Systematic Study of the Photoluminescent and Electroluminescent Properties of Pentacoordinate Carboxylate and Chloro Bis(8-hydroxyquinaldine) Complexes of Gallium(III)

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A detailed analysis of the structural, optical absorption, photoluminescent, and electroluminescent properties of a series of pentacoordinate bis(8-hydroxyquinaldine)gallium(III) complexes, i.e. q'_2GaX with X = acetate, dimethylpropionate, benzoate, and chloro, is presented. These materials are compared with tris(8hydroxyquinaldine)Ga and the tris(8-hydroxyquinolate) complexes of aluminum (Alq₃) and gallium. Structural studies show that the pentacoordinate complexes have significantly less steric congestion than their hexacoordinate analogues, leading to comparatively smaller Franck–Condon shifts in their absorption and emission spectra. Relatively short $\pi - \pi$ stacking distances are observed between the quinolate or quinaldine ligands of adjacent complexes (i.e., 3.3-3.5 Å), which facilitates electron transport in the materials. All of the pentacoordinate complexes had high electroluminescent efficiencies at low drive currents. The benzoate derivative exhibits light output saturation at high drive currents when used in electroluminescent devices, while the other derivatives had characteristics comparable to that of Alq₃ at all drive currents.

Introduction

Considerable research is currently focused on the development of new light-emitting device technologies for flat panel displays. The primary motivation is to replace bulky and energyconsuming cathode ray tubes (CRTs) with energy-efficient flat panels. While liquid crystal displays (LCDs) are a reasonable substitute for CRTs in some applications, it is advantageous for ease of viewing in bright background environments to have an emissive display, rather than the reflective or transmissive panels of LCDs. One emissive technology that shows promise involves organic light-emitting diodes (OLEDs). The interest in organic molecular materials for use in (OLEDs) began with the report of efficient green electroluminescence (EL) from aluminum tris(8-hydroxyquinoline) (Alq₃).^{1,2} Since those reports, other metal chelate systems^{3,4} and polymers⁵ have been found which efficiently produce EL throughout the visible spectrum. Devices prepared with molecular and polymeric materials can be fabricated on virtually any substrate by simple vapor deposition or wet processes, making them economically attractive as well. In this paper we present a systematic study of the optical absorption, photoluminescent (PL), and electroluminescent (EL) properties of a series of pentacoordinate bis-(8-hydroxyquinaldine)gallium(III) complexes, which have potential for use as efficient organic light emitters for flat panel displays (FPDs). Results are compared with the hexacoordinate tris(8-hydroxyquinoline) complexes of Al and Ga (Alq₃ and Gaq₃) and tris(8-hydroxyquinaldine)gallium(III) (Gaq'₃).

Alq₃ is the most thoroughly studied molecular emitter material for OLEDs. This hexacoordinate chelate complex exhibits a very high PL quantum efficiency in the solid state ($\phi = 0.32$).⁶ The excited state for Alq₃ is a localized Frenkel exciton,⁷ eliminating the intermolecular interactions that can lead to selfquenching. Although a material must be fluorescent in the solid state in order to exhibit electroluminescence, the efficiency of the fluorescence is only one criterion for determining the usefulness of a material as an emitter in an OLED. The criteria for efficient EL include the material volatility, film forming properties, charge transport properties, energy band offsets relative to the carrier transporting electrodes and organic layers, and environmental stability. These parameters are strongly coupled to molecular structure and the bulk molecular packing characteristics. An example of how these parameters can affect electroluminescence is the comparison of Alq₃ and Gaq₃ OLEDs.⁸ Even though Alq₃ has a 3–4 times larger PL efficiency than Gaq₃ in thin film form, their EL efficiencies are comparable. Furthermore, the Gaq₃ OLEDs exhibit a lower turn-on voltage than the corresponding Alq₃ devices, and thus, a 50% higher power efficiency has been achieved.⁸ It is important to gain a better understanding of how to optimize these parameters in order to design superior emitter materials.

