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Cesar Perez-Bolivar

Victor A. Montes

Pavel Anzenbacher Jr.
Bowling Green State University, pavel@bgsu.edu

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True Blue: Blue-Emitting Aluminum(III) Quinolinolate Complexes

César Pérez-Bolívar, Victor A. Montes, and Pavel Anzenbacher, Jr.*

Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Blue-emitting heteroleptic aluminum(III) bis(2-methyl-8-quinolino-late)phenolate complexes were synthesized. A tunable, blue-to-green emission is achieved by attaching electron-withdrawing modulators to the emisssive quinaldinate ligand. The electronic nature of modulator substituents attached to the position of the highest HOMO (highest occupied molecular orbital) density is used to modulate ligand HOMO levels to achieve effective emission tuning to obtain blue-emitting materials. Optical and electrochemical properties of the resulting complexes were investigated and compared to the results of density functional theory (DFT/B3LYP/6-31G*) studies. The resulting materials may find application as organic light-emitting device materials.

Electroluminescent organometallic complexes are valued emitters for the fabrication of small-molecule-based organic light-emitting devices (SMOLEDs).[1] The unique electron-transport and emissive properties of tris(8-quinolinolate)aluminum(III) (Alq$_3$) and its derivatives resulted in extensive use of Alq$_3$ in OLED fabrication (Figure 1). The advantage of aluminum(III) quinolinolate complexes is in their semiconductor properties, namely, the ability to transport electrons and act as an electron-transport layer material and a host for various dopants. This, together with the ease of deposition by thermal vacuum evaporation, made aluminum(III) quinolinolate complexes widely used OLED materials. An obstacle in the fabrication of SMOLED-based full-color displays so far appears to be the limited availability of a pure blue color.[1] Additionally, in the case of blue-emitting complexes, the blue emission attests to the fact that the HOMO−LUMO gap (energy difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital) is 3.2−3.3 eV regardless of the actual energy level of each molecular orbital. However, for successful device operation, the HOMO and LUMO energy levels of the electron-transporting material must also be aligned with the levels of the other materials in the OLED, namely, the dopant, both hole-blocking and
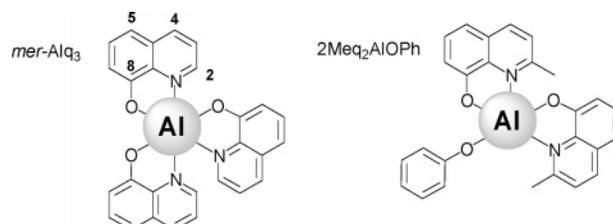

Figure 1. Structures of a *mer* isomer of Alq$_3$ with numbered positions in the ligand and 2Meq$_2$AlOPh.

buffer layers on the cathode side, and the hole-transport layer on the anode side. Few materials satisfy these conditions, which makes them highly desirable.[1]

In the past, numerous research groups investigated aluminum(III) quinolinolate complexes in studies focused on unraveling their photophysical and semiconductor properties.[2] Both the semiconductor and emissive properties are largely defined by HOMO−LUMO levels of the quinolinolate ligand and its lowest electronic $\pi−\pi^*$ transitions.[3] A number of studies aimed at HOMO−LUMO levels and emission color tuning in the Alq$_3$-type materials were attempted with a variable degree of success. Theoretical studies using density functional theory (DFT) calculations provided an insight into the distribution of the HOMO−LUMO densities in the quinolinolate ligand in the *mer* isomer of Alq$_3$ and suggested that the HOMO orbitals are located mostly on the phenoxide side of the ligand, C8 and C5 in particular, while the highest LUMO density is found at the pyridine ring, namely, on C2 and C4 (Figure 1).

