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Color tuning of iridium complexes for organic light-emitting diodes: The electronegative effect and π-conjugation effect

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Abstract

Novel red phosphorescent emitter bis(4-phenylquinazolinato-N,$C^{2'}$) iridium(acetylacetonate) [(pqz)$_2$Ir(acac)], bis(1-(1′-naphthyl)-5-methylisoquinolinato-N,$C^{2'}$)iridium(acetylacetonate) [(1-mniq)$_2$Ir(acac)] and bis(1-(2′-naphthyl)-5-methylisoquinolinato-N,$C^{2'}$)iridium(acetylacetonate) [(2-mniq)$_2$Ir(acac)] have been synthesized and fully characterized. The electronegative effect of (pqz)$_2$Ir(acac) ligand shows almost the same influence as the extended π-conjugation effect of (2-mniq)$_2$Ir(acac). Density functional theory (DFT) was applied to calculate the Kohn–Sham orbitals of HOMOs and LUMOs in the iridium complexes to illustrate the N(1) electronegative atom effect. Finally, lowest triplet state (T_1) energies calculated by time-dependent DFT (TDDFT) were compared with the experimental electroluminescent data. The calculated data for the iridium complexes agreed fairly well with experimental data. Electroluminescent devices with a configuration of ITO/NPB/CBP:dopant/BCP/AlQ$_3$/LiF/Al were fabricated. The device using (pqz)$_2$Ir(acac) as a dopant showed deep-red emission with 1931 CIE (Commission International de L'Eclairage) chromaticity coordinates $x = 0.70$, $y = 0.30$.

Keywords: Iridium; Red emitter; Organic light-emitting diodes

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1. Introduction

Organic light-emitting diodes (OLEDs) are one of the most important low cost full-color flat panel display alternatives to liquid crystal displays. Since the red-emitting phosphorescent dopants have been reported, OLEDs have made great progress and received considerable attention [1–5]. High-efficiency red emission could be anticipated for display applications by carefully designing appropriate ligands to form light-emitting iridium complexes [6,7]. Okada et al. [8] demonstrated a high efficiency red OLED using Ir(piq)$_3$ [iridium(III) tris(1-phenylisoquinolinato-N,$C^{2'}$)] as the dopant, which exhibited a maximum emission peak at 623 nm. The efficiency of the electroluminescence device was 8.0 lm/W, 9.3 cd/A at 100 cd/m^2 and 6.3 lm/W, 8.4 cd/A at 300 cd/m^2, and the CIE (Commission International de L'Eclairage) coordinate was (0.68, 0.33). Photophysical properties can be affected by extending the π-conjugation system of the ligand. Recently, by modifying the ligands, we have successfully shifted the red emission from 624 nm to 680 nm [9].

Quinazoline alkaloid can be found in *Dichroa febriguga* Lour., it contains antimalarial constituents and has been used in Chinese medicine [10]. Although quinazoline derivatives abound in the nature, investigations focused on using quinazoline as a ligand for iridium complex for OLEDs are very limited. Because of the similarity in the structures of 1-phenylisoquinoline and 4-phenylquinazoline, it is interesting to study the effect of the N(1) electronegative atom of the 4-phenylquinazoline on the properties of its iridium complex. In this paper, we compared the

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4-phenylquinazoline ligand to a series of phenyl-methylisoquinoline ligands and applied the density functional theory (DFT) to calculate the Kohn–Sham orbitals of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for these complexes, and lowest triplet state (T_1) energies calculated by time-dependent DFT in order to get a better understanding on the N(1) electronegative effect.

2. Experimental

^{1}H NMR and ^{13}C NMR spectra were measured in CD_2Cl_2 solution on Bruker Avance-300 (300 MHz) or AMX-400 (400 MHz) NMR spectrometers with tetramethylsilane (TMS) as the internal standard. The EI-Mass spectra were recorded on a Bruker APEX II. The UV–Vis spectra were measured in CH_2Cl_2 solution on an Agilent 8453 spectrophotometer, and the photoluminescence spectra were recorded in CH_2Cl_2 solution with a HITACHI model F-2500 fluorescence spectrophotometer. Melting points were measured using capillary melting point apparatus. HRMS spectra were obtained using a MAT-95XL high-resolution mass spectrometer. Elemental analyses have been carried out by using an Elementar vario EL III analyzer. Phenyl-methylisoquinoline ligands and 4-phenylquinazoline were synthesized using the process reported by Yang [9] and Uff [11], respectively. Cyclometalated Ir(III) μ-chloro-bridged dimers were synthesized by the method reported by Lamansky [4].

2.1. *4-phenylquinazoline (4-pqz)*

4-pqz ligand was obtained from the condensation reaction of 2-aminobenzophenone and formamide, according to the literature method [11]. $T_m = 95.0–97.0\ °C$; EIMS: *m/z* 206, $[M]^+$; HREIMS calcd for $C_{14}H_{10}N_2$, 206.0844, found 206.0843. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.39 (s, 1H), 8.13–8.16 (m, 2H), 7.93 (t, $J = 7.7$ Hz, 1H), 7.78–7.79 (m, 2H), 7.65–7.57 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.6, 154.3, 150.7, 136.9, 133.9, 130.2, 130.0, 128.6, 127.9, 127.1, 123.1.