Experimental Section

Synthesis and Preparation of Materials. All reagents were obtained from Aldrich Chemical Co. The $Ga(NO_3)_3 \cdot xH_2O$ was high purity grade (99.999%). 8-Hydroxyquinaldine was recrystallized from ethanol/water before use. The syntheses for all of the compounds reported herein are shown schematically in Figure 1. Alq₃, Gaq₃,⁹ and phenolatobis(8-hydroxyquinaldine)aluminum(III),¹⁰ as well as two of the pentacoordinate q'₂-GaX complexes (X = OAc, Cl),^{11,12} were prepared using published procedures. Spectroscopic and analytical data for these materials matched those reported previously. All of the

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 TABLE 1: Crystallographic Coordinates and Thermal

 Parameters for All Nonhydrogen Atoms of Gaq'3

			-	
	х	у	z	$U(eq)^a$
Ga	3012(1)	5481(1)	2183(1)	34(1)
N(1)	2746(2)	5960(2)	712(2)	35(2)
C(2)	2270(2)	5774(3)	-269(3)	43(2)
C(3)	2248(2)	6196(3)	-1066(3)	49(2)
C(4)	2696(2)	6807(3)	-878(3)	49(3)
C(4a)	3201(2)	7024(3)	131(3)	40(2)
C(5)	3688(2)	7655(3)	419(3)	50(3)
C(6)	4150(2)	7828(3)	1426(3)	49(3)
C(7)	4156(2)	7386(3)	2196(3)	41(2)
C(8)	3691(2)	6765(2)	1970(3)	34(2)
O(8)	3676(1)	6353(2)	2683(2)	40(1)
C(8a)	3203(2)	6576(3)	914(3)	34(2)
C(9)	1756(2)	5115(3)	-510(3)	60(3)
N(1')	3580(2)	5013(2)	3717(2)	31(2)
C(2')	3627(2)	5239(2)	4576(3)	36(2)
C(3')	4111(2)	4863(3)	5520(3)	41(2)
C(4')	4550(2)	4284(3)	5599(3)	44(2)
C(4a')	4526(2)	4041(3)	4713(3)	37(2)
C(5')	4960(2)	3449(3)	4705(3)	44(2)
C(6')	4891(2)	3264(3)	3805(3)	47(3)
C(7')	4395(2)	3651(3)	2883(3)	41(2)
C(8')	3964(2)	4238(2)	2853(3)	34(2)
O(8')	3495(1)	4636(2)	1998(2)	36(1)
C(8a')	4020(2)	4427(2)	3786(3)	29(2)
C(9')	3176(3)	5916(3)	4521(3)	53(3)
N(1")	2115(2)	4561(2)	1688(2)	37(2)
C(2")	1994(2)	3755(3)	1446(3)	45(2)
C(3'')	1367(2)	3387(3)	1137(3)	54(3)
C(4'')	866(2)	3842(3)	1067(3)	56(3)
C(4a'')	971(2)	4696(3)	1344(3)	44(2)
C(5")	497(2)	5209(3)	1347(4)	60(3)
C(6'')	650(3)	6020(3)	1614(4)	64(3)
C(7")	1280(2)	6365(3)	1892(3)	53(3)
C(8")	1762(2)	5880(3)	1905(3)	39(2)
O(8")	2359(1)	6176(2)	2164(2)	40(2)
C(8a'')	1611(2)	5019(3)	1641(3)	36(2)
C(9'')	2519(3)	3219(3)	1471(5)	70(4)

materials were purified by vacuum sublimation at 225 °C at 10^{-4} Torr, prior to OLED fabrication. Elemental analyses for all of the materials were obtained from Robertson Microlit Laboratories, Inc., Madison, NJ.

