Inorganic Chemistry

Synthesis and Characterization of Hemicage 8-Hydroxyquinoline Chelates with Enhanced Electrochemical and Photophysical Properties

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A new hexadentate, tripodal 8-hydroxyquinoline ligand (QH_3) and its trivalent metal chelates (MQ, M = Al^{3+}, Ga^{3+}, In^{3+}) with hemicage structures have been prepared and the electrochemical and photophysical properties systematically studied. The hemicage structure of the metal complexes was characterized by ^{1}H NMR, indicating a pure facial geometry, in contrast to their uncaged cousins with 8-hydroxyquinoline (Mq_3) and 3-methyl-8-hydroxyquinoline ($M(3Meq)_3$), which all exist only as the meridional form in fluid solutions at room temperature. The photoluminescence quantum efficiency for the three hemicage complexes is 1.48, 1.79, and 1.26 times higher for AlQ, GaQ, and InQ, respectively, than their corresponding 3-methyl-8-hydroxyquinoline complexes, likely due to the rigidity of the ligand system, which can efficiently decrease the nonradiative decay of the excited states. The improved electrochemical stability of the hemicage complexes has been demonstrated by cyclic voltammetry, showing an increasingly reversible behavior from InQ to GaQ to AlQ (E_{red} = -2.15, -2.17, and -2.22 V vs Fc/Fc^+ in DMSO). We infer that the degree of reversibility and redox potential result from the metal–ligand bond strength, which is largest in the case of aluminum.

Introduction

Since the first report on small molecule-based organic light-emitting diodes (OLEDs) by Tang and VanSlyke, tris-(8-hydroxyquinoline) aluminum (Alq_3) has become an archetype molecule used as an electron-transport and light-emitting material in OLEDs.[1] Many derivatives of Alq_3 have been investigated with respect to charge-transporting characteristics and luminescent properties, including the substitution of Al(III) by Ga(III) and In(III)[2] and substitution of the quinolinolate ligand (substituents can be halogen, cyano, nitro, alkyl, and aryl groups at various positions).[3–6] For example, after tris(4-methyl-8-hydroxyquinoline) aluminum was found to exhibit higher photoluminescence and electroluminescence efficiency[7,8] than Alq_3, the Forrest group[9] reported the effects of systematic methyl substitution of Al^{3+} and Ga^{3+} tris-8-hydroxyquinoline chelates on the device performance. The Anzenbacher group[10] demonstrated effective color tuning from red to blue of the Alq_3 derivatives with electron-donating or electron-withdrawing aryl and aryl−ethynylene groups to the five-position of the quinolinolate ligand.

The molecular modification strategy provides an effective means of device optimization, but the commercial application of Alq_3-based devices is still limited mostly by short device lifetime, prompting the investigation of degradation phenomena in Alq_3-based devices. In addition to the degradation at device electrodes, usually referred to as dark spots,[11,12] Popovic et al. and Aziz et al.[13,14] have reported that the major intrinsic decrease in the electroluminescence efficiency

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results from the instability of cationic Alq_3 species produced by the injection of holes into the electron-transport and emitter layer. Furthermore, it is well-known that Alq_3 thin films are very sensitive to atmospheric moisture and oxygen at elevated temperature.[15−20] In particular, Alq_3 is susceptible to ligand-exchange reactions with H_2O (hydrolytic decomposition), producing nonemissive species which act as luminescence quenchers, as illustrated by Papadimitrako-poulos et al.[21−24] Electrochemical experiments also showed that Alq_3 is vulnerable to reducing environments, especially in the presence of oxygen, which may cause the degradation of OLEDs.[15]

Various strategies have been employed to enhance the device stability, mostly through engineering techniques, such as multilayer configuration,[25−27] substrate pretreatment,[28−31] postfabrication annealing,[32] device encapsulation,[11] modification of the deposition process,[33,34] and application of new dopants[35,36] and electrodes.[26,37] Modification of Alq_3 at the molecular level provides another solution to affect and potentially achieve better molecular intrinsic stability. One method is to apply a caged ligand structure to the quinolinolate ligand system. Caged ligand structures present a number of advantages; in particular, their substitutional inertness reduces ligand dissociation in solution, as demonstrated by their stabilization of labile trisdiimine complexes of Fe(II) or Zn(II).[38] Additionally, the rigid structure provided by caged ligands can greatly assist in reducing the rate

constant for nonradiative decay (k_{nr}) and thus improve the quantum efficiency of luminescent metal complexes.[38−40]

In this paper, we focus on the design of a new hemicage coordination ligand (**QH₃**) by connecting three individual 8-hydroxyquinoline ligands at the C-3 position (see Scheme 1) through a benzene unit. A metal ion (Al^{3+}, Ga^{3+}, or In^{3+}) can be encapsulated rigidly in the central cavity of the ligand without changing the basic metal−ligand coordination sphere. In the systematic studies of photoluminescence and electrochemical properties, these novel hemicage complexes demonstrate superior electrochemical stability and show great promise for reducing the thermal hydrolysis and electrochemical degradation of Alq_3-based devices.