2.2. *1-(1′-naphthyl)-5-methylisoquinoline (1-mniq)*

1-mniq ligand was prepared by a modified method [9]. First, naphthalene-1-carboxylic acid phenethyl-amide was synthesized and introduced with a cyclization process to obtain 1-naphthalen-1-yl-3,4-dihydro-isoquinoline. After deprotonation of this, the white solid product was obtained in a 38.7% yield. $T_m = 140.9–141.7\ °C$; EIMS: *m/z* 269, $[M]^+$; HREIMS calcd for $C_{20}H_{15}N$, 269.1204, found 269.1206. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.72 (d, $J = 5.9$ Hz, 1H), 7.99–7.87 (m, 3H), 7.63–7.44 (m, 5H), 7.37–7.24 (m, 3H), 2.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.2, 135.9, 133.7, 133.6, 132.3, 130.6, 128.7, 128.3, 128.2, 127.6, 126.7, 126.2, 126.0, 125.9, 125.8, 125.1, 18.9.

2.3. *1-(2′-naphthyl)-5-methyl isoquinoline (2-mniq)*

2-mniq ligand was prepared as described in 1-mniq, and the white solid product was obtained in a 19.6% yield. $T_m = 115.8–117.0\ °C$; EIMS: *m/z* 269, $[M]^+$; HREIMS calcd for $C_{20}H_{15}N$, 269.1204, found 269.1204. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.69 (d, $J = 5.9$ Hz, 1H), 8.17 (s, 1H), 8.01–7.81 (m, 6H), 7.58–7.53 (m, 3H), 7.42 (t, $J = 7.4$ Hz, 1H), 2.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 141.9, 137.1, 136.4, 133.9, 133.2, 133.1, 130.5, 129.5, 128.5, 128.0, 127.7, 127.6, 126.9, 126.8, 126.5, 126.3, 125.8, 19.0.

2.4. *Bis(4-phenylquinazolinato-N,C$^{2'}$)-iridium(acetylacetonate), (4-pqz)$_2$Ir(acac)*

(4-pqz)$_2$Ir(acac) was dried and column chromatography was used to give red solid product in a 63.5% yield. EIMS: *m/z* 702, $[M]^+$; HREIMS calcd for $C_{33}H_{25}IrO_2N_4$, 702.1607, found 702.1613. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 9.14 (s, 2H), 8.93 (d, $J = 8.5$ Hz, 2H), 8.40 (d, $J = 7.7$ Hz, 2H), 8.17 (d, $J = 8.5$ Hz, 2H), 7.95 (t, $J = 7.8$ Hz, 2H), 7.82 (t, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 7.7$ Hz, 1H), 6.76 (t, $J = 7.6$ Hz, 2H), 6.51 (d, $J = 7.7$ Hz, 2H), 5.35 (s, 1H), 1.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 175.7, 165.3, 146.2, 142.7, 141.4, 134.7, 124.6, 122.3, 121.1, 119.1, 118.5, 116.3, 111.9, 111.4, 91.3, 18.3. Anal. Calc. for $C_{33}H_{25}O_2N_4Ir$: C, 56.48; H, 3.59; N, 7.98. Found: C, 56.11; H, 3.73; N, 7.75%.

2.5. *Bis(1-(1′-naphthyl)-5-methylisoquinolinato-N,C$^{2'}$)-iridium(acetylacetonate), (1-mniq)$_2$Ir(acac)*

Dark red solid. Yield: 56.8%; EIMS: *m/z* 828, $[M]^+$; HREIMS calcd for $C_{45}H_{35}IrO_2N_2$, 828.2328, found 828.2330. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.37–8.45 (m, 2H), 8.04 (d, $J = 8.6$ Hz, 2H), 7.74–7.79 (m, 4H), 7.50–7.55 (m, 4H), 7.32–7.37 (m, 2H), 7.02–7.18 (m, 6H), 6.92–7.00 (m, 2H), 2.76 (s, 6H), 1.82 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 175.3, 161.4, 146.9, 130.3, 127.0, 123.7, 121.9, 119.2, 118.9, 118.5, 117.8, 115.7, 114.6, 114.5, 112.7, 106.7, 90.9, 18.6, 9.3. Anal. Calc. for $C_{45}H_{35}O_2N_2Ir$: C, 65.28; H, 4.26; N, 3.38. Found: C, 65.15; H, 4.52; N, 3.19%.

2.6. *Bis(1-(2′-naphthyl)-5-methylisoquinolin ato-N,C$^{2'}$)-iridium(acetylacetonate), (2-mniq)$_2$Ir(acac)*

Red solid. Yield: 62.6%; EIMS: *m/z* 828, $[M]^+$; HREIMS calcd for $C_{45}H_{35}IrO_2N_2$, 828.2328, found 828.2330. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.96 (d, $J = 8.0$ Hz, 2H), 8.62 (s, 2H), 8.53 (d, $J = 6.7$ Hz, 2H), 7.72 (d, $J = 6.7$ Hz, 2H), 7.60–7.68 (m, 6H), 7.06–7.08 (m, 6H), 6.61 (s, 2H), 5.32 (s, 1H), 2.70 (s, 6H), 1.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.5, 136.1, 133.7, 130.1, 126.4, 124.3, 124.2, 121.7, 120.1, 119.2, 118.0, 117.8, 116.8, 115.4, 115.3, 113.1, 106.8, 90.1, 19.5, 9.3. Anal.