The studies aimed at investigating the effect of quinolinolate substituents on photophysical properties revealed that the attachment of electron-donating substituents to the phenolate ring results in red-shifted emission, while the attachment of electron-donating substituents to the pyridine ring results in blue-shifted emission from the complex. While the parent Alq$_3$ emits at 525 nm,[2] a methyl group on C2, C3, C4, and C5 results in emission shifting to 495,[4] 520,[5] 505,[6] and 545 nm,[5] respectively. Attachment of the π-electron-

* To whom correspondence should be addressed. E-mail: pavel@bgnet.bgsu.edu.
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rich substituents in the C5 position resulted mostly in red-shifted emission. For example, C5 phenyl, fluoro, chloro, and cyano substituents resulted in complexes with emission maxima at 550,[7] 535,[8] 540,[2] and 520 nm,[9] respectively. An example of effective blue emission from an Alq$_3$ derivative is the C5 piperidine sulfonamide emitting at 480 nm.[10]

Recently, our group performed extensive studies aimed at emission color tuning in Alq$_3$-type materials.[11] We used simple quinolinolate complexes with electron-donating or electron-withdrawing aromatic moieties connected either directly[12a] or via an acetylene spacer[12b] to the C5 of the ligand. We have demonstrated that electron-deficient moieties cause a blue shift in emission while the electron-donating substituents result in red-shifted emission. We also showed that these materials retain their semiconductor properties and may be used for OLED fabrication.[13]

Unfortunately, none of the above efforts yielded a high-purity blue emitter, one with emission centered around 450−470 nm while possessing a high emission quantum yield. Such an emitter, however, is required for the fabrication of full-color displays to generate the red−green−blue signal.[1] Also, recently discovered high-efficacy (∼18%) white OLEDs for interior lighting require a good-quality blue emitter.[14] We have realized that it is unlikely that a single substituent on the quinolinolate ligand would exert such a strong effect to yield a blue emitter of sufficient quality and that we may need to use a combined effect of two substituents. The question was, how much the substituent effects that modulate the quinolinolate emission were additive, which is the subject of this study.

Here we explore the properties of fluorescent quinolinolate complexes, in which the quinolinolate ligand bears two substituents to modulate the emission. First, we decided to use the 2-methyl substituent (2Meq), which is known to blue shift the emission for ca. 0.2 eV compared to the parent Alq$_3$ through a combination of electronic and geometrical effects.[2] The 2Meq ligand, however, is too sterically demanding to form a tris-complex. Therefore, the 2-methylquinolinolate complexes of Al(III) are complexes comprising two 2Meq ligands and one ancillary ligand. We used a phenolate as an ancillary ligand and used the reaction of aluminum(III) phenoxide[15] with two 2-methyl-8-hydroxyquinoline ligands and its C5-substituted derivatives[16] to prepare the complexes described in Figure 2.

The C5 substituents are divided into two groups: electron-poor substituents were chosen to maximize the blue shift in
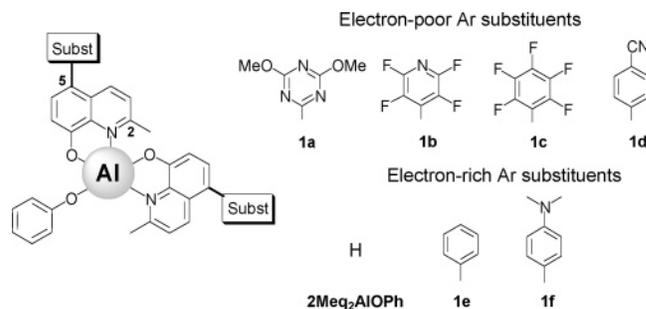

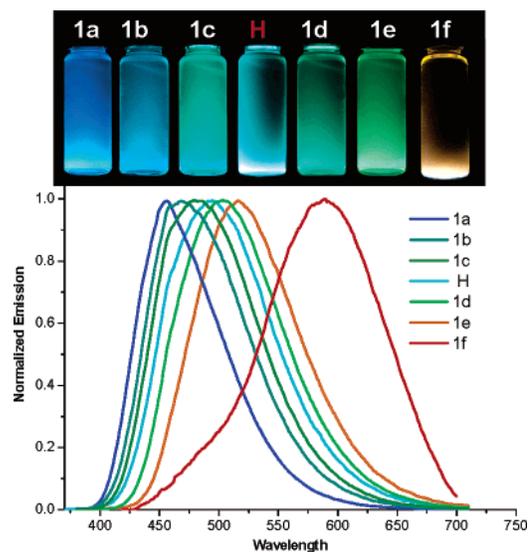**Figure 2.** Structure of C5-substituted derivatives and 2Meq$_2$AlOPh.