It also needs to be emphasized that only the facial configuration is predicted for hemicage complexes, which is in contrast to uncaged metal quinolinonate complexes (Mq_3 and $M(3Meq)_3$, where M = Al^{3+}, Ga^{3+}, In^{3+}, and 3Meq = 3-methyl-8-hydroxyquinoline), which contain both facial (*fac*) and meridional (*mer*) isomers. It was established by NMR[41−43] and X-ray diffraction studies[44−46] that the latter is the stable form at room temperature.[47] Only recently has *fac*-Alq_3 been prepared, existing in crystalline phase γ- and δ-Alq_3, by sublimation[48,49] of mixed polymorphs of Alq_3, or thermal conversion of commercial Alq_3 followed by acetone[50] and chloroform treatment,[51,52] or configuration-specific synthesis[53] of refluxing AlO(OH) and 8-hydroxyquinoline in water for long periods of time. Although *fac*-Alq_3 has been characterized by many methods (e.g., X-ray diffraction,[45,49] NMR,[50,52,54] photoluminescence,[45,50] and infrared and Raman measurements[55]), it has not been possible to directly observe the ^{1}H NMR behavior in solution at room temperature because *fac*-to-*mer* isomerization via the ligand-flip mech-

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Scheme 1. Synthesis of the Hemicage 8-Hydroxyquinoline Ligand (**QH₃**) and Complexes (**MQ**)
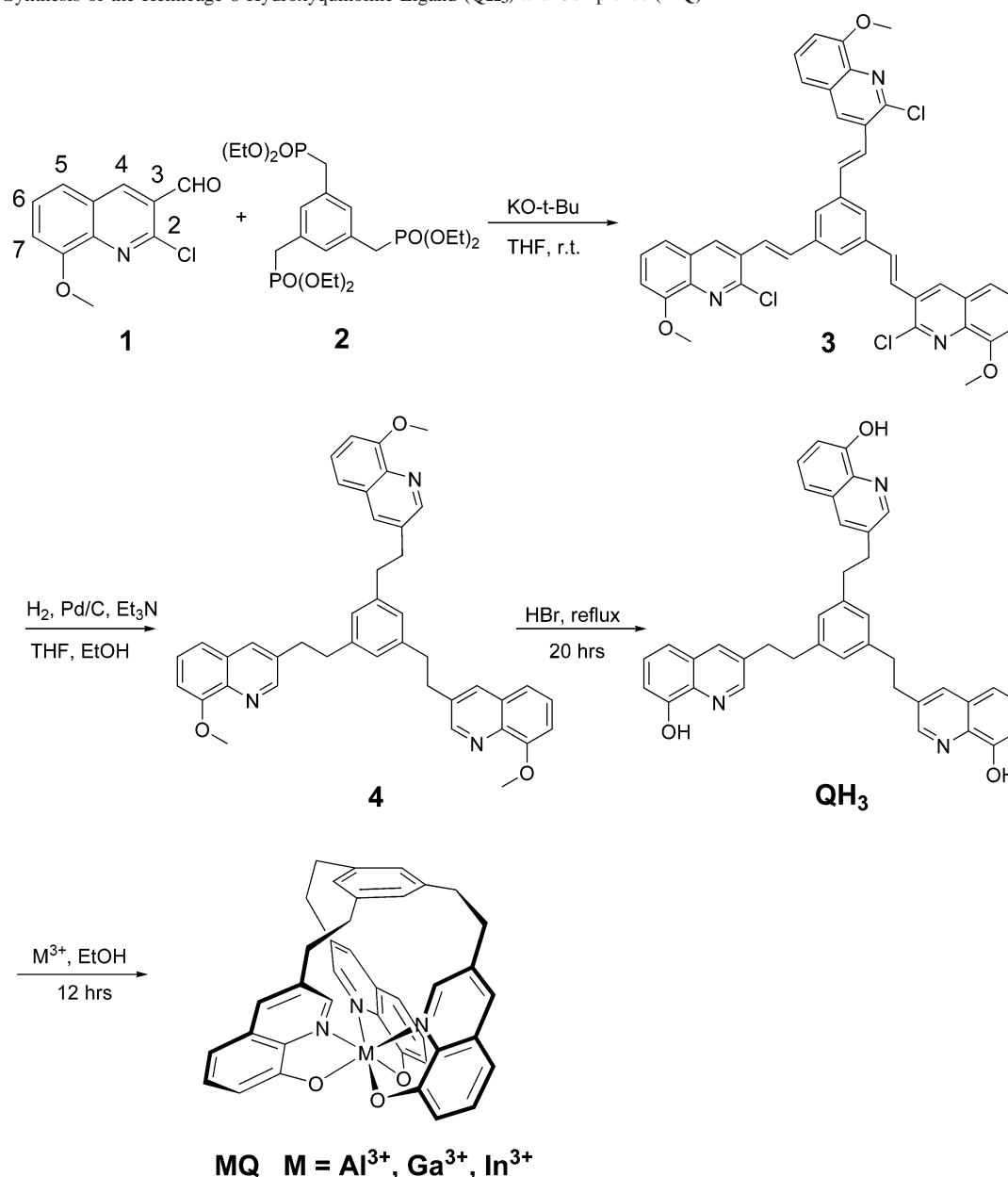
anism is exceedingly fast compared with the reverse step.[54] Therefore, the discovery of enforced *fac* isomerism in the hemicage structure containing not only Al^{3+} but also Ga[3+] and In[3+] opens the way toward a deeper fundamental understanding of Mq₃ complexes, including a full characterization of ¹H NMR spectra in any form. It is also notable that only the *mer* isomer is obtained during the regular process of OLED fabrication, while the *fac* isomer is particularly desirable for its blue-shifted fluorescence and high quantum yield, and it could be of great technological importance in device performance.

