8-Quinolinolates as Ligands for Luminescent Cyclometalated Iridium Complexes

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Received November 9, 2006
Revised Manuscript Received February 7, 2007

Cyclometalated iridium(III) complexes have attracted considerable attention because of possible applications in oxygen sensing purposes[1] and, in particular, organic light-emitting devices (OLEDs).[2] Since the pioneering work of Forrest et al.,[2] enormous experimental and theoretical efforts have focused on the design, synthesis, and characterization of different classes of homoleptic and heteroleptic iridium(III) complexes resulting in improved materials and device structures and, therefore, in increased efficiencies and enhanced brightness, as well as extended operational lifetimes of OLEDs fabricated from the corresponding phosphorescent compounds.[3]

Concerning practical applications such as flat panel displays, tuning of the emission color to cover the entire visible spectrum is very desirable. Although a powerful color tuning from blue to red has been realized by modifications of the cyclometalating ligand, this approach suffers from the draw back of difficulties in the preparation of several μ-chloro bridged precursor materials and sometimes harsh conditions required for the formation of *tris*-cyclometalated iridium(III) complexes.[3] An alternative approach is based on heteroleptic iridium(III) complexes incorporating ancillary ligands such as acetylacetonate, picolinate, triazolate, and tetrazolate derivatives.[3a] In most cases emission properties are still dominated by the nature of the cyclometalating ligands, but preparation of the corresponding heteroleptic compounds is noticeably facilitated compared to the synthesis of *tris*-cyclometalated complexes.[3,4]

While there are numerous reports on luminescent metal complexes containing different derivatives of 8-hydroxyquinoline (e.g., complexes of Al, B, Pd, etc.),[5] to our best knowledge investigations on iridium(III) complexes containing quinolinolates are still rare.[6] Because of the possibility of tuning the energy gap by the attachment of electron-withdrawing or electron-donating groups, ligand centered excited states, and the commercial availability of many 8-hydroxyquinoline derivatives,[5] this class of ligands seems to be a promising candidate for the preparation of corresponding organoiridium(III) complexes.

In this communication we wish to report the synthesis, structure, and thermal and photophysical as well as electroluminescent properties of an up to date barely described class of iridium(III) complexes, namely, derivatives of bis($\kappa^2(C^2,N)$-2-phenylpyridine)($\kappa^2(N,O)$-8-quinolinolate)iridium(III). We demonstrate that these easily prepared compounds exhibit emission characteristics controlled by the quinolinolate ligand and present a powerful tool for tuning materials properties affecting the absorption and emission characteristics as well as the thermal stability and OLED performance by simple modifications of the quinolinolate ligand. Therefore, the herein introduced results line up with recent reports on synthetically tailored iridium(III) compounds[7] and offer a versatile, cheap, and convenient approach for the fine tuning of iridium(III) complexes.

All compounds under investigation were prepared from the μ-chloro bridged precursor material di-μ-chloro-tetrakis-

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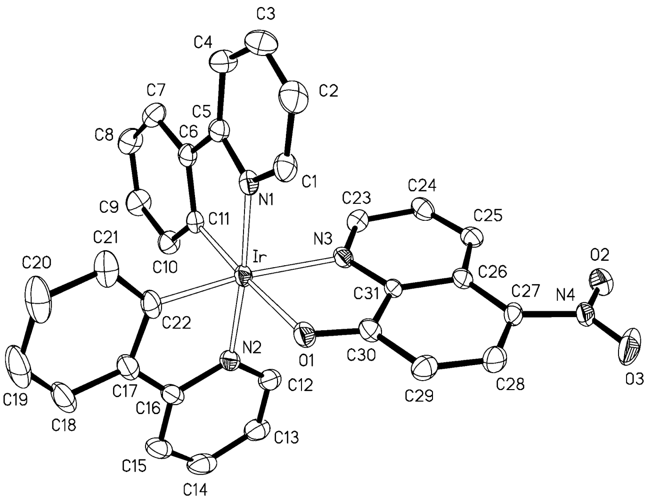

Figure 1. ORTEP of **3** (20% ellipsoids, H atoms omitted). Selected bond lengths (Å) and angles (deg): Ir−C(11) 1.989(6), Ir−C(22) 1.997(6), Ir−N(1) 2.030(5), Ir−N(2) 2.044(5), Ir−N(3) 2.131(5), Ir−O(1) 2.181(5), O(1)−C(30) 1.266(8), C(28)−C(29) 1.362(10), C(27)−N(4) 1.416(8), O(2)−N(4) 1.265(10), O(3)−N(4) 1.196(9), N(1)−Ir−C(11) 80.9(2), N(2)−Ir−C(22) 81.0(3), O(1)−Ir−N(3) 76.8(2), O(1)−Ir−C(11) 176.4(2), N(1)−Ir−N(2) 174.5(2), C(22)−Ir−N(3) 170.6(2).