Figure 3. Top: Emission of **1a**−**f** in CH$_2$Cl$_2$ solutions illuminated with black light (365 nm). Bottom: Emission spectra of complexes **1a**−**f**.

the emission, while the two electron-rich substituents were included for the purpose of investigating the additivity of the substituent effects. The 2-methyl induces a blue shift, while the 5-phenyl and, namely, the 5-(4-dimethylaminophenyl) induce a red shift.[12,13]

The substituent-mediated emission color tuning in complexes **1a**−**f** can be observed by a naked eye. Upon excitation of CH$_2$Cl$_2$ solutions with black light (365 nm), complexes **1a**−**f** show bright photoluminescence (PL) that shifts from blue to green and red, depending on the electronic nature of the aryl substituent (Figure 3).

Table 1 summarizes the properties of complexes **1a**−**f** determined from UV−visible and fluorescence measurements. The data for the parent complex 2Meq$_2$AlOPh (substituent = H) are also included for comparison.

The emission maxima of complexes **1a**−**f** span over 120 nm between 455 and 575 nm, while showing strong emission in the blue region of the visible light spectrum. In general, we found that the C5 substituents provide a stronger emission-tuning effect compared to 2-methyl. It appears that the substituents on the phenoxide and pyridine rings induce an additive effect on the emission wavelength. The combina-

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(16) The synthesis of the C5-substituted 2-methyl-8-hydroxyquinoline ligands used to synthesize **1a**−**f** is reported in the Supporting Information.

Table 1. Photophysical Properties of Complexes **1a−f**[a]

complex	A_{max} (ϵ)[b]	λ_F (nm)	Φ_F[c]	λ_{FSS} (nm)	optic band gap (eV)
H	357 (7.0 × 10⁴)	495	0.40	492	3.47
1a	377 (1.04 × 10⁵)	455	0.60	467	3.29
1b	364 (1.44 × 10⁴)	468	0.40	487	3.40
1c	363 (1.37 × 10⁴)	484	0.60	485	3.41
1d	368 (7.39 × 10⁴)	504	0.30	504	3.37
1e	370 (1.04 × 10⁴)	515	0.10	513	3.35
1f	353 (1.06 × 10³)	574	>0.01	ND	3.51

[a] Absorption maximum (A_{max}), fluorescence emission maximum (λ_F), and quantum yield (Φ_F) in a CH_2Cl_2 solution at room temperature. Solid-state fluorescence maximum (λ_{FSS}) measured in 20% (w/w) poly(methyl methacrylate) in a CH_2Cl_2 suspension. Refer to the Supporting Information for emission spectra. The optical band gap was estimated from the UV−visible spectra. [b] Units: mol⁻¹ cm⁻¹. [c] Determined using quinine sulfate in 0.05 M H_2SO_4 as a standard.

Table 2. Electrochemical Properties of Complexes **1a−f**[a]

complex	E^{ox} (V)	E^{red} (V)	HOMO (eV)	LUMO (eV)	HOMO−LUMO (eV)
H	1.70	−1.43	−6.27	−3.14	3.13
1a	1.90	−1.36	−6.47	−3.21	3.26
1b	1.86	−1.38	−6.43	−3.18	3.24
1c	1.85	−1.37	−6.42	−3.19	3.22
1d	1.57	−1.37	−6.14	−3.19	2.94
1e	1.57	−1.37	−6.14	−3.20	2.94
1f	<1.69[b]	−1.39	<−6.20[b]	−3.18	<3.00[b]

[a] E^{ox} and E^{red} were determined using CV of 1.0 mM solutions in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate. See the Supporting Information for more details. [b] The redox chemistry of the dimethylamino moiety prevented the exact determination of the E^{ox}, HOMO, and HOMO−LUMO gap values.

tion of both types of substituents may be used to achieve a desired blue emission. For example, when compared to Alq₃ ($\lambda_F \sim$ 525 nm), **1a** (455 nm) shows a ~0.4 eV blue shift. This shift appears to be a combined effect of the 2-methyl and 5-dimethoxytriazinyl substituents, both known to induce a ~0.2 eV shift when individually attached to Alq₃ separately.[11] Also, in agreement with the energy gap law,[17] we found a decreasing fluorescence quantum yield with a decreasing emission energy (Table 1).