Experimental Section

All starting materials were obtained from Aldrich and used without further purification. 1,3,5-Tris(diethoxyphosphinylmethyl)-benzene (**2**) was synthesized according to literature procedures,[56–58]

starting from trimethylbenzene-1,3,5-tricarboxylate. The reference ligand 3-methyl-8-hydroxyquinoline was prepared by a previously published method.[59] The ¹H NMR spectra were acquired on Varian/ INOVA 400 or 500 MHz spectrometers. A Bruker Avance-II 500 MHz spectrometer was utilized to obtain ¹³C NMR data of metal complexes. Mass spectral data were collected using a Hewlett-Packard 5898B (electrospray) MS engine. Elemental analyses (CHN) were performed by the Microanalytical Laboratory at the University of Illinois, Urbana-Champaign.

Cyclic voltammetry measurements were made using a CH Instrument model 600C electrochemical analyzer/workstation at a potential sweep rate of 100 mV/s. A homemade platinum-disk electrode served as the working electrode, a coiled platinum wire

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was used as the counter electrode, and a silver wire was used as a quasi-reference electrode. Electrochemical measurements were carried out in a home-built, one-compartment cell at approximately 1 mM concentration of the metal complex in 0.1 M tetra-*n*-butylammonium hexafluorophosphate in DMSO (DMSO = dimethylsulfoxide). Solutions were purged with nitrogen for 10 min prior to each measurement to ensure that they were oxygen-free. Ferrocene was added as an internal standard ($E^{\circ\prime}$ =0.31 V).[60]

UV−vis spectra were obtained in DMF (DMF = dimethylformamide) at a concentration of 10 μmol/L with a HP 8453 spectrometer equipped with a diode-array detector.

Emission spectra were recorded using a Jobin-Yvon Fluorolog-3 spectrometer equipped with double monochromators and a Hamamatsu-928 photomultiplier tube as the detector. All complexes were excited at 390 nm. All emission spectra were adjusted according to the calibrated correction factors of the instrument.

The emission quantum yield (Φ_{em}) was calculated for each complex according to the equation: $\Phi_s = \Phi_r (I_s/I_r)(A_r/A_s)$, where Φ_s is the quantum yield of the sample, A_s and A_r are the absorbance of the sample and the reference at the excitation wavelength, and I_s and I_r represent the points of maximum intensity in the corrected emission spectra. Φ_r is the quantum yield for the reference complex Alq$_3$, whose value is 11%.[61]

Synthesis. 2-Chloro-8-methoxyquinoline-3-carbaldehyde (1). This compound was prepared with a higher yield by a modification of the procedure of Tarnowski.[62] To the Vilsmeier−Haack reagent, prepared from DMF (5.8 mL, 75 mmol) and POCl$_3$ (16.3 mL, 175 mmol) at 0 °C, *N*-(2-methoxyphenyl) acetamide (4.13 g, 25 mmol) was added. The reaction mixture was heated at 85 °C with stirring in a sealed tube for 2 days. Then it was cooled, poured onto crushed ice, and neutralized with concentrated NaOH solution slowly. The precipitated yellow solid was filtered and washed with water. Recrystallization from THF gave a needlelike, light yellow product (2.75 g, 49.6%). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 10.55 (s, 1H), 8.70 (s, 1H), 7.58−7.52 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (500 MHz, CDCl$_3$) δ = 189.52, 154.76, 149.42, 141.31, 140.31, 128.63, 127.88, 127.00, 121.25, 111.90, 56.48.

1,3,5-Tris[3′-(1,2-ethanediyl)-8-methoxyquinoline)]benzene (4). A solution of potassium *tert*-butoxide (0.971 g, 8.65 mmol) in 10 mL of dry THF was added dropwise to the suspension of compound **1** (1.763 g, 7.95 mmol) and **2** (1.051 g, 1.99 mmol) in 80 mL of dry THF under the protection of nitrogen. The reaction mixture dissolved, turned red-brown, and was stirred at room temperature for 3 days. Then, 20 mL of water was added to quench the reaction, and most of the THF was evaporated. The resulting precipitate was filtered, washed with water, and dissolved in CH$_2$Cl$_2$, which was further washed with water. The organic layer was then dried over MgSO$_4$, treated with charcoal, filtered, and evaporated to dryness. Approximately 10 mL of ethyl acetate was added to suspend the solids, and the suspension was filtered after cooling in an ice−water bath. The light yellow solid contained **3** with sufficient purity to be carried on to the next step. The crude compound **3** was suspended in 15 mL of THF and 15 mL of EtOH, to which a Pd catalyst (10% on activated carbon, 0.1 g) and 0.75 mL of triethylamine were added. The mixture was stirred at room temperature under 1 atm of H$_2$ for 12 h. After the filtering off of the catalyst, the light yellow solution was evaporated to dryness