(κ^2(C^2,N)-2-phenylpyridine)diiridium(III)[8] by refluxing with the corresponding ligand in a solvent mixture of CH_2Cl_2, EtOH, and triethylamine under inert argon atmosphere at 80 °C for 24 h (cf. Supporting Information). After removal of the solvent mixture, product purification was achieved by washing the residue with hot methanol several times, giving rise to bis(κ^2(C^2,N)-2-phenylpyridine)(κ^2(N,O)-8-quinolinolate)iridium(III) (**1**),[6a] the corresponding 5-formyl-8-quinolinolate (**2**), and 5-nitro-8-quinolinolate (**3**) derivatives in yields of 75−84%. **1**−**3** were characterized by ^{1}H and ^{13}C NMR spectroscopy, cyclic voltammetry, and absorption and fluorescence measurements as well as matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS to determine the exact mass. Thermal behavior and stability were further studied by simultaneous thermal analysis (STA) measurements (cf. Supporting Information).

Crystals of **3** suitable for X-ray diffraction were obtained from ether diffusion into saturated CH_2Cl_2 solutions. The X-ray crystal structure of **3** is depicted in Figure 1. Coordination chemistry of the central atom can be described as a slightly distorted octahedron with *OC*-6-42 stereochemistry. The trans disposition of the two nitrogen atoms and the Ir−C bond lengths of the metalated phenylpyridine ligands correspond with related *bis*(phenylpyridine)(acac) iridium complexes, while the bite angle of the quinolinolate moiety is distinctly smaller compared to the bite angle of the *acac* ligand in similar complexes.[9]

To determine the thermal stability of **1**−**3**, combined heat flux DSC/TGA experiments were performed under inert helium atmosphere. The temperature at 5% weight loss was chosen for comparison of the thermal stability. From the corresponding temperature values (136.1 °C for **1**, 354.1 °C for **2**, and 394.5 °C for **3**) a significant impact of ligand modifications on thermal properties becomes evident. As it is known from practical applications that materials with good thermal stability extend device lifetimes,[10] our approach provides a simple tool for tuning thermal properties of organoiridium quinolinolates. For applications in working electroluminescent devices another critical parameter is the stability of the phosphorescent compound in the presence of acidic layers.[11] ^{1}H NMR experiments of **1** after exposure to concentrated trifluoroacetic acid (TFA) suggest an increased stability compared to other commonly used ligands such as acetylacetonate and demonstrate another advantage of these quinolinolate ligands (cf. Supporting Information).[11]

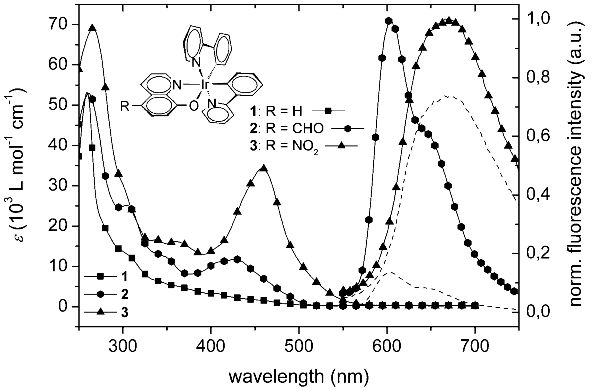

Figure 2. Absorption and emission spectra of **1**−**3**. The dashed lines represent the emission spectra in aerated solutions.

UV−vis absorption and photoluminescence (PL) spectra of all complexes were recorded in diluted solutions of $CHCl_3$ at room temperature in aerated and degassed solutions. As depicted in Figure 2, the photophysical properties of **1**−**3** are strongly affected by the electron-withdrawing formyl and nitro group. Concerning absorption spectra, absorption bands between 400 and 550 nm with noticeable high coefficients of extinction (11 750 L mol^{-1} cm^{-1} at 427 nm for **2** and 34 270 L mol^{-1} cm^{-1} at 459 nm for **3**) are present in **2** and **3**, while in **1** comparable absorption features are missing. These new absorption bands, attributed to the electronic influence of the formyl- and nitro-substituents on the quinolinolate ligand,[12] facilitate the selection of appropriate host materials for OLED fabrication. Additionally, the modifications of the quinolinolate ligand result in changes in the emission wavelengths of the corresponding complexes.

While **1** is not luminescent in aerated as well as degassed solutions, **2** and **3** emit orange to red light upon photoexcitation. **2** gives a structured emission band with the maximum at 603 nm and a shoulder at 645 nm, whereas **3** provides a broad and unstructured emission band ranging from 600 to 800 nm in solution (cf. Figure 2). Although in both cases the emission intensity is increased upon degassing of the solvent, PL quantum yields of these materials remain below 1% in solution. Additionally, thin film spectra of **2** and **3**

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were measured by blending 2 wt % of the metal complexes in polystyrene. The emission spectra of **2** remain virtually unchanged in thin films, contrary to **3**, which gives structured emission bands with a maximum at 619 nm and a broad shoulder around 660 nm (cf. Supporting Information). The apparent lifetimes under ambient conditions and under inert nitrogen atmosphere were determined using coated capillaries of **2** and **3**.[13] The corresponding measurements reveal apparent lifetimes of **2** of 11 μs under ambient conditions and 24 μs under nitrogen atmosphere at a modulation frequency of 5 kHz. The same experimental setup gives apparent lifetimes of 8 μs (air) and 16 μs (nitrogen atmosphere) for **3**.

