4))</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 \times 10^4))</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 \times 10^4))</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 \times 10^4))</td>
<td>537</td>
<td>0.234</td>
<td>12.76</td>
<td>2.797</td>
</tr>
<tr>
<td>1f</td>
<td>402 ((1.0 \times 10^4))</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 \times 10^4))</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 \times 10^4))</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 \times 10^4))</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 \times 10^4))</td>
<td>612</td>
<td>0.008</td>
<td>1.49</td>
<td>2.473</td>
</tr>
</tbody>
</table>

\(^a\) Absorption maximum (Amax), emission maximum (\(\lambda_{max}\)), fluorescence quantum yield (\(\Phi_F\)), and lifetime (\(\tau_F\)) 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 \((30 \mu\text{M} \text{in } 0.05 \text{ M H}_2\text{SO}_4)\) 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, 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).

**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.

References:


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

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 ($\sigma_p$)$^{12}$ 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 the photophysical properties of the complexes 1a–j was correct.

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 ($\sigma_p$)$^{12}$ 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 4](image)

**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.

![Figure 5](image)

**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$^{14}$ 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](image)

**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-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.

**Acknowledgment.** This work was supported by NSF (DMR-0306117 and NER-0304320 grants to P.A.), BGSU (TIE and FRC grants to P.A.), Kraft Foods, Inc grant to P.A., and the Petroleum Research Fund (ACS-PRF No. 38110-G to P.A.). We would like to thank Dr. L. Zou, formerly of the USDOE Ames Laboratory and the Physics and Astronomy Department of ISU, for fabrication of the OLEDs.

**Supporting Information Available:** Experimental procedures for the preparation and characterization of compounds, their UV–vis and fluorescence spectra, numeric values for $k_r$ and $k_{sr}$ 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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$^{14}$ The OLEDs were fabricated by using the standard vapor deposition method. Device configuration: glass-ITO cathode, CuPh-thalocyanine (100 Å), NPD (N,N′-di-1-naphthyl-N,N′-diphenyl-1′-biphenyl-4,4′-diamine, 400 Å), electroluminophore (500 Å), CsF (10 Å), Al (2000 Å). Forward bias for Alq$_3$ = 4.5 V, 1c = 6 V, 1i = 6 V.