and dissolved in CH$_2$Cl$_2$ and was then washed with water. After drying over Na$_2$SO$_4$, the organic layer was evaporated to give a yellow oil. The crude product was purified by silica gel column with the developing solvent: ethyl acetate/methanol = 15:1. The pure compound **4** was obtained as a yellow oil: 0.145 g, 12%. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.65 (s, 3H), 7.66 (s, 3H), 7.36 (t, *J*= 8.2, 7.6 Hz, 3H), 7.23 (d, *J*= 8.2 Hz, 3H), 6.91 (d, *J*= 7.6 Hz, 3H), 6.68 (s, 3H), 4.00 (s, 9H), 2.88−2.81 (m, 12H). ^{13}C NMR (500 MHz, CDCl$_3$) δ = 155.4, 150.7, 141.1, 138.7, 134.8, 134.5, 129.2, 126.85, 126.82, 119.2, 106.9, 55.9, 37.3, 35.2. MS (ESI) *m/z*: [M + H]$^+$ 634.

Hemicage Ligand (QH$_3$). HBr 48% (3 mL) was added to compound **4** (0.145 g) and refluxed for 30 h, then cooled and neutralized by 3 M NaOH. The light green solid was filtered, washed with water, and recrystallized from methanol to give the pure product: 0.113 g, 83%. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 8.48 (d, *J*= 1.4 Hz, 3H), 7.78 (s, 3H), 7.42 ("t", *J*= 7.9, 7.6 Hz, 3H), 7.24 (d, *J*= 9.3 Hz, 3H), 7.12 (d, *J*= 7.6 Hz, 3H), 6.70 (s, 3H), 2.89−2.91 (m, 12H). ^{13}C NMR (400 MHz, CDCl$_3$ and CD$_3$-OD) δ = 151.26, 147.64, 141.26, 139.61, 135.89, 129.95, 129.58, 127.73, 118.54, 112.94, 37.43, 35.17. MS (ESI) *m/z*: [M + H]$^+$ 592.

Synthesis of the Uncaged Complexes. The metal uncaged trischelates were prepared by combining AlCl$_3$, Ga(NO$_3$)$_3$, or In(NO$_3$)$_3$ hydrate salt and the appropriate ligand (8-hydroxyquinoline and 3-methyl-8-hydroxyquinoline) in a 1:3 molar ratio in aqueous solution buffered with ammonium acetate.[41] The crude materials were purified by recrystallization from methanol and methylene chloride. The ^{1}H NMR spectra of Al(3Meq)$_3$ and Ga(3Meq)$_3$ are consistent with published values.[41] The unpublished ^{1}H and ^{13}C NMR data include the following: For **Al(3Meq)$_3$**, ^{13}C NMR (500 MHz, APT, CD$_2$Cl$_2$) even-order carbons: δ = 159.55, 159.33, 159.06, 138.78, 138.53, 138.29, 132.22, 131.55, 129.91, 129.77; odd-order carbons: δ = 146.90, 146.17, 144.43, 139.11, 138.72, 138.67, 131.59, 131.32, 131.20, 111.61, 111.55, 111.42, 111.34, 111.23, 19.16, 18.97, 18.91. For **Ga(3Meq)$_3$**, ^{13}C NMR (500 MHz, APT, CD$_2$Cl$_2$) even-order carbons: δ = 159.31, 159.01, 158.77, 136.91, 136.43, 136.57, 132.15, 132.08, 132.06, 130.08, 130.07, 130.00; odd-order carbons: δ = 146.37, 145.72, 143.98, 139.42, 139.20, 139.01, 131.50, 131.30, 131.12, 111.86 (br), 111.59, 111.44, 111.20, 19.06, 18.90 (br). For **In(3Meq)$_3$**, ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ = 8.37 (s, 3H), 8.12 (s, 3H), 7.46 (t, *J*= 8.2, 7.9 Hz, 3H), 6.99 (d, *J*= 8.2 Hz, 3H), 6.98 (d, *J*= 7.9 Hz, 3H), 2.45 (s, 9H); ^{13}C NMR (500 MHz, APT, CD$_2$Cl$_2$) even-order carbons: δ = 159.79, 137.28, 131.72, 130.48; odd-order carbons: δ = 146.97, 139.85, 131.04, 113.47, 111.49, 18.80. (Note: Unlike the Al and Ga complexes, which exhibit complicated NMR spectra in solution at room temperature, In(3Meq)$_3$ shows one set of proton and carbon resonances that could be misconstrued as that of the *fac* isomer but actually result from rapid ligand exchange in the *mer* isomer as in Inq$_3$.[42,46] The reason is that the chemical shift of H$_2$ (the pyridyl proton next to nitrogen) does not reflect the strong ring current effects expected for a facial geometry.[43])