Bis(8-hydroxyquinaldine)gallium 2,2-dimethylpropionate (q'2-GaDMP) was prepared by the following procedure. A solution of 2.0 g (7.82 mmol) of Ga(NO₃)₃·xH₂O in 200 mL of water was stirred rapidly with warming, while a solution of 2.452 g (15.4 mmol) of 8-hydroxyquinaldine and 7.99 g (78.2 mmol) of 2,2-dimethylpropionic acid in 600 mL of water was added over 1 h. A precipitate formed immediately, and stirring was continued for an additional 1 h after all of the reactants had been added. The precipitate was filtered, washed with hot water, air-dried, and recrystallized from methanol to yield 1.03 g (35%) of large green-yellow crystals, mp = 264-265 °C. ¹H NMR [250 MHz, CDCl₃ data reported as assignment = δ in ppm (multiplicity) (coupling constant in Hz)]: H3 = 7.42 (d) (8.55); H4 = 8.24 (d); H5 = 7.14 (d) (8.24); H6 = 7.43 (t) (7.93); H7= 7.10 (d); $CH_3-q' = 3.03$ (s); $(CH_3)_3CCO_2 = 1.02$ (s). FT-IR (KBR): 1652, 1507, 1465, 1457, 1431, 1394, 1344, 1272, 1116, 833, 756, 528. Anal. Calcd for C₂₅H₂₅GaN₂O₄: C, 61.64; H, 5.17; N, 5.75. Found: C, 61.44; H, 5.13; N, 5.74.

Bis(8-hydroxyquinaldine)gallium benzoate (q'₂GaBen) was prepared by the following procedure. A solution of 1.0 g (3.9 mmol) of Ga(NO₃)₃·xH₂O in 50 mL of water was stirred rapidly while a solution of 1.226 g (7.7 mmol) of 8-hydroxyquinaldine and 6.185 g (38.6 mmol) of potassium benzoate in 280 mL of ethanol/water (50:50) was added over 30 min. Precipitation of the product occurred immediately, and the reaction mixture was stirred an additional 30 min after all the reactants had been



Figure 1. Synthetic scheme for the q'_2GaX complexes investigated in this study.

added. The precipitate was filtered, washed with ethanol, airdried, and recrystallized from chlorobenzene to yield 1.982 g (50%) of small green-yellow crystals, mp = 340 °C (dec). ¹H NMR [250 MHz, CDCl₃ data reported as assignment = δ in ppm (multiplicity) (coupling constant in Hz)]: H3 = 7.39 (d) (8.55); H4 = 8.24 (d); H5 = 7.16 (d) (8.24); H6 = 7.46 (t) (7.93); H7 = 7.15 (d); CH₃-q' = 3.04 (s); H8-ArCO₂ = 7.92 (d) (7.02); H9-ArCO₂ = 7.27 (t) (6.41); H10-ArCO₂ = 7.35–7.50 (m). FT-IR (KBR): 1634, 1610,1509, 1467, 1453, 1433, 1389, 1340, 1305, 1274, 1112, 839, 755, 729, 693, 649, 528. Anal. Calcd for C₂₇H₂₁GaN₂O₄: C, 63.94; H, 4.17; N, 5.52. Found: C, 63.81; H, 4.11; N, 5.55.

X-ray Crystallographic Characterization of Gaq'3. The X-ray diffraction analysis of Gaq'3 was performed on a Siemens P4 four-circle diffractometer employing graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Unit cell constants were determined by a least-squares fit of the 2θ values for 25 centered reflections having $25^{\circ} < 2\theta < 39^{\circ}$. Systematic absences were consistent with the monoclinic space group C2/c. A total of 4683 reflections were measured (ω scan mode, $4^{\circ} < 2\theta < 50^{\circ}$) and corrected for Lorentz-polarization and absorption effects. Of these, 4394 were unique ($R_{\text{int}} = 1.32\%$) and 3116 reflections having $F > 3\sigma(F)$ were considered observed.

The structure of Gaq'₃ was solved by direct methods and refined using the SHELXTL Plus package of programs. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients; hydrogen atoms were included with a riding model [C-H = 0.96 Å, U(H) = 1.2U(C)]. The methyl hydrogen atoms were located in a difference-Fourier map and idealized, and each CH₃ group was refined as a rigid group. The refinement converged to R = 4.60%, wR = 4.91%, and S = 1.08, with 343 variables and 9.1 reflections per refined parameter. The atom positions for all nonhydrogen atoms are given in Table 1, and a thermal ellipsoid plot for Gaq'₃ is shown in Figure 2. The unit cell for Gaq'₃ (C₃₀H₂₄GaN₃O₃) was refined



Figure 2. Thermal ellipsoid figure of Gaq'3.

to a = 23.712(3) Å, b = 16.057(2) Å, c = 15.722(2) Å, $\beta = 124.049(8)^{\circ}$, volume = 4959.9(10) Å³, Z = 8, and density (calcd) = 1.458 g/cm³.