While the photophysical data confirmed that the optical HOMO−LUMO gap is sufficient for a blue emission, we performed cyclic voltammetry (CV) experiments to determine the absolute HOMO and LUMO levels (Table 2).[18]

The data in Table 2 show that the reduction potentials and the corresponding LUMO levels in **1a−f** are not significantly changed across the series. On the other hand, the oxidation potentials and HOMO levels underwent systematic changes, reflecting the tuning of the HOMO−LUMO gap (Figure 4, left panel). We reason that this is due to the 2-methyl substituent in the C2 position with the highest LUMO density in all derivatives, while the varying substituents in the C5 position affect predominantly the HOMO levels because C5 is the site with high HOMO density. The magnitudes of the HOMO−LUMO gap for **1a−f** correlate with the observed emission properties. Thus, the most blue complex **1a** shows the highest HOMO−LUMO gap of 3.26 eV, and the most red-shifted emission of complex **1f** corresponds to a gap of
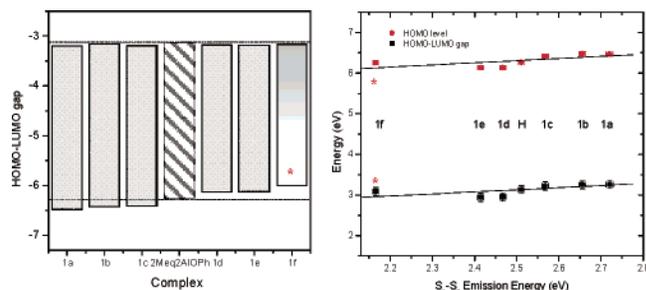
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Figure 4. Left: HOMO−LUMO band gap for **1a−f** and 2Meq₂AlOPh, estimated by CV. Right: Correlation between the HOMO level and HOMO−LUMO obtained from redox potentials as a function of the fluorescence emission energy. The asterisk in **1f** indicates the potential uncertainty due to the redox chemistry of the dimethylamino moiety.

3.08 eV calculated from electrochemistry measurements. Figure 4 shows a systematic decrease in the HOMO−LUMO gaps across the series **1a−f**.

There is a good correlation between the photophysical data and the data derived from electrochemistry (Figure 4, right panel). As mentioned before, this is partially due to the fact that the photophysical properties of these materials are defined by their HOMO−LUMO gap, with the $S_0 \rightarrow S_1$ electronic transition having a large character of HOMO→LUMO. The linear dependence of the HOMO levels and the HOMO−LUMO gap on the S_1-S_0 emission energy attests to the uniform photophysical and semiconductor behavior of the complexes within the series.

Also, the above findings were supported by the DFT calculations of the HOMO levels and the HOMO−LUMO gap at the B3LYP/6-31G* level of theory in vacuum. The absolute values of the HOMO levels were uniformly overestimated in the DFT calculations, presumably because of the fact that the calculations were carried out for **1a−f** in vacuum. Otherwise, the DFT calculations showed the same decrease in the HOMO levels as that observed in electrochemistry.

In conclusion, a new class of quinolinolate complexes **1a−f** with tunable properties was prepared. Complexes **1a−d** show strong blue emission ($\Phi_{FL} = 30-60\%$) and emission maxima at 455−504 nm, which makes them comparable with most small-molecule blue emitters.[1,2] We have shown that the electronic nature of the aryl substituent affects the emission color, predominantly via effective modification of the HOMO levels located on C5 of the quinolinolate ligand. The optical properties of the complexes **1a−f** also correlate well with the electrochemical properties. All of our observations suggest that the electronic effects that modulate the emissive properties in quinolinolate complexes are additive and the effects of individual substituents may be combined to obtain emitters of desired properties. The charge-transport and electroluminescence properties of the complexes **1a−f** are under investigation.

Supporting Information Available: Experimental data for the preparation of **1a−f**, their UV−visible and PL spectra, CV curves, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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