Synthesis of the Hemicage Complexes. The ethanol solution of AlCl$_3$, Ga(NO$_3$)$_3$, or In(NO$_3$)$_3$ hydrate salt (0.05 mmol) was added dropwise to the solution of the ligand **QH$_3$** (29.6 mg, 0.05 mmol) and 20 mL of ethanol at 80 °C. The reaction mixture turned cloudy with the addition of the metal. Two to three drops of triethylamine were then added to complete the precipitation. After refluxing overnight, the total volume was reduced to about 5 mL on a rotary evaporator, and the yellow-green solid was filtered, washed with methanol, and dried in air. **AlQ**: yield = 18.3 mg, 59%. Anal. Calcd for C$_{39}$H$_{30}$AlN$_3$O$_3$·H$_2$O: C, 73.92; H, 5.09; N, 6.63. Found:

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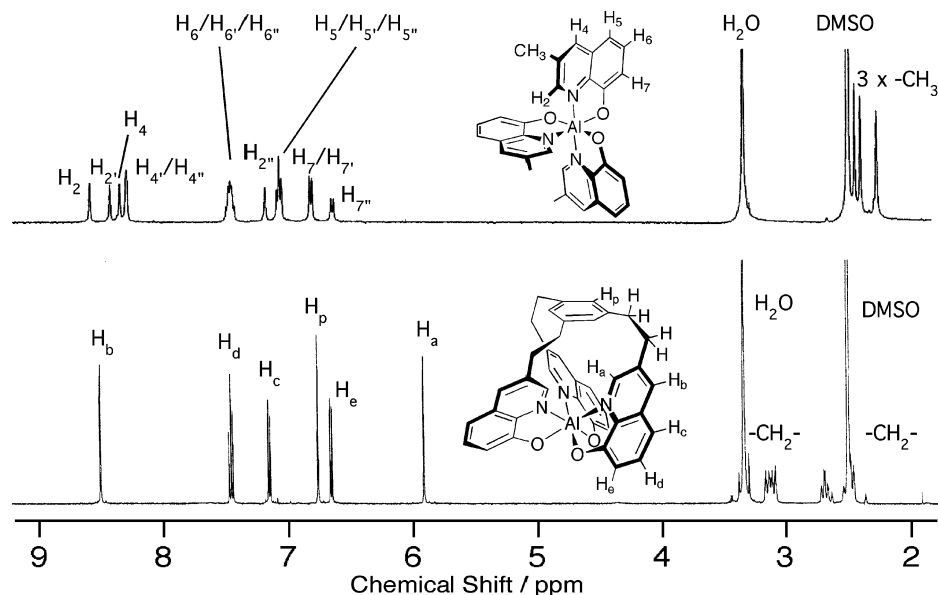
Figure 1. ^{1}H NMR spectra of Al(3Meq)$_3$ (top) and AlQ (bottom) in DMSO. Insets show the structure of the complexes and proton assignments. The assignment of Al(3Meq)$_3$ is made according to that of Alq$_3$ by Baker and Sawyer.[43]

C, 73.44; H, 4.21; N, 6.31. ^{1}H NMR (500 MHz, DMSO) δ = 8.50 (s, 3H), 7.45 (t, J= 7.9 Hz, 3H), 7.15 (d, J= 7.9 Hz, 3H), 6.76 (s, 3H), 6.65 (d, J= 7.6 Hz, 3H), 5.91 (s, 3H), 3.15 (d, J= 13.4 Hz, 3H), 3.10 (d, J= 13.4 Hz, 3H), 2.69 (t, J= 9.8, 13.1 Hz, 3H);[†] (Note: The other "triplet" from the 1,2-ethanediyl is submerged under the solvent (DMSO) signal, and this is also observed for GaQ and InQ. In the ^{1}H NMR spectra in CD$_2$Cl$_2$, all four signals show up clearly.) ^{13}C NMR (500 MHz, APT,CD$_2$Cl$_2$) even-order carbons: δ = 158.97, 140.51, 138.68, 134.94, 130.23, 38.35, 34.09; odd-order carbons: δ = 144.93, 139.15, 131.70, 128.69, 112.54, 111.71; MS (ESI) m/z: [M + H]$^+$ 616. **GaQ**: yield = 19.9 mg, 57%. Anal. Calcd for C$_{39}$H$_{30}$GaN$_3$O$_3$·H$_2$O: C, 69.25; H, 4.77; N, 6.21. Found: C, 69.31; H, 4.39; N, 6.06. ^{1}H NMR (500 MHz, DMSO) δ = 8.53 (s, 3H), 7.47 (t, J= 7.9 Hz, 3H), 7.14 (d, J= 8.2 Hz, 3H), 6.80 (s, 3H), 6.71 (d, J= 7.6 Hz, 3H), 6.06 (s, 3H), 3.16 (d, J= 13.4 Hz, 3H), 3.11 (d, J= 13.1 Hz, 3H), 2.76 (t, J= 9.8, 13.1 Hz, 3H); ^{13}C NMR (500 MHz, APT,CD$_2$Cl$_2$) even-order carbons: δ = 158.75, 140.48, 136.62, 134.68, 130.41, 38.22, 33.86; odd-order carbons: δ = 144.20, 139.51, 131.56, 128.62, 112.67, 111.47; MS (ESI) m/z: [M + H]$^+$ 658. **InQ**: yield = 25.2 mg, 69%. Anal. Calcd for C$_{39}$H$_{30}$InN$_3$O$_3$·3H$_2$O: C, 61.83; H, 4.79; N, 5.55. Found: C, 61.46; H, 4.02; N, 5.37. ^{1}H NMR (500 MHz, DMSO) δ = 8.55 (s, 3H), 7.47 (t, J= 7.9 Hz, 3H), 7.14 (d, J= 8.2 Hz, 3H), 6.89 (s, 3H), 6.85 (d, J= 7.9 Hz, 3H), 6.49 (s, 3H), 3.20 (d, J= 13.7 Hz, 3H), 3.12 (d, J= 13.4 Hz, 3H), 2.89 (t, J= 10.7, 13.1 Hz, 3H); ^{13}C NMR (500 MHz, APT, CD$_2$Cl$_2$) even-order carbons: δ = 159.68, 140.72, 137.17, 134.59, 130.96, 38.12, 33.72; odd-order carbons: δ = 145.50, 140.27, 131.31, 128.63, 114.27, 111.70; MS (ESI) m/z: [M + H]$^+$ 704.