Optical Characterization. Absorption spectra were recorded with a Hewlett-Packard spectrophotometer. Photoluminescent and excitation spectra were obtained with a Perkin-Elmer LS-100 Fluorimeter for both chloroform solution (filtered and degassed) and thin film samples on quartz (thin films were prepared as described previously).^{7,8} The emission spectra were recorded using an excitation wavelength of 365 nm, and the excitation spectra were recorded by detecting emission at 500 nm. Alq₃ was used as the reference for quantum yield (ϕ_{PL}) calculations based on the reported $\phi_{PL}(Alq_3)$ in chloroform (0.04).¹³ The thin film ϕ_{PL} for q'₂GaCl was measured as described previously.⁶

Devices were grown on glass slides precoated with ITO (sheet resistance of 15 Ω /square). Substrates were ultrasonically cleaned in detergent solution for about 1 min, followed by thorough rinsing in deionized water. They were then boiled in 1,1,1-trichloroethane, rinsed in acetone followed by methanol, and dried in pure nitrogen gas between each step. Devices were formed by sequential, high vacuum ($< 2 \times 10^{-6}$ Torr) vapor deposition of of a 350 Å thick layer of the preferentially holetransporting organic material, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1-biphenyl-4,4'-diamine (TPD), and a 400 Å layer of the emitter complex.^{7,8} Deposition was carried out by thermal evaporation from a baffled Ta crucible at a nominal deposition rate of 2–4 Å/s. An array of circular 250 μ m diameter electroninjecting electrodes of approximately 10:1 Mg:Ag atomic ratio was subsequently deposited by coevaporation from separate Ta boats at a vacuum of 10^{-5} Torr. Without breaking the vacuum, a 500 Å layer of Ag was deposited to inhibit atmospheric oxidation of the electrode. All possible steps, such as substrate cleaning and electrode deposition, were performed in parallel to minimize sample-to-sample variations.

Electrical pressure contact to the devices was by means of a 25 μ m diameter Au wire. Current–voltage characteristics were measured with a Hewlett-Packard HP4145 semiconductor parameter analyzer, and EL intensity was measured with a Newport 835 power meter with a broad spectral bandwidth (400–1100 nm) photodetector placed directly below the glass substrate. Although this measurement underestimates the total power since much is lost by wave guiding to the edges of the glass substrate, it nevertheless accurately measures the *relative* efficiency between devices. Electroluminescence spectra were

recorded with an EG&G optical multichannel analyzer on a 0.25 focal length spectrograph.

Results and Discussion

Synthesis and Characterization. Substitution of a methyl group into the 2-position of 8-hydroxyquinoline ligand (i.e., 2-CH₃-8-OH-C₉H₅N = 8-hydroxyquinaldine, abbreviated q') sufficiently increases the steric bulk of the bidentate ligands such that it is not possible to make a stable tris complex with aluminum. However, trigonal bipyramidal aluminum complexes can be prepared with q' ligands, in which four sites are taken up by two bidentate q' ligands and the fifth site is filled by a monodentate ligand, such as phenoxide.¹⁰ Due to its larger ionic radius, it is possible to make a tris complex of q' with gallium, i.e. Gaq'₃, as well as analogues of the trigonal bipyramidal Al complexes, i.e. q'_2GaX , where X = carboxylate or halide. Gaq'_3 is significantly less stable than either the Mq₃ or q'_2MX complex. While Gaq'_{3} is initially stable in air, it degrades over a period of weeks, giving an orange/brown solid. This is adequate for the photophysical measurements described below but makes Gaq'₃ a poor candidate for OLEDs where a long device lifetime is essential to their practical application.

All q'₂GaX complexes prepared in this work are air-stable, pale green-yellow powders. The solubilities of the complexes vary, for $X = OOCCH_3$ (OAc) and OOC(CH₃)₃ (DMP) are soluble in methanol (similar to Alq₃, Gaq₃, and Gaq'₃). Recrystallization of q'₂GaOAc from methanol results in large pale yellow prism-shaped crystals, which contain one methanol per molecule of complex based on ¹H NMR, elemental analysis, and crystal structure data. Recrystallization of q'₂GaDMP also results in large pale yellow prisms. The complexes with X =OOCC₆H₅ (Ben) and Cl are less soluble, and recrystallization from chlorobenzene was the most advantageous, resulting in small pale yellow microcrystals.