Cyclic voltammetry (CV; cf. Supporting Information) was applied to estimate the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). With some restrictions the reduction and oxidation onsets of the CV peaks can be used to estimate the electron affinity ($E_A \approx$ LUMO energy) and the ionization potential ($I_P \approx$ HOMO energy).[14] Assuming that the absolute level of the ferrocene/ferrocenium redox pair is 4.8 eV below the vacuum level gives LUMO energies of −3.5 eV for all complexes. For **1**−**3** HOMO energies were found to be −5.0 eV, −5.2 eV, and −5.3 eV, respectively.

To determine the electroluminescent properties of **1**−**3**, OLEDs were fabricated on glass substrates in a device configuration of indium tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonte)/host material:iridium(III) complex (**1**−**3**)/Ca/Al under an inert argon atmosphere in a glovebox. With this experimental setup no electroluminescence (EL) using standard host materials such as polyphenylenes or polyvinylcarbazole (PVK) is obtained for **1**. In contrast, the absorption peaks of **2** and **3** at 427 and 459 nm are in good accordance with the emission wavelengths of the polymeric host materials PVK (λ_{max} = 410 nm) and poly[6,9,15,18-tetrahydro-6,6,9,9,15,15,18,18-octakis(4-octylphenyl)-*s*-indaceno[1,2-b:5,6-b′]difluorene-2,11-diyl] (LPPP, λ_{max} = 447 nm).[15] Devices fabricated from **2** using PVK as host material give bright EL with an emission maximum at 608 nm and a shoulder around 650 nm with onset voltages of approximately 6 V. Significant concentration quenching is observed for this class of materials, for example, a maximum luminance of 940 cd/m^2 at 13 V is obtained for devices containing 1 wt % of **2**, whereas devices prepared with 3 wt % of **2** give luminance values around 200 cd/m^2 at the same voltage (cf. Figure 3). However, devices prepared from **3** using PVK as host material give weak EL at 620 nm with a shoulder around 675 nm and onset voltages between 8 and 9 V. The luminance of 9 cd/m^2 at 16 V is low compared to devices of **3** fabricated with LPPP as host material, which provides a better spectral overlap of the host and guest material. These devices with 1 wt % complex loading exhibit onset voltages of 11 V with an increased luminance of 490 cd/m^2 at 16 V (cf. Supporting Information).

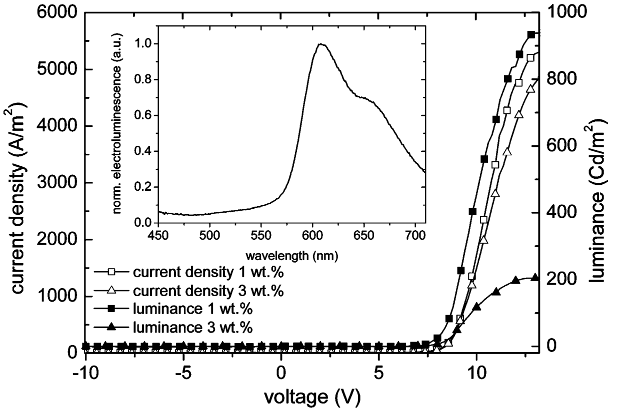

Figure 3. Bias/current characteristics, bias/electroluminescence characteristics, and normalized electroluminescence of OLEDs prepared from **2** with different complex loadings.

Herein a new approach for tuning materials properties of organoiridium(III) complexes toward particular needs has been established. By introduction of electron-withdrawing groups to the quinolinolate ligand a significant impact on structure, thermal, and photophysical as well as electroluminescent properties becomes evident. While **1** is not luminescent in solution and provides no characteristic absorption features for finding appropriate host materials for device applications,[16] **2** and **3** give orange to red luminescence combined with absorption maxima suitable for different polymeric host systems. OLEDs fabricated from **2** and **3** give bright orange to red EL with luminance intensities of 940 and 490 cd/m^2 in nonoptimized device structures. This class of materials offers the possibility of tuning materials properties by simple modifications of the quinolinolate ligand and provides a versatile and cheap approach to iridium(III) complexes with emission characteristics dominated by the quinolinolate ligand.

Acknowledgment. Financial support by the Austrian Science Fund in the framework of the Austrian Nano Initiative RPC ISOTEC - RP 0701 and 0702 is gratefully acknowledged. We thank G. Trimmel for thermal analysis.

Supporting Information Available: Synthetic procedures, NMR spectra, MALDI-TOF MS data, TGA runs, lifetime measurements, CV runs, OLED characteristics of **3**, ^{1}H NMR spectra after exposure to TFA (PDF), and crystallographic data for **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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