Results and Discussion

Synthesis. To design a suitable structure that allows for further ligand modification, we chose the C-3 position of the 8-hydroxyquinoline ligand as the connection point for two reasons. First, the coordination sites are naturally aligned toward the center of the cavity, thereby facilitating the formation of a highly compact cage. Second, this configuration leaves open the two, four, five, and seven positions, which may be utilized for effective color tuning.[6] The

synthesis of the new hemicage ligand (**QH$_3$**, Scheme 1) involved a 3-fold Wittig reaction of compounds **1** and **2**. The former precursor was synthesized by using a procedure improved from the literature.[62] Since any direct activation (including lithiation, bromination, and oxidation) of the 3-methyl group in 8-methoxy-3-methyl quinoline was unsuccessful, connection of the phenyl cap and the chelate ligands through nucleophilic attacks to 1,3,5-tribromomethylbenzene was excluded, despite its use in the synthesis of other caged ligands.[38,40] In addition, the chloride at the C-2 position of the quinoline is found to be crucial due to its electron-withdrawing ability, which activates the aldehyde and favors the Wittig reaction. The subsequent Pd-catalyzed hydrogenation removed the chloride from the quinoline moiety and saturated the double bonds, followed by demethylation in refluxing HBr, yielding compound **QH$_3$** in 10% yield. The hemicage metal complexes (**MQ**, M = Al^{3+}, Ga^{3+}, In^{3+}) were obtained by reacting **QH$_3$** with the corresponding metal salts in refluxing ethanol. All the compounds were characterized by ^{1}H and/or ^{13}C NMR and mass spectrometry.

^{1}H NMR Spectra. The ^{1}H NMR spectrum of AlQ is shown in Figure 1 (bottom), and the peak assignments for the aromatic and methylene protons are shown on the inset. A single set of sharp peaks show that the three chelate rings are geometrically and magnetically equivalent, indicating a cage structure with C_3 symmetry. This is in contrast to the Al(3Meq)$_3$ complex that exhibits the meridional configuration with typical C_1 symmetry in the NMR spectrum (Figure 1, top), which shows three sets of signals from three different chelate ligands. This observation is consistent with the NMR spectrum of *mer*-Alq$_3$ in the literature.[41] In particular, the pyridyl proton adjacent to the nitrogen is well resolved and often used to distinguish the difference of the three ligands as well as the difference between facial and meridional configurations. Compared with the chemical shift of 5.91 ppm (H$_a$) in AlQ, signals of this proton on the uncaged

**Table 1.** Photophysical Data in DMF Solution (10 μM) at Room Temperature

compounds	$\lambda_{max,abs}$ (nm)	$\lambda_{max,abs}$ (10^3 M^{-1} cm^{-1})	$\lambda_{max,PL}$ (nm)	Φ_{PL}
Alq$_3$	388	3.1	515	0.11
Al(3Meq)$_3$	390	3.3	519	0.114
AlQ	385	3.1	508	0.17
Gaq$_3$	392	3.2	536	0.033
Ga(3Meq)$_3$	392	3.4	537	0.036
GaQ	390	2.8	530	0.065
Inq$_3$	396	3.1	538	0.039
In(3Meq)$_3$	397	3.3	543	0.042
InQ	392	3.1	533	0.053