The crystal structures of q'2GaOAc,¹¹ q'2GaCl,¹² Alq3. (MeOH),⁹ and Gaq₃•(MeOH)⁹ have been reported. We have determined the crystal structures of Gaq'₃, shown in Figure 1. Structural data for q'2GaOAc•(MeOH),¹⁴ q'2GaOAc, and q'2-GaCl show that the Ga-N bond lengths [2.093(3), 2.086(3), 2.110(8) Å, respectively] and Ga–O bond lengths [1.874(3), 1.877(2), 1.882(8) Å] are very similar, as expected for the three closely related complexes. The average Ga-N bond length for Gaq'₃ [2.214(4) Å] is significantly longer that of Gaq₃ [2.085 (4) Å] or for the q'₂GaX complexes. The increase in Ga–N bond length observed for Gaq'₃ is due to steric hindrance of the 2-Me substitution of the quinolate ring. The Ga-N bond lengths of the q'2GaX complexes are close to the values seen in Gaq₃, suggesting that the absence of the third quinaldine ligand in the complexes lessens the effects of steric congestion due to the 2-Me group in the molecules. The average Ga-O bond length is shortened in the Gaq'₃ complex [1.904 (3) Å] compared to the Ga–O bond length of Gaq₃ [1.955(3) Å]. The average Ga-O bond lengths observed in q'2GaX complexes (1.875 Å) are shorter than the Ga–O bonds in either Gaq₃ and Gaq'₃. The greater steric congestion of Gaq'₃ may be responsible for the lowered stability of the complex both in solution and the solid-state relative to Gaq_3 and the q'_2GaX complexes.

An examination of the solid-state packing of Alq₃, Gaq₃, and Gaq'₃ shows that there are close $\pi - \pi$ stacking interactions between the quinolate ligands of adjacent molecules, with ligand stacking distances ranging from 3.29(2) to 3.52(2) Å. Good overlap between adjacent molecules facilitates carrier transport in these materials. The packing observed in crystals of q'₂-GaX shows that the quinaldine ligands of adjacent molecules also have short $\pi - \pi$ distances, e.g. 3.38–3.45 Å for q'₂GaOAc,

 TABLE 2: Photoluminescence and Absorbance Data for q'2GaX Complexes

	λ_{\max} (nm)			fluorescence quantum efficiency		
emitter	abs	PL^a	Δ (cm ⁻¹)	CHCl ₃	thin film	
Alq	388	520	6542	0.04	0.36	
Gaq	392	540	7161	0.01	-	
Gaq' ₃	362	520	8393	_	-	
q'2GaCl	366	495	7120	0.08	0.3	
q'2GaAc	366	500	7322	0.05	-	
q'2GaDMP	366	500	7322	0.07	-	
q′2GaBen	366	500	7322	0.06	-	

 $^{\it a}$ Emission wavelength of thin films with excitation wavelength of 365 nm.



Figure 3. Photoluminescence spectra of thin films of q'_2GaX complexes.

suggesting that carrier transport may be reasonable in the q'_2 -GaX materials as well.

Electronic Properties. Sizable blue-shifts are observed in both the absorption and emission spectra of Gaq'₃ relative to Gaq₃ (see Table 2 and Figure 3). The absorption maxima for Gaq'₃ and Gaq₃ are 362 and 392 nm, respectively,^{15,16} corresponding to a difference of 2114 cm⁻¹. A smaller difference is observed in the PL spectra of these two complexes. Gaq'₃ emits at a shorter wavelength (520 nm) than Gaq₃ (545 nm),¹⁵ giving an energy difference of 883 cm⁻¹. The energy difference between the absorption and emission maxima for Gaq'₃ (8393 cm⁻¹) is significantly larger than for Gaq₃ (7161 cm⁻¹). This is due to the structural differences between the ground- and excited-state geometries for Gaq'₃, which are larger than for Gaq₃. This is not surprising considering the degree of steric congestion observed in Gaq'₃.