reference Al(3Meq)$_3$ (*mer* isomer) were observed at 8.59 ppm (H$_2$), 8.42 ppm (H$_{2'}$), and 7.18 ppm (H$_{2''}$) from three different chelate ligands, confirming its C_1 symmetry. The chemical shift for H$_2$ in *fac*-Alq$_3$ is believed to be in the region of 7.1−7.4 ppm[50] because H$_2$ on each ligand is close to the heterocyclic ring of the neighboring ligands in the facial geometry. However, the chemical shift of H$_a$ in caged AlQ moves more upfield than that in *fac*-Alq$_3$ because it is located under the capping phenyl group and is strongly influenced by the ring currents. It is important to note that a similar phenomena was also observed in hemicages composed of 2,2′-bipyridine and derivatives.[40] The chemical shift for H$_2$ in GaQ and InQ is also displaced upfield to 6.06 and 6.49 ppm, respectively. The relatively small shift in InQ can be explained by the greater distance of the proton from the capping phenyl ring, owing to the larger atomic radius of indium. The NMR spectrum of the methylene region has four unique signals (approximately two doublets and two triplets, but one triplet is submerged by the solvent DMSO signal) indicating that the three methylene linkages are equivalent and structurally rigid in the hemicage with a staggered conformation described by Beeston et al.[40] in a ruthenium−bipyridine caged structure. In addition, the expected four resonances can be seen clearly in the ^{1}H NMR spectra (CD$_2$Cl$_2$) in all three hemicage complexes.

^{13}C NMR spectra also confirm the facial geometry of the hemicage structure with a single set of 13 signals, in contrast to the three-line splitting observed in the uncaged Al(3Meq)$_3$ and Ga(3Meq)$_3$. In(3Meq)$_3$ is an exception similar to its unsubstituted Inq$_3$, whose solution NMR spectrum at room-temperature exhibits one set of resonances due to rapid ligand exchange resulting from a relatively weak metal−ligand coordination interaction, although the geometry is actually meridional.[9,42] In fact, when Alq$_3$ and Gaq$_3$ are heated in solution (e.g., to about 115 °C), the spectrum reduces to a single set of resonances. In other words, the spectrum is the average of the three separate ligand spectra at low temperature.[41,43]

UV−Vis and Emission Spectra. The photophysical properties of the hemicage chelates were determined by UV−vis and fluorescence spectroscopy and are summarized in Table 1 and the emission spectra shown in Figure 2. The 3-methyl-substituted (M(3Meq)$_3$) and nonsubstituted 8-hydroxyquinoline complexes (Mq$_3$) were used as controls. Their electronic absorption properties are very similar, as shown in Table 1. The hemicage complexes of all three metals emit at a slightly shorter wavelength than the control, about 11
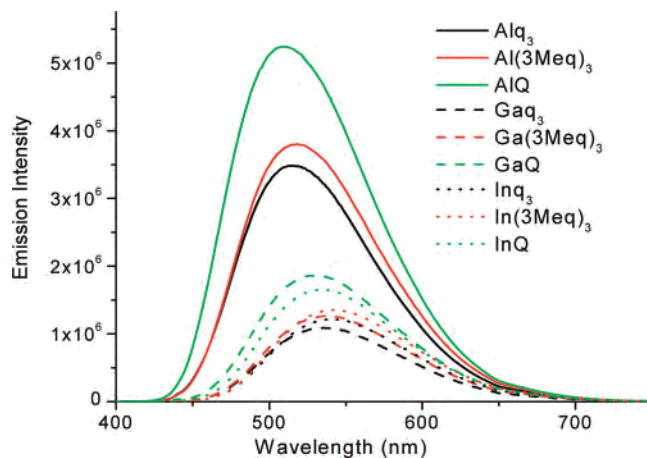
Figure 2. Emission spectra of metal (Al^{3+}, Ga^{3+}, In^{3+}) hemicage complexes and corresponding controls of 10 μM solution in DMF at room temperature.

nm in the case of Al^{3+}. This is consistent with the fact that *fac*-Alq$_3$ shows blue-shifted luminescence over its *mer* isomer, as observed by Muccini et al.[50] where the blue shift is 46.6 nm in solution at −50 °C and 61.2 nm in solid state at room temperature. Although different measurement conditions like temperature and morphology may diminish the change in emission wavelength, this smaller blue shift is also probably due to the steric constraints in the hemicage complex as well as the solvent effects. However, the quantum efficiency of the hemicage complexes increases greatly (by 1.48, 1.79, and 1.26 times for AlQ, GaQ, and InQ, respectively, relative to their corresponding uncaged cousins). This improvement results from the slower nonradiative decay of the hemicage molecule caused by its rigid structure and could be especially valuable for substituted Alq$_3$ complexes that display red-shifted emission,[10] where the quantum efficiency is very low due to the optical energy gap law.