The substitution of one of the q' ligands in Gaq'₃ with a carboxylate or chloro ligand leads to a small red-shift in their absorption spectra relative to Gaq'₃ and a significant blue-shift in the PL spectra, Table 2 and Figure 3. The pentacoordinate q'₂GaX complexes (X = carboxylate, Cl) have absorption maxima at 366 nm, and emission maxima at 500 nm for q'₂-Ga(carboxylate) complexes and 495 nm for q'₂GaCl (see Figure 3). The energy differences between absorption and emission maxima for these bisquinaldine complexes are 7322 cm⁻¹ for the carboxylate derivatives and 7120 cm⁻¹ for the chloro derivative. The fact that the energy differences between the absorption and emission maxima observed for q'₂GaX and that reported for Gaq₃ are very close is consistent with the similar

CHART 1



bonding parameters observed in these complexes and similar degrees of structural distortion in their excited states.¹⁷ A similar situation is observed for the aluminum analogues of the q'_2 -GaX complexes. The pentacoordinate q'_2 AlOPh complex gives absorption and emission spectra that are blue-shifted relative to Alq₃ (by 1401 and 1602 cm⁻¹, respectively).¹⁰ The energy differences between the absorption and emission maxima for each compound are very similar (6341 cm⁻¹ for q'_2 AlOPh and 6542 cm⁻¹ for Alq₃), again consistent with similar levels of steric congestion in the q'_2 MX and Mq₃ complexes. All q'_2 -GaX complexes, as well as Alq₃ and Gaq₃ exhibit excitation spectra that are very similar to their optical absorption profiles.

The PL quantum yields (ϕ_{PL}) for Alq₃, Gaq₃, and q'₂GaX in chloroform and for Alq₃ and q'₂GaCl thin films are listed in Table 2. The q'₂GaX complexes exhibited a 1.3–2 times larger solution ϕ_{PL} than Alq₃, with q'₂GaCl exhibiting the largest value of all the compounds studied. Halogens and carbonyl moieties are known to cause fluorescence quenching;^{18–20} however, the chloro and carboxylate moieties in q'₂GaX do not interact with the quinaldine ligands where the PL is centered, and thus seem to have little effect. The thin film quantum efficiency of q'₂-GaCl is 0.3. This value is very high relative to most organic solids and similar to that found for Alq₃, showing that self-quenching is not important in these q'₂GaX complexes.

Molecular orbital calculations are very valuable for probing the origins of electronic transitions in small molecules. We have used semiemperical INDO methods (INDO = intermediate neglect of differential overlap). The program has been parametrized by Zerner from electronic spectra of metal complexes (referred to as ZINDO)²¹ and has been used to very effectively probe the molecular orbital structure of Alq₃ and related complexes.⁷ The visible bands in the absorption and emission spectra of these metal complexes are due to transitions involving the π system of the quinolate ligands. Configuration interaction leads to extensive mixing of the three quinolate π systems in the low-energy transitions, giving a substantial red-shift for absorption and emission bands of the trisquinolate complexes, relative to those of a metal complex with a single quinolate ligand.

ZINDO is not parametrized for Ga, preventing us from examining q'2GaX complexes using ZINDO; however, calculations on analogous Al complexes, i.e. q'_2AIX (X = Cl, OAc), have been carried out and suggest an explanation for the observed blue-shift in q'_2MX (M = Al, Ga) complexes relative to Mq'₃. In these calculations, the first step is to adjust the atom positions to give a minimum energy. An electronic structure calculation is then carried out, including configuration interactions (CI, 10 filled and 10 empty states used in CI). All of the q'2MX compounds that have been crystallographically characterized have a structure similar to that shown in Chart 1.^{11,12,14} This structure was used as the starting point for our geometry minimizations of q'2AlCl and q'2AlOAc. The geometryminimized structures are very similar to those determined crystallographically, all giving small deviations from the ideal trigonal bipyramidal structure (N–Al–N angles = 165° – 170° and $O-Al-O = 118^{\circ}-125^{\circ}$). For both the chloro and acetate derivatives, CI leads to complete mixing of the π systems of both quinaldine ligands in the low-energy transitions, which is very similar to the situation seen for metal trisquinolates.⁷ For example, the lowest energy transition for q'2AlCl is calculated



Figure 4. Current versus voltage plots for Alq₃, Gaq₃, and q'_2GaX OLEDs.

TABLE 3: Electroluminescene Data for q'2GaX OLEDs

 Alq ₃	Gaq ₃	q'GaAc	q'GaDMP	q′GaBen	q'GaCl
532	535	500	500	500	500
1.0	0.58	0.65	1.04	0.73	0.73
16.9	15	16.7	16.2	21	13.8

^{*a*} EL quantum efficiencies are normalized to Alq = 1 for clarity.

to be at 342 nm (oscillator strength = 0.22), which is composed of equal amounts of the $\pi - \pi^*$ transitions of each quinaldine. The likely reason for the blue-shift observed in absorption and luminescence of q'₂MX relative to Mq₃ is that, while CI leads to extensive mixing of ligand states for both complexes, it involves mixing of two quinaldine ligands for q'₂MX and the mixing of three such ligands for Mq₃. The transitions for q'₂-MX originate from a smaller and thus higher energy system than those of Mq₃.

Electroluminescence. The light outputs from the OLEDs of the q'2GaX complexes are blue-green, while those of Alq3 and Gaq₃ are green to green-yellow. The EL spectra of q'_2 -GaX are identical with their PL spectra, consistent with holeelectron recombination in the q'2GaX layer in the multilayer device. The current versus voltage characteristics of the OLEDs are shown in Figure 4. The device operational voltages (at fixed current)—or $V_{\rm T}$ —increase in the order q'₂GaCl < Gaq₃ < q'₂-GaDMP < Alq₃ \approx q'₂GaOAc < q'₂GaBen (Table 3). Figure 5 shows the dependence of the optical output power on drive current for each of the OLEDs. At low drive current (<100 μ A, 2 mA/cm²), the EL output at a given current decreases in the order $q'_2GaBen > q'_2GaDMP > Alq_3 > q'_2GaCl > q'_2 GaOAc > Gaq_3$ (Figure 5a). At higher drive currents (>100 μ A), the order is significantly different, where the EL output at a given current level decreases in the order $Alq_3 > q'_2GaDMP$ $> q'_2GaCl > Gaq_3 > q'_2GaOAc > q'_2GaBen$ (Figure 5b). The q'2GaBen and q'2GaDMP complexes are significantly brighter than Alq₃ and Gaq₃ at low drive currents; however, while the q'2GaDMP complex consistently exhibits an increase in EL output with increasing drive current, the q'2GaBen complex exhibits saturation of the EL output above 200 μ A. This saturation is completely reversible, showing no decay or hysteresis on cycling between 0 and 300 μ A.

The saturation behavior for the q'_2GaBen complex and the lower efficiencies for the other q'_2GaX complexes may be an intrinsic property of the material (low electron mobility or high heterojunction energy barriers) or may be due to impurities. While the materials were purified by sublimation prior to device fabrication, we cannot rule out that the differences are extrinsic in nature, i.e. they are due to impurities. However, if impurities



Figure 5. Light output versus voltage plots for Alq₃, Gaq₃, and q'_{2} -GaX OLEDs.

are responsible for the saturation behavior, It is interesting to note that they do not lead to significant fluorescence quenching. Further purification procedures are currently underway, and reanalysis of these complexes is warranted to better understand their device properties. We are also investigating the crystal structures of the q'_2GaX complexes to see if there are any obvious relationships between the intermolecular interactions and device properties.

Conclusions

The PL and EL spectra for the q'₂GaX complexes (X = Cl, OAc, DMP, Ben) are very similar and are blue-shifted substantially from those of Alq₃ and Gaq₃. The solution PL quantum efficiencies determined for the q'₂GaX complexes are greater than those reported for Alq₃ and Gaq₃. As observed for Mq₃based devices; however, an increase in PL efficiency does not lead directly to an increase in EL efficiency. While all of the q'₂GaX-based OLEDs performed well relative to Alq₃ and Gaq₃ at low drive currents, at higher drive currents, the Mq₃ devices showed higher EL quantum efficiencies. The q'₂GaBen OLED has the best EL quantum efficiency at low drive currents but shows saturation behavior at higher currents.

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