Electrochemistry. The enhanced stability of the hemicage complexes is apparent from their electrochemistry as shown in Figure 3. By observation of the voltammetric behavior in DMSO, the reference Al(3Meq)$_3$ undergoes a single reduction process within the solvent window, with a peak potential at −2.22 V vs Fc/Fc$^+$ followed by the reoxidation on the anodic potential at −1.10 V vs Fc/Fc$^+$, which is assigned to be the reverse oxidation peak of the chelate. As expected, this redox behavior is very similar to the nonsubstituted Alq$_3$ with E_{p_c} = −2.17 V and E_{p_a} = −1.04 V vs Fc/Fc$^+$, where the large separation between cathodic and anodic peaks reveals the chemically irreversible behavior resulting from the instability of Alq$_3$$^{\bullet-}$. The results are consistent with literature findings[63] where the half-life of Alq$_3$$^{\bullet-}$ anions was estimated to be ca. 0.05 s via intermediate sweep-rate experiments. By contrast, hemicage AlQ exhibits a reversible behavior under the same conditions with $E^{1/2}$ = −2.22 V vs Fc/Fc$^+$ with a half-wave separation ΔE_p of 90 mV.

(63) Anderson, J. D.; McDonald, E. M.; Lee, P. A.; Anderson, M. L.; Ritchie, E. L.; Hall, H. K.; Hopkins, T.; Mash, E. A.; Wang, J.; Padias, A.; Thayumanavan, S.; Barlow, S.; Marder, S. R.; Jabbour, G. E.; Shaheen, S.; Kippelen, B.; Peyghambarian, N.; Wightman, R. M.; Armstrong, N. R. *J. Am. Chem. Soc.* **1998**, *120*, 9646.
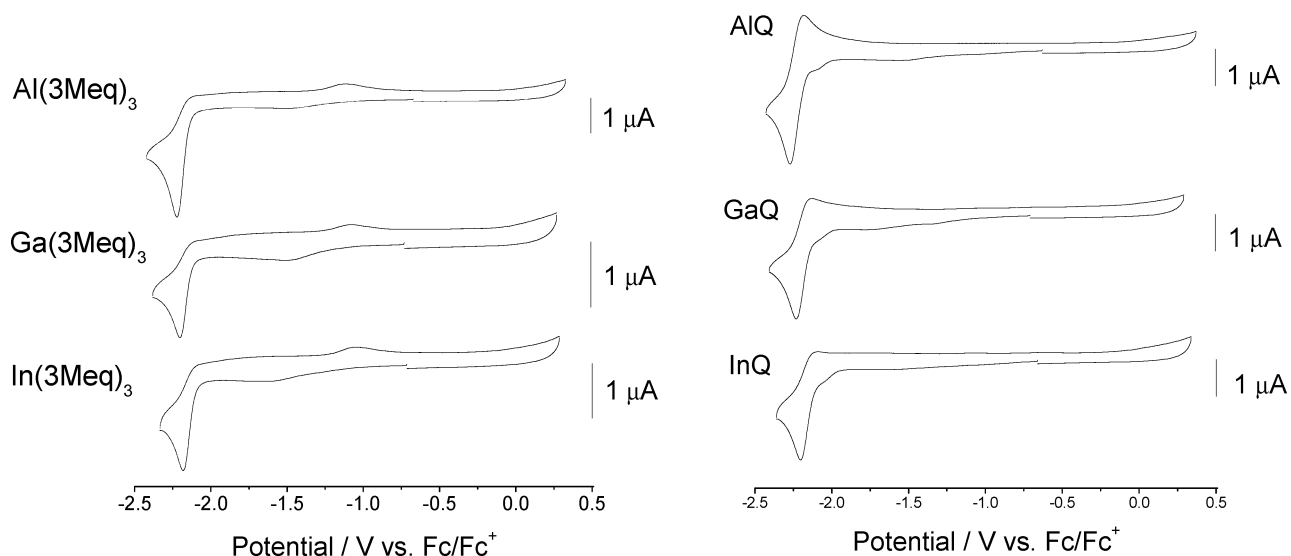
Figure 3. Cyclic voltammograms for M(3Meq)₃ (left) and MQ (right, M = Al³⁺, Ga³⁺, In³⁺) of 10⁻³ M solutions in DMSO containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The sweep rate was 100 mV/s.

Very similarly, the other two trivalent metal hemicages GaQ and InQ show improved electrochemical stability over their uncaged references Ga(3Meq)₃ and In(3Meq)₃ but to a decreased extent compared with AlQ. The intensity of anodic current decreases stepwise from AlQ to InQ, together with enlarged wave separation ΔE_p from 90 to 104 to 114 mV, indicating decreasing stability of the reduced hemicage complexes. This observation is believed to result from the increased strength of the metal−ligand binding (Al³⁺ > Ga³⁺ > In³⁺) in both MQ and M(3Meq)₃ complexes according to the differences in M−N and M−O bond lengths in Mq₃ complexes.[46]

Conclusion

In summary, the unique structure of the hemicage complexes enables a synergistic integration of several desirable properties for OLED applications. The use of hemicage chelates opens a general route toward the formation of pure

fac-Alq₃ complexes, which have been shown to provide favorable OLED performance. The cage structure also leads directly to superior thermal and chemical stability and quantum efficiency enhancement. Further research is under way to (a) better understand the structure−property relationships of this class of complexes and (b) conduct judicious ligand engineering for device performance optimization purposes.

Supporting Information Available: ¹H NMR spectra of selected new compounds (hemicage ligand QH₃, GaQ, and InQ). This material is available free of charge via the Internet at http://pubs.acs.org.

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